CSGI

Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase

Report 2011

Last update May 2011
Editing by Filippo Baldereschi
Printed in July 2011

Summary

CSGI Research Activity *1*
Structure and Organization of CSGI *3*
Current Academic Collaborations *4*
Previous and Current Industrial Partners *5*
CSGI Patents *6*
List of Publications 2009-2011 .... *8*
Conferences 2009-2011 .... *39*
Theses (undergraduate, PhD, master, post-doc) *59*

1A: Hard Matter (Nanomaterials and Solid Interfaces)

Electrochemical Energy Conversion without platinum group metal catalysts *69*
Effect of oxidation level of n+-type nanoporous silicon surface on lipase adsorption and activity *71*
Ordered Mesoporous Materials. Part 1: Synthesis, characterization, and sustained lysozyme release *73*
Synthesis, characterization and functionalevaluation of light hydrides-based nanostructuredcomposites for solid state hydrogen storage. (PRIN Project 2008) *75*
Functionalized Silicon Nanoparticles: a Theoretical Multilevel Approach *77*
Design, synthesis and applications of new organic sensitizers for non-conventional photovoltaic cells *79*
Anchoring of SWCNT-SH on gold surface *81*
Multilayered Nanostructures for OLED devices *83*
Third generation solar cells: nano-fabrication of polymer heterojunctions and Dye Sensitized Solar Cells (DSSC) *85*
COOL-Coverings: Development of a novel and cost-effective range of nanotech improved coatings to substantially improve NIR (Near Infrared Reflective) properties of the building envelope *87*
Nanosensors based on ultrathin organic films *89*
Self Aggregation and transport properties in polyoxomolybdate species *91*
Influence of Cellulose Derivatives on Hydration Kinetics and Water Dynamics in Cement Pastes *93*
Dynamics of water in hydrated cement pastes by time resolved elastic neutron scattering *95*
Hydration and structural properties of cement mortars in presence of inorganic and polymeric additives *97*
Supramolecular architectures for tailoring of surface properties *99*
Physico-chemical characterization of self-assembled thin films on oxide surfaces *101*
Affinity-based sensing for clinical and anti-doping analysis *103*

1B: Soft Matter (Nanomaterials and Liquid Interfaces)

Nucleotide and nucleolipids specific interactions at a lipid cubic interface *104*
Role of the stabilizing agent on morphology and cytotoxicity in nanoparticles preparation *106*
Tuning of the surfactant film curvature through ionic liquids *108*
Interaction of short modified peptides involved in degenerative diseases with phospholipid membranes *110*
Design and Characterization of Ruthenium-based Supramolecular Systems as Nano-devices with antineoplastic activity *111*
Study of the formation of eumelanin and its intermediates *112*
Characterization of vesicles formed by lipopolysaccharides *113*
Accurate Force Fields for Computer Simulations *114*
Interaction of Bioactive Peptides with Membranes *116*

Protein-Matrix Coupling: the Photosynthetic Reaction Center embedded in Solid Matrices 118
Dynamic response of a shear banding wormlike micellar system in transient shear flows 120
Hollow polyelectrolyte nanocapsules assembled on liposomal templates 122
Hydrogel for human lens substitution 124
Nanostructured media for the synthesis of bio-inspired anionic lipids 126
Nucleic Acid condensation onto nucleolipids doped liposomes 128
Photosynthetic Reaction Centers Embedded in Polyelectrolyte Multilayer as an Optical Biosensor for Herbicide Detection 130
Self-organizing processes of Amphiphilic Peptides 132
Nanostructuring of surfaces: tunable size nanopores 134
Nanopatterned surfaces by LB phospholipid/polymer films 136
Hybrid bilayer by sputtered gold nanoparticles onto diblock-copolymer template 138
Substrate Induced Ordering in Poly(3-hexylthiophene) Thin Crystalline Films 140
Interfacial Free Energy and Nanostructuring of Poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric Acid Methyl Ester Thin 142
Soft membranes for specific surface recognition 144
Surface Imaging of Nanostructures 146
The Boron Neutron Capture Therapy: a new perspective for osteosarcoma 148
Clusters in Concentrated Lysozyme Protein Solutions 150
Self assembly of chiral surfactants 152
Self-Assembly of β-Cyclodextrin in Water. Formation of Pseudopolyrotaxanes. 154
Nucleolipid-based DNA vectors: complexation with nucleic acids and interaction with cell membrane model systems. 156
Magnetoliposomes for controlled drug release 158
Using liposomes as carriers for plant derived polyphenolic antibacterial compounds 160
Molecular depth profiling of polymer materials by surface mass spectrometry techniques ...162

1C: Theory and Modelling

Ordered Mesoporous Materials Part 2: Specific ion effects on Protein adsorption and surface charge density 164
Bio-mimetic and Photochemical Switches 166
Multicriteria thermodynamic Analysis for Environmental Impact Assessment 168
Energy Efficiency, Energy Growth and Complexity Leap 170
QM/MM characterization of amino acid radical species involved in biological electron transfer and catalytic processes 172
Specific Ion Effects 174
Measure and modelling the hydrometereology of a shallow lake (Lake of Montepulciano, Siena) 176
Modelling the spectral shape of CDOM 178
Climate change impacts on Mediterrranean coastal lakes and lagoons 180

2A: Art Restoration, Environmental Remediation and Textile Chemistry

Enzymes for green chemistry 182
Silica Gelatin composite for removal of chromate from water solutions 184
Calcium and barium hydroxide nanoparticles for the consolidation of wall paintings 186
Nanotechnology for the deacidification of books and manuscripts 188
Microemulsions and micellar solution for the cleaning of wall paintings 190
Deacidification of waterlogged wood: the Vasa shipwreck case studies 192
Chemical gel for the restoration of canvas paintings 194
Study of the technique in Mesoamerican mural painting: characterization of binders and their behavior. 196

Ionic liquid/Brij 30/nonane microemulsions: Characterization and applications 198
Surfactant for environmental remediation 200
Nanoparticles for biodeterioration control 201
Polyvinyl alcohol highly viscoelastic dispersions: a new class of cleaning tools for works of art 203
Silver nanoparticles on fabrics: synthesis and antimicrobial effect.......................................205
Surface functionalization of textiles 207
Dynamics of chromophoric dissolved organic matter and dissolved organic carbon in lakes209
Interaction study of indigo carmine with albumin and dextran by NMR Relaxation 211
The controlling factors of productivity in African Great Lakes 213

2B: Metals and Ceramics

New doped materials for technological applications 215
MANUDIRECT – Direct ultraprecision manufacturing 217

2C: Biotechnology

Expression and purification of the recombinant mustard trypsin inhibitor 2 (MTI2) in Escherichia coli 219
Proteolysis controls the assembly of Escherichia coli DNA polymerase III catalytic core 221
Shine-Dalgarno sequence enhances the efficiency of lacZ repression by artificial anti-lac antisense RNAs in Escherichia coli 223
Ordered Mesoporous Materials. Part 3: Biodiesel synthesis and phenolic compounds oxidation 225
Bioprocess of rhamnolipid synthesis from glycerol, byproduct of biodiesel production 227
Polyelectrolyte Multilayer Films containing Silver Nanoparticles as antibacterial and antiadhesive coatings 228
New perspectives in bacterial retention study 230
"Phage-displayed" peptides application to recognize L. monocytogenes in dairy products .231
Research of serotype-specific epitopes of Group B Coxsackievirus for development of new diagnostics 232
High quality oil for biodiesel production and biomass yields from a microalga Coccomyxa sp. by autotrophic growth 233
Biodegradable Plastics from Brassica Carinata Oil and from Very Long Chain Fatty Acids: Synthesis and Characterization 234
Influence of ion strength and viability in bacterial self-assembly pattern on abiotic surface: preliminary models 235
PHA synthesis by Pseudomonas aeruginosa ATCC 27853 in magnesium and nitrogen starvation 237
Conformational epitopes on monoclonal mouse anti-Yersinia pestis F1 antigen YPF19 identified by peptide phage display and molecular modeling 238
ToF-SIMS Imaging of Surface Self-Organized Fractal Patterns of Bacteria 239
Physico-Chemical Properties of Pharmaceutical Systems...240
BIoprocessing for Sustainable production of COLoured textiles (BISCOL) 242
Renewable energies from agriculture..244
Structural and Dynamic Studies of Metal Complexes with Ligands of Biological Interest 246
Structure-Activity Relationship Studies on Enzymes of Biotechnological Interest 248
Casein-divalent ions interaction: a solvent exchange study 250
Stability and nanostructure of food emulsions and veiled extra virgin olive oil 251
The role of the interface in the radical induced oxidation in emulsions and liposomes 253
Model systems for saccharide-based biosensor 255
Increasing photostability and water-solubility of carotenoids: synthesis and characterization of β-carotene-humic acid complexes 257

Antibacterial activity of plant extracts towards cagA positive and cagA negative Helicobacter pylori clinical isolates 259
Substitutes of human vitreous 261
In vivo NMR study of yeast fermentative metabolism in the presence of Ferric iron 263
Structural and dynamic NMR studies of oligopeptides mimicking nur77 binding site 265
Interaction between vine pesticides and serum albumin studied by nuclear spin relaxation data 267
In vitro biocompatibility of new PVA-based hydrogels as vitreous body substitutes 269
Microbial synthesis and structural characterization of biodegradable polyesters from fatty acids with odd number of carbon atoms 271

Author Index 273

CSGI Research Activity

Outline

CSGI (Research Center for Colloids and Nanoscience) was established in Firenze, in December 1993. It has been officially recognized by the Italian Government in 1994, and is under the supervision and control of the Italian Ministry for University and Scientific Research (MIUR). Since 1995 CSGI began its scientific activity, devoted to basic research and to the development of high-tech new processes, and is supporting the activities of the small and medium size business industrial companies, that cannot afford the financial costs of an independent research activity.

In the last 18 years, CSGI has sponsored several different research programs, mainly supported by European Union grants, and partly also by other international and national Institutions, such as the Italian “Articolo 10, Law 46/1982”, PRIN, PNR, FISR, FIRB, CNR, and so forth.

CSGI has signed numerous contracts that involve about 75 national and international industrial companies, and some highly qualified research Centers, such as Procter & Gamble, Siemens, Tecnotessile SpA, Massachusetts Institute of Technology, Pharmacia-Upjon, Elf-Atochem, Ansaldo, Glaxo-Wellcome, Sintech, Inver, Cover, Tooling International Ltd, Industrial Materials Technology GmbH, MBN SpA, Inteti, Icmese, Comune di Firenze, VTT, etc.. Such lively activity has brought to several International Patents and research agreements.

CSGI has reached a very qualified standard, and its level has been acknowledged abroad, in several fields. For example, CSGI is a leader in a number of applications of Nanotechnology, in the conservation of cultural heritage, and in the production of nanophasic powders (with MBN) for the production of special materials for aeronautics, high resistance coatings, etc. CSGI supports the local authorities for the safeguard and conservation of works or art (“Sovrintendenze Artistiche”) in Tuscany and other Italian districts, with a set of technologies that have been developed for this aim. Similar actions have been promoted in agreement with the Mexican Federal Government for the conservation of monuments (Puebla Cathedral, Maya and Aztec heritage, the archaeological site of Calakmul, Campeche).

CSGI is active also in the training of specialized researchers, has granted several fellowships, PhD supporting programs, post-doc grants, and other education projects, and has organized several national and international Meetings. In particular, during the year 2010, CSGI has issued 10 PhD scholarships, 42 fellowships, and 7 post-doc grants, and is actively participating in two European Master Programs: EMASCO-COSOM (European Master in Supramolecular and Colloidal Chemistry) and IMES (International Master on Bioenergy and Environment). CSGI has co-sponsored national and international congresses (International Workshop on Dynamic Crossover Phenomena in Water and Other Glass-forming Liquids and CSGI National Meeting).

The CSGI financial plan is solid, with a strong growth of its financial assets, mainly due to EU funding.

The main topics of CSGI research activity are:

1) development of processes for the production of nanophasic systems, for the production of innovative textiles, for the synthesis of nanophasic alloys, ceramics and nanophasic or nanostructured composites (low temperature and low energy costs)
2) setup of new additives for cement products. These projects are mainly carried out in collaboration with Italcementi and MIT, and are aimed at investigating and optimizing the cement hydration process and the production of new, ceramics-like materials for the cement-related industry
3) formulation of dispersions in fluids, emulsions and inverted emulsions (paints, adhesives, sealing materials, detergents, etc.)
4) development of systems for the confinement of proteins and for the controlled release of pharmaceutics
5) development of food-related industrial processes (for example the treatment of milk and milk derivatives in supercritical phase)
6) development of innovative procedures for the conservation and restoration of works of art (paintings, frescoes and stone-based materials). CSGI is a world leader in this research activity, and is involved in a significant campaign for the recover of archaeological treasures in Mexico (Calakmul), in the largest Maya sites, and with the Maritime Museum in Stockholm for the conservation of the Vasa ship. New methods are under development for the removal of polymer and grime from oil paintings (relining) in collaboration with the Louvre Museum (Paris). CSGI is currently involved in the conservation of Annunciation Grotto (Nazareth).

Fields of Interest

- Nanostructured and ultrafine materials.
- Structure and dynamics of supramolecular assemblies (monolayers, micelles, liposomes, microemulsions, Langmuir-Blodgett films, host-guest systems).
- Nanophasic ternary oxides.
- Structural analysis of biomolecules in solution, interaction processes, recognition of ligands with macromolecular surfaces, theoretical and experimental analysis of cellular metabolism, interactions between metals and ligands, characterization of the interaction sites.
- Formulation of nanophasic systems.
- Innovative processes for the conservation and restoration of cultural heritage (stone materials, wood materials, paintings, frescoes, paper, photographic material).

Structure and Organization of CSGI

Management Offices
President, Council, Director, Audit Council, Technical-Scientific Board.

Director of CSGI
Prof. Piero Baglioni, Department of Chemistry, University of Florence.

President of CSGI
Prof. Giovanni Marletta, Department of Chemical Sciences, University of Catania.

Website
http://www.csgi.unifi.it/

Foundation
December 21st, 1993

Official recognition by the Italian Government
November 15th, 1994 (G.U. Nr. 267)

Academic Units and Associated Centers

University of Florence (headquarter)
Scuola Normale Superiore in Pisa
University of Bergamo
University of Catania
University of Cagliari
University of Molise (Campobasso)
University of Pavia
University of Siena
University of Udine
Laboratory CSGI of Treviso
Polytechnic Institute of Milan
University of Bologna
University of Milan, Bicocca
University of Naples "Federico II"
University of Perugia
University of Rome, La Sapienza
University of Venice

Personnel

CSGI gathers about 300 researchers including Full Professors, Associate Professors, University Researchers, that belong to the academic members.
Moreover, CSGI employs 75 researchers and 3 administration employees on its own. Several PhD and post-doc students are financially supported through CSGI fellowships. CSGI hosts researchers hired by industrial companies for training and specific research activities, in the framework of particular projects.
CSGI owes two research Laboratories, located in Vascon di Carbonera (Nanophases Laboratory) and in Prato (Laboratory for the refinement and surface modification of textiles). These plants collaborate closely with the local industrial activities.

Current Academic Collaborations

ANU (Australian National University)
Argonne National Laboratory
Aston University (Birmingham)
Brookhaven National Laboratory
California Institute of Technology (CalTech)
Centro di Istochimica del CNR di Pavia
Collège de France
Columbia University
CNIC (Cuba)
CSIC (Sevilla)
East China Normal University (Shangai)
École Normale Supérieure (Lion)
Escuela Superior Politecnica del Chimborazo
ETH (Zurich)
Hahn-Meitner Institut (Berlin)
Hull University
Inst. Science des Matériaux
Institut Laser Technology
Inst. Nat. Polytechnique de Lorraine (Nancy)
Inst. Scientific Instruments (Czech Rep.)
ITER
Laboratoire Leon Brillouin (Saclay)
Lehstul Fertigungstechnologie
Massachusetts Institute of Technology
Max Planck Institut (Berlin)
Museum of Fine Arts (Boston)
Nuclear Research Institute (Prague)
Oak Ridge National Laboratory
Oklahoma State University
Risø National Laboratory
Technical University di Budapest
Tekniska Hogskolan I Luleå
The Getty Conservation Institute
Università degli Studi Bari
Università degli Studi Camerino
Università degli Studi Chieti
Università degli Studi della Calabria
Università degli Studi di Parma
Università degli Studi Genova
Università degli Studi Padova
Università degli Studi Palermo
Università degli Studi Pisa
Università degli Studi Salerno
Università degli Studi Torino
Università degli Studi Trento
Università degli Studi Urbino
Universitad de Santiago de Compostela
Universitad del Salvador
Universitad Estadual de Campinas
Universität Gesamthoschule Kassel
Universität Heidelberg
Université de Bourgogne
Université de Grenoble
Université “Louis Pasteur” (Strasbourg)
Université de Montpellier II
University College (London)
University of Berkeley
University of Bristol
University of Cambridge
University of Detroit
University of East Anglia
University of Houston
University of Leiden
University of Lund
University of South Florida
University of York
Weizmann Institute (Israel)

Previous and Current Industrial Partners

Alcea
Alfa Test
Alfa Wasserman
Ansaldo
Aprilia
Ascor chimici
Ausimont
Bigagli
Biokimica S.p.A
Bioscreen Technology srl
BTG-Holland
Bitossi
Comune di Firenze
Consorzio delle Buone Idee
Chemia
Cover
D'Appolonia
Dynamotive
Elf-Atochem
ENEA (Energy Department – Casaccia)
Eniricerche
Enitecnologie
EUBIA (Bruxelles)
Flory's
Getty Conservation Institute
Glaxo-Wellcome
Icmese
Instituto Nacional de Antropologìa e Historia - INAH
INASCO-Hellas (Int. Aerosp. Sci. Corp.)
Industrial Materials Technology GmbH
Industrie Casearie Podda
Ineti
Institute for the Care of Hystorical Monuments (Prague)
International Broker
Inver
IRBM
Italcementi S.p.A.
Italfarmaco
Lamberti S.p.A.
Lima
JRC (Joint Research Centre of the European Commission)
Mapei
Mariplast
Martelli S.p.A.
MBN Nanomaterialia
Merk
Microtec (Germany)
National Museum of Denmark
Nicox
Novuspharma Omrod Diesel (UK)
Philips
Pharmacia-Upjon (USA and Sweden)
Pharmaness
Procter & Gamble
Rifiniture BP
Sem
Siemens AG
S.I.F.I.
Sintech
SIR Industriale
Sirio Panel
Solvay
Soprintendenze ai Beni Artistici e Storici di: FI-PO-PT, SI-GR, PI-LU-MS
Soprintendenze ai Beni Ambientali ed Architettonici di:
Arezzo
Firenze-Prato-Pistoia
Roma
Veneto Orientale
Lombardia
Reggio Calabria
Tecnotessile SpA
TIL (Tooling International Ltd UK)
TNO (Netherlands)
3M
Transfergomma (Padova)
WIP (Germany)
VTT (Finland).

CSGI Patents

1) Baglioni Piero, Dei Luigi, Ferroni Enzo, Giorgi Rodorico – "Sospensioni stabili di idrossido di calcio". Italian Patent FI/96/A000255 deposit date 31/10/1996.

2) Matteazzi Paolo, Baglioni Piero, Basset Diego - "Process for Recycling, by Milling, Solid Industrial Waste and Materials at the end of their Service Life" European Patent Application 97203735.2, Priority IT96 FI96A000280.

3) Grassi Giuliano, Chiaramonti David, Baglioni Piero – "Apparato a combustione di etanolo o miscele etanolo per cucine, stufe e illuminazione a uso domestico". Italian Patent FI/98/A42 deposit date 24/ 02/ 98.

4) Ambrosone Luigi, Ceglie Andrea – "Software per l'analisi grafica e numerica di dati di Risonanza Magnetica Nucleare per la determinazione della polidispersità di emulsioni". Italian Patent FI99A000044 deposit date 09/03/1999.

5) Baglioni Piero, Fratini Emiliano, Ricceri Riccardo, Sarti Giuseppe, Chiaramonti David – "Engine fuels consisting of an emulsion comprising mineral and/or natural oils, their preparation and use in internal combustion engine". PCT International Application WO n. 99936473.0 del 02.07.99

6) Baglioni Piero, Carretti Emiliano, Dei Luigi – "Microemulsioni ed emulsioni di olio in acqua, loro uso per la solubilizzazione di resine polimeriche e impacchi contenenti detti microemulsioni o emulsioni". Italian Patent FI99A000071 deposit date 02/ 04/ 99

7) Baglioni Piero, Bardi Ugo, Bonini Massimo -New method for the production of solid powder and films by compartimentalised solution thermal spraying (CSTS). European Patent Application EP 00-105673.8 deposit date 17.03.2000

8) Baglioni Piero, Dei Luigi, Giorgi Rodorigo, Claudio Vinicius Schettino – "Basic Suspensions their Preparation and Use in Processes for Paper Deacidification", European Patent Application EP 02714088.8 deposit date 15/01/02

9) Baglioni Piero, Dei Luigi, Fratoni Laura, Lo Nostro Pierandrea, Moroni Michelangelo - "Processo per la preparazione di nano e microparticelle di ossidi e idrossidi di metalli del secondo gruppo e di transizione, nano e microparticelle così ottenute e loro impiego in campo ceramico, tessile e cartario", Patent Query N. FI2002A000052, deposit date 28/03/2002 – EP 03745367.7

10) Baglioni Piero, Dei Luigi, Fratoni Laura, Lo Nostro Pierandrea, Moroni Michelangelo – "Preparation of nano- and micro-particles of group II and transition metals oxides and hydroxides and their use in the ceramic, textile and paper industries". *PCT Int. Appl.* (2003), 10 pp. CODEN: PIXXD2 WO 2003082742 A2 20031009 CAN 139:278604 AN 2003:796605

11) Baglioni Piero, Dei Luigi, Giorgi Rodorico, Ninham Barry W. – "Process for preparing nano- and micro-sized particles of inorganic compounds" European Patent Application EP 04101822.7, deposit date 29/04/2004.

12) Angelico Ruggero, Ceglie Andrea, Hochoeppler Alejandro, Palazzo Gerardo, Stefan Alessandra – "Macroemulsioni acqua-in olio a lunga stabilità, loro preparazione ed uso" – Patent Query N. FI2001A000016 deposit date 29/01/01.

13) Ambrosone Luigi, Ceglie Andrea – "Materiale assorbente e suoi usi nei processi di bonifica di falde acquifere inquinate da prodotti chimici" – Patent Query FI2003A000236 deposit date 11/09/03.

14) Ambrosone Luigi, Ceglie Andrea – "Gel stabili contenenti gelatina" – Patent Query N. FI2003A000237 deposit date 11/09/03.

15) Fratoni Laura, Lo Nostro Pierandrea – "Composizione detergente a base di un estere dell'acido L-ascorbico" – Patent Query N. TO2003A001032 deposit date 22/12/03.

16) Baglioni Piero, Ambrosi Moira, Dei Luigi, Faneschi Mauro, Mancioli Luciano, Santoni Sergio – "Ceramic products comprising nanoparticles of zirconium hydroxide and/or glass frits" – RIF. Patent Query 7303 PTEP/2006 EP06112439.2 deposit date 10/04/06

17) Ceglie Andrea, Venditti Francesco, Lopez Francesco, Palazzo Gerardo, Colafemmina Giuseppe, Angelico Ruggero, Ambrosone Luigi – "Materiale adsorbente contenente tensioattivo cationico, sua preparazione ed uso per la rimozione di metalli da soluzioni acquose" – Patent Query N. FI 2006 A000113 – RIF. 7490 PTIT deposit date 10/05/2006

18) Ambrosi Moira, Baglioni Piero, Bonini Massimo, Fratini Emiliano – "Nanoparticelle monodisperse di ossidi ed idrossidi metallici e loro applicazione nei settori tessile, cartario e ceramico" – Patent Query FI 2006A000313 – RIF. 7845 PTIT deposit date 11/12/06.

19) Hochkoeppler Alejandro, Baglioni Piero, Stefan Alessandra – "Espressione batterica di un gene artificiale per la produzione di CRM 197 e derivati" – Patent Query FI 2009A000137 – RIF. 9741 PTIT deposit date 25/06/09.

20) Smets Johan, Pintens An, Keijzer Olav Pieter Dora Tony, Bodet Jean-Francois, Lebron Ariel, Fratini Emiliano, Vannucci Chiara, Ambrosi Moira, Baglioni Piero, Guinebretiere Sandra Jaqueline, Yan Nianxi, Liu Hongwei – "Encapsulates" – Attorney's Docket No. 11547P – 21/04/2010.

21) Fernandez Prieto Susana, Smets Johan, Aouad Yousef Georges, Wevers Jean, Baglioni Piero, Ambrosi Moira, Vannucci Chiara – "Particles" – Attorney's Docket No. 11812P2 – 15/04/2011.

CSGI Registered Trade Marks

Nanorestore® International Class 01,37,40 FI2008C00067527508 RIF. 19558

Nanorestore Paper® International Class 01, 16, 40 FI2011C0009935263 RIF. 27175

Prospective CSGI Activity in 2011-2012

CSGI is involved in 5 European programs, in several national projects, and in collaborations with small and medium size industrial companies.

CSGI is developing its own research activity in order to optimize the application of research projects inspired by the urging demands of small and medium size companies.

CSGI is actively working in order to offer a valid support to the Italian industrial system in the setting up and development of projects and pre-industrial processes.

List of Publications 2009-2011

1. Ni based electrodes for hydrogen and oxygen generation. Villa, M.; Milanese, M.; Nelli, P.; Salvi, P.; Verardi, E.; Marini, A.; Zangari, G. *ECS Transactions* 16(50), 9-19 (2009).
2. The apparent capacitance of the electrode “charging” process. Villa, M.; Nelli, P.; Salvi, P.; Kiros, Y.; Zangari, G. ECS Transactions 19 (32), 47-59 (2009).
3. Charge storage and the Oxygen evolution reaction in mixed Ni-Li oxides. Villa, M.; Milanese, M.; Nelli, P.; Salvi, E.; Marini, A.; Zangari, G. Physical Chemistry Chemical Physics 11, 7678-7689 (2009).
4. The regulatory elements of araBAD operon, contrary to lac-based expression systems, afford hypersynthesis of Murine, and Human Interferons in Escherichia coli. Stefan, A., Alfarano, P., Merulla, D., Mattana, P., Rolli, E., Mangino, P., Masotti, L., Hochkoeppler, A. Biotechnology Progress 25, 1612-1619 (2009).
5. Proteolysis of the proofreading subunit controls the assembly of Escherichia coli DNA polymerase III catalytic core. Bressanin, D., Stefan, A., Dal Piaz, F., Cianchetta, S., Reggiani, L., Hochkoeppler, A. Biochimica and Biophysica Acta 1794, 1606-1615 (2009).
6. Expression and purification of the recombinant mustard trypsin inhibitor 2 (MTI2) in Escherichia coli. Stefan, A., Ugolini, L., Martelli, E., Palmieri, S., Hochkoeppler, A. Journal of Bioscience and Bioengineering 108, 282-285 (2009).
7. Orientation and specific interactions of nucleotides and nucleolipids inside monoolein-based liquid crystals. Murgia, S.; Lampis, S.; Angius, R.; Berti, D.; Monduzzi, M. Journal of Physical Chemistry B 113, 9205-9215 (2009).
8. Aerosol-OT forms oil-in-water spherical micelles in the presence of the ionic liquid bmimBF4. Murgia, S.; Palazzo, G.; Mamusa, M.; Lampis, S.; Monduzzi, M. Journal of Physical Chemistry B 113, 9216-9225 (2009).
9. Laccase from Pleurotus sajour-caju on functionalised mesoporous silica: immobilisation and use for the oxidation of phenolic compounds. Salis, A.; Pisano, M.; Monduzzi, M.; Solinas, V.; Sanjust, E. Journal of Molecular Catalysis B: Enzymatic 58, 175-180 (2009).
10. Role of the support surface on the loading and the activity of Pseudomonas fluorescens lipase used for biodiesel synthesis. Salis A.; Bhattacharyya M.S.; Monduzzi M.; Solinas V. Journal of Molecular Catalysis B: Enzymatic 57, 262-269 (2009).
11. Hofmeister Effects in enzymatic activity, colloid stability and pH measurements: ion dependent specificity of intermolecular forces, In Nanoparticles and Nanodevices in Biological Applications. Salis, A.; Monduzzi, M.; Ninham, B.W. Ed S. Bellucci, Springer 159-194 (2009). ISBN: 978-3-540-70943-5
12. Cofactor recycling for the selective enzymatic biotransformation of cinnamaldehyde to cinnamyl alcohol. Zucca, P.; Littarru, M.; Rescigno, A.; Sanjust, E. Bioscience, Biotechnology, and Biochemistry 73, 1224-1226 (2009).
13. Fe(III)-5,10,15,20-tetrakis(pentafluorophenyl)porphine supported on pyridyl-functionalized, crosslinked poly(vinylalcohol) as a biomimetic versatile-peroxidase-like catalyst. Zucca, P.; Sollai, F.; Garau, A.; Rescigno, A.; Sanjust, E. J. Mol. Catal. A: Chemical 306, 89-96 (2009).
14. Bioinspired routes towards delignification. Zucca P.; Sanjust E. La Chimica e l’Industria 7, 150-155 (2009).
15. Influence of ion strength and viability in bacterial self-assembly pattern on abiotic surface: preliminary models. Carnazza, S.; Grasso, L.; Caratozzolo, M.; Guglielmino, S.; Fortuna, L.; Frasca, M.; Marletta, G. IPACS Open Library (http://lib.physcon.ru/?item=2092) (2009).
16. New Advances in Cell Adhesion Technology In Nanoparticles and Nanodevices in Biological Applications. Carnazza, S. Lecture Notes in Nanoscale Science and Technology, S. Bellucci (Ed.), Springer, Vol. 4, pp. 69-130 (2009).
17. Micelles obtained by aggregation of gemini surfactants containing the CCK8 peptide and a gadolinium complex. Accardo, A.; Tesauro, D.; Morisco, A.; Mangiapia, G.; Vaccaro, M.; Gianolio, E.; Heenan, R. K.; Paduano, L.; Morelli, G. Journal of Biological Inorganic Chemistry 14, 587-599 (2009).
18. Quaternary Diffusion Coefficients in a Protein-Polymer-Salt-Water System Determined by Rayleigh Interferometry. Annunziata, O.; Vergara, A.; Paduano, L.; Sartorio, R.; Miller, D. G.; Albright, J. G. Journal of Physical Chemistry B 113, 13446-13453 (2009).
19. Quaternary diffusion coefficients in a protein-polymer-salt-water system determined by rayleigh interferometry. Annunziata, O.; Vergara, A.; Paduano, L.; Sartorio, R.; Miller Donald,

G.; Albright John, G. Journal of Physical Chemistry B 113, 13446-53 (2009).

20. Spinodal Composition of the System Water + Chloroform + Acetic Acid at 25 DegC. Buzatu, F. D.; Lungu, R. P.; Buzatu, D.; Sartorio, R.; Paduano, L. Journal of Solution Chemistry 38, 403-415 (2009).
21. Self-assembling properties of ionic-complementary peptides. D'Auria, G.; Vacatello, M.; Falcigno, L.; Paduano, L.; Mangiapia, G.; Calvanese, L.; Gambaretto, R.; Dettin, M.; Paolillo, L. Journal of Peptide Science 15, 210-219 (2009).
22. Simplified and detailed chemistry modeling of constant-volume diesel combustion experiments. D'Errico, G.; Ettorre, D.; Lucchini, T. SAE International Journal of Fuels and Lubricants 1, 452-465 (2009).
23. Mesoscopic and microstructural characterization of liposomes formed by the lipooligosaccharide from Salmonella minnesota strain 595 (Re mutant). D'Errico, G.; Silipo, A.; Mangiapia, G.; Molinaro, A.; Paduano, L.; Lanzetta, R. Physical Chemistry Chemical Physics 11, 2314-2322 (2009).
24. Interaction of short modified peptides deriving from glycoprotein gp36 of feline immunodeficiency virus with phospholipid membranes. D'Errico, G.; Vitiello, G.; D'Ursi, A. M.; Marsh, D. European Biophysical Journal 38, 873-882 (2009).
25. The in vitro nuclear aggregates of polyamines. Di Luccia, A.; Picariello, G.; Iacomino, G.; Formisano, A.; Paduano, L.; D'Agostino, L. FEBS Journal 276, 2324-2335 (2009).
26. NMR of liquid crystals and micellar solutions. Paduano, L.; D'Errico, G. Nuclear Magnetic Resonance, 38, 491-512 (2009).
27. Binary Mutual Diffusion Coefficients of Isoniazid Aqueous Solutions at (298.15 and 310.15) K. Ribeiro, A.C.F.; Santos, A.C.G.; Lobo, V.M.M.; Veiga, F.J.B.; Cabral, A.M.T.D.P.V.; Esteso, M.A.; Ortona, O. Journal of Chemical and Engineering Data 54, 3235-3237 (2009).
28. Lipid based nanovectors containing ruthenium complexes: a potential route in cancer therapy. Vaccaro, M.; Del Litto, R.; Mangiapia, G.; Carnerup, A. M.; D'Errico, G.; Ruffo, F.; Paduano, L. Chemical Communications, 1404-1406 (2009).
29. Colloidal particles composed of amphiphilic molecules binding gadolinium complexes and peptides as tumor-specific contrast agents in MRI: physico-chemical characterization. Vaccaro, M.; Mangiapia, G.; Radulescu, A.; Schillen, K.; D'Errico, G.; Morelli, G.; Paduano, L. Soft Matter 5, 2504-2512 (2009).
30. Microstructural characterization of lysophosphatidylcholine micellar aggregates: The structural basis for their use as biomembrane mimics. Vitiello, G.; Ciccarelli, D.; Ortona, O.; D'Errico, G. Journal of Colloid and Interface Science 336, 827-833 (2009).
31. Ni – based electrodes for hydrogen and oxygen generation. Villa, M.; Milanese, C.; Nelli, P.; Salvi, P.; Verardi, E.; Marini, A.; Zangari, G. ECS Transaction 16 [50], 9-19 (2009).
32. Physico-chemical characterization of anhydrous D-mannitol. Bruni, G., Berbenni, V., Milanese, C.; Girella, A.; Cofrancesco, P.; Bellazzi, G.; Marini, A. Journal of Thermal Analysis and Calorimetry 95, 871-876 (2009).
33. H2 sorption performance of NaBH4 – MgH2 composites prepared by mechanical activation. Milanese, C.; Girella, A.; Mulas, G.; Enzo, S.; Medici, S.; Garroni, S.; Baró, M.D.; Suriñach, S.; Marini, A. Ecosystems and Sustainable Development VII, Editors: C.A. Brebbia & E. Tiezzi. Series: WIT Transactions on Ecology and the Environment 122, 389-400 (2009).
34. Charge storage and the oxygen evolution reaction in mixed Ni – Li oxides. Villa, M.; Milanese, C.; Salvi, P.; Nelli, P.; Marini, A.; Zangari, G. Physical Chemistry Chemical Physics 11, 7678-7689 (2009).
35. Thermodynamic relationships between nateglinide polymorphs. Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Viganò, E.; Lanfranconi, S.; Marini, A. Journal of Pharmaceutical and Biomedical Analysis 50, 764-770 (2009).
36. SiO2 – P2O5 – CaO glasses and glass-ceramics with and without ZnO: relationships among composition, microstructure and bioactivity. Bini, M.; Grandi, S.; Capsoni, D.; Mustarelli, P.; Saino, E.; Visai, L. Journal of Physical Chemistry C 113, 8821–8828 (2009).
37. Structural, spectroscopic and magnetic investigation of the LiFe1-xMnxPO4 (x = 0 - 0.18) solid solution. Bini, M.; Mozzati, M.C.; Galinetto, P.; Capsoni, D.; Ferrari, S.; Grandi, M.S.; Massarotti, V. Journal of Solid State Chemistry 182, 1972-1981 (2009).
38. Cr and Ni doping of Li4Ti5O12: cation distribution and functional properties. Capsoni, D.; Bini, M.; Massarotti, V.; Mustarelli, P.; Ferrari, S.; Chiodelli, G.; Mozzati, M.C.; Galinetto, P. Journal of Physical Chemistry C 113, 19664–19671 (2009).
39. Structural and spectroscopic characterization of Mo1-xWxO3-d mixed oxides. Morandi, S.; Paganini, M.C.; Giamello, E.; Bini, M.; Capsoni, D.; Massarotti, V.; Ghiotti, G. Journal of

Solid State Chemistry 182, 3342-3352 (2009).

40. The role of accurate quantum mechanical computations in the assignment of vibrational spectra for unstable free radicals: H2CN and F2CN as test cases. Puzzarini, C.; Barone, V. Chemical Physics Letters 467, 276-280 (2009).
41. Validation of the B3LYP/N07D and PBE0/N07D Computational Models for the Calculation of Electronic g-Tensors. Barone, V.; Cimino, P. Journal of Chemical Theory and Computation 5, 192-199 (2009).
42. First principle simulation of vibrationally resolved A2 B1□X2 A1 electronic transition of phenyl radical . Biczysko, M.; Bloino, J.; Barone, V. Chemical Physics Letters 471, 143-147 (2009).
43. Fully Integrated Approach to Compute Vibrationally Resolved Optical Spectra: From Small Molecules to Macrosystems. Barone, V.; Bloino, J.; Biczysko, M.; Santoro, F. Journal of Chemical Theory and Computation 5, 540-554 (2009).
44. Role of surface oxygen vacancies in photoluminescence of tin dioxide nanobelts . Trani, F.; Causà, M.; Lettieri, S.; Setaro, A.; Ninno, D.; Barone, V.; Maddalena, P. Microelectronics Journal 40, 236-238 (2009).
45. Role and Effective Treatment of Dispersive Forces in Materials: Polyethylene and Graphite Crystals as Test Cases . Barone, V.; Casarin, M.; Forrer, D.; Pavone, M.; Sambi, M.; Vittadini, A. Journal of Computational Chemistry 30, 934-939 (2009).
46. On the Performance of Continuum Solvation Methods. A Comment on “Universal Approaches to Solvation Modeling". Klamt, A.; Mennucci, B.; Tomasi, J.; Barone, V.; Curutchet, C.; Orozco, M.; Luque, F.J. Accounts of Chemical Research 42, 489-492 (2009).
47. Theory for Vibrationally Resolved Two-Photon Circular Dichroism Spectra. Application to (R)-(+)-3-Methylcyclopentanone. Lin, N.; Santoro, F.; Rizzo, A.; Luo, Y.; Zhao, X.; Barone, V. Journal of Physical Chemistry A 113, 4198-4207 (2009).
48. UV-Vis Spectra of the Anticancer Campothecin Family Drugs in Aqueous Solution: Specific Spectroscopic Signatures Unraveled by a Combined Computational and Experimental Study. Sanna, N.; Chillemi, G.; Gontrani, L.; Grandi, A.; Mancini, G.; Castelli, S.; Zagotto, G.; Zazza, C.; Barone, V.; Desideri, A. Journal of Physical Chemistry B 113, 5369-5375 (2009).
49. Modified virtual orbitals for CI calculations of energy splitting in organic diradicals. Barone, V.; Cacelli, I.; Ferretti, A.; Prampolini, G. Physical Chemistry Chemical Physics 11, 3854-3860 (2009).
50. Toward spectroscopic studies of biologically relevant systems: Vibrational spectrum of adenine as a test case for performances of long-range/dispersion corrected density functionals. Biczysko, M.; Panek, P.; Barone, V. Chemical Physics Letters 475, 105-110 (2009).
51. Lack of Visible Chromophore Development in the Pulse Radiolysis Oxidation of 5,6-Dihydroxyindole-2-carboxylic Acid Oligomers: DFT Investigation and Implications for Eumelanin Absorption Properties. Pezzella, A.; Panzella, L.; Crescenzi, O.; Napolitano, A.; Navaratnam, S.; Edge, R.; Land, E.J.; Barone, V.; D'Ischia, M. Journal of Organic Chemistry 74, 3727-3734 (2009).
52. agnetic coupling in bis-nitronylnitroxide radicals: The role of aromatic bridges. Barone, V.; Cacelli, I.; Ferretti, A. Journal of Chemical Physics 130, 094306 (2009).
53. Benzothiopyranoindole-Based Antiproliferative Agents: Synthesis, Cytotoxicity, Nucleic Acids Interaction, and Topoisomerases Inhibition Properties. Dalla Via, L.; Marciani Magno, S.; Gia, O.; Marini, A.M.; Da Settimo, F.; Salerno, S.; La Motta, C.; Simorini, F.; Taliani, S.; Lavecchia, A.; Di Giovanni, C.; Brancato, G.; Barone, V.; Novellino, E. Journal of Medicinal Chemistry 52, 5429-5441 (2009).
54. Theoretical Study of the X2NO Systems (X = F, Cl, Br, I): Effects of Halogen Substitution on Structural and Spectroscopic Properties. Puzzarini, C.; Barone, V. Journal of Chemical Theory and Computation 5, 2378-2387 (2009).
55. Existence of energy minimums for thin elastic rods in static helical configurations. Argeri, M.; Barone, V.; De Lillo, S.; Lupo, G.; Sommacal, M. Theoretical and Mathematical Physics 159, 698-711 (2009).
56. Periodic DFT modeling of bulk and surface properties of MgCl2. Credendino, R.; Busico, V.; Causà, M.; Barone, V.; Budzelaard, P.H.M.; Zicovich-Wilsone, C. Physical Chemistry Chemical Physics 11, 6525-6532 (2009).
57. Magneto-Structural Relationships for Radical Cation and Neutral Pyridinophane Structures with Intrabridgehead Nitrogen Atoms. An Integrated Experimental and Quantum Mechanical Study. Williams, F.; Chen, G.F.; Mattar, S.M.; Scudder, P.H.; Trieber II, D.A.; Saven, J.G.; Whritenour, D.C.; Cimino, P.; Barone, V. Journal of Physical Chemistry B 113, 9026-9034

(2009).

58. Elastic rods in life- and material-sciences: A general integrable model. Argeri, M.; Barone, V.; De Lillo, S.; Lupo, G.; Sommacal, M. Physica D: Nonlinear Phenomena 238, 1031-1049 (2009).
59. Quantum Dynamics of the Ultrafast ππ*/nπ Population transfer in Uracil and 5-Fluoro-Uracil in Water and Acetonitrile. Improta, R.; Barone, V.; Lami, A.; Santoro, F. Journal of Physical Chemistry B 113, 14491-14503 (2009).
60. Molecular dynamics simulations in a NpT ensemble using non-periodic boundary conditions. Brancato, G.; Rega, N.; Barone, V. Chemical Physics Letters 483, 177-181 (2009).
61. The Gas Phase Anisole Dimer: A Combined High-Resolution Spectroscopy and Computational Study of a Stacked Molecular System. Pietraperzia, G.; Pasquini, M.; Schiccheri, N.; Piani, G.; Becucci, M.; Castellucci, E.; Biczysko, M.; Bloino, J.; Barone, V. Journal of Physical Chemistry A 113, 14343-14351 (2009).
62. Accurate yet feasible post-Hartree–Fock computation of magnetic interactions in large biradicals through a combined variational/perturbative approach: Setup and validation. Barone, V.; Cacelli, I.; Ferretti, A.; Prampolini, G. Journal of Chemical Physics 131, 224103 (2009).
63. Simulation of electron spin resonance spectroscopy in diverse environments: An integrated approach. Zerbetto, M.; Polimeno, A.; Barone, V. Computer Physics Communications 180, 2680-2697 (2009).
64. A quantum mechanical study of TiCl3 α, β and γ crystal phases: geometry, electronic structure and magnetism. Sementa, L.; D'Amore, M.; Barone, V.; Busico, V.; Causà, M. Physical Chemistry Chemical Physics 11, 11264-11275 (2009).
65. On the stability of X2NO radicals (X = F, Cl, Br, I). Puzzarini, C.; Barone, V. Physical Chemistry Chemical Physics 11, 11463-11470 (2009).
66. Sensors for DNA detection: theoretical investigation of the conformational properties of immobilized single-strand DNA. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini, G. Physical Chemistry Chemical Physics 11, 10644-10656 (2009).
67. PCM/TD-DFT study of the two lowest excited states of uracil derivatives in solution: The effect of the functional and of the cavity model. Improta, R.; Barone, V. Journal of Molecular Structure (Theochem) 914, 87-93 (2009).
68. Magnetic Interactions in Phenyl-Bridged Nitroxide Diradicals: Conformational Effects by Multireference and Broken Symmetry DFT Approaches. Barone, V.; Cacelli, I.; Cimino, P.; Ferretti, A.; Monti, S.; Prampolini, G. Journal of Physical Chemistry A 113, 15150-15155 (2009).
69. Force-Field Modeling through Quantum Mechanical Calculations: Molecular Dynamics Simulations of a Nematogenic Molecule in its Condensed Phases. Cacelli, I.; Lami, C.F.; Prampolini, G. Journal of Computational Chemistry 30, 366-378 (2009).
70. Chemical Detail Force Fields for Mesogenic Molecules. Cacelli, I.; Cimoli, A.; De Gaetani, L.; Prampolini, G.; Tani, A. Journal of Chemical Theory and Computation 5, 1865-1876 (2009).
71. Computational study through atomistic potentials of a partial bilayer liquid crystal: structure and dynamics. De Gaetani, L.; Prampolini, G. Soft Matter 5, 3517-3526 (2009).
72. Solvent-Induced Stereochemical Behavior of a Bile Acid-Based Biphenyl Phosphite: A Computational Study. Cimoli, A.; Prampolini, G.; Tani, A. Journal of Physical Chemistry A 113, 14930-14935 (2009).
73. Mechanical properties and deformation mechanisms of nanocrystalline Fe/Cu 60/40 composites. Tagarielli, V.L.; Fleck, N.A.; Colella, A.; Matteazzi, P. Journal Of Materials Science, 46, 2, 385-393 (2009).
74. Modeling the fluorescence of protein-embedded tryptophans with ab initio multiconfigurational quantum chemistry: the limiting cases of Parvalbumin and Monellin. Pistolesi, S.; Sinicropi, A.; Pogni, R.; Basosi, R.; Ferrè, N.; Olivucci, M. The Journal of Physical Chemistry B 113, 16082-16090 (2009).
75. A novel biomimetic photochemical switch at work: Design of a photomodulable peptide. Sinicropi, A.; Bernini, C.; Basosi, R.; Olivucci, M. Photochemical & Photobiologicla Sciences 8, 1639-1649 (2009).
76. Humanin structural versatility and interaction with model Cerebral Cortex Membranes. Pistolesi, S.; Rossini, L.; Ferro, E.; Basosi, R.; Trabalzini, L.; Pogni, R. Biochemistry 48 (22), 5026–5033 (2009).
77. Protein radicals in fungal versatile peroxidase: Catalytic tryptophan radical in both Coumpound-I and Coumpound-II and studies on W164Y, W164H and W164S variants. Ruiz-Duenas, F.J.; Pogni, R.; Morales, M.; Giansanti, S.; Mate, M.J.; Romero, A.; Martinez, M.J.;

Basosi, R.; Martinez, A.T. Journal of Biological Chemistry 284(12), 7986-7994 (2009).

78. Structural studies in solution and in the solid state on the zinc chelate of 2-hydroxy-(4-methylthio) butanoic acid, an effective mineral supplement in animal feeding. Predieri, G.; Beltrami, D.; Pattacini, R.; Parisi, M.L.; Sinicropi, A.; Valensin, D.; Basosi R. Inorganica Chimica Acta 362, 1115-1121, (2009).
79. Metti il girasole nel motore. Basosi, R. QualEnergia 4, 31-36 (2009).
80. An Hydrogen-solar system for zero emission heating and cooling. Fulini, P.; Cecchini, E.; Baldini, A.; Federici, M.; Basosi, R. International Journal of Heat and Technology 01, 127-132 (2009).
81. Evaluation of the energy efficiency evolution in the European road freight transport sector. Ruzzenenti, F.; Basosi, R. Energy Policy 37, 4079-4085 (2009).
82. Air versus terrestrial transport modalities: an energy and environmental comparison. Federici, M.; Ulgiati, S.; Basosi, R. Energy 34, 1493-1503 (2009).
83. Complexity change and space symmetry rupture. Ruzzenenti, F.; Basosi, R. Ecological Modelling 220, 1880-1885 (2009).
84. The advantages of the local scale: a pilot biodiesel production line in the Province of Siena, Italy. Federici, M.; Spinelli, D.; Basosi, R. Proceedings of Third Energy Management Conference 37-42, Parma (Italy) June, 4-5, (2009).
85. Un approccio teorico al cambiamento di complessità come effetto della rottura di simmetria. Ruzzenenti, F.; Federici, M.; Basosi, R. Proceedings of Third Energy Management Conference 43-48, Parma (Italy) June, 4-5 (2009).
86. Membrane proteins embedded in supported lipid bilayers employed in field effect electronic devices. Angione, M.D.; Mallardi, A.; Romanazzi, G.; Suranna, G.P.; Mastrorilli, P.; Cafagna, D.; De Giglio, E.; Palazzo, G.; Torsi, L. Proceedings of 3rd IEEE International Workshop on Advances in Sensors and Interfaces, IWASI 2009, art. no. 5184798, 218-221, Trani 25-26 June (2009).
87. Aerosol-OT Forms Oil-in-Water Spherical Micelles in the Presence of the Ionic Liquid bmimBF(4). Murgia, S.; Palazzo, G.; Monduzzi, M. Journal of Physical Chemistry B 113, 9216-9225 (2009).
88. Triazine herbicides determination in water with an optical biosensor. Autullo, M.; Mennuni, M.; Giustini, M.; Giomini, M.; Lopez, F.; Mallardi, A.; Palazzo, G. Proceedings of 3rd IEEE International Workshop on Advances in Sensors and Interfaces, IWASI 2009, art. no. 5184798, 213-217, Trani 25-26 June (2009).
89. Ca2+-dependent K+ Efflux is a Key Event in Deoxycholate-induced Apoptosis in BHK-21 and Caco-2 cells. Gerbino, A.; Ranieri, M.; Lupo, S.; Caroppo, R.; Debellis, L.; Maiellaro, I.; Caratozzolo, M.F.; Lopez, F.; Colella, M. Gastroenterology 137, 955-964 (2009).
90. Alkylation of complementary ribonucleotides by 1,2-dodecyl-epoxide in a micellar environment: a liquid chromatography–electrospray ionization–sequential mass spectrometry investigation. Losito, I.; Angelico, R.; Ceglie, A.; Diomede, S.; Palmisano, F. Journal of Mass Spectrometry 44, 1053-1065 (2009).
91. Dodecyl Epoxide - Water Microemulsion for the Synthesis of Novel Nucleo-Lipids. Angelico, R.; Ceglie, A.; Cuomo, F. Colloids and Surfaces B 70, 68-75 (2009).
92. Quenching Efficiency of Pyrene Fluorescence by Nucleotide Monophosphates in Cationic Micelles. Cuomo, F.; Palazzo, G.; Ceglie, A.; Lopez F. Journal of Photochemistry Photobiology A 201, 21-27 (2009).
93. Numerical simulation of dielectric spectra of aqueous suspensions of non-spheroidal differently shaped biological cells. Di Biasio, A.; Ambrosone, L.; Cametti, C. Journal of Physics D 42, art. no. 025401 (2009).
94. Fluorescence spectroscopy of synthetic melanin in solution. Perna, G.; Frassanito, M.C.; Palazzo, G.; Gallone, A.; Mallardi, A.; Biagi, P.F.; Capozzi, V. Journal of Luminescence 129, 44–49 (2009).
95. Aminofunctionalization and sub-micrometer patterning on silicon through silane doped agarose hydrogels. Manso Silvan, M.; Messina, G.M.L.; Montero, I.; Satriano, C.; García Ruiz, J.P.; Marletta, G. J. Mater. Chem. 19, 5226–5233 (2009).
96. A multitechnique study of preferential protein adsorption on hydrophobic and hydrophilic plasma-modified polymer surfaces. Messina, G.M.L.; Satriano, C.; Marletta, G. Colloids and Surfaces B: Biointerfaces 70, 76–83 (2009).
97. Supramolecular Self-Assembled Multilayers of Terpyridine-functionalized Perylene Bisimides Metal Complexes. Tuccitto, N.; Delfanti, I.; Torrisi, V.; Scandola, F.; Würthner, F.; Licciardello, A. Physical Chemistry Chemical Physics 11, 4033-4038 (2009).

98. Nanostructured morphologies of complexes containing porphyrin bridges between Pt(II) acetylide tethers. Amato, M.E.; Licciardello, A.; Torrisi, V.; Ugo, L.; Venditti, I.; Russo M.V. Material Science and Engineering C 29, 1010-1017 (2009).
99. Effect of headgroup chirality in nanoassemblies. Part 2. Thermal behavior of vitamin C-based surfactants. Lo Nostro, P.; Ambrosi, M.; Ninham, B.W.; Baglioni, P. Journal of Physical Chemistry B 113, 8324-8331 (2009).
100. Effect of headgroup chirality in nanoassemblies. Part 1. Self-assembly of D-isoascorbic acid derivatives in water. Ambrosi, M.; Lo Nostro, P.; Fratini, E.; Giustini, L.; Ninham, B.W.; Baglioni, P. Journal of Physical Chemistry B 113 1404-1412 (2009).
101. Soft hybrid nanostructures composed of phospholipid liposomes decorated with oligonucleotides. Banchelli, M.; Bombelli, F.B.; Berti, D.; Baglioni, P. Methods in Enzymology 464, 249-277 (2009).
102. [S-35] GTP gamma S binding studies of amphiphilic drugs-activated Gi proteins: A caveat. Manetti, D.; Mannelli, L.D.; Dei, S.; Guandalini, L.; Martini, E.; Banchelli, M.; Ghelardini, C. Bioorganic & Medicinal Chemistry Letters 19, 2224-2229 (2009).
103. Closed nanoconstructs assembled by step-by-step ss-DNA coupling assisted by phospholipid membranes. Bombelli, F.B.; Betti, F.; Gambinossi, F.; Caminati, G.; Brown, T.; Baglioni, P.; Berti, D. Soft Matter 5, 1639-1645 (2009).
104. Development and validation of europium-sensitized luminescence (ESL) method for the determination of tetracycline residues in milk. Morandi, S.; Focardi, C.; Nocentini, M.; Puggelli, M.; Caminati, G. Food Analytical Methods 2, 271-281 (2009).
105. Adsorption Isotherms of Aqueous C12E6 and Cetyltrimethylammonium Bromide Surfactants on Solid Surfaces in the Presence of Low Molecular Weight Coadsorbents. Shi, L.; Ghezzi, M.; Caminati, G.; Lo Nostro, P.; Grady, B.P.; Striolo, A. Langmuir 25, 5536-5544 (2009).
106. Gels for the Conservation of Cultural Heritage. Baglioni, P.; Dei, L.; Carretti, E.; Giorgi, R. Langmuir 25, 8373-8374 (2009).
107. Poly(vinyl alcohol)-borax hydro/cosolvent gels. Viscoelastic properties, solubilizing power, and application to art conservation. Carretti, E.; Grassi, S.; Cossalter, M.; Natali, I.; Caminati, G.; Weiss, R. G.; Baglioni, P.; Dei L. Langmuir 25 , 8656-8662 (2009). This paper has been cited by:Nature Materials 8, 446 (2009).
108. Soft condensed matter for the conservation of cultural heritage. Baglioni, P.; Giorgi, R.; Dei, L. Compte Rendus Chimie, 12, 61-69 (2009).
109. Lo stato di conservazione delle fibre di lino delle tele di Giovanni Fattori: un contributo di conoscenza per l'operatività nel restauro. Giorgi, R.; Baglioni, P.; Citti, G.; Chelazzi, D.; Mosto, V.; Adoni, E.; Paciulli, L.; Zecchi, S.G.; Pizzorusso, G. Con la matita e col pennello. Giovanni Fattori, Mauro Pagliai editore, 81-85 (2009).
110. Nanoparticles of calcium hydroxide for wood deacidification: decreasing the emissions of organic acid vapors in church organ environments. Giorgi, R.; Baglioni, P.; Chelazzi, D.; Fratini, E.; Langer, S.; Niklasson, A.; Rådemar, M.; Svensson, J.-H. Journal of Cultural Heritage, 10, 206-213 (2009).
111. Nanoscience contribution to preservation of acidic shipwrecks. Giorgi, R.; Chelazzi, D.; Baglioni, P. Proceedings of the 10th ICOM-CC conference on Wet Organic Archaeological Materials - WOAM 2007, Amsterdam on September 10-15, 2007, Editors: K. Straetkvern, D.J. Huisman, RACM: Amersfoort, 525-538 (2009).
112. Surfactant-based photorheological fluids: the effect of the surfactant structure. Baglioni, P.; Braccalenti, E.; Carretti, E.; Germani, R.; Goracci, L.; Savelli, G.; Tiecco. M. Langmuir 25, 5467-5475 (2009).
113. Structural behavior of highly concentrated hyaluronan. Matteini, P.; Dei, L.; Carretti, E.; Volpi, N.; Goti, A.; Pini R. Biomacromolecules 10, 1516-1522 (2009).
114. Noninvasive physicochemical characterization of two 19th century English ferrotypes Carretti, E.; Dei, L.; Milano, M.; Baglioni P. Journal of Cultural Heritage 10, 501-508 (2009).
115. Evidence of dynamic crossover phenomena in water and other glass-forming liquids: experiments, MD, simulations and theory. Chen, S.H.; Zhang, Y.; Lagi, M.; Chong, S.H.; Baglioni, P.; Mallamace, F. Journal of Physics-Condensed Matter 21, 50 (2009).
116. Logarithmic decay in single-particle relaxation of hydrated lysozyme powder. Lagi, M.; Baglioni, P.; Chen, S.H. Physical Review Letters 103, 10 (2009).
117. Receptor-independent modulation of reconstituted G alpha(i) protein mediated by liposomes. Luciani, P.; Berti, D.; Fortini, M.; Baglioni, P.; Ghelardini, C.; Pacini, A.; Manetti, D.; Gualtieri, F.; Bartolini, A.; Di Cesare Mannelli, L. Molecular Biosystems 5, 356-367 (2009).
118. Fluorescent-and Spin-Labeled Sulfonamides as Probe for Carbonic Anhydrase IX.Checchi, A.;

Ciani, L.; Ristori, S.; Supuran, C.T. Drug Design of Zinc-Enzyme Inhibitors ed. Supuran, C.T., Winum, J.Y., John Wiley & Sons, Inc. 9, 223-239 (2009).

119. Electron Spin Resonance Spectroscopy in Drug Delivery. Martini, G.; Ciani, L. Physical Chemistry Chemical Physics 11, 211-254 (2009).
120. Dissecting the Inhibition Mechanism of Cytosolic versus Transmembrane Carbonic Anhydrases by EPR. Ciani, L.; Cecchi, A.; Temperini, C.; Supuran, C.T.; Ristori, S. Journal of Physical Chemistry B 113, 13998-14005 (2009).
121. Carborane derivatives loaded into liposomes as efficient delivery systems for Boron Neutron Capture Therapy. Altieri, S.; Balzi, M.; Bortolussi, S.; Bruschi, P.; Ciani, L.; Clerici, A.M.; Faraoni, P.; Ferrari, C.; Gadan, M.A.; Panza, L.; Pietrangeli, D.; Ricciardi, G.; Ristori, S. Journal of Medicinal Chemistry, Centennial Issue 52, 7829-7835 (2009).
122. Observation of high-temperature dynamic crossover in protein hydration water and its relation to reversible denaturation of lysozyme. Zhang, Y.; Lagi, M.; Liu, D. Z.; Mallamace, F.; Fratini, E.; Baglioni, P.; Mamontov, E.; Hagen, M.; Chen, S. H. Journal of Chemical Physics 130, (13), - (2009).
123. Dynamic susceptibility of supercooled water and its relation to the dynamic crossover phenomenon. Zhang, Y.; Lagi, M.; Fratini, E.; Baglioni, P.; Mamontov, E.; Chen, S. H. Physical Review E 79, (4), - (2009).
124. Water Confined in Cement Pastes as a Probe of Cement Microstructure Evolution. Ridi, F.; Luciani, P.; Fratini, E.; Baglioni, P. Journal of Physical Chemistry B 113, (10), 3080-3087 (2009).
125. Dynamics of Water in Voids between Well-Defined and Densely Packed Spherical Nanocages Acting as Polyprotic Inorganic Acids. Faraone, A.; Fratini, E.; Todea, A. M.; Krebs, B.; Muller, A.; Baglioni, P. Journal of Physical Chemistry C 113, (20), 8635-8644 (2009).
126. Proteins Remain Soft at Lower Temperatures under Pressure. Chu, X. Q.; Faraone, A.; Kim, C.; Fratini, E.; Baglioni, P.; Leao, J. B.; Chen, S. H. Journal of Physical Chemistry B 113, (15), 5001-5006 (2009).
127. Neutron scattering studies of dynamic crossover phenomena in a coupled system of biopolymer and its hydration water. Chen, S. H.; Mallamace, F.; Chu, X. Q.; Kim, C.; Lagi, M.; Faraone, A.; Fratini, E.; Baglioni, P. Journal of Physics: Conference Series 177, 012006 (2009).
128. Gels from a Semifluorinated n-Alkane in Fluorinated Solvents as a Probe for Intermolecular Interactions. Tattini, L.; Lo Nostro, P.; Scalise, L.; Baglioni, P. Journal of Colloid and Interface Science 339, 259-265 (2009).
129. Anion-Specific Partitioning in Two-Phase Finite Volume Systems: Possible Implications for Mechanisms of Ion Pumps. Boström, M.; Lima, E.R.A.; Biscaia Jr.,E.C.; Tavares, E.W.; Lo Nostro, P.; Parsons, D.F.; Deniz, V.; Ninham, B.W. Journal of Physical Chemistry B 113, 8124-8127 (2009).
130. Adsorption Isotherms of Aqueous C12E6 and Cetyltrimethylammonium Bromide Surfactants on Solid Surfaces in the Presence of Low Molecular Weight Coadsorbents. Shi, L.; Ghezzi, M.; Caminati, G.; Lo Nostro, P.; Grady, B.P.; Striolo, A. Langmuir 25, 5536-5544 (2009).
131. Stiffening Agents and Process in Clothing. Lo Nostro, P.; Becheri, A.; Giustini, L.; Rodrigues, L.; Mendes, A. in Transforming Clothing Production into a Demand-Driven, Knowldege-Based, High-Tech Industry, Walter, L.; Kartsounis, G.-A.; Carosio, S. Eds. Springer (Dordrecht) (2009), ISBN 10.1007/978-1-978-1-84882-608-3.
132. Phase Separation Kinetics Of Maya Asphaltene Emulsion And Free-To-Bound Water Transformation. Ridi F.; Verdal, C.; Baglioni, P.; Sheu, E. Fuel, 88, 319-325 (2009).
133. Towards a general organogelator: combining a versatile scaffold and an efficient linking process. Ghini, G.; Lascialfari, L.; Vinattieri, C.; Cicchi, S.; Brandi, A.; Berti, D.; Betti, F.; Baglioni, P.; Mannini, M. Soft Matter 5, 1863-1869 (2009).
134. Intercalation of single-strand oligonucleotides between nucleolipid anionic membranes: a neutron diffraction study. Langmuir 25, 4084-4092 (2009).
135. Study of Bradykinin Conformation in the presence of Model Membrane by NMR and Molecular Modelling. Bonechi, C.; Ristori, S.; Martini, S.; Martini, G.; Rossi, C. BBA Biomembranes 1788, 708-716 (2009).
136. Hydrotropic Solubilization of Gold Nanoparticles Functionalized with Proto-Alkylthioporphyrazines. Ristori, S.; Ricciardi, G.; Pietrangeli, D.; Rosa, A.; Feis A. J. Phys. Chem C 113, 8537–8540 (2009).
137. Structural study of liposomes loaded with a GM3 lactone analogue for the targeting of tumor epitopes. Ristori, S.; Di Cola, E.; Lunghi, C.; Richichi, B.; Nativi, C. BBA Biomembranes,

1788, 2518-2525 (2009).

138. Non-zinc mediated inhibition of carbonic anhydrases: coumarins are a new class of suicide inhibitors. Maresca, A.; Temperini, C.; Vu, H.; Pham, N.B.; Poulsen, S.A.; Scozzafava, A.; Quinn, R.J.; Supuran, C.T. J. Am. Chem. Soc. 131, 3057-3062 (2009).
139. Synthesis and biological evaluation of a new family of anti-benzylanilinosulfonamides as CA IX inhibitors. Thiry, A.; Delayen, A.; Goossens, L.; Houssin, R.; Ledecq, M.; Frankart, A.; Dogné, J.M.; Wouters, J.; Supuran, C.T.; Hénichart, J.P.; Masereel, B. Eur. J. Med. Chem 44, 511-518 (2009).
140. Carbonic anhydrase inhibitors. Cloning, characterization and inhibition studies of the cytosolic isozyme III with anions. Nishimori, I.; Minakuchi, T.; Onishi, S.; Vullo, D.; Cecchi, A.; Scozzafava, A.; Supuran, C.T. J. Enz. Inhib. Med. Chem. 24, 70-76 (2009).
141. Carbonic anhydrase inhibitors. Biphenylsulfonamides with inhibitory action towards the transmembrane, tumor-associated isozymes IX possess cytotoxic activity against human colon, lung and breast cancer cell lines. Morsy, S.M.I.; Badawi, A.M.; Cecchi, A.; Scozzafava, A.; Supuran, C.T. J. Enzyme Inhib. Med. Chem. 24, 499-505 (2009).
142. Crystal structure of human carbonic anhydrase XIII and its complex with the inhibitor acetazolamide. Di Fiore, A.; Monti, S.M.; Hilvo, M.; Parkkila, S.; Romano, V.; Scaloni, A.; Pedone, C.; Scozzafava, A.; Supuran, C.T.; De Simone, G. Proteins 74, 164-175 (2009).
143. Carbonic anhydrase inhibitors. Comparison of chlorthalidone and indapamide X-ray crystal structures in adducts with isozyme II: when three water molecules and the keto-enol tautomerism make the difference. Temperini, C.; Cecchi, A.; Scozzafava, A.; Supuran, C.T. J. Med. Chem. 52, 322-328 (2009).
144. Ligand-based and structure-based virtual screening to identify carbonic anhydrase IX inhibitors. Thiry, A.; Ledecq, M.; Cecchi, A.; Frederick, R.; Dogné, J.-M.; Supuran, C.T.; Wouters, J.; Masereel, B. Bioorg. Med. Chem. 17, 553-557 (2009).
145. Therapeutic applications of glycosidic carbonic anhydrase inhibitors. Winum, J.Y.; Poulsen, S.-A.; Supuran, C.T. Med. Res. Rev. 29, 419-435 (2009).
146. Structure and inhibition of the CO2-sensing carbonic anhydrase Can2 from the pathogenic fungus Cryptococcus neoformans. Schlicker, C.; Hall, R.A.; Vullo, D.; Middelhaufe, S.; Gertz, M.; Supuran, C.T.; Muhlschlegel, F.A.; Steegborn, C. J. Mol. Biol. 385, 1207-20 (2009).
147. Metal based isatin-derived sulfonamides: Their synthesis, characterization, coordination behavior and biological activity. Chohan, Z.H.; Supuran, C.T.; Ben Hadda, T.; Nasim, F.U.; Khan, K.M. J. Enzyme Inhib. Med. Chem. 24, 859-870 (2009).
148. Cloning, characterization, post-translational modifications and inhibition studies of the latest mammalian carbonic anhydrase (CA) isoform, CA XV. Hilvo, M.; Salzano, A.M.; Innocenti, A.; Kulomaa, M.S.; Scozzafava, A.; Scaloni, A.; Parkkila, S.; Supuran, C.T. J. Med. Chem. 52, 646-654 (2009).
149. Carbonic anhydrase inhibitors. The membrane-associated isoform XV is highly inhibited by inorganic anions. Innocenti, A.; Hilvo, M.; Parkkila, S.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 1155-8 (2009).
150. Carbonic anhydrase inhibitors. Inhibition of human erythrocyte isozymes I and II with a series of antioxidant phenols. Şentürk, M.; Gülçin, I.; Daştan, A.; Küfrevioğlu, Ö.I.; Supuran, C.T. Bioorg. Med. Chem. 17, 3207-3211 (2009).
151. Carbonic anhydrase inhibitors. Inhibition studies of a coral secretory isoform with inorganic anions. Bertucci, A.; Innocenti, A.; Zoccola, D.; Scozzafava, A.; Allemand, D.; Tambutté, S.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 650-653 (2009).
152. Carbonic anhydrase inhibitors. Inhibition of the β-class enzyme from the yeast Saccharomyces cerevisiae with sulfonamides and sulfamates. Isik, S.; Kockar, F.; Aydin, M.; Arslan, O.; Ozensoy Guler, O.; Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. 17, 1158-1163 (2009).
153. Carbonic anhydrase inhibitors. Comparison of chlorthalidone, indapamide, trichloromethiazide and furosemide X-ray crystal structures in adducts with isozyme II, when several water molecules make the difference. Temperini, C.; Cecchi, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. 17, 1214-1221 (2009).
154. A thiabendazole sulfonamide with potent inhibitory activity against mammalian and nematode α-carbonic anhydrases. Crocetti, L.; Maresca, A.; Temperini, C.; Hall, R.A.; Scozzafava, A.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 1371-1375 (2009).
155. In Silico Drug Screening Approach for the Design of Magic Bullets: A Successful Example with Anti-HIV Fullerene Derivatized Amino Acids. Durdagi, S.; Supuran, C.T.; Strom, T.A.; Doostdar, N.; Kumar, M.K.; Barron, A.R.; Mavromoustakos, T.; Papadopoulos, M. J. Chem.

Inform. Model. 49, 1139-1143 (2009).

156. Inhibition of carbonic anhydrase isozymes with benzene sulfonamides incorporating thio, sulfinyl and sulfonyl glycoside tail moieties. Singer, M.; Lopez, M.; Bornaghi, L.F.; Innocenti, A.; Vullo, D.; Supuran, C.T.; Poulsen, S.-A. Bioorg. Med. Chem. Lett. 19, 2273-2276 (2009).
157. Carbonic anhydrase activators: Activation of the β-carbonic anhydrase Nce103 from the yeast Saccharomyces cerevisiae with amines and amino acids. Isik, S.; Kockar, F.; Aydin, M.; Arslan, O.; Ozensoy Guler, O.; Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 1662-1665 (2009).
158. Small-molecule suppression of misfolding of mutated human carbonic anhydrase II linked to marble brain disease. Almstedt, K.; Rafstedt, T.; Supuran, C.T.; Carlsson, U.; Hammarström, P. Biochemistry, 48, 5358-5364 (2009).
159. Carbonic anhydrase inhibitors: Two-prong versus mono-prong inhibitors of isoforms I, II, IX, and XII exemplified by photochromic cis-1,2-α-dithienylethene derivatives. Vomasta, D.; Innocenti, A.; König, B.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 1283-1286 (2009).
160. Carbonic anhydrase inhibitors. The nematode α-carbonic anhydrase of Caenorhabditis elegans CAH-4b is highly inhibited by 2-(hydrazinocarbonyl)-3-substituted-phenyl-1H-indole-5-sulfonamides. Güzel, Ö.; Innocenti, A.; Hall, R.A.; Scozzafava, A.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. 17, 3212-3215 (2009).
161. Carbonic anhydrase inhibitors. Inhibition of cytosolic carbonic anhydrase isozymes II and VII with simple aromatic sulfonamides and some azo dyes. Carta, F.; Pothen, B.; Maresca, A.; Tiwari, M.; Singh, V.; Supuran, C.T. Chem. Biol. Drug. Des. 74, 196-202 (2009).
162. Molecular cloning, characterization and inhibition studies of the Rv1284 β-carbonic anhydrase from Mycobacterium tuberculosis with sulfonamides and a sulfamate. Minakuchi, T.; Nishimori, I.; Vullo, D.; Scozzafava, A.; Supuran, C.T. J. Med. Chem. 52, 2226-2232 (2009).
163. Synthesis and evaluation of pharmacological profile of 1-aryl-6,7-dimethoxy-3,4-dihydroisoquinoline-2(1H)-sulfonamides. Gitto, R.; Ferro, S.; Agnello, S.; De Sarro, G.; Russo, E.; Vullo, D.; Supuran, C.T.; Chimirri, A. Bioorg. Med. Chem. 17, 3659-3664 (2009).
164. Carbonic anhydrase inhibitors. Inhibition of the beta-class enzymes from the fungal pathogens Candida albicans and Cryptococcus neoformans with aliphatic and aromatic carboxylates. Innocenti, A.; Hall, R.A.; Schlicker, C.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. 17, 2654-2657 (2009).
165. Carbonic anhydrase inhibitors. Cloning, characterization and inhibition studies of a new β-carbonic anhydrase from Mycobacterium tuberculosis. Nishimori, I.; Minakuchi, T.; Vullo, D.; Scozzafava, A.; Innocenti, A.; Supuran, C.T. J. Med. Chem. 52, 3116-3120 (2009).
166. Carbonic anhydrase inhibitors. Inhibition of cytosolic isoforms I, II, III, VII and XIII with less investigated inorganic anions. Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 1855-1857 (2009).
167. Carbonic anhydrase activators: Activation of human isozymes I, II and IX with phenylsulfonylhydrazido L-histidine derivatives. Abdo, M.-R.; Vullo, D.; Saada, M.-C.; Montero, J.L.; Scozzafava, A.; Winum, J.-Y.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 2440-2443 (2009).
168. Carbonic anhydrase inhibitors. Aromatic/heterocyclic sulfonamides incorporating phenacetyl-, pyridylacetyl- and thienylacetyl- tails act as potent inhibitors of human mitochondrial isoforms VA and VB. Güzel, Ö.; Innocenti, A.; Scozzafava, A.; Salman, A.; Supuran, C.T. Bioorg. Med. Chem. 17, 4894-4899 (2009).
169. Carbonic anhydrase inhibitors. Phenacetyl-, pyridylacetyl- and thienylacetyl-substituted aromatic sulfonamides act as potent and selective isoform VII inhibitors. Güzel, Ö.; Innocenti, A.; Scozzafava, A.; Salman, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 3170-3173 (2009).
170. Drug design studies of the novel antitumor targets carbonic anhydrase IX and XII. Ozensoy Guler, O.; De Simone, G.; Supuran, C.T. Curr. Med. Chem. 17, 1516-1526 (2009).
171. Carbonic anhydrase inhibitors. Inhibition of the human cytosolic isoforms I and II and transmembrane, tumor-associated isoforms IX and XII with boronic acids. Winum, J.Y.; Innocenti, A.; Scozzafava, A.; Montero, J.L.; Supuran, C.T. Bioorg. Med. Chem. 17, 3649-3652 (2009).
172. Taking advantage of tumor cell adaptations to hypoxia for developing new tumor markers and treatment strategies. Ebbesen, P.; Pettersen, E.O.; Gorr, T.A.; Jobst, G.; Williams, K.; Kienninger, J.; Wenger, R.H.; Pastorekova, S.; Dubois, L.; Lambin, P.; Wouters, B.G.; Supuran, C.T.; Poellinger, L.; Ratcliffe, P.; Kanopka, A.; Görlach, A.; Gasmann, M.; Harris, A.L.; Maxwell, P.; Scozzafava, A. J. Enzyme Inhib. Med. Chem. 24 (S1), 1-39 (2009).

173. Which carbonic anhydrases are targeted by the antiepileptic sulfonamides and sulfamates? De Simone, G.; Scozzafava, A.; Supuran, C.T. Chem. Biol. Drug. Des. 74, 317-321 (2009).
174. Dynamic combinatorial libraries in the presence of human carbonic anhydrase: towards hCA II isozyme-specific inhibitors. Nasr, G.; Petit, E.; Supuran, C.T.; Winum, J.-Y.; Barboiu, M. Bioorg. Med. Chem. Lett. 19, 6014-6017 (2009).
175. Carbonic anhydrase-encoded dynamic constitutional libraries: towards the discovery of isozyme-specific inhibitors. Nasr, G.; Petit, E.; Vullo, D.; Winum, J.-Y.; Supuran, C.T.; Barboiu, M. J. Med. Chem 52, 4853-4859 (2009).
176. Carbonic anhydrase inhibitors. Inhibition of the fungal β-carbonic anhydrases from Candida albicans and Cryptococcus neoformans with boronic acids. Innocenti, A.; Winum, J.-Y.; Hall, R.A.; Mühlschlegel, F.A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 2642-2645 (2009).
177. Carbonic anhydrase inhibitors. Inhibition and homology modeling studies of the fungal β-carbonic anhydrase from Candida albicans with sulfonamides. Innocenti, A.; Hall, R.A.; Schlicker, C.; Scozzafava, A.; Steegborn, C.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. 17, 4503-4509 (2009).
178. Discovery of low nanomolar and subnanomolar inhibitors of the mycobacterial β-carbonic anhydrases Rv1284 and Rv3273. Güzel, Ö.; Maresca, A.; Scozzafava, A.; Salman, A.; Balaban, A.T.; Supuran, C.T. J. Med. Chem. 52, 4063-4067 (2009).
179. Carbonic anhydrase inhibitors. Synthesis of 2,4,6-trimethylpyridinium derivatives of 2-(hydrazinocarbonyl)-3-aryl-1H-indole-5-sulfonamides acting as potent inhibitors of the tumor-associated isoform IX and XII. Güzel, Ö.; Maresca, A.; Scozzafava, A.; Salman, A.; Balaban, A.T.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 2931-2934 (2009).
180. Novel organometallic cationic Ru(II) Cp* benzenesulfonamide complexes targeted to inhibit carbonic anhydrase. Loughrey, B.T.; Williams, M.L.; Healy, P.C.; Vullo, D.; Innocenti, A.; Supuran, C.T.; Parsons, P.G.; Poulsen, S.A. J. Biol. Inorg. Chem. 14, 935-945 (2009).
181. Inhibition of Carbonic Anhydrase IX: A New Strategy Against Cancer. Winum, J.Y.; Scozzafava, A.; Montero, J.L.; Supuran, C.T. Anticanc. Agents Med. Chem. 9, 693-702 (2009).
182. Carbonic anhydrase inhibitors. Inhibition studies of a coral secretory isoform by sulfonamides. Bertucci, A.; Innocenti, A.; Zoccola, D.; Scozzafava, A.; Tambutté, S.; Supuran, C.T. Bioorg. Med. Chem. 17, 5054-5058 (2009).
183. Nitric oxide-donating carbonic anhydrase inhibitors for the treatment of open-angle glaucoma. Steele, R.M.; Batugo, M.R.; Benedini, F.; Biondi, S.; Borghi, V.; Carzaniga, L.; Impagnietello, F.; Miglietta, D.; Chong, W.K.M.; Rajapakse, R.; Cecchi, A.; Temperini, C.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 6565-6570 (2009).
184. New macrocyclic amines showing activity as HIV entry inhibitors against wild type and multi-drug resistant Viruses. Rusconi, S.; Lo Cicero, M.; Viganò, O.; Sirianni, F.; Bulgheroni, E.; Ferramosca, S.; Bencini, A.; Bianchi, A.; Ruiz, L.; Cabrera, C.; Martinez-Picado, J.; Supuran, C.T.; Galli, M. Molecules 14, 1927-1937 (2009).
185. Carbonic anhydrase inhibitors. Inhibition of the β-class enzyme from the pathogenic yeast Candida glabrata with anions. Innocenti, A.; Leewattanapasuk, W.; Mühlschlegel, F.A.; Mastrolorenzo, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 4802-4805 (2009).
186. Imaging of CA IX with fluorescent labelled sulfonamides distinguishes hypoxic and (re)-oxygenated cells in a xenograft tumour model. Dubois, L.; Lieuwes, N.G.; Maresca, A.; Thiry, A.; Supuran, C.T.; Scozzafava, A.; Wouters, B.G.; Lambin, P. Radiother. Oncol. 92, 423-428 (2009).
187. Carbonic anhydrase inhibitors. Comparison of aliphatic sulfamate/bis-sulfamate adducts with isozymes II and IX as a platform for designing tight-binding, more isoform-selective inhibitors. Vitale, R.M.; Alterio, V.; Innocenti, A.; Winum, J.-Y.; Monti, S.M.; De Simone, G.; Supuran, C.T. J. Med. Chem. 52, 5990-5998 (2009).
188. Crystal structure of the extracellular catalytic domain of the tumor-associated human carbonic anhydrase IX. Alterio, V.; Hilvo, M.; Di Fiore, A.; Supuran, C.T.; Pan, P.; Parkkila, S.; Scaloni, A.; Pastorek, J.; Pastorekova, S.; Pedone, C.; Scozzafava, A.; Monti, S.M.; De Simone, G. Proc. Natl. Acad. Sci. USA 106, 16233-16238 (2009).
189. The role of carbonic anhydrase 9 in regulating extracellular and intracellular pH in 3-D tumor-cell growths. Swietach, P.; Patiar, S.; Supuran, C.T.; Harris, A.L.; Vaughan-Jones, R.D. J. Biol. Chem. 284, 20299-20310 (2009).
190. Carbonic anhydrase inhibitors. Fluorinated phenyl sulfamates show strong inhibitory activity and selectivity for the inhibition of the tumor-associated isozymes IX and XII over the

cytosolic ones I and II. Winum, J.-Y.; Innocenti, A.; Montero, J.-L.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 5082-5085 (2009).

191. Dissecting the inhibition mechanism of cytosolic versus transmembrane carbonic anhydrases by ESR. Ciani, L.; Cecchi, A.; Temperini, C.; Supuran, C.T.; Ristori, S. J. Phys. Chem. B 113, 13998-14005 (2009).
192. Carbonic Anhydrase Inhibitors: Glycosylsulfanilamides act as subnanomolar inhibitors of the human secreted isoform VI. Winum, J.-Y.; Montero, J.-L.; Innocenti, A.; Supuran, C.T. Chem. Biol. Drug. Des. 74, 636-639 (2009).
193. Sildenafil is a strong activator of mammalian carbonic anhydrase isoforms I – XIV. Coban, T.A.; Beydemir, S.; Gülcin, I.; Ekinci, D.; Innocenti, A.; Vullo, D.; Supuran, C.T. Bioorg. Med. Chem. 17, 5791-5795 (2009).
194. Carbonic anhydrase inhibitors. Inhibition of the Rv1284 and Rv3273 β-carbonic anhydrases from Mycobacterium tuberculosis with diazenylbenzenesulfonamides. Maresca, A.; Carta, F.; Vullo, D.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 4929-4932 (2009).
195. S-glycosyl primary sulfonamides – a new structural class for selective inhibition of cancer-associated carbonic anhydrases. Lopez, M.; Paul, B.; Hofmann, A.; Morizzi, J.; Wu, Q.; Charman, S.A.; Innocenti, A.; Vullo, D.; Supuran, C.T.; Poulsen, S.-A. J. Med. Chem. 52, 6421-6432 (2009).
196. Carbonic anhydrase inhibitors. Characterization and inhibition studies of the most active β-carbonic anhydrase from Mycobacterium tuberculosis, Rv3588c. Carta, F.; Maresca, A.; Suarez Covarrubias, A.; Mowbray, S.L.; Jones, T.A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 6649-6654 (2009).
197. Carbonic anhydrase inhibitors. Diazenylbenzenesulfonamides are potent and selective inhibitors of the tumor-associated isozymes IX and XII over the cytosolic isoforms I and II. Carta, F.; Maresca, A.; Scozzafava, A.; Vullo, D.; Supuran, C.T. Bioorg. Med. Chem. 17, 7093-7099 (2009).
198. The proteoglycan region of the tumor-associated carbonic anhydrase isoform IX acts as an intrinsic buffer optimizing CO2 hydration at acidic pH values characteristic of solid tumors. Innocenti, A.; Pastorekova, S.; Pastorek, J.; Scozzafava, A.; De Simone, G.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 5825-5828 (2009).
199. Intact intracellular tail is critical for proper functioning of the tumor-associated, hypoxia-regulated carbonic anhydrase IX. Hulikova, A.; Zatovicova, M.; Svastova, E.; Ditte, P.; Brasseur, R.; Kettmann, R.; Supuran, C.T.; Kopacek, J.; Pastorek, J.; Pastorekova, S. FEBS Lett. 583, 3563-3568 (2009).
200. Covalent surface modification of titanium oxide with different adhesive peptides: Surface characterization and osteoblast-like cell adhesion. Dettin, M.; Bagno, A.; Gambaretto, R.; Iucci, G.; Conconi, M. T.; Tuccitto, N.; Menti, A. M.; Grandi, C.; Di Bello, C.; Licciardello, A.; Polzonetti, G. J. Biomed. Mater. Res. Part A, 90, 35-45 (2009).
201. Supramolecular Self-Assembled Multilayers of Terpyridine-functionalized Perylene Bisimides Metal Complexes. Tuccitto, N.; Delfanti, I.; Anastasi, E.; Torrisi, V.; Scandola, F.; Chiorboli, C.; Stepanenko, V.; Würthner, F.; Licciardello, A. Physical Chemistry Chemical Physics 11(20), 4033-4038 (2009).
202. Highly conductive extra-long molecular wires. Tuccitto, N.; Ferri, V.; Cavazzini, M.; Quici, S.; Zhavnerko, G.; Licciardello, A.; Rampi, M. A. Nature Materials, 8, 41-46 (2009).
203. Pulsed Radio Frequency Glow Discharge Time of Flight Mass Spectrometry for Molecular Depth Profiling of Polymer-based films. Tuccitto, N.; Tempez, A.; Lobo, L.; Delfanti, I.; Bordel, N.; Chapon, P.; Licciardello A. Rapid Commun. Mass Spectr., 23, 549-556 (2009).
204. 18O/16O isotopic separation in anodic tantala films by glow discharge time-of-flight mass spectrometry. Tempez, A.; Canulescu, S.; Molchan, I. S.; Doebeli, M.; Whitby, J. A.; Lobo, L.; Michler, J.; Thompson, G. E.; Bordel, N.; Chapon, P.; Skeldon, P.; Delfanti, I.; Tuccitto, N.; Licciardello, A. Surface and Interface Analysis, 41(12-13), 966-973 (2009).
205. Supramolecular self-assembled multilayers of terpyridine-functionalized perylene bisimide metal complexes. Tuccitto, N.; Delfanti, I.; Torrisi, V.; Scandola, F.; Chiorboli, C.; Stepanenko, V.; Wuerthner, F.; Licciardello, A. Physical Chemistry Chemical Physics, 11(20), 4033-4038 (2009).
206. Nanostructured morphologies of complexes containing porphyrin bridges between Pt(II) acetylide tethers. Amato, M. E.; Licciardello, A.; Torrisi, V.; Ugo, L.; Venditti, I.; Russo, M. V. Materials Science & Engineering, C: Materials for Biological Applications, 29(3), 1010-1017 (2009).
207. Pulsed radiofrequency glow discharge time-of-flight mass spectrometry for molecular depth

profiling of polymer-based films. Tuccitto, N.; Lobo, L.; Tempez, A.; Delfanti, I.; Chapon, P.; Canulescu, S.; Bordel, N.; Michler, J.; Licciardello, A. Rapid Communications in Mass Spectrometry, 23(5), 549-556 (2009).

208. Effects of the substrate on ToF-SIMS spectra of thin films of some fluorinated compounds deposited on calcarenite. Torrisi, A.; Tuccitto, N.; Licciardello, A. International Journal of Mass Spectrometry, 281(3), 157-166 (2009).
209. Study of bradykinin conformation in the presence of model membrane by Nuclear Magnetic Resonance and molecular modelling. Bonechi, C.; Ristori, S.; Martini, G.; Martini, S.; Rossi C. Biochimica et Biophysica Acta (Biomembranes) 1788, 708-716 (2009).
210. Antibacterial activity of grape extracts towards cagA positive and cagA negative Helicobacter pylori clinical isolates. Martini, S.; D'Addario, C.; Braconi, D.; Bernardini, G.; Bonechi, C.; Figura, N.; Santucci, A.; Rossi, C. Journal of Chemotherapy 21, 507-513 (2009).
211. Interaction Study of Bioactive Molecules with Fibrinogen and Human Platelets Determined by 1H-NMR Relaxation Experiments. Bonechi, C.; Martini, S.; Rossi, C. Bioorganic & Medicinal Chemistry 17, 1630-1635 (2009).
212. Antimicrobial activity against Helicobacter pylori strains and antioxidant properties of blackberry leaves (Rubus ulmifolius) and isolated compounds. Martini, S.; D'Addario C.; Colacevich, A.; Focardi, S.; Borghini, F.; Figura, N.; Santucci, A.; Rossi C. International Journal of Antimicrobial Agents 34 (1), 50-59 (2009).
213. Polysaccharide Based Hydrogels for Biomedical Applications. Leone, G.; Barbucci, R. In "Hydrogels: Biological Properties and Applications", 25-42 (2009).
214. 3D cell scaffolds for tissue engineering. Lamponi, S.; Di Canio, C.; Forbicioni, M.; Guerrini, A.; Barbucci, R. International Journal of Artifical Organs 32, 455-456 (2009).
215. Heterotypic cell-cell interaction on micropatterned surfaces. Lamponi, S.; Di Canio, C.; Barbucci, R. International Journal of Artifical Organs 32, 507-516 (2009).
216. The role of fibronectin in cell adhesion to spiral patterned TiO2 nanoparticles. Lamponi, S.; Forbicioni, M.; Barbucci, R. Journal of Applied Biomaterials and Biomechanics 7, 104-110, (2009).
217. The microalgae Tetraselmis Suecica in Mesocosms under different light regimes. Borghini, F.; Colacevich, A.; Bergamino, N.; Micarelli, P.; Dattilo, A.M.; Focardi, S.; Focardi, S.E.; Loiselle, S.A. Chemistry And Ecology 5, 345-357 (2009).
218. Lakes and reservoirs as regulators of carbon cycling and climate. Tranvik, L.J.; Downing, J.A.; Cotner, J.B.; Loiselle, S.A.; et al. Limnology and Oceanography 54, 2298-2314 (2009).
219. Modelling Upwelling Irradiance using Secchi disk depth in lake ecosystems. Bracchini, L.; Dattilo, A.M.; Hull, V.; Loiselle, S.A.; Tognazzi, A.; Rossi, C. Journal of Limnology 68, 83-91, (2009).
220. The optical characterization of chromophoric dissolved organic matter using the wavelength distribution of absorption spectral slopes. Loiselle, S.A.; Bracchini, L.; Cozar, A.; Ricci, M.; Dattilo, A.M.; Tognazzi, A.; Rossi, C. Limnology and Oceanography 54, 590-597 (2009).
221. Variability in photobleaching yields and their related impacts on optical conditions in subtropical lakes. Loiselle, S.; Bracchini, L.; Cózar, A.; Dattilo, M.D.; Tognazzi, A.; Rossi, C.. Journal of Photochemistry and Photobiology B-Biology 95, 129-137 (2009).
222. Use of a novel transfer function to reduce repolarization interval hysteresis. Halámek, J.; Jurák P.; Novák, T.M.; Vondra, V.; Kara T.; Villa, M.; Fráňa P.; Souček, M.; Somers, V.K.; J Interv. Card Electrophysiol 29, 23–32 (2010).
223. Crystalline and amorphous phases of a new drug, Bruni. G.; Milanese, C.; Berbenni, V.; Sartor, F.; Villa, M.; Marini, A. Journal of Thermal Analysis and Calorimetry 102, 297–303 (2010).
224. Nanoporous Nickel by electrochemical dealloying. Rouya, E.; Mallet, J.J.; Salvi, P.; Villa, M.; Begley, M.; Kelly, R.J.; Reed, M.; Zangari G.; Transaction of the Materials Research of Japan, 35 (1), 23-26 (2010).
225. Shine-Dalgarno sequence enhances the efficiency of lacZ repression by artificial anti-lac antisense RNAs in Escherichia coli. Stefan, A., Schwarz, F., Bressanin, D., Hochkoeppler, A. Journal of Bioscience and Bioengineering 110, 523-528 (2010).
226. Biodiesel from microalgae in Microbiology of Hydrocarbons, oils, lipids and derived compounds. Salis, A.; Nicolò M.; Guglielmino, S.; Solinas, V. Ed. Timmis, K., Springer Berlin Heidelberg 2827-2839 (2010). ISBN: 978-3-540-77584-3
227. Ion Specific Surface Charge Density of SBA-15 Mesoporous Silica. Salis, A.; Parsons, D.F.; Boström, M.; Medda, L.; Barse, B.; Ninham, B.; Monduzzi, M. Langmuir 26, 2484-2490 (2010).

228. Why Direct or Reversed Hofmeister Series? Interplay of Hydration, Non-electrostatic Potentials, and Ion Size. Parsons, D.F.; Boström, M.; Maceina, T.J.; Salis, A.; Ninham, B.W. Langmuir 26, 3323-3328 (2010).
229. Effect of Oxidation Level of n+-type Mesoporous Silicon Surface on the Adsorption and the Catalytic Activity of Candida rugosa Lipase. Salis, A.; Cugia, F.; Setzu, S.; Mula, G.; Monduzzi, M. Journal of Colloid and Interface Science 345, 448-453 (2010).
230. Specific Ion Effects on Adsorption of Lysozyme on Functionalized SBA-15 Mesoporous Silica. Salis, A.; Bhattacharyya, M.S.; Monduzzi, M. The Journal of Physical Chemistry B 114, 7996-8001 (2010).
231. Lysozyme Adsorption and Release From Ordered Mesoporous Materials. Bhattacharyya, M.S.; Hiwale, P.; Piras, M.; Medda, L.; Steri, D.; Piludu, M.; Salis, A.; Monduzzi, M. The Journal of Physical Chemistry C 114 (2010) 19928-19934.
232. A selective, non toxic, OFF-ON fluorescent molecular sensor based on 8-hydroxyquinoline for probing Cd2+ in living cells. Mameli, M.; Aragoni, M. C.; Arca, M.; Caltagirone, C.; Demartin, F.; Farruggia, G.; De Filippo, G.; Devillanova, F.; Garau, A.; Isaia, F.; Lippolis, V.; Murgia, S.; Prodi, L.; Pintus, A.; Zaccheroni, N. Chemistry – A European Journal 16, 919-930 (2010).
233. Iron(III) and aluminum(III) complexes with hydroxypyrone ligands aimed to design kojic acid derivatives with new perspectives. Nurchi, V. M.; Crisponi, G.; Lachowicz, J. I.; Murgia, S.; Pivetta, T.; Remelli, M.; Rescigno, A.; Niclós-Gutíerrez, J.; González-Pérez, J. M.; Domínguez-Martín, A.; Castiñeiras, A.; Szewczuk, Z. Journal of Inorganic Biochemistry, 104, 560-569 (2010).
234. Nanoparticles from lipid-based liquid crystals: emulsifier influence on morphology and cytotoxicity. Murgia, S.; Falchi, A. M.; Mano, M.; Lampis, S.; Angius, R.; Carnerup, A. M.; Schmidt, J.; Diaz, G.; Giacca, M.; Talmon, Y.; Monduzzi M. Journal of Physical Chemistry B 114, 3518-3525 (2010).
235. Nucleotide recognition and phosphate linkage hydrolysis at a lipid cubic interface. Murgia, S.; Lampis, S.; Zucca, P.; Sanjust, E.; Monduzzi M. Journal of the American Chemical Society, 132, 16176-16184 (2010).
236. Is the bleaching of phenosafranine by hydrogen peroxide oxidation catalyzed by silica-supported 5,10,15,20-tetrakis-(sulfonatophenyl)porphine-Mn(III) really biomimetic? Zucca, P.; Vinci, C.; Rescigno, A.; Dumitriu, E.; Sanjust, E. Journal of Molecular Catalysis A: Chemical 321, 27-33 (2010).
237. Evaluation of antioxidant capacity of antioxidant-declared beverages marketed in Italy. Zucca, P.; Sanjust, E.; Trogu, E.; Sollai, F.; Rescigno, A. It. J. Food Sci. 3313-319 (2010).
238. Bacillus subtilis fadB (ysiB) gene encodes an enoyl-CoA hydrataseFrandi, Zucca, P.; Marvasi, M.; Mastromei, M.; Sanjust, E.; Perito, B. Annals of Microbiology IN PRESS (2010).
239. Biodiesel from microalgae. Salis, A.; Nicolò, M.; Guglielmino, S.; Solinas, V. In Multi. Handbook of Hydrocarbon and Lipid Microbiology 32, 2827-2839 (2010).
240. Phage Display technology: new biotechnological applications in synthetic biology. Carnazza S.; Guglielmino S. International Journal Of Medical and Biological Frontiers 1081-3829 (2010).
241. Phage Display as a tool for synthetic biology: new perspectives in nano-biotechnology. Carnazza S.; Guglielmino S. In Synthetic and Integrative Biology: Parts and Systems, Design Theory and Applications, J.T. Genova (Ed.), Nova Science Publishers, Chap. 1 (Hardcover & On-line Book) (2010).
242. Phage Display as a Tool for Synthetic Biology. Carnazza, S.; Guglielmino S. Softcover Book Nova Science Publishers, (2010).
243. New Research Trends in Protein Chip Technology. Carnazza, S.; Guglielmino, S. Special Review Book in Biological Sciences, Research SignPost, (2010).
244. Synthesis and characterization of poly(3-hydroxyalkanoates) from Brassica carinata oil with high content of erucic acid and from very long chain fatty acids. Impallomeni, G.; Ballistreri, A.; Carnemolla, G.; Guglielmino, S.; Nicolò, M.; Cambria, M. International Journal of Biological Macromolecules 137-145 (2010).
245. ToF-SIMS imaging of surface self-organized fractal patterns of bacteria. Tuccitto, N.; Marletta, G.; Carnazza, S.; Grasso, L.; Caratozzolo M.; Guglielmino, S.; Licciardello, A. Surf. Interface Anal. 43, 370-375 (2010).
246. Peptide modified nanocarriers for selective targeting of bombesin receptors. Accardo, A.; Mansi, R.; Morisco, A.; Mangiapia, G.; Paduano, L.; Tesauro, D.; Radulescu, A.; Aurilio, M.; Aloj, L.; Arra, C.; Morelli, G. Molecular BioSystems 6, 878-887 (2010).

247. On the determination of the spinodal curve for the system water + chloroform + acetic acid from the mutual diffusion coefficients. Buzatu, D.; Buzatu, F. D.; Lungu, R. P.; Paduano, L.; Sartorio, R. Romanian Journal of Physics 55, 342-351 (2010).
248. Design, Synthesis and Characterisation of a Fluorescently Labelled CyPLOS Ionophore. Coppola, C.; Paciello, A.; Mangiapia, G.; Licen, S.; Boccalon, M.; De Napoli, L.; Paduano, L.; Tecilla, P.; Montesarchio, D. Chemistry - An European Journal 16, 13757-13772 (2010).
249. Evaluation of alkyl sulfate and sulfonate micellar structure at the water-surfactant interphase with simple geometrical calculations. Del Re, G.; D'Errico, G.; Ortona, O.; Vitagliano, V. Journal of Colloid and Interface Science 349, 230-235 (2010).
250. NMR of liquids crystals and micellar solutions. D'Errico, G.; Paduano, L. Nuclear Magnetic Resonance 39, 424-455 (2010).
251. Characterization of liposomes formed by lipopolysaccharides from Burkholderia cenocepacia, Burkholderia multivorans and Agrobacterium tumefaciens: from the molecular structure to the aggregate architecture. D'Errico, G.; Silipo, A.; Mangiapia, G.; Vitiello, G.; Radulescu, A.; Molinaro, A.; Lanzetta, R.; Paduano, L. Physical Chemistry Chemical Physics 12, 13574-13585 (2010).
252. Role of membranotropic sequences from herpes simplex virus type I glycoproteins B and H in the fusion process. Galdiero, S.; Falanga, A.; Vitiello, G.; Vitiello, M.; Pedone, C.; D'Errico, G.; Galdiero, M. Biochemical and Biophysical Acta, Biomembranes. 1798, 579-591 (2010).
253. Membrane charge dependent states of the beta -amyloid fragment Abeta (16-35) with differently charged micelle aggregates. Grimaldi, M.; Scrima, M.; Esposito, C.; Vitiello, G.; Ramunno, A.; Limongelli, V.; D'Errico, G.; Novellino, E.; D'Ursi, A. M. Biochemical and Biophysical Acta, Biomembranes, 1798, 660-671 (2010).
254. Interaction of poly(vinyl alcohol) with poly(acrylic acid) and with sodium polyacrylate in aqueous solutions: a volumetric study at 25 °C. Molisso, A.; Mangiapia, G.; D'Errico, G.; Sartorio, R. Journal of Solution Chemistry 39, 1627-1635 (2010).
255. Inhomogeneities in sodium decylsulfate doped 1,2-dipalmitoylphosphatidylcholine bilayer. Ortona, O.; Vitagliano, V.; Fessas, D.; Del Vecchio, P.; D'Errico, G. Journal of Colloid and Interface Science 343, 401-407 (2010).
256. Structural characterization of the transmembrane proximal region of the hepatitis C virus E1 glycoprotein. Spadaccini, R.; D'Errico, G.; D'Alessio, V.; Notomista, E.; Bianchi, A.; Merola, M.; Picone, D. Biochemical and Biophysical Acta, Biomembranes 1798, 344-353 (2010).
257. Effect of flavonoids on the Abeta (25-35)-phospholipid bilayers interaction. Tedeschi, A.; D'Errico, G.; Lauro, M. R.; Sansone, F.; Di Marino, S.; D'Ursi, A. M.; Aquino, R. P. European Journal of Medicinal Chemistry 45, 3998-4003 (2010).
258. A diffusion study on the ternary system, sodium cholate-sodium deoxycholate-water. Vitagliano, V.; Sartorio, R.; Ortona, O.; Paduano, L.; D'Errico, G.; Capuano, F.; Mangiapia, G. Journal of Molecular Liquids 156, 70-75 (2010).
259. Interaction of a beta -sheet breaker peptide with lipid membranes. Vitiello, G.; Grimaldi, M.; Ramunno, A.; Ortona, O.; De Martino, G.; D'Ursi, A. M.; D'Errico, G. Journal of Peptide Science 16, 115-122 (2010).
260. Mg – Ni – Cu mixtures for hydrogen storage: a kinetic study. Milanese, C.; Girella, A.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. Intermetallics 18, 203-211 (2010).
261. Solid state synthesis of CuFe2O4 from Cu(OH)2·CuCo3-4FeC2O4·2H2O mixtures: mechanism of reaction and thermal characterization of CuFe2O4. Berbenni, V.; Marini, A.; Milanese, C.; Bruni, G. Journal of Thermal Analysis and Calorimetry 99, 437-442 (2010).
262. Effect Of C (Graphite) Doping On The H2 Sorption Performance of The Mg – Ni Storage System. Milanese, C.; Girella, A.; Garroni, S.; Bruni, G.; Berbenni, V.; Matteazzi, P.; Marini, A. International Journal of Hydrogen Energy 35, 1285-1295 (2010).
263. Mechano-thermally Activated Solid-State Synthesis of Li4Ti5O12 Spinel from Li2CO3-TiO2 Mixtures. Berbenni, V.; Milanese, C.; Bruni, G.; Marini, A. Zeitschrift für Naturforschung B 65, 23-26 (2010).
264. New solid modifications of nateglinide. Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Lanfranconi, S.; Marini, A. Journal of Pharmaceutical and Biomedical Analysis 51, 1054-1059 (2010).
265. Sorption properties of NaBH4/MH2 (M = Mg, Ti) powder systems. Garroni, S.; Milanese, C.; Girella, A.; Marini, A.; Menéndez, E.; Pistidda, C.; Dornheim, M.; Suriñach, S.; Baró, M.D. International Journal of Hydrogen Energy 35, 5434-5441 (2010).
266. Synergetic effect of C (graphite) and Nb2O5 on the H2 sorption properties of the Mg - MgH2 system. Milanese, C.; Girella, A.; Garroni, S.; Bruni, G.; Berbenni, V.; Matteazzi, P.; Marini,

A. International Journal of Hydrogen Energy 35, 9027-9037 (2010).

267. Mechanothermal Solid-State Synthesis of Cobalt (II) Ferrite and determination of Heat Capacity by MTDSC. Berbenni, V.; Milanese, C.; Bruni, G.; Girella, A.; Marini, A. Zeitschrift für Naturforschung B 65, 1434-1438 (2010).
268. Crystalline and Amorphous Phases of a New Drug. Bruni, G.; Milanese, C.; Berbenni, V.; Sartor, F.; Villa, M.; Marini, A. Journal of Thermal Analysis and Calorimetry 102, 297-303 (2010).
269. Drug-excipient compatibility studies in binary and ternary mixtures by physico-chemical techniques. Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Marini, A. Journal of Thermal Analysis and Calorimetry 102, 193-201 (2010).
270. Influence of particle size and crystal orientation on the electrochemical behavior of carbon-coated LiFePO4. Ferrari, S.; Lavall, R.L.; Capsoni, D.; Quartarone, E.; Magistris, A.; Mustarelli, P.; Canton, P. Journal of Physical Chemistry C 114, 12598–12603 (2010).
271. Structural, spectroscopic and electrical features of undoped and Mn doped LiTi2(PO4)3. Capsoni, D.; Bini, M.; Ferrari, S.; Mustarelli, P.; Massarotti, V.; Mozzati, M.C.; Spinella, A. Journal of Physical Chemistry C 114, 13872–13878 (2010).
272. Phase homogeneity and stability in undoped and Mn doped LiFePO4. Galinetto, P.; Mozzati, M.C.; Grandi, M.S.; Bini, M.; Capsoni, D.; Ferrari, S.; Massarotti, V. Journal of Raman Spectroscopy 41, 1276-1282 (2010).
273. Ball-milling and AlB2 addition effects on the hydrogen sorption properties of the CaH2+MgB2 system. Schiavo, B.; Girella, A.; Agresti, F.; Capurso, G.; Milanese, C. Journal of Alloys and Compounds in press, doi:10.1016/j.jallcom.2010.11.045.
274. Characterization of Nicergoline polymorphs crystallized in several organic solvents. Malaj, L.; Censi, R.; Capsoni, D.; Pellegrino, L.; Bini, M.; Ferrari, S.; Gobetto, R.; Massarotti, V.; Di Martino, P. Journal of Pharmaceutical Sciences, accepted for publication.
275. Effects of Electronic and Lattice Polarization on the Band Structure of Delafossite Transparent Conductive Oxides. Vidal, J.; Trani, F.; Bruneval, F.; Marques, M.A.L.; Botti, S. Physical Review Letters 104, 136401 (2010).
276. Band structures of delafossite transparent conductive oxides from a self-consistent GW approach. Trani, F.; Vidal, J.; Botti, S.; Marques, M.A.L. Physical Review B 82, 085115 (2010).
277. DFT Study on Anatase TiO2 Nanowires: Structure and Electronic Properties As Functions of Size, Surface Termination, and Morphology. Iacomino, A.; Cantele, G.; Trani, F.; Ninno, D. Journal of Physical Chemistry C 114, 12389-12400 (2010).
278. Validation of the DFT/N07D computational model on the magnetic, vibrational and electronic properties of vinyl radical. Barone, V.; Bloino, J.; Biczysko, M. Physical Chemistry Chemical Physics 12, 1092-1101 (2010).
279. Absorption and emission UV-Vis spectra of the TRITC fluorophore molecule in solution: a quantum mechanical study. Pedone, A.; Bloino, J.; Monti, S.; Prampolini, G.; Barone, V. Physical Chemistry Chemical Physics 12, 1000-1006 (2010).
280. Time-dependent and time-independent approaches for the computation of absorption spectra of Uracil derivatives in solution. Improta, R.; Lami, A.; Barone, V.; Santoro, F. International Journal of Quantum Chemistry 110, 624-636 (2010).
281. Benchmark calculations for molecules in the gas phase: State-of-the-art coupled-cluster computations. Puzzarini, C.; Barone, V. International Journal of Quantum Chemistry 110, 637-655 (2010).
282. Interpretation of the emission fluorescence spectra of two fluoroionophores: DMABN-Crown4 and DMABN-Crown5. Carlotto, S.; Ferrante, C.; Polimeno, A.; Benzi, C.; Barone, V. International Journal of Quantum Chemistry 110, 368-375 (2010).
283. Computational approach to the study of the lineshape of absorption and electronic circular dichroism spectra. Santoro, F.; Barone, V. International Journal of Quantum Chemistry 110, 476-486 (2010).
284. Unraveling solvent effects on the electronic absorption spectra of TRITC fluorophore in solution: a theoretical TD-DFT/PCM study. Pedone, A.; Barone, V. Physical Chemistry Chemical Physics 12, 2722-2729 (2010).
285. Accurate Harmonic/Anharmonic Vibrational Frequencies for Open-Shell Systems: Performances of the B3LYP/N07D Model for Semirigid Free Radicals Benchmarked by CCSD(T) Computations. Puzzarini, C.; Biczysko, M.; Barone, V. Journal of Chemical Theory and Computation 6, 828-838 (2010).
286. Insight into the mechanism of action of plakortins, simple 1,2-dioxane antimalarials.

Taglialatela-Scafati, O.; Fattorusso, E.; Romano, A.; Scala, F.; Barone, V.; Cimino, P.; Stendardo, E.; Catalanotti, B.; Persico, M.; Fattorusso, C. Organic and Biomolecular Chemistry 8, 846-856 (2010).

287. Coverage-Dependent Architectures of Iron Phthalocyanine on Ag(110): a Comprehensive STM/DFT Study. Casarin, M.; Di Marino, M.; Forrer, D.; Sambi, M.; Sedona, F.; Tondello, E.; Vittadini, A.; Barone, V.; Pavone, M. Journal of Physical Chemistry C 114, 2144-2153 (2010).
288. Environmental Effects in Computational Spectroscopy: Accuracy and Interpretation. Pedone, A.; Biczysko, M.; Barone, V. ChemPhysChem 11, 1812-1832 (2010).
289. On the Calculation of Vibrational Frequencies for Molecules in Solution Beyond the Harmonic Approximation. Cappelli, C.; Monti, S.; Scalmani, G.; Barone, V. Journal of Chemical Theory and Computation 6, 1660-1669 (2010).
290. General Approach to Compute Vibrationally Resolved One-Photon Electronic Spectra. Bloino, J.; Biczysko, M.; Santoro, F.; Barone, V. Journal of Chemical Theory and Computation 6, 1256-1274 (2010).
291. Parameterization and validation of an accurate force-field for the simulation of alkylamine functionalized silicon (111) surfaces. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini, G. Physical Chemistry Chemical Physics 12, 4201-4209 (2010).
292. The excited electronic states of adenine-guanine stacked dimers in aqueous solution: a PCM/TD-DFT study. Santoro, F.; Barone, V.; Lami, A.; Improta, R. Physical Chemistry Chemical Physics 12, 4934-4948 (2010).
293. Interplay of stereo-electronic, environmental, and dynamical effects in determining the EPR parameters of aromatic spin-probes: INDCO as a test case. Cimino, P.; Pedone, A.; Stendardo, E.; Barone, V. Physical Chemistry Chemical Physics 12, 3741-3746 (2010).
294. Cyclic Structural Motifs in 5,6-Dihydroxyindole Polymerization Uncovered: Biomimetic Modular Buildup of a Unique Five-Membered Macrocycle. Arzillo, M.; Pezzella, A.; Crescenzi, O.; Napolitano, A.; Land, E.J.; Barone, V.; D'Ischia, M. Organic Letters 12, 3250-3253 (2010).
295. Harmonic and Anharmonic Vibrational Frequency Calculations with the Double-Hybrid B2PLYP Method: Analytic Second Derivatives and Benchmark Studies. Biczysko, M.; Panek, P.; Scalmani, G.; Bloino, J.; Barone, V. Journal of Chemical Theory and Computation 6, 2115-2125 (2010).
296. Simulating DNA Hybridization on an Amine-Functionalized Silicon Substrate. Monti, S.; Cacelli, I.; Ferretti, A.; Prampolini, G.; Barone, V. Journal of Physical Chemistry B 114, 8341-8349 (2010).
297. Double C—H Activation of Ethane by Metal-Free SO2·+ Radical Cations. de Petris, G.; Cartoni, A.; Troiani, A.; Barone, V.; Cimino, P.; Angelini, G.; Ursini, O. Chemistry - A European Journal 16, 6234-6242 (2010).
298. Extending the Range of Computational Spectroscopy by QM/MM Approaches: Time-Dependent and Time-Independent Routes . Barone, V.; Biczysko, M.; Brancato, G. Advances in Quantum Chemistry 59, 17-57 (2010).
299. Magnetic Properties of Nitroxide Spin Probes: Reliable Account of Molecular Motions and Nonspecific Solvent Effects by Time-Dependent and Time-Independent Approaches. Pavone, M.; Biczysko, M.; Rega, N.; Barone, V. Journal of Physical Chemistry B 114, 11509–11514 (2010).
300. Extension of the AMBER force-field for the study of large nitroxides in condensed phases: an ab initio parameterization. Stendardo, E.; Pedone, A.; Cimino, P.; Menziani, M.C.; Crescenzi, O.; Barone, V. Physical Chemistry Chemical Physics 12, 11697-11709 (2010).
301. Uracil anion radical in aqueous solution: thermodynamics versus spectroscopy. Brancato, G.; Rega, N.; Barone, V. Physical Chemistry Chemical Physics 12, 10736-10739 (2010).
302. An integrated computational protocol for the accurate prediction of EPR and PNMR parameters of aminoxyl radicals in solution. Barone, V.; Cimino, P.; Pedone, A. Magnetic Resonance in Chemistry 48, S11-S22 (2010).
303. A fully automated implementation of VPT2 Infrared intensities. Barone, V.; Bloino, J.; Guido, C.A.; Lipparini, F. Chemical Physics Letters 496, 157-161 (2010).
304. Theoretical multilevel approach for studying the photophysical properties of organic dyes in solution. Barone, V.; Bloino, J.; Monti, S.; Pedone, A.; Prampolini, G. Physical Chemistry Chemical Physics 12, 10550-10561 (2010).
305. DNA hybridization mechanism on silicon nanowires: a molecular dynamics approach. Monti, S.; Cacelli, I.; Ferretti, A.; Prampolini, G.; Barone, V. Molecular BioSystems 6, 2230-2240 (2010).

306. Integrated experimental and computational spectroscopy study on π-stacking interaction: the anisole dimer. Schiccheri, N.; Pasquini, M.; Piani, G.; Pietraperzia, G.; Becucci, M.; Biczysko, M.; Bloino, J.; Barone, V. Physical Chemistry Chemical Physics 12, 13547-13554 (2010).
307. Toward spectroscopic accuracy for open-shell systems: Molecular structure and hyperfine coupling constants of H2CN, H2CP, NH2, and PH2 as test cases. Puzzarini, C.; Barone, V. Journal of Chemical Physics 133, 184301 (2010).
308. Microsolvation of uracil anion radical in aqueous solution: a QM/MM study. Brancato, G.; Rega, N.; Barone, V. Chemical Physics Letters 500, 104-110 (2010).
309. Bottom-Up Approach to Innovative Memory Devices: II. Molecular Adsorption on Electrodes and the Asymmetric Response. Pino, I.; Causà, M.; Barone, V. Journal of Physical Chemistry C 114, 21439–21443 (2010).
310. Geometry Optimization of Large and Flexible van der Waals Dimers: A Fragmentation–Reconstruction Approach. Cacelli, I.; Cimoli, A.; Prampolini, G. Journal of Chemical Theory and Computation 6, 2356-2546 (2010).
311. The microstructural basis for the mechanical properties and electrical resistivity of nanocrystalline Cu-Al2O3. Nachum, S.; Fleck, N.A.; Ashby, M.F.; Colella, A.; Matteazzi, P. J. Materials Science and Engineering: A, 527, Issue 20, 5065-5071 (2010). Submitted.
312. Characterisation and tribological investigation on thermally processed nanostructured Fe-based and Cu-based cermet materials. Basak, A.K.; Eddine, W.Z.; Celis, J.P.; Matteazzi, P. J Nanosci Nanotechnol., 10(2), 1179-84 (2010).
313. Mg – Ni – Cu mixtures for hydrogen storage: a kinetic study. Milanese, C.; Girella, A.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. Intermetallics, 18, 203-211 (2010).
314. Effect of C (Graphite) doping on the H2 sorption performance of the Mg – Ni storage system. Milanese, C.; Girella, A.; Garroni, S.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. International Journal of Hydrogen Energy, 35, 3, 1285-129 (2010).
315. Energy growth, complexity and efficiency. Ruzzenenti, F.; Basosi, R. Energy Efficiency, ed. Jenny Palm, published by Sciyo, 27-48 (2010).
316. Complex Networks and Symmetry I: a review. Garlaschelli, D.; Ruzzenenti, F.; Basosi, R. Symmetry 2, 1683-1709 (2010).
317. Complex Networks and Symmetry II: reciprocity and Evolution of World Trade. Ruzzenenti, F.; Garlaschelli, D.; Basosi, R. Symmetry 2, 1710-1744 (2010).
318. Energy Growth, complexity and efficiency. Basosi, R. Summer School Chemistry for Life and Environment, 7th edition 18 (2010).
319. Mechanistic study on trametes cervina lignin peroxidase having a catalytic tyrosine: unique activation mechanism by veratryl alcohol. Miki, Y.; Calvino, F.R.; Pogni, R.; Ruiz-Duenas, F.J.; Martinez, M.J.; Basosi R.; Romero, A.; Martinez, A.T. Proceedings of the “Oxidative enzymes as sustainable industrial biocatalysts”, 42-46 (2010).
320. Sustainable discoloration of textile chromo-baths by spent mushroom substrate from the industrial production of Plerotus ostreatus. Di Grgorio, S.; Balestri, F.; Basile, M.; Matteini V.; Gini, F.; Giansanti, S.; Tozzi, M.G.; Basosi, R.; Lorenzi, R. Journal of Environmental Protection 1, 85-94 (2010).
321. A Biomimetic Dipole Moment Switch Driven by Double Bond Photoisomerization. Melloni, A.; Rossi Paccani, R.; Donati, D.; Zanirato V.; Sinicropi, A.; Parisi, M.L.; Martin, E.; Ryazantsev, M.; Ding, W.J.; Frutos, L.M.; Basosi, R.; Fusi, S.; Latterini, L.; Ferrè, N.; Olivucci, M. Journal of the American Chemical Society, 132 (27), 9310-9319 (2010).
322. Characterization of LRET Mechanism: Laccase-Mediator and Laccase Precursor System. Baratto, M.C.; Martorana, A.; Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. Summer School Chemistry for Life and Environment, 7th edition 32 (2010).
323. QM/MM Characterization of Trp and Tyr Radicals inside the protein matrix of a P.Eryngii Versatile Peroxidase and its W164Y Mutant. Bernini, C.; Pogni, R.; Ruiz-Duenas, F.J.; Martinez Ferrer, F.J.; Basosi, R.; Sinicropi, A. Summer School Chemistry for Life and Environment, 7th edition 30 (2010).
324. Synthesis and Structural Characterization of a Novel Phenoxazinone Dye by use of a Fungal Laccase. Forte, S.; Polak, J.; Valensin, D.; Taddei, M.; Basosi, R.; Jarosz-Wilkolazka, A.; Pogni, R. Journal of Molecular Catalysis B: Enzymatic 63, 116-120 (2010).
325. Simulation of EPR spectra as a tool for interpreting the degradation pathway of hyaluronan. Busi, E.; Travagli, E.; Zanardi, I.; Gabbrielli, I.; Basosi, R. Applied Magnetic Resonance 37, 325-337 (2010).
326. Tyrosyl Radical in the W164Y Mutant of P. eryngii Versatile Peroxidase: an EPR and

DFT/PCM study. Bernini, C.; Sinicropi, A.; Basosi, R.; Pogni, R. Applied Magnetic Resonance, 37, 279-288 (2010).

327. Distribution of dimorphic yeast species in commercial extra virgin olive oil. Zullo, B.A.; Cioccia, G.; Ciafardini, G. Food microbiology 27, 1035-1042 (2010).
328. XPS characterization of microstructured composites for Cr(VI) removal from polluted environment. Ditaranto, N.; Cioffi, N.; Sabbatini, L.; Palazzo, G.; Lopez, F. ISA 2010, La Chimica e l'Industria, Ottobre 2010, 92-94 (2010).
329. The Dielectric Behavior of Nonspherical Biological Cell Suspensions: An Analytic Approach. Di Biasio, A.; Ambrosone, L.; Cametti, C. Biophysical Journal 99, 163-174 (2010).
330. Complementary amphiphilic ribonucleotides confined into nanostructured environments. Angelico, R.; Ambrosone, L.; Ceglie, A.; Losito, I.; De Zio, D.; Palmisano, F. Physical Chemistry Chemical Physics 28, 7977-7987 (2010).
331. Ordering fluctuations in a shear-banding wormlike micellar system. Angelico, R.; Rossi, O.; Ambrosone, L.; Palazzo, G.; Mortensen K.; Olsson, U. Physical Chemistry Chemical Physics 12, 8856-8862 (2010).
332. Lauric Acid-Induced Formation of a Lyotropic Nematic Phase of Disk-Shaped Micelles. Colafemmina, G.; Recchia, R.; Ferrante, A.; Amin, S.; Palazzo, G. Journal of Physical Chemistry B 114, 7250-7260 (2010).
333. Mushroom tyrosinase in polyelectrolyte multilayers as an optical biosensor for o-diphenols. Fiorentino, D.; Gallone, A.; Fiocco, D.; Palazzo, G.; Mallardi, A. Biosensensors and Bielectronics 25, 2033-2037 (2010).
334. Vesicle-templeted LbL for the production of nanocapsules. Cuomo, F.; Lopez, F.; Miguel, M.G.; Lindman, B. Langmuir 26, 10555–10560 (2010).
335. Slow dynamics of wormlike micelles. Olsson, U.; Borjesson, J.; Angelico, R.; Ceglie, A.; Palazzo, G. Soft Matter 6, 1769-1777 (2010).
336. Lipid oxidation in water-in-olive oil emulsions initiated by a lipophilic radical source. Mosca, M.; Ceglie, A.; Ambrosone, L. Journal of Physical Chemistry B 114, 3550-3558 (2010).
337. Effect of detergent concentration on the thermal stability of a membrane protein: the case study of bacterial reaction center solubilized by N,N,-dimethyldodecylamine-N-oxide. Palazzo, G.; Lopez, F.; Mallardi, A. Biochim. Biophys. Acta Proteins and Proteomics 1804, 137-146 (2010).
338. Effects of sulfate ions and slightly acidic pH conditions on Cr(VI) adsorption onto Silica Gelatin composite. Venditti, F.; Cuomo, F.; Ceglie, A.; Ambrosone, L.; Lopez, F. Journal of Hazardous Material 173, 552-557 (2010).
339. Anchoring Geometry and Surface Reactions of Phosphonate-functionalised terpyridine ligands onto zirconium-containing oxide surfaces. Spampinato, V.; Tuccitto, N.; Quici, S.; Calabrese, V.; Marletta, G.; Torrisi, A.; Licciardello, A. Langmuir 26, 8400-8406 (2010).
340. Kinetic growth mechanisms of sputter-deposited Au films on mica: from nanoclusters to nanostructured microclusters. Ruffino, F.; Torrisi, V.; Marletta, G.; Grimaldi M.G. Applied Physics A-Materials Science and Processing 100, 7-13 (2010).
341. ToF-SIMS images and spectra of biomimetic calcium silicate-based cements after storage in solutions simulating the effects of human biological fluids. Torrisi, A.; Torrisi, V.; Tuccitto, N.; Gandolfi, M.G.; Prati, C., Licciardello, A. International Journal of Mass Spectrometry 289, 150-161 (2010).
342. Chemical imaging of self-assembling structures in Langmuir-Blodgett films of polymer blends. Torrisi, V.; Licciardello, A.; Marletta, G. Materials Science and Engineering B 169, 49-54 (2010).
343. Protein adsorption onto nanopores at the nanometer scale. Messina, G.M.L.; Marletta, G. European Cells and Materials 20, Suppl. 3, 179-183 (2010).
344. Could N,N-(diethylcarbamothioyl)benzamide be a good ionophore for sensor membranes? Lazo Fraga, A. R.; Li Destri, G.; Forte, G.; Rescifina, A.; Punzo, F. Journal of Molecular Structure 981, 86-92 (2010).
345. Evaluation of Plasma Modified Polycaprolactone Honeycomb Scaffolds by Human Mesenchymal Stem Cells Cultured in Vitamin D Differentiation Medium. Formosa, F.; Sanchez Vaquero, V.; Rodríguez Navas, C.; Muñoz Noval, Á.; Tejera Sánchez, N.; Manso Silván, M.; García-Ruiz, J. P.; Marletta, G. Plasma Proc. Polym., 7, 794-801 (2010).
346. Self-assembling pathway of hIAPP fibrils within lipid bilayers. Scalisi, S.; Sciacca, M.F.M.; Zavhnerko, G.; Grasso, D.M.; Marletta, G.; La Rosa, C. Chem Bio Chem 11, 1856–1859 (2010).
347. Application of hybrid agarose-aminosilane gels to the biofunctionalisation of honeycomb

structured polycaprolactone scaffolds. Formosa, F.; Satriano, C.; Garcìa Ruiz, J.P.; Montero, I.; Manso Silvàn, M.; Marletta, G. SIA-Surf.Interf.Anal. 42, 448-451 (2010).

348. Developing Langmuir-Blodgett Strategies Towards Practical Devices. Zhavnerko, G.; Marletta, G. Mat.Sci.Engin.B 169, 43-48 (2010).

349. Ion Beam Modification of Polymer Surfaces for Biological Applications. Marletta, G. in “Materials Science with Ion Beams”, Vol.116 of “Topics in Applied Physics”, Ed. H.Bernas, Springer-Verlag, Heidelberg (Germany), 2010, p.345-369.

350. Surface anchoring of a chiral salen macrocycle on a carboxy-functionalized platform via a multiple site esterification. Torrisi, V.; Amato, M.E.; Ballistreri, F.P.; Tomaselli, G.; Licciardello, A. Surface and Interface Analysis DOI:10.1002/sia3690 (2010).

351. Atomic Force Microscopy investigation of the kinetic growth mecanisms of sputtered nanostructured Au film on mica: towards a nanoscale morphology control. Ruffino, F.; Torrisi, V.; Marletta, G.; Grimaldi, M.G. Nanoscale Research Letters in press (2010).

352. Memory effects in annealed hybrid gold nanoparticles/block copolymer bilayers. Torrisi, V.; Ruffino, F.; Licciardello, A.; Grimaldi, M.G.; Marletta, G. Nanoscale Research Letters in press (2010).

353. ToF-SIMS Imaging of Surface Self-Organised Fractal Patterns of Bacteria. Tuccitto, N.; Marletta, G.; Carnazza, S.; Grasso, L.; Caratozzolo, M.; Guglielmino, S.; Licciardello, A. SIA-Surf.Interf.Anal. (2010) in press.

354. Understanding the properties of the coagel and gel phases: A 2H and 13C NMR study of amphiphilic ascorbic acid derivatives. Borsacchi, S.; Ambrosi, M.; Lo Nostro, P.; Geppi, M. Journal of Physical Chemistry B 114, 15872-15878 (2010).

355. Modulation of density and orientation of amphiphilic DNA anchored to phospholipid membranes. I. Supported Lipid Bilayers. Gambinossi, F.; Banchelli, M.; Durand, A.; Berti, D.; Brown, T.; Caminati, G.; Baglioni, P. Journal of Physical Chemistry B 114, 7338-7347 (2010).

356. Modulation of density and orientation of amphiphilic DNA on phospholipid membranes. II. Vesicles. Banchelli, M.; Gambinossi, F.; Durand, A.; Caminati, G.; Brown, T.; Berti, D.; Baglioni, P. Journal of Physical Chemistry B 114, 7348-7358 (2010).

357. Kinetic analysis of chol-tagged oligonucleotides adsorption onto Supported Lipid Bilayers: from diffusion limited mass-transport to a Tetris scenario. Gambinossi, F.; Banchelli, M.; Berti, D.; Baglioni, P.; Caminati, G. To be submitted to J. Phys. Chem B.

358. Removal of acrylic coatings from works of art by means of nanofluids: understanding the mechanism at the nanoscale. Baglioni, M.; Rengstl, D.; Berti, D.; Bonini, M.; Giorgi, R.; Baglioni, P. Nanoscale, 2, 1723-1732 (2010).

359. New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles. Giorgi, R.; Baglioni, M.; Berti, D.; Baglioni, P. Accounts of Chemical Research, 43 (6), 695-704 (2010).

360. Inorganic nanoparticles for works of art conservation. Baglioni, P.; Giorgi, R. Inorganic Nanoparticles: Synthesis, Applications, and Perspectives; Series: Nanomaterials and their Applications; Editors: C. Altavilla & E. Ciliberto, CRC Press – Taylor & Francis Group: London, 2010.

361. Hydroxide Nanoparticles for Deacidification and Concomitant Inhibition of Iron-Gall Ink Corrosion of Paper. Poggi, G.; Giorgi, R.; Toccafondi, N.; Katzur, V.; Baglioni, P. Langmuir, 26, 19084-19090 (2010).

362. Nanoparticles for Cultural Heritage Conservation: Calcium and Barium Hydroxide Nanoparticles for Wall Painting Consolidation. Giorgi, R.; Ambrosi, M.; Toccafondi, N.; Baglioni, P. Chemistry – A European Journal (Chem. Eur. J.), 16, 9374-9382 (2010).

363. New Frontiers in Materials Science for Art Conservation. Responsive Gels and Beyond. Carretti, E.; Bonini, M.; Dei, L.; H. Berrie, B.; Angelova, L.V.; Baglioni, P.; Weiss, R.G. Accounts of Chemical Research 43, 751-760 (2010).

364. Nanoscience for Art Conservation: o/w microemusions embedded in a Polymeric Network for the Cleaning of Works of Art. Carretti, E.; Fratini, E.; Berti, D.; Dei, L.; Baglioni P. Angewandte Chemie 48, 8966-8969 (2010). This paper has been cited by: http://www.rsc.org/chemistryworld/News/2009/October/22100901.asp; http://www.nature.com/nnano/reshigh/2009/1009/full/nnano.2009.350.html (30 October 2009) doi: 10.1038/nnano.2009.350. Nanocontainers: Clean and spotless art by Ai Lin Chun.

365. A new family of viscoelastic polymeric dispersions for cleaning easel paintings. Carretti, E.; Natali, I.; Matarrese, C.; Bracco, P.; Weiss, R. G.; Baglioni, P.; Dei L. Journal of Cultural Heritage 11, 373-380 (2010).

366. Insights into Mechanical Properties of a Silicone Oil Gel with a ‘Latent’ Gelator, 1-

Octadecylamine, and CO2 as an Activator. Carretti, E.; George, M.; Weiss, R. G. Beilstein Journal of Organic Chemistry 6, 984-991 (2010).

367. DNA induced dimerization of a sulfhydryl surfactant in transfection agents studied by ESR spectroscopy. Ciani, L.; Candiani, G.; Frati, A.; Ristori, S. Biophysical Chemistry 151, 81-85 (2010).
368. Development of new reducible cationic Gemini surfactant - SS14 - containing liposomes for gene delivery. Candiani, G.; Pezzoli, D.; Ciani, L.; Cigada, A.; Chiesa, R.; Ristori, S. Transactions of the Annual Meeting of the Society for Biomaterials 32 Annual Meeting of the Society for Biomaterials: Giving Life to a World of Materials 2, 600 (2010).
369. Boron-neutron capture therapy: research and clinical application. Part 1. Ciani, L.; Bortolussi, S.; Altieri, S.; Ristori, S.; Ferrari, C.; Zonta, A.; Baglioni, P.; Martini, G. Chimica e l'Industria 92, 83-87 (2010).
370. Chemistry and technology. Boron neutron capture therapy: research and clinical application. Part 2. Bortolussi, S.; Ciani, L.; Altieri, S.; Ristori, S.; Ferrari, C.; Zonta, A.; Baglioni, P.; Martini, G. Chimica e l'Industria 92, 117-125 (2010).
371. Bioreducible liposomes for gene delivery: from the formulation to the mechanism of action.Candiani, G.; Pezzoli, D.; Ciani, L.; Chiesa, R.; Ristori, S. PloS one 5, e13430 (2010).
372. Formation of the Dynamic Clusters in Concentrated Lysozyme Protein Solutions. Porcar, L.; Falus, P.; Chen, W. R.; Faraone, A.; Fratini, E.; Hong, K. L.; Baglioni, P.; Liu, Y., Journal of Physical Chemistry Letters 1, (1), 126-129 (2010).
373. Poly(9,9-dioctylfluorene)-Based Conjugated Polyelectrolyte: Extended pi-Electron Conjugation Induced by Complexation with a Surfactant Zwitterion. Pace, G.; Tu, G. L.; Fratini, E.; Massip, S.; Huck, W. T. S.; Baglioni, P.; Friend, R. H. Advanced Materials 22, (18), 2073-+ (2010).
374. A Low-Temperature Crossover in Water Dynamics in an Aqueous LiCl Solution: Diffusion Probed by Neutron Spin-Echo and Nuclear Magnetic Resonance. Mamontov, E.; Faraone, A.; Hagaman, E. W.; Han, K. S.; Fratini, E. Journal of Physical Chemistry B 114, (50), 16737-16743 (2010).
375. Hydrated {Mo72Fe30} clusters: Low-frequency hydrogen modes and self-aggregation. Fratini, E.; Faraone, A.; Todea, A. M.; Baglioni, P. Inorganica Chimica Acta 363, (15), 4234-4239 (2010).
376. Experimental evidence of logarithmic relaxation in single-particle dynamics of hydrated protein molecules. Chu, X. Q.; Lagi, M.; Mamontov, E.; Fratini, E.; Baglioni, P.; Chen, S. H. Soft Matter 6, (12), 2623-2627 (2010).
377. The Dynamic Response Function chi(T)(Q,t) of Confined Supercooled Water and its Relation to the Dynamic Crossover Phenomenon. Chen, S. H.; Zhang, Y.; Lagi, M.; Chu, X. Q.; Liu, L.; Faraone, A.; Fratini, E.; Baglioni, P. Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics 224, (1-2), 109-131 (2010).
378. Dynamics of a globular protein and its hydration water studied by neutron scattering and MD simulations. Chen, S. H.; Lagi, M.; Chu, X. Q.; Zhang, Y.; Kim, C.; Faraone, A.; Fratini, E.; Baglioni, P. Spectroscopy-an International Journal 24, (1-2), 1-24 (2010).
379. Cellulose as a renewable resource for the synthesis of wood consolidants. Cipriani, G.; Salvini, A.; Baglioni, P.; Bucciarelli, E. Journal of applied polymer science 118, 2939-2950 (2010).
380. Self-sorting chiral organogels from a long chain carbamate of 1-benzyl-pyrrolidine-3,4-diol. Cicchi, S.; Ghini, G.; Lascialfari, L.; Brandi, A.; Betti, F.; Berti, D.; Baglioni, P.; Di Bari, L.; Pescitelli, G.; Mannini, M.; Caneschi, A. Soft Matter 6, 1655-1661 (2010).
381. Small-angle neutron scattering of percolative perfluoropolyether water in oil microemulsions. Laurati, M.; Gambi, C.M.C.; Giordano, R.; Baglioni, P.; Teixeira, J. The Journal of Physical Chemistry B 114, 3855-3862 (2010).
382. Asymmetric Partitioning of Anions in Lysozyme Dispersions. Lo Nostro, P.; Peruzzi, N.; Severi, M.; Ninham, B.W.; Baglioni, P. Journal of the American Chemical Society 132, 6571-6577 (2010).
383. Molecular Forces and Self Assembly. In Colloid, Nano Sciences and Biology. Ninham, B.W.; Lo Nostro, P. Cambridge University Press (Cambridge), 2010, ISBN: 978-0-521-89600-9.
384. Understanding the properties of the coagel and gel phases: a 2-H and 13-C NMR study of amphiphilic ascorbic acid derivatives. Borsacchi, S.; Ambrosi, M.; Lo Nostro, P.; Geppi, M. Journal of Physical Chemistry B 114, 15872-15878 (2010).
385. Piezoelectric PZT nanodevices from a hybrid ligand burning method. Tattini, L.; Lo Nostro, P.; Ravalli, A.; Stirner, M.; Baglioni, P. Journal of Nanoparticle Research, 13, 1791-1800 (2010). Available Online. DOI 10.1007/s11051-010-9930-5.

386. Magnetoliposomes for controlled drug release in the presence of low-frequency magnetic field. Nappini, S.; Baldelli Bombelli, F.; Bonini M.; Nordèn, B.; Baglioni, P. Soft Matter, 6, 154-162 (2010).
387. Carborane-Conjugated 2-Quinolinecarboxamide Ligands of the Translocator Protein for Boron Neutron Capture Therapy. Cappelli, A.; Valenti, S.; Mancini, A.; Giuliani, G.; Anzini, M.; Altieri, S.; Bortolussi, S.; Ferrari, C.; Clerici, A.; Zonta, C.; Carraro, F.; Filippi, I.; Giorgi, G.; Donati, A.; Ristori, S.; Vomero, S.; Concas, A.; Biggio, G.; Bionconj. Chem., 21, 2213–2221 (2010).
388. Surface-enhanced Raman spectra of dimethoate and omethoate. Guerrini, L.; Sanchez-Cortes, S.; Cruz, V.L.; Martinez, S.; Ristori, S.; Feis, A.J. Raman Spectroscopy, DOI 10.1002/jrs.2823 (2010).
389. Carboranylporphyrazines for anti-cancer therapies: synthesis and physicochemical properties. Pietrangeli, D.; Ristori, S.; Rosa, A.; Ricciardi, G.J. Porphyrins Phthalocyanines 14, 678-688 (2010).
390. Carbonic anhydrase activators. Activation of the membrane-associated isoform XV with amino acids and amines. Innocenti, A.; Hilvo, M.; Parkkila, S.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 3420-3433 (2010).
391. The protein tyrosine kinase inhibitors imatinib and nilotinib strongly inhibit several mammalian α-carbonic anhydrase isoforms. Parkkila, S.; Innocenti, A.; Kallio, H.; Hilvo, M.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 19, 4102-4106 (2010).
392. Deciphering the mechanism of carbonic anhydrase inhibition with coumarins and thiocoumarins. Maresca, A.; Temperini, C.; Pochet, L.; Masereel, B.; Scozzafava, A.; Supuran, C.T. J. Med Chem. 53, 335-344 (2010).
393. Carbonic anhydrase IX: biochemical and crystallographic characterization of a novel antitumor target. De Simone, G.; Supuran, C.T. Biochim. Biophys. Acta 1804, 404-409 (2010).
394. Identification of 3,4-Dihydroisoquinoline-2(1H)-sulfonamides as Potent Carbonic Anhydrase Inhibitors: Synthesis, Biological Evaluation and Enzyme-ligand X-ray studies. Gitto, R.; Agnello, S.; Ferro, S.; Vullo, D.; Brynda, J.; Mader, P.; Supuran, C.T.; Chimirri, A. J. Med. Chem. 53, 2401-2408 (2010).
395. Carbonic anhydrase inhibitors induce ceramide-mediated apoptosis in human tumor cells. Cianchi, F.; Vinci, M.C.; Supuran, C.T.; Peruzzi, B.; De Giuli, P.; Fasolis, G.; Perigli, G.; Pastorekova, S.; Masini, E.; Puccetti, L. J. Pharmacol. Exp. Ther. 334, 710-719 (2010).
396. The coumarin-binding site in carbonic anhydrase accommodates structurally diverse inhibitors: the antiepileptic lacosamide as an example. Temperini, C.; Innocenti, A.; Scozzafava, A.; Parkkila, S.; Supuran, C.T. J. Med. Chem. 53, 850- 854 (2010).
397. Carbonic anhydrase inhibitors. Identification of selective inhibitors of the human mitochondrial isozymes VA and VB over the cytosolic isozymes I and II from a natural product-based phenolic library. Davis, R.A.; Innocenti, A.; Poulsen, S.A.; Supuran, C.T. Bioorg. Med. Chem. 18, 14-18 (2010).
398. Carbonic anhydrase inhibitors. Inhibition of human erythrocyte isozymes I and II with a series of phenolic acids. Öztürk Sarıkaya, S.B.; Gülçin, I.; Supuran, C.T. Chem. Biol. Drug Des. 75, 515-520 (2010).
399. Carbonic anhydrase inhibitors. X-Ray crystal studies of the carbonic anhydrase II – trithiocarbonate adduct – An inhibitor mimicking the sulfonamide and urea binding to the enzyme. Temperini, C.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 474-478 (2010).
400. Carbonic anhydrase activators. The first activation study of a coral secretory isoform with amino acids and amines. Bertucci, A.; Zoccola, D.; Tambutté, S.; Vullo, D.; Supuran, C.T. Bioorg. Med. Chem. 18, 2300-2303 (2010).
401. Characterization of the first beta-class carbonic anhydrase from an arthropod (Drosophila melanogaster) and phylogenetic analysis of beta-class carbonic anhydrases in invertebrates. Syrjänen, L.; Tolvanen, M.; Hilvo, M.; Olatubosun, A.; Innocenti, A.; Scozzafava, A.; Leppiniemi, J.; Niederhauser, B.; Hytönen, V.P.; Gorr, T.A.; Parkkila, S.; Supuran, C.T. BMC Biochemistry 11, 28 (2010).
402. Carbonic anhydrase activators: Activation of the β-carbonic anhydrase from the pathogenic yeast Candida glabrata with amines and amino acids. Innocenti, A.; Leewattanapasuk, W.; Manole, G.; Scozzafava, A.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 1701-1704 (2010).
403. Carbonic anhydrase activators: Activation of the β-carbonic anhydrases from the pathogenic fungi Candida albicans and Cryptococcus neoformans with amines and amino acids. Innocenti,

A.; Hall, R.A.; Scozzafava, A.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. 18, 1034-1037 (2010).

404. Polyamines inhibit carbonic anhydrases by anchoring to the zinc-coordinated water molecule. Carta, F.; Temperini, C.; Innocenti, A.; Scozzafava, A.; Kaila, K.; Supuran, C.T. J. Med.Chem. 53, 5511-5522 (2010).

405. Carbonic anhydrase inhibitors. Inhibition of transmembrane isoforms IX, XII and XIV with less investigated inorganic anions. Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 1548-1550 (2010).

406. Carbonic anhydrase inhibitors. Synthesis and inhibition of the human cytosolic isozymes I and II and transmembrane isozymes IX, XII (cancer-associated) and XIV with 4-substituted 3-pyridinesulfonamides. Brzozowski, Z.; Sławiński, J.; Sączewski, F.; Innocenti, A.; Supuran, C.T. Eur. J. Med. Chem. 45, 2396-2404 (2010).

407. Cloning, characterization and inhibition studies of a b-carbonic anhydrase from Brucella suis. Joseph, P.; Turtaut, F.; Ouahrani-Bettache, S.; Montero, J.-L.; Nishimori, I.; Minakuchi, T.; Vullo, D.; Scozzafava, A.; Köhler, S.; Winum, J.-Y.; Supuran, C.T. J. Med. Chem., 53, 2277-2285 (2010).

408. The first example of significant active site reorganization in a carbonic anhydrase-inhibitor adduct: the carbonic anhydrase I–topiramate complex. Alterio, V.; Monti, S.M.; Truppo, E.; Pedone, C.; Supuran, C.T.; De Simone, G. Org. Biomol. Chem. 8, 3528-3533 (2010).

409. Identification of i potent and selective human carbonic anhydrase VII (hCA II) inhibitors. Gitto, R.; Agnello, S.; Ferro, S.; Vullo, D.; Supuran, C.T.; Chimirri, A. ChemMedChem 5, 823-826 (2010).

410. Sulfonamide linked neoglycoconjugates – a new class of inhibitors for cancer-associated carbonic anhdyrases. Lopez, M.; Bornaghi, M.F.; Innocenti, A.; Vullo, D.; Supuran, C.T.; Poulsen, S.-A. J. Med. Chem. 53, 2913-2926 (2010).

411. Nanoscale enzyme inhibitors: Fullerenes inhibit carbonic anhydrase by occluding the active site entrance. Innocenti, A.; Durdagi, S.; Doostdar, N.; Strom, T.A.; Barron, A.R.; Supuran, C.T. Bioorg. Med. Chem. 28, 2822-2828 (2010).

412. Putative anion transporter-1 (Pat-1, Slc26a6) contributes to intracellular pH regulation during H+-dipeptide transport in the villous epithelium. Simpson, J.E.; Walker, N.M.; Supuran, C.T.; Soleimani, M.; Clarke, L.L. Am. J.Physiol. Gastrointest. Liver Physiol. 298, G683-G691 (2010).

413. Carbonic anhydrase inhibitors. Inhibition of mammalian isoforms I – XIV with a series of natural product polyphenols and phenolic acids. Innocenti, A.; Öztürk Sarıkaya, S.B.; Gülçin, I.; Supuran, C.T. Bioorg. Med. Chem. 18, 2159-2164 (2010).

414. Inhibition studies of a b-carbonic anhydrase from Brucella suis with a series of water soluble glycosyl sulfanilamides. Vullo, D.; Nishimori, I.; Scozzafava, A.; Köhler, S.; Winum, J.-Y.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 2178-2182 (2010).

415. Carbonic Anhydrase Inhibitors: Gd(III) complexes of DOTA- and TETA- sulfonamide conjugates targeting the tumor associated carbonic anhydrase isozymes IX and XII. Rami, M.; Montero, J.-L.; Dubois, L.; Lambin, P.; Scozzafava, A.; Winum, J.-Y.; Supuran, C.T. New J. Chem. 34, 2139-2144 (2010).

416. A new purification method for human serum paraoxonase 1 and its interaction with sulfonamides. Ekinci, D.; Şentürk, M.; Beydemir, S.; Küfrevioğlu, Ö.I.; Supuran, C.T. Chem. Biol. Drug. Des. 76, 552-558 (2010).

417. Inhibition and binding studies of carbonic anhydrase isozymes I, II and IX with benzimidazo[1,2-c] [1,2,3] thiadiazole-7-sulphonamides. Baranauskiene, L.; Hilvo, M.; Matuliene, J.; Golovenko, D.; Manakova, E.; Dudutiene, V.; Michailoviene, V.; Torresan, J.; Jachno, J.; Parkkila, S.; Maresca, A.; Supuran, C.T.; Grazulis, S.; Matulis, D. J. Enzyme Inhib. Med. Chem. 25, 863-870 (2010).

418. Carbonic anhydrase inhibitors. The β-carbonic anhydrases from the fungal pathogens Cryptococcus neoformans and Candida albicans are strongly inhibited by substituted-phenyl-1H-indole-5-sulfonamides. Güzel, Ö.; Maresca, A.; Hall, R.A.; Scozzafava, A.; Mastrolorenzo, A.; Mühlschlegel, F.A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 2508-2511 (2010).

419. New Hydroxypyrimidinone-containing Sulfonamides as Carbonic Anhydrase Inhibitors also acting as MMP inhibitors. Esteves, M.A.; Ortet, O.; Capelo, A.; Supuran, C.T.; Marques, S.M.; Santos, M.A. Bioorg. Med. Chem. Lett. 20, 3623-3627 (2010).

420. Affinity of sulfamates and sulfamides to Carbonic Anhydrase II isoform: experimental and molecular modeling approaches. Gavernet, L.; Ramale, J.L.; Bruno Blanch, L.; Estiu, G.; Maresca, A.; Supuran, C.T. J. Chem. Inform. Model. 50, 1113-1122 (2010).

421. NO-releasing esters show carbonic anhydrase inhibitory action against human isoforms I and II. Ekinci, D.; Çavdar, H.; Talaz, O.; Şentürk, M.; Supuran, C.T. Bioorg. Med. Chem., 18, 3559-3563 (2010).
422. Analysis of a shortened form of human Carbonic Anhydrase VII expressed in vitro compared to the full-length enzyme. Bootorabi, F.; Jänis, J.; Smith, E.; Waheed, A.; Kukkurainen, S.; Hytönen, V.;Valjakka, J.; Supuran, C.T.; Vullo, D.; Sly, W.S.; Parkkila, S. Biochimie 92, 1072-1080 (2010).
423. The X-ray structure of the adduct between NAMI-A and carbonic anhydrase provides insights into the reactivity of this metallodrug with proteins. Casini, A.; Temperini, C.; Gabbiani, C.; Supuran, C.T.; Messori, L. ChemMedChem. 5, 1989-1994 (2010).
424. Carbonic anhydrase inhibitors. Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 3467-3474 (2010).
425. Mutation of Phe91 to Asn in human carbonic anhydrase I unexpectedly enhances both catalytic activity and affinity for sulfonamide inhibitors. Kockar, F.; Aydın, M.; Maresca, A.; Işık, S.; Turkoglu, S.; Sinan, S.; Arslan, O.; Özensoy Güler, Ö.; Turan, Y.; Supuran, C.T. Bioorg. Med. Chem. 18, 5498-5503 (2010).
426. Carbonic anhydrase inhibitors. The X-Ray crystal structure of human isoform II in adduct with an adamantyl analogue of acetazolamide resides in a new hydrophobic binding pocket. Avvaru, B.S.; Wagner, J.M.; Maresca, A.; Scozzafava, A.; Robbins, A.H.; Supuran, C.T.; McKenna, R. Bioorg. Med. Chem. Lett. 20, 4376-4381 (2010).
427. Carbonic anhydrase inhibitors. X-ray crystallographic and solution binding studies for the interaction of a boron containing aromatic sulfamide with mammalian isoforms I-XV. Di Fiore, A.; Monti, S.M.; Innocenti, A.; Winum, J.-Y.; De Simone, G.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 3601-3605 (2010).
428. Synthesis and biological evaluation of a 99mTc-labelled sulfonamide conjugate for in vivo visualization of carbonic anhydrase IX expression in tumor hypoxia. Akurathi, V.; Dubois, L.; Lieuwes, N.G.; Chitneni, S.K.; Cleynhens, B.J.; Vullo, D.; Supuran, C.T.; Verbruggen, A.M.; Lambin, P.; Bormans, G.M. Nuclear Med. Biol. 37, 557-564 (2010).
429. Bidentate Zinc Chelators for α-Carbonic Anhydrases that Produce a Trigonal Bipyramidal Coordination Geometry. Schulze Wischeler, J.; Innocenti, A.; Vullo, D.; Agrawal, A.; Cohen, S.M.; Heine, A.; Supuran, C.T.; Klebe, G. ChemMedChem 5, 1609-1615 (2010).
430. Coumarins incorporating hydroxy- and chloro- moieties selectively inhibit the transmembrane, tumor-associated carbonic anhydrase isoforms IX and XII over the cytosolic ones I and II. Maresca, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 4511-4514 (2010).
431. Crystal structure of the C183S/C217S mutant of human CA VII in complex with acetazolamide. Di Fiore, A.; Truppo, E.; Supuran, C.T.; Alterio, V.; Dathan, N.; Bootorabi, F.; Parkkila, S.; Monti, S.M.; De Simone, G. Bioorg. Med. Chem. Lett. 20, 5023-5026 (2010).
432. Carbonic anhydrase inhibitors. Regioselective synthesis of novel 1-substituted 1,4-dihydro-4-oxo-3-pyridinesulfonamides and their inhibition of the human cytosolic isozymes I and II and transmembrane cancer-associated isozymes IX, XII. Brzozowski, Z.; Sławiński, J.; Innocenti, A.; Supuran, C.T. Eur. J. Med. Chem. 45, 3656-3661 (2010).
433. Coumarinyl-substituted sulfonamides strongly inhibit several human carbonic anhydrase isoforms: solution and crystallographic investigations. Wagner, J.; Avvaru, B.S.; Robbins, A.H.; Scozzafava, A.; Supuran, C.T.; McKenna, R. Bioorg. Med. Chem. 18, 4873-4878 (2010).
434. Carbonic anhydrase inhibitors. Antioxidant polyphenols effectively inhibit mammalian isoforms I-XV. Innocenti, A.; Gülçin, I.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 5050-5053 (2010).
435. Carbonic anhydrases: again, and again, and again. Supuran, C.T. Curr. Pharm. Des. 16, 3231-3232 (2010).
436. Carbonic anhydrase inhibition/activation: trip of a scientist around the world in the search of novel chemotypes and drug targets. Supuran, C.T. Curr. Pharm. Des. 16, 3233-3245 (2010).
437. Carbonic anhydrase inhibitors developed through 'click tailing'. Lopez, M.; Salmon, A.J.; Supuran, C.T.; Poulsen, S.-A. Curr. Pharm. Des. 16, 3277-3287 (2010).
438. The β-carbonic anhydrases from Mycobacterium tuberculosis as drug targets. Nishimori, I.; Minakuchi, T.; Maresca, A.; Carta, F.; Scozzafava, A.; Supuran, C.T. Curr. Pharm. Des. 16, 3300-3309 (2010).
439. Hyperchlorhidrosis caused by homozygous mutation in CA12, encoding carbonic anhydrase. Feldshtein, M.; El Krinawi, S.; Yerushalmi, B.; Marcus, B.; Vullo, D.; Romi, H.; Ofir, R.; Landau, D.; Sivan, S.; Supuran, C.T.; Birk, O.S. Am. J. Hum. Gen. 87, 713-720 (2010).
440. Brucella carbonic anhydrases: New targets for designing anti-infective agents. Winum, J.Y.;

Kohler, S.; Supuran, C.T. Curr. Pharm. Des. 16, 3310-3316 (2010).

441. 3-Phenyl-1H-indole-5-sulfonamides: structure-based drug design of a promising class of carbonic anhydrase inhibitors. Güzel, Ö.; Innocenti, A.; Vullo, D.; Scozzafava, A.; Supuran, C.T. Curr. Pharm. Des. 16, 3317-3326 (2010).
442. Saccharomyces cerevisiae β-carbonic anhydrase inhibition and activation studies. Isik, S.; Ozensoy Guler, O.; Kockar, F.; Aydin, M.; Arslan, O.; Supuran, C.T. Curr. Pharm. Des. 16, 3327-3336 (2010).
443. Pteridine-Sulfonamide Conjugates as Dual Inhibitors of Carbonic Anhydrases and Dihydrofolate Reductase with Potential Antitumor Activity. Marques, S.M.; Enyedy, E.A.; Supuran, C.T.; Krupenko, N.I.; Krupenko, S.A.; Santos, M.A. Bioorg. Med. Chem. 18, 5081-5089 (2010).
444. Recent advances in structural studies of the carbonic anhydrase family: The crystal structure of human CA IX and CA XIII. Supuran, C.T.; Di Fiore, A.; Alterio, V.; Monti, S.M.; De Simone, G. Curr. Pharm. Des., 16, 3246-3254 (2010).
445. Modulation of Carbonic Anhydrase 9 (CA9) in Human Brain Cancer. Said, H.M.; Supuran, C.T.; Hageman, C.; Staab, A.; Polat, B.; Katzer, A.; Scozzafava, A.; Anacker, J.; Flentje, M.; Vordermark, D. Curr. Pharm. Des. 16, 3288-3299 (2010).
446. Inhibition of the R1 fragment of the cadmium- containg ζ class carbonic anhydrase from the diatom Thalassiosira weissflogii with anions. Viparelli, F.; Monti, S.M.; De Simone, G.; Innocenti, A.; Scozzafava, A.; Xu, Y.; Morel, F.M.M.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 4745-4748 (2010).
447. Design, solid-phase synthesis and biological evaluation of novel 1,2-diarylpyrrole-3-carboxamides as carbonic anhydrase IX inhibitors. Gluszok, S.; Frédérick, R.; Supuran, C.T.; Vullo, D.; Scozzafava, A.; Masereel, B.; Depreux, P.; Goossens, L. Bioorg. Med. Chem. 18, 7392-7401 (2010).
448. Selective hydrophobic pocket binding observed within the carbonic anhydrase II active site accommodate different 4-substituted-ureido-benzenesulfonamides and correlate to inhibitor potency. Pacchiano, F.; Aggarwal, M.; Avvaru, B.S.; Robbins, A.H.; Scozzafava, A.; McKenna, R.; Supuran, C.T. Chem. Comm. 46, 8371-8373 (2010).
449. Paraoxon, 4-nitrophenyl phosphate and acetate are substrates of α- but not of β-, γ- and ζ-carbonic anhydrases. Innocenti, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 6208-6212 (2010).
450. 7,8-Disubstituted- but not 6,7-disubstituted coumarins selectively inhibit the transmembrane, tumor-associated carbonic anhydrase isoforms IX and XII over the cytosolic ones I and II in the low nanomolar/subnanomolar range. Maresca, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 20, 7255-7258 (2010).
451. Polymer screening by radiofrequency glow discharge time-of-flight mass spectrometry. Lobo, L.; Tuccitto, N.; Bordel, N.; Pereiro, R.; Pisonero, J.; Licciardello, A.; Tempez, A.; Chapon, P.; Sanz-Medel, A. Analytical and Bioanalytical Chemistry 396, 2863-2869 (2010).
452. ToF-SIMS images and spectra of biomimetic calcium silicate-based cements after storage in solutions simulating the effects of human biological fluids. Torrisi, A.; Torrisi, V.; Tuccitto, N.; Gandolfi, M. G.; Prati, C.; Licciardello, A. International Journal of Mass Spectrometry, 289(2-3), 150-161 (2010).
453. Differentiation of O-18- and O-16-rich layers in anodic alumina films by glow discharge time-of-flight mass spectroscopy. Molchan, I.S.; Thompson, G.E.; Skeldon, P.; Trigoulet, N.; Tempez, A.; Chapon, P.; Tuccitto, N.; Licciardello, A. Surface and Interface Analysis, 42; 211-214 (2010).
454. Chemical imaging of self-assembling structures in Langmuir-Blodgett films of polymer blends. Torrisi, V.; Licciardello, A.; Marletta,G. Material Science and Engineering B-Solid State Materials forAdvanced Technology, 169; 49-54 (2010).
455. Surface anchoring of a chiral salen macrocycle on a carboxy-functionalized platform via a multiple site esterification. Torrisi, V.; Amato, M. E.; Ballistreri, F. P.; Tomaselli, G.; Toscano, R. M.; Licciardello, A. Surface and Interface Analysis ISSN: 0142-2421, doi: 10.1002/sia.3690 (2010).
456. ToF-SIMS imaging of surface self-organized fractal patterns of bacteria. Tuccitto, N.; Marletta, G.; Caratozzolo, M.; Grasso, L.; Carnazza, S.; Guglielmino, S.; Licciardello, A. Surface and Interfaces Analysis, DOI: 10.1002/sia.3555 (2010).
457. Depth profiling analysis of barrier-type anodic aluminium oxide films formed on substrates of controlled roughness. Trigoulet, N.; Tuccitto, N.; Delfanti, I.; Licciardello, A.; Molchan, I. S.; Skeldon, P.; Thompson, G. E.; Tempez, A.; Chapon, P. Surface and Interfaces Analysis, DOI:

10.1002/sia.3410 (2010).

458. Interaction between vine pesticides and serum albumin studied by nuclear spin relaxation data. Martini, S.; Bonechi, C.; Rossi, C. Journal of Agricultural and Food Chemistry 58, 10705-10709 (2010).

459. Realisation and chemical characterisation of a model system for saccharide-based biosensor. Leone, G.; Consumi, M.; Tognazzi, A.; Magnani, A. Thin Solid Films 519, 462-470 (2010).

460. PVA/STMP based hydrogels as potential substitutes of human vitreous. Leone, G.; Consumi, M.; Aggravi, M.; Donati, A.; Lamponi, S.; Magnani, A. Journal of Materials Science: Materials in Medicine 21:2491–2500 (2010).

461. Evaluation of in vitro biocompatibility of hydrogels as vitreous body substitutes. Lamponi, S.; Leone, G.; Consumi, M.; Greco, G.; Magnani, A. International Journal of Artifical Organs 33, 142-142 (2010).

462. Chemistry and topographic domains: micropatterned surfaces. Production, physico-chemical and biological characterisation. Lamponi, S.; Di Canio, C.; Barbucci, R. In Cell mechanochemistry Transworld Research Network Eds Trivandrum, India 55 – 74 (2010).

463. Heterotypic interaction of fibroblasts and endothelial cells on restricted area. Lamponi, S.; Di Canio, C.; Forbicioni, M.; Barbucci, R. Journal of Biomedical Materials Research. Part A 92A, 733 – 745 (2010).

464. Spiral and square microstructured surfaces: the effect of the decreasing size of photo-immobilised hyaluronan domains on cell growth. Di Canio, C.; Lamponi, S.; Barbucci, R. Journal of Biomedical Materials Research. Part A 92A, 276 – 284 (2010).

465. Spatial and seasonal changes in optical properties of autochthonous and allochthonous chromophoric dissolved organic matter in a stratified mountain lake. Bracchini, L.; Dattilo, A.M.; Hull, V.; Loiselle, S.A.; Nannicini, L.; Picchi, M.P.; Ricci, M.; Santinelli, C.; Seritti, A.; Tognazzi, A.; Rossi, C. Photochemical & Photobiological Sciences 9, 304-314 (2010).

466. Optimized extraction of daily bio-optical time series derived from MODIS/Aqua imagery for Lake Tanganyika, Africa. Horion, S.; Bergamino, N.; Stenuite, S.; Descy, J.P.;Plisnier, P.D.; Loiselle, S.A.; Cornet, Y. Remote Sensing of Environment 114, 781-791 (2010).

467. Increasing photostability and water-solubility of carotenoids: synthesis and characterization of Beta-carotene-humic acid complexes. Martini, S.; Daddario, C.; Bonechi, C.; Leone, G.; Tognazzi, A.; Consumi, M.; Magnani, A.; Rossi C. Journal of Photochemistry and Photobiology B-Biology 101, 355-361 (2010).

468. H. pylori (HP) strains isolated from patients with gastric carcinoma (GC) show an increased susceptibility to resveratrol (Res) in vitro. Martini, S.; Bonechi, C.; Figura, N.; Nardi, P.; Santucci, A.; Rossi, C. Helicobacter 15, 336 (2010).

469. Spatial dynamics of chromophoric dissolved organic matter in nearshore waters of Lake Victoria. Loiselle, S.A.; Azza, N.; Gichuki, J.; Bracchini L.; Tognazzi, A.; Dattilo, A.M.; Rossi, C. Aquatic Ecosystem Health & Management 13, 1-11 (2010).

470. Sensitivity analysis of CDOM Spectral Slope in artificial and natural samples. An application in the central eastern Mediterranean Basin. Bracchini, L.; Tognazzi, A.; Dattilo, A.M.; Decembrini, F.; Rossi, C.; Loiselle, S.A. Aquatic Sciences 72, 485-498 (2010).

471. Spatio-temporal dynamics of phytoplankton and primary production in Lake Tanganyika using a MODIS based bio-optical time series. Bergamino, N.; Horion, S.; Stenuite, S.; Cornet, Y.; Loiselle, S.; Plisnier, P.-D.; Descy, J.-P. Remote Sensing of Environment 114, 772-780 (2010).

472. A new three-band algorithm for estimating chlorophyll concentrations in turbid inland lakes. Duan, H.; Ma, R.; Zhang, Y.; Loiselle, S.A.; Zhao, J.X.C.; Zhou, L.; Shang, L. Environ. Res. Lett. 5 044009 (2010).

473. Carborane-Conjugated 2-Quinolinecarboxamide Ligands of the Translocator Protein for Boron Neutron Capture Therapy. Cappelli, A.; Valenti, S.; Mancini, A.; Giuliani, G.; Anzini, M.; Altieri, S.; Bortolussi, S.; Ferrari, C.; Clerici, A.M.; Zonta, C.; Carraro, F.; Filippi, I.; Giorgi, G.; Donati, A.; Ristori, S.; Vomero, S.; Concas, A.; Biggio, G. Bioconjugate Chemistry. 21 (12), 2213-2221 (2010).

474. Structure-Property Relationships in π-Stacked Polymer Brushes. Cappelli, A.; Polino, A.; Anzini, A.; Giuliani, G.; Valenti, S.; Aggravi, M.; Donati, A.; Mendichi, R.; Zetta, L.; Boccia, A.C.; Bertini, F.; Samperi, F.; Battiato, S.; Paccagnini, E.; Vomero, S. Journal of polymer science. Part a, polymer chemistry 48 (11), 2446-2461 (2010).

475. A New Approach To Study In Vivo Cellular Metabolism Using A Modellistic Analysis Of Magnetic Resonance Spectra. Gastaldelli, A.; Martini, S.; Donati, A.; Marchettini, N.; Rossi, C.; Bastianoni, S. Mathematical Biosciences, Vol. 222; P. 36-41 (2010).

476. TOF-SIMS Characterization of Pigments and Binders in 'The Martyrdom of St. Catherine' in

Zejtun (Malta). Tognazzi, A.; Lapucci, R.; Martini, S.; Leone, G.; Magnani, A.; Rossi C. Surface and Interface Analysis (2010). In press.

477. TOF-SIMS investigation of ancient ceramics from Quartaia Site, Tuscany. Tognazzi, A.; Dattilo, A.M.; Bracchini, L.; Aggravi,M.; Benetti, F.; Magnani, A.; Rossi, C. Surface And Interface Analysis (2010). In press.
478. Assessing the optical changes in dissolved organic matter in humic lakes by spectral slope distributions. Galgani, L.; Tognazzi, A.; Rossi, C.; Ricci, M.; Galvez, J.A.; Dattilo, A.M.; Cozar, A.C.; Bracchini, L.; Loiselle, S.A. Journal of Photochemistry and Photobiology B-Biology, ISSN: 1011-1344 (2010).
479. In vitro biocompatibility of new PVA based hydrogels as vitreous body substitutes. Lamponi, S.; Leone, G.; Consumi, M.; Greco, G.; Magnani, A. Journal of Biomaterials Science: Polymer Edition (accepted on 1st Jan 2011).
480. Cartilage replacement implants using hydrogels. Leone, G. In Biomedical hydrogels Biochemistry, manufacture and medical applications. Ed. Steve Rimmer. Woodhead Publishing Limited, Abington Hall, Granta Park, Great Abington, Cambridge, UK. 2011 (correcting proofs).
481. Non-nucleoside inhibitors of human adenosine kinase (NNhAKIs): synthesis and biological studies. Butini, S.; Gemma, S.; Brindisi, M.; Borrelli, G.; Lossani, A.; Ponte, A.; Torti, A., Maga, G.; Marinelli, L.; La Pietra, V.; Fiorini, I.; Lamponi, S.; el al. Journal of Medicinal Chemistry (2011). Submitted.
482. In vitro biocompatibility of new PVA-based hydrogels as vitreous body substitutes. Lamponi, S.; Leone, G.; Consumi, M.; Greco, G.; Magnani, A. Journal of Biomaterials Science. Polymer Edition (2011). In press.
483. New Perspectives in cellular communication: bioelectromagnetic interactions. Rossi, C.; Foletti, A.; Magnani, A.; Lamponi, S. Seminars in Cancer Biology (2011). In press.
484. Viable But Nonculturable State of Foodborne Pathogens in Grapefruit Juice: A Study of Laboratory. Nicolo`, M.; Gioffré, A.; Carnazza, S.; Platania, G.; Di Silvestro, I.; Guglielmino, S. Foodborne Pathogens and Disease 8, 11-17 (2011).
485. Natural Product-Based Phenols as Novel Probes for Mycobacterial and Fungal Carbonic Anhydrases. Davis, R.A.; Hofmann, A.; Osman, A.; Hall, R.A.; Mühlschlegel, F.A.; Vullo, D.; Innocenti, A.; Supuran, C.T.; Poulsen, S.-A. J. Med. Chem. 54, 1682-1692 (2011).
486. Characterization and inhibition studies of an α-carbonic anhydrase from the endangered sturgeon species Acipenser gueldenstaedti. Kolayli, S.; Karahalil, F.; Sahin, H.; Dincer, B.; Supuran, C.T. J. Enz. Inhib. Med. Chem. 26 (2011). In press.
487. Inhibition of β-carbonic anhydrases with ureido-substituted benzenesulfonamides. Pacchiano, F.; Carta, F.; Vullo, D.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21, 102-105 (2011).
488. Kinetic and docking studies of phenol-based inhibitors of carbonic anhydrase isoforms I, II, IX and XII evidence a new binding mode within the enzyme active site. Durdagi, S.; Şentürk, M.; Ekinci, D.; Türker Balaydın, H.; Göksu, S.; Küfrevioğlu, Ö.İ.; Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. 19, 1381-1389 (2011).
489. Determination of the nateglinide polymorphic purity through DSC. Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Lanfranconi, S.; Marini, A.; Journal of Pharmaceutical and Biomedical Analysis 54, 1196-1199 (2011).
490. Mn influence on the electrochemical behaviour of Li3V2(PO4)3 cathode material. Bini, M.; Ferrari, S.; Capsoni, D.; Massarotti, V. Electrochimica Acta 56, 2648-2655 (2011).
491. Hydrogen evolution reaction in PTFE bonded Raney-Ni electrodes. Salvi, P.; Nelli, P.; Villa, M.; Kiros, Y.; Zangari, G.; Bruni, G.; Marini, A.; Milanese, C. International Journal of Hydrogen Energy 36, 7816-7821 (2011).
492. Thermal, spectroscopic and ab-initio structural characterization of carprofen polymorphs. Bruni, G.; Gozzo, F.; Capsoni, D.; Bini, M.; Macchi, P.; Simoncic, P.; Berbenni, V.; Milanese, C.; Girella, A.; Ferrari, S.; Marini, A. Journal of Pharmaceutical Sciences 100, 2321-2332 (2011).
493. Thermodynamic and kinetic investigations on pure and doped NaBH4 – MgH2 system. Milanese, C.; Garroni, S.; Girella, A.; Mulas, G.; Berbenni, V.; Bruni, G.; Suriñach, S.; Baró, M.D.; Marini, A. Journal of Physical Chemistry C 115, 3151-3162 (2011).
494. Hydrogen sorption performance of MgH_2 doped with mesoporous nickel- and cobalt-based oxides. Cabo, M.; Garroni, S.; Pellicer, E.; Milanese, C.; Girella, A.; Marini, A.; Rossinyol, E.; Suriñach, S.; Baró, M.D. International Journal of Hydrogen Energy 36, 5400-5410 (2011).
495. Optical properties of sol-gel prepared Cerium doped Lutetium and Yttrium oxyorthosilicates.

Ricci, P.C.; Carbonaro, C.M.; Stagi, L.; Anedda, A.; Ferrari, S.; Capsoni, D.; Magistris, A. Journal of Non-Crystalline Solids 357, 1908-1911 (2011).

496. Characterization of Nicergoline polymorphs crystallized in several organic solvents. Malaj, L.; Censi, R.; Capsoni, D.; Pellegrino, L.; Bini, M.; Ferrari, S.; Gobetto, R.; Massarotti, V.; Di Martino, P. Journal of Pharmaceutical Sciences 100, 2610-2622 (2011).
497. Quantification methods of amorphous/crystalline fractions in high-energy ball milled pharmaceutical products. Bruni, G.; Berbenni, V.; Sartor, F.; Milanese, C.; Girella, A.; Franchi, D.; Marini, A. Journal of Thermal Analysis and Calorimetry (2011) in press, doi: 10.1007/s10973-011-1504-y.
498. Preliminary evaluation of particle systems visualization on the skin surface by scanning electron microscopy and transparency profilometry. Perugini, P.; Vettor, M.; Bleve, M.; Bruni, G.; Mondelli, A.; Secchi, G.F.; Pavanetto, F. Skin Research and Technology (2011) in press, doi: 10.1111/j.1600-0846.2011.00529.x.
499. Therapeutic approach to avoid periprosthetic bone loss: preliminary study of HA-ALN composites. Capra, P.; Dorati, R.; Colonna, C.; Bruni, G.; Genta, I.; Conti, B. Journal of Microencapsulation (2011). In press.
500. Characterization of Nicergoline polymorphs crystallized in several organic solvents. Malaj, L.; Censi, R.; Capsoni, D.; Pellegrino, L.; Bini, M.; Ferrari, S.; Gobetto, R.; Massarotti, V.; Di Martino, P. Journal of Pharmaceutical Sciences (2011). Accepted for publication.
501. Hydrogenation of carbon monoxide over nanostructured systems: a mechanochemical approach. Mulas, G.; Campesi, R.; Garroni, S.; Delogu, F.; Milanese, C. Applied Surface Science (2011). Accepted for publication.
502. Synthesis of $YFeO_3$ by Thermal Decomposition of Mechanically Activated Mixtures $Y(CH_3COO)_3•4H_2O-FeC_2O_4•H_2O$. Berbenni, V.; Milanese, C.; Bruni, G.; Girella, A.; Marini, A. Termochimica Acta (2011). Accepted for publication.
503. Synthesis, characterization, biological studies and X-ray crystal structure of sulfonamide Schiff's bases and some of their metal derivatives. Chohan, Z.H.; Shad, H.A.; Supuran, C.T. J. Enz. Inhib. Med Chem (2011). In press.
504. Carbonic anhydrase activators: gold nanoparticles coated with derivatized histamine, histidine and carnosine show enhanced activatory effects on several mammalian isoforms. Saada, M.C.; Montero, J.L.; Winum, J.Y.; Vullo, D.; Scozzafava, A.; Supuran, C.T. J. Med. Chem. 54, 1170-1177 (2011).
505. Targeting Tumor Hypoxia: Suppression of Breast Tumor Growth and Metastasis by Novel Carbonic Anhydrase IX Inhibitors. Lou, Y.; McDonald, P.C.;Oloumi, A.; Chia, S.; Oslund, C.; Ahmadi, A.; Kyle, A.; auf dem Keller, U.; Leung, S.; Huntsman, D.; Clarke, B.; Sutherland, B.W.; Waterhouse, A.D.; Bally, M.; Roskelley, C.; Overall, C.M.; Minchinton, A.; Pacchiano, F.; Carta, F.; Scozzafava, A.; Touisni, N.; Winum, J.Y.; Supuran, C.T.; Dedhar, S. Cancer Res. (2011). In press.
506. A new carbonic anhydrase in the coral Stylophora pistillata. Bertucci, A.; Tambutté, S.; Supuran, C.T.; Allemand, D.; Zoccola, D. Mar. Biotechnol. (NY) (2011). In press.
507. A new Brucella suis β-carbonic anhydrase, bsCA II: inhibition of bsCA I and II with sulfonamides and sulfamates inhibits the pathogen growth. Joseph, P.; Ouahrani-Bettache, S.; Montero, J.L. Nishimori, I.; Vullo, D.; Scozzafava, A.; Winum, J.Y.; Köhler, S.; Supuran, C.T. Bioorg. Med. Chem. 19, 1172-1178 (2011).
508. Hofmeister Effects: Interplay of Hydration, Non-Electrostatic Potentials, and Ion Size. Parsons, D.F.; Boström, M.; Lo Nostro, P.; Ninham, B.W.; Baglioni, P. Physical Chemistry Chemical Physics, in press (2011).
509. Quntitative Structure-Activity Relationship (QSAR) studies of carbonic anhydrase inhibitors and activators. Khadikar, P.V.; Supuran, C.T.; Manikpuri, A.D.; Singh, S.; Lakhwani, M. J. Indian Chem. Soc. 88, 25-85 (2011).
510. Carbonic anhydrase inhibition with natural products: novel chemotypes and inhibition mechanisms. Supuran, C.T. Mol. Divers. (2011). In press.
511. Inhibition of the b-carbonic anhydrase from Streptococcus pneumoniae by inorganic anions and small molecules: towards innovative drug design of antiinfectives? Burghout, P.; Vullo, D.; Scozzafava, A.; Hermans, P.W.M.; Supuran, C.T. Bioorg. Med. Chem. 19, 243-248 (2011).
512. Pyridinium derivatives of histamine are potent activators of cytosolic carbonic anhydrase isoforms I, II and VII. Dave, K.; Scozzafava, A.; Vullo, D.; Supuran, C.T.; Ilies, M.A. Org. Biomol. Chem. (2011). In press.
513. Controlled drug release under a low-frequency magnetic field: effect of the citrate coating on

the magnetoliposome stability. Nappini, S.; Bonini M.; Baldelli Bombelli, F.; Pineider, F.; Sangregorio, C.; Nordèn, B.; Baglioni, P. Soft Matter, 7, 1024-1037 (2011).

514. Magnetically triggered release from giant unilamellar vesicles: visualization by means of confocal microscopy. Nappini, S.; Al Kayal, T.; Berti, D.; Nordèn, B.; Baglioni, P. J. Phys. Chem. Lett., 2, 713-718 (2011).
515. Honey, polen and propolis extracts show potent inhibitory activity against the zinc metalloenzyme carbonic anhydrase. Sahin, H.; Aliyazicioglu, R.; Yildiz, O.; Kolayli, S.; Innocenti, A.; Supuran, C.T. J. Enz. Inhib. Med. Chem. 26 (2011). In press.
516. An inhibitor-like binding mode of a carbonic anhydrase activator within the active site of isoform II. Dave, K.; Ilies, M.A.; Scozzafava, A.; Temperini, C.; Vullo, D.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21 (2011). In press.
517. Characterization and anions inhibition studies of an α-carbonic anhydrase from the teleost fish Dicentrarchus labrax. Ekinci, D.; Buğrahan Ceyhun, S.; Şentürk, M.; Erdem, D.; Küfrevioğlu, Ö.İ.; Supuran, C.T. Bioorg. Med. Chem. 19, 744-748 (2011).
518. (R)-/(S)-10-Camphorsulfonyl-substituted aromatic/heterocyclic sulfonamides selectively inhibit mitochondrial over cytosolic carbonic anhydrases. Maresca, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21, 1334-1337 (2011).
519. In Vitro Inhibition of Human Carbonic Anhydrase I and II Isozymes with Natural Phenolic Compounds. Şentürk, M.; Gülçin, I.; Beydemir, S.; Küfrevioğlu, Ö.I.; Supuran, C.T. Chem. Biol. Drug Des. (2011). In press.
520. Carbonic anhydrase inhibitors. Inhibition studies with anions and sulfonamides of a new cytosolic enzyme from the scleractinian coral Stylophora pistillata. Bertucci, A.; Innocenti, A.; Scozzafava, A.; Tambutté, S.; Zoccola, D.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21, 710-714 (2011).
521. Cement: A two thousand year old nano-colloid. Ridi, F.; Fratini, E.; Baglioni, P. Journal of Colloid and Interface Science 357, 255-264 (2011).
522. A tri-block copolymer templated synthesis of gold nanostructures. Falletta, E.; Ridi, F.; Fratini, E.; Vannucci, C.; Canton, P.; Bianchi, S.; Castelvetro, V.; Baglioni, P. Journal of Colloid and Interface Science 357, (1), 88-94 (2011).
523. Structure and permeability of magnetoliposomes loaded with hydrophobic magnetic nanoparticles in the presence of a low frequency magnetic field. Nappini, S.; Bonini, M.; Ridi, F.; Baglioni, P. Soft Matter 7, 4801-4811 (2011).
524. Functional liposomes and supported lipid bilayers: towards the complexity of biological archetypes. Berti, D.; Caminati, G.; Baglioni, P. Physical Chemistry Chemical Physics 13, 8769-8782 (2011).
525. Euopium in phospholipid nanoscaffolds for the photophysical detection of antibiotic traces in solution. Caminati, G.; Puggelli, M. Europium: Compounds, Production and Applications, Ed. Moreno, L.M.; Nova Science Publisher, 203-228 (2011).
526. Plant Oil Bodies: Novel Carriers to Deliver Lipophilic Molecules. Bonsegna, S.; Bettini, S.; Pagano, R.; Zacheo, A.; Vergaro, V.; Giovinazzo, G.; Caminati, G.; Leporatti, S.; Valli, L.; Santino, A. Applied Biochemistry and Biotechnology 163, 792-802 (2011).
527. Studio dell'alterazione di superfici bronzee attraverso misure di angolo di contatto. Caminati, G.; Gambinossi, F.; Sagarese, V.; Dei, L. in AA. VV., "Progetto Battistero. Studio dell'impatto ambientale sulle Porte del Battistero di Firenze. Risultati finali.", a cura di M. Matteini e R. Rimaboschi, Opera del Duomo di Firenze. In fase di pubblicazione (2011).
528. Design, Synthesis and Biological Evaluation of Novel Carbohydrate-based Sulfamates as Carbonic Anhydrase Inhibitors. Lopez, M.; Trajkovic, J.; Bornaghi, L.F.; Innocenti, A.; Vullo, D.; Supuran, C.T.; Poulsen, S.A. J. Med. Chem. 54, 1481-1489 (2011).
529. Selection of Carbonic Anhydrase IX Inhibitors from One Million DNA-Encoded Compounds. Buller, F.; Steiner, M.; Frey, K.; Mircsof, D.; Scheuermann, J.; Kalisch, M.; Bühlmann, P.;. Supuran, C. T ; Neri, D. ACS Chem. Biol. (2011). In press.
530. Ureido-substituted benzenesulfonamides potently inhibit carbonic anhydrase IX and show antimetastatic activity in a model of breast cancer metastasis. Pacchiano, F.; Carta, F.; McDonald, P.C.; Lou, Y.; Vullo, D.; Scozzafava, A.; Dedhar, S.; Supuran, C.T. J. Med. Chem. 54, 1896-1902 (2011).
531. Macroscopic Dynamics as Reporter of Mesoscopic Organization: The Belousov–Zhabotinsky Reaction in Aqueous Layers of DPPC Lamellar Phases. Biosa, G.; Ristori, S.; Spalla, O.; Rustici, M.; Hauser, M.J.B. J. Phys. Chem. A, ASAP web publ. date: March 24 (2011).
532. D-sorbitol, a structurally simple, low molecular-mass gelator. Grassi, S.; Carretti, E.; Dei, L.; Branham, C. W.; Kahr, B.; Weiss, R. G. New Journal of Chemistry, in press 35, 445-452

(2011).

533. Multiple binding modes of inhibitors to the carbonic anhydrases: how to design specific drugs targeting 15 different isoforms ? Alterio, C.; Di Fiore, A.; D'Ambrosio, K.; Supuran, C.T.; De Simone, G. Chem. Rev. (2011). In press.

534. Sulfonamides incorporating 1,3,5-triazine moieties selectively and potently inhibit carbonic anhydrase transmembrane isoforms IX, XII and XIV over cytosolic isoforms I and II: solution and X-ray crystallographic studies. Carta, F.; Garaj, V.; Maresca, A.; Wagner, J.; Avvaru, B.S.; Robbins, A.H.; Scozzafava, A.; McKenna, R.; Supuran, C.T. Bioorg. Med. Chem. (2011). In press.

535. Carbonic anhydrase inhibitors. Inhibition of the β-class enzymes from the fungal pathogens Candida albicans and Cryptococcus neoformans with branched aliphatic- and aromatic carboxylates. Innocenti, A.; Hall, R.A.; Mühlschlegel, F.A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21 (2011). In press.

536. Structural basis for the interaction between carbonic anhydrase and 1,2,3,4-tetrahydroisoquinoline-2ylsulfonamides. Mader, P.; Brynda, J.; Gitto, R.; Agnelo, S.; Pachl, P.; Supuran, C.T.; Chimirri, A,; Řezáčová, P. J. Med. Chem. 54 (2011). In press.

537. Purification and inhibition studies with anions and sulfonamides of an α-carbonic anhydrase from the Antarctic seal Leptonychotes weddellii. Cincinelli, A.; Martellini, T.; Innocenti, A.; Scozzafava, A.; Supuran, C.T. Bioorg. Med. Chem. 19, 1847-1851 (2011).

538. Carbonic anhydrase inhibitors. Purification and inhibition studies of red blood cell pigeon (Columba livia var. domestica) carbonic anhydrase with sulfonamides. Ozensoy, O.; Arslan, M.; Supuran, C.T. J. Enz. Inhib. Med. Chem. 26 (2011). In press.

539. Virtual Screening-Driven Identification of Human Carbonic Anhydrase Inhibitors carrying an Original Pharmacophore. Pala, N.; Dallocchio, R.; Dessì, A.; Brancale, A.; Carta, F.; Ihm, S.; Maresca, A.; Sechi, M.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21 (2011). In press.

540. Generation and characterization of the first inhibitory antibody targeting tumour-associated carbonic anhydrase XII. Battke, C.; Kremmer, E.; Mysliwietz, J.; Gondi, G.; Dumitru, C.; Brandau, S.; Lang, S.; Vullo, D.; Supuran, C.; Zeidler, R. Cancer Immunol. Immunother (2011). In press.

541. Sulfonamides incorporating boroxazolidone moieties are potent inhibitors of the transmembrane, tumor-associated carbonic anhydrase isoforms IX and XII. Rami, M.; Maresca, A.; Zhora Smaine, F.; Montero, J.-L.; Scozzafava, A.; Winum, J.-Y.; Supuran, C.T. Bioorg. Med. Chem. Lett. 21 (2011). In press.

542. Temperature dependence of Calcium and Magnesium induced caseinate precipitation in H2O and D2O. Cuomo, F.; Ceglie, A.; Lopez, F. Food Chemistry 126, 8-14 (2011).

543. Polyadenylic acid binding on cationic liposomes doped with the non-ionic nucleolipid Lauroyl-Uridine. Cuomo, F.; Ceglie, A.; Colafemmina, G.; Germani, R.; Savelli, G.; Lopez, F. Colloids and Surfaces B 82, 277-282 (2011).

544. Kojic Acid Derivatives as Powerful Chelators for Iron(III) and Aluminium(III). Nurchi V.M.; Lachowicz, J.I.; Crisponi, G.; Murgia, S.; Arca, M.; Pintus, A.; Gans, P.; Niclos-Gutierrez, J.; Dominguez-Martin, A.; Castineiras, A.; Remelli, M.; Szewczuk, Z.; Lis, T.; Dalton Transactions 40, 5984-5998 (2011).

545. Aerosol-OT in water forms fully-branched cylindrical direct micelles in the presence of the ionic liquid 1-butyl-3-methylimidazolium bromide. Murgia, S.; Palazzo, G.; Mamusa, M.; Lampis, S.; Monduzzi, M. PCCP 13, 9238-9245 (2011).

546. Environmental and Life Cycle Analysis of a biodiesel production line from sunflower in the Province of Siena (Italy). Spinelli, D.; Jez, S.; Pogni, R.; Basosi, R. Biomass & Bioenergy (2011). In press.

547. Life Cycle Assessment of a Micromorph Photovoltaic System. Bravi, M.; Parisi, M.L.; Tiezzi, E.; Basosi, R.; Energy. DOI: 10.1016/j.energy.2011.04.012. (2011). In press.

548. Crystallographic, kinetic, and spectroscopic study of the first ligninolytic peroxidase presenting a catalytic tyrosine. Miki, Y.; Calvino, F.R.; Pogni, R.; Giansanti, S.; Ruiz-Duenas, F.J.; Martinez, M.J.; Basosi, R.; Romero, A.; Martinez, A.T.; The Journal of Biological Chemistry 286, 17, 15525-15534. DOI: 10.1074/jbc.M111.220996. (2011). In press.

549. EPR Parameters of amino acid radicals in P. eryngii versatile peroxidase and its W164Y variant computed at the QM/MM level. Bernini, C.; Pogni, R.; Ruiz-Duenas, F.J.; Martinez Ferrer, A.T.; Basosi, R.; Sinicropi, A. Physical Chemistry Chemical Physics 13 (11), 5078-5098, (2011). DOI:10.1039/C0CP02151B (2011). In press.

550. A novel environmental indicator for monitoring of pesticides. Luchi, F.; Vigni, V.; Basosi, R.; Busi, E. Environmental Monitoring and Assessment 177, 151-163 (2011) DOI:

10.1007/s10661-010-1626-x.

551. Life Cycle Assessment of advanced technologies for photovoltaic panels production. Bravi, M.; Parisi, M.L.; Tiezzi, E.; Basosi, R. International Journal of Heat & Technologies 28, 2, 133-140 (2011).
552. Approximate bottom contribution to remote sensing reflectance in Taihu Lake, China. Ma, R.; Duan, H.; Liu, Q.; Xi, H.; Zhang, Y.; Loiselle, S.A. Journal of Great Lakes Research 37, 18-25 (2011).
553. Competition for spectral irradiance between epilimnetic optically active dissolved and suspended matter and phytoplankton in the metalimnion. Consequences for limnology and chemistry. Bracchini, L.; Dattilo, A.M.; Falcucci, M.; Hull, V.; Tognazzi, A.; Rossi, C.; Loiselle, S.A. Photochemical & Photobiological Sciences (2011) doi.org/10.1039/C0PP00291G.
554. Effective upwelling irradiance depths in turbid waters: a spectral analysis of origins and fate. Ma, R.; Jiang, G.; Duan, H.; Bracchini, L.; Loiselle, S.A. Optics Express 19, 7127-7138 (2011).
555. Unusual links between inherent and apparent optical properties in shallow lakes, the case of Taihu Lake. Ma, R.; Duan, H.; Lu, C.; Loiselle, S.A. Hydrobiologia 667,149–158 (2011).
556. On the antibacterial activity of roots of Capparis spinosa L. Boga, C.; Forlani, L.; Calienni, R.; Hindley, T.; Hochkoeppler, A.; Tozzi, S.; Zanna, N. Natural Product Research 25, 417-421 (2011).
557. pGOODs: new plasmids for the co-expression of proteins in Escherichia coli. Conte, E.; Landolfi, G.; Vincelli, G.; Stefan, A.; Hochkoeppler, A. Biotechnol Lett. DOI 10.1007/s10529-011-0624-6 (2011).
558. A PVA/PVP hydrogel for human lens substitution: synthesis, rheological characterisation and in vitro biocompatibilità. Leone, G.; Consumi, M.; Greco, G.; Bonechi, C.; Lamponi, S.; Magnani, A.; Rossi, C. Journal of Biomedical Materials Research part B: Applied Biomaterials 97B, 278-288 (2011).
559. Interaction study of indigo carmine with albumin and dextran by NMR Relaxation. Bonechi, C.; Martini, S.; Rossi, C. Journal of Materials Science 46, 2541-2547 (2011).
560. Effect of trans-Resveratrol on induced oxidative stress in human sperm and in rat germinal. Collodel, G.; Federico, M.G.; Geminiani, M.; Martini, S.; Bonechi, C.; Rossi, C.; Figura, N; Moretti, E. Reproductive Toxicology 31, 239-246 (2011).
561. *In vivo* NMR study of yeast fermentative metabolism in the presence of Ferric iron. Ricci, M., Martini, S.; Bonechi, C.; Braconi, D.; Santucci, A.; Rossi, C. Journal of Biosciences 36, 97-103 (2011).
562. Fluorescence spectra of organic dyes in solution: a time dependent multilevel approach. Barone, V.; Bloino, J.; Monti, S.; Pedone, A.; Prampolini, G. Physical Chemistry Chemical Physics 13, 2160-2166 (2011).
563. Singlet–triplet energy gap of a diarylnitroxide diradical by an accurate many-body perturbative approach. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini G. Physical Chemistry Chemical Physics 13, 4709-4714 (2011).
564. The proton affinity and gas-phase basicity of sulfur dioxide. De Pretis, G.; Cartoni, A.; Rosi, M.; Barone, V. ; Puzzarini, C.; Troiani, A. Physical Chemistry Chemical Physics 12, 112-115 (2011).
565. Dirichlet to Neumann map for a nonlinear diffusion equation. Barone, V.; De Lillo, S.; Lupo, G.; Polimeno, A. Studies in Applied Mathematics 126, 145-155 (2011).
566. Methyl Phosphate Dianion Hydrolysis in Solution Characterized by Path Collective Variables Coupled with DFT-Based Enhanced Sampling Simulations. Branduardi, D.; De Vivo, M.; Rega, N.; Barone, V.; Cavalli, A. Journal of Chemical Theory and Computation 7, 539-543 (2011).
567. An Integrated Protocol for the Accurate Calculation of Magnetic Interactions in Organic Magnets. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini G. Journal of Chemical Theory and Computation 7, 699-706 (2011).
568. Silicon Nanocrystal Functionalization: Analytic Fitting of DFTB Parameters. Trani, F.; Barone, V. Journal of Chemical Theory and Computation 7, 699-706 (2011).
569. Organic Functionalization and Optimal Coverage of a Silicon(111) Surface in Solvent: A Computational Study. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini G. Journal of Physical Chemistry C 115, 4145-4154 (2011).
570. Extending the molecular size in accurate quantum-chemical calculations: The equilibrium structure and spectroscopic properties of uracil. Puzzarini, C.; Barone, V. Physical Chemistry

Chemical Physics 13, 7189-7197 (2011).

571. Interactions of Nucleotide Bases with Decorated Si Surfaces from Molecular Dynamics Simulations Monti, S.; Prampolini, G.; Barone, V. Journal of Physical Chemistry C 115, 9146-9156 (2011).

572. The fluorine environment in bioactive glasses: ab initio molecular dynamics simulations. Christie, J. K.; Pedone, A.; Menziani, M. C.; Tilocca, A. Journal of Physical Chemistry B 115, 2038-2045 (2011).

573. Insight into the Structure of Vanadium containing Glasses: a Molecular Dynamics Study. Ori, G.; Montorsi, M.; Pedone, A.; Siligardi, C. Journal of Non-Crystalline Solids DOI:10.1016/j.jnoncrysol.2011.02.002.

574. The bioactivity of SiO2–CaO and SiO2–CaO–P2O5 glasses explained by molecular dynamic simulations. Malavasi, G.; Menabue, L.; Menziani, M.C.; Pedone, A.; Salinas, A.; Vallè-Regi, M. Journal of Sol-Gel Science and Technology DOI:10.1007/s10971-011-2453-4.

Conferences 2009-2011

1. Ambrosone, L. XXXIX Congresso Nazionale di Chimica Fisica, Stresa 20-24/09/2010. “The dielectric response of non-spherical live cells in suspension”. Oral Presentation.
2. Angelico, R.; Ambrosone, L.; Losito, I.; Palmisano, F. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. “Smart organized molecular assemblies”. Poster.
3. Arroyo, M.C.; Baglioni, P.; Berti, D.; Fratini, E.; Giorgi, R. XXIX Congresso Nazionale di Chimica Fisica – Stresa, VB, 20-24/09/2010. “Ionic liquid/Brij 30/nonane microemulsions: Characterization and Applications”. Poster.
4. Baglioni, M.; Rengstl, D.; Berti, D.; Bonini, M.; Giorgi, R.; Baglioni, P. XII Congresso Nazionale di Chimica dell’Ambiente e dei Beni Culturali, Taormina, 26-30/09/2010 “Nano-structured fluids for the removal of polymer coatings from wall paintings – a study of the mechanism down to the nanoscale”. Oral presentation.
5. Baglioni, M.; Rengstl, D.; Berti, D.; Giorgi, R.; Baglioni, P. XXIII Congresso Nazionale S.C.I., Sorrento, 9/07/2009. “Microemulsions and micellar solutions for the removal of polymers from painted surfaces: Investigation on the cleaning mechanism”. Poster.
6. Baglioni, M.; Rengstl, D.; Berti, D.; Giorgi, R.: Bonini, M.; Baglioni, P. CSGI - Ottava riunione scientifica annuale delle Unità Operative, Chianciano Terme (SI), 28/06-01/07/2010. “Micellar systems for the removal of polymer coatings from wall paintings – a study on the nano-structure and the cleaning mechanism”. Poster.
7. Baglioni, M.; Rengstl, D.; Berti, D.; Teixeira, J.; Bonini, M.; Giorgi, R.; Baglioni, P. PhD-Day, 1° Meeting dei Dottorandi del Polo Scientifico Sesto Fiorentino, 22/06/2010. “Sistemi acquosi nano-strutturati per la rimozione di polimeri organici da dipinti murali”. Oral presentation.
8. Baglioni, P. 3rd EuCheMS Chemistry Congress 2010, Chemistry – The Creative Force, Nürnberg (Germany), 29/08-02/09/2010. “Soft and hard nanoparticles for restoration and conservation of Cultural Heritage”. Invited lecture.
9. Baglioni, P. 7th Lipidomics Congress: Lipids in all states, Anglet – Biarritz (France), 03-06/10/2010. “Hybrid Lipid-DNA Self-Assemblies”. Invited lecture.
10. Baglioni, P. ACS 239th National Meeting, San Francisco (USA), 21-25/03/2010. “Conservation of cultural heritage: there is plenty of room for colloids science”. Invited lecture.
11. Baglioni, P. Florens 2010 - Beni culturali: scienza, istituzioni e nuova industria (sessione “Restauro e Conservazione”); Palazzo Vecchio, Salone dei Dugento, Firenze, 14/11/2011. “Enzo Ferroni - Omaggio ai maestri della scuola di conservazione di beni culturali di Firenze”. Invited lecture.
12. Baglioni, P. International School of Molecular and Structural Archaelogy, 3rd Course: Non-invasive analysis of painting materials, Erice (TP), 14-21/06/2010. “New frontiers in material science for art conservation. Responsive gels and beyond”. Invited lecture.
13. Baglioni, P. International Workshop 14th Annual Meeting Swedish Neutron Scattering Society and Bio-Interfaces: from molecular understanding to application, Lund (Svezia), 24-27/08/2010. “Hybrid Lipid/DNA Self-Assemblies”. Invited lecture.
14. Baglioni, P. International Year of Chemistry 2011, Ambasciata Italiana, Washington DC, 04/04/2011. “Chemistry for the Conservation of Cultural Heritage: Preserving our Past for a Better Future”. Invited lecture.
15. Baglioni, P. International Year of Chemistry 2011, Institut de Science et d’Ingénierie Supramoléculaires, Université de Strasbourg, 02/05/2011. “Chemistry for the Conservation of Cultural Heritage: Preserving our Past for a Better Future”. Invited lecture.
16. Baglioni, P. International Year of Chemistry 2011, Lafayette College, Pennsylvania (USA), 29/03/2011. “Chemistry for the Conservation of Cultural Heritage: Preserving our Past for a Better Future”. Invited lecture.
17. Baglioni, P. International Year of Chemistry 2011, Lund University, 03/02/2011. “Chemistry for the Conservation of Cultural Heritage: Preserving our Past for a Better Future”. Invited lecture.

18. Baglioni, P. Recent Advances on Supramolecular Systems Involving Biological Molecules and/or Bioinspired Compounds, Centre de Recherches Paul Pascal, Pessac (France), 14-15/10/2010. “Lipid membranes functionalized with nucleobases”. Invited lecture.
19. Baglioni, P. Seminar on Nanotechnology for art Conservation, Northwestern University (MRSEC), 28/10/2010. “New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions and Hydroxide Nanoparticles”. Invited lecture.
20. Baglioni, P. Seminar series in Conservation Science: Nanotechnology for research and art conservation, Northwestern University, Chicago (USA), 27-28/10/2010. “Nanogels for cleaning and consolidation”. Invited lecture.
21. Baglioni, P. Workshop on Manipulation of DNA with cosolutes, Kumarakom, Kerala (India), 13-16/01/2010. “Lipid membranes functionalized with DNA”. Invited lecture.
22. Ballistreri, A; Impallomeni, G.; Carnemolla, G. M.; Guglielmino, S.; Nicolò, M.; Cambria, M. G. XXIII congresso nazionale società chimica italiana Sorrento 5-10/07/2009. “Microbial synthesis and structural characterization of biodegradable polyesters from fatty acids with odd number of carbon atoms”. Poster.
23. Ballistreri, A.; Impallomeni, G.; Carnemolla, G.; Guglielmino, S.; Nicolò, M.; Cambria, M. IBS 2010 – 14th International Biotechnology Symposium and Exhibition, Rimini, 14-18/09/2010. “Biodegradable Plastics from Brassica Carinata Oil and from Very Long Chain Fatty acids: Synthesis and Characterization”. Poster.
24. Banchelli, M.; Gambinossi, F; Berti, D; Caminati, G.; Roelens, S.; Baglioni, P. 10° Sigma Aldrich Young Chemists Symposium: 10° SAYCS, Pesaro 18-20/10/2010. “Processi di riconoscimento molecolare su membrane lipidiche funzionalizzate”. Poster.
25. Banchelli, M.; Gambinossi, F.; Berti, D.; Caminati, G.; Baglioni, P. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento 5-10/07/2009. “Modulation of DNA grafting density and double strand orientation in phospholipid bilayers”. Oral Presentation.
26. Banchelli, M.; Gambinossi, F.; Berti, D.; Caminati, G.; Brown, T.; Baglioni, P. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. “Modulation of DNA grafting density and double strand orientation in phospholipid bilayers”. Oral Presentation.
27. Banchelli, M.; Gambinossi, F.; Berti, D.; Caminati, G.; Roelens S.; Baglioni, P. VIII Riunione Scientifica Annuale delle Unità Operative del Consorzio per lo Sviluppo dei Sistemi a grande Interfase (CSGI), Chianciano Terme (SI), 29-30/06/2010. “Soft membranes for specific surface recognition”. Poster.
28. Baratto, M.C.; Lipscomb, D.A.; Allen C.R., Larkin, M.J.; Pogni, R.; Basosi, R. Summer School: Chemistry for Life and Environment, VI Edition, Siena 1/06-4/07/2009. “Spectroscopic Studies on a Novel Naphthalene Dioxygenase from Rhodococcus sp.”. Poster.
29. Baratto, M.C.; Lipscomb, D.A.; Allen, C.; Larkin, M.J.; Pogni, R.; Basosi, R. 42nd Annual International Meeting of the Electron Spin Resonance Spectroscopy Group of the Royal Society of Chemistry, Norwich (England) 19-23/04/2009. “Spectroscopic Studies on a Novel Naphthalene Dioxygenase from Rhodococcus sp.”. Poster.
30. Baratto, M.C.; Martorana, A.; Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “Characterization of catalytic mechanism in laccase-mediator and laccase precursor systems” . Poster.
31. Baratto, M.C.; Martorana, A.; Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, Italia 20-24/09/2010. “Spectroscopic characterization of 4-(methylamino)-benzoic acid, a small precursor for the synthesis of new dyes”. Poster.
32. Barbucci, R.; Arturoni, E.; Di Canio, C.; Lamponi, S.; Mercuri, D. 22nd European Conference on Biomaterials, Losanna (Svizzera) dal 7-11/09 2009. “New amido phosphonate derivatives of carboxymethylcellulose with a osteogenic activity capable of interacting strongly with any Ti surface”. Poster.
33. Barbucci, R.; Arturoni, E.; Di Canio, C.; Lamponi, S.; Panariello, G. VII Convegno Nazionale sulla Scienza e Tecnologia dei Materiali, Tirrenia (Italia) dal 9-12/06/2009. “New amido phosphonate derivatives of carboxymethylcellulose with a osteogenic activity capable of interacting strongly with any Ti surface”. Presentazione Orale.

34. Barbucci, R.; Guerrini, A., Panariello, G.; Lamponi, S. 22nd European Conference on Biomaterials, Losanna (Svizzera) 7-11/09/2009. “InterPenetrating Hydrogels (IPH): A novel class of biohydrogels based on their thixotropic properties”. Presentazione Orale.
35. Barbucci, R.; Guerrini, A.; Lamponi, S.; Di Canio, C. VII Convegno Nazionale sulla Scienza e Tecnologia dei Materiali, Tirrenia (Italia) dal 9-12/06/2009. “Thixotropy for the formulation of new interpenetrating hydrogels (IPH) as cell scaffolds”. Poster.
36. Barone, V. 13th International Congress of Quantum Chemistry, Helsinki (Finland) June 22-27, 2009. "Accuracy and Interpretation: the Difficult Binomial of Computational Spectroscopy". Lecture.
37. Barone, V. Euchem 2010: Conference on Organic Free Radicals, Bologna (Italy) June 28 - July 2, 2010. "Spin Labels and Spin Probes: a Computational Journey". Lecture.
38. Barone, V. I Venerdì del CEINGE, Napoli (October 19, 2009). "Il Ruolo della Teoria nelle Scienze Molecolari". Lecture.
39. Barone, V. PhD School on Biological and Molecular Sciences, Pisa (Italy) March 4, 2010. "Computational Spectroscopy: Status and Perspectives". Lecture.
40. Barone, V. Theoretical chemistry modelling reactivity from gas phase to biomolecules and solids - Celebrating 25 years of the Theoretical Chemistry Network of Catalonia, Barcelona (Spain) June 29 - July 3, 2009. "Time-independent and time-dependent approaches to computational spectroscopy". Lecture.
41. Barone, V. XXII Congresso Nazionale di Chimica analitica, Como (Italy) September 13-16, 2010. "Applicazioni della Modellistica Computazionale allo Studio di Sensori e Biosensori". Lecture.
42. Barone, V. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (Italy) July 5-10, 2009. "Time-independent and time-dependent approaches to computational spectroscopy". Lecture.
43. Barone, V. XXVIII Congresso Interregionale Toscana, Umbria, Marche, Abruzzo, TUMA 2009, Tirrenia (Italy) September 20-22, 2009. "Computational Spectroscopy: a Tool of Increasing Impact in Molecular Sciences" Lecture.
44. Barone, V.; Biczysko, M.; Brancato, G.; Carnimeo, I.; Trani, F. BIOPHYS 10, Biology and beyond, Arcidosso (Italy) September 9-11, 2010. "Molecular modeling of structural, dynamic and spectroscopic properties of bio-molecules using first-principle methods". Poster.
45. Barone, V.; Biczysko, M.; Cimino, P. 13th International Congress of Quantum Chemistry, Helsinki (Finland) June 22-27, 2009. "Calculation of structural and magnetic properties of free radicals using DFT and TD-DFT approaches and the new N07D basis set". Poster.
46. Barone, V.; Bloino, J.; Cacelli, I.; Ferretti, A.; Monti, S.; Pedone, A.; Prampolini, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (Italy) September 20-24, 2010. "Accurate Force Fields for Soft Matter Computer Simulations". Oral Communication.
47. Barone, V.; Brancato, G.; Cimino, P.; Crescenzi, O.; Pavone, M.; Rega, N. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (Italy) July 5-10, 2009. "Spectroscopic properties of molecules in solution: an effective computational approach based on non-periodic boundary conditions". Poster.
48. Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini, G. Winter Modeling 2010, Pisa (Italy) February 26, 2010. "Multilevel approach to the study of DNA biosensors". Poster.
49. Barone, V.; Cacelli, I.; Ferretti, A.; Prampolini, G. Winter Modeling 2010, Pisa (Italy) February 26, 2010. "Theoretical study of magnetic exchange interactions". Poster.
50. Barone, V.; Cimino, P.; Crescenzi, O.; Menziani, M.C.; Pedone, A.; Stendardo, E. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (Italy) July 5-10, 2009. "Parameterization of the AMBER force-field to study nitroxide systems in vacuo and in condensed phase". Poster.
51. Barone, V.XX Congresso Nazionale della Società Italiana di Biofisica Pura ed Applicata (SIBPA), Arcidosso (Italy) September 11-14, 2010. "Computational Spectroscopy: A Versatile Tool for Biophysics". Lecture.
52. Bellissima F.; Bonini, M.; Fratini, E.; Giorgi, R.; Baglioni, P. CSGI annual meeting, Chianciano Terme (SI) 28/06/2010-01/07/2010. “Nanosystems for the control of biodeterioration of manufactered lithoic materials ”. Poster.
53. Bellissima, F.; Carta F.; Innocenti, A.; Supuran, C.; Scozzafava, A.; Berti, D.; Baglioni, P. 10° Sigma Aldrich Young Chemists Symposium: 10° S.A.Y.C.S., Pesaro 18-20/10/2010. XXXIX Congresso Nazionale di Chimica Fisica 2010, Stresa (VB) 20-23/09/2010. “Gold

nanoparticles cated with a carbonic anhydrase inhibitor: size and functionalization control". Poster.

54. Berbenni, V.; Bruni, G.; Milanese, C.; Girella, A.; Marini, A. Ottava Riunione Scientifica Annuale delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 28/06-1/07/2010. "Mechanosynthesis of yttrium iron perovskite oxide (YFeO3) from mixtures of Y(CH3COO)3.4H2O-FeC2O4.2H2O". Oral presentation.
55. Bernini L. VIII Riunione Scientifica Annuale della Unita' Operative CSGI, Chianciano T. (SI), 28/06-01/07/2010, "Mesoamerican mural paintings. Physico-chemical characterization of natural exudate gums"; "Mesoamerican mural paintings. Physico-chemical characterization of materials and application of calcium hydroxide nanoparticles for consolidation". Posters.
56. Bernini L. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, 20-24/09/2010 "Mesoamerican mural paintings. Physico-chemical characterization of natural exudate gums"; "Mesoamerican mural paintings. Physico-chemical characterization of materials and application of calcium hydroxide nanoparticles for consolidation". Posters.
57. Bernini L. YOCOCU 2010, Youth in the Conservation of Cultural Heritage, Palermo, 24-26/05/2010. "Mesoamerican mural paintings. Physico-chemical characterization of materials and application of calcium hydroxide nanoparticles for consolidation". Oral presentation.
58. Bernini, C.; Pogni, R.; Ruiz-Duenas, F.J.; Martinez, A.Y.; Basosi, R.; Sinicropi, A. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. "QM/MM characterization of Trp and Tyr radicals inside the protein matrix of a P. eryngii Versatile Peroxidase and its W164Y mutant". Poster.
59. Bernini, C.; Sinicropi, A.; Basosi, R.; Pogni R. X Convegno Nazionale GIRSE, Rimini, Italia 26-29/09/2010. "Quantum chemical calculations of EPR properties of radical species involved in the catalytic activity of oxidative enzymes". Poster.
60. Bernini, C.; Sinicropi, A.; Basosi, R.; Pogni, R. V Scuola GIRSE di Spettroscopia EPR, Firenze 23-30/09/2009. "EPR and DFT/PCM characterization of Tryptophan vs Tyrosyl Radical in native and W164Y mutant of Fungal Versatile Peroxidase". Poster.
61. Berti, D.; Baglioni, M.; Teixeira, J.; Giorgi, R.; Baglioni, P. XXXIX Congresso Nazionale della Divisione Chimica Fisica della Società Chimica Italiana, Stresa, 20-24/09/2010. "The nano-structure of cleaning systems for the removal of organic polymers from wall paintings – a SANS study". Oral presentation.
62. Berti, D.; Bombelli, F. B.; Banchelli, M.; Gambinossi, F.; Caminati, G.; Brown, T.; Baglioni, P. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. "Closed Nanoconstructs Assembled by Step-by-Step ssDNA Coupling Assisted by Phospholipid Membranes". Poster.
63. Bettini, S.; Bonsegna, S.; Pagano, R.; Zacheo, A.; Vergaro, V.; Giovinazzo, G.; Caminati, G.; Leporatti, S.; Valli, L.; Santino, A. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. "Plant oil bodies as novel carriers to deliver lipophilic molecules." Oral presentation.
64. Biczysko, M.; Bloino, J.; Panek, P.; Santoro, F.; Barone, V. 13th International Congress of Quantum Chemistry, Helsinki (Finland) June 22-27, 2009. "Fully Integrated Approach to Compute Vibrationally Resolved Optical Spectra: From Small Molecules to Macrosystems". Poster.
65. Bini, M.; Capsoni, D.; Ferrari, S.; Mustarelli, P.; Massarotti, V.; Mozzati, M.C. VIII Riunione scientifica annuale delle unità operative CSGI, Chianciano Terme (SI) 28/06-1/07/2010. "Undoped and Mn doped LiTi2(PO4)3: structural, spectroscopic and electrical investigation". Oral presentation.
66. Bini, M.; Grandi, S.; Capsoni, D.; Mustarelli, P.; Quartarone, E.; Saino, E.; Visai, L. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5-10/07/2009. "SiO2-based bioglasses with and without ZnO: relationships among composition, microstructure and bioactivity". Poster.
67. Bleve, M.; Bruni, G.; Mondelli, A.; Secchi, G.; Pavanetto, F.; Perugini, P. Skin Forum 12th Annual Meeting, Frankfurt, 28-29/3/2011. "SLN capability to deliver actives in the dermal epidermal junction : Preliminary investigation". Poster.

68. Bloino, J.; Biczysko, M.; Barone, V. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (Italy) July 5-10, 2009. "First principle simulation of vibrationally resolved optical spectra". Poster.
69. Bonechi, C.; Martini, Rossi, C. VIII Congresso Nazionale CSGI, Chianciano Terme (SI) 28/06-1/07/2010. "Interaction study of natural dye (indigo carmine) with albumin and dextran as determined by NMR Relaxation Data”. Poster.
70. Bonechi, C.; Martini, S.; Ristori, S.; Donati, A.; Rossi, C. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento 5-10/07/2009. “Study of the aggregation behaviour of resveratrol in solution and its interaction with membrane proteins”. Poster.
71. Bonechi, C.; Martini, S.; Rossi, C. VIII Congresso Nazionale CSGI, Chianciano Terme (SI) 28/06-1/07/2010. “Conformational analysis of Atrial Natriuretic Peptide (ANP) in solution by NMR techniques”. Poster.
72. Bravi, .M.; Parisi, M.L.; Tiezzi, E.; Basosi, R. Advances in Energy Studies 2010 - 7th biennal International Workshop, Barcellona (Spagna) 19-21/10/2010. “Life cycle assessment of advanced technologies for photovoltaic panels production”. Poster.
73. Bravi, M.; Parisi, M.L.; Tiezzi, E.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “Life Cycle Assessment of a Micromorph Photovoltaic System” Poster.
74. Bravi, M.; Parisi, M.L.; Tiezzi, E.; Basosi, R. IV Congresso Nazionale AIGE, Roma 26-27/05/2010. “Life cycle assessment of advanced technologies for photovoltaic panels production”. Poster.
75. Bressanin, D.; Stefan, A.; Dal Piaz, F.; Cianchetta, S.; Reggiani, L.; Hochkoeppler, A. 28th National Meeting SIMGBM, Spoleto (Italy)11-13/06/2009. “The assembly of Escherichia coli DNA polymerase III catalytic core”. Poster.
76. Bruni, G.; Capsoni, D.; Bini, M.; Berbenni, V.; Gozzo, F.; Milanese, C.; Girella, A.; Ferrari, S.; Marini, A. Ottava Riunione Scientifica Annuale delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 28/06-1/07/2010. “Thermal, spectroscopic and diffractometric characterization of carprofen polymorph”. Poster.
77. Busi, E.; Travagli, V.; Zanardi, I.; Gabbrielli, A.; Basosi, R. Summer School: Chemistry for Life and Environment, VI Edition, Siena 1/06-4/07/2009.“Simulation of EPR spectra as a tool for interpreting the degradation pathway of hyaluronan”. Poster.
78. Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini, G.VIII Riunione Scientifica Annuale delle Unità operative CSGI, Chianciano Terme (Italy) June 28 - July 1, 2010. "Accurate Force Fields for Soft Matter Computer Simulations". Poster.
79. Cambria, M.; Frezza, C.; Ballistreri, A.; Impallomeni, G.; Guglielmino, S. Congresso CSGI 2010 Chianciano Terme (Si) 28/06-01/07/2010. “Bioprocess of rhamnolipids synthesis from glicerol, byproduct of biodiesel production”. Poster.
80. Caminati, G.; Al Kayal, T.; Berti, D.; Baglioni, P. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. “Phospholipid bilayer composition modulates protein/liposome interactions: amyloid-like fibrils versus liposome/protein aggregates.” Poster.
81. Caminati, G.; Gambinossi, F.; Stadler, A.-M.; Baglioni, P.; Lehn, J.-M. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. “Construction of novel [2x2] grid-like mechanoresponsive architectures: molecular organization at the liquid-air interface and in nanofilm”. Poster.
82. Campesi, R.; Garroni, S.; Milanese, C.; Girella, A.; Delogu, F.; Napolitano, E.; Mulas, G. European Materials Research Society (E-MRS) Fall Meeting, Warsaw (Poland) 13-17/09/2010. “Sorption properties of NaBH4 - MgH2 powders prepared by ball milling and by impregnation in mesoporous scaffolds”. Oral presentation.
83. Campesi, R.; Milanese, C.; Delogu, F.; Napolitano, E.; Mulas, G. International Symposium on Metal – Hydrogen Systems MH 2010, Moscow (Russia) 19-23/07/2010. “Sorption properties of dispersed MBH4-MgH2 (M=Na, Li) systems in nano-mesoporous scaffolds”. Oral presentation.
84. Campiani, G.; Butini, S.; Bonechi, C.; Donati, A.; Rossi, C. XXXIX Congresso Nazionale Chimica Fisica, Stresa 20-24/09/2010. “Strategies to Potential Anticancer Agents Functionally Mimicking Activity of Nur-77 on Bcl-2: NMR studies of new oligopeptide PEP2”. Poster.

85. Campo, F.; Panza, L.; Morel, S.; Jessica, E.; Ciani, L.; Ristori, S. 14th International Congress on Neutron Capture Therapy, Buenon Aires (Argentina) 25-29/11/2010. “Synthesis of self-assembled boronated nanoparticles for BNCT”. Poster.
86. Candiani, G.; Pezzoli, D.; Ciani, L.; Frati, A.; Battistini, C.; Chiesa, R.; Ristori, S. 22nd European Conference on Biomaterials, Lausanne, (CH) 07-11/09/2009. “Development of Cationic Gemini-like Surfactant –SS14– Containing Liposomes for Gene Delivery”. Poster.
87. Candiani, G.; Ristori, R.; Pezzoli, D.; Ciani, L.; Chiesa, R. Congresso Nazionale Biomateriali, Camogli, Genova (Italy) 24-26/05/2010. “New gemini surfactant -SS14- containing liposomes for gene delivery”. Poster.
88. Capra, P.; Genta, I.; Bruni, G.; Visai, L.; Perugini, P.; Modena, T.; Pavanetto, F.; Conti, B. AI.t.U.N. Annual Meeting, Salerno 6-7/03/2009. “Fabrication and characterization of scaffold from PLGA-HAp microspheres”. Poster.
89. Capra, P.; Genta, I.; Bruni, G.; Visai, L.; Perugini, P.; Modena, T.; Pavanetto, F.; Conti, B. 36th Annual Meeting & Exposition of the Controlled Release Society, Copenhagen 18-22/07/2009. “PLGA-HAp scaffolds: a mouldable system from microspheres to 3D complex structure for bone regeneration”. Poster
90. Capsoni, D.; Bini, M.; Ferrari, S.; Massarotti, V.; Di Martino, P.; Gobetto, R.; Censi, R.; Malaj, L.; Pellegrino, L. XXXVIII Congresso Nazionale dell’Associazione Italiana di Cristallografia, Salerno 20-23/09/2009. “Polymorphism and thermal stability of nicergoline”. Poster.
91. Capsoni, D.; Bini, M.; Ferrari, S.; Mustarelli, P.; Massarotti, V.; Mozzati, M.C.; Spinella, A. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. “The role of Mn doping in LiTi2(PO4)3 material for lithium batteries”. Poster.
92. Caratozzolo, M.; Carnazza, S.; Frasca, M.; Grasso, L.; Guglielmino, S.; Marletta, G.; Fortuna, L. 4th International Scientific Conference on Physics and Control (Physcon 2009) Catania 1-4/09/2009. “Influence of ion strength and viability in bacterial self-assembly pattern on abiotic surface: preliminary models”. Poster.
93. Carnazza, S.; Guglielmino, S. The International School of Advanced Molecular BioMedicine: Complex Systems BioMedicine. Molecules, Signals, Networks, Diseases Aci Trezza (Catania) 2-6/10/2009. “Mappatura di Epitopi Conformazionali di Coxsackie Virus di Gruppo B Tramite Tecnologia del Phage-Display”. Oral Presentation.
94. Carrai, P.; Bufalo, G.; Ambrosone, L. Ottavo congresso Internazionale di igiene industriale, Roma 28/09-02/10/2010. “A novel approach for recognizing of workplace hazards”. Poster.
95. Carretti, E.; Baglioni, P.; Dei, L.; Natali I. XVI Salone del Restauro, Ferrara 25-28/03/2009. “Gel innovativi per la pulitura di superfici dorate”, nell’ambito del Convegno “Metallici riflessi. Le lamine metalliche nella pittura murale. Tecnica, Degrado, Restauro, alcuni casi di studio”. Oral Presentation.
96. Carretti, E.; Fratini, E.; Berti, D.; Dei, L.; Baglioni, P. XXIX Congresso Nazionale di Chimica Fisica – Stresa, VB, 20-24/09/2010. “Nanoscience for Art Conservation: Oil-in-Water Microemulsions Embedded in a Polymeric Network for the Cleaning of Works of Art”. Poster.
97. Carretti, E.; Natali, I.; Angelova, L.; Weiss, R. G.; Baglioni, P.; Dei, L. 1st ChemCH Congress, Ravenna, 30/06– 2/02/2010. “Poly vinylalchol hydrogels for cleaning works of art: recent developments”. Oral Presentation.
98. Carretti, E.; Natali, I.; Matarrese, C.; Caminati, G.; Weiss, R. G.; Baglioni, P.; Dei, L. XXII Congresso Nazionale della Società Chimica Italiana, Sorrento (Na) 5-10/07/2009. “Poly(vinyl alcohol)-borax hydro/cosolvent gels. Viscoelastic properties, solubilizing power, and application to art conservation”. Oral Presentation.
99. Cavaciocchi, L.; Gambinossi, F.; Baglioni, P.; Caminati, G. VIII Riunione Scientifica Annuale delle Unità Operative del Consorzio per lo Sviluppo dei Sistemi a grande Interfase (CSGI), Chianciano Terme (SI), 29-30/06/2010. “Layer-by-Layer solar cell based on a polymer/fullerene bulk heterojunction”. Poster.
100. Cavaciocchi, L.; Gambinossi, F.; Baglioni, P.; Caminati, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB), 20-24/09/2010. “Layer-by-Layer solar cell based on a polymer/fullerene bulk heterojunction”. Poster.
101. Cavigli, P.; Gambinossi, F.; Baglioni, P.; Caminati, G. VIII Riunione Scientifica Annuale delle Unità Operative del Consorzio per lo Sviluppo dei Sistemi a grande Interfase

(CSGI), Chianciano Terme (SI), 29-30/06/2010. “Phosphorescent Organic Light Emitting Diodes of PVK-Iridium complexes in LB nanoassemblies”. Poster.

102. Cavigli, P.; Gambinossi, F.; Baglioni, P.; Caminati, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB), 20-24/09/2010. “Phosphorescent Organic Light Emitting Diodes of PVK-Iridium complexes in LB nanoassemblies”. Poster.
103. Ciani, L.; Martini, G.; Ristori, S. Ottava Riunione Scientifica Annuale delle Unità Operative - Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme, Siena (Italy) 28/06-01/07/2010. “The Boron Neutron Capture Therapy: a new perspective for osteosarcoma”. Poster.
104. Ciani, L.; Ristori, S.; Martini, G. X Convegno Nazionale GIRSE, Rimini (Italy) 26-29/09/2010. “Nitrossidi come sonde per sistemi soft matter biologici”. Invited oral presentation.
105. Ciullini, I.; Gullotto, A.; Tilli, S.; Sannia, G.; Basosi, R.; Scozzafava, A.; Briganti, F. OXIZYMES & 9th International Symposium on Peroxidases, Leipzig (Germany) 14-16/06/2010. “Biodecolorization of exhausted textile dyeing baths composed by mixtures of synthetic dyes and additives”. Poster.
106. Colella, A.; Bianchin, A.; Matteazzi, P.; Milanese, C. HYdrogen – POwer THeoretical and Engineering Solutions International Symposium - Hypothesis VIII, Lisbon (Portugal) 1-3/04/2009. “Mg–Ni based material for hydrogen storage optimized for an industrial tank prototype”. Poster.
107. Consumi, M.; Matteucci, M.; Menichetti, L.; Kusmic, C.; L’Abbate, A.; Rossi, C.; Bonechi, C.; Magnani, A. 17th International Conference on Secondary Ion Mass Spectrometry, Toronto 14-18/09/2009. “Imaging ToF-SIMS of biomarker’s distribution in thin cryosections of tissues and its application for the assessment of microvascular perfusion in isolated murine heart”. Poster.
108. Conte, E.; Vincelli, G.; Shaaper, R.M.; Stefan, A.; Hochkoeppler, A. Evolving DNA polymerases 2010, Locarno (Switzerland) 9-14/05/2010. “Auxiliary proteins improve stability of the proofreading subunit (epsilon) of Escherichia coli DNA polymerase III”. Poster.
109. Conte, E.; Vincelli, G.; Shaaper, R.M.; Stefan, A.; Hochkoeppler, A. Ottava Riunione Scientifica Annuale delle Unità Operative, Chianciano Terme (Italy) 28/06-1/07/2010. “Auxiliary proteins improve stability of the proofreading subunit (epsilon) of Escherichia coli DNA polymerase III”. Oral presentation.
110. Costantino A.; Simeone, L.; Mangiapia, G.; Montesarchio, D.; D’Errico, G.; Ortona, O; Sartorio, R.; Paduano, L. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB). “A new class of potential antineoplastic agents based on ruthenium amphiphilic nanostructures”. Poster.
111. Costantino, A.; Simeone, L.; Mangiapia, G.; Montesarchio, D.; Radulescu, A.; Frielinghaus, H.; Paduano, L. User Meeting at FRM II on October 15th, 2010. “A new class of potential antineoplastic agents based on ruthenium amphiphilic nanostructures”. Invited lecture.
112. Cugia, F.; Salis, A.; Barse, A.; Monduzzi, M.; Mascini M. ESAC 2010: 13th International Conference on Electroanalysis, Gijon (Oviedo) - Spain 20-24/06/2010. "Determination of the toxicity of surfactants with an electrochemical DNA biosensor". Poster
113. Cugia, F.; Salis, A.; Monduzzi, M.; Mascini, M. 3rd Workshop of the Sensors Divisional Group of the Italian Chemical Society, GS2010, Sesto Fiorentino (FI) 26–28/10/ 2010 . "DNA-based biosensor, and surfactant toxicity: a FTIR investigation". Oral Presentation
114. Cuomo, F.; Ceglie, A.; Lopez, F. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. “Nanocapsules from polyelectrolyte deposition on vesicular template”. Oral Presentation.
115. Cuomo, F.; Ceglie, A.; Lopez, F.; Miguel, M. G.; Lindman B. 24th Conference of the European Colloid and Interface Society (ECIS). Book of abstract, Prague (Czech Republic) 5-10/09/2010. “Polyelectrolyte nanocapsules through LbL on vesicular templates”. Oral Presentation.
116. D’Errico, G.; Paduano, L.; Ortona, O.; Mangiapia, G.; D’Ursi, A.M.; Marsh, D.; Vitiello, G. XXIII Congresso Nazionale della Società Chimica Italiana - SCI 2009, Sorrento (NA) 05-10/07/2009. “Interaction of short modified peptides deriving from glycoprotein gp36 of feline immunodeficiency virus with phospholipid membranes”. Poster.
117. Ditaranto, N.; Cioffi, N.; Sabbatini, L.; Palazzo, G.; Lopez, F. Incontri di spettroscopia analitica ISA 2010, Rimini 16-18 Giugno 2010. “Caratterizzazione XPS di compositi

micro-strutturati per la rimozione di cromo(VI) da comparti ambientali inquinati". Oral Presentation.

118. Dr. José M. Bellosta von Colbe, Institute of Materials Research - GKSS Research Centre – Geesthach, Germany, "Hydrogen Storage: New Materials and New Perspectives for the Future", Department of Physical Chemistry, University of Pavia, 4/10/2010.
119. Dr. Leonid A. Bendersky, Leader of the "Hydrogen Storage Materials Program", Thin Film and Nanostructure Processing Group - Metallurgy Division - National Institute of Standards and Technology, Gaithersburg, Maryland, USA, "Combinatorial Approach and Measurements of Hydrogen Storage Materials", Department of Physical Chemistry, University of Pavia, 25/06/2010.
120. Dr. Prof. Andreas Züttel, Head of the section "Hydrogen & Energy" at the Swiss National Institute for Materials Research and Testing, EMPA, Dubendorf, Switzerland. "Synthetic Energy Carriers", Department of Physical Chemistry, University of Pavia, 1/06/2010.
121. Fantozzi, F.; Pasqui, D.; Lamponi, S.; Arturoni, E., Ciani, S.; Barbucci, R. 22nd European Conference on Biomaterials, Losanna (Svizzera) dal 7-11/09/2009. "The influence of the TiO2 nanoparticles polysaccharide coating on the cytotoxicity and cell permeation through electroporation". Poster.
122. Faraone, A.; Fratini, E.; Muller, A.; Baglioni P. 9th International Conference on Quasielastic Neutron Scattering, Bad Zurzach, CH, 10-13/02/2009. "Single particle dynamics of water hydrating a {Mo72Fe30} nanocapsule". Oral presentation.
123. Faraone, A.; Zhang, Y.; Chen, S.-H.; Liu, K.-H.; Mou, C.-Y.; Fratini, E.; Baglioni, P.; Muller, A.; Todea, A.M.; Krebs, B. American Conference on Neutron Scattering, Ottawa, ON, Canada 26-30/06/2010. "Combined Use of QENS Techniques for the Investigation of Interfacial Water Dynamics". Oral Presentation.
124. Ferrari, S.; Bruni, G.; Gozzo, F.; Bini, M.; Capsoni, D.; Massarotti, V. 2nd Meeting of the Italian and Spanish Crystallographic Associations (MISCA II), Oviedo (Spain) 30/06–3/07/2010. "Ab-initio structural determination of carprofen polymorphs from synchrotron diffraction data". Oral presentation.
125. Floris, P.; Casula, M. F.; Monduzzi, M.; Murgia S. IX Convegno Nazionale Materiali Nanofasici, Iglesias (CI), 03-05/06/2009. "Silanisation of magnetic nanocrystals in microemulsion". Poster.
126. Forrer, D.; Sedona, F.; Di Marino, M.; Sambi, M.; Vittadini, A.; Casarin, M.; Tondello, E.; Pavone, M.; Barone, V. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (Italy) July 5-10, 2009. "Iron Phtalocyanine self-assembly on Ag(110): a combined STM/DFT study". Poster.
127. Fratini, E.; Chu, X.-Q.; Chen, S.-H.; Baglioni, P. XXIII Congresso Nazionale della Società Chimica Italiana - SCI 2009, Sorrento, 05-10/07/2009. "Proteins Remain Soft at Lower Temperatures under Pressure". Oral Presentation.
128. Fratini, E.; Faraone, A.; Muller, A.; Baglioni P. XXIII Congresso Nazionale della Societa' Chimica Italiana - SCI 2009, Sorrento, 05-10/07/2009. "Single particle dynamics of water hydrating a {Mo72Fe30} nanocapsule". Poster.
129. Frezza, C.; Ferreri, A.; Impallomeni, G.; Ballistreri, A.; Carnemolla, G. M.; Guglielmino, S. SIMGBM 28th National Meeting Proceedings. Spoleto 11-13/06/2009 "PHA synthesis by Pseudomonas aeruginosa ATCC 27853 in magnesium and nitrogen starvation". Oral Presentation.
130. Fulini, P.; Cecchini, E.; Baldini, A.; Basosi, R. IV Congresso Nazionale AIGE, Roma 26-27/05/2010. "Integrazione di efficienza energetica e fonti rinnovabili nella progettazione di un edificio OFF GRID". Poster.
131. Galinetto, P.; Grandi, M.S.; Mozzati, M.C.; Bini, M.; Capsoni, D.; Ferrari, S.; Massarotti, V. XXI Congresso Gruppo Nazionale Spettroscopia Raman (GNSR), Milano 10-13/02/2009. "Phase homogeneity and stability in undoped and Mn doped LiFePO4". Oral presentation.
132. Gambi, C.M.C.; Marchetti, S.; Fratini, E.; Sennato, S. 6th International Discussion Meeting on Relaxations in Complex Systems, Rome, 30/08-05/09/2009. "Cluster phases of patchy micelles". Oral Presentation.
133. Gambi, C.M.C.; Marchetti, S.; Fratini, E.; Sennato, S.; Cametti, C.; Zaccarelli, E.; Rossi, B.; Cazzolli, G.; Viliani, G.; Sciortino, F. XII International Workshop on Complex Systems, Andalo, Trento (Italy), 15-18/03/2010. "Cluster phases of patchy micelles". Oral Presentation.
134. Gambinossi, F.; Banchelli, M.; Berti, D.; Baglioni, P.; Caminati, G. VIII Riunione Scientifica Annuale delle Unità Operative del Consorzio per lo Sviluppo dei sistemi a Grande

Interfase (CSGI), Chianciano Terme (SI), 29-30/06/2010. “Sequential adsorption of amphiphilic DNA onto Supported Phospholipid Bilayers: a ‘Tetris-like’ scenario”. Oral Presentation.

135. Gambinossi, F.; Banchelli, M.; Berti, D.; Baglioni, P.; Caminati, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB), 20-24/09/2010. “Sequential adsorption of amphiphilic DNA onto Supported Phospholipid Bilayers: a ‘Tetris-like’ scenario”. Poster.
136. Gambinossi, F.; Salvatori, D.; Lorenzelli, L.; Baglioni, P.; Caminati, G. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. “Functionalized Self-Assembled Nanosensors for microcantilever-based detection of food contaminants in fluid matrices”. Poster.
137. Garroni, S.; Menendez, E.; Ortega, A.L.; Estrader, M.; Nogues, J.; Milanese, C.; Nolis, P.; Suriñach, S.; Baró, M.D. MRS Fall Meeting, Symposium W: Hydrogen storage materials, Boston (USA), 30/11-4/12/2009. “Sorption properties of the NaBH4/MgH2 system: kinetic enhancement”. Oral presentation.
138. Garroni, S.; Menéndez, E.; Pistidda, C.; Brunelli, M.; Vaughan, G.; Nolis, P.; Mulas, G.; Milanese, C.; Girella, A.; Marini, A.; Suriñach, S.; Baró, M.D. Gordon Research Conference 2009 on “Hydrogen in Metal Systems”, Il Ciocco, Castelvecchio Pascoli (LU) 12-17/07/2009. “Hydrogen desorption mechanism and sorption properties of NaBH4/MgH2 composite”. Poster.
139. Garroni, S.; Milanese, C.; Girella, A.; Marini, A.; Campesi, R.; Suriñach, S.; Baró, M.D.; Mulas, G. Faraday Discussion 151: Hydrogen Storage Materials, Rutherford Appleton Laboratory, Didcot (Oxon, United Kingdom) 18-20/04/2011. “Kinetic, thermodynamic and spectroscopic exploration on the NaBH4 – MgH2 RHC system”. Poster.
140. Garroni, S.; Milanese, C.; Marini, A.; Girella, A.; Mulas, G.; Menéndez, E.; Dornheim, M.; Pistidda, C.; Suriñach, S.; Baró, M.D. 4th International Symposium Hydrogen & Energy, Wildhaus (Switzerland) 24-29/01/2010. “Sorption properties of NaBH4/MH2 (M = Mg, Ti) systems”. Oral presentation.
141. Garroni, S.; Milanese, C.; Marini, A.; Girella, A.; Mulas, G.; Menéndez, E.; Pistidda, C.; Dornheim, M.; Pottmaier, D.; Baricco, M.; Suriñach, S.; Baró, M.D. VI Rencontre Franco-Espagnole Sur La Chimie Et La Physique De L'état Solide - VI Encuentro Franco-Español De Química Y Física Del Estado Sólido, Tarragona (Spain) 17-19/03/2010. “Sorption properties of NaBH4/MgH2 system”. Oral presentation.
142. Garroni, S.; Milanese, C.; Marini, A.; Pottmaier, D.; Baricco, M.; Orlova, M.; Surinyach, S.; Baró, M.D. 17th International Symposium on Metastable, Amorphous and Nanostructured Materials ISMANAM 2010, Zurich (Switzerland) 4-9/07/2010. “Hydrogen Sorption Properties of the NaBH4/MgH2 System”. Oral presentation.
143. Garroni, S.; Milanese, C.; Pistidda, C.; Pottmaier, D.; Orlova, M.; Dolci, F.; Brunelli, M.; Vaughan, G.; Mulas, G.; Girella, A.; Baricco, M.; Dornheim, M.; Marini, A.; Suriñach, S.; Baró, M.D. Joint Final Event of the European Integrated Project NESSHY (Novel Efficient Solid Storage for Hydrogen) and the European Marie Curie Research Training Network COSY (Complex Solid State Reactions for Energy Efficient Hydrogen Storage) & International Workshop and Exhibition “Solid State Hydrogen Storage, From Fundamental Research to Industrial Application”, Torino 5-6/10/2010. “Hydrogen Sorption Properties of the NaBH4 / MgH2 Reactive Hydride Composite”. Oral presentation.
144. Giansanti, S.; Fatarella, E.; Cioni, I.; Bani, S.; Pogni, R.; Basosi, R. OXIZYMES & 9th International Symposium on Peroxidases, Leipzig (Germany) 14-16/06/2010. “Combined use of ultrasound-laccase system to treat industrial wastewaters”. Poster.
145. Giansanti, S.; Fatarella, E.; Cioni, I.; Bonucci, A.; Pogni, R.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “Methodologies to improve laccase oxidative activity towards industrial wastewaters”. Poster.
146. Giansanti, S.; Pogni, R.; Ruiz-Duenas, F.J.; Martinez, A.T.; Basosi, R. COST Action 868 Biotechnical Functionalisation of Renewable Polymeric Materials, Isola D’Elba (LI) 18-19/05/2009. “A Catalytic Study of Ligninolytic Enzymes: Protein Radical Intermediates in Versatile Peroxidases”. Poster.
147. Gilmore, I.; Lee, J.; Shard, A.; Gray, G.; Licciardello, A. 7th European Workshop on Secondary Ion Mass Spectrometry, Muenster (Germania) 19-21/09/2010. “Organic depth profiling – recent progress and future needs for industrial analysis”. Oral Presentation.

148. Giorgi R. Escuela Nacional de Conservacion, Restauracion y museografia Manuel del Castillo negrete, Citta' del Messico, 2-3/02/2009. "Nanotecnologia aplicada a la conservacion del patrimonio cultural". Oral presentation.
149. Giorgi R. International congress on Archeology and preservation of old shipwrecks, Stoccolma, 1/12/2009. "Inhibition of cellulose corrosion from iron salts by means of ph control". Oral presentation.
150. Giorgi R. IX Convegno Nazionale Materiali Nanofasici, Iglesias, 3-5/06/2009. "Nanoscience contribution for the conservation of cultural heritage". Oral presentation.
151. Giorgi R. Storia della Chimica Applicata alla Conservazione dei Beni Culturali, Roma, 14/06/2010. "L'Esperienza dello scienziato al servizio della conservazione del patrimonio artistico: il contributo pioneristico di Enzo Ferroni al restauro". Oral presentation.
152. Giorgi R. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, 20-24/09/2010. "Nanotechnology for the restoration of art masterpieces". Oral presentation.
153. Giustini, L.; Carretti, E.; Lo Nostro, P.; Baglioni, P. XXIII Congresso della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. "Rheological properties of gels from ascorbic acid-based surfactants". Poster.
154. Grasso, L.; Carnazza, S.; Guglielmino S. Congresso CSGI 2010. Chianciano Terme (Si) 28/06-01/07/2010. "New perspectives in bacterial retention study". Poster.
155. Grasso, L.; Carnazza, S.; Pisagatti, I.; Spadaio, S.; Barreca, F.; Cascio, A.; Currò, G.; Neri, F.; Guglielmino, S. Congresso CSGI 2010 Chianciano Terme (Si) 28/06-01/07/2010. "Polyelectrolyte Multilayer Films containing Silver Nanoparticles as antibacterial and antiadhesive coatings". Poster.
156. Hiwale, P.; Murgia, S.; Lampis, S.; Conti, G.; Monduzzi M. 2nd Conference "Innovation in Drug Delivery: From Preformulation to Development through Innovative Evaluation Process", Aix-en Provence, 03-06/10/2010. "In vitro release of lysozyme from gelatin microspheres suspended in pluronic F127 thermoreversible gel". Poster.
157. Hiwale, P.; Steri, D.; Medda, L.; Piras, M.; Piludu, M.; Bhattacharyya, M.S.; Salis, A.; Monduzzi, M. NanoBiotech Montreux - Switzerland 15-17/11/2010. "Nanostructured Mesoporous Silica Materials for Adsorption and Release of Lysozyme". Poster.
158. La Lia, M.; Caratozzolo, M.; Caglioti, C.; Gioffrè, G.; Guglielmino, S. Congresso CSGI 2010 Chianciano Terme (Si) 28/06-01/07/2010. "Phage-displayed" peptides application to recognize L. monocytogenes in dairy products. Poster.
159. Lampis, S.; Murgia, S.; Zucca, P.; Sanjust, E.; Monduzzi M. "Nucleotide recognition and phosphate linkage hydrolysis induced by specific interactions at a lipid interface". Poster.
160. Lamponi, S.; Di Canio, C.; Forbicioni, M.; Guerrini, A.; Barbucci, R. XXXVI Annual Meeting of European Society for Artificial Organs (ESAO), Compiègne, Francia 2-5/09/2009. "3D cell scaffolds for tissue engineering". Poster.
161. Lamponi, S.; Di Canio, C.; Guerrini, A.; Barbucci, R. Congresso Nazionale Biomateriali, Salice Terme (PV) (Italia) 15-17/06/2009. "InterPenetrating Hydrogels (IPH) as 3D scaffold for tissue engineering". Poster.
162. Lamponi, S.; Leone, G.; Consumi, M.; Greco, G.; Magnani, A. XXXVII Annual Meeting of European Society for Artificial Organs (ESAO), Skopje, Macedonia 8-11/09/2010. "Evaluation of in vitro biocompatibility of hydrogels as vitreous body substitutes". Poster.
163. Lavall, R.L.; Ferrari, S.; Capsoni, D.; Quartarone, E.; Magistris, A.; Mustarelli, P.; Canton, P. 33a Reunião Anual da Sociedade Brasileira de Química, Águas de Lindóia – SP (Brasil) 28-31/05/2010. "Síntese e comportamento eletroquímico de LiFePO4-MWCNT como material do cátodo para baterias de íons-lítio". Oral presentation.
164. Li Destri, G.; Punzo, F; Keller, T.; Jandt, K.D.; Marletta, G. 9th International Symposium on π-conjugated Systems, Atlanta (USA), 23-28/05/2010. "Interfacial Free Energy and Nanostructuring of Poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric Acid Methyl Ester Thin Films. Poster.
165. Li Destri, G.; Punzo, F.; Keller, T.; Jandt, K.D.; Marletta, G. 111th International Conference on Advanced Materials, Rio de Janeiro (Brazil) 20-25/09/2009. "Substrate Induced Phase Separation and Crystals Orientation in P3HT-PCBM Thin Films". Oral presentation.
166. Li Destri, G.; Punzo, F.; Marletta, G. XIV International Conference of Small Angle Scattering, Oxford (UK) 13-18/09/2009. "Effect of Substrate on the Nanostructure of Poly(3-hexylthiophene) PCBM Thin Films". Poster.
167. Licciardello, A. 17th International Conference on Secondary Ion Mass Spectrometry – SIMS XVII, Toronto (Canada), Sept. 2009. "ToF-SIMS of molecular materials: from polymers to supramolecular systems". Invited lecture.

168. Lo Nostro, P.; Ambrosi, M.; Fratini, E.; Giustini, L.; Baglioni, P. 239th A.C.S. National Meeting, San Francisco (CA, USA), 19-26/03/2010. "Levo ds. Dextro. Effect of the headgroup chirality on nanoassemblies". Oral Presentation.
169. Lo Nostro, P.; Ambrosi, M.; Fratini, E.; Giustini, L.; Ninham, B.W.; Baglioni, P. XXIII Congresso della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. "Levo versus Dextro: effect of the headgroup chirality on nanoassemblies". Poster.
170. Lo Nostro, P.; Giustini, L.; Fratini, E.; Ninham, B.W.; Ridi, F.; Baglioni, P. 239th A.C.S. National Meeting, San Francisco (CA, USA), 19-26/03/2010. "Threading, growth and aggregation of pseudopolyrotaxanes". Oral Presentation.
171. Lo Nostro, P.; Peruzzi, N.; Lagi, M.; Baglioni, P. Symposium "Dynamic crossover phenomena in water and other glass-forming liquids", Firenze, 11-13/11/2010. "Specific Ion Effects on the Cloud Point of diC8PC". Oral Presentation.
172. Lo Nostro, P.; Peruzzi, N.; Lagi, M.; Ninham, B.W.; Baglioni, P. XXIII Congresso della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. "Ion partitioning in self-assembled systems". Poster.
173. Lo Nostro, P.; Peruzzi, N.; Lagi, M.; Ninham, B.W.; Baglioni, P. 23rd ECIS (European Colloid and Interface Science) Conference, Antalya (Turchia), 6-11/09/2009. "Ion partitioning at interfaces: a Hofmeister series study". Oral Presentation.
174. Lo Nostro, P.; Peruzzi, N.; Severi, M.; Ninham, B.W.; Baglioni, P. 239th A.C.S. National Meeting, San Francisco (CA, USA), 19-26/03/2010. "Asymmetric partitioning of anions at interfaces: a Hofmeister series study". Oral Presentation.
175. Lo Nostro, P.; Tattini, L.; Bonini, M.; Baglioni, P. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, 20-24/09/2010. "PZT Nanoparticles for Piezoelectric Devices". Poster.
176. Lopez, F.; Cuomo, F.; Colafemmina, G.; Savelli, G.; Germani, R.; Ceglie, A. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. "Novel liposomal formulations based on a nucleobase-functionalized lipid". Poster.
177. Lopez, F.; Venditti, F.; Cuomo, F.; Ambrosone, L.; Ceglie, A. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. "Adsorption of Cr(VI) onto the silica gelatin composite in the presence of sulfate ions and at slightly acidic pH". Poster.
178. Marchetti, S.; Gambi, C.M.C.; Sbrana, F.; Fratini, E.; Carlà, M.; Vassalli, M.; Tiribilli, B.; Pacini, A.; Toscano, A. "Poly-Ig fragments of beta-connectin from human cardiac muscle: folding, unfolding and clustering". Poster.
179. Marletta, G. E-MRS 2009, Strasbourg (France), 8-12/06/2009. "Biointerfaces: Self-assembling systems and other surface patterning strategies". Invited lecture.
180. Marletta, G. Fourth International Conference on Electroactive Polymers: Materials and Devices" (ICEP 2010), Surujkund (India), 21-26/11/2010. "Tayloring the structure at the nanometric scale in electroactive polymer thin films". Invited lecture.
181. Marletta, G. Huntsville Ion Beam Institute, Huntsville (USA), 12-15/07/2009. "Ion beams for bio-active surfaces: from nanometric to mesoscopic level". Invited lecture.
182. Marletta, G. Huntsville Ion Beam Institute, Huntsville (USA), 4-8/08/2010. "Protein onto irradiated surfaces: from cell expression to epitope orientation". Invited lecture.
183. Marletta, G. Int. Conf. on Materials Science and Engineering 2010 (MSE 2010), Darmstadt (Germany), 24-26/08/2010. "Surface Engineering for Cell driving". Invited lecture.
184. Marletta, G. Invited lecture, University of Izmir; Izmir (Turkey), 12-18/07/2010. "Biomolecules Immobilization Strategies for Bio-active Surfaces". Invited lecture.
185. Marletta, G. Radiation in Matter (REM-2010), Gramado (Brasil), 24-28/10/2010. "Ion beams for bio-active surfaces: from nanometric to mesoscopic level". Invited lecture.
186. Marletta, G. University of Izmir; Izmir (Turkey), 12-18/07/2010. "Surface Functionalisation Strategies for Biomedical Applications". Invited lecture.
187. Marletta, G. University of Izmir; Izmir (Turkey), 12-18/07/2010. "Ion Beam Modification of Biopolymers". Invited lecture.
188. Marletta, G. XXV LIAC Congress, Matera (Italy), 1-4/09/2009. "Surface Functionalisation Strategies for Biomedical Applications". Invited lecture.
189. Marletta, G. XXV LIAC Congress, Toulouse (France), 29/09-2/10/2010. "Surface Functionalisation Strategies for Biomedical Applications". Invited lecture.
190. Martina, M.R.; Al Kayal, T.; Sadafi, F. Z.; Berti, D.; Caminati, G. VIII Riunione Scientifica Annuale delle Unità Operative del Consorzio per lo Sviluppo dei Sistemi a grande

Interfase (CSGI), Chianciano Terme (SI), 29-30/06/2010. “Models for lipid rafts: a study in synthetic lipid vesicles”. Poster.

191. Martina, M.R.; Al Kayal, T.; Sadafi, F. Z.; Berti, D.; Caminati, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. “Models for lipid rafts: a study in synthetic lipid vesicles”. Poster.
192. Martina, M.R.; Al Kayal, T.; Sadafi, F.Z.; Berti, D.; Caminati, G. 2010 CSGI Conference, Chianciano Terme (SI) 28/06-01/07/2010. “Models for lipid rafts: a study in synthetic lipid vesicles”. Poster.
193. Martina, M.R.; Al Kayal, T.; Sadafi, F.Z.; Berti, D.; Caminati, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. “Models for lipid rafts: a study in synthetic lipid vesicles”. Poster.
194. Martini, S.; Bonechi, C.; Figura, N.; Rossi, C. VIII Congresso Nazionale CSGI, Chianciano Terme (SI) 28/06-1/07/2010. “Increased susceptibility to resveratrol of Helicobacter pylori strains isolated from patients with gastric carcinoma”. Poster.
195. Martini, S.; Bonechi, C.; Rossi, C.; Ristori, S. VIII Congresso Nazionale CSGI, Chianciano Terme (SI) 28/06-1/07/2010. “Interaction between Resveratrol and model proteins in solution”. Poster.
196. Martorana, A.; Baratto, M.C.; Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. X Convegno Nazionale GIRSE, Rimini, Italia 26-29/09/2010. “Spectroscopic characterization of catalytic cycle in laccase mediator/precursor system”. Poster.
197. Massarotti, V.; Capsoni, D.; Bini, M.; Ferrari, S.; Mozzati, M.C.; Galinetto, P. IX Convegno Nazionale Materiali Nanofasici, Loc. Monteponi, Iglesias (CI) 3-5/06/2009. “Microstructure and impurity phases control in the synthesis of LiFePO4”. Oral presentation.
198. Massarotti, V.; Capsoni, D.; Bini, M.; Ferrari, S.; Mustarelli, P.; Mozzati, M.C.; Galinetto, P.; Chiodelli, G. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5-10/07/2009. “Cr and Ni doped Li4Ti5O12: a magnetic, spectroscopic and electrical investigation”. Oral presentation.
199. Matteazzi, P.; Bianchin, A.; Colella, A.; Milanese, C.; Marini, A. Euronanoforum 2009, Prague (Czech Republic) 2-5/06/2009. “Nanostructured bulk magnesium compounds for hydrogen storage”. Poster.
200. Matteazzi, P.; Bianchin, A.; Colella, A.; Milanese, C.; Marini, A. EuroNanoForum 2009, Prague (Czech Republic). “Nanostructured bulk magnesium compounds for hydrogen storage”.
201. Matteazzi, P.; Bianchin, A.; Colella, A.; Rolli, R. EuroNanoForum 2009, Prague (Czech Republic). “Nanostructured materials integration in microcomponents by direct ultraprecision manufacturing”.
202. Matteazzi, P.; Prior, F.; Colella, A. “Direct Laser Micro Manufacturing: The Manudirect Machine” (2010). 1581-1583, Annals of Direct Laser Micro Manufacturing: The Manudirect Machine Daaam for 2010 & Proceedings of the 21st International DAAAM Symposium, ISBN 978-3-901509-73-5, ISSN 1726-9679, pp 0791, Editor B. Katalinic, Published by DAAAM International, Vienna, Austria 2010.
203. Matteazzi, P.; Schäfer, M. 18th International Scientific And Technical Conference “Design and Technology of Drawpieces and Die Stampings” Poznań-Wąsowo, 9-11/06/2011. “The New Manufacturing Era: Virtual Design To Functional Products. The Manudirect Project Pioneer”.
204. Messina, G.M.L.; Dettin, M.; Marletta, G. E-MRS 2010 Spring Meeting Strasbourg (France) 7 –11/06/2010. “Multiscale Self-Assembling Processes of Amphiphilic Peptides”. Oral presentation.
205. Messina, G.M.L.; Marletta, G. E-MRS 2010 Spring Meeting Strasbourg (France) 7–11/06/2010. “Structuring adsorption at the nanometer scale: Tunable Nanopores”. Oral presentation.
206. Messina, G.M.L.; Marletta, G. Gordon Research Conference-Biointerface Science, Les Diablerets (Switzerland) 5-10/09/2010. “Protein adsorption onto nanopores at the nanometer scale”. Poster.
207. Messina, G.M.L.; Marletta, G. Third International NanoBio Conference, ETH Zurich (Switzerland) 24-27/08/2010. “ Protein adsorption onto nanopores at the nanometer scale”. Poster.

208. Messina, G.M.L.; Satriano, C.; Marletta, G. E-MRS 2010 Spring Meeting, Strasbourg (France) 8-12/06/2009. “Fabrication of confined supported lipid bilayers into bidimensional nanopore arrays”. Oral presentation.
209. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Colella, A.; Bianchin, A.; Matteazzi, P.; Marini, A. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. “The “Nanostore” project: development of an innovative Mg – based material for solid state hydrogen storage”. Poster.
210. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Marini, A. 4th International Symposium Hydrogen & Energy, Wildhaus (Switzerland) 24-29/01/2010. “Catalysis/destabilization studies on the magnesium/magnesium hydride system: from lab scale to the realization of a portable prototype”. Oral presentation.
211. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Marini, A. Convegno Nazionale “Chimica Verde, Chimica Sicura”, Pavia, 20-22/10/2009. “Nanomateriali a base Mg per lo stoccaggio di idrogeno: dagli studi di laboratorio alla realizzazione di un prototipo pre-industriale”. Poster.
212. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Marini, A. Hydrogen Show, Milano, 25-27/11/2009. “Nanostore: development of an innovative Mg – based material for solid state hydrogen storage”. Poster + Esposizione del prototipo dimostrativo realizzato nell’ambito del progetto FISR “Nanostore: stoccaggio di idrogeno in nanomateriali”.
213. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Marini, A. International Symposium on Metal – Hydrogen Systems MH 2010, Moscow (Russia) 19-23/07/2010. “Synergetic effect of C (graphite) and Nb2O5 on the H2 sorption properties of the Mg - MgH2 system”. Flash oral presentation + poster.
214. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Marini, A.; Colella, A.; Bianchin, A.; Matteazzi, P. Ottava Riunione Scientifica Annuale delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 28/06-1/07/2010. “The “Nanostore” project: development of an innovative Mg – based material for solid state hydrogen storage”. Poster.
215. Milanese, C.; Girella, A.; Bruni, G.; Berbenni, V.; Matteazzi, P.; Marini, A. International Conferences on Modern Materials and Technology (CIMTEC 2010), 5th Forum on New Materials – Materials and process innovation in hydrogen production and storage – Hydrogen storage Symposium, Montecatini Terme (PT) 13-18/06/2010. “From lab-scale optimization of Mg-based composites for H2 storage to the realization of a portable prototype”. Oral presentation.
216. Milanese, C.; Girella, A.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. HYdrogen – POwer THeoretical and Engineering Solutions International Symposium - Hypothesis VIII, Lisbon (Portugal) 1-3/04/2009. “The effect of C (graphite) addition on the H2 sorption performances of the Mg – Ni system”. Oral presentation.
217. Milanese, C.; Girella, A.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. Gordon Research Conference 2009 on “Hydrogen in Metal Systems”, Il Ciocco, Castelvecchio Pascoli (LU) 12-17/07/2009. “Ball milled Mg – Ni – C (graphite) composites for H2 storage: From lab scale analyses to the realization of an industrial tank prototype”. Flash oral presentation + poster.
218. Milanese, C.; Girella, A.; Bruni, G.; Cofrancesco, P.; Berbenni, V.; Matteazzi, P.; Marini, A. 42nd IUPAC Congress, Hydrogen Storage Symposium, Glasgow (Scotland), 2-7/08/2009. “Mg – based composites for H2 storage optimized for the realization of an industrial prototype”. Flash oral presentation + poster.
219. Milanese, C.; Girella, A.; Campesi, R.; Garroni, S.; Doppiu, S.; Napolitano, E.; Mulas, G. 5th International Symposium Hydrogen & Energy, Stoos (Switzerland) 23-28/01/2011. “Investigation of the H_2 sorption properties of $NaBH_4$ – MgH_2 nanocomposites confined into mesoporous SBA-15. Poster.
220. Milanese, C.; Girella, A.; Garroni, S.; Mulas, G.; Campesi, R.; Suriñach, S.; Baró, M.D.; Marini, A. The International Chemical Congress of Pacific Basin Societies - Pacifichem 2010, Honolulu (USA) 15-17/12/2010. “Hydrogen storage in NaBH4 - MgH2 mixtures: kinetic, thermodynamic, and mechanistic studies”. Invited oral presentation.
221. Milanese, C.; Girella, A.; Garroni, S.; Mulas, G.; Napolitano, E.; Suriñach, S.; Baró, M.D.; Marini, A. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. “Hydrogen Sorption Properties of the NaBH4 - MgH2 System”. Oral presentation.
222. Milanese, C.; Girella, A.; Garroni, S.; Mulas, G.; Suriñach, S.; Baró, M.D.; Marini, A. 5th International Symposium Hydrogen & Energy, Stoos (Switzerland) 23-28/01/2011.

"Kinetic and Thermodynamic Investigations on Pure and Doped $NaBH_4$ - MgH_2 System". Oral presentation.

223. Milanese, C.; Girella, A.; Marini, A. Medicta 2009, 9th Mediterranean Conference on Calorimetry and Thermal Analysis, Marseille (France) 15-18/06/2009. "High pressure differential scanning calorimetry studies on solid state H2 storage nanomaterials". Poster.
224. Milanese, C.; Girella, A.; Marini, A.; Garroni, S.; Suriñach, S.; Baró, M.D. Ottava Riunione Scientifica Annuale delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 28/06-1/07/2010. "Hydrogen sorption properties of the NaBH4 – MgH2 system: kinetic and thermodynamic studies". Oral presentation.
225. Milanese, C.; Girella, A.; Mulas, G.; Enzo, S.; Medici, S.; Garroni, S.; Baró, M.D.; Suriñach, S.; Marini, A. Ecosud 2009, Seventh International Conference on Ecosystems and Sustainable Development, Chianciano Terme (SI) 8-10/07/2009. "H2 sorption performance of NaBH4 – MgH2 composites prepared by mechanical activation". Oral presentation.
226. Montis, C.; Milani, S.; Baglioni, P.; Berti, D. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. "Anionic Liposomes and DNA: Molecular Recognition and Reentrant Condensation". Poster.
227. Montis, C.; Milani, S.; Baglioni, P.; Berti, D. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010. "Nucleolipoplexes: interaction with GUV as cell membrane model systems. A Confocal Microscopy study". Poster.
228. Mosca, M.; Ceglie, A. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. "Lipid oxidation in emulsions and liposomes: role of the interface". Oral Presentation.
229. Mulas, G.; Delogu, F.; Campesi, R.; Milanese, C.; Garroni, S. IX Convegno Nazionale sui Materiali Nanofasici, Loc. Monteponi, Iglesias (CI) 3-5/06/2009. "Hydrogen sorption by nanostructured materials under thermal and mechanical activation". Poster.
230. Mulas, G.; Enzo, S.; Medici, S.; Delogu, F.; Garroni, S.; Barò, M.D.; Surinach, S.; Milanese, C.; Marini, A. 3rd International Symposium Hydrogen & Energy, Braunwald (Switzerland) 25-30/01/2009. "Kinetic features in the hydrogen sorption by NaBH4 + MgH2 composites under mechanical activation conditions". Poster.
231. Murgia, S.; Falchi, A. M.; Lampis, S.; Talmon, Y.; Monduzzi M. 24th ECIS Conference, Prague, 05-10/09/2010. "Nanoparticles from lipid-based liquid crystals: emulsifier influence on morphology and cytotoxicity". Poster.
232. Murgia, S.; Lampis, S.; Berti, D.; Monduzzi, M. IX Convegno Nazionale Materiali Nanofasici, Iglesias (CI), 03-05/06/2009. "Orientation, specific interactions, and hydrolisis of mononucleotides inside monoolein based liquid crystals". Poster.
233. Murgia, S.; Lampis, S.; Hiwale, P.; Monduzzi M. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB), 20-24/09/2010. "Nanostructures for innovative drug delivery". Poster.
234. Murgia, S.; Palazzo, G.; Mamusa, M.; Lampis, S.; Monduzzi M. IX Convegno Nazionale Materiali Nanofasici, Iglesias (CI), 03-05/06/2009. "The striking phase behavior of Aerosol-OT in an ionic liquid". Poster.
235. Nachum, S.; Fleck, N.A.; Colella, A.; Santin, L.; Noelke, C.; Matteazzi, P. 2nd international conference Super High Strength Steel, Peschiera del Garda (VR) 17-20/10/2010. "The microstructure and mechanical properties of a ballmilled stainless steel powder consolidated by a micro-laser beam".
236. Nappini, S.; Baldelli Bombelli, F.; Bonini M.; Nordèn, B.; Baglioni, P. XXIII National Congress of the Italian Chemical Society, Sorrento (Na), 05-10/07/2009. "Magnetoliposomes for controlled drug release in the presence of low-frequency magnetic field". Poster.
237. Nappini, S.; Bonini M.; Baldelli Bombelli, F.; Pineider, F.; Sangregorio, C.; Nordèn, B.; Baglioni, P. 10° SAYCS, Pesaro, 18-20/10/2010. Poster.
238. Natali, I.; Carretti, E.; Angelova, L.; Weiss, R. G.; Baglioni, P.; Dei, L. II Congresso YOCOCU, Palermo 24-26/05/2010. "Poly vinylalchol hydrogels for cleaning works of art: recent developments". Poster.
239. Natali, I.; Pizzorusso, G.; Carretti, E.; Fratini, E.; Giorgi, R.; Dei L.; Baglioni, P. XII Congresso Nazionale di Chimica dell'ambiente e dei Beni Culturali, Taormina, 27/09/2010. "Innovative aqueous gels and polymeric dispersions for cleaning works of art". Oral presentation.

240. Natali, I.; Pizzorusso, G.; Carretti, E.; Fratini, E.; Giorgi, R.; Dei, L.; Baglioni, P. XII Congresso Nazionale di Chimica dell'Ambiente e dei Beni Culturali, Taormina, 26-30/09/2010. "Innovative aqueous gels and polymeric dispersions for cleaning works of art". Oral Presentation.
241. Nelli, P.; Salvi, P.; Villa, M.; Zangari, G. Abstract 3034, 216th Electrochemical Society Meeting Vienna 5-9 Oct 2009. "Hydrogen evolution on Ni electrodes and the formation of Ni hydrides". Oral presentation.
242. Nicolò, M.; Columbro, G.; La Porta, S.; Cicero, N.; Dugo, G.; Guglielmino, S. IBS 2010 – 14th International Biotechnology Symposium and Exhibition, Rimini, 14-18/09/2010. "High quality oil for biodiesel production and biomass yields from a microalga coccomyxa sp. by autotrophic growth". Poster.
243. Palazzo, G.; Colafemmina, G. Association in Solution-II-Structure, Function & Performance –ECI conference, Tomar (Portugal) 26-30/07/2009. "Interfacial composition and microstructure in quaternary microemulsions: a pulsed gradient spin-echo NMR approach". Oral Presentation.
244. Palazzo, G.; Mallardi, A.; Giustini, M. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. "Biosensors and bioassays based on immobilized proteins and nanoparticle synthesis". Poster.
245. Palazzo, G.; Venturoli, G.; Mallardi, A. Ottava riunione annuale delle unità operative del consorzio interuniversitario per lo sviluppo dei sistemi a grandi interfase (GSGI), C. 14, Chianciano Terme (SI) 28/06-1/07/2010. "Functionality of the bacterial reaction center in trehalose solutions and glasses". Oral Presentation.
246. Parisi, M.L.; Spinelli, D.; Busi, E.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. "Life cycle assessment and sustainability analysis of recovery options for plastic parts from end-of-life vehicles". Poster.
247. Pendolino, F.; Garroni, S.; Milanese, C.; Girella, A.; Borgschulte, A.; Baró, M.D.; Marini, A.; Züttel, A. 4th International Symposium Hydrogen & Energy, Wildhaus (Switzerland) 24-29/01/2010. "Hydrogen evolution from decomposition of borohydrides: the boron effect". Poster.
248. Pendolino, F.; Milanese, C.; Züttel, A. International Conferences on Modern Materials and Technology (CIMTEC 2010), Marie Curie Conference 2010, Creative Design for Innovation in Sceince and Technology, Torino 1-2/07/2010. "Borohydrides: hydrogen storage materials". Poster.
249. Perugini, P.; Bruni, G.; Vettor, M.; Bleve, M.; Corsini, E.; Pavanetto, F. 7th World Meeting on Pharmaceutics, Biopharmaceutics and Pharmaceutical Technology, La Valletta, Malta, 8-11/03/2010. "Preparation, characterization and in vitro tolerability of SLN intended for the regeneration of hyaluronan into skin: preliminary investigation". Poster.
250. Peruzzi, N.; Lo Nostro, P.; Severi, M.; Ninham, B.W.; Baglioni, P. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, 20-24/09/2010. "A Phase Separated System can act as a Chemical Sponge: Asymmetric Partitioning of Anions in Lysozyme Dispersions". Poster.
251. Pirker, K.F.; Baratto, M.C.; Goodman, B.A. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, Italia, 20-24/09/2010."Multifrequency EPR study of GA-and EGCG-Cu(II) complexes". Poster.
252. Pistolesi, S.; Rossini, L.; Ferro, E.; Basosi, R.; Trabalzini, L.; Pogni, R. 7th European Federation of EPR Gropus Meeting and Closing Meeting of COST P15, Anversa (Belgio) 6-11/09/2009. "Humanin structural versatility and interaction with model Cerebral Cortex Membranes". Poster.
253. Pizzorusso, G.; Giorgi, R.; Fratini, E.; Eiblmeier, J.; Baglioni, P. XXIII Congresso Nazionale S.C.I., Sorrento, 09/07/2009. "Magnetic Chemical Gels for the Restoration of Canvas Paintings". Oral presentation.
254. Pizzorusso, G.; Giorgi, R.; Fratini, E.; Eiblmeier, J.; Baglioni, P. XXIII Congresso Nazionale della Societa' Chimica Italiana - SCI 2009, Sorrento, 05-10/07/2009. "Magnetic Chemical Gels for the Restoration of Canvas Paintings". Oral Presentation.
255. Pizzorusso, G.; Neubauer, M.; Fratini, E.; Giorgi, R.; Baglioni, P. VIII Riunione Scientifica Annuale delle Unità Operative del CSGI, Chianciano Terme, 28/06-01/07/2010. "Chemical gels for the cleaning of easel paintings". Poster.

256. Pizzorusso, G.; Neubauer, M.; Fratini, E.; Giorgi, R.; Baglioni, P. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, 20-24/09/2010. “Chemical gels for the cleaning of easel paintings”. Poster.
257. Pizzorusso, G.; Neubauer, M.; Fratini, E.; Giorgi, R.; Baglioni, P. XXIX Congresso Nazionale di Chimica Fisica – Stresa, VB, 20-24/09/2010. “Chemical gels for the cleaning of easel paintings”. Poster.
258. Pogni, R.; Basosi, R. OXIZYMES & 9th International Symposium on Peroxidases, Leipzig (Germany) 14-16/06/2010. “The catalytic cycle of versatile peroxidases: an EPR story”. Oral Presentation.
259. Pogni, R.; Basosi, R. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, Italia 20-24/09/2010. “The catalytic cycle of versatile peroxidases: a EPR story”. Oral presentation.
260. Pogni, R.; Sinicropi, A.; Bernini, C.; Basosi, R. Summer School: Chemistry for Life and Environment, VI Edition, Siena 1/06-4/07/2009. “EPR and DFT/PCM characterization of Tryptophan vs Tyrosyl Radical in native and W164Y mutant of Fungal Versatile Peroxidase”. Poster.
261. Pogni, R.; Sinicropi, A.; Bernini, C.; Ruiz-Duenas, F.J.; Martinez, A.T.; Basosi, R. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5-10/07/2009. "Comparison between Catalytic Tryptophan Radical in Fungal Versatile Peroxidase and its W164Y variant: EPR and DFT/PCM approaches”. Poster.
262. Pogni, R.; Valensin, D.; Jarosz-Wilkolazka, A.; Parisi, M.L.; Basosi, R. IBS2010, 14th International Biotechnology Symposium and Exhibition, Rimini (Italia) 14-18/09/2010. “Synthesis. Structural characterization and LCA analysis of a novel phenoxazinone dye by use of a fungal laccase”. Poster.
263. Puliafico, M.; Bianco, F.; Carnazza, S.; Guglielmino, S. Congresso CSGI 2010 Chianciano Terme (Si) 28/06-01/07/2010. “Research of serotype-specific epitopes of Group B Coxsackievirus for development of new diagnostics”. Poster.
264. Puliafico, M.; Carnazza, S.; Bianco, F.; Guglielmino, S. SIMGBM 28th National Meeting Proceeding Spoleto 11-13/06/2009. “Conformational epitopes on monoclonal mouse anti-Yersinia pestis F1 antigen YPF19 identified by peptide phage display and molecular modelling”. Poster.
265. Quartarone, E.; Lavall, R.L.; Ferrari, S.; Capsoni, D.; Mustarelli, P.; Magistris, A.; Canton, P. Materials Research Society Spring Meeting, San Francisco (California) 5-9/04/2010. “Particle Size and Crystal Orientation Effects on the Electrochemical Behavior of Carbon-coated LiFePO4”. Poster.
266. Ridi, F. 13th IACIS International Conference on Surface and Colloid Science & 83rd ACS Colloid & Surface Science Symposium, New York, USA, 14-19/06/2009. “Effect of organic polymers on the cement hydration reaction: thermodynamics and structure”. Oral Presentation.
267. Ridi, F.; Cottone F.; Bonini M.; Baglioni P. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, Italy, 20-24/09/2010. “Study of interactions between a cellulosic polymer and polycarboxylate superplasticizers”. Poster.
268. Ruffino, F.; Torrisi, V.; Marletta, G.; Grimaldi, G.M. European Materials Research Society Fall Meeting 2010, Varsavia (Polonia) 13-17/09/2010. “Atomic force microscopy investigation of the kinetic growth mechanisms of sputtered nanostructured Au film on mica: towards a nanoscale morphology control”. Poster.
269. Ruiz-Duenas, F.J.; Morales, M.;Pogni, R.; Basosi, R.; Martìnez, M.J.; Piontek, K.; Martìnez, A.T. 1st Symposium on biotechnology applied to lignocelluloses, Reims (Francia) 28/03-1/04/2010. “Pleurotus versatile peroxidase”. Poster.
270. Ruzzenenti, F.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “On benefits and perspectives of applying Network Theory to Energy Systems”. Oral presentation.
271. Ruzzenenti, F.; Garlaschelli, D.; Basosi, R. Advances in Energy Studies 2010 - 7th biennal International Workshop, Barcellona (Spagna) 19-21/10/2010. “On benefits and perspectives of applying network theory to energy systems”. Poster.
272. Sala Mariet, E.; Ruzzenenti, F.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “The rebound effect and globalization: phase transition in the WTW”. Poster.

273. Salis, A.; Bhattacharyya, M.S.; Solinas, V.; Monduzzi M. 16th International Zeolite Conference and 7th International Mesostructured Materials Symposium, IZC-IMMS 2010 Sorrento (NA) 4-9/07/2010 “Lipase on SBA-15 mesoporous silica as a biocatalyst for Biodiesel synthesis”. Oral Presentation.
274. Salis, A.; Parsons, D.F.; Bostrom, M.; Ninham, B.W.; Monduzzi, M. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB) 20-24/09/2010 “Specific Ion Effects at SBA-15 Mesoporous Silica solid/liquid Interface: Protein Adsorption and Surface Charge Density”. Oral Presentation.
275. Salvi, P.; Nelli, P.; Villa, M.; Kiros, Y.; Bruni, G.; Marini, A.; Milanese, C. 3rd World Congress of Young Scientists on Hydrogen Energy, Torino, 7-9/10/2009. “Hydrogen evolution reaction in PTFE bonded Raney-Ni electrodes”. Oral presentation.
276. Salvi, P.; Nelli, P.; Villa, M.; Kiros, Y.; Bruni, G.; Marini, M. Paper A-2F., Hysydays 2009, (3rd World Congress of Young Scientists on Hydrogen Energy Systems) Turin 6-9 Oct 2009. “Hydrogen evolution reaction in PTFE bonded Raney-Ni electrodes”. Oral presentation.
277. Sapuppo, D.; Zappalà, G.; Spampinato, V.; Tuccitto, N.; Licciardello A. 7th European Workshop on Secondary Ion Mass Spectrometry, Muenster (Germania) 19-21/09/2010. “Nitric oxide-assisted cluster-SIMS depth profiling of polymers”. Oral Presentation.
278. Sapuppo, D.; Zappalà, G.; Spampinato, V.; Tuccitto, N.; Licciardello A. Congresso congiunto della Società Chimica Italiana, sezione Sicilia e Calabria, Palermo 2-3/12/2010. “Uso di gas reattivi nel cluster-SIMS di materiali polimerici”. Oral Presentation.
279. Sawada, H. (Department of Frontier Material Chemistry, Hirosaki University, Japan), Dipartimento di Chimica, Sesto Fiorentino (FI), 11/06/2009. “Preparation and properties of novel fluorinated polymeric nanocomposites”.
280. Schiavo, B.; Agresti, F.; Capurso, G.; Milanese, C. International Symposium on Metal – Hydrogen Systems MH 2010, Moscow (Russia) 19-23/07/2010. “Hydrogen sorption in the CaH2+MgB2 system”. Flash oral presentation + poster.
281. Schiavo, B.; D’Alì Staiti, G.; Milanese, C.; Agresti, F.; Principi, G. European Energy Conference, Barcelona (Spain) 20-23/04/2010. “Hydrogen sorption properties of the composed system calcium hydride – magnesium boride”. Oral presentation.
282. Schiavo, B.; Girella, A.; Joseph, B.; Milanese, C. Faraday Discussion 151: Hydrogen Storage Materials, Rutherford Appleton Laboratory, Didcot (Oxon, United Kingdom) 18-20/04/2011. Hydrogen storage properties of the CaH2-MgB2-AlB2 system”. Poster.
283. Schiavo, B.; Milanese, C.; Agresti, F. International School of Solid State Physics - “Materials for Renewable Energy”, Erice (TP) 28/05-2/06/2010. “Formation of calcium borohydride based systems for solid state hydrogen storage”. Poster.
284. Sfuncia, G.; Li Destri, G.; Marletta, G. Carbomat workshop, Catania (Italia), 06-08/10/2010. “Structuring of Single Wall Carbon Nanotubes/Poly(3-hexylthiophene) nano-composite at the air/water interface”. Poster.
285. Sinicropi, A.; Bernini, C.; Basosi, R.; Olivucci, M. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5-10/07/2009. "Design and computational investigation of a photomodulable peptide containing the RGD sequence and a Z/E photoisomerizable biomimetic switch”. Poster.
286. Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. 13th International Conference on the Applications of Density Functional Theory in Chemistry and Physics, Lione (Francia), 31/08-4/09/2009. “A QM/MM investigation of molecular factors influencing the properties of radical intermediates in a Fungal Versatile Peroxidase”. Poster.
287. Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. 7th European Federation of EPR Gropus Meeting and Closing Meeting of COST P15, Anversa (Belgio) 6-11/09/2009. “Experimental and computational characterization of Tryptophan vs Tyrosyl Radical in native and W164Y mutant of P. eryngii Versatile Peroxidase: an EPR, DFT/PCM and QM/MM investigation”. Poster.
288. Sinicropi, A.; Bernini, C.; Pogni, R.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “Quantum chemical calculations of EPR properties of a radical species involved in the catalytic activity of oxidative enzymes”. Poster.
289. Sinicropi, A.; Bernini, C.; Ruiz-Duenas, F.J.; Martinez, A.T.; Pogni, R.; Basosi, R. OXIZYMES & 9th International Symposium on Peroxidases, Leipzig (Germany) 14-

16/06/2010. “A QM/MM investigation of radical intermediates in a fungal versatile peroxidase and its W164Y variant”. Poster.

290. Sinicropi, A.; Bernini, C.; Ruiz-Duenas, F.J.; Martinez, A.T.; Pogni, R.; Basosi, R. X Convegno Nazionale GIRSE, Rimini, Italia 26-29/09/2010. “QM/MM characterization of Trp and Tyr radicals inside the protein matriz of a P. eryngii versatile peroxidase and its W164Y variant”. Poster.

291. Sinicropi, A.; Parisi, M.L.; Melloni, A.; Rossi Paccani, R.; Donati, D.; Zanirato, V.; Fusi, S.; Latterini, L.; Basosi, R.; Olivucci, M. XXIII Congresso Nazionale della Società Chimica Italiana, Sorrento (NA) 5-10/07/2009. “Computer modeling, synthesis and spectroscopical characterization of a zwitterionic bio-mimetic and photochemical switch”. Poster.

292. Spampinato, V.; Corallo, V.; Tuccitto, N.; Quici, S.; Torrisi, A.; Licciardello A. 7th European Workshop on Secondary Ion Mass Spectrometry, Muenster (Germania) 19-21/09/2010. “ToF-SIMS of engineered oxide surfaces”. Poster.

293. Spampinato, V.; Tuccitto, N.; Giamblanco, N.; Defrancq, E.; Licciardello, A.; Marletta, G. XXIII Congresso Nazionale SCI, Sorrento (NA) 5-10/07/2009. “Patterned Non-covalent Surface Anchoring of Terpyridine-tagged Oligonucleotides”. Poster.

294. Spampinato, V.; Tuccitto, N.; Giamblanco, N.; Quici, S.; Defrancq, E.; Licciardello, A.; Marletta, G. IX Congresso Nazionale di Chimica Supramolecolare, Parma 7-9/09/2009. “Supramolecular Surface Anchoring and Coverage Tuning of Terpyridine-tagged Oligonucleotides”. Poster.

295. Spampinato, V.; Tuccitto, N.; Giamblanco, N.; Quici, S.; Defrancq, E.; Licciardello, A.; Marletta, G. XV Scuola Nazionale di Scienza dei Materiali, Bressanone (BZ) 21-30/09/2009. “Uniform patterning of ss-DNA for microarray applications”. Poster.

296. Spampinato, V.; Tuccitto, N.; Giamblanco, N.; Quici, S.; Defrancq, E.; Torrisi, A.; Licciardello, A.; Marletta, G. International School of Solid State Physics 47th Course, Erice (TP) 28/05-2/06/2010. “Surface Engineering by Metal-Complex Supramolecular Coordination”. Poster.

297. Spinelli, D.; Giansanti, S.; Pogni, R.; Basosi, R. V Scuola GIRSE di Spettroscopia EPR, Firenze 23-30/09/2009. “Use of Anionic HRP (Horseradish Peroxidase) for polymer biosynthesis”. Poster.

298. Spinelli, D.; Jez, S.; Pogni, R.; Basosi, R. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “Environmental and life cycle analysis of a biodiesel production line from sunflower”. Poster.

299. Spinelli, D.; Jez, S.; Pogni, R.; Basosi, R. IBS2010, 14th International Biotechnology Symposium and Exhibition, Rimini (Italia) 14-18/09/2010. “Environmental and CLA analysis of a biodiesel production line from sunflower in the Province of Siena (Italy)" . Poster.

300. Stefan, A.; Conti, M.; Rubboli, D.; Ravagli, L.; Hochkoeppler, A. Ottava Riunione Scientifica Annuale delle Unità Operative, Chianciano Terme (Italy) 28/06-1/07/2010. “Espression and purification of Diphtheria toxin variant CRM197 in Escherichia coli”. Poster.

301. Stefan, A.; Conti, M.; Rubboli, D.; Ravagli, L.; Hochkoeppler, A. 14th International Biotechnology Symposium and Exibition, Rimini (Italy) 14-18/09/2010. “Espression and purification of Diphtheria toxin variant CRM197 in Escherichia coli”. Poster.

302. Stefan, A.; Ugolini, L.; Martelli, E.; Palmieri, S.; Hochkoeppler, A. 28th National Meeting SIMGBM, Spoleto (Italy)11-13/06/2009. “Expression and purification of the recombinant mustard trypsin inhibitor 2 (MTI2) in Escherichia coli”. Oral presentation.

303. Suriñach, S.; Milanese, C.; Girella, A.; Marini, A.; Mulas, G.; Garroni, S.; Baró, M.D. 11th International Conference on Advanced Materials (ICAM), Rio de Janeiro (Brazil), 20-25/09/2009. “Sorption properties of the NaBH4/MgH2 system milled with different additives”. Poster.

304. Tattini, L.; Lo Nostro, P.; Bonini, M.; Baglioni, P. XXIII Congresso della Società Chimica Italiana, Sorrento (NA), 5-10/07/2009. “Synthesis and characterization of piezoelectric nanoparticles”. Poster.

305. Tognazzi, A.; Leone, G.; Magnani, A.; Aggravi,a M.; Dattilo, A.M.; Bracchini, L.; Rossi, C. Interim meeting Scientific Research Working Group, Pisa 7-8/10/2010. “A new tool for the assessment of ancient ceramic production technologies. ToF-SIMS investigation of the ceramic impasto in fragments from the archaeological site of Quartaia (Italy)”. Poster

306. Tognazzi, A.; Magnani, A.; Donati A.; Rossi C. Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase – CSGI - VIII Riunione Scientifica Annuale delle Unità

Operative Chianciano Terme (SI) 28/06-01/07/2010. “Study of anthraquinoid, indigoid and curcuminoid compounds employed as pigments in cultural heritage”. Presentazione Orale.

307. Tognazzi, A.; Magnani, A.; Leone G.; Rossi C. Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase – CSGI - VIII Riunione Scientifica Annuale delle Unità Operative Chianciano Terme (SI) 28/06-01/07/2010. “Analysis of polysaccharide paint binders by chromatographic techniques”. Poster.
308. Tognazzi, A.; Magnani, A.; Martini, S.; Leone, G.; Lapucci, R.; Rossi C. SIMS XVII - 17th International Conference on Secondary Ion Mass Spectrometry, Toronto (CANADA) 14-18/09/2009. “ToF-SIMS characterization of pigments and binders in painting microsamples”. Poster.
309. Torrisi, V.; Amato, M.E.; Ballistreri, F.P.; Tomaselli, G.; Toscano, R.M.; Licciardello. A. European Materials Research Society Spring Meeting 2009, Strasburgo (Francia) 8-12/06/2009. “Gold Surface Anchoring of a Chiral Salen Macrocycle as a Sensor for Enanctioselective Recognition”. Poster.
310. Torrisi, V.; Licciardello, A.; Marletta. G. European Materials Research Society Spring Meeting 2009, Strasburgo (Francia) 8-12/06/2009. “Langmuir- Blodgett films of polymer blends: modular feature of surface science”. Oral presentation.
311. Torrisi, V.; Marletta, G.; Da Ros, T.; Prato. M. Carbomat, Catania 6-8/10/2010. “Anchoring of SWCNT-SH on gold surface”. Oral Presentation.
312. Torrisi, V.; Ruffino, F.; Licciardello, A.; Grimaldi, M.G.; Marletta. G. European Materials Research Society Spring Meeting 2010, Strasburgo (Francia) 7-11/06/2010. “Hybrid bilayer by sputtered gold nanoparticles onto diblock-copolymer template”. Poster.
313. Torrisi, V.; Ruffino, F.; Licciardello, A.; Grimaldi, M.G.; Marletta G. European Materials Research Society Fall Meeting 2010, Varsavia (Polonia) 13-17/09/2010. “Hybrid bilayer by sputtered gold nanoparticles onto diblock-copolymer template”. Oral Presentation.
314. Trani, F.; Barone, V. Winter Modeling 2010, Pisa (Italy) February 26, 2010. "Functionalized semiconductor nanoparticles for biosensing applications: a theoretical multilevel approach". Poster.
315. Trani, F.; Carnimeo, I.; Barone, V. VIII Riunione Scientifica Annuale delle Unità operative CSGI, Chianciano Terme (Italy) June 28 - July 1, 2010. "Functionalized Silicon Nanoparticles: a Theoretical Multilevel Approach.". Oral Communication.
316. Trani, F.; Vidal, J.; Bruneval, F.; Marques, M.A.L.; Botti, S. TCM 2010, 3rd International Symposium on Transparent Conductive Materials, Analipsi, Crete (Greece) October 17-21, 2010). "Effects of Electronic and Lattice Polarization on the Band Structure of Delafossite Transparent Conductive Oxides". Oral Communication.
317. Trigoulet, N.; Tuccitto, N.; Delfanti, I.; Licciardello, A.; Molchan, I. S.; Skeldon, P.; Thompson, G. E.; Tempez, A.; Chapon, P. 17th International Conference on Secondary Ion Mass Spectrometry – SIMS XVII, Toronto, Sept. 2009 ”Depth profiling analysis of barrier-type anodic aluminium oxide films formed on substrates of controlled roughness”. Poster.
318. Tuccitto, N.; Delfanti, I.; Spampinato, V. and Licciardello, A. 17th International Conference on Secondary Ion Mass Spectrometry – SIMS XVII, Toronto, Sept. 2009. “C60 depth profiling of polymer-based multilayers”. Oral Presentation.
319. Tuccitto, N.; Marletta, G.; Caratozzolo, M.; Grasso, L.; Guglielmino, S.; Licciardello, A. 17th International Conference on Secondary Ion Mass Spectrometry – SIMS XVII, Toronto, Sept. 2009. “ToF-SIMS imaging of surface self-organized fractal patterns of bacteria”. Poster
320. Tuccitto, N.; Marletta, G.; Licciardello, A.; Carnazza, S.; Caratozzolo, M.; Grasso, L.; Guglielmino, S. 17th International Conference on Secondary Ion Mass Spectrometry (SIMS XVII) Toronto, Canada 14-18/09/2009. “ToF-SIMS Imaging of Surface Self-Organized Fractal Patterns of Bacteria”. Poster.
321. Tuccitto, N.; Marroccia, M. and Licciardello, A. 17th International Conference on Secondary Ion Mass Spectrometry – SIMS XVII, Toronto (Canada), Sept. 2009. “Effect of chemical composition in cluster beam molecular depth profiling of copolymer films”. Poster.
322. Turro, Nicholas J. (Department of Chemistry Columbia University, New York, USA). Dipartimento di Chimica, Sesto Fiorentino (FI), 06/07/2010. “Trapping and Magnetic Manipulation of the Spin Isomers of H2@C60”.
323. Vaccaro, M.; Del Litto, R.; Costantino, A.; Paduano, L.; D’Errico, G.; Ortona, O.; Montesarchio, D.; Ruffo, F.; Simeone, L.; Sartorio, R. XXIII Congresso Nazionale della

Società Chimica Italiana - SCI 2009, Sorrento (NA) 05-10/07/2009. “Lipid Based Nanovectors Containing Ruthenium Complexes: A Potential Route in Cancer Therapy”. Poster.

324. Vanhulle, S.; Balducci, G.; Basosi, R.; Booth, S.; Coppens, P.; Cludts M.; Flores, O.; Francois, B.; Grieder, K.; Jaeger, I.; Jarosz-Wilkolazka, A.; Keshavarz, T.; Leboulc’h, V.; Marvsik, W.; Pede, V.; Prunty, C.; Sandrelli, A.; Sannia, G.; Scheibner, K.; Schlosser, D.; Karaaslan, R.; Tamerler, C.; Tron, T.; Martins, L.; Bols, C.M. COST 868 Meeting on Biotechnology and Biopolymers in Textile, Packaging, Cosmetics and Medical Applications, Istanbul (Turchia) 19-20/02/2009. “Sustainable ecocolourants for the textile and cosmetic industries”. Poster.
325. Vaselli, E.; D’Errico, G.; Silipo, A.; Molinaro, A.; Lanzetta, R.; Radulescu, A.; Paduano, L.; Mangiapia, G. User Meeting at FRM II on October 15th, 2010. “Characterization of vesicles formed by lipopolysaccharides: from the molecular structure to the aggregate architecture”. Poster.
326. Vettor, M.; Bruni, G.; Mondelli, A.; Bleve, M.; Pavanetto, F.; Perugini, P. XXI Simposio Adritelf, Cagliari 10-13/09/2009. “Evaluation of SLN skin surface distribution by scanning electron microscopy and transparency profilometry techniques. Poster.
327. Vettor, M.; Bruni, G.; Mondelli, A.; Secchi, G.; Pavanetto, F.; Perugini, P. Skin and Formulation 3rd Symposium & Skin Forum, 10th Annual Meeting, Versailles, Francia, 9-10/03/2009. “Evaluation of colloidal system distribution on the skin surface by scanning electron microscopy and transparency profilometry”. Poster.
328. Villa, M.; Pesenti, R.; Salvi, P.; Nelli, P.; Kiros, Y. Abstract 277 - 215th Electrochemical Society Meeting San Francisco (CA), 24-29 May 2009. “Electrochemical pressure spectroscopy; a tool to characterize porous air electrodes”. Oral Presentation.
329. Vitiello, G.; Busi, E.; Coppola, C.; Montesarchio, D.; Basosi, R.; Paduano, L.; D’Errico, G. CSGI Annual conference, 8a Riunione Scientifica delle Unità Operative del Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Chianciano Terme (SI) 29-30/06/2010. “A study on the mechanism of ion transport through membrane by CyPLOS”. Poster.
330. Vitiello, G.; Merlino, A.; Sica, F.; Busi, E.; Basosi, R.; Paduano, L.; D’Errico, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa (VB). “A combined experimental and molecular dynamics simulation study on the interaction between a peptide deriving from glycoprotein gp36 of feline immunodeficiency”. Poster.
331. Vitiello, G.; Merlino, A.; Sica, F.; Busi, E.; Basosi, R.; Paduano, L.; D’Errico, G. XXXIX Congresso Nazionale di Chimica Fisica, Stresa, Italia 20-24/09/2010. “A combined experimental and molecular dynamics simulation study on the interaction between a peptide deriving from glycoprotein gp36 of feline immunodeficiency virus and phospholipid membranes”. Poster.
332. Wirth, E.; André, R.; Levchenko, A.; Gross, K.; Milanese, C.; Le Parlouër, P. International Symposium on Metal – Hydrogen Systems MH 2010, Moscow (Russia) 19-23/07/2010. “Coupling of manometric and calorimetric measurements to probe unique characterization of solid hydrogen storage systems”. Poster.

Theses (undergraduate, PhD, master, post-doc)

U.O. Bergamo

- De Ruschi, D.: Laurea magistrale in Ingegneria Informatica "Database management for an electrical distribution network of intermediate complexity (CERN – Genève)" 2010 (Relatore M. Villa).
- Longo, M.: Laurea magistrale in Ingegneria Informatica "Controllo degli esperimenti e ottimizzazione degli algoritmi di trattamento dati per un laboratorio di elettrochimica" 2009 (Relatore M. Villa).
- Pesenti, R.: Laurea magistrale in Ingegneria Informatica "Problematiche di sistema e di trattamento dati per banchi di misure elettrochimiche" 2009 (Relatore M. Villa).

U.O. Bologna

- Bressanin, D.: PhD Thesis "Studio della subunità ε della DNA polimerasi III di Escherichia coli: stabilità e interazione con la subunità polimerasica" 2009.
- Lemma, S.: Laurea Triennale "Studio di metodi continui e discontinui per la determinazione dell'attività DNA polimerasica in vitro" 2009.
- Presta, E.: Laurea Specialistica "Espressione in Escherichia coli e caratterizzazione della variante della tossina difterica CRM197" 2010.
- Vincelli, G.: Laurea Specialistica "Ruolo di proteine accessorie nella stabilizzazione della subunità esonucleasica della DNA polimerasi III di Escherichia coli" 2010.

U.O. Cagliari

- Cocco, G.: Laurea Triennale "Purificazione di una laccasi inducibile dal fungo ligninolitico Pleurotus sajor-caju" 2009/10.
- Fadda, P.: PhD Thesis "Microemulsioni innovative per formulazioni biocompatibili" 2009.
- Gottardi, G.: Laurea Specialisitca "Attività di una laccasi fungina verso alcuni idrossiantrachinon i e idrossiantraceni" 2009/10.
- Loi, M.: Laurea Triennale "Analisi elettroforetica di una laccasi da Pleurotus sajor-caju" 2009/10.
- Mamusa, M.: Laurea Magistrale "Implicazioni del controione del liquido ionico sulle nanostrutture osservate nel sistema ternario NaAOT/acqua/bmimBr" 2010.
- Nardone, J.L.: Laurea Triennale "Estrazione e purificazione di laccasi da Pleurotus sajor-caju" 2009/10.
- Sanna, M.: Laurea Triennale "Cromatografia a scambio ionico di una laccasi da Pleurotus sajor-caju" 2009/10.
- Zurru, I.: laurea Triennale "Assimilazione dell'ammonio da parte del lievito ambientale Sakaguchia dacryoidea" 2009/10.

U.O. Campobasso

- Colalillo, A.: Laurea Triennale "Ossidazione di Lipidi in sistemi colloidali" 2009 (Univ. Molise).
- Diantom, A.: Laurea Triennale "Ossidazione lipidica in emulsioni e in olio di oliva velato" 2010 (Univ. Molise).
- Facchini, L.: Laurea Triennale "Messa a punto di un saggio colorimetrico per la determinazione degli zuccheri basato sulla sintesi di nanoparticelle di oro" 2010 (Univ. Bari).
- Guastamacchia, M.: Laurea Triennale "Glucosio come riducente nella preparazione di nano-particelle di Pd°: aspetti cinetici" 2010 (Univ. Bari).

- Iapalucci, F.: Laurea Triennale “Utilizzo dei sottoprodotti dell’industria olearia per il disinquinamento delle acque da metalli pesanti” 2010 (Univ. Molise).
- Sacco, P.: Laurea Triennale “Rimozione di cromato da soluzioni acquose mediante un nuovo materiale assorbente composto da CTAB, Gelatina e Silice” 2009 (Univ. Molise).

U.O. Catania

- Arangio, A.M.: Laurea Triennale “Deposizioni di monostrati di Langmuir-Blodgett di miscele fosfolipide-polimero” 2010 (Relatore G. Marletta).
- Campisi, A.: Laurea Triennale “Preparazione di multistrati polimerici e loro caratterizzazione mediante cluster-SIMS” 2009.
- Corallo, V.: Laurea Specialistica “Architetture supramolecolari di complessi metallici su superfici” 2010.
- Crifò, S.: Laurea Magistrale “Strategie di auto-aggregazione per strutture di nano contenitori” 2010 (Relatore G. Marletta).
- Cristaudo, V.: Laurea Triennale “Influenza dei gas reattivi nel SIMS dinamico di polimeri” 2010.
- Cunsolo, F.: Laurea Magistrale “Metodologie di organizzazione supramolecolare per transistors organici” 2010 (Relatore G. Marletta).
- Fusari, I.: Laurea Triennale “Crescita e caratterizzazione di multistrati di complessi metallici su ossidi trasparenti” 2010.
- Intilla, L.: Laurea Triennale “Metodologie di preparazione e caratterizzazione di film Langmuir-Blodgett” 2010 (Relatore G. Marletta).
- Li Destri, G.: PhD Thesis “Self-organization processes in conjugated polymer films” 2010.
- Marroccia, M.: Laurea Specialistica “Profili di profondità molecolari di strati polimerici mediante sputtering con fasci di fullerene” 2009.
- Messina, F.G.: Laurea Triennale “Metodologie di nanopatterning di superfici” 2009 (Relatore G. Marletta).
- Messina, G.M.L.: PhD Thesis “A study of molecular self-organizing processes at surfaces” 2009 (Relatore G. Marletta).
- Paternò, G.: Laurea Triennale “Processi di auto-assemblaggio di film di Langmuir di copolimeri coniugati” 2009 (Relatore G. Marletta).
- Privitera, S.: Laurea Triennale “Auto-organizzazione di peptidi anfifilici su superfici” 2009 (Relatore G. Marletta).
- Sfuncia, G.: Laurea Magistrale “Metodologie per la nanostrutturazione di sistemi molecolari fotoattivi” 2010 (Relatore G. Marletta).
- Vitale, S.: Laurea Triennale “Caratterizzazione chimico-fisica di film ultrasottili auto assemblati su substrati di ossido semiconduttore” 2009.
- Zappalà, G.: Laurea Specialistica “Applicazioni del cluster-SIMS allo studio di materiali polimerici” 2010.
- Zuccarello, E.G.: Laurea Triennale “Ancoraggio di nanotubi di carbonio mediante self assembly su superfici” 2010 (Relatore G. Marletta).

U.O. Firenze

- Anfuso, I.: Laurea Triennale “Determinazione dello stato di ossidazione di materiale cartaceo mediante tecniche di spettrofotometria” 2009.
- Antonazzo, E.D.: Laurea Triennale “Sintesi ed applicazione di nanoparticelle di $Sr(OH)_2$ per la conservazione ed il restauro di manufatti cartacei” 2010.
- Augugliaro, G.: Laurea Triennale “Caratterizzazione chimico-fisica di vernici naturali impiegate da Vincenzo Coronelli (XVII secolo) sui globi celesti e terrestri conservati presso il Museo Galileo di Firenze” 2010.
- Baglioni, M.: PhD Thesis “Development of Nano-Systems for the Cleaning of Wall Paintings” 2010.
- Baldoneschi, V.: Laurea Triennale “Stabilizzazione di inchiostri metallo-gallici mediante deacidificazione con nanoparticelle alcaline” 2009.

- Balducci, S.: Laurea Triennale in Tecnologia per la Conservazione e il Restauro dei Beni Culturali “Caratterizzazione chimico-fisica di idrogel a base di polivinil acetato parzialmente idrolizzato” 2009.
- Bandoli, A. C.: Laurea Specialistica in Scienze per i Beni Culturali “Sistemi polimerici per la pulitura di superfici pittoriche: proprietà reologiche, fenomeni di swelling e rilascio controllato di solventi” 2010.
- Bausi, F.: Laurea Specialistica “Studio dell'idratazione e della struttura di malte cementizie in presenza di additivi inorganici e polimerici” 2010.
- Bellissima, F.: Laurea Specialistica “Nanoparticelle di oro funzionalizzate con un inibitore dell’anidrasi carbonica: sintesi e caratterizzazione” 2009.
- Berlangieri, C.: Laurea Triennale in Tecnologia per la Conservazione e il Restauro dei Beni Culturali “Gel a base di polivinl alcol e borace per la pulitura di superfici artistiche: inglobamento di tensioattivi e microemulsioni” 2009.
- Bernacchioni, C.: Laurea Triennale in Tecnologia per la Conservazione e il Restauro dei Beni Culturali “Caratterizzazione chimico fisica di pellicole cinematografiche in triacetato di cellulosa” 2010.
- Boscagli, C.: Laurea Specialistica “Nanodispositivi fotovoltaici” 2011.
- Castri, E.: Laurea Triennale “Applicazione di nanorestore per la deacidificazione di manoscritti contenenti inchiostri metallo-gallici” 2010.
- Cavaciocchi, L.: Laurea Specialistica “Materiali organici nanostrutturati per dispositivi fotovoltaici” 2010.
- Cavigli, P.: Laurea Specialistica “Nanoarchitetture polimeriche per dispositivi OLED fosforescenti” 2010.
- Cottone, F.: Laurea Triennale “Polimeri a Base Acrilica e Cellulosica in Acqua di Calce: Autoassociazione e Influenza nella Formazione di Nanostrutture Inorganiche” 2010.
- Dankesreiter, S.: German Diploma Thesis “Synthesis and Characterization of Nanoparticles” 2009.
- De Tuglie, D.: Laurea Triennale “Caratterizzazione chimico-fisica del degrado di opere cartacee conservate presso la Biblioteca Nazionale Centrale di Firenze” 2009.
- Del Buffa, S.: Laurea Triennale “Dinamica dell’acqua di idratazione confinata in nanostrutture di silicato tricalcico” 2010.
- Di Biase, F.: Laurea Triennale “Formulazione e caratterizzazione di liposomi cationici per il trasporto di DNA plasmidico” 2009.
- Di Lorenzo, F.: Tesi di Laurea Triennale “Sintesi di nanoparticelle di oro tramite derivati anfifilici della vitamina C” 2009.
- Dolle, C.: German Diploma Thesis “Physico-Chemical Characterization of Epimeric Vitamin-C Bolaamphiphiles” 2010.
- Eiblmeier, J.: Laurea Quinquennale “Formulation and characterization of hydrogels for the cleaning of works of art” 2009, (Università degli Studi di Firenze - University of Regensburg).
- Fantoni, G.: Laurea Triennale “Determinazione del contenuto di carbossili e carbonili nella carta e loro effetti di degrade” 2010.
- Ferretti, I.: Laurea Triennale “Deacidificazione di materiale cartaceo mediante dispersioni fluorurate di nanoparticelle alcaline” 2009.
- Fraticelli, G.: Laurea Triennale “Gli inchiostri al rame nei manoscritti: analisi storica e problemi conservative” 2009.
- Gambinossi, F.: “Nanoarchitetture a funzionalità modulabile” Assegno di ricerca 2009-2011.
- Ghezzi, M.: Laurea Magistrale “Hybrid Nanoarchitectures for OLED Devices (Nanoarchitetture ibride per dispositivi OLED)” 2010.
- Ghezzi, M.: Tesi di Laurea Magistrale “Hybrid nanoarchitectures for OLED devices” 2010.
- Giannetti, A.: Laurea Triennale “Manoscritti di Giuseppe Ungaretti al Gabinetto Scientifico Letterario G.P. Vieusseux: *indagini conoscitive sperimentali sui materiali e inchiostri”* 2010.
- Giustini, L.: PhD Thesis “Nanostrutture da Tensioattivi Chirali” 2011.
- Gori, M.: Laurea Triennale “Deacidificazione di legno archeologico: uso di nanoparticelle per il trattamento di grandi volume” 2009.
- Guarducci, J.: Laurea Triennale “Caratterizzazione chimico-fisica di un tessuto di cotone trattato con metodologia innovativa in ammoniaca liquida.

- Kaiser, J.: German Diploma Thesis “Formation of Polypseudorotaxane from Cyclodextrins and Polyethylene Glycol” 2009.
- Luci, L.: Master IMES “Indagine botanica su colture arboree oleaginose tropicali e caratterizzazione chimico/fisica degli oli derivati” 2010.
- Marinelli, F.: Laurea Triennale in Tecnologia per la Conservazione e il Restauro dei Beni Culturali “Dispersioni di Polivinil acetati a vario grado di idrolisi in acqua: proprietà reologiche ed applicazioni per la pulitura di superfici artistiche” 2009.
- Martina, M.R.: Laurea Magistrale “Modelli per raft lipidici: uno studio in vescicole lipidiche sintetiche” 2009.
- Martina, M.R.: XXV Ciclo di Dottorato in Scienze Chimiche, “Interazioni tra biomolecole e membrane fosfolipidiche”, 2010.
- Mercatelli, E.: Laurea Triennale “Nanosensori per la diagnostica precoce di amiloidosi degenerative” 2011.
- Migliaccio, M.: Laurea Triennale in Tecnologia per la Conservazione e il Restauro dei Beni Culturali “Applicazione di dispersioni polimeriche acquose di poli vinil alcol in presenza di cosolventi per la pulitura di superfici pittoriche” 2010.
- Montis, C.: Laurea Specialistica in Chimica “Sistemi Ibridi Nucleolipidi-Acidi Nucleici: Preparazione e Caratterizzazione” 2009.
- Nappini, S.: PhD Thesis “Magnetoliposmes for controlled drug release” 2011.
- Natali, I.: PhD Thesis in Scienza per la Conservazione dei Beni Culturali, ssd CHIM/12 “Green Nanostructured Systems for the Conservation of Artistic and Architectonic Artefacts” 2010.
- Neubauer, M.: Laurea Quinquennale “Synthesis and physico-chemical characterization of novel hydrogels for cultural heritage conservation” 2010, (Università degli Studi di Firenze - University of Regensburg).
- Nuccio, A.: Laurea Specialistica in Scienze per i Beni Culturali “Sistemi compositi nanocalce-copolimeri acrilici per la conservazione di superfici architettoniche” 2010.
- Palmieri, F.: Laurea Triennale “Le pitture murali Maya della Acropolis Chik-Naab in Calakmul” 2009.
- Paoli, D.: Laurea Quinquennale “Sintesi di particelle di idrossido di stronzio micro- e nano-strutturato e potenziali applicazioni nel restauro” 2009.
- Peruzzi, N.: Tesi di Laurea Triennale “La serie di Hofmeister e il comportamento di fase del lisozima” 2009.
- Pieralli, E.: Laurea Triennale “Degrado e Conservazione di Beni Artistici Precolombiani Trattati con Resine Sintetiche” 2011.
- Pistolesi, S.: Tesi di Laurea Magistrale “L’impronta della serie di Hofmeister sull’alocromismo di coloranti azoici: sviluppi sull’effetto specifico degli anioni” 2009.
- Pizzorusso, G.: PhD Thesis “Synthesis and characterization of systems for the micro-confinement of detergents for the cleaning of canvas paintings” 2011.
- Progetto/titolo PhD thesis “Interazioni tra biomolecole e membrane fosfolipidiche”. (Relatore G. Caminati).
- Raudino, M.: Laurea Triennale “Sintesi e caratterizzazione di organogel chimici per la pulitura di quadri su tela” 2010.
- Rengstl, D.: Thesis “Microemulsion and Micellar Solution for the Removal of Polymers form Painting Surfaces: Investigation on the Cleaning Mechanism” 2009.
- Rossi, F.: Laurea Triennale “Caratterizzazione chimico-fisica di derivati del Guar come additivi per materiali da costruzione” 2011.
- Salvatore, A.: Laurea Triennale “Nanoparticelle di idrossido di stronzio per la desolfatazione e il consolidamento degli intonaci” 2009.
- Salvatori, D.: Laurea Triennale “Nanosistemi funzionali come sensori per residui tossici nel settore alimentare” 2009.
- Sampaolo, S.: Laurea Triennale “Studio del degrado e del comportamento termico di pergamena sottoposta ad invecchiamento accelerato” 2010.
- Sarri, F.: Laurea Triennale “Nanodispositivi Organici Per Diodi Ad Emissione” 2011.
- Stirner, M.: German Diploma Thesis “Synthesis and Characterization of Piezoelectric Nano-Powders” 2009.

- Tattini, L.: PhD Thesis “Synthesis and Characterization of Nanosystems for Polyfunctional Textiles” 2010.
- Zahn, S.: German Diploma Thesis “Synthesis and Physico-chemical Characterization of L-6-O-ascorbyl oleate and of its Nanoassemblies” 2009.

U.O. Messina

- Anghelone, D.: Laurea Magistrale “Ottimizzazione della produzione di Ramnolipidi da parte di Pseudomonas aeruginosa L05” 2009.
- Bianco, F.: Laurea Magistrale “Studio della dinamica molecolare di mimotopi di F1 di Yersia pestis” 2010.
- Caratozzolo, M.: PhD Thesis “Fattori chimico-fisici e fisiologici influenzanti l’adesione cellulare: modellizzazione dell’interazione cellula-substrato e cellula-cellula nel self-assembly di cellule procariotiche” 2010.
- De Santis, R.: Laurea Triennale “Biocelle Microbiche” 2009.
- Franco, D.: Laurea Triennale “Nuove prospettive nella progettazione delle Celle a Combustibile Microbico” 2010.
- Frezza, C.: Laurea Magistrale “Effetti della starvation di azoto e di magnesio sulla produzione di PHA in Pseudomonas aeruginosa” 2010.
- Grasso, L.: Laurea Magistrale “Influenza della forza ionica nel processo di adesione batterica su superfici abiotiche” 2010.
- La Lia, M.: Laurea Magistrale “Applicazioni di peptidi ricombinanti selezionati tramite Phage Display per la cattura di L. monocytogenes in prodotti lattierocaseari” 2010.
- Romeo, L.: Laurea Triennale “Biosensoristica e Medicina innovativa” 2009.
- Rossitto, M. F.: Laurea Magistrale “Utilizzo della diagnostica molecolare per valutare la riattivazione di JC Virus in pazienti trattati con immuno-soppressori” 2009.

U.O. Napoli

- Chiacchio, F.: Undergraduated thesis “Studio di aggregati supramolecolari a base nucleosidica con potenziale attività antitumorale” 2010.
- Costantino, A.: Master thesis “Sviluppo e caratterizzazione di aggregati supramolecolari ad attività antineoplastica” 2010.
- Di Nardo, G.: Undergraduated thesis “Effetto del colesterolo nell’interazione tra un peptide derivante dalla gp36 del FIV e membrane lipidiche” 2009.
- Emendato, A.: Undergraduated thesis “Interazione tra il frammento 665-683 della gp41 di HIV e membrane fosfolipidiche” 2010.
- Gentile, F.: Master thesis “Caratterizzazione di liposomi pH modulabili in fase gel” 2010.
- Lombardi, L.: Undergraduated thesis “Caratterizzazione spettroscopica e reologica di idrogeli nano strutturati di acido ialuronico” 2009.
- Luchini, A.: Undergraduated thesis “Studio di un complesso di rutenio ad attività antitumorale in sistemi nanostrutturati” 2010.
- Noviello, D.: Undergraduated thesis “Caratterizzazione del processo di fibrillazione del peptide b-amiloide in presenza di membrane liposomiali” 2009.
- Santagata R.A.: Undergraduated thesis “Cinetica di accrescimento di nanogeli di PVA in presenza di sali diversi” 2010.

U.O. Pavia

- Cipollini, C.: Laurea Specialistica in Farmacia “I co-cristalli farmaceutici: una strategia per migliorare le proprietà chimico-fisiche dei farmaci” 2010.
- Ferrari, S.: PhD Thesis in Chemical Sciences “Synthesis and Characterization of Materials for Electrochemistry” 2010.
- Fulcheri, M.C.: Laurea Specialistica in Farmacia “La microscopia elettronica a scansione e le sue applicazioni in campo farmaceutico” 2010.

- Maietta, M.: Laurea Specialistica in Farmacia “Preparazione e caratterizzazione chimico-fisica di co-cristalli di carprofen” 2010.
- Mazzoni, A.: Laurea Triennale in Scienze Chimiche " Sintesi in situ di compositi a base di alluminio: attivazione termica, meccanica e meccano-termica di reazioni chimiche" 2009.
- Paturzo, C.E.: Laurea Triennale in Tecnologie chimiche per l’ambiente e le risorse “Studio di Parametri Termodinamici Relativi allo Stoccaggio Geologico della CO2” 2010.
- Quaroni, D.: Laurea Triennale in Tecnologie chimiche per l’ambiente e le risorse “Caratterizzazione di Membrane Metalliche al Palladio per la Separazione dell’Idrogeno da Miscele di Gas” 2010.
- Sfondrini, A.: Laurea Specialistica in Farmacia “Determinazione della purezza polimorfica della nateglinide” 2011.
- Sichel, B.M.: Laurea Triennale in Tecnologie chimiche per l’ambiente e le risorse “Sintesi e Caratterizzazione di Polimorfi della Rifaximina” 2010.
- Zanni, F.: Laurea Triennale in Scienze Chimiche “I Metodi Termici di Indagine: Fondamenti ed Esempi Pratici” 2009.

U.O. Siena

- Arcuri, M.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Studio dell’interazione tra coloranti naturali e macromolecole modello nei processi di tintura delle stoffe mediante spettroscopia d risonanza magnetica nucleare” a.a 2008/2009 (Relatore C. Bonechi).
- Arezzini, E.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Studio delle variazioni spaziali e stagionali della materia organica disciolta e il loro impatto sulla distribuzione dei pigmenti fotosintetici in un lago stratificato” 2009 (Relatore S. Loiselle).
- Bersotti, C.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Valutazione in vitro della citotossicità di idrogeli di PVA da utilizzare come sostituti del corpo vitreo” 2010 (Relatore S. Lamponi).
- Bidini, A.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Derivati polivinilici fosfatati come sostituti artificiali dell’umor vitreo” a.a. 2008/2009 (Relatore G. Leone).
- Bonucci, A.: Laurea Magistrale “Spectroscopic characterization of antimicrobial peptide HNP1 in solution and in presence of model membranes” 2009.
- Bravi, M.: Assegno di Ricerca post-doc “Pianificazione e gestione di un sistema energetico locale ad alta concentrazione di produzione da fonte rinnovabile e di cogenerazione, integrata con sistemi di accumulo, orientata all’ottimizzazione energetico-economica e alla fornitura di servizi di rete mediante sistemi “smart grids”” 2011.
- Calderoni, E.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Valutazione in vitro della citocompatibilità di idrogeli di PVA da utilizzare come sostituti del corpo vitreo” 2010 (Relatore S. Lamponi).
- Casaccia A., Laurea Triennale in Chimica e Tecnologia dei Materiali. “Analisi delle metodologie di trasformazione delle biomasse lignocellulosiche: processi termici, chimici e biologici”. 2009 (Relatore C. Rossi).
- De Ricco, R.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Sintesi e caratterizzazione chimico-fisica di idrogel a base di polivinilalcol e polivinilpirrolidone” a.a 2008/2009 (Relatore C. Bonechi).
- Della Porta, E.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Comportamento cellulare sui SAM” 2010 (Relatore S. Lamponi).
- Forte, S.: PhD Thesis “Sviluppo di processi enzimatici per la decontaminazione e la produzione industriale” 2010.
- Fulini, P.: PhD Thesis “Integrazione dell’efficienza energetica e fonti rinnovabili nella progettazione di un edificio off grid” 2010.
- Giansanti, S.: Assegno di Ricerca post-doc “Bioprocessing for sustainable production of coloured textiles” 2010.
- Giansanti, S.: Assegno di Ricerca post-doc “Caratterizzazione strutturale e funzionale di laccasi, perossidasi versatili e diossigenasi: identificazione degli intermedi del meccanismo catalitico e della specificità di substrato” 2009.

- Lambardi, F.: Ph.D. Thesis “Interactome Explorer: un nuovo WEB TOOL Informatico per l'analisi interattomica” e “NOESolver: una applcazione web per l'analisi della Complete Relaxation Matrix” 2009 (Relatore A. Donati).
- Mariani, B.: Ph.D. Thesis “Caratterizzazione chimica di matrici vegetali e studio dei complessi tra componenti antiossidanti e macromolecole biologiche. Valutazione degli effetti biologici degli estratti vegetali e delle principali componenti chimiche identificate” 2010 (Relatore C. Rossi).
- Nelli, N.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Realizzazione e caratterizzazione di sensori a base polimerica per il rilevamento di inquinanti ambientali” a.a. 2008/2009 (Relatore G. Leone).
- Parisi, M.L.: Assegno di Ricerca post-doc “Studio di nuovi processi industriali per lo sviluppo di metodi di riciclaggio e riuso per residui plastici delle automobili e ricerca e trasferimento tecnologico di nuovi impianti, strutture e macchinari finalizzati alla corretta gestione del fine vita dell’auto nella realtà Toscana” 2009.
- Parisi, M.L.: Borsa di Studio post-doc “Progettazione e sintesi di nuovi sensibilizzatori organici per la produzione di celle fotovoltaiche non convenzionali” 2010.
- Parisotto, C.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Estrazione e caratterizzazione di pigmenti organici utilizzati nel settore dei beni culturali” 2009 (Relatore A. Magnani).
- Pelliccia, T.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Sviluppo di sistemi modello per biosensori” a.a. 2008/2009 (Relatore G. Leone).
- Rocchigiani, G.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Analisi composizionale di leganti pittorici a base di polisaccaridi naturali mediante tecniche cromatografiche” 2009 (Relatore C. Rossi).
- Rossini D. Laurea Triennale in Chimica e Tecnologia dei Materiali. “Sviluppo di un modello matematico per la degradazione del glucosio nel Saccharomyces cerevisiae in condizioni di stress dovute alla presenza di metalli” 2010 (Relatore C. Rossi).
- Ruzzenenti, F.: Assegno di Ricerca post-doc “Efficienza e fonti rinnovabili per l’Università di Siena e rebound effect” 2009.
- Sorci, F.: PhD Thesis “Analisi dei processi fotochimici della materia organica disciolta, DOM, indotti dalla radiazione solare, nei sistemi acquatici” 2010 (Relatore C. Rossi).
- Sordi, F.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Analisi dei processi di interazione tra fungicidi utilizzati in viticoltura e albumina mediante misure di risonanza magnetica nucleare” a.a 2008/2009 (Relatore C. Bonechi).
- Spannocchi, A.: Laurea Triennale in Chimica e Tecnologia dei Materiali “Analisi conformazionale del peptide natriuretico atriale (ANP) con tecniche di risonanza magnetica nucleare” ”a.a 2008/2009 (Relatore C. Bonechi).

RESEARCH PROJECTS

1A: Hard Matter (Nanomaterials and Solid Interfaces)..69

1B: Soft Matter (Nanomaterials anl Liquid Interfaces)..104

1C: Theory and Modelling...164

2A: Art Restoration, Environmental Remediation and Textile Chemistry.............182

2B: Metals and Ceramics..215

2C: Biotechnology...219

1A – Electrochemical Energy Conversion without platinum group metal catalysts

M. Villa, P. Nelli, R. Pesenti, P. Salvi
G. Zangari (Dept. MSI- Un. of Virginia),
Y. Kiros (Dept. Chem. Eng KTH – Stockholm)

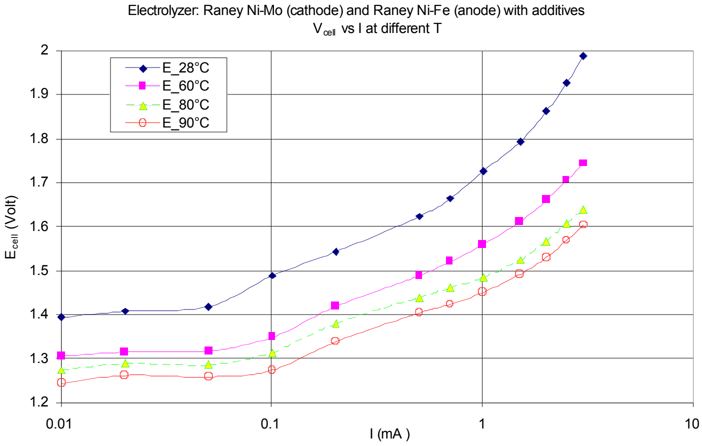
Aims

To develop electrochemical alkaline cells for energy conversion which may use abundant non-Platinum-Metal-Group (PMG) ,catalysts while competing in performance/cost with PMG-based Proton Exchange Membrane (PEM) devices. In particular, we are chiefly interested in the technological exploitation of the $2H_2O \leftrightarrow 2H_2+O_2$ reaction and will contribute to the following areas: 1) advanced alkaline electrolysers, 2) alkaline fuel cells.

Results

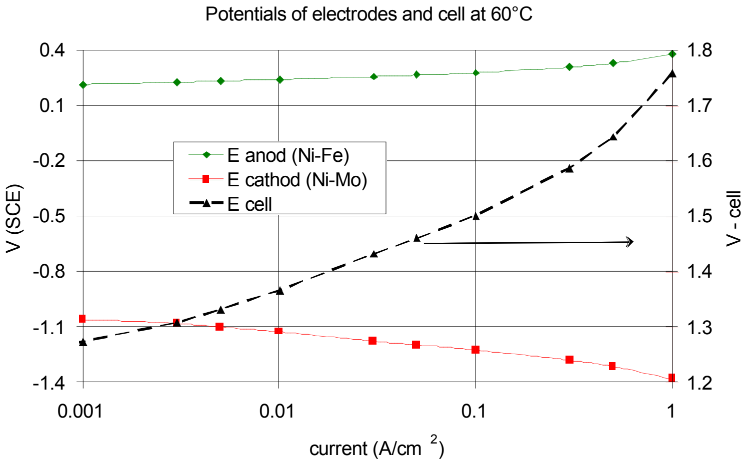
In a water electrolyser we have, at the cathode (–), the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER) at the anode (+). In a typical fuel cell, gaseous oxygen is reduced at the cathode (Oxygen Reduction Reaction – ORR) while gaseous hydrogen is consumed at the anode (Hydrogen Oxidation Reaction, HOR). Most of our work has focused upon membrane electrodes with PTFE bonded catalysts on a conducting net, and optional layers for gas-electrode separation (at the electrolyte side) and gas diffusion (at the other side). Such an architecture is suitable for both electrolysers and fuel cells, and simplifies system architecture.

Our main result is an advanced alkaline electrolyser operating at moderate temperatures (below 100°C), which sustains current densities up to ~300 mA/cm^2 when $V_{cell} \cong 1.6$ V (i.e., near the thermoneutral point) The figure below shows the cell voltages at different currents and temperatures for a 10 cm^2 cell using two gas diffusion electrodes. This 77% cell efficiency (attained at 90°C) leaves an 8% margin to achieve the 2012 D.O.E. goal of a 69% efficiency for the whole electrolyser.

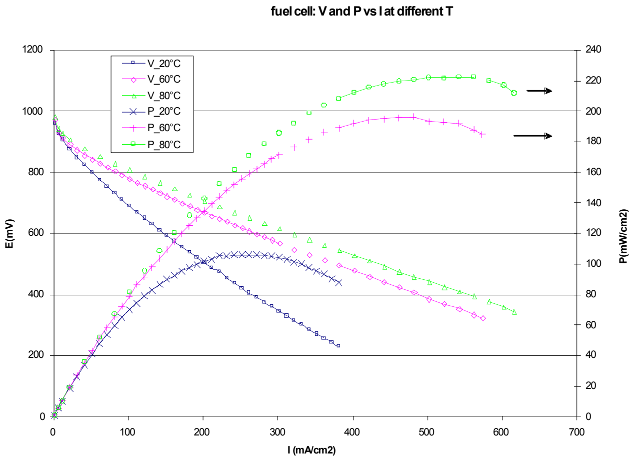


Electrolyzer: Raney Ni-Mo (cathode) and Raney Ni-Fe (anode) with additives
V_{cell} vs I at different T

Furthermore, we feel that these performances may be further improved: a) by reducing the ohmic losses in the electrolyte and separators, b) by increasing the electrochemical roughness of the electrode (active area per unit geometric area) with suitable changes of wettability and morphology. For example, the figure below shows, as a function of current density, the potential of anode, cathode and full cell of a zero-gap electrolyser with full immersion electrodes at 60°C. Relative to the cell with gas diffusion electrodes, at 300 mA/cm^2 and 60°C we have a voltage gain of almost 150 mV, and achieve at 60°C the performances that the other electrolyser attains at 90°C.



The next figure shows the behaviour vs current density of voltage and power density for a H_2/O_2 fuel cell based upon our non-PGM gas diffusion electrodes.



We believe that the power density of this cell may be improved several times by a better choice of the ORR catalyst, a hot topic in the current research, and by suitable modification of the pore structures of anode and cathode.

References

Hurst, H. "In pursuit of water oxidation catalysts" Science 328, 315-316 (2010).
Yin Q., Tan, J.M.; Besson C.; Geletii Y.V.; Musaev D.J.; Kusnetsov A.E.; Luo Z.; Hardcastle K.I. and Hill G.L. "A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals", Science 328, 342-345 (2010).
US Dept. Of Energy and US Dept. Of Transportation "Hydrogen Posture Plan; An integrated Research, Development and Demonstration Plan" (2006).
Lu, S.; Pan, J.; Huang A.; Zhuang, L. and Lu, J. "Alkaline polymer electrolyte fuel cells completely free from noble metal catalysts" PNAS 105, 20611-20614 (2008).
Spendelow, J.S. and Wieckowski, A. "Electrocatalysis of oxygen reduction and small alcohol oxidation in alkaline media", Phys. Chem. Chem. Phys. 9, 2654-2675 (2007).

1A – Effect of oxidation level of n+-type nanoporous silicon surface on lipase adsorption and activity

A. Salis, F. Cugia, S. Setzu, G. Mula, M. Monduzzi

Aims

Nanoporous silicon. Physico-Chemical characterization. Surface oxidation. Lipase adsorption and activity.

Results

Porous silicon (PSi), discovered by Uhlir in 1956, is currently finding interesting applications as transducer for biosensing devices. PSi forms as a result of electrochemical etching of crystalline silicon in aqueous HF solution. In the field of biosensors, porous silicon shows great potentialities. The very large specific area, and the possibility to choose pores size from few nm to more than 100 nm represent peculiar characteristics. Consequently, the adsorption of a large amount of biomolecules onto small volumes can easily be performed, and the fabrication of small devices such as biosensors may become a valuable development.
In this work, we present the synthesis and the characterization of n^+-type porous silicon (PSi) layers, being the final aim of the work the fabrication of a biosensor that exploits the semiconductive properties of this material. PSi wafers were used as a matrix for enzyme adsorption. These wafers, as a result of their porous nanostructure had a high surface area (360 m^2/g) and pore size in the range 5 - 20 nm.

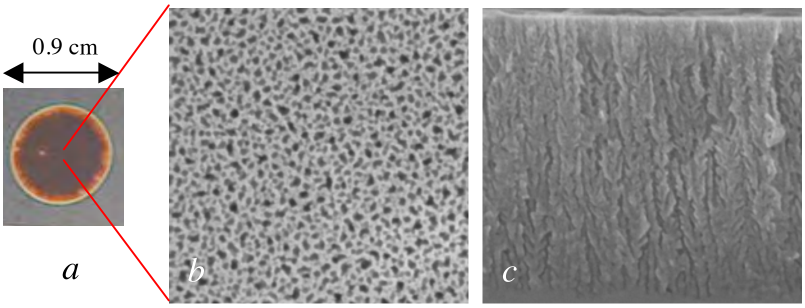
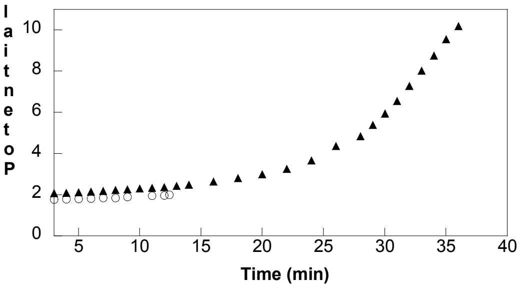
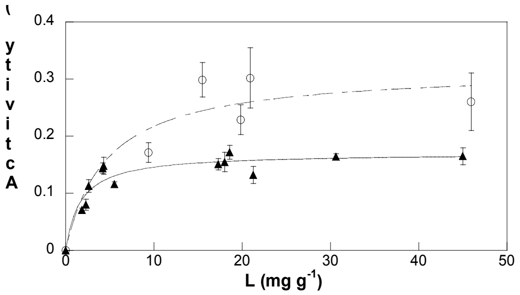


Figure *a* shows a PSi slab and Figure *b* and *c* show the SEM micrographs of the top view and the side view of the nano-pores. The freshly prepared PSi was stabilized through controlled anodic oxidation. Two classes of samples differing for the level of oxidation were prepared. The first class was oxidized up to 2V (LO-PSi), whereas the second class was oxidized up to 10 V (HO-PSi).



Both samples were used for the adsorption of *Candida rugosa* lipase. A significantly higher loading was ascertained for LO-PSi (140 mg/g) compared to HO-Si (47 mg/g). The different hydrophobic-hydrophilic balance of the PSi surfaces induced by the different oxidation voltage affects the physical interactions that address the adsorption process of the lipase.



The higher loading achieved with the LO-PSi resulted in a higher activity of the immobilized biocatalyst but in a lower catalytic efficiency. The two biocatalysts showed an acceptable stability towards storage (pH 5 buffer solution at 5°C) within two weeks.

References

Salis, A.; Cugia, F.; Setzu, S.; Mula, G.; and Monduzzi, M. "Effect of Oxidation Level of n^+-type Mesoporous Silicon Surface on the Adsorption and the Catalytic Activity of *Candida rugosa* Lipase", J. Colloid Interface Sci., 345, 448-453, (2010).

1A – Ordered Mesoporous Materials. Part 1: Synthesis, characterization, and sustained lysozyme release

A. Salis, M.S. Bhattacharyya, P. Hiwale, D. Steri, M. Piras, L. Medda, M. Piludu, M. Monduzzi

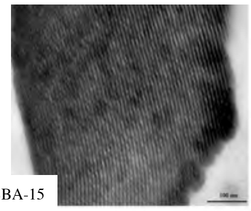
Aims

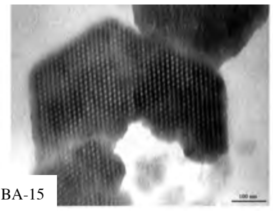
Nanostructured silica. Physico-chemical characterization. Protein adsorption on solid surfaces. Sustained Release.

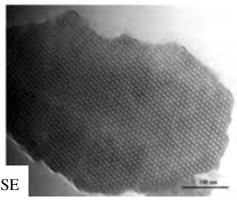
Results

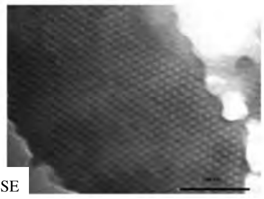
Ordered mesoporous materials (OMMs) have unique features, namely high surface area, high pore volume, and a narrow pore size distribution. This last feature is particularly useful for the adsorption of proteins since their dimension often matches the OMMs pore size. For these reasons OMMs are becoming of high interest in important fields such as nanomedicine, bioadsorption, and biocatalysis.

Here two OMMs namely, SBA-15 mesoporous silica and MSE periodic mesoporous organosilica (whose silicon atoms are alternatively connected by means of -Si-O-Si- and -Si-CH_2-CH_2-Si- groups), were synthesized and characterized. Both OMMs have a hexagonal ordered mesoporous structure and texture, as confirmed by SAXS, TEM and N_2 adsorption isotherms, but differ for the chemical composition and surface charge density, as determined by ATR-FTIR spectroscopy and potentiometric titrations, respectively.


SBA-15


SBA-15


MSE


MSE

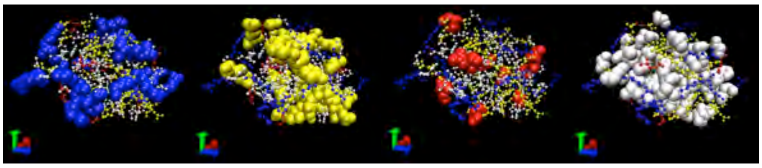
Characterization of OMMs Obtained Through N_2-Adsorption/Desorption Isotherms and SAXS.

	S_{BET} [a] (m^2/g)	V_p [b] (cm^3/g)	d_{BJH} [c] (Å)	d_{BJH} [d] (Å)	a [e] (Å)
SBA-15	718	1.2	86	65	112
MSE	1752	2.2	76	58	119

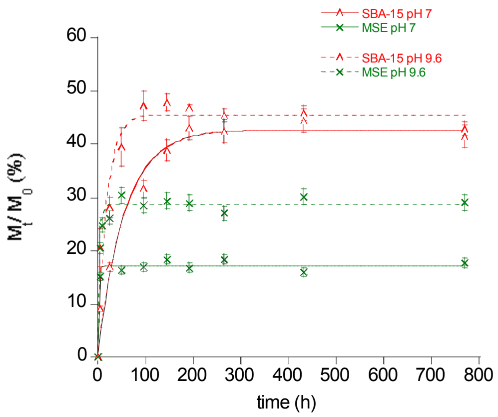
[a]Specific surface area; [b]Cumulative pore volume; [c]Pore diameter calculated by the adsorption branch; [d]Pore diameter calculated by the desorption branch; [e]Lattice parameter.

These OMMs were used for the adsorption (pH 7.0 and 9.6) and *in vitro* release (pH 7.4; T = 37°C) of hen egg white lysozyme, a therapeutic protein.

The very different nature of the surface,



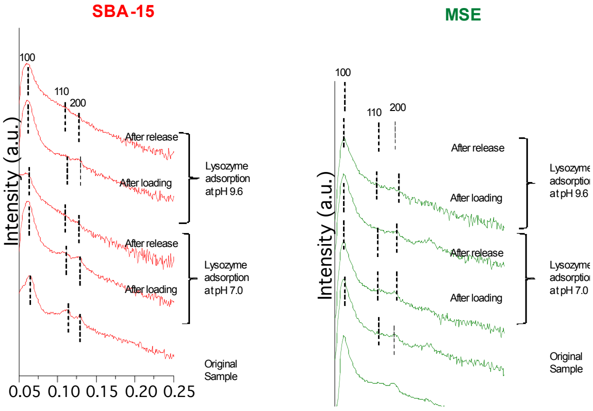
in terms of surface charge, implies different types of host-guest (surface-protein) interactions. The van der Waals interactions, mainly involved in the adsorption/release process at Lysozyme/MSE interface, seem to produce stronger protein binding than the electrostatic forces that dominate the Lysozyme/SBA-15 interface.



$$\frac{M_t}{M_0}(\%) = A(1 - e^{-k_1 t})$$

Besides adsorption, different intermolecular forces involved in lysozyme binding to OMMs surface differently affect its desorption in the release medium. As a matter of fact, the strong protein binding in Lysozyme-loaded MSE matrix decreases both the time over which release occurs, and the released amount of protein, significantly. It is remarkable that a short burst release, in all cases, suggests that only a small amount of adsorbed protein is located on the outer surface of the OMM particle. Another very significant parameter that affects both adsorption and release is the pH of the adsorbing solution. This allows for a potential modulation of the global performance, in terms of loaded amount of protein, and rate of release. In other words, a personalized sustained release may be produced. Another important consideration concerns the longer shelf-life in physiological medium observed for MSE compared to SBA-15. Silica materials tend to dissolve in biological fluids, and this can develop toxicity when accumulation above certain concentrations occurs. Hence, if a silica-based drug delivery system has to be projected in view of possible innovative applications (cfr. protein drug delivery) and performances (cfr. sustained release), it is relevant to introduce structural features that can prolong the shelf-life and attenuate dangerous, though not fatal, side effects.

Finally, the last comment in favor of MSE OMM to be used as a sustained drug release carrier is given by the relatively easy and reproducible synthesis - this is a peculiar feature of all OMMs - that does not involve any post-synthesis functionalization step.



References

Bhattacharyya, M.S.; Hiwale, P.; Piras, M.; Medda, L.; Steri, D.; Piludu, M.; Salis, A. and Monduzzi, M. "Lysozyme Adsorption and Release From Ordered Mesoporous Materials", J. Phys. Chem. C ,114, 19928-19934, (2010).

1A – Synthesis, characterization and functionalevaluation of light hydrides-based nanostructuredcomposites for solid state hydrogen storage. (PRIN Project 2008)

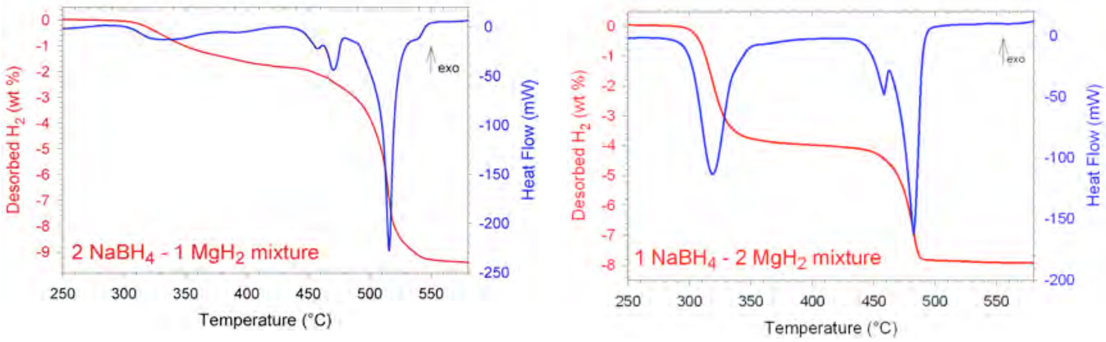
C. Milanese, A. Girella, V. Berbenni, G. Bruni, A. Marini,
E. Napolitano, S. Enzo*, S. Doppiu*, G. Mulas**
*(*University of Sassari, Department of Chemistry)*

Aims

Ideation, preparation, kinetic and thermodynamic characterization of light hydrides (borohydrides, alanates, amidoboranes) - based composites for solid state hydrogen storage.

Results

In the field of materials for solid state hydrogen storage, particular attention has recently been paid to *Reactive Hydride Composites* (RHC), where the combination of an alkaline borohydride with a metallic hydride and/or another complex hydride induces a mutual thermodynamic destabilization and a decrease of the H_2 desorption temperatures with respect to the component phases, maintaining high gravimetric H_2 capacities (the target for on-board applications is 5.5 wt % H_2). The $NaBH_4$ – MgH_2 system is considered a good model for the study of the sorption mechanism of RHC since $NaBH_4$ is cheaper and more stable upon exposure to air than other borohydrides. In this work, a deep investigation on the sorption properties of $NaBH_4$ – MgH_2 RHC with 2:1 and 1:2 molar ratio (the two stoichiometries resulted more favourable from thermodynamic calculations) prepared by high energy ball milling have been performed by coupled manometric – calorimetric measurements up to 600 °C under different H_2 pressures (from 0.1 bar to 60 bar).



Coupled manometric – calorimetric profiles recorded at heating rate β = 2 °C/min and P H_2= 0.1 bar for the 2:1 (a) and the 1:2 (b) mixture respectively.

For both mixtures, two desorption steps are present, attributable to the dehydrogenation of MgH_2 (starting from 300 °C) and $NaBH_4$ (from 450 °C) respectively. In particular, the decomposition of this last hydride occurs via the formation of the destabilizing compound MgB_2 at a temperature that is 50 °C lower than that of the pure phase. For the first time in literature we obtained a reliable value for the melting enthalpy of $NaBH_4$ and demonstrated that the decomposition of this hydride takes place mainly after melting (melting – decomposition mechanism) in the 2:1 mixture, while evolves fully in solid state for the 1:2 stoichiometry. By a simple thermodynamic model we determined the decomposition enthalpy of $NaBH_4$ as destabilized by MgB_2 and showed that the melting-decomposition process is thermodynamically more favourable than the solid state one. The total amount of released hydrogen is 9.4 wt % and 8.1 wt % respectively for the 2:1 and the 1:2 stoichiometries, to be compared with theoretical values of 9.9 wt % and 8.9 wt %.

The dehydrogenation kinetics of the two mixtures has been explored by thermal programmed desorption measurements up to 450 °C (the minimum temperature at which $NaBH_4$ decomposes). In these conditions, the process takes about 12 h for completion for the 2:1 stoichiometry and about a third of the time for the 1:2 mixture. Recharging (450 °C, 60 bar) takes place in about 90 min in both the cases but the amount of absorbed hydrogen (6 wt % and 5 wt % H_2 for the 2:1 mixture and the 1:2 stoichiometry respectively) is limited by the formation of the mixed phase $NaMgH_3$ together with the two component hydrides. Work is in progress to find suitable pressure and temperature conditions to avoid the formation of the ternary hydride.

By fitting the kinetic profiles by Avrami – type equations, the kinetic constants and qualitative information on the microscopic processes limiting the sorption reactions (nucleation and growth for desorption, H_2 diffusion for absorption) have been obtained for the first time in literature and the activation energies for the sorption processes have been evaluated.

Among the different dopants tested as catalyzing/destabilizing agents (fluorides, chlorides, hydroxides, fluoborates), the most promising results have been obtained for MgF_2, that is able to decrease both the desorption temperatures of the two hydrides and the temperature lag between the two processes. Moreover, it works as good catalyst for the borohydride decomposition.

References

Garroni, S.; Milanese, C.; Girella, A.; Marini, A.; Menéndez, E.; Pistidda, C.; Dornheim, M.; Suriñach, S. and Baró, M.D. "Sorption properties of $NaBH_4/MH_2$ (M = Mg, Ti) powder systems", International Journal of Hydrogen Energy 35, 5434-5441 (2010).

Milanese, C.; Garroni, S.; Girella, A.; Mulas, G.; Berbenni, V.; Bruni, G.; Suriñach, S.; Baró, M.D. and Marini, A. "Thermodynamic and kinetic investigations on pure and doped $NaBH_4$ – MgH_2 system", Journal of Physical Chemistry C, accepted for publication.

1A – Functionalized Silicon Nanoparticles: a Theoretical Multilevel Approach

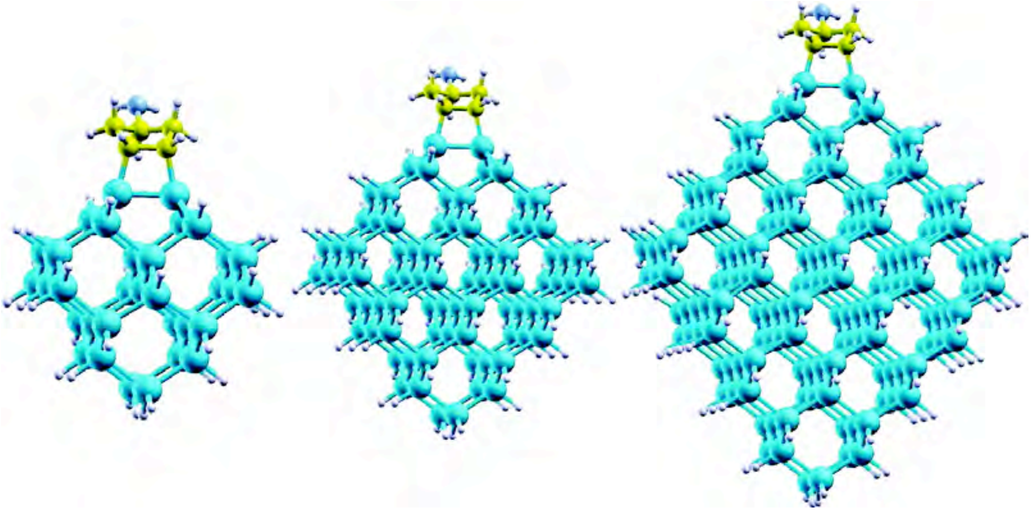
F. Trani, I. Carnimeo, M. Biczysko, G. Prampolini, V. Barone
Scuola Normale Superiore di Pisa

Aims

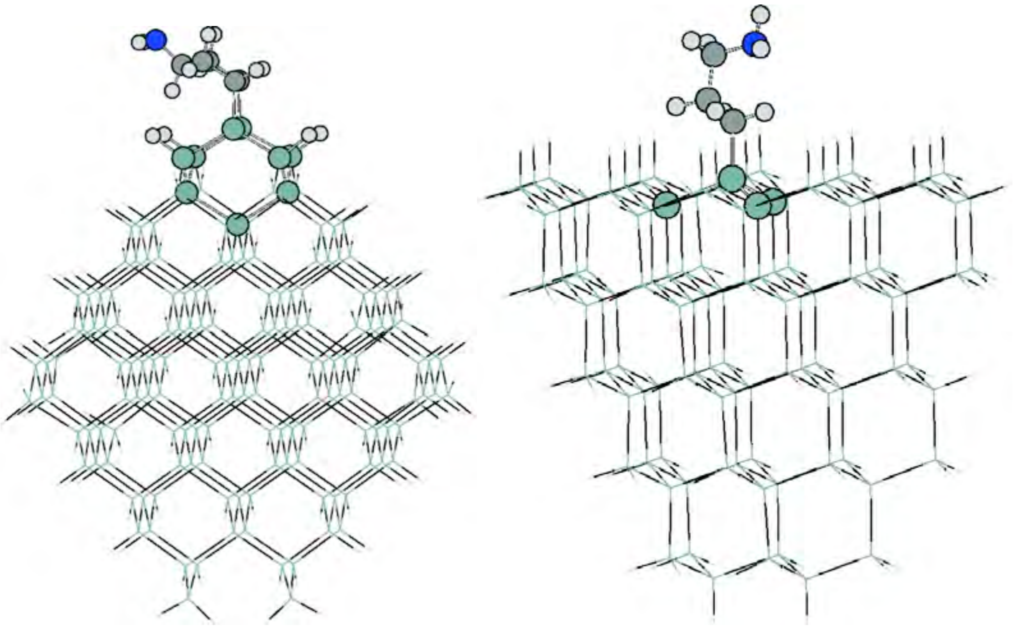
Functionalized silicon nanocrystals are becoming widely used in applications concerning important technological fields, from optoelectronics to biomedicine, from solar cell technology to chemical sensing. In particular, they can be used as a diagnostic tool for the detection of cancer cells. The theoretical understanding of functionalized silicon nanocrystals requires the development of new integrated computational schemes, that bring together the accuracy of DFT approaches and the efficiency of semiempirical models.

Results

The synthesis of bright, stable, biocompatible water soluble silicon nanocrystals has opened the route to realistic biomedical applications of functionalized silicon nanoparticles as cellular probes. The recent chemical synthesis techniques allow for an excellent control of nanoparticle size and shape. The fabrication of nanocrystals has thus become reproducible, with easy control of their fluorescent properties. A multilevel approach has been proposed, which combines density functional calculations (DFT) with a semiempirical tight binding scheme (DFTB), to study the functionalization of silicon nanocrystals by organic molecules upon increasing the nanocrystal size [in the picture, 1-amino-3-cyclopentene (ACP) adsorbed on $Si_{33}H_{32}$, $Si_{82}H_{60}$, and $Si_{158}H_{96}$].



An ONIOM(DFT/DFTB) approach has been proposed to study functionalized silicon nanocrystals. The structure has been divided into a nanocrystal core, that is studied using DFTB (low level approach), well tested for large systems, and the molecule + the nanocrystal adsorption site, that is described within DFT, by using an hybrid exchange-correlation functional (high level approach). In the following picture the ball-and-stick model represents the nanocrystal portion described using the high level approach. The method has been applied to the functionalization of Si(100) and Si(111) surfaces, by ACP and Propylamine, respectively.



Due to the lightness of DFTB approach, based on a semiempirical approximation of the Coulomb integrals, the ONIOM method has been used to describe the functionalization of thousands-of-atoms structures. A comparison with full DFT calculations has been done for small nanocrystals, obtaining excellent results, with an error smaller than 0.004 Å and 1 kcal/mol, on the bond lengths and binding energies, respectively.

References

Trani, F. and Barone, V. "Silicon Nanocrystal Functionalization: Analytic Fitting of DFTB Parameters", Journal of Chemical Theory and Computation (2011), in press.

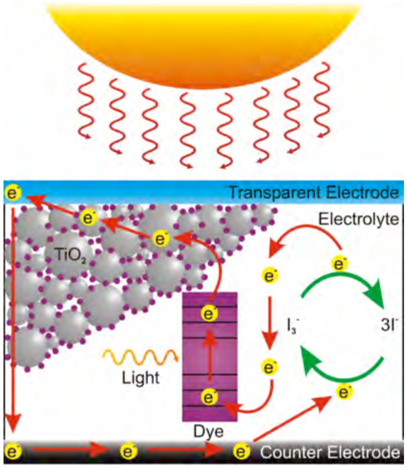
1A – Design, synthesis and applications of new organic sensitizers for non-conventional photovoltaic cells

M.L. Parisi, A. Sinicropi, M. Bravi, G. Giannuzzi, M. Taddei, R. Basosi

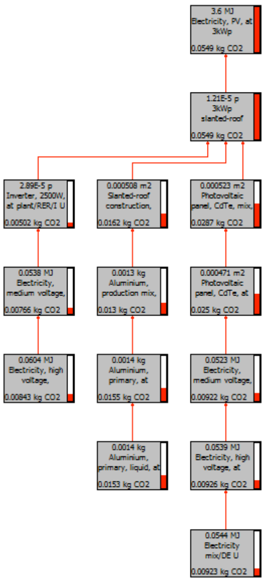
Aims

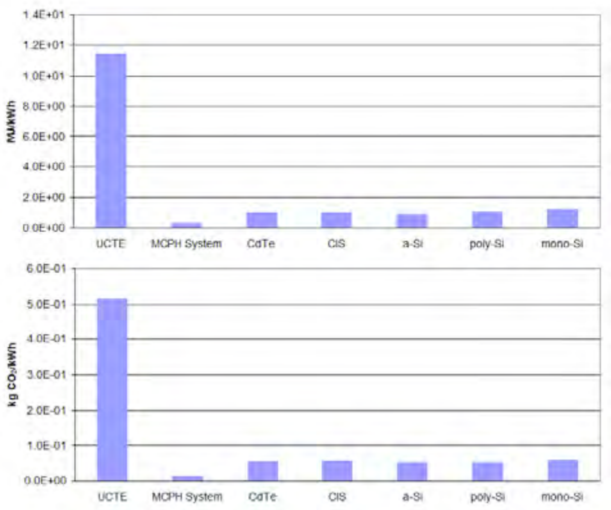
The aim of the project is the design, computational characterization and synthesis of new organic dyes and their use for the production of Grätzel-type solar cells, as well as an in-depth life cycle assessment of all the stages of their production process.

Results



The first report concerning the construction of an efficient dye-sensitized solar cell (DSSC) was published by Grätzel and O'Reagan in 1991(1). From then on, research in the area of photovoltaic cells based on hybrid sensitizer/nanocrystalline semiconductor systems has undergone some major developments. The present project is based on a multidisciplinary approach for the production of new organic dye sensitizers for DSSCs that could result to be competitive in comparison with the already available systems. This approach takes benefit from the synergic employment of state-of-the-art computational methods and innovative eco-compatible synthetic strategies that together with the spectro-, photo- and electrochemical characterization of the synthesized compounds will permit the development of a new and accurate protocol for the study and design of organic sensitizers to be employed in photovoltaic cells. A life cycle analysis of all the steps constituting the whole DSSC production process on a lab scale will be performed in order to achieve a systematic and complete assessment of environmental impacts and burdens (in energetic and pollution terms) deriving from all inputs to the process, and to highlight the critical points of the process itself. The LCA will be pivotal in understanding the environmental dynamics, the benefits and drawbacks associated with the production of DSSCs in comparison with other photovoltaic crystalline silicon and thin film technologies recently analysed in our studies. Through the LCA and a detailed analysis of available data in the international literature, we tried to better understand the nature and the extent of risks related to all the stages of photovoltaic panels life cycle for the best commercially available photovoltaic technologies. In particular, we focused on the Cadmium Telluride (CdTe) thin film photovoltaic technology which is very promising from an economic and energetic point of view, but it shows challenges and risks related to the presence of potentially very dangerous heavy metals, whose utilization has been actually banned in many products. The analysis on small-scale grid-connected CdTe PV system plant allowed to assess that the environmental performance of photovoltaic system must be evaluated on a precautionary principle base in order to account for all the impact indicators in the right way.





The LCA analysis of production and use of a novel photovoltaic micromorph (a-Si/μc-Si) system compared to other photovoltaic technologies, allowed to assess the better environmental performance of the micromorph technology. Results obtained for the case study showed a significant decrease in the gross energy requirement, a lower level of CO_2 emissions and a shorter energy pay-back time due to the smaller amount of materials produced by energy intensive processes

References

Bravi, M.; Parisi, M.L.; Tiezzi, E. and Basosi, R. ”Life Cycle Assessment of a Micromorph Photovoltaic System”, Energy, in press (2011).

Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L. and Pettersson, H. “Dye-sensitized solar cells”, Chem. Rev., 110, 6595 (2010).

Bravi, M.; Parisi, M.L.; Tiezzi, E. and Basosi, R. “Life Cycle Assessment of Advanced Technologies for Photovoltaic Panels Production”, Int. J. of Heat and Technology, in press (2010).

O'Regan, B. and Grätzel, M. “A low cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films”, Nature, 353, 737 (1991).

1A – Anchoring of SWCNT-SH on gold surface

V. Torrisi, G. Marletta

Aims

1) Positioning of SWCNT-SH;
2) Understanding the effect of thiols self assembly onto SWCNT-SH self assembly;
3) Understanding the difference between SWCNT-SH insertion and mixing with thiols;
4) Understanding the advantages of direct printing of CNTs on their positioning.

Results

The bottom-up approach has been gaining a significant momentum in the field of nanometer-sized device fabrication and it leads to develop a variety of smart nanoscale building blocks. Among various nanoscale building blocks, nanotubes and nanowires have been synthesized with desired physical properties to be incorporated in electronic and optical devices.

Whereas the carbon nanotubes (CNTs) synthesis has been explored extensively, the effort to address CNTs onto specific locations of the substrates for the device fabrications has just begun.[1-3] The integration of carbon nanotubes in solid state devices is crucial for many applications. In particular, controlling the distribution of CNTs and their positioning on surfaces is of paramount importance in taking advantage of their outstanding physical and electrical properties in a wide range of fields. For this reason it is necessary the development of processes of preferential orientation, self assembly and positioning of CNT and CNT bundles characterized by tunable size.

Many kind of interactions, among which molecular recognitions, were applied for positioning CNTs in specific regions on substrates.

We report on the use of three anchoring strategies (A,B,C) of single-walled CNTs functionalised with thiols (SWCNT-SH), both involving the use of strong thiol-based chemical bonds. The length of used SWCNT-SH ranged from 10 nm to 10 μm. A)We employed mixtures of SWCNT-SH and alkane- or aromatic thiols to obtain the SWCNT-SH self-assembly onto polycrystalline Au surfaces. B) We performed the SWCNT-SH insertion within a previously self-assembled alkane-thiol monolayer. Finally, C) we carried out the “click anchoring” (that means the direct printing from a polydimethylsiloxane stamp) of SWCNT-SH suspension onto gold coated substrates.

In this work, we describe the assembly of thiolated nanotubes by using a strong thiol-Au interaction.[4] The morphology of thiol films and SWCNT-SH/thiol systems has been studied by Atomic Force Microscopy. It was found that the nature of the employed thiols affects the SWCNT-SH organization in the first strategy, while the percentage of SWCNT-SH insertion within a given thiol film depends on the molar fraction of SWCNT-SH in the treating solution as well as on the thiol chain length.

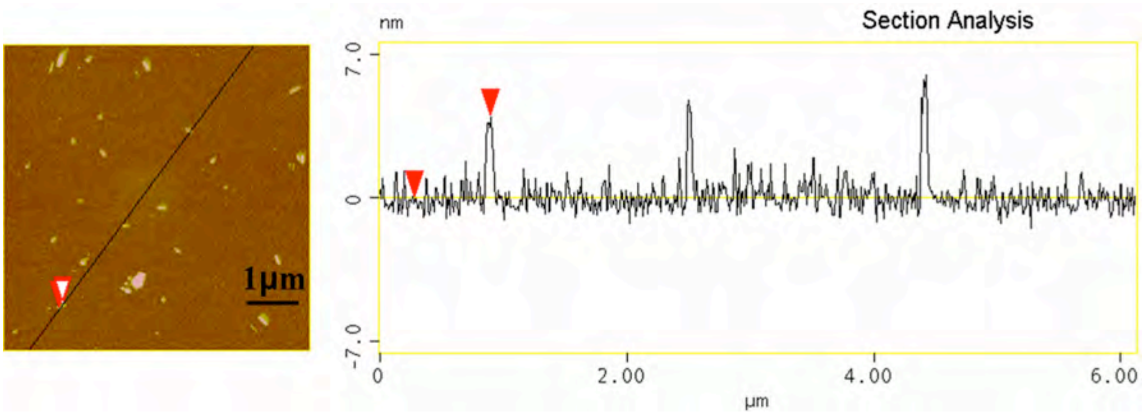


Figure 1: Height AFM image and section analysis of SWCNT-SH anchored on Au/mica surface.

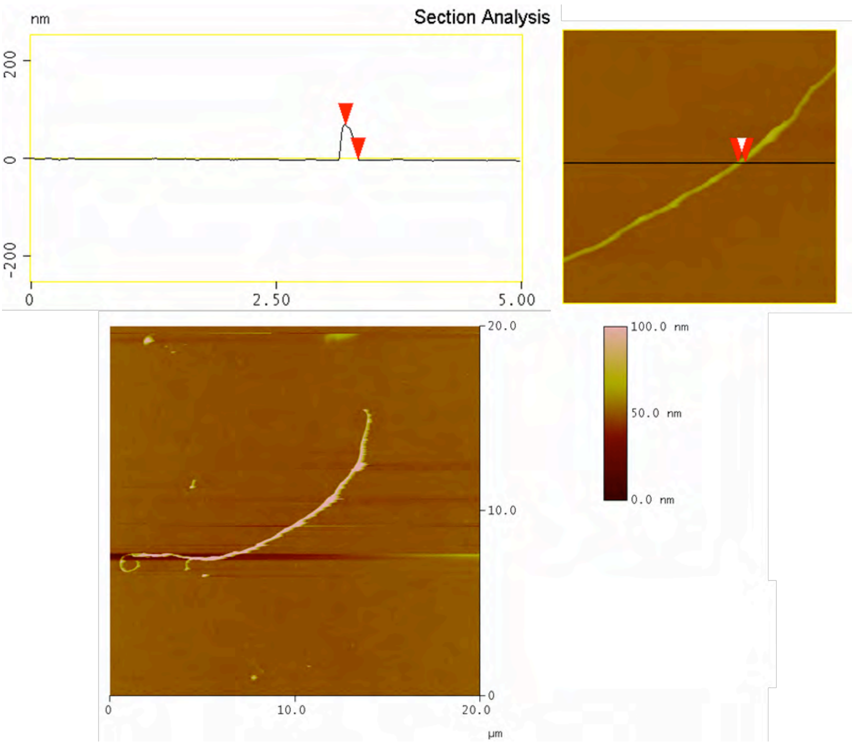


Figure 2: AFM image and section analysis of SWCNT-SH bundles anchored by direct printing form PDMS stamp on Au/mica surface.

References

[1] Rao, S.G.; Huang, L.; Setyawan, W. and Hong, S. "Large-scale assembly of carbon nanotubes", Nature, 425, 36-37, (2003).

[2] Banerjee, I.A.; Yu, L.; MacCuspie, R.I. and Matsui, H. "Thiolated Peptide Nanotube Assembly as Arrays on Patterned Au Substrates", NanoLetters, 4, 2437-2440, (2004).

[3] LeMieux, M.C.; Sok, S.; Roberts, M.E.; Opatkiewicz, J.P.; Liu, D.; Barman, S.N.; Patil, N.; Mitra, S. and Bao, Z. "Solution Assembly of Organized Carbon Nanotube Networks for Thin-Film Transistors", ACS Nano, 3, 4089-4097, (2009).

[4] Tuccitto, N.; Torrisi, V.; Cavazzini, M.; Morotti, T.; Puntoriero, F.; Quici, S.; Campagna, S. and Licciardello, A. "Stepwise formation of ruthenium(II) complexes by direct reaction on organized assemblies of thiol-terpyridine species on gold", ChemPhysChem, 8, 227-230, (2007).

1A – Multilayered Nanostructures for OLED devices

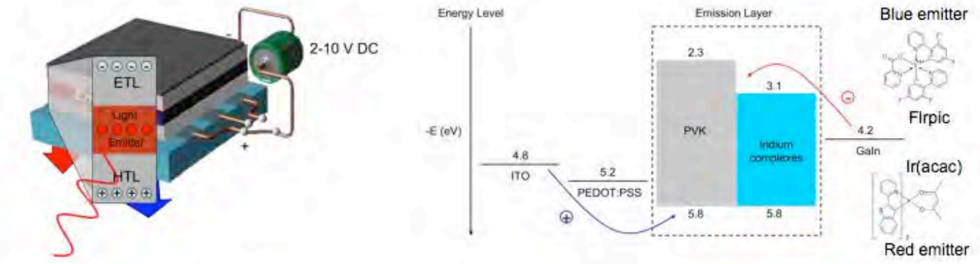
G. Caminati, F. Gambinossi, P. Cavigli, M. Ghezzi

Aims

Aim of this work is the design and the realization of novel Phosphorescent Organic Light Emitting Devices (PhOLED) composed of poly(9-vinylcarbazole) (PVK) nanostructures doped with light-emitting iridium(III) complexes. We employed two different kinds of nanostructured system: planar Langmuir-Blodgett (LB) films and nanoparticles (NPs) with the PVK/Ir couple embedded either in the NPs of PVK or in a PVK shell surrounding polypyrrole NPs.

Results

The hetero-structures were built using the same sequence of active layers reported schematically in figure 1 together with the corresponding diagram of energy levels.



(a) (b)

Fig 1. Schematic representation of the PhOLED structure (a) and energy levels (b).

Planar Films of PVK-Ir. Nanofilms of PVK were immobilized onto solid supports either by spin-coating techniques and by the Langmuir-Blodgett method. The behavior of Langmuir monolayers of PVK and PVK diluted in an amphiphilic matrix (SA) was preliminary studied at the water-air interface to select the optimal scaffold for the LB deposition. The 2D polymer film was successfully transferred onto ITO evaporated quartz slides and examined by means of fluorescence microscopy, Atomic Force Microscopy (AFM), Brewster Angle Microscopy (BAM) and ellipsometric thickness determination.

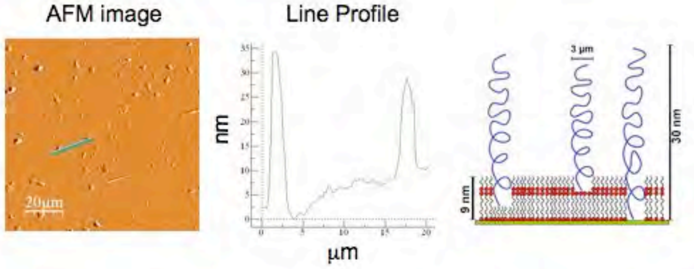
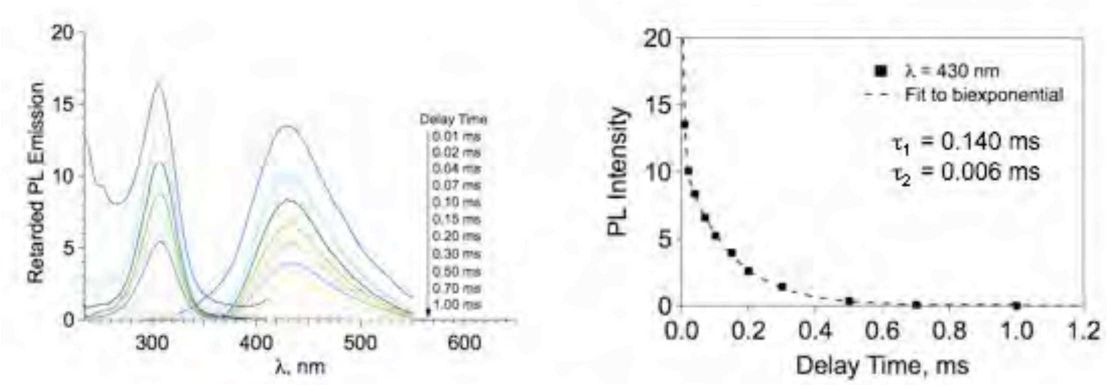


Fig. 2 AFM characterization of 3 LB layers of PVK/SA (left). Cartoon of LB structure (right).

Such characterization showed that PVK forms stable patterned nanostructures, whose morphology significantly varies as a function of the preparation procedure spanning from 'spaghetti-like' patterns coexisting with spherical structures to high density of round shaped aggregated domains. The addition of Iridium complexes to PVK in the LB film changes the morphology of PVK nanostructures without altering their photophysical characteristics as shown by the spectroscopic investigation on the nanostructured films.



(a) (b)

Fig. 3 Time-resolved spectra (a) and decay profiles (b) for 3 LB layers of PVK/SA/Ir.

Time-resolved emission spectra revealed the unexpected contribution of PVK phosphorescence at room temperature whose intensity and lifetime depend on the confinement of PVK in the ordered matrix.

PVK/Ir nanoparticles.

Doping PVK NPs with Ir(III) complexes was obtained by reprecipitation, the structural characterization of the system showed that the dimensions of the aggregates correlate with the structure and concentration of the specific Iridium complex used.

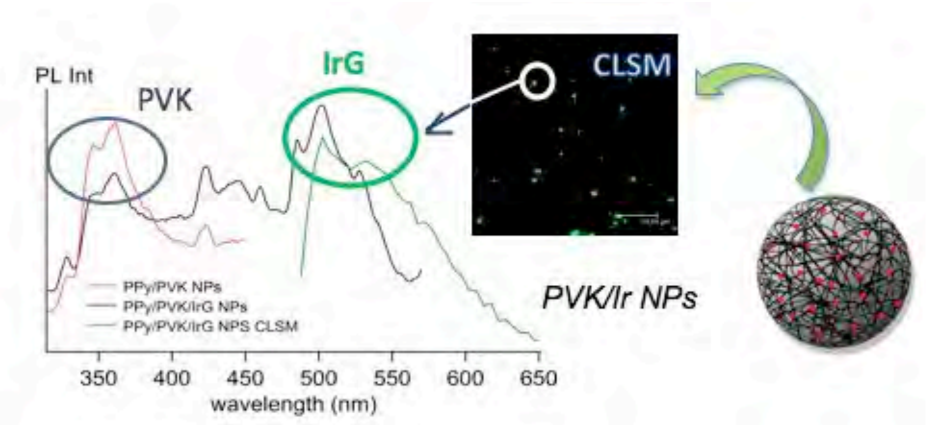


Fig. 4 Phosphorescence spectra and CLSM images of PVK/Ir Nanoparticles.

Photophysical characterization demonstrated the occurrence of the desired energy transfer process between PVK and the Iridium complexes both in aqueous suspension and in spin-coated samples.

1A – Third generation solar cells: nano-fabrication of polymer heterojunctions and Dye Sensitized Solar Cells (DSSC)

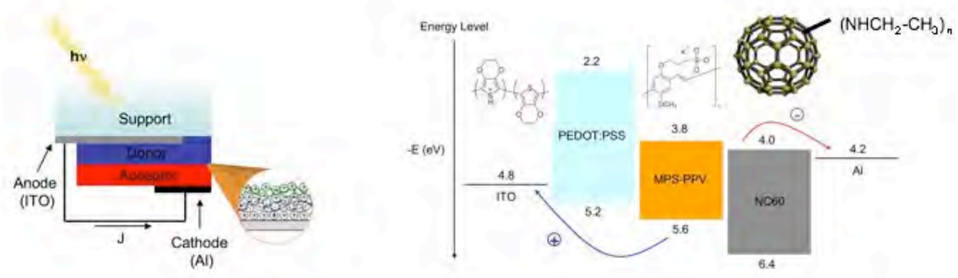
G. Caminati, F. Gambinossi, L. Cavaciocchi, C. Boscagli

Aims

The target of the project is the design and the realization of novel nano-architectures with tunable functionality. In particular, we focused on organic photovoltaic nano-devices (OPC, *Organic Photovoltaic Cell*) for the conversion of light to electrical energy with two different approaches that involve either a polymer-based design or the use of dye-sensitizers, in both cases a fullerene derivative was used as an electron acceptor unit.

Results

Polymer-based solar cells. New bulk heterojunctions solar cells based on conjugated polymers and fullerene derivatives were prepared using unconventional deposition techniques, such as Layer-by-Layer (LbL) adsorption of polyelectrolytes. The hetero-structures were made up using a conjugated polyelectrolyte, poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylene vinylene] potassium salt, MPS-PPV, as an electron donor. A water-soluble C60 derivative: N-ethyl-polyamino-C60, NC60, was used as an electron acceptor. In particular, we studied NC60 mixed with poly(methacrylic acid), PMA.

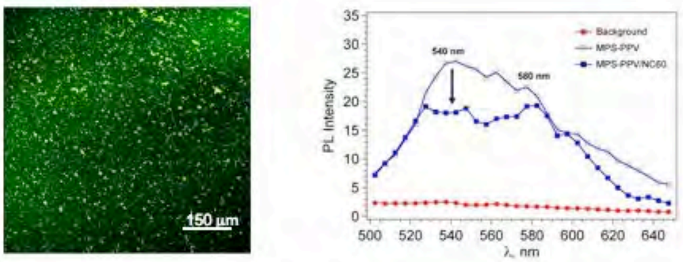


(a) (b)

Fig. 1 Schematic representation of a multi-functional solar nanodevice (a) and corresponding energy level diagram (b).

The nanodevices were prepared by sequential deposition of MPS-PPV and PMA/C60 by layer-by-layer deposition as a function of C60 concentration and positioning in the sequence. The process was monitored through Quartz Crystal Microbalance (QCM-Z) measurements that provided information on the kinetics of the process as well as on the structural features of the resulting assembly.

The structural and photophysical investigation of the resulting LbL films showed a regular distribution of the chromophore and, more importantly, that modulation of the Photoinduced Electron Transfer (P.E.T.) efficiency can be achieved by tuning the polymer concentration and by varying the number of spacer layers.



(a) (b)

Fig. 2 CLSM images of MPS-PPV in LbL (a) and space-resolved fluorescence emission with and without NC60 (b).

DSSC Solar cells. Nanostructures containing different Ru(II) complexes were prepared by planar LbL deposition or by nanocapsules (NCs) fabrication using a Graetzel-inspired solar cell designed as shown in figure 3.

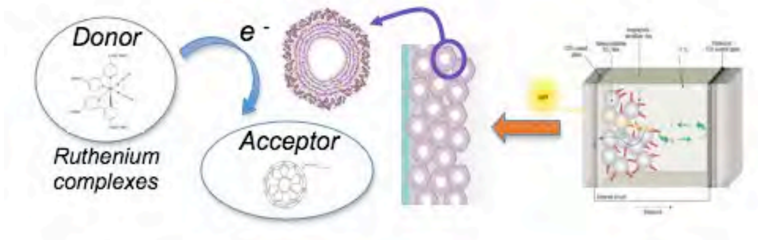
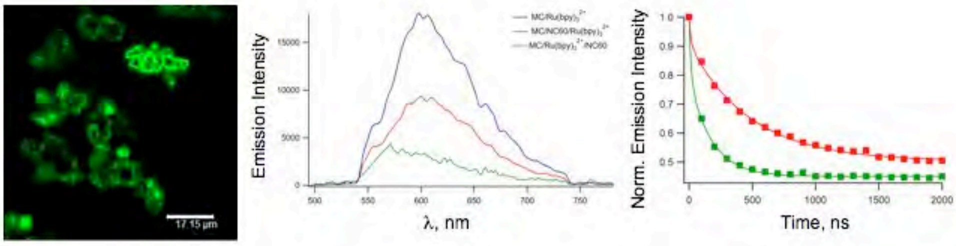


Fig. 3 Design and components of the proposed nanostructured DSSC.

Combined AFM, CLSM and Fluorescence investigation on the analog planar systems showed that the P.E.T was achieved with different efficiencies that depend on the layer sequence. The redox couple was immobilized in a polyelectrolyte shell surrounding inorganic nanoparticles (NPs), dissolution of the NPs core resulted in empty nanocapsules bearing the donor and the acceptor in different corona layers.



(a) (b)

Fig 4. (a) CLSM imaging on polymer nanocapsules with embedded redox couple. (b) Steady-state and time-resolved fluorescence spectroscopy for NCs with different layer ordering.

The photophysical characterization demonstrated that efficient vectorial electron transfer occurs between the donor and the acceptor in the polyelectrolyte layers allowing for the construction of mesoporous polymer materials at the anode of the DSSC.

1A – COOL-Coverings: Development of a novel and cost-effective range of nanotech improved coatings to substantially improve NIR (Near Infrared Reflective) properties of the building envelope

P. Matteazzi, A. Colella

Aims

This project is funded by the European Commission' 7 Framework Programme, under the area of New nanotechnology-based high performance insulation systems for energy efficiency (EeB. NMP.2010-1).

The NIR reflective COOL-Coverings Project led by "*KERABEN GRUPO SA"* aims to develop an easy to use and cost-effective range of coatings that can be rapidly offered in the market of retrofitting and new constructions:

(1) on the external walls;

(2) on façades ceramics;

(3) on the roofs, for which an already existing new generation membrane will incorporate nanotechnological-based NIR reflecting coating;

(4) on the internal walls and tiles, since the NIR-Reflecting nanocrystalline oxides can be developed in such a reflection range that may also cover the radiation from indoor heating systems.

Results

Project has started in the second half of 2010. First simulations showed that NIR reflective solutions allow interesting savings in cooling and heating bills, and pay off rapidly the initial investment. The more competitive target will be air-conditioned buildings with flat roof in hot Mediterranean coast, while there is a clear evidence that also buildings in northern continental climates will payoff the additional investment in the NIR technology, due to reflective properties of the internal walls.

To achieve these properties, suitable nanoparticles like ZnO and Al_2O_3 (Figure 1) have being investigated as main components for the primer coating, as well as an appropriate hydrophobic material, which will provide water protection to the substrate surface. The final coating will instead be based on NIR reflecting nanoparticle formulations, UV anti-aging, and pigments responsible for controlled thermal emittance, incorporated in an appropriate binder that will contributed to the enhanced mechanical and chemical properties of the coating itself.

Characterization work in COOL-Coverings exploits the experiences available from project partner in paint additives and special painting products as well as recent advances in coatings for the automotive sector with special emphasis on nanocrystalline metal oxides such as ZnO, MgO, TiO2, Al2O3, Cr2O3, CeO2 and Fe2O3, with crystalline size less than 7 nm.

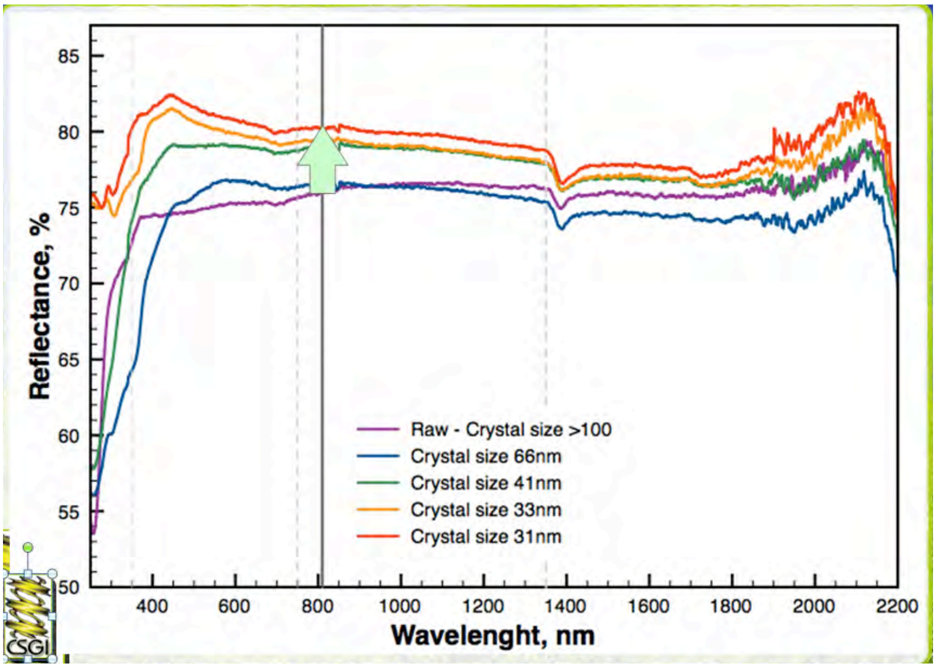


Figure1: behavior of Nano Alumina reflectance properties

It is worth emphasizing that the components of COOL-Coverings solutions for insulating envelopes will be studied, adapted and optimised starting from existing solutions, developed for other applications or in scattered attempts to renew the currently used insulating materials.

It is worth noticing that each of these components will have high performances and functionalities, and can be combined in different ways according to the needs and requirements of the application, thus optimising the cost-benefits of the intervention.

1A – Nanosensors based on ultrathin organic films

G. Caminati, F. Gambinossi, M. R. Martina

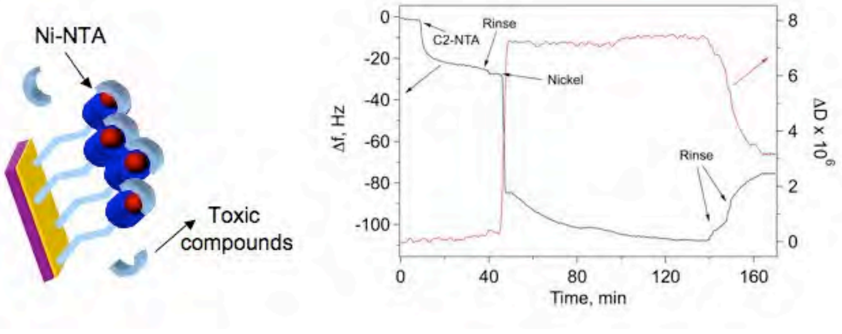
Aims

The research is focused on the preparation of new molecular devices for sensor applications by means of different nanotechniques tailored to meet the specific requirements of several detection systems. In particular we explored hybrid architectures formed by a combination of Supported Lipid Bilayers (SLB), Langmuir-Blodgett (LB), Self-Assembly (SA) and Layer-by-Layer (LbL) systems.

Results

Nanosensor for stress-based determination of toxic substances.

We developed a functionalization procedure for silicon oxide surfaces used in microcantilever-based sensors dedicated to the detection of food contaminants in fluid matrices. The surface functionalization was obtained by direct self-assembly of long chain molecules bearing at one end a complexing moiety for metal ions and a chemical function for specific chemisorption to the desired surface. The selected chelating molecule, the nitrilotriacetic acid (NTA), was immobilized onto silicon oxide surfaces using a three-step process involving the consecutive addition of an organosilane, glutaraldehyde and a NTA derivative solutions (SAN). QCM measurements indicated that the functionalized molecule forms a rigid self-assembled film on both substrates.

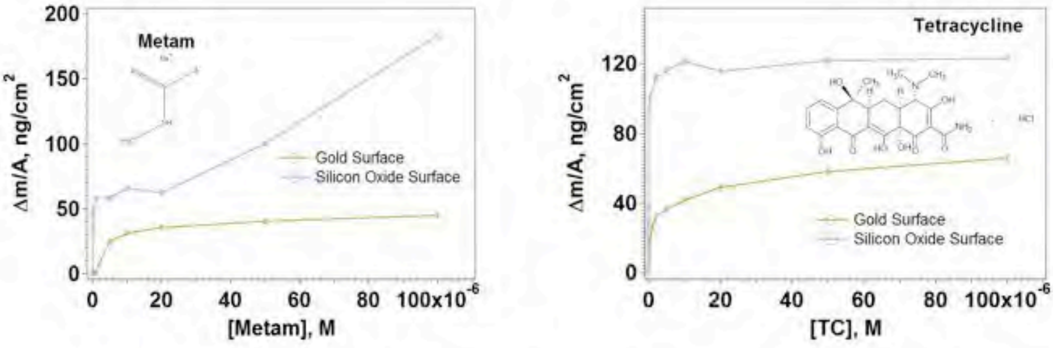


(a) (b)

Fig. 1 Schematic structure of the SAN-functionalized surface (a) and QCM monitoring of SAN formation on gold substrate (b).

Data analysis provided the layer thickness and the molecular orientation of the chemisorbed layers at the interface.

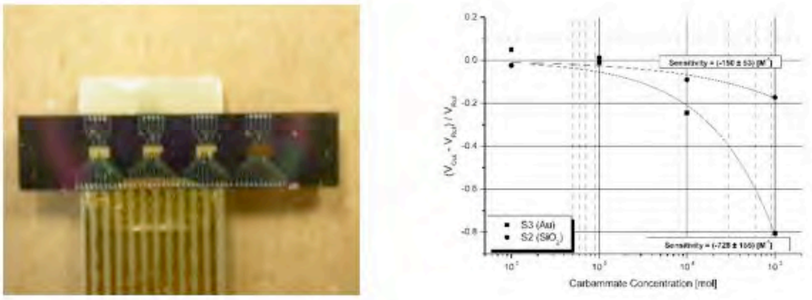
Quantitative determination of pesticides (Metam) and antibiotics (Tetracycline) by complexation at the surface was achieved adding the desired solution in the QCM measuring chamber and recording the adsorbed mass change as a function of the concentration. The results allowed for the determination of concentrations of the contaminants well below the Maximum Residue Limit imposed by current European Legislation.



(a) (b)

Fig 2. QCM titration curve for a carbamate pesticide and for tetracycline antibiotics.

The optimized procedure was tentatively applied to functionalize the silicon oxide outer surface of an array of microwells each containing four microcantilevers.



(a) (b)

Fig. 3 Microcantilever array layout (a) and surface stress plot for the determination of Metam onto gold and silicon surfaces.

Nanosensors for the determination of FKBP12.

FKBP12 is a protein overexpressed in the initial stages of amiloyd-dependent pathologies that binds effectively small ligand molecules such as Rapamycin or Tacrolimus. This latter molecule is known to insert quantitatively in phospholipid bilayers, we therefore designed and fabricated a nanosensor device where the ligand is immobilized in a solid Supported Lipid Bilayer (SLB) formed by rupture and adsorption of phospholipid liposomes. Addition of the protein to this system results in ligand-mediated binding of FKBP12 to the surface of the SLB. QCM sensors covered with SLB/Tacrolimus system allows for the determination of traces of the protein in buffered solution.

(a) (b)

Fig 4. (a) Structure of FKBP12/Tacrolimus complex. (b) Scheme of formation of SLB followed by ligand adsorption at the surface.

1A – Self Aggregation and transport properties in polyoxomolybdate species

E. Fratini, A. Faraone (NIST), A. Müller (U. Bielefeld), P. Baglioni

Aims

Translational dynamics of water inside $\{Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\ [Mo_2O_7(H_2O)]_2\ [H_2Mo_2O_8(H_2O)]\ (H_2O)_{91}\}$ •150 H_2O shortly $\{Mo_{72}Fe_{30}\}$ monomer. Self-aggregation properties of $\{Mo_{72}Fe_{30}\}$ monomer in water solution.

Results

The translational dynamics of the water molecules in the compound is profoundly different from that of bulk water at the same temperature showing a non-Debye relaxation behavior. The temperature dependence of the relaxation time can be described in terms of an Arrhenius law, indicating that the dynamics is triggered by the breaking of the bonds connecting the crystal water molecules with the hydrophilic nanocapsule surfaces.[1]

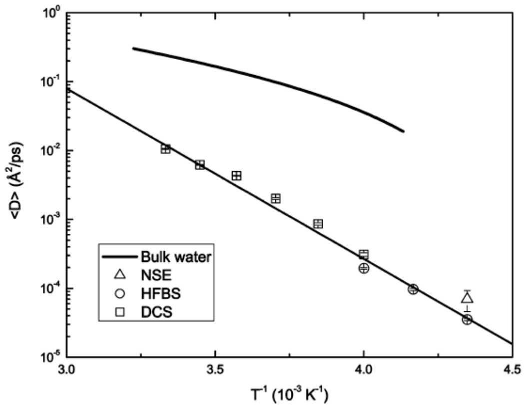


Figure 1. Temperature dependence of the average diffusion coefficient of water molecules contained in $\{Mo_{72}Fe_{30}\}$ monomer. The thick line represents the diffusion coefficient of bulk water measured by NMR. The straight line is a fit of the whole set of data to an Arrhenius law, which gives an activation energy of 47.3 kJ/mol.

Inelastic neutron scattering spectra confirm the attenuation of water translational modes with respect to the bulk water case due to the strong destructuring effect imposed by the nanocage interface and the enhancement of the highest frequency librational mode as already found in hydrated Vycor or Gelsil matrix[2]. Small angle X-ray scattering on freshly prepared aqueous solution evidences the presence of nanocapsule structures proper of the monomer (2.5 nm in diameter) that coexist with a small amount of oligomers. After 1 month the polyoxomolibdate specie self-assembles in a supramolecular structure with a polydisperse distribution of dimensions spanning from the monomer to a ‘‘blackberry” vesicular structure of about 10-60 nm. The aggregation properties can be tuned by changing the pH, ionic dissolved species and the polarity of the solvent offering unique opportunities for both fundamental studies and practical applications in many different fields.

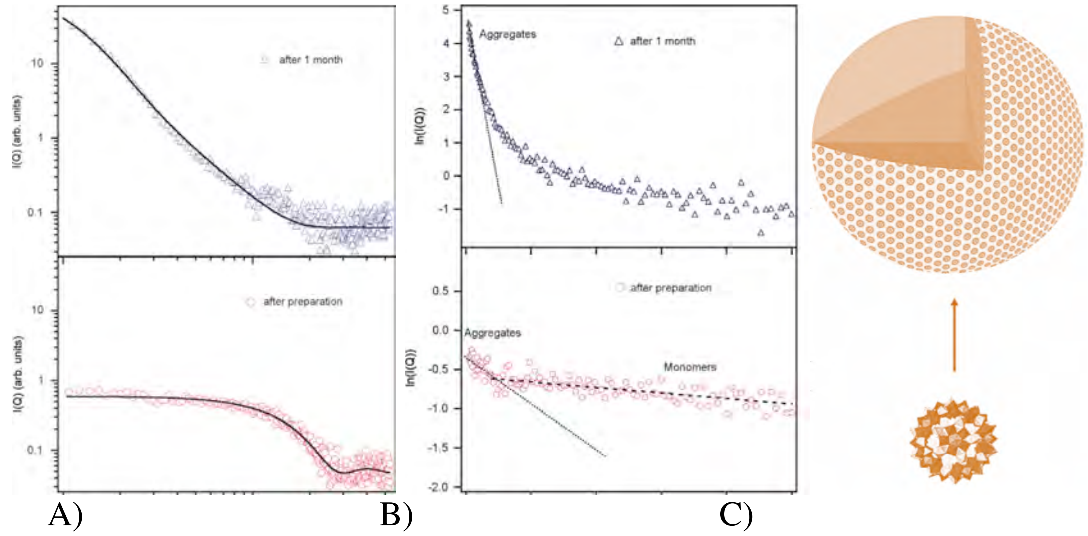


Figure 2. A) Scattering curve of 0.5 mg/mL $\{Mo_{72}Fe_{30}\}$ nanocapsules water solution at 25°C. Lower panel: freshly prepared. Upper panel: 1 month old. Continuous lines are the best fit according to the model described by spherical core–shell model has been implemented considering a polydispersity on the inner radius as described by a Schulz distribution. B) Guinier plot of scattering curves reported in A) Dashed line is the best fit according to the Guinier approximation for $\{Mo_{72}Fe_{30}\}$ monomers. Dotted lines are the best fit according to the Guinier approximation for aggregates. C) Monomer (2.5 nm) to “blackberry” soft aggregate (about 40 nm).

References

[1] Faraone, A.; Fratini, E.; Todea, A.M.; Krebs, B.; Muller, A. and Baglioni, P. “Dynamics of Water in Voids between Well-Defined and Densely Packed Spherical Nanocages Acting as Polyprotic Inorganic Acids”, Journal of Physical Chemistry C, 113, 8635-8644 (2009).

[2] Fratini, E.; Faraone, A.; Todea, A.M. and Baglioni, P. “Hydrated {Mo72Fe30} clusters: Low-frequency hydrogen modes and self-aggregation”, Inorganica Chimica Acta, 363, 4234-4239 (2010).

1A – Influence of Cellulose Derivatives on Hydration Kinetics and Water Dynamics in Cement Pastes

E. Fratini, S. Del Buffa, F. Ridi, P. Baglioni

Aims

Understanding the effect of hydrophobic modified cellulose derivatives (Methyl-Hydroxy-Ethyl Cellulose, MHEC) on the cement hydration kinetics.

Results

C_3S/MHEC pastes have been already studied by DSC, SEM and NMR [1]. MHEC addition in calcium silicate pastes produces an increase in the induction time. kB/kG ratio (transformation of nucleated boundary area against the non-nucleated ''grains'' between the boundaries) approaches the conditions of spatially random nucleation specified by the standard Avrami equation as the MHEC % increases.

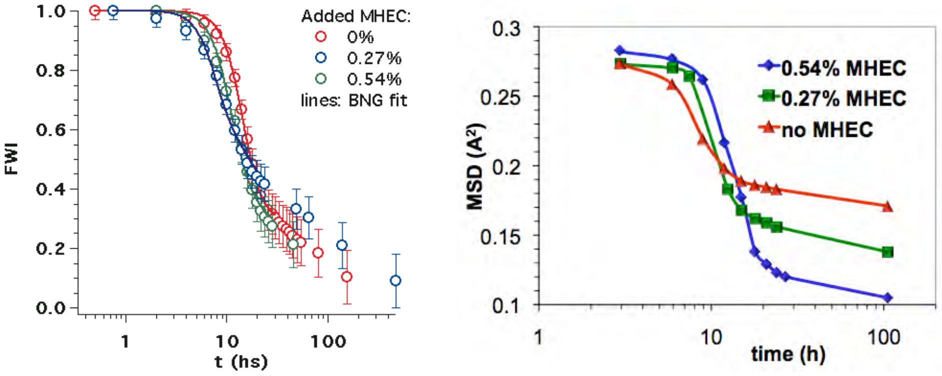


Figure 1. Left Panel: Isothermal hydration kinetic as obtained by DSC at different MHEC concentration. Right Panel: Isothermal evolution of mean square displacement of mobile hydrogenated species at different MHEC concentration.

Mean-square displacement (MSD) evolution mirrors the three stages of the hydration kinetics. While the initial MSD value is about 0.28 Å2 in all cases, MHEC addition causes a reduction in the plateau value from 0.17 Å2 in pure water to 0.1 Å2 in the case of 0.54% of MHEC added as a results for the extra confining effect introduced by the polymer network.

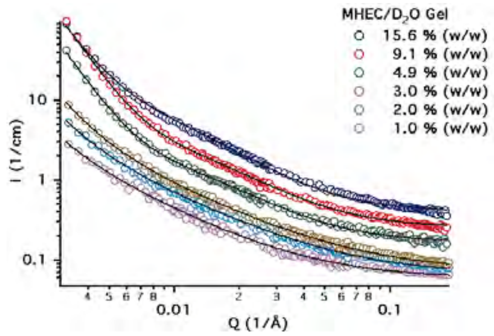


Figure 2. SANS curve of MHEC/D2O physical gel phase from 1 to 15.6%w/w of polymer phase.

SANS experiment on the pure MHEC/D2O physical gel phase evidenced that the mesh size, z, of the gel decreases from 190 to 12 nm as MHEC passes from 1% (FWI=1) to 15% (FWI=0.1)). I(Q) = a*Q-a+b*(1+(z*Q)b)-1+c Accordingly, LT-DSC (figure not shown) detected a greater amount of Large Gel Pore water (peak at -25°C) already at 24 hs as a consequence of the MHEC network re-structuring.

References

Ridi, F. et. al. J. Phys. Chem. B, 107, 1056 (2003).
Ridi, F. et al. J. Phys. Chem. B, 109, 14727 (2005).
M. Alesiani, et. al. J. Phys. Chem. B, 108, 4869 (2004).
Thomas, J.J. J. Am. Ceram. Soc., 90 3282 (2007).
Fratini, E.; Del Buffa, S.; Ridi, F. and Baglioni, P. manuscript in preparation.

1A – Dynamics of water in hydrated cement pastes by time resolved elastic neutron scattering

E. Fratini, A. Faraone (NIST) and P. Baglioni

Aims

A detailed microscopic description of water dynamics in curing tricalcium silicate by Elastic Neutron Scattering.

Results

A new model to fit ENS data has been implemented and tested on the C3S/H2O system[1]. This new approach based on the random-jump diffusion model allows both to extract the bound water index, BWI, (i.e. the water that is "immobile" in the dynamic range of IN13 instrument at ILL: 0.1 ps to few hundred ps) and the self-diffusion coefficient, D, of the H-species (mainly the unreacted water). D evolution mirrors the trend of BWI, with an induction, acceleration, and diffusion limited region.

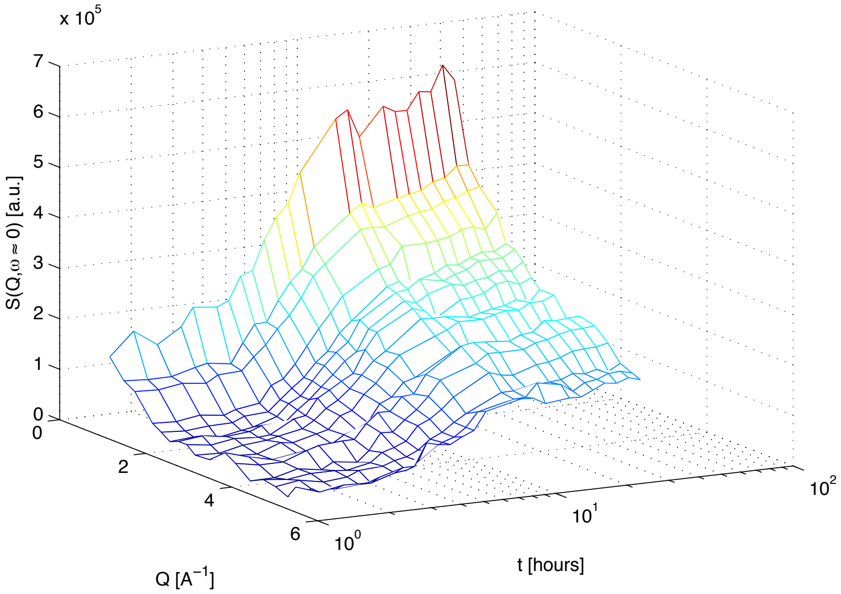


Figure 1. Time evolution of elastic scans as obtained on a curing tricalcium silicate paste by IN13 (ILL).

In particular, D decreases from about $4\text{x}10^{-9}$ m^2/s after few hours to $4\text{x}10^{-10}$ m^2/s after 2 days of curing [1]. MD on bulk water: $2.3\text{x}10^{-9}$ m2/s (FF: Simple Point Charge). MD for SPC water on the surface of tobermorite (C-S-H nano-pores model) for all C-S-H surface-associated H_2O: 1.0x10–10 m^2/s[2]. Similar values were determined by ^{1}H-NMR field cycling relaxation experiments[3]. It is clear that QENS and ENS probe all the water molecules present in the sample and in particular monitors the bulk-like water consumption in favor of the nano-confined water lasting in the C-S-H gel porosity.

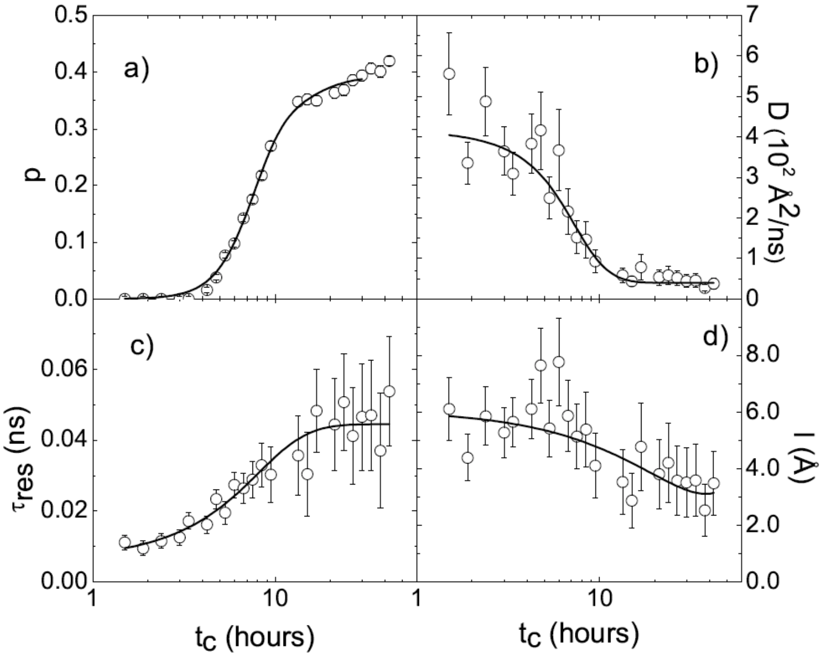


Figure 2. Evolution of extracted parameters, according to equation 6 in ref.[1]: a) bound water index, p, b) diffusion coefficient, D, c) residence time, τ_{res}, d) average jump distance, l.

References

[1] Fratini, E.; Faraone, A.; Chen, S.H. and Baglioni, P. "Dynamics of water in hydrated cement pastes by time resolved elastic neutron scattering", JPCB. Submitted.

[2] Kalinichev, A.G. et al. Cem. Conc. Res., 37, 337 (2007).

[3] Korb, J.-P. et al. Cem. Conc. Res., 37, 348 (2007).

1A – Hydration and structural properties of cement mortars in presence of inorganic and polymeric additives

F. Ridi, F. Bausi and P. Baglioni (CSGI - Florence)

Aims

The need for cement pastes having optimized performances to be used for specific applications requires investigating the influence of inorganic and polymeric additives on the hydration process and on the structure of the hydrated phases.

Results

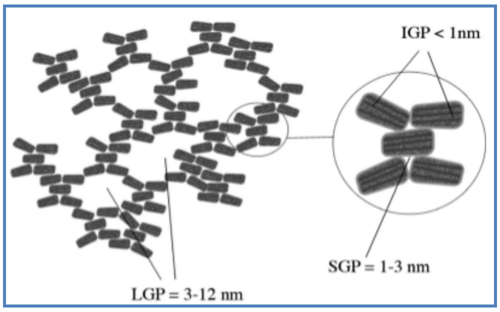
The influence of inorganic additions (limestone, inert sand) and of a polymeric superplasticizer on the hydration of CEM I type Ordinary Portland Cement (OPC) was studied both from thermodynamic and structural points of view. The use of limestone in the cement formulations is a widely used practice, as it enhances the stability and the flow of fresh mortar and concrete and also enhances the rheological properties of the fresh concrete, especially in the sense of a higher cohesion and better plasticity. In order to better reproduce the actual composition of an industrial mortar, we introduced an inert coarser additive (sand) in our formulations. Finally an organic superplasticizer was mixed to the paste. The introduction of this class of polymers is essential in the real formulations, because they allow the fluidification of the pastes without increasing of the water amount, avoiding a worsening of the mechanical properties.

The hydration kinetics were followed by means of calorimetry, by monitoring the water consumption due to the reaction with cement [1;2]. We obtained the Free Water Index (FWI) vs time curves for all the investigated samples at four different curing temperatures and each curve was then fitted according to the most recent model describing the nucleation and the growth process of cementitious materials, the Boundary Nucleation and Growth Model (BNGM). The fitting allowed us to obtain the values of the rate constants related to the nucleation (kB) and to the growth (kG) of the hydrated phases for each formulation. We observed that inorganic additions modify the thermodynamics of the OPC hydration process. In particular we found that the rate constant kB (controlling the nucleation process) has a classical Arrhenius dependence with the temperature in the case of the OPC sample, with an activation energy of 28.6±1.2 kJ/mol. When the calcium carbonate and the sand are mixed in the paste, a super-Arrhenius model has to be used to fully describe the behaviour. In these cases the activation energy is no more constant in the investigated temperature range, but it decreases on increasing the temperature.

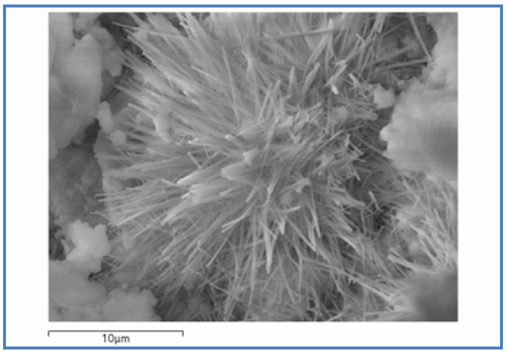
The superplasticizer produces an important delay in the beginning of the acceleration period, i.e. it strongly prolongs the induction period.

In order to investigate the evolution of the microstructure of the samples, we performed Low Temperature Differential Scanning Calorimetry (LT-DSC) experiments. The samples have been slowly cooled down to -80°C and then heated again to room temperature. The obtained thermograms were interpreted according to the Jennings Colloidal Model II (CM II, see the sketch below) describing the C-S-H microstructure.

We observed that the admixtures produce a modification in the microstructure evolution of the pastes. In particular the carbonate addition produces a more effective consumption of water, during the first 28 days of hydration, compared to the unadditivated Calusco sample. Interestingly, the sand is observed to counteract the carbonate effects.



The hydrated phases formed in the samples during the hydration have been characterized by means of spectroscopic and microscopic techniques. In particular we used X-Ray powder Diffraction (XRD) to observe the evolution of the hydrated products during the hydration process. We confirmed the data already reported in previous literature, showing that the carbonate is not an inert additive, but it participates in the formation of carboaluminate hydrated phases. It also inhibits the formation of monosulfoaluminate phase. The Scanning Electron Microscopy (SEM) shows the presence of the amorphous C-S-H and of lamellar hexagonal structures, attributable to Portlandite. Ettringite crystals were also often detected. In the presence of carbonate a massive presence of a characteristic fibrous structure is visible after seven days of hydration. This phase has the typical morphology of AFt aluminate phases: as it is present only when carbonate is mixed in the paste, we believe that it is attributable to an AFt carboaluminate hydrated phase, as thaumasite [3].



References

[1] Damasceni, A.; Dei, L.; Fratini, E.; Ridi, F.; Chen, S.H. and Baglioni, P. “A novel approach based on differential scanning calorimetry applied to the study of tricalcium silicate hydration kinetics”, J Phys Chem B, 106 (44), 11572-11578 (2002).

[2] Ridi, F.; Fratini, E.; Chen, S.H. and Baglioni, P. “Hydration kinetics of tri-calcium silicate in the presence of superplasticizers”, J. Phys. Chem. B, 107 (4), 1056-1061 (2003).

[3] Bonavetti, V.L.; Rahhal, V.F. and Irasser, E.F. “Studies on the carboaluminate formation in limestone filler-blended cements”, Cement and concrete Research, 31 (6), 853-859 (2001).

1A – Supramolecular architectures for tailoring of surface properties

V. Spampinato, N. Tuccitto, G. Zappalà, A. Licciardello

Aims

Tailoring of surface properties is one of the major issues in the development of devices in the micro- and nanometer scale. In particular, many efforts are currently produced for integrating on solid surfaces some interesting features, such as electronic properties or molecular recognition properties, exhibited by isolated molecules and/or supramolecular systems. In our laboratory we are working to the development of methodologies that transfer to the surface the approaches typical of supramolecular chemistry for the construction of functional, nanometer-sized structures.

Results

The general approach we use is that of anchoring a self assembled monolayer of suitable molecules on the surface to be modified and to use such a layer as the base "platform" for the construction of supramolecular architectures with the desired electrical or sensor properties. For example we have shown that a mixed component thiolate SAM on gold, containing a terpyridine ligand, is a very reproducible "platform" system that can be used as a platform for subsequent surface reactions, as sketched in Figure 1 in the case of the construction of a supramolecular wire.

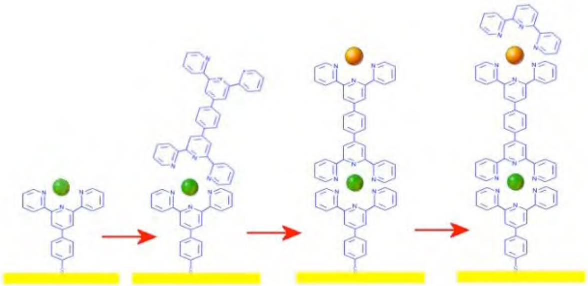


Figure 1. Scheme for the stepwise preparation of a metal-containing molecular wire, based on coordination chemistry of terpyridine (see also figure 4 for electrical properties).

This approach has been exploited for the direct surface synthesis of heteroleptic ruthenium complexes (useful for light harvesting), for the incorporation of metal cations able to drive the specific adsorption of proteins (see fig. 2), for the controlled anchoring of single strand oligonucleotides capable of DNA recognition (Figure 3). The same platform can be successfully exploited for the stepwise construction, at the

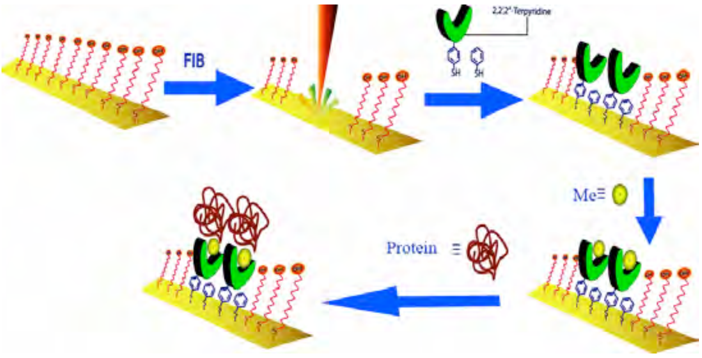


Figure 2. Pictorial scheme of the preparation of a patterned metal-ion containing surface capable of spatially selective adsorbtion of a specific protein (in the present case metal is Fe^+ and protein is lactoferrin).

Figure 3. Pictorial representation of anchoring, on the terpyridine-containing platform, of a single strand oligonucleotide and its subsequent hybridization with the complementary sequence.

surface, of self-assembled, Fe(II)- or Co(II)-containing molecular wires, exhibiting outstanding conduction (Figure 4) and optical properties.

Of course the development of the above described methodologies requires a detailed compositional control – at molecular level - of each preparation step. For this purpose we use time-of-flight secondary ion mass spectrometry (ToF-SIMS), that provides a unique capability in providing a large amount of molecular information from organic-based materials, together with other surface characterisation techniques, such as AFM and XPS.

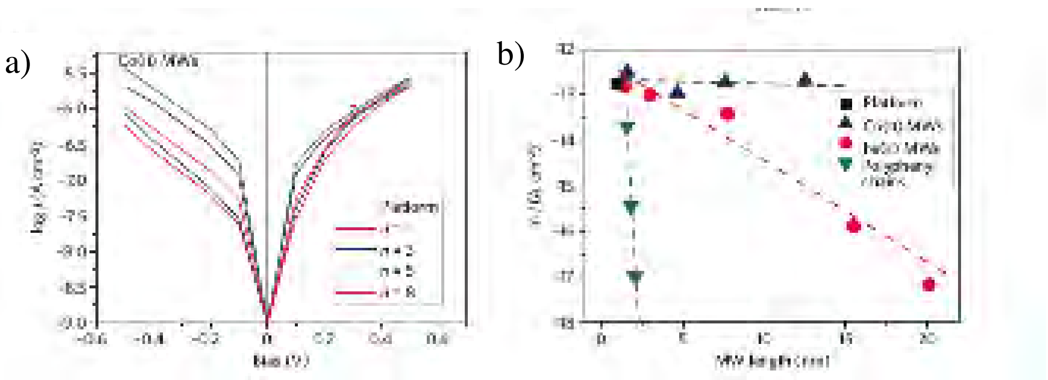


Figure 4. a) J–V curves for a Co(II)-based molecular wire. b), ln J versus length of Fe(II)- and Co(II)-based molecular wires. Data for polyphenyl chains, showing much worse characteristics, are reported for comparison.

References

Auditore, A.; Tuccitto, N.; Marzanni, G.; Quici, S.; Puntoriero, F.; Campagna, S. and Licciardello, A. “Organized assemblies of thiol-terpyridine and thiophenol on gold surfaces: preferential composition of mixed species evidenced”, Chem. Commun. 19, 2494 (2003).

Tuccitto, N.; Torrisi, V.; Cavazzini, M.; Morotti, T.; Puntoriero, F.; Quici, S.; Campagna, S. and Licciardello, A. “Stepwise Formation of Ruthenium(II) Complexes by Direct Reaction on Organized Assemblies of Thiol-Terpyridine Species on Gold” ChemPhysChem 8, 227-230 (2007).

Tuccitto, N.; Giamblanco, N; Licciardello, A. and Marletta, G. “Patterning of lactoferrin using functional SAMs of iron complexes”, Chem. Commun., 2621-2623 (2007).

Tuccitto, N.; Ferri, V.; Cavazzini, M.; Quici, S.; Zhavnerko, G.; Licciardello, A. and Rampi, M.A. “Highly conductive ~40-nm-long molecular wires assembled by stepwise incorporation of metal centres”, Nature Materials 8, 41-46 (2009).

Tuccitto, N.; Delfanti, I.; Torrisi, V; Scandola, F; Chiorboli, C.; Stepanenko, V.; Würtner, F. and Licciardello, A. “Supramolecular self-assembled multilayers of terpyridine-functionalized perylene bisimide metal complexes”, Phys. Chem. Chem. Phys. 11, 4033-4038 (2009)

1A – Physico-chemical characterization of self-assembled thin films on oxide surfaces

V. Spampinato, N. Tuccitto, A. Torrisi, G. Marletta,
A. Licciardello

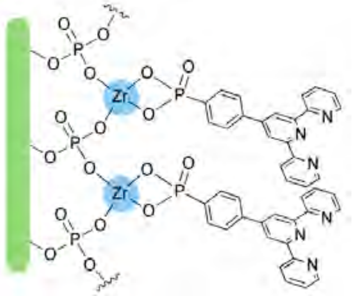
Aims

Development of a methodology for engineering of oxide surfaces by metal complex coordination, involving the creation of a general-purposes surface functionalization platform based on direct attachment of phosphate groups onto hydroxylated surfaces and subsequent formation of a terpyridine-based monolayer.

Results

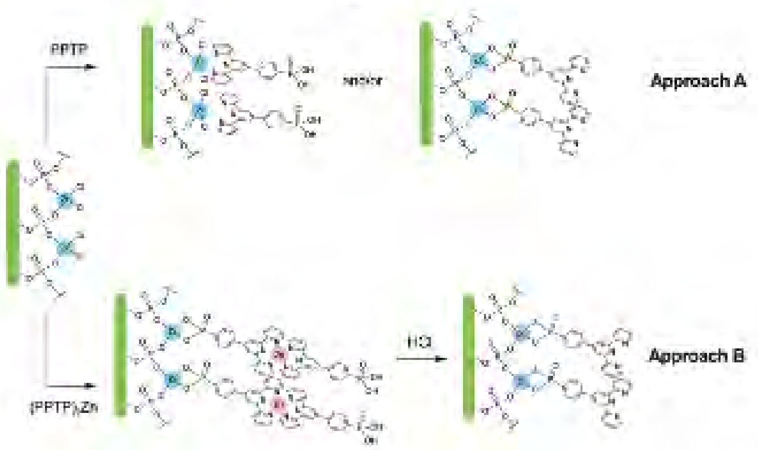
Self-assembled monolayers of molecules containing polypyridinic functional groups are suitable systems for mediating the subsequent formation, at the surface, of opto- and/or electroactive metal complexes that could be of some interest in several application fields, such as molecular electronics or sensing devices.

In order to exploit the well-known and often interesting optical properties of many transition metal complexes, possibly in conjunction with electrical or redox properties, their anchoring onto oxide surfaces is very attractive. Indeed several transparent semiconductor oxides are widely used for the emerging fields of organic photovoltaic and organic electronics/optoelectronics.



Scheme 1

A methodology for engineering oxide surfaces by metal complex coordination is used for creating a surface functionalization platform based on direct attachment of phosphate groups onto hydroxylated surfaces and subsequent formation of a terpyridine-based monolayer (scheme 1). For this purpose a bifunctional ligand, bringing both a terpyridine moiety and a phosphonic acid group (PPTP), was attached onto oxide surfaces, namely quartz and Indium Tin Oxide (ITO), previously functionalized by means of Zr-phosphate groups. Two alternative anchoring approaches were explored (Scheme 2), involving a one-step reaction (approach A) and a three-step pathway (approach B),



Scheme 2

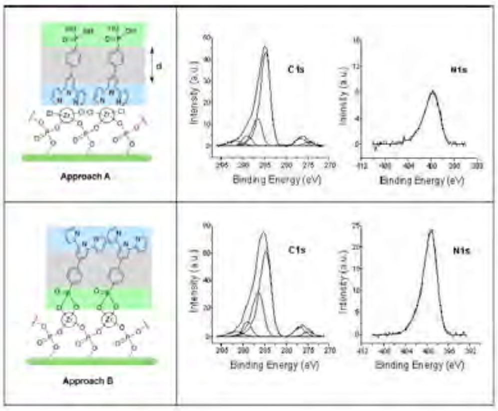


Figure 1

the latter involving the protection and successive deprotection of the terpyridinic moiety. The second approach leaves the terpyridine function available for further reactions. In order to check the availability of the terpyridine function for further coordination reactions, X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) were used. In particular, XPS allowed us to demonstrate the right orientation of the layer is obtained only *via* approach B since only in this case the pyridine functions are exposed as outermost layer. The availability of such functions for subsequent coordination reactions was demonstrated by ToF-SIMS. In particular it is shown that only the layer prepared by approach B can be exploited as a platform for the assembly of additional layers. Indeed, after their preparation, the PPTP layers were allowed to interact, consecutively, first with Fe(II) and, immediately after, with terpyridine (tpy), in order to form on the surface the PPTP-Fe(II)-tpy heteroleptic complex. The complex is formed only on the surfaces prepared by approach B, as shown by the presence, only in this case, of the (quasi)molecular ions in the ToF-SIMS spectra shown in Figure 2.

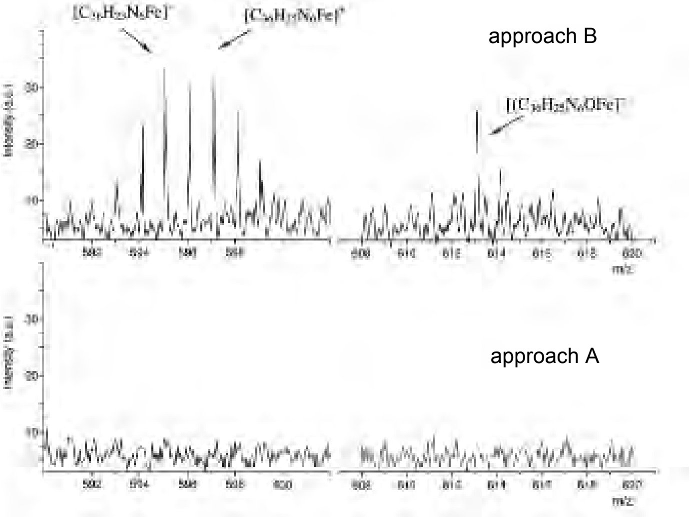


Figure 2

References

Spampinato, V.; Tuccitto, N.; Quici, S.; Calabrese, V.; Marletta, G.; Torrisi, A. and Licciardello A. “Functionalization of Oxide Surfaces by Terpyridine Phosphonate Ligands: Surface Reactions and Anchoring Geometry”, Langmuir 26, 8400-8406 (2010).

Tuccitto, N.; Torrisi, V.; Cavazzini, M.; Morotti, T.; Puntoriero, F.; Quici, S.; Campagna, S. and Licciardello, A. “Stepwise Formation of Ruthenium(II) Complexes by Direct Reaction on Organized Assemblies of Thiol-Terpyridine Species on Gold”, ChemPhysChem 8, 227-230 (2007).

1A – Affinity-based sensing for clinical and anti-doping analysis

M.L. Ermini, S. Scarano S. Mariani, A. Vestri, M. Minunni

Aims

The research is focused on the development of affinity sensors based label-free and real-time transduction with application to analytical chemistry. The transduction principles used are mainly piezoelectric i.e. Quartz Crystal Microbalances (QCM) and optical i.e. Surface Plasmon Resonance (SPR) and SPR imaging.

The receptor used for surface immobilization are, respectively, antibodies in the development of immunosensor, nucleic acid probes for DNA-based sensing and aptamer in aptasensing applications.

The development of affinity based sensing requires optimization of the immobilization chemistry of the receptor to be coupled to the surface. Thiol-based chemistry is employed for protein and nucleic acid molecules, including aptamers) immobilizations mainly on gold surfaces.

Signal sampling and management as well as signal amplification are also crucial aspects in sensors' optimization. On going research is devoted to very sensitive detection of proteins and nucleic acids in complex matrices.

Application dedicated to protein detection for clinical diagnostic and anti-doping analysis are under development. Among others, hepcidin detection in bodily fluids. Hepcid is an emerging marker in Erythropoiesis Stimulators Abuse, it is synthesized primarily by hepatocytes and released into blood. Affinity-based sensing for Erythropoietin and Hepcidin is under development within a World Anti-doping Agency (WADA) funded project (Grant 2010).

Regarding nucleic-acid sensing, sensitive point mutation detection by SPRimaging-based transduction is also under development for applications in theranostic (i.e, pain treatment).

References

Ermini, M.L.; Scarano, S.; Bini, R.; Banchelli, M.; Berti, D.; Mascini, M. and Minunni, M. "A rational approach in probe design for nucleic acid-based biosensing", Biosensors and Biolectronics, in press (2011), BIOS-D-11-00497.

1B – Nucleotide and nucleolipids specific interactions at a lipid cubic interface

S. Murgia, S. Lampis, R. Angius, P. Zucca, D. Berti, E. Sanjust, M. Monduzzi

Aims

Phase behavior of the monoolein/water/nucleotides-nucleolipids ternary systems. Nucleotide recognition and specific interactions at a lipid cubic interface.

Results

The entrapment of AMP, GMP, CMP and UMP nucleotides along with two different AMP-based nucleolipids (hydrophobically functionalized nucleotides) inside the liquid crystalline phases of the monoolein (MO)/water system is investigated through optical microscopy, FT-IR, SAXRD and NMR techniques. As ascertained mainly through ^{31}P NMR experiments (see Fig. 1), when included within the cubic phase, in spite of their natural inertness towards hydrolysis, the various nucleotides undergo a slow hydrolysis of the sugar-phosphate ester bond induced by specific interactions at the MO-water interface. Differently, neither hydrolysis nor alterations of the monoolein self-assembly is observed when the nucleolipids are included within the cubic liquid crystalline phase.

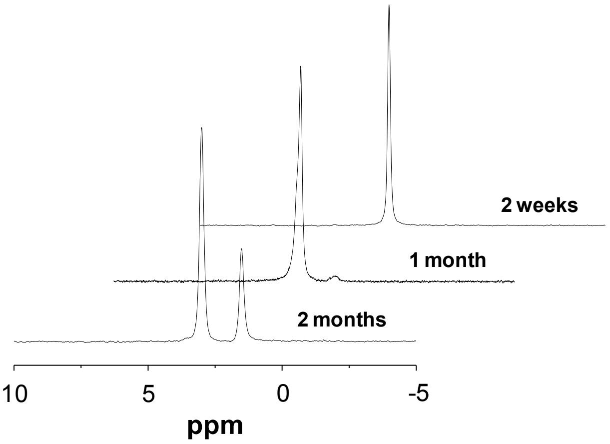


Figure 1. ^{31}P NMR stack plot spectra of a cubic MO/D/CMP sample (30 wt% deuterated water, D, content) recorded upon ageing.

Kinetics of the hydrolysis reaction and interactions between the lipid matrix and the mononucleotide adenosine 5'-monophosphate disodium salt (AMP) and its 2'-deoxy derivative (dAMP) are thoroughly investigated in order to shed some light on the mechanism of the nucleotide recognition and phosphate ester hydrolysis. Experiments evidenced that molecular recognition occurs essentially through the *sn-2* and the *sn-3* alcoholic OH groups of MO. It is also worth noticing that the nucleotide phosphoryl was not transferred onto whatever nucleophile present in our system (water, monoolein and (deoxy)ribose hydroxyl groups), but exclusively to water: no transphosphorylation products were found at all, but only (deoxy)adenosine and hydrogen phosphate dianion. The last observation, taken together with the others above, indicates that a hydroxyl group of monoolein is involved in the phosphoester bond hydrolysis through a dissociative mechanism (possibly through a six-membered transition state). As deduced from the apparent activation energies, the mechanism underlying the hydrolysis reaction is the same for AMP and dAMP. Nevertheless, the reaction proceeds slower for the latter, highlighting a substantial difference in the chemical behavior of the two nucleotides. The nucleotides-induced phase behavior can be visualized as follows. Anchorage of nucleotides to MO molecules at the lipid-water interface via hydrogen bonds reduces the thermal motions of the MO polar heads, thus causing a shrink of the effective polar head areas. In turn, this phenomenon leads either to an intercubic *Ia3d* to *Pn3m* or to a cubic to hexagonal phase transitions (see Fig. 2). Upon ageing, the released hydrogen phosphate dianion accelerates the cubic to hexagonal phase transition. Remarkably, the hydrolysis mechanism appears to be highly specific for the *Ia3d* phase.

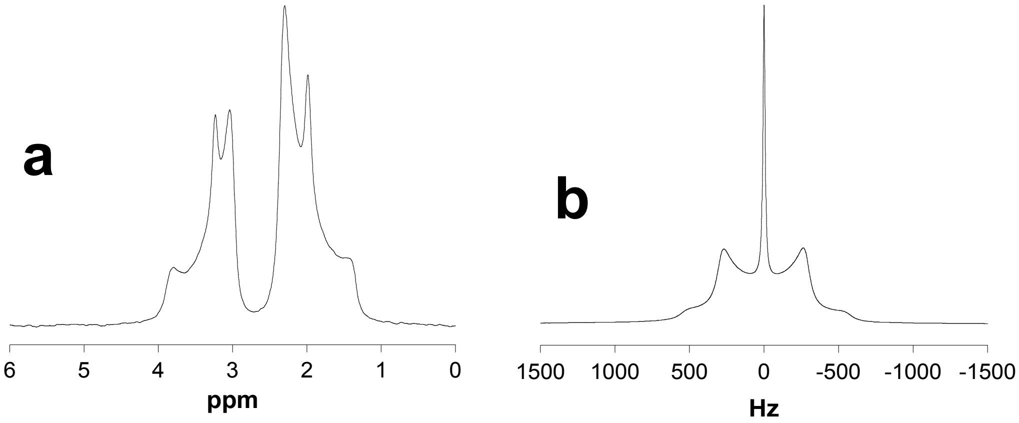


Figure 2. NMR spectra showing the cubic to hexagonal phase transition induced by the XMP hydrolysis. MO/D/UMP (D indicates deuterated water) sample after 5 months ageing: (a) ^{31}P NMR spectrum, (b) ^{2}H NMR spectrum.

References

Murgia, S.; Lampis, S.; Angius, R.; Berti, D. and Monduzzi, M. “Orientation and specific interactions of nucleotides and nucleolipids inside monoolein-based liquid crystals” J. Phys. Chem. B, 113, 9205-9215 (2009).

Murgia, S.; Lampis, S.; Zucca, P.; Sanjust, E. and Monduzzi M. “Nucleotide recognition and phosphate linkage hydrolysis at a lipid cubic interface” J. Am. Chem. Soc., 132, 16176-16184 (2010).

1B – Role of the stabilizing agent on morphology and cytotoxicity in nanoparticles preparation

S. Murgia, A.M. Falchi, M. Mano, S. Lampis, R. Angius, A.M. Carnerup (Lund University, Sweden), J. Schmidt (Technion, Haifa, Israel), G. Diaz, M. Giacca, Y. Talmon (Technion, Haifa, Israel), M. Monduzzi

Aims

Highlighting the role of the stabilizing agent in the preparation of lipid-based nanoparticles and evaluating its impact in biological systems.

Results

Monoolein (MO)-based nanoparticles (NPs), obtained through fragmentation of bulk liquid crystalline phases, and stabilized by two different emulsifiers, namely Pluronic F127 (PF127) and lauroylcholine chloride (LCh), are investigated for structural features, and for short term in-vitro cytotoxicity. Depending on the emulsifiers, different morphologies of the lipid NPs (cubosomes and liposomes) are obtained, as demonstrated by the cryo-TEM images shown in Fig. 1.

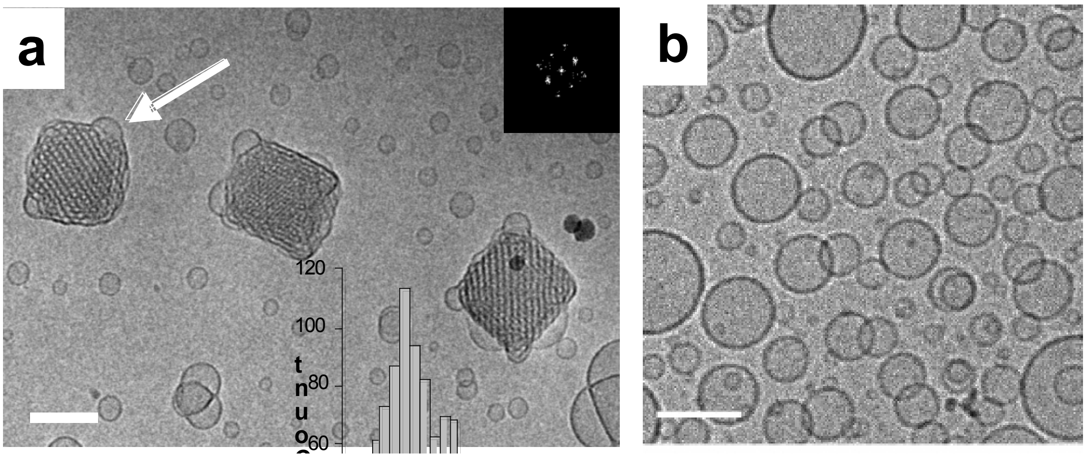


Figure 1. (a) Cryo-TEM image of cubic phase nanoparticles (cubosomes) dispersed in the aqueous solution of PF127. Fast Fourier transformation of the domain indicated by the arrow is shown in the inset. (b) Cryo-TEM image of the LCh-based dispersion showing unilamellar liposomes. Scale-bars correspond to 100 nm.

Whereas PF127 allows for the formation of cubosomes as reported in previous works, upon LCh addition the original cubic liquid crystalline matrix is lost. This finding may be explained calling into play the effective packing parameter (P_{eff}). Taking into account that MO LC aggregates in water show $P_{\text{eff}} \geq 1.0$, while a suitable P_{eff} value for the vesicular arrangement of the bilayer is 0.5-1.0, according to our experimental result it is clear that LCh incorporation into the MO/W system must induce a consistent decrease of P_{eff}. This logical deduction is also supported by the broadening of the L_α region and the disappearance of the C_D phase from the pseudo-binary

MO/W/LCh diagram (C_G has a smaller P_{eff} than C_D). Moreover, the intercalation of the short-chain LCh molecule within the MO palisade will disturb the regular arrangement of both the lipid tails and the polar head thus increasing the bilayer flexibility. During the dispersion process, these two effects (decreased P_{eff} and increased bilayer flexibility) cooperatively act to allow for the bilayer folding towards the liposomal nanostructure. Two different protocols to evaluate the impact of these lipid NPs on biological systems are presented in Fig. 2. Results show that nanoparticles stabilized by PF127 (cubosomes) display a relevant toxicity towards different cell lines, whereas those stabilized by LCh (liposomes) affect cell viability at a much lesser extent.

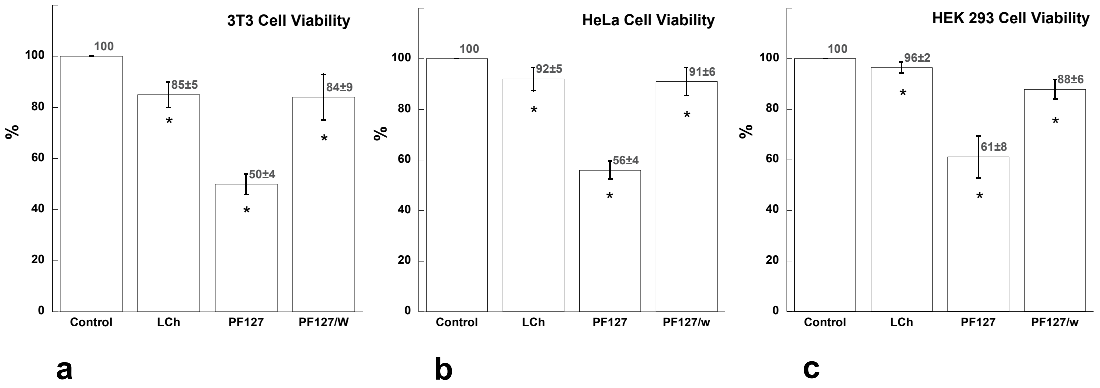


Figure 2. Effect of the MO/W dispersions stabilized by PF127 and LCh on the cell viability of (a) 3T3 cells (Hoechst 33258 data analysis), (b) HeLa cell line (Alamar Blue assay), (c) HEK 293 cell lines (Alamar Blue assay). (*) $p < 0.05$, compared to non-treated control cells.

References

Murgia, S.; Falchi, A. M.; Mano, M.; Lampis, S.; Angius, R.; Carnerup, A. M.; Schmidt, J.; Diaz, G.; Giacca, M.; Talmon, Y. and Monduzzi M. “Nanoparticles from lipid-based liquid crystals: emulsifier influence on morphology and cytotoxicity” J. Phys. Chem. B 114, 3518-3525 (2010).

1B – Tuning of the surfactant film curvature through ionic liquids

S. Murgia, G. Palazzo, M. Mamusa, S. Lampis, M. Monduzzi

Aims

Phase behavior of the sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT)/water/1-butyl-3-methylimidazolium tetrafluoborate ($bmimBF_4$) ternary system.

Results

The ternary diagram sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT)/water/1-butyl-3-methylimidazolium tetrafluoborate ($bmimBF_4$), a polar room temperature ionic liquid, is explored through optical microscopy in polarized light, SAXRD and NMR PGSTE techniques (see Fig. 1). The analysis of SAXRD and self-diffusion data reveals that the $bmim^+$ cation is strongly adsorbed at the interface. Data are accounted for by the Hill's model for cooperative binding (see Fig. 2). The overall processes is described as a co-micellization of AOT^- and $bmim^+$ involving roughly two cations for AOT^- ion. The $bmim^+$ is severely involved in the structural arrangement of the interface. Indeed, a huge modification of the interfacial geometry resulting in the occurrence of micelles having positive curvature is inferred from the analysis of the self-diffusion coefficients. The analysis of the water diffusion data in the L_1 phase (according to the Effective Cell Model) allows to exclude the presence of oblate and/or discoid micelles (Fig. 3). Finally, the study of the oil diffusion in samples doped with *p*-xylene permits to asses furthermore not only the formation of AOT aggregates of the oil-in-water type but also the occurrence of dynamic percolation phenomena.

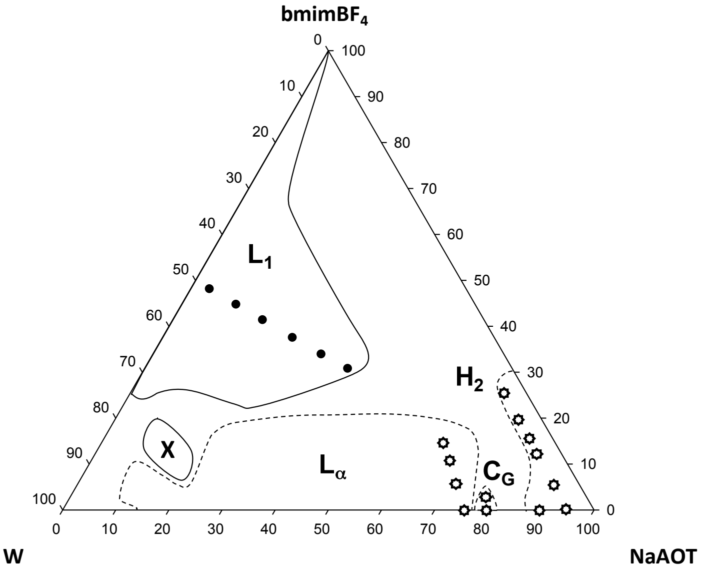


Figure 1. Ternary diagram of the NaAOT/W/$bmimBF_4$ system at 25 °C. Also displayed are the samples analyzed through SAXRD (open symbols) and NMR PGSTE (closed symbols) techniques.

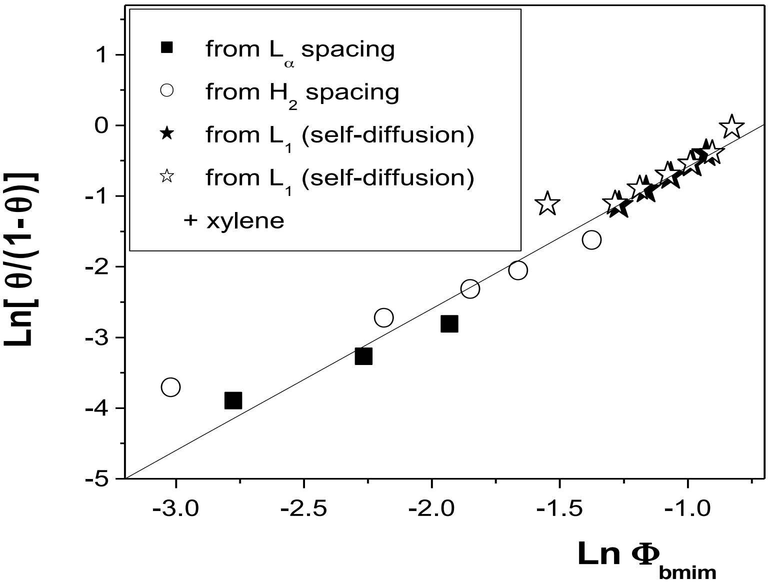


Figure 2. Hill's plot: the linearity of the plot and its slope are a graphical confirm of the cooperative process.

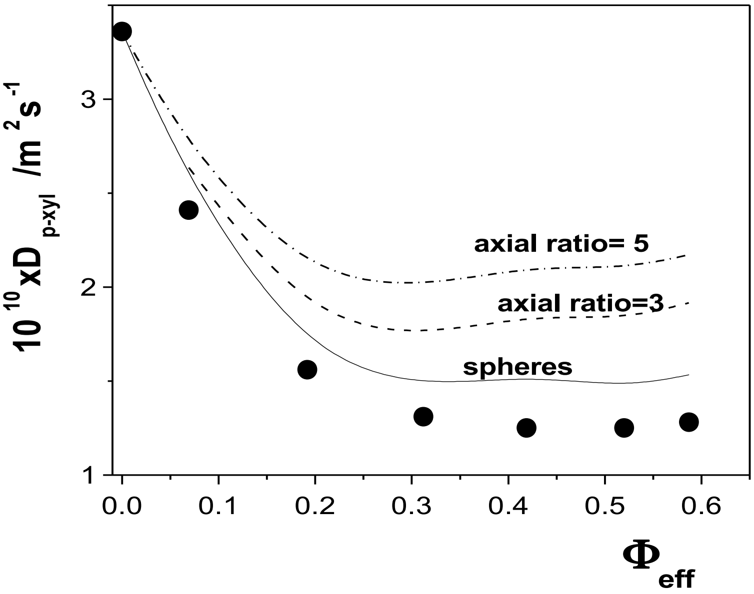


Figure 3. Self-diffusion coefficents of *p*-xylene as a function of the micellar volume fraction. Solid curve is the prediction for spherical micelles; dashed curves are the prediction for prolate spheroids with axial ratio = 3 or 5.

References

Murgia, S.; Palazzo, G.; Mamusa, M.; Lampis, S. and Monduzzi, M. "Aerosol-OT forms oil-in-water spherical micelles in the presence of the ionic liquid bmimBF$_4$" J. Phys. Chem. B, 113, 9216-9225 (2009).

1B – Interaction of short modified peptides involved in degenerative diseases with phospholipid membranes

G. D'Errico, G. Vitiello, L. Paduano, R. Sartorio, O. Ortona, G. Mangiapia.

Aims

There is mounting evidence that the lipid matrix of neuronal cell membranes plays an important role in the accumulation of β-amyloid peptides into senile plaques, one of the hallmarks of Alzheimer's disease (AD). Other degerative diseases involve interaction between some particular proteins and phosholipidic double layer as step for propagate the pathology. Thus, it is important to clarify the molecular basis and the mechanism of the interaction between proteins, or their representative fragments and cellular membranes, that could open a new view for the design of a therapy to prevent or to stop the degenerative processes.

Results

We have studied the interaction between Ab peptide and lipid membranes, showing that Aβ(25-35) fragment inserts in bilayers formed by phospholipid dilauroyl phosphatidylcholine (DLPC), positioning between the outer part of the hydrophobic core and the external hydrophilic layer. This process is not significantly influenced by the inclusion of the anionic phospholipid phosphatidylglycerol (DLPG) in the bilayer, indicating the peptide insertion to be driven by hydrophobic rather than electrostatic interactions. Cholesterol plays a fundamental role in regulating the peptide/membrane association, inducing a membrane transition from a fluid-disordered to a fluid-ordered phase. At low cholesterol content, in the fluid-disordered phase, the insertion of the peptide in the membrane causes a displacement of cholesterol towards the more external part of the membrane, probably because of a direct cholesterol-peptide association. The crowding of cholesterol enhances its rigidifying effect on this region of the bilayer. Finally, the cholesterol-rich fluid-ordered membrane looses the ability to include Aβ(25-35).

About the study on the interaction between viral fusion peptides and lipid bilayers, we have investigated the effect of a tryptophan-rich octapeptide, named C8, deriving from the gp36 MPER domain of feline immunodeficiency virus (FIV) on the structure of different phospholipid membranes. Experimental results indicated that C8 adsorbs on the bilayer surface, positioning between phospholipid polar groups and perturbs the lipid packing and chain motion in the membranes, assuming an helical conformation in which the Trp residues are exposed on the same side of the helix. We have also studied the action of different peptides deriving from glycoprotein gB and gH of Herpes Simplex Virus (HSV) and from gp41 of Human Immunodeficiency Virus on lipid membranes. Our results indicated that viral-derived membrane interacting peptides all act via a similar mechanism, which is substantially different from that of the non-cell selective lytic peptide melittin.

1B – Design and Characterization of Ruthenium-based Supramolecular Systems as Nano-devices with antineoplastic activity

G. D’Errico, G. Vitiello, L. Paduano, R. Sartorio, O. Ortona, G. Mangiapia.

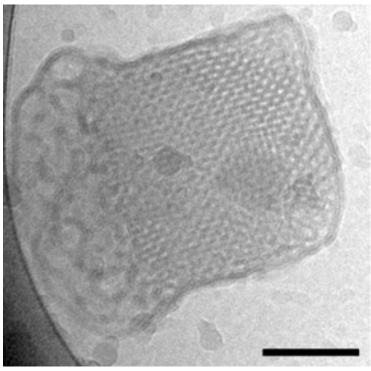
Aims

Metal complexes have had an enormous impact in medicine, especially in the treatment of cancer. It has been estimated that 50–70% of all cancer patients in the world are treated with Cisplatin or its analogues. Because of the platinum-based drug high side effects, the research has been prompted to develop more effective and less toxic metal-based antitumor agents. Among metals, one of the most promising is Ruthenium, since some Ru(III) complexes show high *in vitro* and *in vivo* antitumor activity and some compounds, such as NAMI-A and KP1019, are currently under clinical trials. This research is focused on the design and physico-chemical characterization of Ruthenium based supramolecular aggregates (micelles, liposomes, etc.) with potential antineoplastic activity.

Results

Recently we have synthesized a new series of amphiphilic unimers able to form stable complexes with ruthenium. It has been shown their ability to form, in the presence as well as in the absence of phospholipids, stable multilamellar vesicles and a rich variety of more complex aggregates, such as the formation of bicontinous cubic liquid crystalline (see figure below). A theoretical model to analyze small angle scattering data arising from such systems has also been developed.

The findings in the present study open up new vistas for the application of lipid based supramolecular systems in Ruthenium anti-cancer therapy.



1B – Study of the formation of eumelanin and its intermediates

G. D'Errico, G. Vitiello, L. Paduano, R. Sartorio, O. Ortona, G. Mangiapia.

Aims

Melanins are polymeric pigments widely distributed throughout the animal kingdom. Our research is focusing on the investigation of characteristics of eumelanin, as well as on the kinetic evolution of its formation, starting from its precursor 5,6-dihydroxyindole. The interest arises from involvement of eumelanin in skin photoprotection, and in non linear optical properties of melanin intermediates and their potential connection with the pigment functional role.

Results

Through a combine SANS and DLS analysis, it has been possible to derive a model describing the formation of eumelanin in solution. This model describes the eumelanin growth through a series of additions of the unimer and/or a cluster formed by a small amount of unimers to the polymeric backbone. It has also been found the possibility to modulate the polymeric growth by adding an appropriate quantity of poly-(vinyl alcohol) that stops the growth and reduces the growth rate.

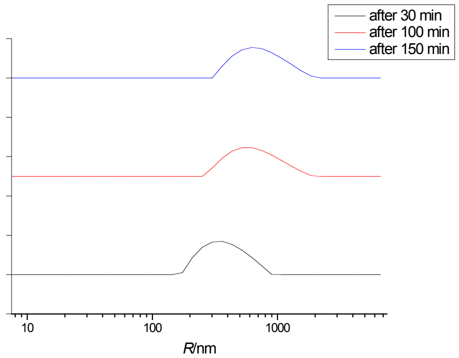


Figure 1 – Distribution function of the hydrodynamic radii found during the oxidation of 5,6-dihydroxyindole (1mmol/dm^3), at 298 K and at various elapsed times.

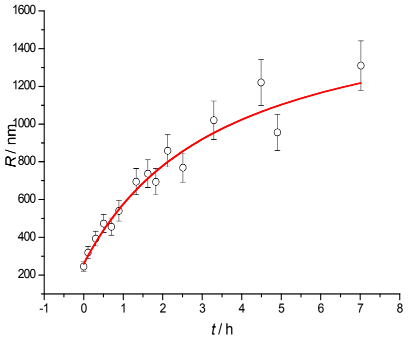


Figure 2 – Hydrodynamic radii of diffusing aggregates found during the oxidation of 5,6-dihydroxyindole (1mmol/dm^3), at 298 K and at various elapsed times.

1B – Characterization of vesicles formed by lipopolysaccharides

G. Mangiapia, G. D'Errico, R. Lanzetta, A. Molinaro, A. Silipo, L. Paduano

Aims

Lipopolysaccharides (LPSs) are amphiphilic macromolecules indispensable for the growth and the survival of Gram-negative bacteria, one of the most diffuse classes of pathogenic bacteria. LPS are composed of a hydrophilic heteropolysaccharide unit, covalently linked to a lipophilic moiety called lipid A, which is embedded in the outer leaflet and anchors these macromolecules to the lipid membrane (see figure below). Recent studies have revealed that presumably the physical characteristics of these molecules are correlated to their biological activity.

Results

We have been able to highlight the relationships between the molecular structure of some LPS molecules and the structure of their aggregates. Interestingly, the relationship is often not obvious, in that the aggregate architecture and dynamics is the final result a complex interplay of all the possible interaction (hydrophobic, electrostatic, steric) set up among the LPS molecules. In the biological context, our results suggest that the rich biodiversity of LPS molecular structure could be fundamental to finely tune the structure and functional properties of the outer membrane of Gram negative bacteria and, consequently, their biological behavior.

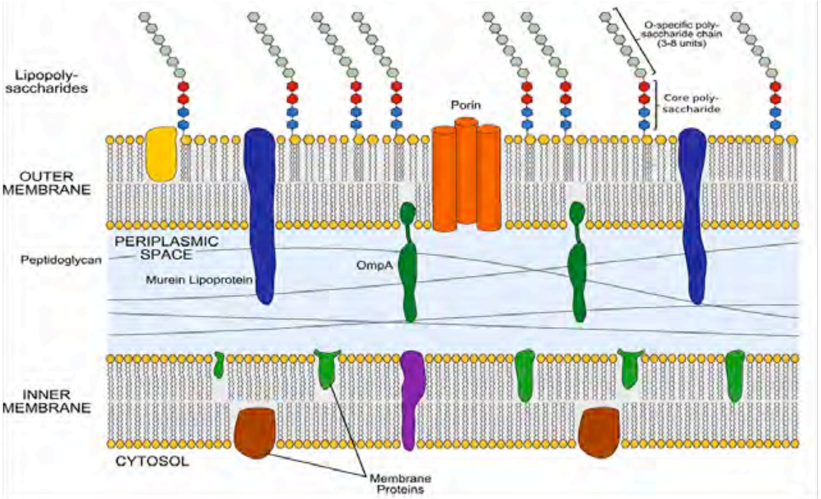


Figure 1 – Schematic representation of a Gram negative bacterium cell membrane

1B – Accurate Force Fields for Computer Simulations

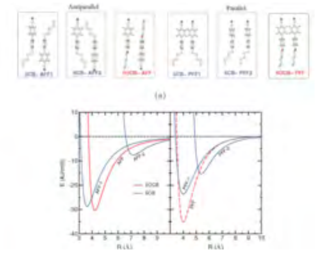
V. Barone, I. Cacelli°, J. Bloino, A. Ferretti [a], S. Monti [a], A. Pedone*, and G. Prampolini**
*(°Dip. di Chimica, Università di Pisa; [a] CNR, Pisa; *SNS, Pisa)*

Aims

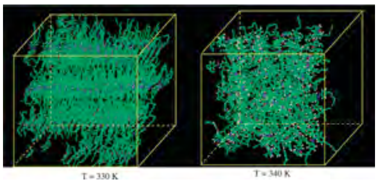
Nowadays molecular dynamics (MD) simulation is a powerful computational tool, which allows us to gain a microscopic insight into soft matter in experimental conditions. However, highly accurate force fields (FF) are requisite, if macroscopic structural and dynamic material properties are to be reproduced successfully. Unfortunately, literature FF parameters are not always reliable, and their use in computer simulation may yield unsatisfactory results.

Results

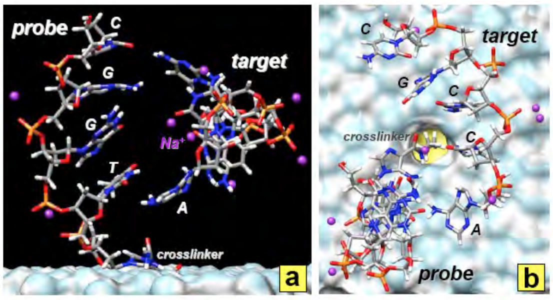
In these cases, a FF parameterization from accurate quantum mechanical (QM) calculations can be attempted, allowing us to maintain MD simulations intrinsic predictive properties, which can be in turn employed to aid the design of novel materials. In this picture, the Fragmentation Reconstruction Method (FRM), developed in our lab, allows the accurate QM calculation of large molecular dimers and it has been used to create a database that can be employed in the parameterization of FF intermolecular parameters.

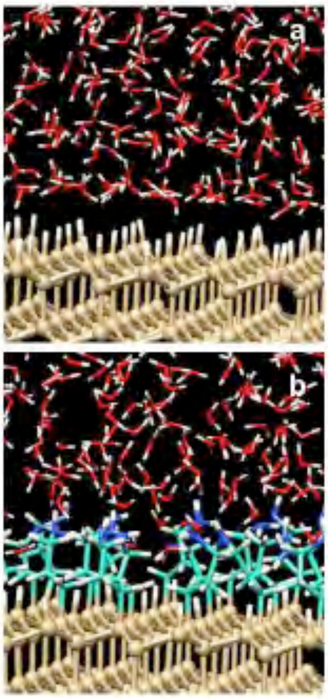


The latter FF's have been successfully adopted in the simulation of several liquid crystalline materials, reproducing different structural and dynamic properties, within a good level of accuracy.

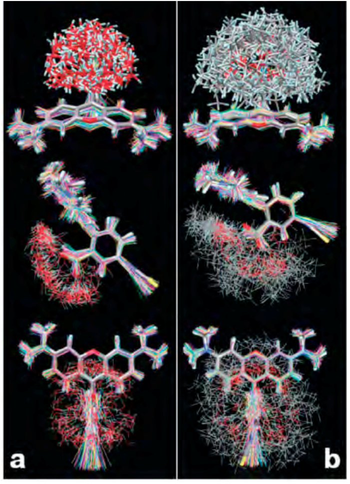


A similar QM based approach can be adopted for the intra-molecular parameterization, either to correct specific part of existing FF, or for a complete re-parameterization of the whole FF. A recent application of the former type, has been applied in the parameterization of the torsional potential of a cross-linker moiety in a single-strand DNA bio-sensor,





whereas the latter choice was made in the study of the optimal coverage of a alkyl functionalized Si (111) surface and in the case of time-dependent approach to the calculation of the absorption and fluorescence spectra of an organic dye in different solvents.



References

Cacelli, I.; Lami, C.F. and Prampolini, G. "Force-Field Modeling through Quantum Mechanical Calculations: Molecular Dynamics Simulations of a Nematogenic Molecule in its Condensed Phases", Journal of Computational Chemistry 30, 366-378 (2009).

Cacelli, I.; Cimoli, A.; De Gaetani, L.; Prampolini, G. and Tani, A. "Chemical Detail Force Fields for Mesogenic Molecules", Journal of Chemical Theory and Computation 5, 1865-1876 (2009).

De Gaetani, L. and Prampolini, G. "Computational study through atomistic potentials of a partial bilayer liquid crystal: structure and dynamics", Soft Matter 5, 3517-3526 (2009).

Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S. and Prampolini, G. "Sensors for DNA detection: theoretical investigation of the conformational properties of immobilized single-strand DNA", Physical Chemistry Chemical Physics 11, 10644-10656 (2009).

Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S. and Prampolini, G. "Parameterization and validation of an accurate force-field for the simulation of alkylamine functionalized silicon (111) surfaces", Physical Chemistry Chemical Physics 12, 4201-4209 (2010).

Monti, S.; Cacelli, I.; Ferretti, A.; Prampolini, G. and Barone, V. "Simulating DNA Hybridization on an Amine-Functionalized Silicon Substrate", Journal of Physical Chemistry B 114, 8341-8349 (2010).

Monti, S.; Cacelli, I.; Ferretti, A.; Prampolini, G. and Barone, V. "DNA hybridization mechanism on silicon nanowires: a molecular dynamics approach", Molecular BioSystems 6, 2230-2240 (2010).

Pedone, A.; Bloino, J.; Monti, S.; Prampolini, G. and Barone, V. "Absorption and emission UV-Vis spectra of the TRITC fluorophore molecule in solution: a quantum mechanical study", Physical Chemistry Chemical Physics 12, 1000-1006 (2010).

Barone, V.; Bloino, J.; Monti, S.; Pedone, A. and Prampolini, G. "Theoretical multilevel approach for studying the photophysical properties of organic dyes in solution", Physical Chemistry Chemical Physics 12, 10550-10561 (2010).

1B – Interaction of Bioactive Peptides with Membranes

R. Pogni, A. Bonucci, S. Pistolesi, R. Basosi, L. Trabalzini

Aims

The aims of this work is to study the interaction of bioactive peptides with membranes using the SDSL-EPR (Site Directed Spin Labeling – Electron Paramagnetic Resonance) technique in order to clarify the mechanism that regulates this interaction.

Results

We have analyzed the interaction of antimicrobial peptide CM15 that is a linear peptide, synthetic hybrid AMP (Antimicrobial Peptide) composed of the first seven residues of the cecropin A and residues 2-9 of the bee venom melittin. The rationale for the use of the SDSL-EPR technique is based on the use of a spin label that is bound to a cysteine in the aminoacidic sequence of a protein (Fig. 1)

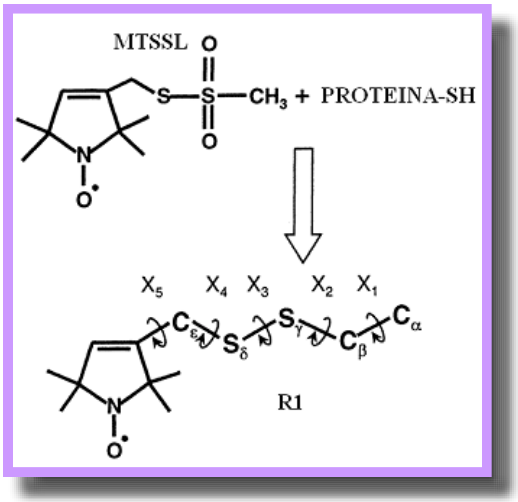


Figure 1. Structure of the MTSL (Methane-ThioSulfonate Spin Label)
and the resulting side chain produced by reaction with the peptide cysteine residue.

Antimicrobial peptides (AMPs) are an essential part of innate immune defense against microbial infection. Naturally occurring AMPs are basic peptides composed of 12–50 aminoacids that are ubiquitously distributed throughout all kingdoms of life. AMPs display a broad spectrum of antimicrobial activity against both Gram-negative and Gram-positive bacteria, fungi, and enveloped viruses (5). Importantly, they retain activity against antibiotic-resistant strains and do not readily elicit resistance. In this study we have used site-directed spin labelling (SDSL) electron paramagnetic resonance (EPR) spectroscopy to investigate the behavior of a spin-labeled analog of CM15 as a function of increasing peptide concentration and utilized phospholipid-analog spin labels to examine the effects of CM15 binding and accumulation on physical properties of membrane lipids. We find that as the concentration of membrane-bound CM15 is increased, the N-terminal domain of the peptide becomes more deeply immersed in the lipid bilayer. Changes in the rotational dynamics of membrane lipids are minimal and confined primarily to near the membrane surface. However, peptide binding dramatically increases interaction of the lipid-analog spin labels with the polar relaxation agent NiEDDA (nickel (II) ethylenediaminediacetate), indicating that there are significant changes in the physical state of the lipid bilayer that are not readily detected by methods that examine motional dynamics. These results are discussed in relation to the molecular mechanism of membrane disruption by CM15.

Another study is based on the interaction with membranes by Humanin (HN) a recently identified neuroprotective peptide, able to inhibit neurotoxicity induced by various insults which can be related to Alzheimer Disease as well as death induced by other stimuli. Here we apply the site directed spin labeling technique coupled to EPR spectroscopy to study the aggregation state and aggregate stability of humanin peptide in solution. This technique was previously used to study AMP's and fibrillogenic proteins behavior in aqueous environment, such as aggregation states and dynamics, and in presence of model bacterial membranes.
The purpose of this paper is the study of the conformational properties of humanin in different conditions in solution and in presence of model membranes.

References

Pistolesi, S.; Rossini L.; Ferro, E.; Basosi, R.; Trabalzini, L. and Pogni R. "Humanin behavior in solution and in model neuronal membranes: a SDSL-EPR study", Biochemistry, submitted (2008).
Ferro, E.; Magrini, D.; Guazzi, P.; Fischer, T.H.; Pistolesi, S.; Pogni, R.; White II, G.C. and Trabalzini, L. "G-Protein Binding Features and Regulation of the RALGDS Family Member RGL2", Journal of Biochemistry, 415(1), 145-154 (2008).
Pistolesi, S.; Pogni, R. and Feix, J.B. "Membrane insertion and bilayer perturbation by antimicrobial peptide CM15", Biophysical Journal, 93, 1651-1660 (2007).
Pistolesi, S.; Ferro, E.; Santucci, A.; Basosi, R.; Trabalzini, L. and Pogni R. **"**Molecular motion of spin labeled side chains in the C-terminal domain of RGL2 protein: a SDSL-EPR and MD study"**,** Biophysical Chemistry, 123, 49-57 (2006).

1B – Protein-Matrix Coupling: the Photosynthetic Reaction Center embedded in Solid Matrices

G. Palazzo, M. Giustini, F. Lopez, A. Mallardi (Dip. Chimica, Università di Bari), G. Venturoli (Dip. BES, Università di Bologna)

Aims

Study of the coupling of intra-protein electron transfer to protein dynamics in bacterial reaction centers embedded in glassy or polymer matrix.

Results

Proteins are soft materials. Indeed, a protein is not rigid, rather it can undergo a variety of (fast) vibrations and (slower) structural rearrangements, these latter being called *protein-specific motions*. A protein share with supercooled liquids and glasses the existence of a very large number of non-identical conformation (substates)and separated by free-energy barriers. All possible substates together form the energy landscape, where a substate is pictured as a valley in the landscape. We have investigated the coupling of protein motions to intra-protein long-range electron transfer and to inter-protein interactions. All the investigations were carried out on a given protein: the *bacterial photosynthetic reaction center* of purple bacterium *Rhodobacter sphaeroide*s.

This protein provides an excellent model system for the detailed study of reaction substates and the free-energy barriers between them. The reactions can be probed by means of spectroscopical techniques, and it is possible to initiate electron-transfer in reaction centers (RC) with a pulse of light. This allows synchronized, single turnover measurements over a wide range of time scales. Reactions are reversible, allowing signal averaging.

Hindering of protein specific motions coupled to long-range electron transfer has been detected in RC embedded in trehalose glasses at room temperature. According to our investigations, conformational relaxations occurring in response to primary charge separation decrease both the free energy gap and the electronic coupling between acceptor and donor states, resulting in the observed stabilisation of the charge-separated state. Fig 1 shows the decay kinetics of laser induced charge separated state

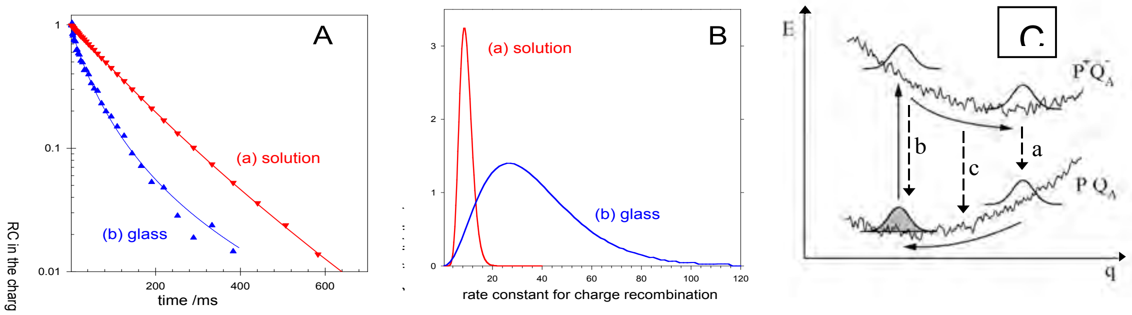


Fig. 1 *Kinetic analysis of charge recombination following laser flash excitation of RC in a trehalose solution and glass.* ***(A)*** *Normalized decay of the charge separated state measured in a 0.4 M trehalose solution (trace a), and in a dry glass (water/trehalose mole ratio of 0.47; trace b).* ***(B)*** *The corresponding distribution functions.* ***(C)*** *The corresponding evolution of the protein ensembles in a simplified diagram showing relaxation on the energy surfaces associated with the neutral (PQ_A) and the charge separated state ($P^+Q_A^-$); the abscissa q represents a generic conformational coordinate.*

(panel A) and the corresponding rate distribution functions (panel B) obtained in solution (a) and in trehalose glass (b). Incorporation of the protein into a rigid the trehalose-water matrix leads to a substantial increase of mean rate of charge recombination and of the distribution width. Both the acceleration and the spreading of the recombination kinetics observable at room temperature in extremely dried trehalose-water matrices are quite comparable with those detected upon cooling the RC in the dark below 60 K. The coupling between relaxation and electron transfer is shown schematically in Panel C, which depicts simplified free energy surfaces of the electronic states of neutral and charge-separated RC as a function of a generic conformational coordinate q. Within the Franck-Condon approximation, transitions between the $P^+Q_A^-$ and PQ_A electronic states are vertical in this diagram. The electron transfer rate is controlled by the energy gap ε, i.e. by the vertical separation between the two surfaces. Since ε varies with q, the charge recombination kinetics reflects the evolution of the protein ensemble on the lower or upper energy surfaces. In trehalose glass, the RC relaxation from the *dark-adapted* to the *light-adapted* conformation, which stabilises primary charge separation in solution at room temperature (see transition *a* in Fig2C), is prevented over the time scale of $P^+Q_A^-$ recombination. This results in an accelerated charge recombination, occurring in a structurally inhomogeneous population of essentially non-relaxed *dark-adapted* proteins (see transition *b* in Fig.2C). In moderately 'soft' matrices, a partial relaxation takes place over the time scale of charge recombination, leading to intermediate recombination kinetics (see transition *c* in Fig. 2C).

References

Palazzo, G.; Francia, F.; Mallardi, A.; Giustini, M.; Lopez, F. and Venturoli, G. “Water Activity Regulates the QA- to QB Electron Transfer in Photosynthetic Reaction Centers from Rhodobacter sphaeroides”, Journal of American Chemical Society, 130, 9353- 9363, (2008).

Veronesi, G.; Giachini, L.; Francia, F.; Mallardi, A.; Palazzo, G.; Boscherini, F. and Venturoli G. “The Fe2+ site of photosynthetic reaction centers probed by multiple scattering x-ray absorption fine structure spectroscopy: Improving structure resolution in dry matrices”, G. Biophysical Journal, *95*, 814-822 (2008).

Francia, F.; Dezi, M.; Mallardi, A.; Palazzo, G.; Cordone, L. and Venturoli, G. “Protein-Matrix Coupling/Uncoupling in “Dry” Systems of Photosynthetic Reaction Center Embedded in Trehalose/Sucrose: The Origin of Trehalose Peculiarity”, Journal of American Chemical Society, 130, 10240-10246 (2008).

Cordone L.; Cottone G.; Giuffrida S.; Palazzo G.; Venturoli G. and Viappiani C., “Internal Dynamics and Protein-Matrix Coupling in Trehalose Coated Proteins”, Biochim. Biophys. Acta, *1749*, 252-281 (2005).

Francia F.; Palazzo G.; Mallardi A.; Cordone L. and Venturoli G., “Probing light-induced conformational transitions in bacterial photosynthetic reaction centers embedded in trehalose amorphous matrices”, Biochim. Biophys. Acta, *1658*, 50-57 (2004).

1B – Dynamic response of a shear banding wormlike micellar system in transient shear flows

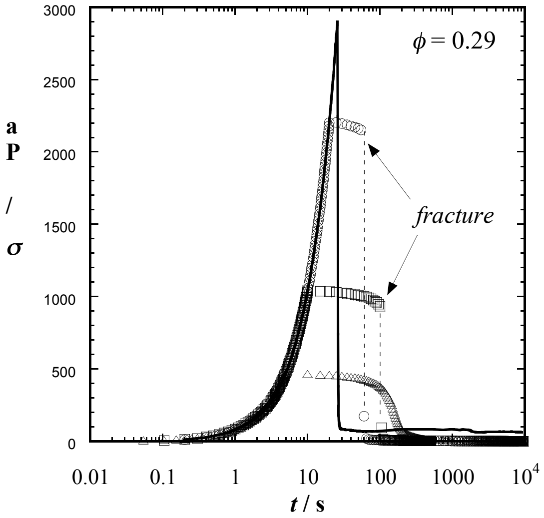
R. Angelico, A. Ceglie, L. Ambrosone, G. Palazzo, U. Olsson (Chemical Center, Lund University, Sweden), C. Oliviero Rossi, G.A. Ranieri (Dip. Chimica, Univ. Cosenza)

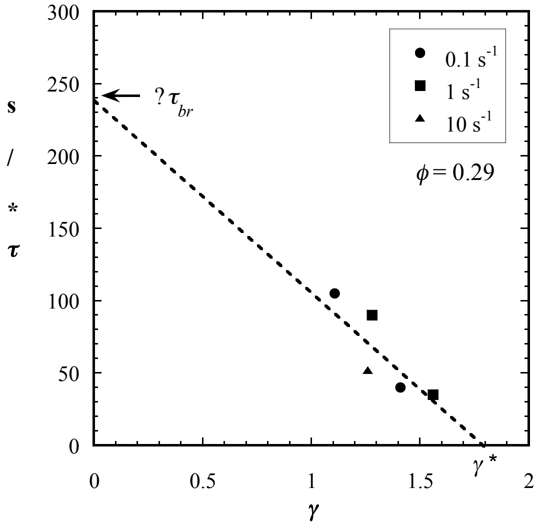
Aims

Non-linear flow properties of living polymer systems. Shear induced Isotropic-Nematic phase transition. Fracture of micellar network. Micellar breaking time.

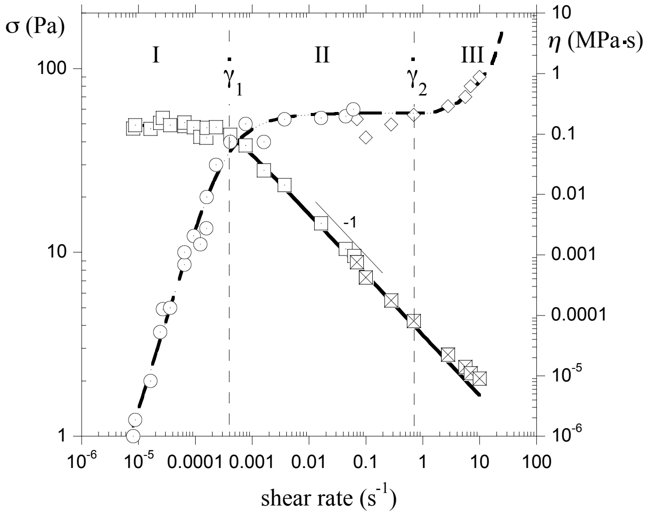
Results

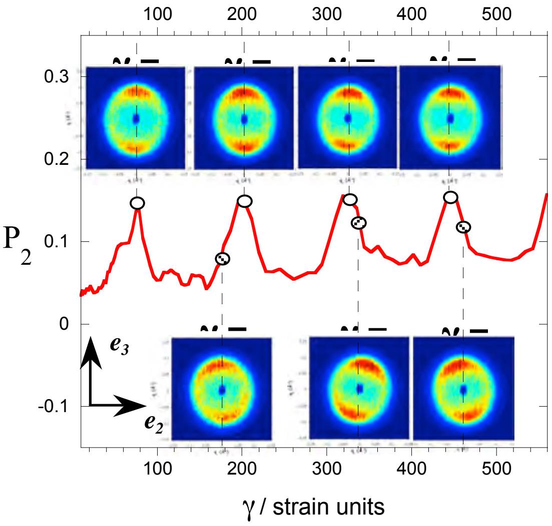
An extensive rheology study of the wormlike micelle system lecithin-water-cyclohexane is carried out together with a combined Rheo-SANS investigation. In this system the micelles, which are long and flexible cylindrical aggregates, break and recombine with no signs of micellar branching, as it has previously been demonstrated by NMR self-diffusion experiments. When branching is highly unfavorable, micelle recombination reactions only involve micelle ends, the concentration of which are very low when the micelles are very long. Hence, the break and recombination kinetics is very slow for true wormlike micelles. In the present system, the stress relaxation times are of the order of an hour. This is about three to four orders of magnitude longer than what commonly is observed in systems claimed to contain wormlike micelles. Larger deformations result in a fracture of the micellar network at a critical strain $\gamma^* \sim \phi^{-1}$, where ϕ is the micelle volume fraction. For $\gamma < \gamma^*$ we may still obtain fracture, although with a lag time, τ^*, that decreases with increasing γ, and vanishes when $\gamma = \gamma^*$. Extrapolating τ^* to zero deformation we estimate $\tau^* \approx 250$ s at the highest concentration $\phi = 0.29$. We interpret this time as the equilibrium micellar breaking time at rest, a quantity not previously measured.





At a concentration near to the zero-shear Isotropic-Nematic phase transition ($\phi = 0.29$), the stress plateau has been found shifted to very low values of the applied shear rate $\dot{\gamma}$, compared to most of the concentrated living polymer systems reported in the literature. Rheo-Small Angle Neutron Scattering (Rheo-SANS) experiments performed in the flow-vorticity plane revealed periodical fluctuations of both the order parameter P_2 and the angular deviation ϕ from the vorticity axis as determined from the scattering peaks. The periods of the oscillations were not found to depend on imposed $\dot{\gamma}$. A theoretical model has been also developed to explain the oscillatory dynamics of the shear-induced nematic order parameter in terms of the presence of standing waves of the director orientation profile along the circumference of the Couette cell. The experimental results of the periodic order parameter fluctuations together with their theoretical modelling shed significant new insights on the shear banding phenomenon, particularly its microscopic mechanism.





References

Olsson, U.; Borjesson, J.; Angelico, R.; Ceglie, A. and Palazzo, G. “Slow dynamics of wormlike micelles”, Soft Matter, 6, 1769-1777 (2010).

Angelico, R.; Oliviero Rossi, C.; Ambrosone, L.; Palazzo, G.; Mortensen K. and Olsson, U. “Ordering fluctuations in a shear-banding wormlike micellar system”, Physical Chemistry Chemical Physics, 12, 8856-8862 (2010).

1B – Hollow polyelectrolyte nanocapsules assembled on liposomal templates

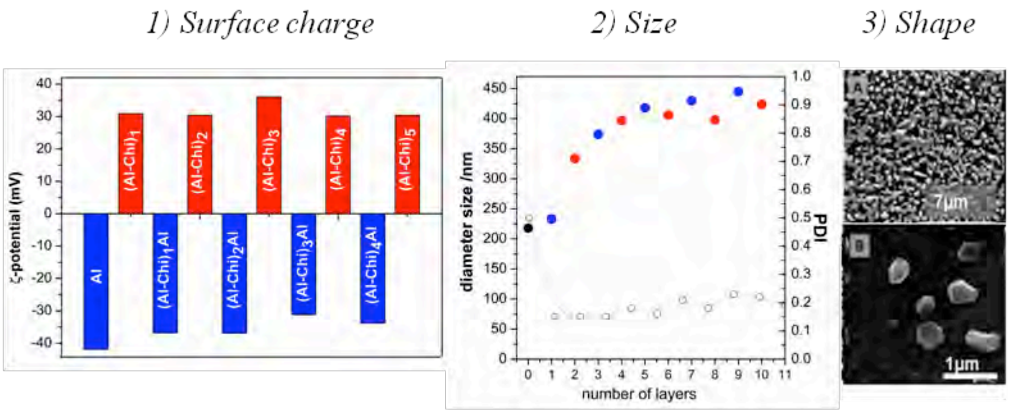
F. Cuomo, F. Lopez, A. Ceglie, B. Lindman (Physical Chemistry, Lund University, Sweden), M.G. Miguel (Dept. of Quimica, Coimbra University, Portugal)

Aims

The main goal is the production of biocompatible nanocapsules useful for drug-delivery applications. We are developing appropriate protocols to assemble biocompatible polyelectrolyte onto liposomal templates with the Layer-by-Layer (LbL) technique.

Results

Hollow spheres on the submicrometer scale (nm) are obtained with the LbL assembly of polyelectrolytes. The polymers alginate and chitosan were alternatively adsorbed on colloidal templates such as vesicles or liposomes made of surfactants or lipids. The vesicle-templated construction offers the advantage of a cheap, easy way to produce core-shell and hollow nanostructures. The core-removal process is based on a vesicle-to-mixed micelle transition determined by the interaction of a nonionic surfactant with the double-chained surfactant forming the vesicles. The obtained nanostructures were characterized by means of DLS, the ζ potential, and SEM in order to establish their size, surface charge, and shape.


1) Surface charge *2) Size* *3) Shape*

1) ζ-potential values with respect to the alternate adsorption of polyelectrolyte layers; 2) Average particle size and PDI with respect to the adsorption of polyelectrolyte layers onto vesicles. The first point refers to the bare vesicles; 3) SEM pictures of nanoparticles with two different magnifications. The dimension of the bar is 7 µm for panel A and 1 µm for panel B.

Moreover, the data collected suggested the hollow nanocapsules are suitable thermostable aggregates and that the presence of high ionic strength (0.4M) does not affect the size of the aggregates. Some characteristics such as the stability of the capsule or the release of loaded molecule in response to the temperature increase are the subjects of investigation in progress.

A further investigation has been started on the polyelectrolyte deposition on liposomal template made of DPPC and DDAB with dimensions of about 85nm and with the adsorption of nucleic acids into the multishell. After the deposition of eight layers the core-shell particles have diameters of 300nm.

References

Cuomo, F.; Lopez, F.; Miguel M.G. and Lindman, B. “Vesicle-Templated Layer-by-Layer Assembly for the Production of Nanocapsules”, Langmuir, 26(13), 10555-10560 (2010).

1B – Hydrogel for human lens substitution

G. Leone, M. Consumi, G. Greco, C. Bonechi, S. Lamponi, C. Rossi, A. Magnani.

Aims

Cataract surgery is the most frequently performed surgical intervention, pursued by replacement of the opacified natural lens by a polymeric intraocular lens (IOL).
This research concerns the synthesis of a new thixotropic poly(vinyl alcohol) (PVA) /poly(N-vinyl-2- pyrrolidinone) (PVP) based hydrogel with the aim of realising a human lens substitute.

Results

The crystalline lens is a viscoelastic tissue. The rheological analysis in terms of the □G*□ value (Tab1), phase shift and dynamic viscosity (Fig 1a and 1b) underlines that PPS31075 hydrogel behaves as a lens substitute. Furthermore, it shows a good accommodation capability since the stress rapidly decays up to 99% within 1 second followed by a much slower decay independently of the strain percentage. In particular, higher the strain higher the residual tension but faster relaxation can be observed (Fig 1c).
Thixotropic behaviour of PPS31075 hydrogel permits to foresee its injectability (Fig 1d).

Table 1: Magnitude of the complex shear modulus |G*| of hydrogels at a frequency of 10Hz

Sample	|G*| (Pa)
PPS31075	57±3
Young human lens*	50*

*: average steady-state moduli

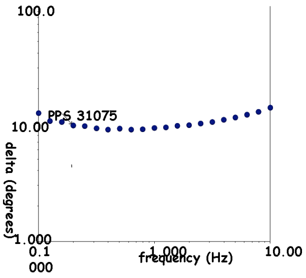


Figure 1a

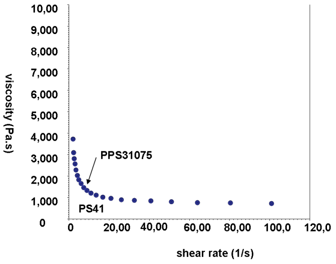


Figure1b

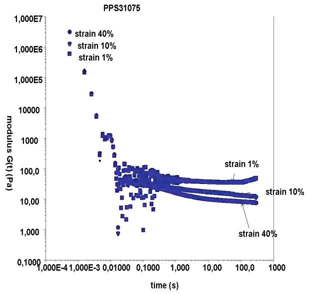


Figure 1c

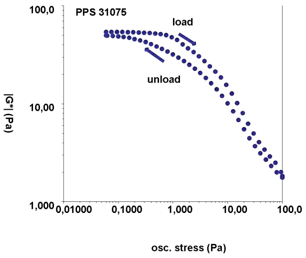


Figure 1d

PPS31075, characterised by very high water content (94.5±2.7%) and transparency (93±1%) and able to inhibit cell adhesion responsible of opacification, shows optimal rheological behaviour comparable to that of young human lens. The obtained results can foresee for the developed material a potential application as human lens substitute.

References

Leone, G.; Consumi, M.; Greco, G.; Bonechi, C.; Lamponi, S.; Rossi, C. and Magnani, A. "A PVA/PVP hydrogel for human lens substitution: synthesis, rheological characterisation and in vitro biocompatibility", J Biomed Mater Res: Part B: Appl Biomater (correcting proof).

1B – Nanostructured media for the synthesis of bio-inspired anionic lipids

R. Angelico, A. Ceglie, I. Losito, F. Palmisano (Dip. Chimica, Univ. Bari)

Aims

Oil-in-Water microemulsions as nanoreactors to produce alkylated nucleobases.
Effect of base-pairing on the reaction of alkylation of complementary ribonucleotides.

Results

Evidences of a subtle role of base-base interaction upon a reaction of alkylation of complementary ribonucleotides – giving rise to their amphiphilic derivatives – have been experimentally obtained in a model ternary microemulsion. The aliphatic epoxide 1,2-Dodecyl-Epoxide (DE) has been used as alkylating agent, which can be finely dispersed in a microemulsion of Oil-in-Water spherical micelles, provided by the cationic surfactant Cetyl-Trimethyl-Ammonium-Bromide (CTAB).

The presence of a charged interface not only overcomes the mutual immiscibility between the apolar epoxide and aqueous solutions of AMP and UMP, but also provides a suitable domain where both reactants meet and react.

The corresponding reaction products have been identified through HPLC-ESI-MS and MS^n as mixtures of mono- and di-chained (α or β hydroxyl) derivatives of the nucleobases, with some peculiar differences depending on whether the starting microemulsions were incubated with AMP, UMP or their equimolar mixture.

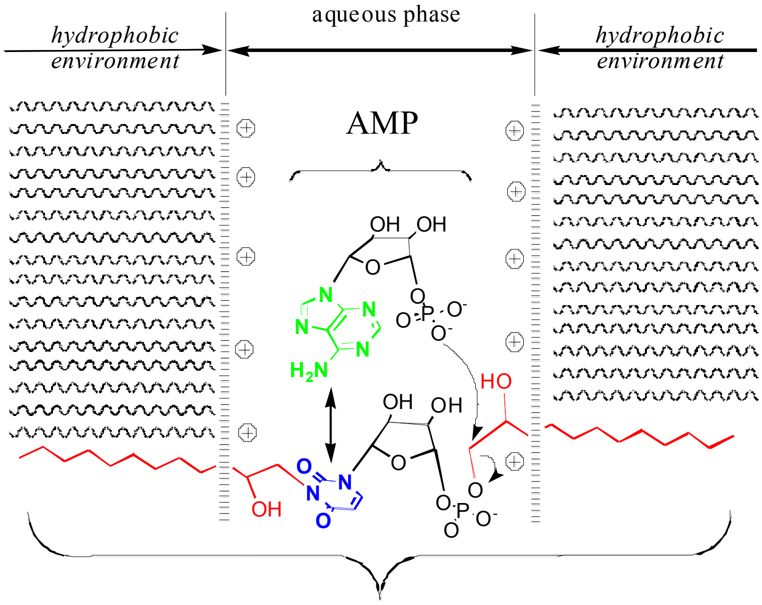
In particular, MS/MS data gave indication about the sites of alkylation occurring, e.g., at level of uracil/phosphate OH groups in doubly-alkylated UMP, whereas in the case of alkylated derivatives of AMP, adenine NH_2 group and phosphate or ribose OH groups were found to be involved as such (single alkylation) or in combination (di-chained products).

In the system incubated with both complementary nucleotides, the absence of α-hydroxyl-derivatives has been considered as a signature of a weak base-base preferential interaction between uridine and adenine nucleobases occurring at micellar interface.

After several days, the initial isotropic microemulsions, incubated with both nucleotides and DE, transformed into milky suspensions identified by optical microscopy as a system of Multi-Layered-Vesicular (MLV) structures.

The interface of these aggregates is constituted presumably by cationic CTAB monomers and the novel anionic mono- and di-chained C_{12}-amphiphiles, bearing nucleobases in their head polar groups.

The major implication of the present study indicates that simple ribonucleotides may give rise to slightly different kinetic mechanisms, for reactions involving complementary nucleobases as reactants themselves. This is a consequence that molecular recognition between UMP and AMP can be significatively achieved in a nanostructured environment, such as micelles and growing vesicles, thanks to favorable cation-π interactions, π–π stacking and electrostatic interactions occurring between the anionic (NMP-ions) guests and the cationic (CTAB-colloidal particle) host.



[2-U]

References

Losito, I.; Angelico, R.; Ceglie, A.; Diomede, S. and Palmisano, F. “Alkylation of complementary ribonucleotides by 1,2-dodecyl-epoxide in a micellar environment: a liquid chromatography–electrospray ionization–sequential mass spectrometry investigation”, Journal of Mass Spectrometry, 44, 1053-1065 (2009).

Angelico, R.; Ambrosone, L.; Ceglie, A.; Losito, I.; De Zio, D. and Palmisano, F. “Complementary amphiphilic ribonucleotides confined into nanostructured environments”, Physical Chemistry Chemical Physics, 28, 7977-7987 (2010).

1B – Nucleic Acid condensation onto nucleolipids doped liposomes

F. Cuomo, F. Lopez, A. Ceglie

Aims

Investigation on the ability to form lipoplexes with liposomes containing nucleolipids and highlighting an eventual crucial role of the nucleobase's derivatives surfactants.

Results

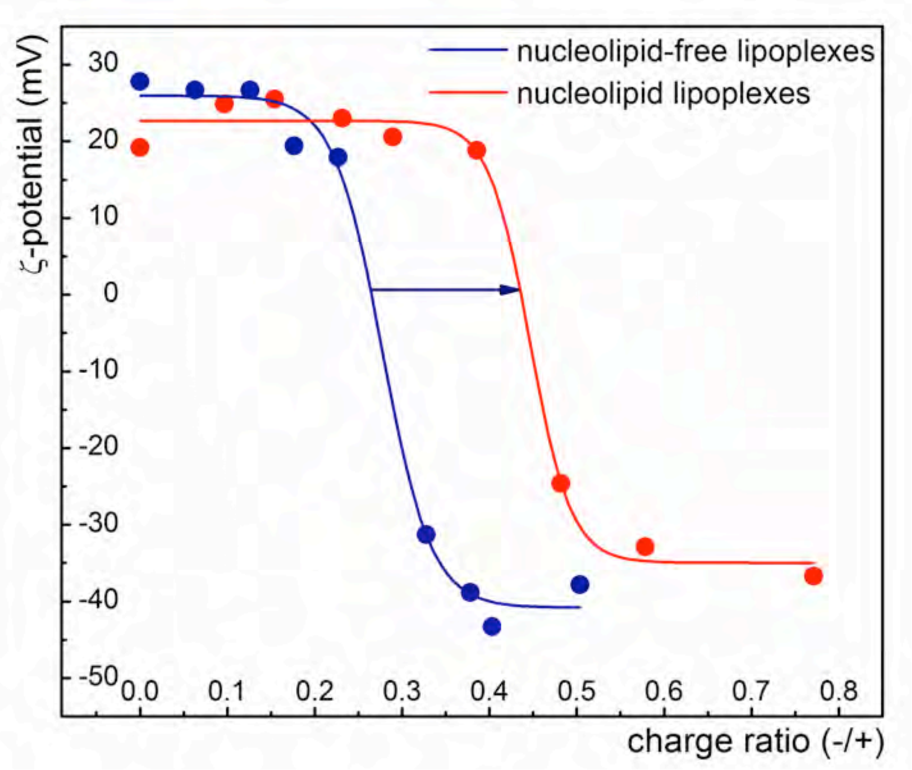
The formulation of complexes obtained with liposomes and nucleic acid (lipoplexes) has been in the last few years and still is of major concern, because of the enormous utilization for items related to the investigation of biotechnological aspects.

In general, the future of non-viral delivery of nucleic acids depends on the understanding of the barriers to delivery. Since, these naked macromolecules are often prone to degradation and do not reach their target site, their formulation needs special care. For instance to produce a successful genetic material delivery the vectors should have nanometric diameters, the particles should be stable and resistant to non-specific uptake in the circulation.

In a previous investigation liposomes containing a novel nucleolipid, the non-ionic amphiphile LU obtained by functionalization of Uridine in the 5' position the existence of a preferential interaction between poly-A and liposome doped with the nucleolipid containing the complementary bases was demostrated by ^{1}HNMR experiments. This study has investigated on several spectral and charge properties of the new LU liposomes and on LU lipoplexes obtained in the presence of the polynucleotide poly-A.

In the current project we also perform ζ-potential and DLS measurements on liposomes containing the lipidic nucleobase's derivatives to investigate on their interaction with anionic polyelectrolytes i.e. oligonucleotides and polynucleotides.

The tritration performed with the addition of DNA onto liposomes cationic surface results in a decreasing of zeta potential. We verify that the zeta potential decreasing allows us to check for the isoelectric point. The point of maximum instability of assemblies corresponds to the charge inversion point where the whole surface charge is neutralized. The positive zeta potentials' region is considered the most efficient concerning the transfection's capabilities. The negative zeta-potential values correspond to the whole cationic vesicles' surface wrapped with the polyanion. Complexes with negative surface charge have reduced tranfection efficiency because of the repulsion interactions with the negative cellular membranes. The graphs reported, as an example, show the charge inversion points on liposomes formulation with and without the nucleolipid and subsequently that the useful amount of adsorbed DNA is shifted toward an higher value in nucleolipid enriched liposomes.



ζ-potential values vs. charge ratio. The figure shows the surface charge inversion with the addition of DNA on liposomal formulation without the nucleolipid (blue points) and with nucleolipid (red points). Liposomes enriched with the nuclebases' derivative allow the binding of higher amount of DNA.

References

Cuomo, F.; Ceglie, A.; Colafemmina, G.; Germani, R.; Savelli, G. and Lopez, F. "Polyadenylic acid binding on cationic liposomes doped with the non-ionic nucleolipid Lauroyl-Uridine", Colloids and Surfaces, B 82, 277-282 (2011).

1B – Photosynthetic Reaction Centers Embedded in Polyelectrolyte Multilayer as an Optical Biosensor for Herbicide Detection

G. Palazzo, M. Giustini, F. Lopez, A. Mallardi (Dip. di Chimica, Università di Bari) G. Venturoli (Dip. BES, Università di Bologna)

Aims

Development of an herbicide biosensor based the bacterial reaction center (a photosynthetic protein) immobilized on glass substrates through layer-by-layer adsorption.

Results

Herbicides are widely used on a variety of crops for the control of broadleaf weeds but can be highly toxic for human and animal health. Their wide use in agriculture has resulted often in the herbicide pollution of water and the level of herbicides allowed in drinking water is subject to regulation, at least in the industrialized countries. Different attempts have been made to introduce biological detection systems in order to overcome the high cost of time consuming HPLC analysis.
Here we present an optical biosensor based on a photosynthetic protein deposited on a quartz surface. The protein is the Reaction Center (RC) purified from *Rhodobacter sphaeroides* and for the preparation of the solid specimen its deposition is alternated with the cationic polymer poly(dimethyl diallyl) ammonium chloride (PDDA). The RC-herbicides interaction can be easily monitored since the steady-state attained by RCs under continuous light is different in the presence and in the absence of an inhibitor as shown in Fig. 1.

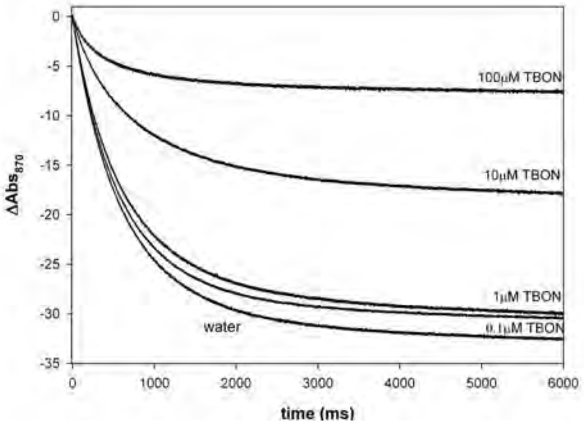


Figure 1. *Time course of RC photobleaching induced by continuous illumination at 870 nm and measured on the same specimen immersed in solutions of herbicide (TBON) at different concentration.*

The bound herbicide can be easily removed from PEM, thus allowing the reuse of the same sample.
The composite material developed has been previously characterized from a physico-chemical point of view.[1] The full characterization of their analytical

properties regarding the broad family of PSII herbicides will be here presented together with the critical evaluation of costs and benefits of their use.

Among the most striking features are the long lifetime of the specimen (> 12 months) and the high reproducibility. The RC layered on quartz can be also used to test potentially active herbicides of new synthesis.

Its long time stability, easiness of handling, low demanding instrumental setup, let the RC/quartz assembly particularly appealing for the realization of a stand alone analytical apparatus.

References

Lopez F.; Mennuni M.; Giustini M.; Giomini M.; Dezi M.; Venturoli G.; Mallardi A. and Palazzo G. “Photosynthetic reaction centers embedded in polyelectrolyte multilayers as a tool in the determination of PSII herbicides”, Proceedings of 2nd IEEE International Workshop on Advances in Sensors and Interfaces, IWASI 2007, Bari 26-27 June 2007, 237-242.

Mallardi A.; Giustini M.; Lopez F.; Dezi M.; Venturoli G. and Palazzo G. “Functionality of Photosynthetic Reaction Centers in Polyelectrolyte Multilayers: Towards an Herbicide Biosensor”, Journal of Physical Chemistry B, 111, 3304-3314 (2007).

Autullo, M.; Mennuni, M.; Giustini, M.; Giomini, M.; Lopez, F.; Mallardi, A. and Palazzo, G. “Triazine herbicides determination in water with an optical biosensor”, Proceedings of 3rd IEEE International Workshop on Advances in Sensors and Interfaces, IWASI 2009, Trani 25-26 June 2009, art. no. 5184798, 213-217.

1B – Self-organizing processes of Amphiphilic Peptides

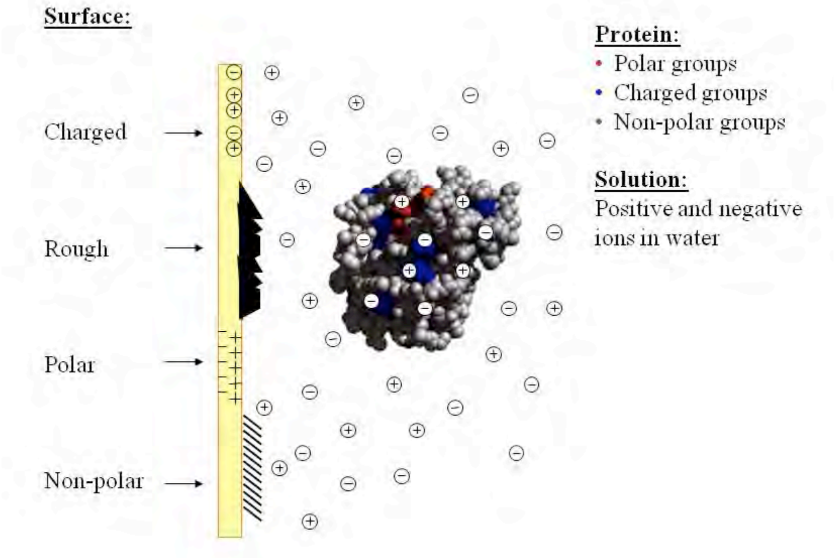
G.M.L. Messina, G. Marletta

Aims

Study of self-organizing processes of amphiphilic peptides

Results

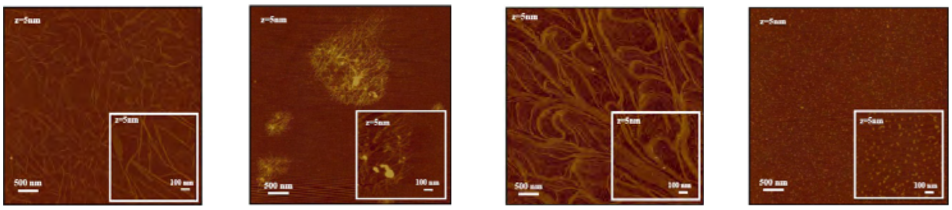
Biomolecules adsorption is a widespread event occurring at biological interfaces. There is a general tendency for biomolecules to accumulate spontaneously at aqueous interfacial regions. This tendency is due to the large number of atoms in biomolecules and their large size compared to possible single binding sites on the surface. This allows peptides to expose several sites that can interact with a surface and the exposed sites might change in number and nature. The transition of biomolecules from the bulk of the liquid to the adsorbed state may pass through a number of intermediate states, with changing conformation and/or orientation of protein. The figure below shows the complexity of the biomolecules-adsorption process, considering a protein molecule with different charge and surface with different region of roughness, charge, polarity, etc…



Peptides consisting of alternated hydrophilic and hydrophobic amino acids have a natural tendency to generate ordered structures by self-assembling, a property which makes them promising materials for synthetic scaffolds in the preparation of artificial tissues and biosensors. Self-assembling oligopeptides belong to a novel class of biomaterials that has been recently discovered. These materials are self complementary amphiphilic oligopeptides that have regular repeating units of positively charged residues (lysine or arginine) and negatively charged residues (aspartate or glutamate) separated by hydrophobic residues (alanine or leucine). The alternation of polar and non polar pending groups and of positively and negatively charged residues makes self-complementary amphiphilic peptides capable of self-assembling.

Molecular self-assembly has become a widely used method for fabrication of biological and biocompatible structures at the nano- and micrometer range. In particular, amphiphilic peptides have been shown to self-assemble into a variety of cylindrical nanostructures, with diameter of a few nanometer and micrometer scale lengths. In the present paper the self-assembling behavior on surfaces of two classes such peptides, both composed of alanine (A), Aspartic acid (D) and Lysine (D), with different structure has been studied by using Atomic Force Microscopy. These compounds were a 5-amino acid amphiphilic peptide (AcA_4DOH), characterized by single tail, and a 10-amino acid one ($(AcA_4)_2KDOH$) having a double tail. The peptides showed different organization patterns ranging from unstructured round shape aggregates to 1D-wires. The following surfaces of different wettability and charge state have been investigated: mica as reference surface, two positively charged polyelectrolyte surfaces, polyethylenimine and poly(diallyl dimethylammonium) chloride, and a negative one, poly(sodium styrene sulfonate). The effect of pH values on the aggregation state of the single and double-tail peptides has been also investigated. The self-organization process is shown to be severely affected by the type of peptide and surface properties, including specifically the charge state at a given pH.

The results strongly support a self-assembly mechanism based onto a very specific organization processes at the liquid-solid interface, based onto the active role played by the surfaces to promote the orientation and organization of single molecules as the prime processes at nanometer scale, followed by the aggregation process at the mesoscopic scale.



References

Baumann, M.K.; Textor, M. and Reimhult, E.; “Understanding Self-Assembled Amphiphilic Peptide Supramolecular Structures from Primary Structure Helix Propensity”, Langmuir 24 (15), 7645-7647, (2008).

Deng, M.; Yu, D.; Hou, Y. and Wang, Y. “Self-assembly of Peptide-Amphiphile C12-Aβ (11-17) into Nanofibrils”, J Phys Chem B. 113(25), 8539-8544, (2009).

Jiang, H.; Guler, M. O. and Stupp, S. I. “The internal structure of self-assembled peptide amphiphiles nanofibers”, Soft Matter 3, 454-462, (2007).

Shera, J. N. and Sun, X.S. “Effect of Peptide Sequence on Surface Properties and Self-Assembly of an Amphiphilic pH-Responsive Peptide” Biomacromolecules 10 (9), 2446–2450, (2009).

1B – Nanostructuring of surfaces: tunable size nanopores

G.M.L. Messina, G. Marletta

Aims

The aim of this work is to develop new techniques to achieve reproducible and cost-effective chemical and topographical patterns of polymeric and silicon substrates at nanometer scale for biological application. In particular, two-dimensional (2D) porous substrates are developed for a wide range of applications including chemical microcontainers, surface-plasmon resonance biosensors, catalytic supports and photonic crystals. including as nanocontainers, trapping sites, etc… Two main requirements were defined: flexibility in terms of lateral pattern dimension, which is indeed ranging from the micrometer to the sub-micrometer scale, and the compatibility with respect to preservation of biological activity of the adsorbed biomolecules.

Results

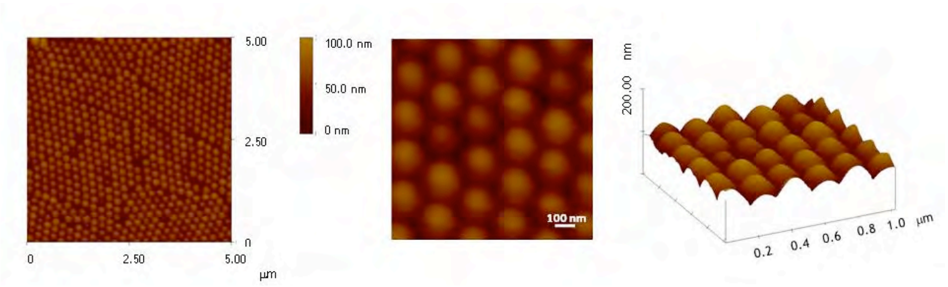
Today nanoscience is fed from a number of subdisciplines: nanoelectronics, nanomaterials, molecular nanotechnology, bionanotechnology and development of tools for analysis, especially scanning probe microscopies all contribute. The development of nanoelectronics and materials mostly relies on top-down methodology. Molecular and bionanotechnology have a more bottom-up approach.

A pure self-assembly approach towards spatial organization, to provide a complementary paradigm to the currently available top-down methodologies, including lithographic techniques, would in itself be a very desirable goal. Other parameters like cost and ease of fabrication only seem to be speaking more in favor of such an approach. Self-assembly, defined as the spontaneous, thermodynamically controlled, organization of individual molecules into a (meta) stable and (spatially) well-defined aggregate usually is a complicated and not very well understood phenomenon.

It critically relies on a delicate interplay of many interactions, often of different nature. It is exactly for this reason that self-assembly approaches have been put forward as an alternative to top-down methodology in nanotechnology. Self-assembly promises to be a cheap and potentially extremely easy methodology to decorate surfaces with all kinds of interesting templates. In general it would be highly desirable to be able to control interfacial properties, as interfaces play such a prominent role in many processes, e.g. in catalysis, molecular recognition, and as sites of nucleation, both in natural and synthetic systems.

We present a versatile and simple approach for rapidly fabricating nanopatterned surfaces on micrometer scale. Monodisperse silica nanoparticles were spin-coated onto gold surfaces.

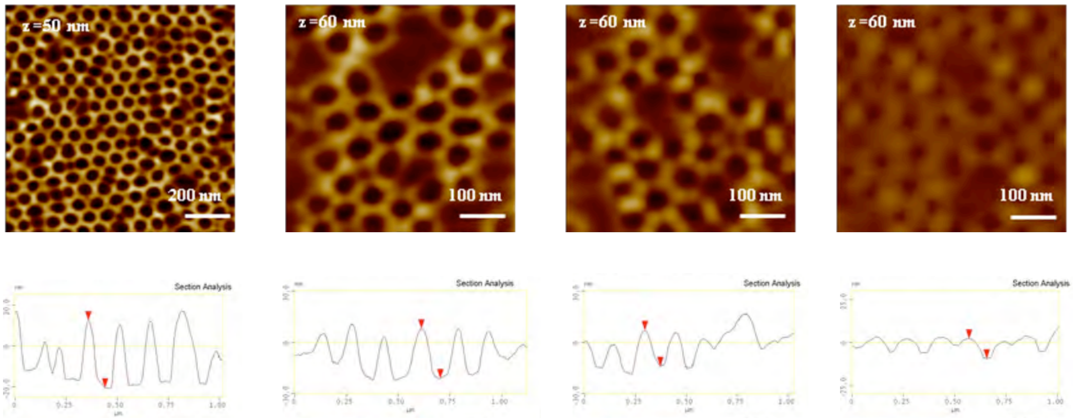
Silica spheres, with an average diameter (D) in the range of 147-403 nm, self-organised in the classical bidimensional hexagonal lattice structure. The produced arrays are in general not perfect, as intrinsic point and line defects appear in the resulting structure. Typically, defect-free domains have size in the 10-50 μm2 range.



AFM image of 2D and 3D hexagonal silica spheres on gold substrate.

A polymer layer is then deposited on samples, embedding the nanoparticle distribution. Finally, the selective removal of the silica nanospheres leads to the formation of nanostructured micron-sized area. The nanopatterned surfaces consisted of 2D nanopore arrays, having internal area of gold surrounded by polymeric matrix. The nanopores depth can be modulated by using UV-ozone treatment, in particular by increase time treatment, decrease pore depth.

The preferential adsorption of proteins, e.g., Human Lactoferrin (Lf) and Human Serum Albumin (HSA), having different physico-chemical properties, was investigated onto the nanostructured surfaces prepared from different spin-coated polymers. The adsorption was studied as a function of the pore geometrical features, including volume, aspect ratio and diameter, as well as the chemical contrast. The driving chemical factors were identified in terms of surface free energy gradients and chemical termination of the pore bottom and walls.



References

Xia, D.; Li, D.; Luo, Y. and Brueck, S. R. J. “An Approach to Lithographically Defined Self-Assembled Nanoparticle Films”, Adv. Mater. 18, 930-933 (2006).

Cheung, C.L.; Nikolíc, R.J.; Reinhardt, C.E. and Wang, T.F. “Fabrication of nanopillars by nanosphere Lithography”, Nanotechnology 17, 1339-1343 (2006).

Jiang, P. “Wafer-scale fabrication of periodic polymer attolitre microvial arrays”, Chem. Commun., 1699-1701 (2005).

1B – Nanopatterned surfaces by LB phospholipid/polymer films

G.M.L. Messina, G. Marletta

Aims

The aim is to obtain the fabrication of well-ordered mesoscopic structural surfaces over large areas by the LB technique, which focused on obtaining uniform and defect-free films. Dynamic self-organization and template-directed self-assembly may be able to successfully control and modify the surface patterning. The mesoscopic structural surfaces may serve as a platform in engineering the biological/material interface.

Results

The formation of patterned surfaces is a universal and fascinating phenomenon in nature, for example, regular stripes on the surface of zebras and the wings of butterflies. Moreover, surface patterning has become an increasingly important part in modern science and technology, such as in the areas of micro-electronics, information processing and storage, nano/microfluidic devices, and biodetection. Fabrication and investigation of patterned surfaces are active areas of research in chemistry, physics, materials science, and biology. Methods used for pattern fabrication are commonly summarized as “top–down” and “bottom–up”.

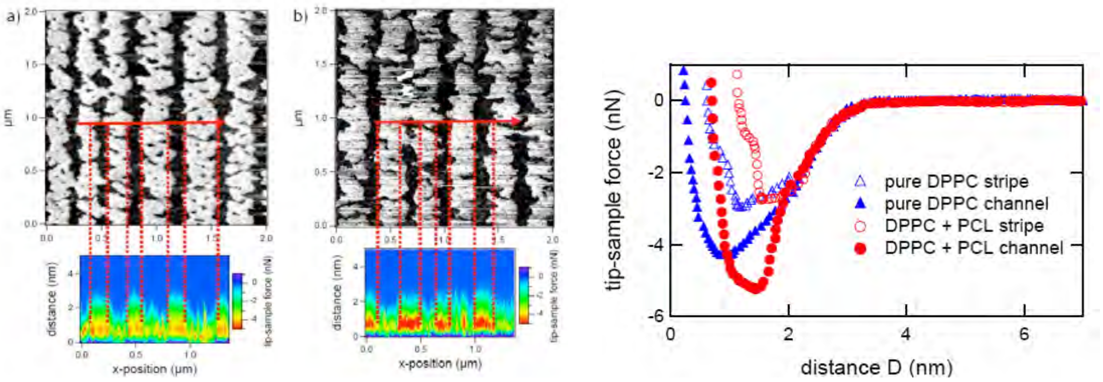
The Langmuir–Blodgett (LB) technique is a well established and sophisticated method to control interfacial molecular orientation and packing. Moreover, it is an efficient approach toward the controllable fabrication of laterally patterned structures on solid supports, termed LB patterning. Laterally structured LB monolayers are normally generated by the deposition of ordered two-dimensional (2D) domains formed at the air–water interface onto solid substrates

Langmuir-Blodgett technique was used to obtain a regular patterned large-area with mesostructured features. This strategy uses a simple fabrication technique to control the alignment, size, shape, and periodicity of self-organized phospholipid monolayer patterns with feature sizes down to 100 nm over surface areas of square centimeters. Because of the anisotropic wetting behavior of the patterns, they can be used as templates to direct the self-assembly of functional molecules and nanocrystals. The described mesoscopic structured surfaces may serve as a platform in engineering the biological/material interface and constructing biofunctionalized structures.

L-α-dipalmitoylphosphatidylcholine (DPPC) was used to obtain a regular patterning of surface on nanometer scale. DPPC, one of the major lipid components of biological membranes, shows a typical phase behavior of a Langmuir monolayer at the air-water interface, characterized by a liquid-expanded (LE) phase, a liquid-condensed (LC) phase, and a LE-LC phase transition, as visible by the surface pressure-molecular area (π-A) isotherm. In the LE phase, the DPPC monolayer behaves as a quasi-2D liquid, where the head groups of DPPC molecules are translationally disordered and chains are conformationally disordered. When the molecular areas are decreased, DPPC molecules begin to condense and a co-existing phase of LE and crystalline LC occurs at the plateau region of the isotherm. Finally, a homogeneous well-packed condensed monolayer (LC phase) appears at larger molecular areas. This fabrication approach uses the LB transfer process to induce phase transitions and create pattern near the three-phase contact line from a homogeneous DPPC Langmuir monolayer at the LE phase. The resulting mesostructured DPPC, detected on surfaces by an atomic force microscope (AFM), consists of alterning stripes with widths of about 800 nm separated by channels of about 200 nm in width .

The height difference between the stripes and channels is about 1 nm, and the stripes are composed of condensed (LC phase) DPPC molecules. The length of a DPPC molecule is about 2 nm, so it can be possible to attribute the material in the channels to the expanded (similar to LE phase) DPPC molecules, which are characterized by a larger tilt angle compared to condensed DPPC molecules in the stripe. This hypothesis can be confirmed by tip-sample interaction forces by using dynamic force spectroscopy. The size and shape of the DPPC patterns can be controlled by simply adjusting the transfer velocity, surface pressure, temperature, substrate chemistry, monolayer composition and transfer method.

The striped pattern formation of the mixed monolayers of L-α-dipalmitoylphosphatidylcholine (DPPC) and poly-ε-caprolactone (PCL) onto a mica surface by Langmuir-Blodgett (LB) transfer have been investigated. The addition of the second component, PCL, strongly affects the formation of DPPC stripe patterns in term of pressure and transfer rate values. Self-assembled monolayers of DPPC and DPPC/PCL adsorbed on mica are examined by dynamic force spectroscopy under ambient conditions. By a systematic recording of the frequency shift caused by the tip–sample interaction we determine the corresponding tip–sample potential and force curves. Due to the systematic mapping of the tip–sample interaction it is possible to compute contour maps of the tip-surface potential of the DPPC films and to extract local properties like contact stiffness and adhesion force.



References

Chen, X.; Chen, Z.; Fu, N.; Lu, G. and Yang, B. Adv. Mater. "Versatile nanopatterned surfaces generated via three-dimensional colloidal crystal" 15, 1413-1417 (2003).

Chen, X.; Lu, N.; Zhang, H.; Hirtz, M.; Wu, L.; Fuchs, H. and Chi, L. "Langmuir-Blodgett Patterning of phospholipid microstripes: effect of second component", J. Phys. Chem. B 110, 8039-8046 (2006).

Schmutz, J.-E.; Hölscher, H.; Ebeling, D.; Schäfer, M.M. and Anczykowski, B. "Mapping the tip-sample interactions on DPPC and DNA by dynamic force spectroscopy under ambient conditions", Ultramicroscopy 107, 875-881 (2007).

1B – Hybrid bilayer by sputtered gold nanoparticles onto diblock-copolymer template

V. Torrisi, G. Marletta

Aims

1) Directing gold nanopartcles onto block copolymer template;
2) Investigation of the effect of thermal treatments on the organization of the hybrid bilayers;
3) Understanding and exploiting conductive properties of hybrid bilayers.

Results

The polymers/nanoparticles mixing opens routes for engineering flexible composites that exhibit unique electrical, optical, or mechanical properties. The interactions between block copolymers and NPs can lead to highly organized hybrid materials.

Recent advances in the patterning of polymers have enabled to fabricate integrated micro- and nanosystems with high degree of functionality. For example, block copolymers have attracted huge interest for nanotechnology applications because of easy processability. The immiscible polymer blocks in block copolymers microphase separate. This soft nano and micro-structured polymer film can further be used as a template for patterning of hard inorganic materials such as metal NPs.

Patterning of metal NPs within polymer films has been achieved using many routes. The first method is vapour phase co-deposition of polymers/nanoparticles in high vacuum followed by thermal annealing.[1] Annealing of the polymer film above the glass transition temperature (*T*g) of the polymer allows structural relaxation of the polymer matrix and was proven to be responsible for the dispersion of the metal nanoparticles within the polymer film. The second method is based on the deposition from a mixture of block copolymer and organic-coated nanoparticles in solution onto a solid surface followed by the annealing step.[2] The third method employs the dewetting of polymer films made from low concentrations of mixed solutions of polymer and polymer-grafted nanoparticles to create metal nanostructures.[3] The fourth method uses the self-organization characteristic of evaporated nanoparticles on a self-assembled polymer film to create nanopatterning by selective adsorption.[4]

Our method consists in using the self-organization characteristic of sputtered NPs on a self-assembled block-copolymer film.

Physical vapour deposition methods, in particular sputtering process, are one of the promising methods used for preparing nanocomposite films in a dry system.

Horizontal precipitation Langmuir-Blodgett (HP-LB) method allows us to obtain nano and microstructured thin films of diblock copolymer. [5, 6]

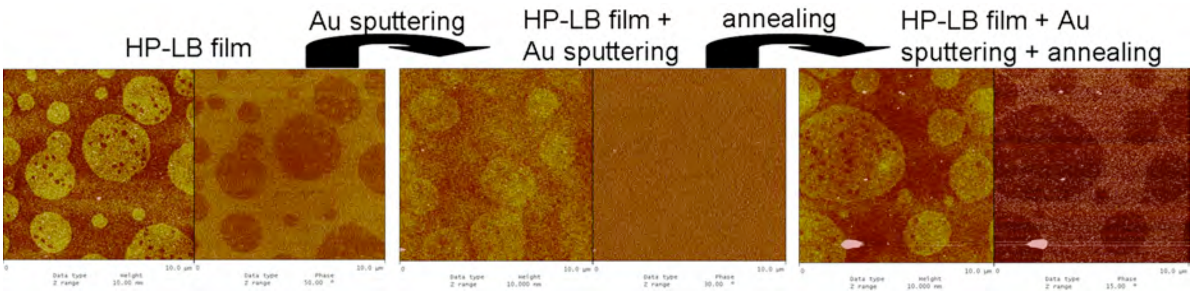


Figure 1. AFM images of HP-LB film of pnBA-b-pAA, of the same film after sputtering and after annealing.

In this work, we use the sputtering technique to investigate the behaviour of gold onto self assembled diblock copolymer film obtained by HP-LB method. We studied the morphology and the phase-separation of the PAA-*b*-PnBuA film before and after gold sputtering. To understand the effect of the increased mobility of the polymer chain onto the organization of gold atoms the behaviour of the bilayer after heating at $T>T_g$ has been also studied.

The nanoparticles distribution onto the block copolymer domains, studied by Atomic Force Microscopy and Time of Flight Secondary Ion Mass Spectrometry, seems strongly affected by the bilayer annealing. In particular, hybrid bilayers exhibit memory effects as a conseguence of thermal annealing. Such effects are proved by morphological and compositional experimental evidence of Au NPS/Block copolymer hybrid bilayer and can be explained by the hypothesis that take into account a modified surface-tip interaction induced by thermal annealing. Such hypothesis is supported by the comparison of the nanomorphologies of the block copolymer film, of hybrid bilayer and annealed hybrid bilayer showed in the AFM images. In fact, after thermal annealing, above Tg temperatures of both of the blocks, the uppermost modified nanostructered gold layer become sensitive to the immediately underlying block copolymer film, probably due to the increased diffusion of gold onto diblock copolymer film during the annealing (higher mobility of polymer chains) and, in particular, sensitive to polar and non polar chains of two blocks. Furthermore, annealing at T >Tg doesn't induce polymer mixing between two blocks or between blocks and gold.

Finally the conductive properties of these film have been explored, the electrical behaviour shows a Schottky-like I-V characteristics, suggesting the formation of hybrid polymer-metal junctions.

References

[1] Takele, H.; Schurmann, U.; Greve, H.; Paretkar, D.; Zaporojtchenko, V. and Faupel, F., Eur. Phys. J. Appl. Phys. 33, 83-89 (2006).

[2] Lauter-Pasyuk, V.; Lauter, H. J. ; Ausserre, D.; Gallot, Y.; Cabuil, V.; Hamdoun, B. and Kornilov, E.I., Physica B, 248, 243-245 (1998).

[3] Abul Kashem, M.M.A.; Perlich, J.; Schulz, L.; Roth, S.V.; Petry, W. and Müller-Buschbaum, P., Macromolecules 40, 5075-5083 (2007).

[4] Lopes, W.A., Phys. Rev. E 65, 031606 (2002).

[5] Torrisi, V.; Licciardello, A. and Marletta, G., Materials Science and Engineering B, 169, 49-54 (2010).

[6] Torrisi, V.; Tuccitto, N.; Delfanti, I.; Audinot, J.N.; Zhavnerko, G.; Migeon, H.-N. and Licciardello, A., Applied Surface Science 255, 1006-1010 (2008).

1B – Substrate Induced Ordering in Poly(3-hexylthiophene) Thin Crystalline Films

G. Li Destri, F. Punzo, G. Marletta

Aims

Tuning the crystalline ordering in polymeric ultrathin films.

Results

The effect of two different substrates, a strongly hydrophilic one and a strongly hydrophobic one, on the crystalline structure of thermally annealed poly(3-hexylthiophene) (P3HT) thin films was investigated by atomic force microscopy (AFM) and grazing incidence X-ray diffraction analysis (GIXRD). Annealing above the melting temperature of the polymer produced numerous polymer lamellar crystals in both cases [1]. However, the average orientation of the lamellae markedly differed as a function of the interfacial energy with better reciprocal and in plane orientation of the lamellae onto hydrophobic substrate than on hydrophilic one. Fast Fourier Transform (FFT) of AFM images shows indeed a preferential direction of repetition of closely packed lamellae on hydrophobic substrates (Fig. 1).

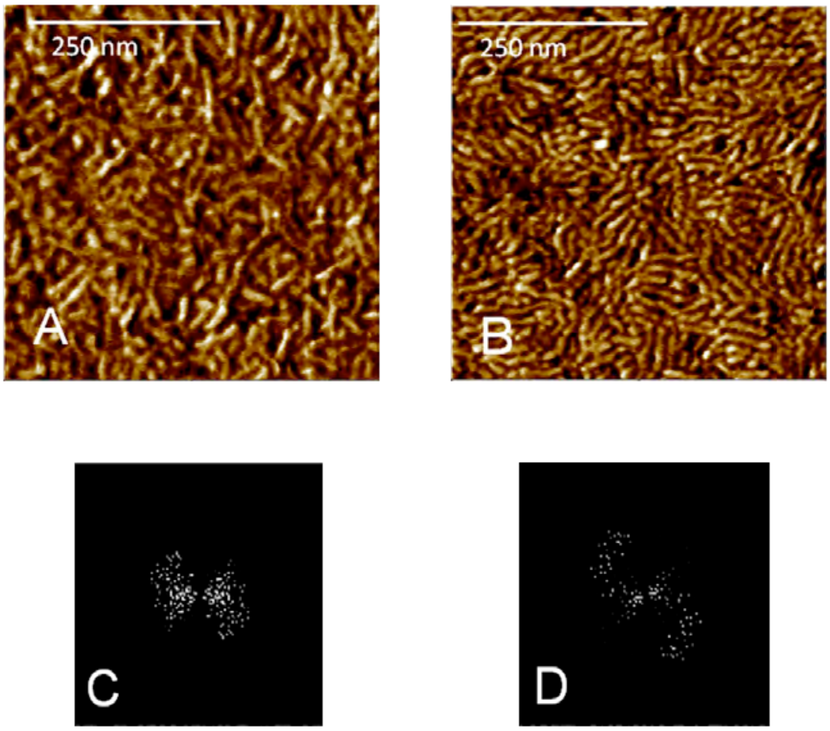


Figure 1. 500 nm x 500 nm AFM phase pictures of P3HT films annealed at 250°C on hydrophilic (A) and hydrophobic (B) substrates and the corresponding 2-D Fast Fourier Transform (C and D). The outer part of FFT spectra show isotropic (random) distribution of lamellae on hydrophilic substrate and anisotropic distribution on hydrophobic one.

Rocking curves of lamellar <100> peak (Fig. 2) reveal a more parallel orientation of lamellae with respect to the hydrophobic substrate plane too.

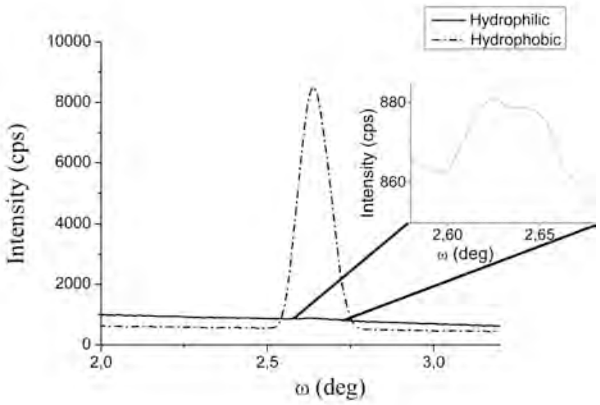


Figure 2. Rocking curves of 100 peak of 250°C annealed P3HT films on hydrophilic and hydrophobic substrate. The much higher signal to noise ratio reveals a better "edge on" orientation of lamellae on hydrophobic substrate. In the inset is shown the very weak peak of rocking curve on hydrophilic substrate

The effect is interpreted in terms of the markedly different interface free energy between the polymer and the two substrates as proved by means of static contact angle measurements. Because of the lower interface free energy between the polymer and the hydrophobic substrate the molecular mobility is enhanced [2] thus leading to the more efficient observed crystallization in terms of both in plane and reciprocal orientation. The model was further confirmed by slowing the cooling rate after annealing, i.e. by increasing the molecular mobility, on hydrophilic substrate, leading to crystalline ordering comparable with the one found for fast cooled hydrophobic substrate. Interestingly the ordering effect of the substrate nature is kept also when film thickness exceeds the single lamella thickness thus suggesting a sort of vertical lamellar packing. To our best knowledge, the reported data are the first experimental evidence of the propagation of substrate-induced lamellar orientation to the polymer-atmosphere interface. This ordering effect may cause the observed increased efficiency of P3HT based field effect transistors when hydrophobic dielectric are employed: it is indeed known that crystal in-plane orientation [3], grain boundaries [4] and interconnectivity [5] have beneficial effects on FET mobilities, the second effect being probably the most relevant, due to the predominant contribution of intra-chain processes to the overall charge transport mechanism [6].

References

[1] Sirringhaus, H.; Brown, P.J.; Friend, R.H.; Nielsen, M.M.; Bechgaard, K.; Langeveld-Voss, B.M.W.; Spiering, A.J.H.; Janssen, R.A.J.; Meijer, E.W.; Herwig, P. and De Leeuw, D.M., Nature, 401, 685-688 (1999).
[2] Fryer, D.S.; Peters, R.D.; Kim, E.J.; Tomaszewski, J.E.; De Pablo, J.J.; Nealey, P.; White, C.C. and Wu, W., Macromolecules, 34, 5627-5634 (2001).
[3] Kline, R.J.; McGehee, M.D. and Toney, M.F., Nat. Mater., 5, 222-228 (2006).
[4] Jimison, L.H.; Toney, M.F.; McCulloch, I.; Heeney, M. and Salleo, A., Adv.Mater., 21, 1568-1572 (2009).
[5] Yang, H.; Shin, T.J.; Cho, K.; Ryu, C.Y. and Bao, Z., Adv. Funct. Mater., 15, 671-676 (2005).
[6] Lan, Y.K. and Huang, C.I., J. Phys. Chem. B, 112, 14857-14862 (2008).

1B – Interfacial Free Energy and Nanostructuring of Poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric Acid Methyl Ester Thin

G. Li Destri, F. Punzo, G. Marletta

Aims

Structural characterization of thin films.

Results

We have investigated the effect of the substrate/film interfacial free energy on the nanostructuring process of annealed poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) composite thin films. Recent studies have shown the effect of substrate on the vertical phase separation [1,2] of P3HT-PCBM as a critical parameter in the design of high efficiency cells but no attention has been paid to the effect of interfacial free energy on the phase separation degree. In this work we have studied the phase separation and crystalline evolution of P3HT:PCBM thin films annealed at different temperatures respectively onto strongly hydrophobic and strongly hydrophilic substrates.

At any given annealing temperature up to 250 °C, the phase separation degree resulted higher for hydrophilic substrates than for hydrophobic ones (Fig. 1).

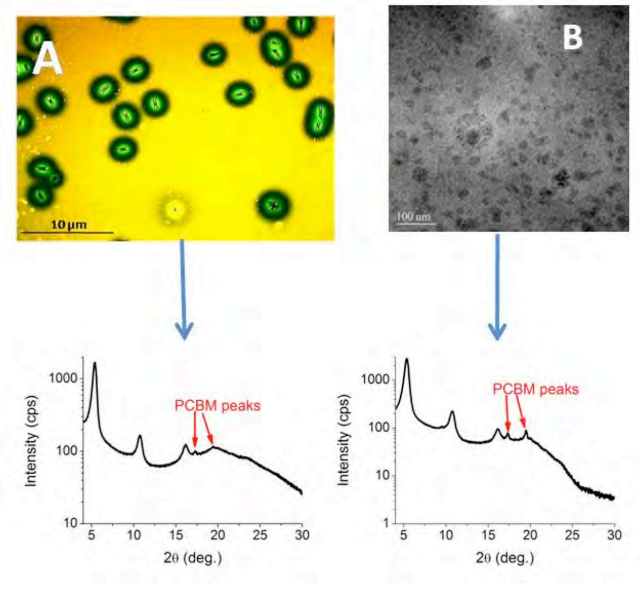


Figure 1. Microscopic (A) and nanoscopic (B) phase separation of 200°C annealed P3HT:PCBM thin films on hydrophilic (A) and hydrophobic (B) substrates. Below the two corresponding diffractograms show a better degree of crystallinity of PCBM on the hydrophobic substrate.

Moreover, better crystalline structure of PCBM aggregates as well as better in plane orientation of P3HT polymeric lamellae (Fig.2) were observed on hydrophobic substrates.

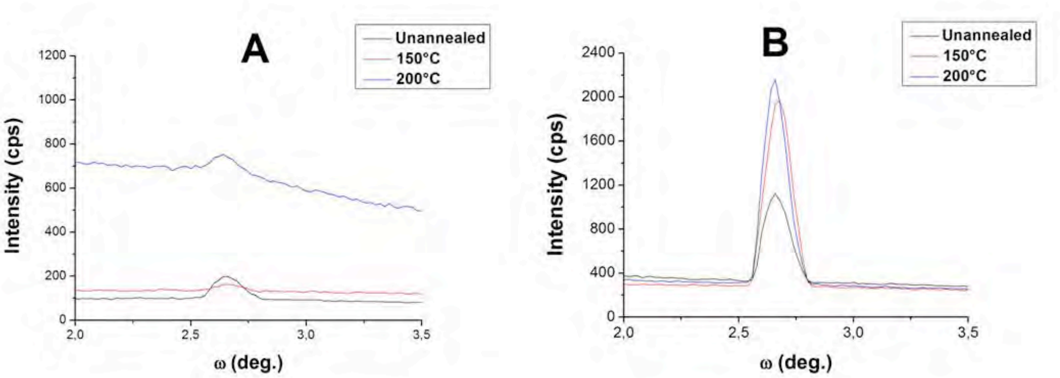


Figure 2. Rocking curves of 100 P3HT peak in P3HT/PCBM thin films on hydrophilic (A) and hydrophobic substrate (B) annealed at different temperatures. The much higher signal to noise ratio reveals a better "edge on" orientation of lamellae on hydrophobic substrate with increasing temperature. On the contrary on the hydrophilic substrate thermal annealing decrease the in-plane order of P3HT lamellae.

The effect is explained in terms of the different interface free energy between substrates and thin film. In P3HT-PCBM thin films, PCBM molecules may quickly migrate away from the high surface free energy substrates, i.e., the hydrophilic ones, increasing their concentration at the film-air interface and causing a strong phase separation. This suggests that developing high efficiency solar cells implies the tailoring of the substrate nature in view of both the different P3HT crystals orientation as well as the extent of PCBM phase separation. The very limited, if any, phase separation onto hydrophobic substrates would in fact allow higher annealing temperature than on hydrophilic ones, leading to higher crystallinity and in turn to higher light absorption yield and conductivity without any loss in charge transfer. In fact, the occurrence of a large phase separation, deriving from the PCBM diffusion, is well known to be the limiting process in high efficiency solar cells [3].

References

[1] Campoy-Quiles, M.; Ferenczi, T.; Agostinelli, T.; Etchegoin, P.G.; Kim, Y.; Anthopoulos, T.D.; Stavrinou, P.N.; Bradley, D.D.C. and Nelson, J., Nature Materials, 7, 158-164 (2008).

[2] Yao, Y.; Hou, J.H.; Xu, Z.; Li, G. and Yang, Y., Advanced Functional Materials, 18, 1783- 1789 (2008).

[3] Nguyen, L.H.; Hoppe, H.; Erb, T.; Günes, S.; Gobsch, G. and Sariciftci, N.S., Advanced Functional Materials, 17, 1071-1078 (2007).

1B – Soft membranes for specific surface recognition

M. Banchelli, F. Gambinossi, D. Berti, G. Caminati and P. Baglioni

The self-organization of molecules leads to supramolecular systems and is responsible for their functions. Liquid-crystalline membranes are such functional units formed by self-organization and they are a prerequisite for the development of life and the ability of cells to function. In this regard we discuss the molecular architecture of two examples of functionalized phospholipid membranes with specific recognition properties, as new materials in nanotechnology and as well as for the simulation of biomembrane processes. In fact we performed a systematic study on the anchoring of cholesterol-tagged oligonucleotides to phospholipids bilayers followed by membrane-assisted hybridization of the complementary strand in solution. By exploring a wide range of oligonucleotide-derivative concentrations, different peculiar scenarios emerge at different hydrophobicity of the amphiphilic DNA guest molecules on phospholipid vesicles (Fig. 1), in terms of distribution and conformation of the single strand and consequent coupling properties with the complementary strand in solution.[1]

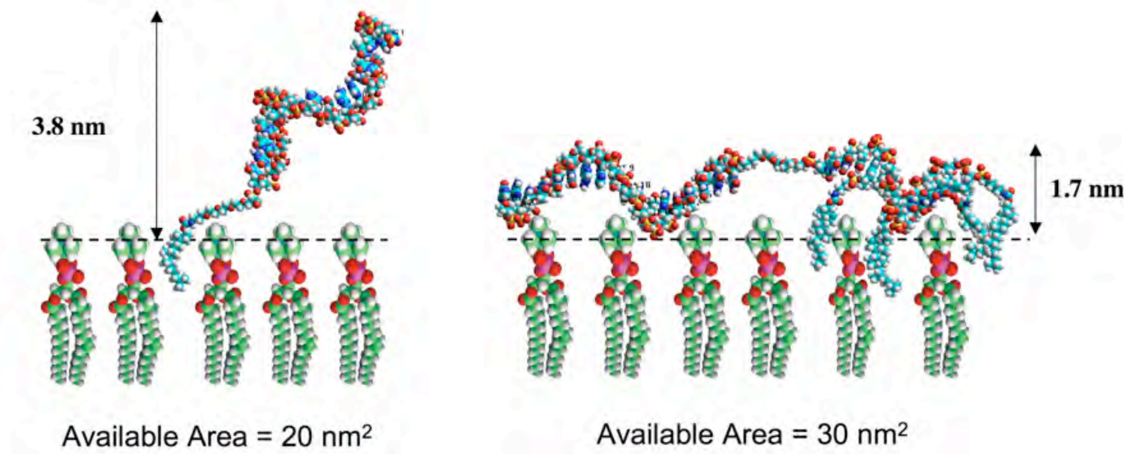


Figure 1. Oligonucleotide anchorage to supported lipid bilayers of POPC: by changing the number of the anchoring function and the concentration of the added solution we can control the grafting density of the oligonucleotide and the single strand orientation

As a second example we considered a model membrane system for the selective recognition of glucosides [2] in aqueous environment, obtained by the incorporation of an alkylic pyrrolic receptor in POPC vesicles. Preliminary results showed that the membrane-assisted interaction between receptor and glucoside in the bilayer of complementary vesicles leads to the formation of clusters and aggregated states of the vesicles (Fig. 2).

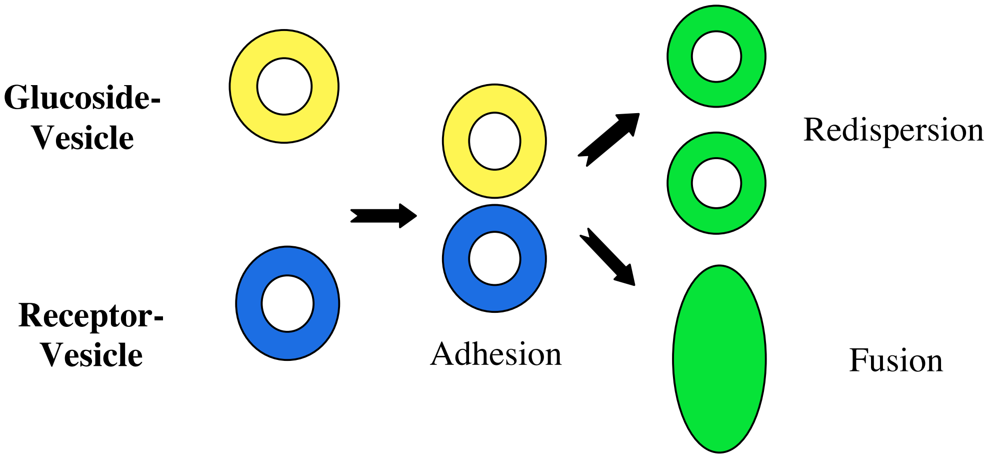


Figure 2. Scheme of the interaction between complementary Glucoside/POPC and Receptor/POPC vesicles. Glucoside and Receptor are synthetic amphiphiles incorporated into the vesicle membranes and interacting through several hydrogen bonds and electrostatically.

References

Banchelli, M.; Gambinossi, F.; Durand, A.; Caminati, G.; Brown, T.; Berti, D. and Baglioni, P. “Modulation of density and orientation of amphiphilic DNA on phospholipid membranes. II. Vesicles”, The Journal of Physical Chemistry B, 114, 7348-7358 (2010)

Gambinossi, F.; Banchelli, M; Durand, A.; Berti, D.; Brown, T.; Caminati, G. and Baglioni, P. “Modulation of density and orientation of amphiphilic DNA on phospholipid membranes. I. Supported lipid bilayers”, The Journal of Physical Chemistry B, 114, 7338-7347 (2010).

Nativi, C.; Cacciarini, M.; Francesconi, O.; Moneti, G. and Roelens, S. “A β-Mannoside-Selective Pyrrolic Tripodal Receptor”, Organic Letters 9, 4685-4688 (2007).

1B – Surface Imaging of Nanostructures

G. Caminati, F. Gambinossi, M. R. Martina

Aims

A synergic combination of different imaging techniques such as Confocal Laser Scanning Microscopy (CLSM), Brewster Angle Microscopy (BAM), Ellipsometric mapping and conventional Atomic Force Microscopy (AFM) can be successfully used to describe the structural organization and the bidimensional morphology of thin films at liquid and solid interfaces as well as spherical nanostructures.

Results

Mapping of the ellipsometric thickness is an invaluable tool in the characterization of functional nanodevices such as Organic Solar Cell devices (OPC) and Organic Light Emitting Diodes (OLED), since this measurement allows the discrimination between homogenous surfaces and domains with poor emission efficiency. Ellipsometric measurements support and complement other imaging techniques such as CLSM and AFM as shown in figure 1.

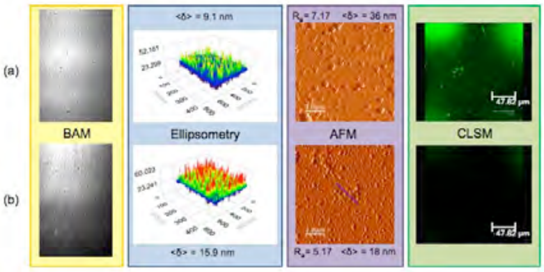


Figure 1. Comparative description of a nanodevice of MPS-PPV (a) and MPS-PPV/NC60 (b) for Polymer Solar cells applications by means of different imaging techniques.

In particular, Brewster Angle Microscopy (BAM) offers unique possibilities to explore the bidimensional morphology of ordered nanofilms at water-air interface identifying surface phase transitions and domains with different molecular packing or orientation. On the other hand, although the CLSM technique is widely used in biological studies, it also represents a precious tool for the investigation of nanostructures such as LB, LbL films or Supported Bilayers (see for example 1A - Multilayered Nanostructures for OLED devices and 1A – Third generation solar cells: nanostructures fabrication of polymer heterojunction and DSSC cells).

High-resolution surface imaging studies of nanostructured films can be easily performed also with conventional AFM techniques, representative results obtained for polymer nanofilm fabricated by means of the LB technique are reported in figure 2.

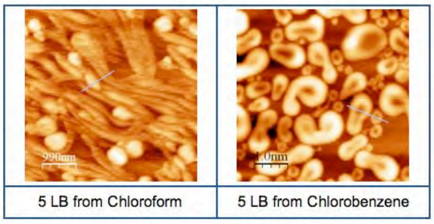


Figure 2. AFM images (5 μm x 5 μm) of PKV nanofilm for OLED applications.

Imaging of spherical nanostructures as nanoparticles, nanocapsules and Giant Unilamellar Vesicles is easily accomplished by CLSM technique provided a suitable fluorescent probe is inserted in the system. Examples of Ru(II) containing polyelectrolyte nanocapsules and of arrays of core-shell nanoparticles for OLED applications are described in figure 3.

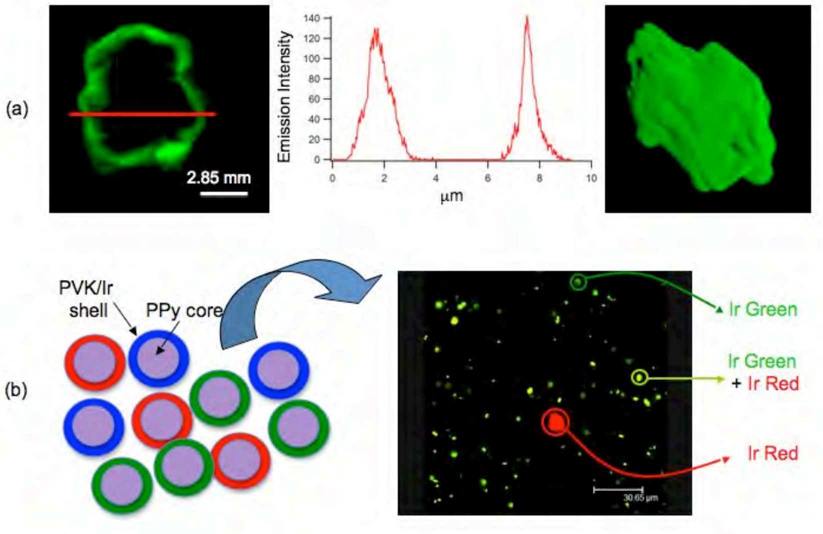
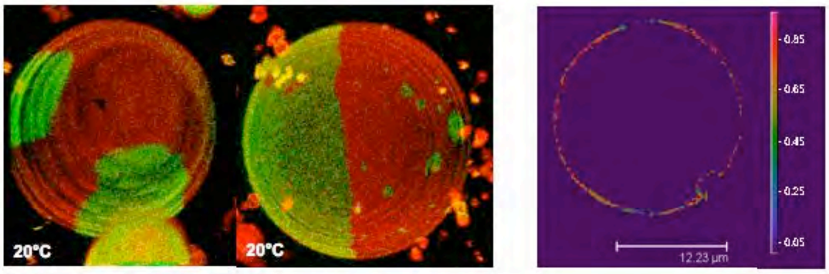


Figure 3. (a) PAH/PSS Nanocapsules containing a Ru(II) complex. (b) Surface mixture of core-shell NPs of PPy/PVK with different Iridium complexes.

Direct visualization of lipid domains of different fluidity can be easily achieved with CLSM imaging of the surface of GUVs (Giant Unilamellar Vesicles), in this case the fluorescent probes are selected to give preferential partition only in one of the two phases. Typical results obtained for DSPC/DOPC/Chol (36:36:28) system are reported in figure 4 together with a Fluorescence Resonance Energy Transfer (FRET) analysis of the surface. Such information is of unvaluable importance in the study on lipid rafts formation or bilayer-protein interactions in biomimetic membranes.



(a) (b)

Figure 4. (a) CLSM images of liquid-ordered and liquid-disordered phopholipid domains in Giant Unilamellar Vesicles. (b) FRET imaging of the same system.

CLSM imaging also allows for the detection of thermoreversible phase domain separation in the bilayer depending on the lipid composition and on their relative concentration.

1B – The Boron Neutron Capture Therapy: a new perspective for osteosarcoma

L. Ciani, S. Bortolussi [1], G. Martini, L. Panza [2], S. Altieri [1], S. Ristori
[1]Dip. di Fisica Nucleare e Teorica, Univ. Pavia
[2]Dip. Scienze Chimiche, Alimentari, Farmaceutiche e Farmacologiche, Univ. Piemonte Orientale

Aims

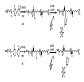
This project opens a new issue in BNCT, by applying this therapy to osteosarcoma, due to the intrinsic infiltrative properties of this sarcoma. The principal aims of this project are the design and characterization of improved boronated-nanovectors, the establishment of the conditions for clinical applications and the onset of clinical research by planning patient irradiation at the TRIGA facility in Pavia.

Results

Boron Neutron Capture Therapy is an anticancer radiotherapy whose fundamental characteristics is selectivity, i.e. the possibility to bombard cancer cells, while sparing healthy ones. This treatment is mainly based on boron fission and features the accumulation of ^{10}B in tumor cells with subsequent neutron irradiation of the region around the tumor by a thermal neutron beam. Selectivity is ensured by higher absorption of boronated molecules in tumor tissues with respect to normal ones. This project open a new issue in BNCT by applying this therapy to osteosarcoma, due to the intrinsic infiltrative properties of this sarcome and to the major incidence of this tumor in young people. Nowadays, with the introduction of pre- and post-operative chemotherapy, the survival of patients affected by osteosarcoma has been sensibly increased. New surgical techniques allow to avoid the limb amputation and to perform, instead, "limb salvage" operations. However, in spite of expectations increase in the cure of osteosarcoma, the mean survival percentage is not higher than 60%. It would be useful, then, to experiment a new therapeutic approach inorder to increase the survival of the young osteosarcoma patients, limit the recurrences and allow a less aggressive surgery.

Our experience and perspective will be especially focused on bioconjugated borocompounds carried by nanosize vectors, such as liposomes and other nanoparticles. The rationale for using this systems as carriers for anticancer agents, is the high permeability of blood vessels in tumors. The mechanisms by which particles with typical size in the range 10-200 nm are preferentially accumulated in tumor tissues is Enhanced Permeability and Retentions (EPR effect). Tumor tissues generally do not develop a lymphatic system and this favors the accumulation of drugs in the tumor itself.

In latest years, we have prepared and characterized liposome-based formulations loaded with lactose and porphyrazine molecules, which have given encouraging results in comparison with borophenilalanine (BPA), which is the standard borocarrier for clinical trials. In particular, the use of cationic liposomes increased the cellular concentration of ^{10}B by at least 30 times more than that achieved by BPA in murine



carcinoma cell cultures, with negligible toxic effects. [1].

In this project our main task will be the design and preparation of new therapeutic formulations as carriers of BNCT-active compounds. We decided to exploit the ability of poly(ethylene oxide)-*b*-poly(e-caprolactone) (PEO-b-PCL) block copolymers to self-assemble into micelles in aqueous solution for boron delivery to tumor cells. These formulations are currently being characterized and tested in order to optimize their application to osteosarcoma *in vitro* and *in vivo*. The newly synthesized block copolymer micelles, containing polyethylene oxide as hydrophilic crown and carborane cages as hydrophobic core. These carriers are able to prevent interaction with cytokines, thus prolonging the circulation time *in vivo* [2].

Preliminary physico-chemical characterization of these micelles evidenced a remarkable stability of both polymersunder different conditions of osmotic pressure and temperature tested in order to mimic a physiological environment. This is a fundamental pre-requisite for *in vitro* administration as well as for *in vivo* long circulation time.

References

Altieri, S.; Balzi, M.; Bortolussi, S.; Bruschi, P.; Ciani, L.; Clerici, A.M.; Faraoni, P.; Ferrari, C.; Gadan, M.A.; Panza, L.; Pietrangeli, D.; Ricciardi, G. and Ristori, S. "Carborane derivatives loaded into liposomes as efficient delivery systems for Boron Neutron Capture Therapy", J. Med. Chem. 52 (Centennial Issue), 7829-7835 (2009).
Campo, F.; Panza, L.; Morel, S.; Jessica, E.; Ciani, L. and Ristori, S. "Synthesis of self-assembled boronated nanoparticles for BNCT", Proceeding 14th ICNCT, Buenos Aires (Argentina) (2010).

1B – Clusters in Concentrated Lysozyme Protein Solutions

E. Fratini, Y. Liu (NIST), L. Porcar (ILL), P. Baglioni

Aims

The comprehension of the phenomenon of protein clustering is of fundamental importance in various diseases and in new promising routes for drug delivery based on storing high concentrated functioning protein.

Results

Neutron spin echo (NSE) and small angle neutron scattering (SANS) were used to investigate the correlation between structure and short-time dynamics of lysozyme solutions. It was found that, upon increasing protein concentration, the self-diffusion coefficient at the short time limit becomes much smaller than that of the corresponding hard-sphere and charged colloidal suspensions at the same volume fraction. Contrary to literature conclusions, we find that, at relatively low concentrations, the system consists mostly of monomers or dimers, while, at high concentrations, large dynamic clusters dominate.[1] From the estimation of the mean square displacement by using short-time and long-time diffusion coefficient measured by NSE and NMR, we find that these clusters are not permanent but have a finite lifetime longer than the time required to diffuse over a distance of a monomer diameter.

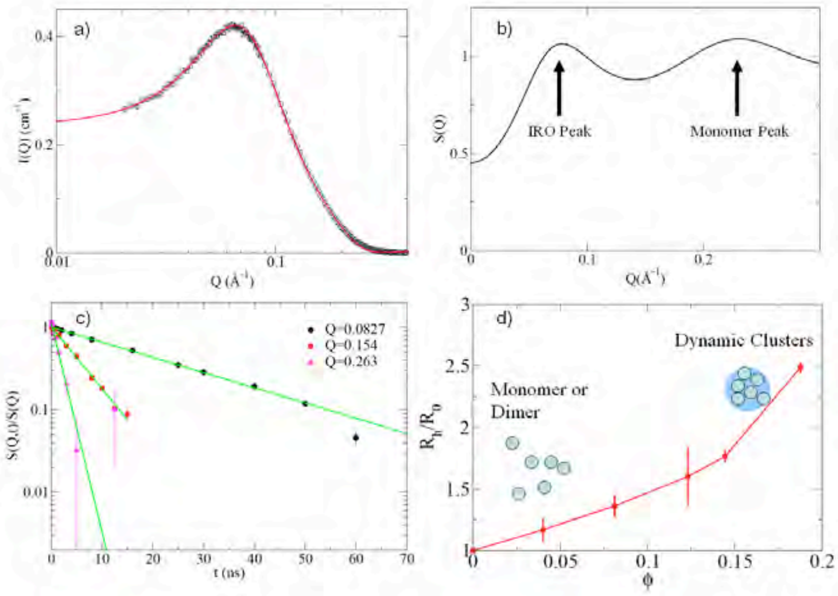


Figure 1. Panel a): Fitting curve (solid line) together with the experimental points of 5 wt% lysozyme solution measured by SANS. Panel b): Extracted inter-particle structure factor, S(Q), for the 5 wt% sample. Panel c): S(Q,t)/S(Q) vs t in the Q range 0.08 to 0.26 Å^{-1} as extracted by NSE on the 5 wt% sample. Panel d): Normalized hydrodynamic radius as a function of protein volume fraction.

By using statistical mechanics models[2], it is clear that the appearance of a low-Q peak is not a signature of the formation of clusters. Rather, it is due to the formation of an intermediate range order structure governed by a short-range attraction and a long-range repulsion.

References

Porcar, L.; Falus, P.; Chen, W. R.; Faraone, A.; Fratini, E.; Hong, K. L.; Baglioni, P. and Liu, Y. “Formation of the Dynamic Clusters in Concentrated Lysozyme Protein Solutions”, Journal of Physical Chemistry Letters, 1, (1), 126-129 (2010).

Liu, Y., Porcar, L.; Chen, J.; Chen, W.-R.; Falus, P.; Faraone, A.; Fratini, E.; Hong, K. and Baglioni, P. “Lysozyme Protein Solution with an Intermediate Range Order”, J. Phys. Chem. B, ASAP (2011).

1B – Self assembly of chiral surfactants

P. Lo Nostro, M. Ambrosi, E. Fratini, V. Mazzini, B.W. Ninham, P. Baglioni

Aims

Effect of chirality on self assembly, different kinds of hydration water.

Results

Chirality plays a crucial role in molecular recognition and in other functions that pertain to higher hierarchical structures, especially in biological systems. Alkanoyl-L-(+)-Ascorbic acid esters act as radical scavengers like Vitamin C (Figure 1), and can be easily dispersed in hydrophobic or aqueous media.

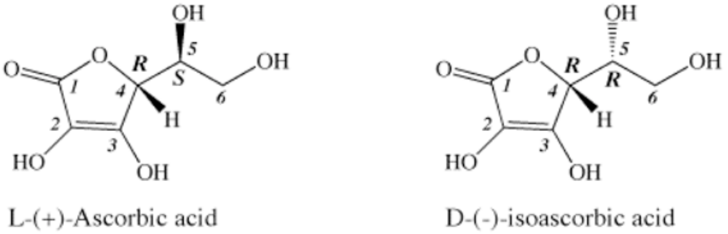


Figure 1. Molecular structures of L-ascorbic (left) and D-isoascorbic acid (right), showing the atom numbering and the configuration of the chiral centers (C_4 and C_5).

We synthesized single chained, double chained, and bolaform surfactants that bear either L-ascorbic or D-isoascorbic acid residues as polar headgroups (Figure 1). Depending on their structure and temperature, these derivatives form different nanoassemblies in water. Single chain surfactants produce micellar solutions or gels, depending on the side chain length, and upon cooling form hydrated crystalline phases (*coagels*) (Figure 2) [1]. The bolaamphiphile forms monodispersed nanotubes in aqueous dispersions [2], while the more hydrophobic double chain surfactant produces stable organogels [3].

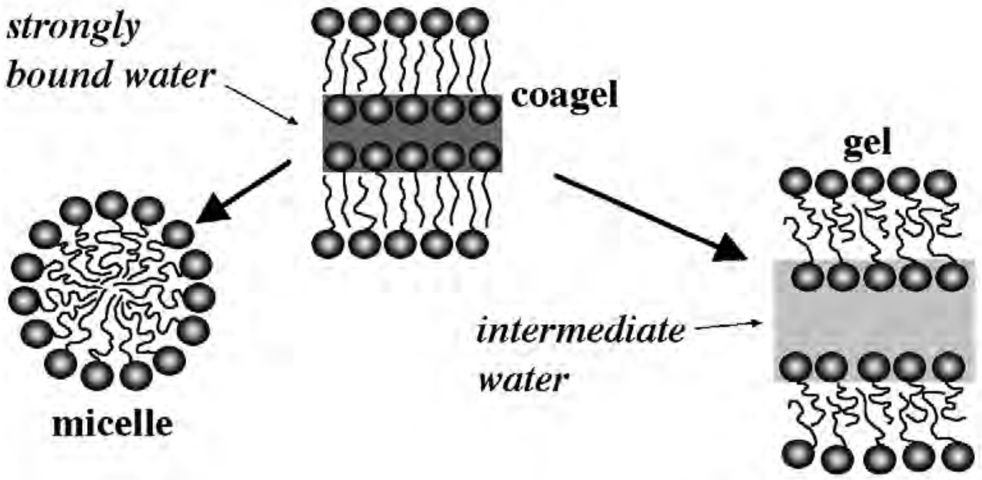


Figure 2. Structures formed by the single-chained surfactants in water dispersions, and different kinds of hydration water.

These nanoassemblies have been carefully studied through SAXS, XRD, DSC, SEM, surface tension isotherms, and conductivity experiments. [1-4].

We explored the properties of single chain surfactants that carry a D-(-)-Isoascorbic acid moiety (Figure 1) as polar headgroup. The amphiphilic derivatives D-ASCn produce the same kinds of nanoaggregates in water, but present significantly different properties from the epimeric L-isomers, due to the different sets of inter- and intramolecular interactions that involve the surfactant molecules and the solvent [5]. Interestingly, D-ASCn and L-ASCn produce eutetics in the pure and in the coagel state [6].

More recently the coagel and gel phases formed by the two diastereoisomer derivatives were studied through solid state NMR. The dynamic properties of water and surfactant chains were investigated by 2-H and 13-C NMR static spectra, respectively. Two different kinds of water were found in the coagel phase, due to the strongly-bound and bulk water. Only one kind of "intermediate" water was found in the gel phase, suggesting that the merging of the two types of water in the interlayers between the surfactant lamellae occurs at the coagel-to-gel transition [7].

References

[1] Lo Nostro, P.; Ninham, B.W.; Fratoni, L.; Palma, S.; Manzo, R.; Allemandi, D. and Baglioni, P. "Effect of Water Structure on the Formation of Coagels from Ascorbyl-Alkanoates", Langmuir 19, 3222 (2003).

[2] Ambrosi, M.; Fratini, E.; Alfredsson, V.; Ninham, B.W.; Giorgi, R.; Lo Nostro, P. and Baglioni, P. "Nanotubes from a Vitamin C-Based Bolaamphiphile", J. Am. Chem. Soc. 128, 7209 (2006).

[3] Lo Nostro, P.; Ramsch, R.; Fratini, E.; Lagi, M.; Ridi, F.; Carretti, E.; Ambrosi, M.; Ninham, B.W. and Baglioni, P. "Organogels from a Vitamin C-Based Surfactant", J. Phys. Chem. B 111, 11714 (2007).

[4] Ambrosi, M.; Lo Nostro, P.; Fratoni, L.; Dei, L.; Ninham, B.W.; Palma, S.; Manzo, R.; Allemandi, D. and Baglioni, P. "Water of hydration in coagels", Phys. Chem. Chem. Phys. 6, 1401 (2004).

[5] Ambrosi, M.; Lo Nostro, P.; Fratini, E.; Giustini, L.; Ninham, B.W. and Baglioni, P. "Effect of headgroup chirality in nanoassemblies. Part 1. Self-assembly of D-isoascorbic acid derivatives in water", J. Phys. Chem. B 113, 1404 (2009).

[6] Lo Nostro, P.; Ambrosi, M.; Fratini, E.; Ninham, B.W. and Baglioni, P. "Effect of headgroup chirality in nanoassemblies. Part 2. Thermal behavior of Vitamin C-based surfactants", J. Phys. Chem. B 113, 8324 (2009).

[7] Borsacchi, S.; Ambrosi, M.; Lo Nostro, P. and Geppi, M. "Understanding the properties of the coagel and gel phases: a 2-H and 13-C NMR study of amphiphilic ascorbic acid derivatives", J. Phys. Chem. B 114, 15872 (2010).

1B – Self-Assembly of β-Cyclodextrin in Water. Formation of Pseudopolyrotaxanes.

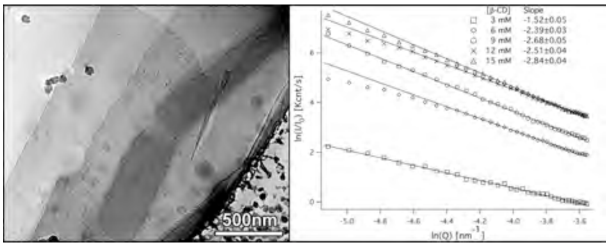
M. Bonini, S. Rossi, P. Lo Nostro, L. Giustini, P. Baglioni,
G. Karlsson[1], M. Almgren [1]
[1]: Dept. Physical Chemistry, Uppsala University, Sweden

Aims

Although cyclodextrins (CDs) have been extensively studied for more than four decades, the self-aggregation of cyclodextrins in water has been postulated only recently. The aim of this investigation is to confirm the presence of supramolecular assemblies in b-CD/water dispersions, and to evaluate the main structural and geometrical features of such mesoscopic structures, through dynamic and static light scattering, cryo-TEM, and electron spin resonance experiments. The formation and precipitation of pseudopolyrotaxanes obtained from a- or b-CD and linear polymers were investigated through turbidity and SAXS measurements.

Results

Our results definitely confirm that β-CD monomers do aggregate in water at room temperature in differently shaped particles, depending on the concentration. A critical aggregation concentration (c.a.c.) between 2 and 3 mM was determined by using Dynamic (DLS) and Static (SLS) Light Scattering. Above 3 mM, aggregates are formed in water, with a minimum hydrodynamic radius of about 90 nm. These particles are in equilibrium with larger objects at higher solute concentrations. Transmission Electron Microscopy at cryogenic temperature (Cryo-TEM) was used to detect the structural features of cyclodextrin self-aggregates.

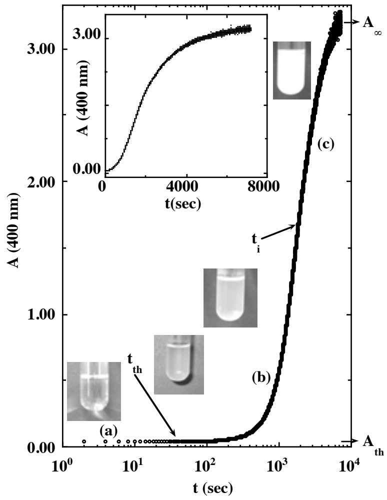


Left: Cryo-TEM micrograph showing the planar aggregates formed by β-CD in water . Right: Static Light Scattering results of β-CD solutions in water.

The results show the occurrence of polymorphism depending on the β-CD concentration: polydisperse objects with diameters of about 100 nm are present at lower concentrations, while micrometer planar aggregates are predominant at higher concentrations. Upon sonication, the large bidimensional sheets turn into entangled long fibers and folded lamellae. Static light scattering experiments were performed to evaluate the fractal nature of the particles.

In order to explore the aggregation of β-cyclodextrin in water and its influence on the inclusive properties, the interaction of amphipilic spin labels with b-cyclodextrin has been investigated using conventional electron spin resonance (ESR) spectroscopy. Stearic acid spin probes (n-DSA) which contain a doxyl group, a cyclic nitroxide with unpaired electrons, covalently linked to the aliphatic chain carbon in position 5, 7, 12 or 16 were used. The most relevant finding from the ESR experiments is the detection of two spectral components differing in line-width, and thus in dynamics. The faster ESR component (Component 1), which was detected in all the investigated n-DSA/b-CD systems, has been simulated in order to extract the dynamic and polarity properties experienced by the spin probes (t, <A>).

The formation and precipitation of pseudopolyrotaxanes (PPR) were studied through turbidimetric and SAXS experiments. The formation and growth of the PPRs can be interpreted in terms of the Avrami model. The precipitation of large structures depends on the nature of the guest polymer. The aggregation of the PPRs was explained in terms of spatial dielectric anisotropy.



The effects of dissolved gases and electrolytes have been investigated also.

References

Bonini, M.; Rossi, S.; Karlsson, G.; Almgren, M.; Lo Nostro, P. and Baglioni, P. "Self-Assembly of β-Cyclodextrin in Water. Part 1: Cryo-TEM and Dynamic and Static Light Scattering", Langmuir 22, 1478 (2006).

Rossi, S.; Bonini, M.; Lo Nostro, P. and Baglioni, P. "Self-Assembly of β-Cyclodextrin in Water. 2. Electron Spin Resonance", Langmuir 23, 10959 (2007).

Lo Nostro, P.; Giustini, L.; Fratini, E.; Ninham, B.W.; Ridi, F. and Baglioni, P. "Threading, Growth, and Aggregation of Pseudopolyrotaxanes", J. Phys. Chem. B 112, 1071 (2008).

Becheri, A.; Lo Nostro, P.; Ninham, B.W. and Baglioni, P. "The Curious World of Polypseudorotaxanes: Cyclodextrins As Probes of Water Structure", J. Phys. Chem. B 107, 3979 (2003).

Ceccato, M.; Lo Nostro, P. and Baglioni, P. "α-Cyclodextrin/Polyethylene Glycol Polyrotaxane: A Study of the Threading Process", Langmuir 13, 2436 (1997).

1B – Nucleolipid-based DNA vectors: complexation with nucleic acids and interaction with cell membrane model systems.

C. Montis, P. Baglioni, D. Berti

Aims

Preparation of DNA vectors based on anionic nucleolipid liposomes. Investigation on DNA complexation process and on the structure of nucleolipoplexes. Interaction of nucleolipoplexes with cell membrane model systems.

Results

The complexation of DNA by anionic liposomes mediated by multivalent cations is of outmost interest for the application of these non-cytotoxic vectors in gene therapy. The study of anionic nucleolipid liposomes is of particular relevance in this context, for the possibility to use specific interactions between nucleolipid polar heads and DNA nucleobases.

Previous studies in our group highlighted, both in solution and in low-water content regime, the presence of specific interactions between nucleolipid assemblies and nucleic acids attributable to a molecular recognition process between nucleobases and nucleolipids polar headgroups complementary according to Watson and Crick, notwithstanding the electrostatic repulsion between systems all negatively charged.

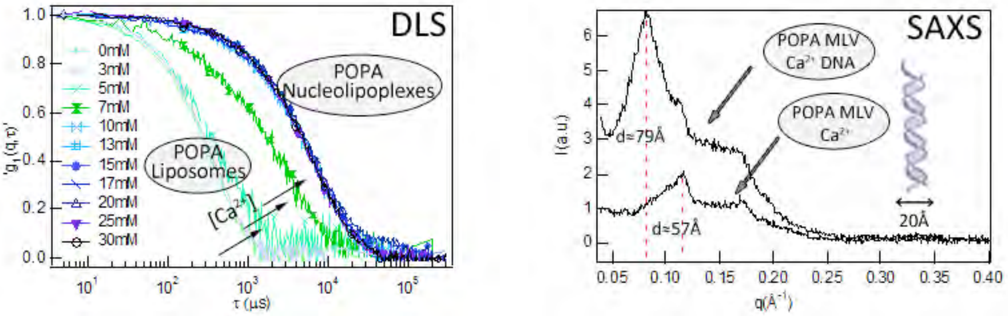


Figure 1. POPA Nucleolipoplexes formation followed by DLS with increasing Ca^{2+} concentration *(left)* and by SAXS with the comparison of POPA MLV-Ca^{2+} SAXS patterns before and after the addition of DNA *(right)*.

We prepared anionic nucleolipids' liposomes containing POPA mixed with different zwitterionic "helper" lipids, POPC or DOPE, efficient nucleic acids complexation was achieved with a contribution of divalent cations, capable to bridge phosphate groups of nucleic acids' backbone and on liposomal surface. QELS measurements on POPA liposomes/Ca^{2+}/polyU samples revealed the presence of large aggregates attributable to the formation of nucleolipoplexes. Interestingly, the molecular recognition interaction between polyU uridine monomeric units and POPA adenosine was found to be strictly necessary to achieve polyU complexation, for similar samples containing the common anionic phospholipid POPG instead of POPA didn't show the formation of complexes for any Ca^{2+} amount added. DNA complexation process can be followed through QELS and ζ-potential measurements, to investigate POPG lipoplexes' and POPA nucleolipoplexes' size and charge, factors that strongly affect transfection efficiency and cytotoxic effects, as a function of liposomes' surface charge density tuned with the anionic/zwitterionic lipid molar ratio chosen, and of M^{2+} concentration. We found that it is possible to rationalize POPG lipoplexes formation according to the reentrant condensation model while, amazingly, for POPA nucleolipoplexes formation an additional attractive contribution between liposomes and dsDNA has to be taken into account, attributable to the specific molecular recognition capabilities of POPA, that can be further highlighted through CD measurements.

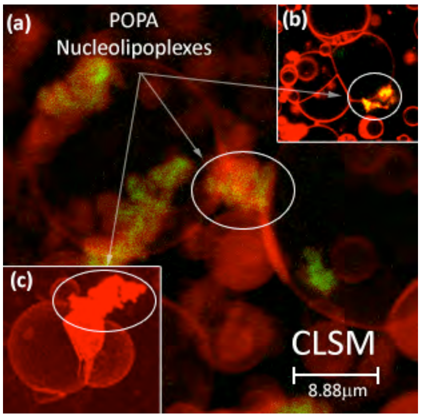


Figure 2. CLSM 2D and 3D images of POPA nucleolipoplexes stained with fluorescein-labeled DNA (a, b. yellow) or not stained (c) incubated with POPG:POPC 1:1 negatevely charged GUV stained with lipophilic Liss-Rhod PE within the bilayer (red).

A prominent issue in non-viral vectors' DNA delivery is the interaction between DNA complexes and cell membrane, closely related to the zwitterionic helper lipid chosen in liposomes' formulation and to lipoplexes' structure obtained e.g. through SAXS, in order to achieve cellular internalization and to complete transfection process. In this field, Giant Unilamellar Vesicles can be a valuable cell membrane model system, for GUV made of different lipid mixtures (e.g. negatively charged, uncharged, structurally homogeneous or not) can highlight different properties of cell membrane, highlighting hence the main factors affecting transfection efficiency. A CLSM study on the interaction between nucleolipoplexes and GUV has highlighted the fusogenic capabilities of nucleolipoplexes with GUV as a function of nucleolipoplexes' features, as the helper lipid chosen in liposomes formulation, and GUV characteristics. Moreover, Fluorescence Correlation Spectroscopy can be a useful technique to highlight the possible presence of bound or free fluorescently labeled-DNA within the aqueous pool of the GUV, due to the interaction between nucleolipoplexes and the GUV membrane and, above all, to specifically highlight the modifications in GUV bilayer properties provoked by the interaction with nucleolipoplexes.

References

Banchelli, M.; Berti, D. and Baglioni, P. "Molecular Recognition Drives Oligonucleotide Binding to Nucleolipid Self-Assemblies", Angewandte Chemie- Int. Edition, 46, 3070 (2007).

Bombelli, F. B.; Berti, D.; Milani, S.; Lagi, M.; Barbaro, P.; Karlsson, G.; Brandt, A. and Baglioni, P. "Collective headgroup conformational transition in twisted micellar superstructures", Soft Matter, 4, 1102 (2008).

Milani, S.; Berti, D.; Dante, S.; Hauss, T. and Baglioni, P. "Intercalation of Single-Strand Oligonucleotides between Nucleolipid Anionic Membranes: A Neutron Diffraction Study", Langmuir, 25, 4084 (2009).

1B – Magnetoliposomes for controlled drug release

S. Nappini, M. Bonini, F. Ridi, T. Al Kayal, D. Berti, P. Baglioni, B. Nordèn (Department of Chemistry and Bioscience, Chalmers University of Technology, Gothenburg, Sweden)

Aims

Effects of a low-frequency magnetic field (LF-AMF) on the permeability and release properties of magnetic nanoparticle-embedded vesicles.

Results

Large (LUVs) and giant (GUVs) unilamellar vesicles loaded with three different Cobalt Ferrite Nanoparticles ($CoFe_2O_4$ NPs): uncoated, citrate and oleic acid coated Nps were prepared and characterized. The hydrophilic nanoparticles (uncoated and citrate coated NPs) were embedded in the aqueous pool of liposomes, while the hydrophobic ones (coated with oleic acid) were entrapped in the lipid bilayer of liposomes. According to their sub-micrometer diameter, LUVs or liposomes are used for in vivo applications, while GUVs are used as cellular models to study membrane perturbations in the presence of an external *stimulus*. A number of investigations have been reported on exploiting superparamagnetic NPs in targeted and controlled release of drugs: in fact, magnetic NPs can be efficiently encapsulated inside lipid vesicles and used for targeting a specific location of the body by an external magnetic force.

A way to promote drug release and to tune magnetoliposome permeability is the application of an alternating magnetic field. In most cases a high-frequency alternating magnetic field (HF-AMF) was used to promote local heating, or magnetic fluid hyperthermia (MFH) of Nps, which are located in the targeted tumor cells, causing their thermal ablation without damaging the healthy tissues. In this project, for the first time, a low frequency alternating magnetic field (LF-AMF, frequency < 10 kHz) was used in order to minimize the temperature contribution and investigate mainly the field effect.

Cobalt Ferrite NPs were produced introducing some modifications to the method originally proposed by Massart and characterized by SAXS (Small Angle X-Rays Scattering), DLS (Dynamic Light Scattering) and TEM (Transmission Electron Microscopy).

Magnetoliposomes were prepared by extrusion method and characterized by DLS, while magnetic GUVs were prepared by electroformation and analyzed by Confocal Laser Scanning Microscopy (CLSM).

The increase of magnetoliposome permeability upon exposure to LF-AMF was evaluated as the self-quenching decrease of the fluorescent molecule Carboxyfluorescein (CF) entrapped in the liposome pool. Liposome leakage was monitored as a function of field frequency, time of exposure, size, charge, concentration and different coatings of NPs.

To gain further knowledge into the leakage mechanism induced by LF-AMF, Confocal Laser Sanning Microscopy (CLSM) experiments were performed on magnetic GUVs labeled with the fluorescent probe $DiIC_{18}$ and filled with the water-soluble fluorescent dye Alexa 488-maleimide.

All magnetoliposome samples have shown an effective response to LF-AMF exposure in terms of CF release. The release kinetics were monitored during time after the magnetic field application and the drug release kinetics were analyzed by Ritger and Peppas equation in order to understand the drug transport mechanism.

The results have indicated that, in the presence of LF-AMF, both nanoparticles'oscillations and hyperthermic effect due to the magnetic field anisotropy of the magnet effectively alter the bilayer structure promoting CF release. In particular, for liposomes loaded with hydrophobic NPs, kinetics monitored by Differential Scanning Calorimetry (DSC) have suggested that nanoparticles' oscillations in the presence of LF-AMF alter the bilayer structure promoting a initial weak release of CF during the first hours, followed by a stronger destabilization of the lipid membrane due to the formation of larger pores and to the rupture of some vesicles approximately 8-10 hours after the LF-AMF application.

These results were also confirmed by CLSM experiments, which have shown a progressive leakage of Alexa 488 fluorescent dye during the application of LF-AMF as consequence of the formation of pores at the lipid bilayer.

Moreover fluorescent and magnetic particles were also prepared and used as a system for locating their position in GUVs and to study the effect of a LF-AMF on the permeability of magnetic vesicles by Confocal Laser Scanning Microscopy (CLSM). Silica-coated Cobalt ferrite nanoparticles incorporating Rhodamine B isothiocyanate MP@SiO$_2$(RITC) were synthesized by a sol-gel method and adsorbed on GUVs' membrane.

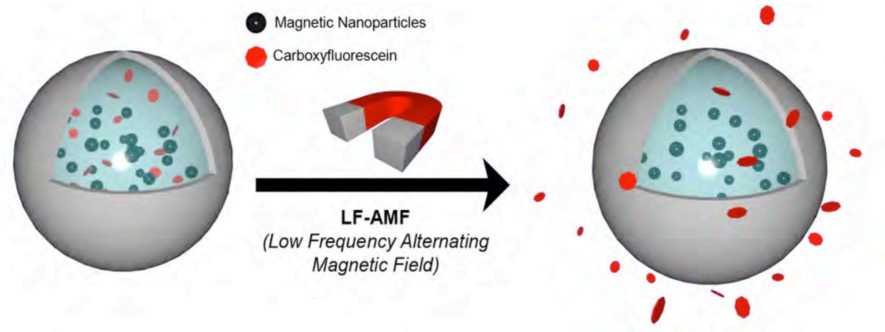


Figure 1. Sketch of CoFe$_2$O$_4$ nanoparticles-embedded liposomes containing carboxyfluorescein (CF) and subsequent CF release upon application of LF-AMF.

References

Nappini, S.; Baldelli Bombelli, F.; Bonini M.; Nordèn, B. and Baglioni, P., Soft Matter, 6, 154-162 (2010).

Nappini, S.; Bonini M.; Baldelli Bombelli, F.; Pineider, F.; Sangregorio, C.; Nordèn, B. and Baglioni, P., Soft Matter, 7, 1024-1037 (2011).

Nappini, S.; Al Kayal, T.; Berti, D.; Nordèn, B. and Baglioni, P., J. Phys. Chem. Lett., 2, 713-718 (2011).

1B – Using liposomes as carriers for plant derived polyphenolic antibacterial compounds

C. Bonechi, L. Ciani, N. Figura [1], S. Lamponi, S. Martini,
S. Ristori, C. Rossi
[1]Dip. Medicina interna Scienze endocrino-Metaboliche e
Biochimica, Università di Siena.

Aims

There is considerable interest in alternative/adjuvant approaches for the eradication of *Helicobacter pylori (Hp)* by using biologically active compounds, especially antioxidants from plants. *Hp* is a Gram-negative helical-shaped bacterium (Fig 1) which has evolved together with man and has adapted to survive in the hostile gastric environment. It nowadays represents the major cause of gastroduodenal pathologies, such as ulcer, autoimmune gastritis and cancer.

Figure 1

This project aims at evaluating the bactericidal activity of polyphenols administered through biocompatible liposomes.

Specific liposomal formulations have to be used to trigger the interaction with bacterial membranes. In particular, cationic lipids will be used to target the negatively charged plasma membranes of bacteria, while glycolipids will be used due to the well documented surface recognition phenomena elicited by sugar groups.

Polyphenol extracts will be obtained from edible plants or their derivatives, such as grapes, onions and red wines.

The bactericidal activity of polyphenols loaded into liposomes will be tested against *Hp* strains with different virulence.

Results

Drugs and biomolecules with a rigid aromatic core are not easily loaded into liposomes possessing a fluid bilayer. This limitation also applies to trans-Resveratrol (trans-3,5,4’-trihydroxystilbene, Fig. 2), which is the parent compound of plant derived polyphenols.

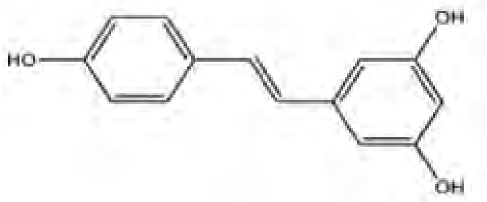


Figure 2

To circumvent limited compatibility between Resveratrol and standard liposome formulations we have chosen lipid bilayers made of di-palmitoyl chain and cholesterol or cholesterol derivatives. In particular, we have found that the cationic DPPC/DC-CHOL and zwitterionic DPPC/CHOL mixtures are able to incorporate Resveratrol with ~ 30-40% loading ratio, as determined by spectrophotometric titration. *Ad hoc* protocols based on repeated cycles of sonication and extrusion have been used to obtain a well defined liposome population, with size in the range 100-300 nm. Preliminary results have shown that the minimum bactericidal concentration of Resveratrol toward *Hp* can be reduced by using liposomes as delivery agents.

The next steps of this project will be to establish both the bactericidal activity and the radical scavenging effect of different polyphenols loaded into liposome formulations that are optimized with respect to the type of lipids and their mutual molar fraction.

References

Martini, S.; D'Addario, C.; Braconi, D.; Bernardini, G.; Salvini, L.; Bonechi, C.; Figura, N.; Santucci, A. and Rossi, C. "Antibacterial Activity of Grape Extracts on cagA-Positive and Negative Helicobacter pylori Clinical Isolates", Chemotherapy, 5, 86-92 (2009).

1B – Molecular depth profiling of polymer materials by surface mass spectrometry techniques

Davide Sapuppo, Nunzio Tuccitto, Valentina Spampinato,
Gabriella Zappalà, Antonino Licciardello

Aims

Development of methods for in-depth molecular characterisation of polymer-based materials by ToF-SIMS and rfGDMS. Study of fundamental aspects of interaction of plasma and polyatomic ions with polymer surfaces.

Results

Analysis of polymer-based films is extremely central in the field of materials science since polymers are currently used for a multiplicity of manufactured goods and technological applications. Characterization of paints and pigment films, study of coating performance, development of polymer-based electronic devices such as poly-LED displays or organic photovoltaic systems, detailed analysis of food packaging, and investigation of ion-exchange membranes, are some important fields of interest that require detailed depth-resolved investigation of polymer-based materials. Such investigations often require not only knowledge of the elemental depth profile, but also detailed molecular information along the depth, i.e. 'molecular depth profiling'. Molecular depth profiling of polymers is presently obtained by means of secondary ion mass spectrometry using polyatomic primary ions (*cluster*-SIMS). The achievement of a molecular depth profile, however, is strongly dependent on the radiation chemistry of the polymer and on the energy density deposited by the primary beam close to the sample surface. For example PMMA is easily profiled with fullerene ions, but polystyrene (PS) does not. Also, we demonstrated that profiling behaviour is dependent on temperature, as illustrated in figure 1 for poly-α-methylstyrene that switches from non-profilability to profilability by increasing temperature.

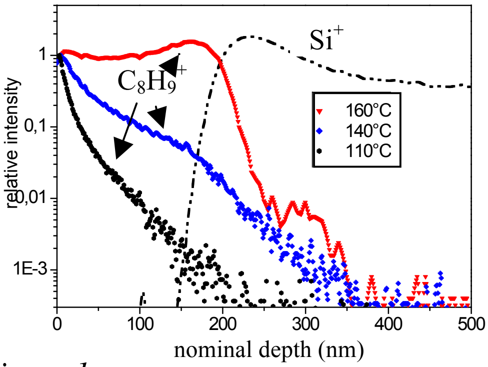


Figure 1

Such behaviour is often connected with the competition among radiation induced reactions, some of these leading to crosslinking (causing damage accumulation and preventing molecular depth profiling) and others leading to chain scission and formation of volatile products. The latter processes are believed to favour depth profiling by helping in the removal of ion-beam-induced damage. We have recently demonstrated that it is possible to interfere positively with the above described processes by introducing in the vacuum chamber of the SIMS apparatus a proper reactive gas, typically a radical scavenger such as NO. For example, in the case of

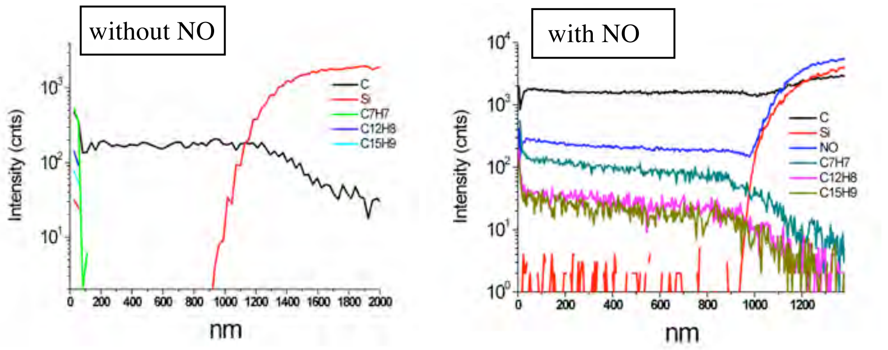


Figure 2

PS, the presence of nitric oxide during C_{60}^+ SIMS depth profiling allows a successful molecular depth profile of the polymer (see Figure 2).

Interesting results can be obtained by using, for sample erosion, a properly modulated plasma source. In the framework of an EU project, we demonstrated that it is possible to obtain molecular depth profiles of various polymer layers and multilayers by means of pulsed radiofrequency glow discharge time-of-flight mass spectrometry (rfGDTOFMS). Examples of molecular depth profiles obtained by means of such technique are reported in figure 3 for approx. 300 nm-thick films of (a) PMMA, (b) PS, (c) PETi, and (d) PAMS, on silicon substrates. This work has been recently awarded with the "RCM Beynon Prize" as the innovative advance in mass spectrometric instrumentation or methodology that has had the greatest immediate impact in its particular sub-discipline over years 2009-2010.

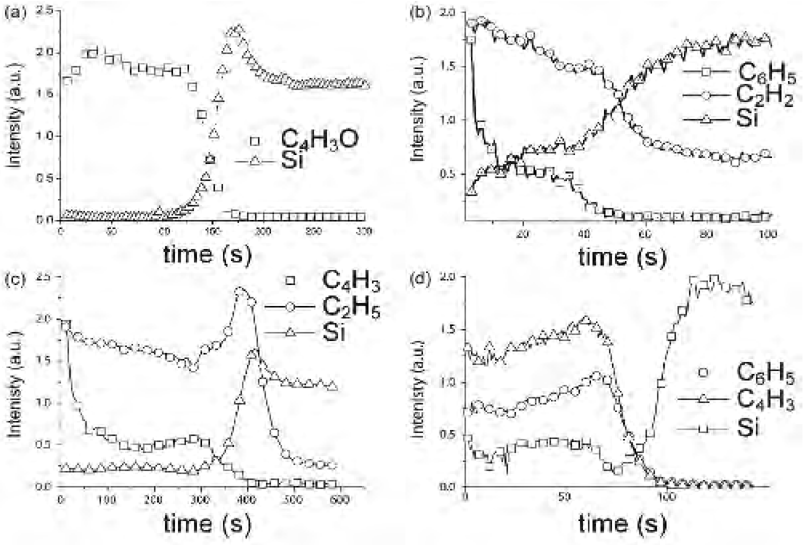


Figure 3

References

Moellers, R; Tuccitto, N; Torrisi, V.; Niehuis, E. and Licciardello, A. "Chemical effects in C_{60} irradiation of polymers", Appl Surf Sci, 252, 6509-6512 (2006).

Tuccitto, N; Lobo, L.; Tempez, A.; Delfanti, I.; Chapon, P.; Canulescu, S.; Bordel, N.; Michler, J. and Licciardello, A. "Pulsed radiofrequency glow discharge time-of-flight mass spectrometry for molecular depth profiling of polymer-based films", Rapid Commun. Mass Spectrom. 23, 549-556 (2009).

1C – Ordered Mesoporous Materials Part 2: Specific ion effects on Protein adsorption and surface charge density

A. Salis, M.S. Bhattacharyya, M. Boström, D.F. Parsons (ANU, Australia), L. Medda, B. Barse, B.W. Ninham (ANU, Australia), M. Monduzzi

Aims

Specific Ion Effects at solid/liquid interface. Surface charge density of nanostructured silica. Protein adsorption on solid surfaces.

Results

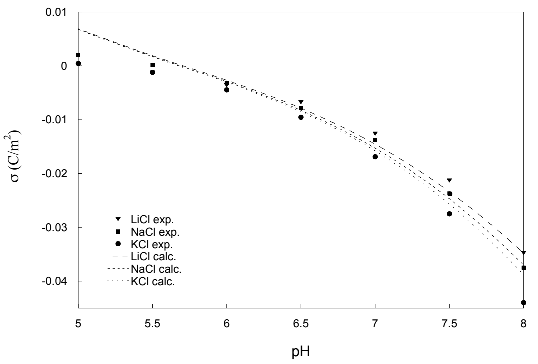
Ordered mesoporous materials have been widely used as protein adsorbents. Previous works have shown how to tune the amount of adsorbed protein by changing pH or ionic strength of the adsorbing solution. Actually, there is no awareness of what is the effect of different salts used to fix ionic strength. Such effects, Hofmeister phenomena, reflecting both co- and counter-ion specificity, are universal.

In the present work a comparison is made between the experimental and theoretical surface charge density (σ) of SBA-15 mesoporous silica. Experimental σ values were obtained through potentiometric titration measurements. It was found that surface charge depends both on cation type, following a Hofmeister series ($Cs^+<$ Guanidinium$^+$ $< K^+ < Na^+ < Li^+$), and on salt concentration (in the range 0.05-1 M).

Theoretical dispersion *B* coefficients and ion radii *a*. For reference, ionic polarizabilities are also given (at the lowest optical, that is the first nonzero, frequency,$\omega_1=3.9\times10^{13}$ Hz, used in the calculation of *B*).

Ion	ion radius (Å)	hard sphere ion radius (Å)	Intrinsic α_1 (Å^3)	Excess α_1* (Å^3) (in water)	*B* (10^{-50} Jm^3)
H_3O^+	0.97	1.07	0.963	0.205	-0.79
unhydrated Li^+	0.38	0.42	0.0285	0.000421	-0.041
hydrated Li^+	2.18	2.40	7.155	0.950	-4.32
unhydrated Na^+	0.61	0.67	0.139	0.0139	-0.18
hydrated Na^+	1.64	1.81	4.415	0.918	-3.01
K^+	0.96	1.06	0.814	0.159	-0.73
Cl^-	1.69	1.86	4.859	1.011	-1.70

The surface charge series is reproduced by theoretical calculations performed using a modified Poisson-Boltzmann equation that includes ionic dispersion potentials ($U_{disp}(x)$) through dispersion coefficients (B_i) calculated by ab initio ion polarizabilities (α_1*) and hydrated ion radii (*a*).

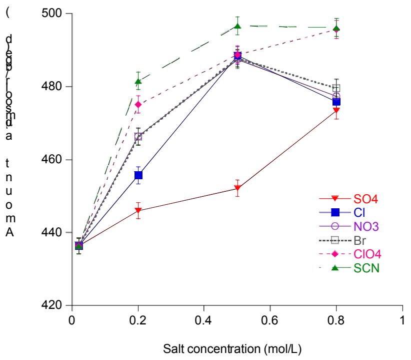


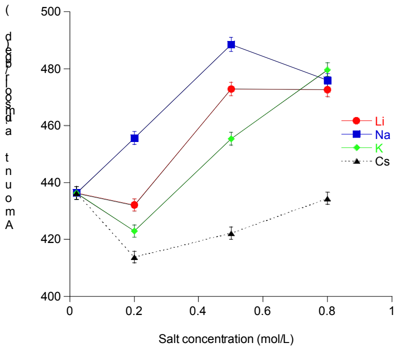
$$U_{disp}(x)=\frac{B_i f(x)}{x^3}$$

$$B_i=\frac{kT}{4}\sum_{n=0}\left(2-\delta_{0,n}\right)\frac{\alpha_i^*(i\omega_n)}{\varepsilon_w(i\omega_n)}\left(\frac{\varepsilon_w(i\omega_n)-\varepsilon_c(i\omega_n)}{\varepsilon_w(i\omega_n)+\varepsilon_c(i\omega_n)}\right)$$

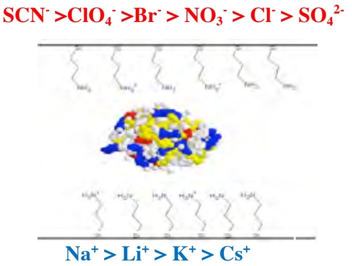
$$f(x)=1+\frac{2x}{\sqrt{\pi}a}\left[\frac{2x^2}{a^2}-1\right]\exp\left(\frac{-x^2}{a^2}\right)-\left[1+\frac{4x^4}{a^4}\right]\mathrm{erfc}\left(\frac{x}{a}\right).$$

The Hofmeister series appears to be due to the combination of ion surface dispersion interactions and ion hydration. Then, the adsorption of lysozyme on a functionalized SBA-15 (SBA-15-NH_2) as a function of added salts was investigated. It was ascertained that the amount of adsorbed protein follows a reversed Hofmeister series for anions (sodium salts): $SCN^- > ClO_4^- > Br^- > NO_3^- > Cl^- > SO_4^{2-}$ whereas for cations (chloride salts) the sequence was: $Na^+ > Li^+ > K^+ > Cs^+$.





As more precise theoretical modeling is now in sight due to the recent availability of ab initio dynamic polarizabilities, it is possible to make quantitative comparison with different experiments. This should provide better insights into the correctness and usefulness of the theoretical modeling. The discovery that the charging of mesoporous silica surfaces is ion specific has huge impact for applications like catalysis and drug delivery. It is now clear that for example protein adsorption in SBA-15 and other mesoporous structures could be effectively manipulated by the choice of background salt solution. These findings demonstrate the importance of specific ion effects occurring at solid/liquid interface between mesoporous silica and proteins.



References

Salis, A.; Parsons, D.F.; Boström, M.; Medda, L.; Barse, B.; Ninham, B. and Monduzzi, M. "Ion Specific Surface Charge Density of SBA-15 Mesoporous Silica", Langmuir, 26, 2484-2490, (2010).

Salis, A.; Bhattacharyya, M.S. and Monduzzi, M. "Specific Ion Effects on Adsorption of Lysozyme on Functionalized SBA-15 Mesoporous Silica", J. Phys. Chem. B, 114, 7996-8001, (2010).

Salis, A.; Monduzzi, M. and Ninham, B.W. "Hofmeister Effects in enzymatic activity, colloid stability and pH measurements: ion dependent specificity of intermolecular forces", In "Nanoparticles and Nanodevices in Biological Applications", Ed. S. Bellucci, Springer, 159-194 (2009). ISBN: 978-3-540-70943-5

1C – Bio-mimetic and Photochemical Switches

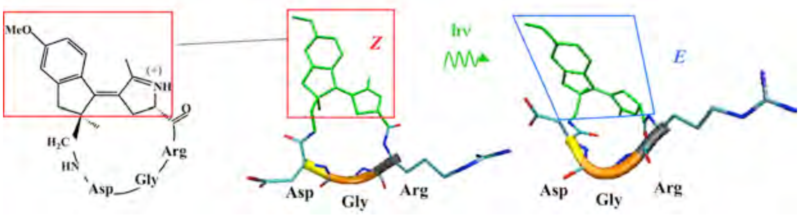
A. Sinicropi, M.L. Parisi, C. Bernini, R. Basosi, M. Olivucci

Aims

Design, synthesis and characterization of novel synthetic molecules that mimic the behavior of biological photoreceptors and can be employed as bio-mimetic molecular devices.

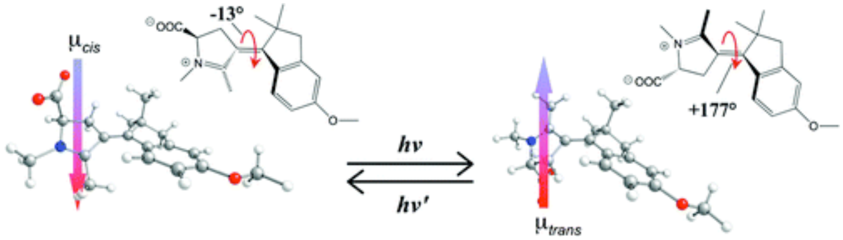
Results

A new class of light-driven biomimetic switch (N-alkylated indanylidenepyrroline (NAIP) Schiff bases) has been designed, synthesized and characterized by experimental and computational investigation in solution featuring (i) the electronic structure and photoisomerization mechanism of the protonated Schiff base of retinal, (ii) the same bis-pentanylidene locked skeleton of diarylidenes single-molecule motor and (iii) a reduced molecular size and higher polarity when compared to the widely used azobenzene switch. These molecules undergo a UV-visible light-driven Z/E isomerization along the central C-C double bond. Complementary ab initio multiconfigurational quantum chemistry-based computations and time-resolved spectroscopy have been used to follow the light-induced isomerization of the switch in methanol. The results show that, similar to rhodopsin, the isomerization occurs on a 0.3-ps time scale and is followed by <10-ps cooling and solvation. The entire (2-photon-powered) switch cycle was traced by following the evolution of its infrared spectrum. These measurements indicate that a full cycle can be completed within 20 ps. Furthermore, the photochemical investigation of NAIPs revealed that the composition of the photostationary state is wavelength dependent. Indeed, by changing the irradiation wavelength from 360 to 440 nm the Z/E ratio can be inverted. In particular, at 440 nm, the E form becomes dominant. The property of inverting the composition of the photostationary state upon irradiation at a given wavelength figures out different applications of NAIPs where the control of the percentage in solution of the two forms is needed. With this aim we designed a novel "functional" cyclic peptidomimetics formed by the switch conjugated to a biologically active peptide (the RGD sequence involved in the control of cell adhesion processes) whose conformation can be modulated by irradiation at a given wavelength.



Structural properties of the construct have been investigated in aqueous solution using molecular dynamics (MD) simulations. Analysis of MD trajectories reveals that, for each diastereoisomer of the switch (E or Z), different conformations are stabilized. Electrostatic and spectroscopic properties of such conformers have been evaluated by means of ab initio multiconfiguration quantum chemical method implemented in a quantum-mechanical/molecular-mechanic (CASPT2//CASSCF/6-31G*/AMBER) scheme.

More recently, a multidisciplinary research effort, combining the methods of computational photochemistry and retrosynthetic analysis/synthesis, have contributed to the preparation of a novel N-alkylated indanylidene-pyrroline Schiff base featuring an exocyclic double bond and a permanent zwitterionic head. We showed that, due to its large dipole moment and efficient photoisomerization, such a system may constitute the prototype of a novel generation of electrostatic switches achieving a reversible light-induced dipole moment change on the order of 30 D. The modeling of a peptide fragment incorporating the zwitterionic head into a conformationally rigid side chain showed that the switch can effectively modulate the fluorescence of a tryptophan probe.



References

Melloni, A.; Rossi Paccani, R.; Donati, D.; Zanirato V.; Sinicropi, A.; Parisi, M.L.; Martin, E.; Ryazantsev, M.; Ding, W.J.; Frutos, L.M.; Basosi, R.; Fusi, S.; Latterini, L.; Ferrè, N. and Olivucci, M. “A Biomimetic Dipole Moment Switch Driven by Double Bond Photoisomerization”, Journal of the American Chemical Society, 132 (27), 9310-9319 (2010).

Sinicropi, A.; Bernini, C.; Basosi, R. and Olivucci, M. “A novel biomimetic photochemical switch at work: Design of a photomodulable peptide”, Photochemical & Photobiological Sciences 8, 1639-1649 (2009).

Pistolesi, S.; Sinicropi, A.; Pogni, R.; Basosi, R.; Ferrè, N. and Olivucci, M. “Modeling the fluorescence of protein-embedded tryptophans with ab initio multiconfigurational quantum chemistry: the limiting cases of Parvalbumin and Monellin”, The Journal of Physical Chemistry B 113, 16082-16090 (2009).

Sinicropi, A.; Martin, E.; Ryasantsev, M.; Helbing, J.; Briand, J.; Sharma, D.; Léonard, J.; Haacke, S.; Canizzo, A.; Chergui, M.; Zanirato, V.; Fusi, S.; Santoro, F.; Basosi, R.; Ferré, N. and Olivucci, M. “An Artificial Molecular Switch that Mimics the Visual Pigment and Completes its Photocycle in Picoseconds”, Proc. Nat. Acad. Sci., 105, 17642-17647 (2008).

1C – Multicriteria thermodynamic Analysis for Environmental Impact Assessment

N. Graniglia, P. Fulini, C. Daniele, S. Jez, R. Basosi,

Aims

Using different thermodynamic methodologies (Material Flow Accounting, Energy, Exergy and LCA) the project aims to develop an integrated approach to evaluate the environmental impacts and the environmental sustainability of antropic systems.

Results

Sustainability evaluation of antropic system can be performed by means of analytical methodologies deeply rooted on Thermodynamic laws: Material Flow Accounting, Energy, Exergy, Emergy and Life Cycle Assessment.

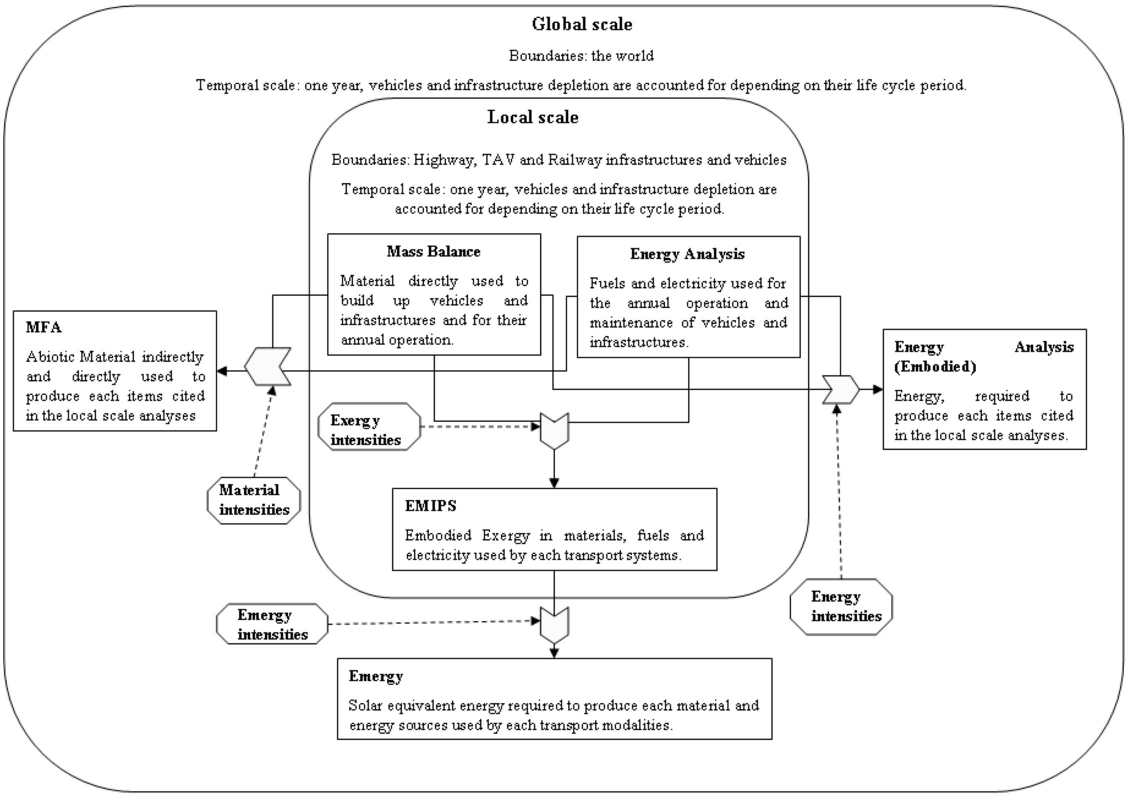


Figure 1. Local scale framework encompasses the direct inputs supporting the transport activities: Mass Balance, Energy Analysis and EMIPS are used in this context. Global scale framework takes into account the indirect and hidden material and energy flows supporting the transportation process. Specific material, energy and emergy intensities are used to shift from local to global scale.

These methodologies are based on different paradigms (for instance MFA and Energy are based on the First Law of Thermodynamic, while Exergy and Emergy are based on the second one) and different time-space windows, so the use of just one methodology lead to neglect some aspects and impacts linked to the process or the product with misleading indication about optimization policies.

In our study, we try to get a comprehensive and coherent integration among the cited methodologies in order to obtain an "investigation tool" able to encompass, virtually, all the environmental impacts. The validity of this method has been tested evaluating two kind of processes:

1. Passenger and commodity transport systems;

In this work, we perform a comparison among several transport options, not considering only the nominal performances of vehicles or modalities, but instead we focus on the useful outputs of the transport systems as a whole, namely the average demand for resources and environmental support related to the functional units, identified as one person transported per km (p-km) and one tonne of commodities transported per km (t-km). In so doing, by means of a "system approach", we are able to measure and compare the material and energy depletion required as well as the environmental impact generated per functional unit in each analysed transport systems, taking into account all the system's components.

2. Territorial Energy Planning and development of local renewable energy chains.

In this case, our multicriteria approach is used to evaluate different *energy planning* options and the environmental advantage/disadvantage coming from the development of local renewable energy chains as biomass, biofuel and wind energy.

References

Federici, M.; Ulgiati, S. and Basosi, R. "Air versus terrestrial transport modalities: an energy and environmental comparison", Energy, 34, 1493-1503 (2009).

Federici, M.; Ulgiati, S. and Basosi, R. "A Thermodynamic and Material Flow Analysis of the Italian Highway and Railway Transport Systems", Energy, 33, 760-775 (2008).

Federici, M.; Basile, M.; Pogni, R. and Basosi, R. "Environmental and economical advantages of the local scale: a pilot biodiesel production line in the Province of Siena, Italy", First European Workshop on biotechnology for lignocellulose biorefineries, 154-160 (2008).

Verdesca, D.; Federici, M.; Torsello, L. and Basosi, R. "Exergy-economic accounting for sea-coastal systems: A novel approach", Ecological Modelling, 193, 132-139 (2006).

Graniglia, R.; Federici, M.; Graniglia, N. and Basosi, R. "Integration of Renewable Energy Production in Historical Downtown Centers: The Case of Siena", World Renewable Energy Congress IX, Elsevier, 142-149 (2006).

Federici, M.; Verdesca, D. and Basosi, R. "Thermodynamic and Economic Analysis of Biomass Energy Recovering Processes. Siena Case Study", World Renewable Energy Congress IX, Elsevier, 313-332 (2006).

1C – Energy Efficiency, Energy Growth and Complexity Leap

F. Ruzzenenti, F. Picciolo, D. Garlaschelli, R. Basosi

Aims

The aims of this project is to study the dynamic interplay between energy efficiency, energy growth and structural complexity of macroscopic thermodynamic systems – human made or biological, on an evolutionary time-scale.

Methodology

The research project aims at studying the energy-evolutionary pattern of complex systems by means of network theory and information theory. Network theory is an evolution of graph theory and information theory extends statistical mechanics to non-experimental analysis. Information theory applied to network theory is commonly defined statistical mechanics of networks. Complex systems are therefore approached as complex networks and information theory -or to better say: statistical mechanics of networks, is employed to define a reference state whence the system can evolve (symmetry breaking).

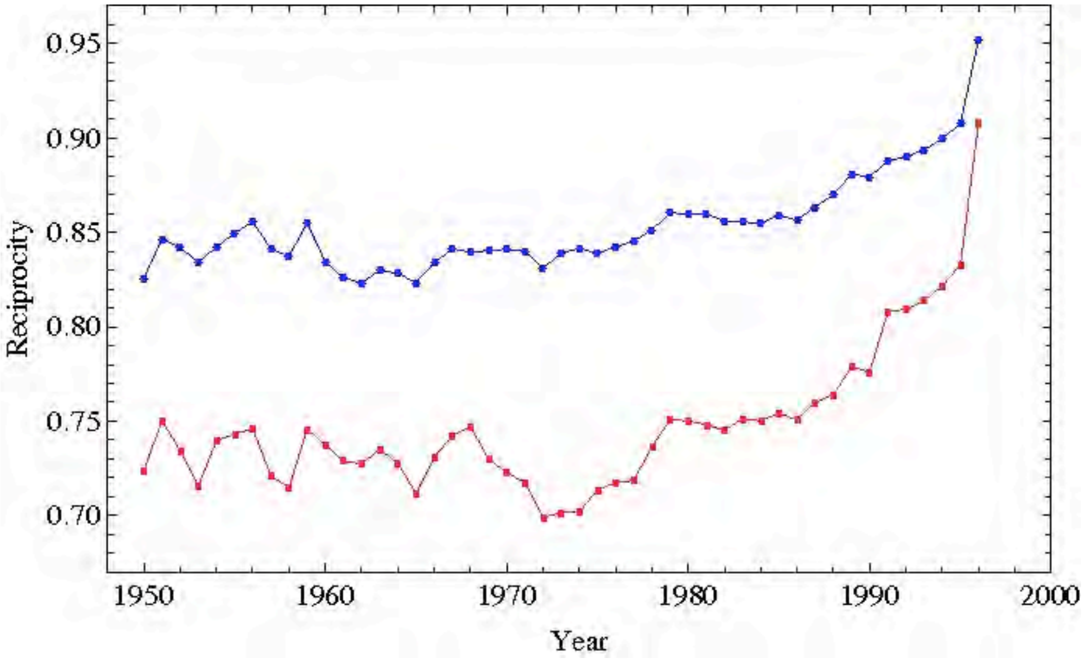


Figure 1. Symmetry breaking in the WTW, the blue line whereby detection is possible. The second line investigates the occurrence of saturation in systems' growth depicts the trend measure in the topology of the network and the red line portrays the same trend implemented within a statistical framework – Source: Ruzzenenti, F.; Garlaschelli, D.; Basosi, R. "Complex Networks and Symmetry II: reciprocity and Evolution of World Trade", Symmetry 2, 1710-1744 (2010)

The research project develops two major lines:

1. Investigating complexity leap as a result of symmetry breaking in the system' space that eventually affects the topological space of the network.
2. Investigating the role of saturation in the symmetry breaking.

The first line assumes that symmetry breaking occurs in a underlying space of system's interacting components that would inevitably affects the topology of the describing network, whereby detection is possible. The second line investigates the occurrence of saturation in systems' growth stage and the hypothesis that saturation determines symmetry breaking.

Results

The analysis applied to the World Trade Web -here considered as the describing network, highlighted that a symmetry breaking in the topology of the network occurred between the late 1970's and the mid 1980's. According to our analysis the symmetry breaking actually occurred in the economic space of the productive structure and the transition reflected in the topological space of the WTW. A dramatic energy efficiency change affected delivery costs of firms and the economic space changed thereafter. The hypothesis is that the efficiency changed was driven by the saturation of industrial sector. Further analysis focused on the concept -and related analytical tools, of symmetry in networks. Symmetry breaking was thus firstly approached in terms of reciprocity of the binary network, and then in terms of euclidean embedding space and reciprocity of the weighted network. These symmetries' analysis was further extended to several networks in order to investigated an evolutionary pattern.

References

Ruzzenenti, F. and Basosi, R. “Energy growth, complexity and efficiency”, Energy Efficiency, ed. Jenny Palm, published by Sciyo, 27-48 (2010).
Garlaschelli, D.; Ruzzenenti, F. and Basosi, R. “Complex Networks and Symmetry I: a review”, Symmetry 2, 1683-1709 (2010).
Ruzzenenti, F.; Garlaschelli, D. and Basosi, R. “Complex Networks and Symmetry II: reciprocity and Evolution of World Trade”, Symmetry 2, 1710-1744 (2010).
Basosi, R. “Energy Growth, complexity and efficiency”, Summer School Chemistry for Life and Environment, 7th edition 18 (2010).
Ruzzenenti, F. and Basosi, R. “Evaluation of the energy efficiency evolution in the European road freight transport sector”, Energy Policy 37, 4079-4085 (2009).
Ruzzenenti, F. and Basosi, R. “Complexity change and space symmetry rupture”, Ecological Modelling 220, 1880-1885 (2009).
Ruzzenenti, F.; Federici, M. and Basosi, R. “Un approccio teorico al cambiamento di complessità come effetto della rottura di simmetria”, Proceedings of Third Energy Management Conference 43-48, Parma (Italy) June, 4-5 (2009).
Ruzzenenti, F. and Basosi, R. “On the relationship between energy efficiency and complexity: Insight on the causality chain from the study of the rebound effect”, International Journal of Ecodynamics, 3, 95-108 (2008).
Ruzzenenti, F. and Basosi, R. “The role of the power/efficiency misconception in the rebound effect’s size debate: Does efficiency actually lead to a power enhancement?” Energy Policy, 36, 3626-3632 (2008).
Ruzzenenti, F. and Basosi, R. “The rebound effect: An evolutionary perspective”, Ecological Economics, 67, 526-537 (2008).

1C – QM/MM characterization of amino acid radical species involved in biological electron transfer and catalytic processes

A. Sinicropi, C. Bernini, R. Pogni, R. Basosi

Aims

Combined use of DFT-based quantum mechanics/molecular mechanics (QM/MM) calculations and multifrequency EPR for the characterization of amino acid radicals that act as redox-active cofactors in enzymatic reactions.

Results

Molecular g-tensors, hyperfine coupling constants (hfcc) and Mulliken spin densities for organic radicals embedded in solution or in a protein matrix can be calculated with high accuracy using Density Functional Theory (DFT) methods. The inclusion of the effects of the whole protein surrounding and of the solvent is particularly important for the calculations of spectroscopic properties, such as EPR magnetic parameters, that are strongly influenced by the environment.
State-of-the-art DFT-based QM/MM computations have been used to characterize Trp and Tyr radicals involved in the Long Range Electron Transfer pathways of *P. eryngii* Versatile Peroxidase (VP) and its W164Y variant.

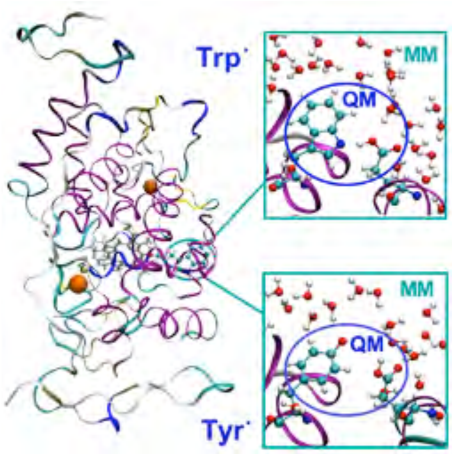


Figure 1. Trp and Tyr radical intermediates in *P. eryngii* Versatile Peroxidase and its W164Y variant.

The proper modeling of the environmental effects within a QM/MM approach has made possible to: i) achieve a good agreement between QM/MM computed and measured EPR parameters; ii) support and complement the experimental data, iii) determine the geometric and electronic structure of the radical and iv) evaluate, at a high degree of details, the interactions that mainly contribute to the overall magnetic properties of the radical species. In particular, the computed set of g-tensors, hfcc and the Mulliken spin densities, compared to the experimental data, confirmed the formation of a neutral Trp radical (W164•) in VP, N1-deprotonated and hydrogen bonded to the nearby E243 residue. Computations also demonstrated that the formation of W164• is exothermic with a barrier (~2-4 kcal mol^{-1}) compatible with a stepwise electron and proton transfer and with the existence of a short-lived transient Trp radical cation having a lifetime of few ps. On the contrary, for W164Y, it has been shown that the Tyr oxidation proceeds via a concerted electron and proton transfer and that the proton is transferred in an ultrafast way to the E243 residue. Besides, QM/MM MD simulations showed that in W164Y the hydrogen bond between Y164• and E243 is broken that both Y164• and E243 make new hydrogen bonds with solvent water molecules.

The different hydrogen bond network that were found for the models of VP and W164Y enzymes (Fig. 1) might be linked to the different catalytic behaviour of W164Y variant compared to the native VP. In particular, in VP, the transferred proton remains hydrogen bonded to the Trp indolic N1 and thus it can be easily recovered by the catalytic residue in its subsequent reduction. On the other hand, in W164Y variant, the different conformation of E243 and the major reorganization of the surroundings suggest that the back proton transfer might be slower. The achieved results have provided insight into the difference in catalytic activity of W164Y as compared to VP and may very well make possible *de novo* design of new variants or enzymes with higher activity or different desirable properties.

References

Bernini, C.; Pogni, R.; Ruiz-Dueñas, F.J.; Martínez, A.T.; Basosi, R. and Sinicropi, A. “EPR Parameters of Amino Acid Radicals in P. eryngii Versatile Peroxidase and its W164Y variant computed at the QM/MM level”, PCCP, ISSN: 1463-9076, doi: 10.1039/C0CP02151B, in press (2011).

Bernini, C.; Sinicropi, A.; Basosi, R. and Pogni, R. “Tyrosyl Radical in the W164Y Mutant of P. eryngii Versatile Peroxidase: an EPR and DFT/PCM Study”, Appl. Magn. Reson., 37, 279-288 (2010).

Ruiz-Dueñas, F.J.; Pogni, R.; Morales, M.; Giansanti, S.; Mate, M.J.; Romero, A.; Martínez, M.J.; Basosi, R. and Martínez, A.T. “Protein radicals in fungal versatile peroxidase: Catalytic tryptophan radical in both Coumpound-I and Coumpound-II and studies on W164Y, W164H and W164S variants”, J. Biol. Chem., 284, 7986-7994 (2009).

Pogni, R.; Baratto, M.C.; Teutloff, C.; Giansanti, S.; Ruiz-Dueñas, F.J.; Choinowski, T.; Piontek, K.; Martínez, A.T.; Lendzian, F. and Basosi, R. “A Tryptophan Neutral Radical in the Oxidized State of Versatile Peroxidase from Pleurotus eryngii”, J. Biol. Chem., 28, 9517-9526 (2006).

1C – Specific Ion Effects

P. Lo Nostro, B. W. Ninham, N. Peruzzi, P. Baglioni, A. Salis,
M. Monduzzi, M.C. Pinna, D. Bilanicova

Aims

Hofmeister effect in bulk solutions and at interfaces

Results

The effect of electrolytes in a moderate concentration range (between 0.1 and 1 M) was investigated in bulk solutions and at interfaces:

1. the ion binding and partitioning at lysozyme/SDS interfaces in water (Fig. 1) [1]
2. the cloud point of dioctanoyl-phosphatidylcholine/water dispersions (Fig. 2) [2]
3. the kinetics of formation of pseudopseudorotaxanes (Fig. 3) [3]
4. the phase transitions in water dispersions of ascorbyl-alkanoates (Fig. 4) [4]
5. the growth of *Staphylococcus aureus* and *Pseudomonas aeruginosa* (Fig. 5) [5]
6. the spreading monolayers of calix[n]arenes (Fig. 6) [6]
7. the water absorbency of natural fibers (Fig. 7) [7]
8. the optical rotation of glucose and α-amino acids (Fig. 8) [8]
9. the UV-vis absorption spectra of congo red in aqueous dispersions (Fig. 9)
10. the pH of buffered solutions (phosphate and cacodylate) (Fig. 10) [9]

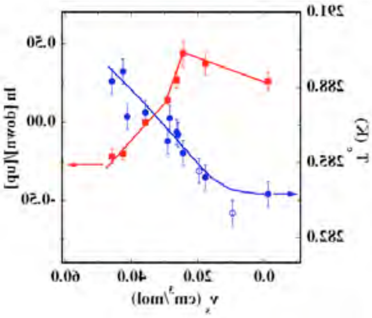


Figure 1

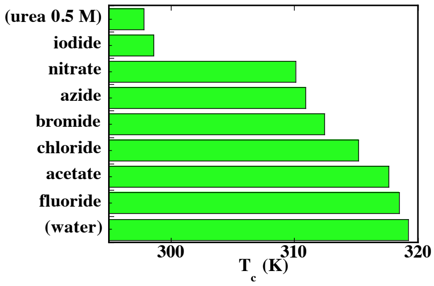


Figure 2

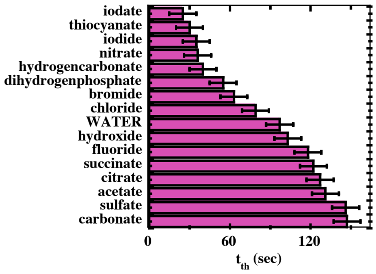


Figure 3

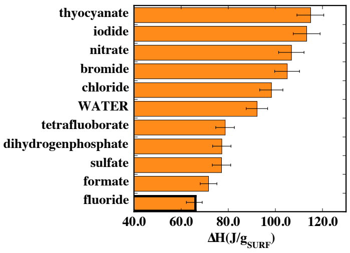


Figure 4

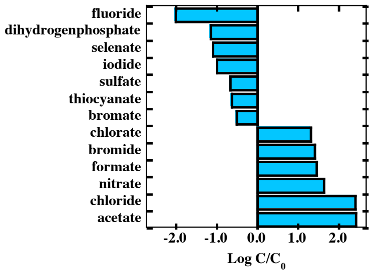


Figure 5

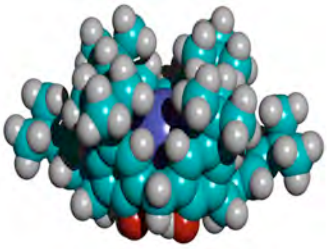


Figure 6

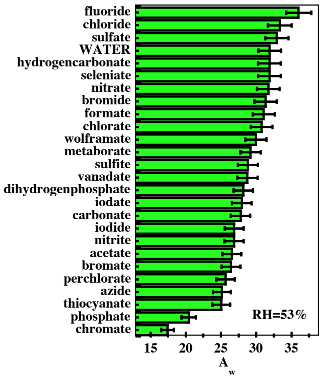


Figure 7

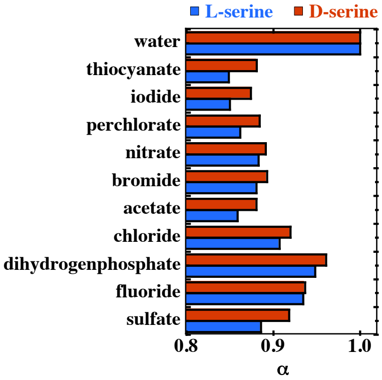


Figure 8

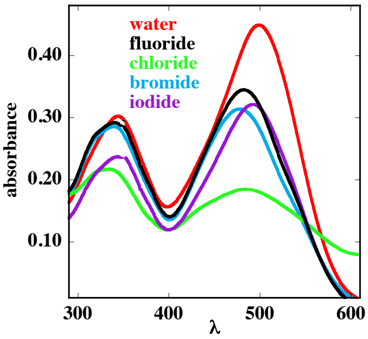


Figure 9

In each case the variation of a characteristic parameter was related to the free energy of hydration, partial molar volume, surface tension increment, polarizability and lyotropic number. The results indicate that in all these cases the phenomenon is ruled by dispersion forces, that originate from the different microscopic atomic properties of the single ions (polarizability and ionization potential).

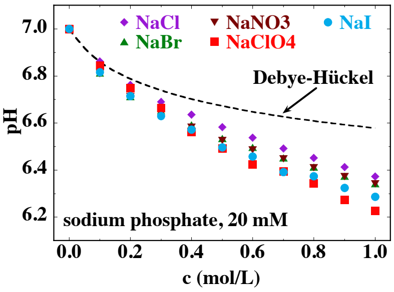


Figure 10

References

Lo Nostro, P.; Peruzzi, N.; Severi, M.; Ninham, B.W. and Baglioni, P. "Asymmetric Partitioning of Anions in Lysozyme Dispersions", J. Am. Chem. Soc. 132, 6571 (2010).

Lagi, M.; Lo Nostro, P.; Fratini, E.; Ninham, B.W. and Baglioni, P. " Insights into Hofmeister Mechanisms: Anion and Degassing Effects on the Cloud Point of Dioctanoylphosphatidylcholine/Water Systems", J. Phys. Chem. B, 111, 589 (2007).

Lo Nostro, P.; Lopes, J.R.; Ninham B.W. and Baglioni P. "Effect of Cations and Anions on the Formation of Polypseudorotaxanes", J. Phys. Chem. B, 106(9), 2166 (2002).

Lo Nostro, P.; Ninham, B.W.; Ambrosi, M.; Fratoni, L.; Palma, S.; Allemandi, D. and Baglioni P. "Hofmeister Effect in Coagels of Ascorbic Acid-based Surfactants", Langmuir 19, 9583 (2003).

Lo Nostro, P.; Ninham, B.W.; Lo Nostro, A.; Pesavento, G.; Fraton, L. and Baglioni, P. "Specific ion effects on the growth rates of *St. aureus* and *Ps. aeruginosa*", Phys. Biol. 2, 1 (2005).

Lonetti, B.; Lo Nostro, P.; Ninham, B.W. and Baglioni, P. "Anion Effects on Calixarene Monolayers: A Hofmeister Series Study", Langmuir 21, 2242 (2005).

Lo Nostro, P.; Fratoni, L.; Ninham, B.W. and Baglioni, P. "Water Absorbency by Wool Fibers: Hofmeister Effect", Biomacromolecules 3, 1217 (2002).

Rossi, S.; Lo Nostro, P.; Lagi, M.; Ninham, B.W. and Baglioni, P. "Specific Anion Effects on the Optical Rotation of a-Amino Acids", J. Phys. Chem. B 111, 10510 (2007).

Salis, A.; Pinna, M.C.; Bilanicova, D.; Monduzzi, M.; Lo Nostro, P. and Ninham, B.W. "Specific Anion Effects on Glass Electrode pH Measurements", J. Phys. Chem. B 110, 2949 (2006).

1C – Measure and modelling the hydrometereology of a shallow lake (Lake of Montepulciano, Siena)

A.M. Dattilo, L. Bracchini, S.A. Loiselle, A. Tognazzi, C. Rossi

Aims

To better understand the tele-connection between metereological forcing and hydrology of a shallow lake. Set a "protocol alert" for Province of Siena.

Results

We develop a unique hydrometereological station inside the Lake of Montepulciano to collect at the same time metereological and hyrological data.

Figure 1. The hydrometereological station inside the Montepulciano lake

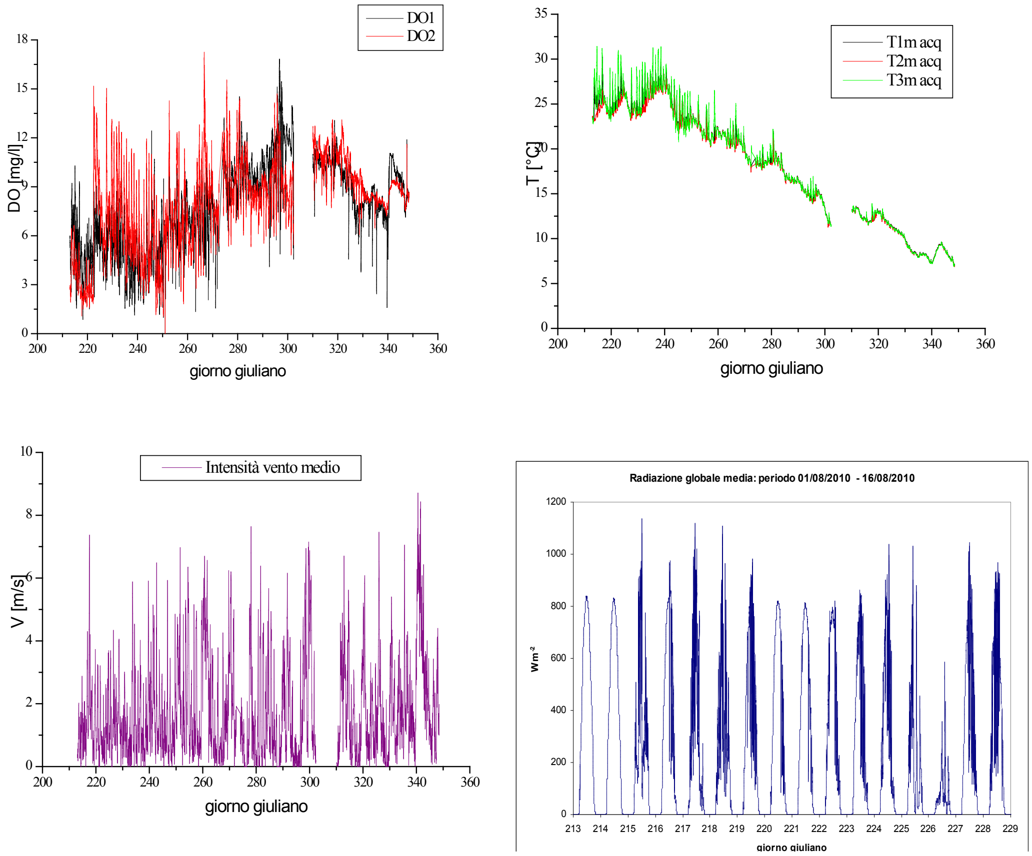


Figure 2. An example of collected data(DO, Oxygen two depths; T, Water Temperature three depths; V, Wind speed; Global Radiation).

The develop of the model of evaporation and the data of wind, rain and others permitted us to predict the level of the lake and sudden inform the Province.

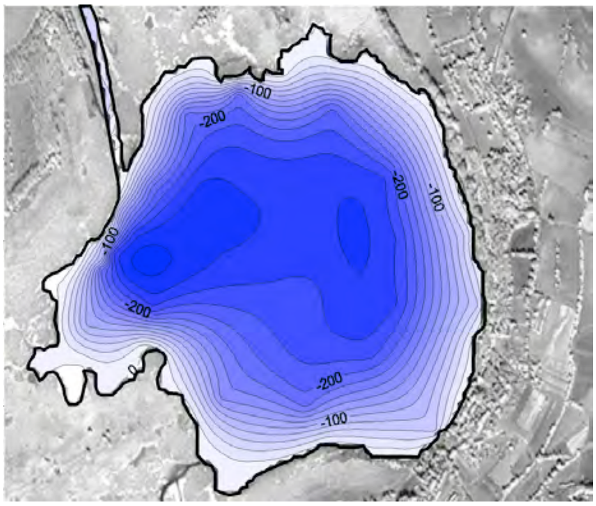


Figure 3. The predicted level of Montepulciuano Lake in July by using an integrated model between evaporation data model and hydrometereological data.

1C – Modelling the spectral shape of CDOM

L. Bracchini, A.M Dattilo, S.A. Loiselle, M. Ricci, A. Tognazzi, C. Rossi

Aims

Study the best way to modelling the spectral shape of chromophoric dissolved organic matter.

Results

We develop two new methods to analyse the CDOM shape. The first is related to the use of an exponential function ($S(\lambda)$). The second do not use this supposition ($\sigma(\lambda)$).
The first method use a nonlinear fitting approach. It was possible to determine the variation of spectral slope over a wide range of wavelengths in UV and visible. The resulting spectral slope curve ($S(\lambda)$) displays some characteristics which are similar in both standard and lake samples, in particular to spectral slopes calculated near 270 and 380 nm. In lake samples, numerous degradation mechanisms will influence the spectral absorption characteristics of the CDOM produced by both allochthonous and autochthonous sources.
We show spectral slope curves for standard solutions and compare them to several lake ecosystems, as well as samples that have undergone photodegradation. Clearly, further studies are required to identify how specific sinks and sources influence the spectral slope curve in natural environments, but working from a common basis, such comparisons are greatly facilitated. We believe that this approach may help standardize the analysis of the CDOM absorption curve and provide more complete information on the chemical composition of CDOM (Figure 1).
With the second method we introduce a new approach to determine the CDOM absorption slope without assuming an exponential behaviour. The resultant $\sigma(\lambda)$ curve shows the wavelength dependent variability of spectral slope data, allowing for comparison with published values made in different wavelength intervals. Differences in $\sigma(\lambda)$ appear to be linked to changes in average chemical composition and aromaticity more specifically to different source and sink mechanisms (e.g. photobleaching).
While the $\sigma(\lambda)$ approach is facilitated by the use of the more sensitive long path spectrophotometer, we show that is can also be applied to standard spectrophotometric absorbance data, after applying the opportune signal smoothing. The resultant spectral distribution curve is consistent with that obtained using a long path spectrophotometer (Figure 2).

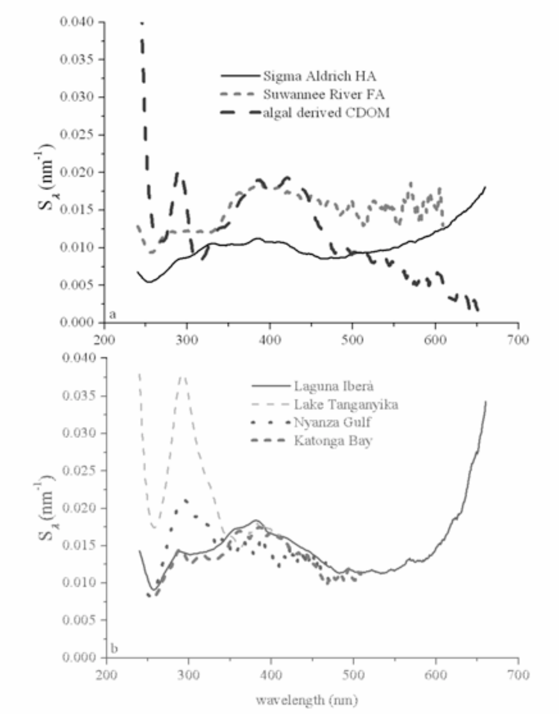


Figure 1. The S(λ) curve generated for different aquatic ecosystems and for CDOM standards

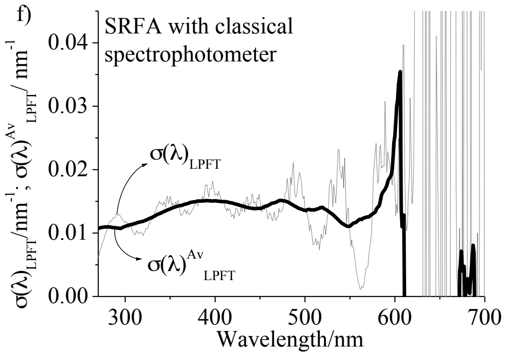


Figure 2. The σ(λ) curve generated with theory of signals.

References

Loiselle, S.A.; Bracchini, L.; Cozar, A.; Ricci, M.; Dattilo, A.M.; Tognazzi, A. and Rossi, C. "The optical characterization of chromophoric dissolved organic matter using the wavelength distribution of absorption spectral slopes", Limnology and Oceanography 54, 590-597 (2009).

1C – Climate change impacts on Mediterrranean coastal lakes and lagoons

S. Loiselle, L. Bracchini, A.M. Dattilo, A. Tognazzi, C. Rossi

Aims

The UNISI research unit is working closely with leading researchers in France, Italy and Morocco to develop long term monitoring and management approaches for coastal aquatic ecosystems. Major activities include the construction of a common database, scenario analysis workshops with local stakeholders in three ecosystems (Pontine Lakes (IT), Camargue (FR), Sidi Boughaba (MO), hydrodynamic and ecological modelling of key energy and matter fluxes in coastal ecosystem dynamics in relation to primary climate drivers, until 2050.

Coastal transitional aquatic ecosystems have a strategic role in meeting the needs and aspirations of current and future populations. Proper functioning of coastal lakes, wetlands, estuaries and lagoons is fundamental for water resources, food production and biodiversity. Yet, they have been witness to a progressive and occasionally irreversible degradation, in particular to their hydrological and biogeochemical cycles, which is further complicated by their sensitivity to climate change. To avoid further losses in resource availability and basic environmental services, an appropriate long term strategy must be developed.

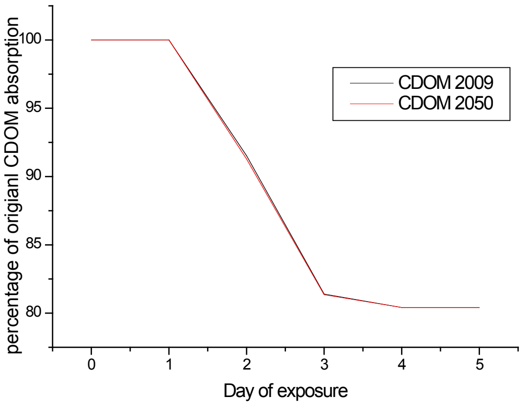
Results

The Medcodyn database structure was completed in May 2009 and the database has been on line since, http://www.medcodyn.unisi.it/. The Medcodyn research team has been uploading data continuously and used the data to examine temporal trends in chemical, biological and physical parameters in the three coastal sites

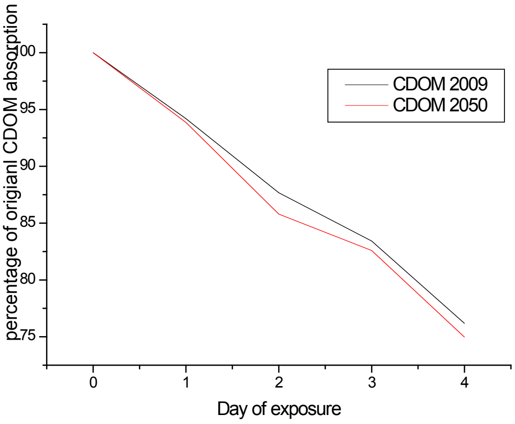
Ecological and hydrological models were developed to study management options and potential impacts of climate change in coastal ecosystems. In Fogliano Lake, a dissolved oxygen model was developed to examine the impacts of changes in water temperature, sea/lake exchange, wind stress and organic matter load on oxygen concentrations in the water column and sediment, and in particular with respect to anoxia. An organic matter / photodegradation model was developed for each ecosystem considering estimated changes in cloudiness until 2050, with present day optical conditions measured in each ecosystem.

For Sidi Boughaba (Morocco), the lack of long term data made modeling and trends analysis difficult. An intensive baseline analysis of this ecosystem was made and used to set up a long term monitoring plan for local stakeholders and scientists to examine monthly trends in key ecological, hydrological and chemical characteristics of the lake.

Past and future trends in ecosystem dynamics, ecosystem services and climate were used to explore adaptation measures for the three coastal ecosystems studied. Through a process of consultation with stakeholders, indicator and model development, different adaptation options were identified in relation to their potential success within the context of local and regional environmental change.



Change in absorption of chromophoric dissolved organic matter (CDOM) due to photodegradation by solar radiation in Fogliano Lake for the years 2009 and 2050



Change in absorption of chromophoric dissolved organic matter (CDOM) due to photodegradation by solar radiation in Etang de Vaccares for the years 2009 and 2050

References

Bracchini, L.; Dattilo, A.M.; Loiselle, S.A.; Tognazzi, A.; Hull, V. and Rossi C. “Temporal and spatial dynamics of inherent and apparent optical properties in a shallow coastal lake (Fogliano Lagoon, Circeo National Park)”, Transitional Water Bulletin 3, 1-24 (2008).

Loiselle, S. A.; Bracchini, L.; Dattilo, A.M.; Ricci, M.; Tognazzi, A.; Cozar, A. and Rossi, C. “The optical characterization of chromophoric dissolved organic matter using the wavelength distribution of absorption spectral slopes”, Limnology and Oceanography 54, 590-597 (2009).

Bracchini, L.; Dattilo, A.M.; Hull, V.; Loiselle, S.A.; Tognazzi, A. and Rossi, C. “Modelling Upwelling Irradiance using Secchi disk depth in lake ecosystems”, Journal of Limnology 68, 83-91 (2009).

2A – Enzymes for green chemistry

R. Pogni, S. Giansanti, M.C. Baratto, A. Martorana, R. Basosi

Aims

The aim of this research is to address the catalytic properties of different oxidative enzymes for the bio-synthesis of new compounds and for bioremediation.

Results

Biocatalytic processes differ from conventional chemical processes, owing mainly to enzyme kinetics, protein stability under technical conditions and catalyst features that derive from their role in cell's physiology.

Laccase based treatment method received much attention in treatment of various recalcitrant pollutants. Many studies demonstrated the effectiveness of crude and purified forms of laccase in dye decolourization. Previously reported results describe laccase ability in oxidation of single dye, while few attempts were made on real effluents due to difficulties derived from their complex composition, extremely variable even within the same factory and containing compounds which often inhibit laccase activity. Laccases are not able to oxidize all dyes and real wastewaters, and depending on pH, the time of reaction could be very long. A methodology to improve the range of substrates of these enzymes is the use of mediators. In reality the laccase-mediator system must answer to existing concerns about the possible toxicity of some of the most powerful laccase mediators, such as the –N(OH)- compounds or their reaction products.

An efficient alternative to the use of mediators is the UltraSound(US)-laccase system: when US are combined with laccase, short frequencies (150 kHz) are required. We have tested this combined system on a model wastewater containing dye and auxiliaries.The hydorxyl radical produced by US work as mediator radicals, destroying the levelling-agent – dye complex and avoiding the problem of laccase activity inhibition. The enzymatic treatment which follows, acts on dye molecules in short time (few minutes) and at great extent, comparable to ozone methods. Furthermore, preliminary results on treated model effluent, obtained immobilizing laccase on Eupergit C, show a decrease of values of COD, anionic and non – anionic additives and suspended solids.

Another alternative to the use of commercial mediators is the design of new molecules for laccase-catalysed reactions taking into account the following properties for the redox mediator: a) it should be a good enzyme substrate showing high turnover numbers, b) it should produce stable free radicals able to diffuse away of the active site to oxidize the final target compound, and c) the radical produced should have a high redox potential to oxidize a wide range of compounds. In order to achieve this goal around 20 molecules candidates are under study to obtain good redox mediators selected using computational chemistry. To study the approach and interaction of redox mediators molecules and the enzyme active site molecular mechanics studies will be performed. Then the proposed molecules will be synthesized and the radical intermediates formed during the process will be characterized by EPR spectroscopy; studies of the catalytic performance of the proposed mediators will be also carried out.

Furthermore the interest in the potential use of laccases in organic synthesis has increased in the recent years and this application can compete with conventional methods. Several phenolic and amino derivatives were explored in order to find new substrates suitable for the preparation of novel compounds. An example realised in our laboratory is the 3-amino-4-hydroxybenzenesulfonic acid which was bioconverted into a new colored compound using the fungal laccase from Cerrena unicolor. Thus the use of oxidative enzymes represents a convenient and ecofriendly way for synthesis of new molecules. Recently our attention has been focused on the study of the catalytic mechanism of Trametes versicolor laccase in the presence of the precursor Me14 (4-methylamino benzoic acid). It is well known that laccases have great capability in coupling two different molecules to create new low molecular weight products; the enzyme is also able to couple hydroxylated aromatic substrate with a nonlaccase substrate of variable structure to create new heteromolecular hybrid molecules and finally oligomerization and polymerization reactions can lead to new homo- or hetropolymers and biomaterials. The laccase reactions presumably proceed by radical intermediates with subsequent deprotonation of the hydroxyl group to produce a radical species. The destiny of the radical species can be different depending on the experimental conditions and whether a second partner molecule is present in solution. When undefined reaction conditions or in the absence of a second molecule, the radical species generated can undergo intermolecular nucleophilic attack by itself to produce homomolecular dimers, but after longer reaction time, oligomers and polymers can be generated from the dimers. The formation of a well structured radical intermediate centered on the Me14 precursor in the presence of laccase from Trametes versicolor was followed spectroscopically by EPR and spectrophotometrically and the paramagnetic species remains for 20 minutes, after that the solution from violet started to become yellowish.

The assignment of the EPR signal to a dimeric radical intermediate (diazo species) is also supported by theoretical calculations of isotropic hyperfine coupling constants (hfcc) and g values based on density functional theory (DFT). As the final solution is coloured, further spectroscopic measurements have been carried out in order to identify and characterise the product of the biosynthesis obtained from the reaction.

References

Forte, S.; Polak, J.; Valensin, D.; Taddei, M.; Basosi, R.; Vanhulle, S.; Jarosz-Wilkolaska, A. and Pogni, R. “Synthesis and Structural Characterization of a Novel Phenoxazinone Dye by Use of a Fungal Laccase”, J. Mol. Catal. B: Enzym., 63, 116-120 (2010).

Fernandes, A.T.; Damas, J.M.; Todorovic, S.; Huber, R.; Baratto, M.C.; Pogni, R.; Soares, C.M. and Martins, L.O. “The mutlicopper oxidases from the archaeon Pyrobaculum aerophilum shows nitrous oxide reductase activity”, FEBS J. 277, 3176-3189 (2010).

Di Gregorio, S.; Balestri, F.; Basile, M.; Matteini, V.; Gini, F.; Giansanti, S.; Tozzi, M.G.; Basosi, R. and Lorenzi R. “Sustainable discoloration of textile chromo-baths by spent mushroom substrate from the industrial cultivation of Pleurotus ostreatus”, Journal of Environmental protection, 1, 85-94 (2010).

Brogioni, B.; Biglino, D.; Sinicropi, A.; Reijerse, E.J.; Giardina, P.; Sannia, G.; Lubitz, W.; Basosi, R. and Pogni, R. “Characterization of Radical Intermediates in the Laccase-Mediator Systems: A Multifrequency EPR, ENDOR and DFT/PCM study”, Physical Chemistry Chemical Physics, 10, 7284-7292 (2008).

2A – Silica Gelatin composite for removal of chromate from water solutions

F. Lopez, A. Ceglie, F. Venditti (C.O.S.I.B. Termoli)

Aims

The main aim of this project is the removal of toxic ions from wastewater. For this purpose a new composite was fabricated characterized and utilized. A further aim of this project is to study the process of Cr(VI) removal by the new composite and determine whether chromate ions adsorption, could be affected by the presence of sulfate ions and a slightly acidic pH. Finally the possibility to use this matrix as reactor for the conversion of Cr(VI) to Cr(III) is evaluated.

Results

We focused our attention on the removal of chromates ions present in the environment. Several materials have been developed and tested, ranging from low cost waste material, such as moss peat, sawdust, zeolites, clay, hazelnut shell, to more sophisticated adsorbents, such as activated carbon, modified zeolite, modified clay, modified steel slag, nanoscale magnetic material, chitosan based composite.

We proposed a novel composite able to remove hexavalent chromium Cr(VI) from aqueous solutions obtained by adding the silica precursor tetraethoxysilane (TEOS) to the hexadecyltrimethylammonium bromide (CTAB) microemulsion-based gel[1,2]. SEM and NMR analysis showed that this material is made by an interconnected network of gelatin, silicate and surfactant molecules in which water molecules manifest a high mobility. Analyses of the elemental content in the CTAB-silica gelatin composite suggest that the adsorption of chromium takes also places in the internal areas.

Furthermore, we noticed that the composite containing the adsorbed hexavalent chromium left in water for 30 days undergoes a change in colour from yellow to green (Figure 1). This evidence is an indication of the reduction in situ of Cr(VI). X-ray Photoelectron Spectroscopy has been used to characterize the composite materials. Surface analyses performed at different times revealed chromium chemical speciation changes as a function of the pollutant-material interaction time (Figure 2)[3].

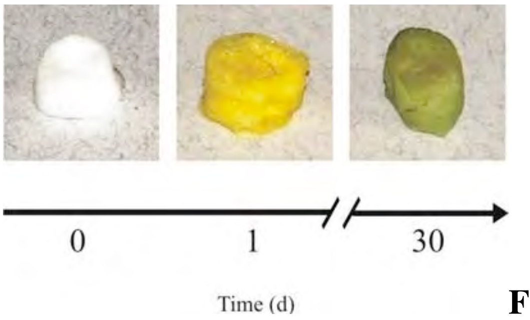


Fig. 1

Moreover, the removal of chromate was assessed also through evaluation of the adsorption kinetics of chromate ions on the composite under equilibrium conditions in the presence of sulfate ions and at a slightly acidic pH condition (pH 5.8)[4]. Adsorption competition tests in the presence of sulfate ions showed that Cr(VI) was still effectively adsorbed from aqueous solution regardless of the presence of the competing anions (Figure 3). The equilibrium adsorption data were fitted by

Freundlich adsorption isotherms and confirmed that the adsorption efficiency of chromium on the CTAB–silica gelatin composite was unchanged in the presence of sulfate ions[4]. These findings demonstrated a high specificity of the CTAB–silica gelatin composite for chromium, and highlight the possibility of using this matrix for efficient removal of chromium from industrial wastewater without the need to eliminate contaminant sulfate ions.

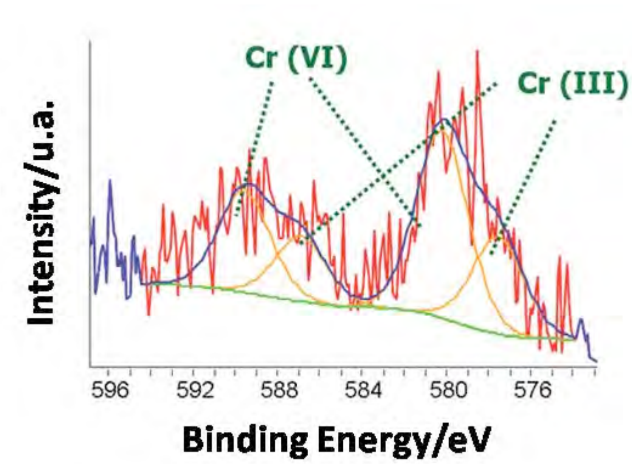


Fig.2

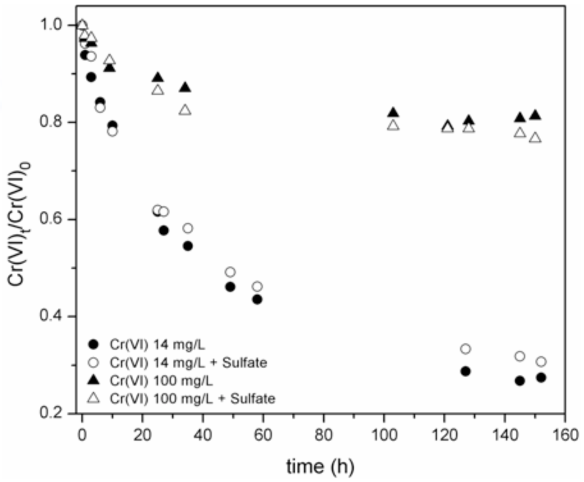


Fig.3

References

Venditti, F.; Lopez, F.; Palazzo, G.; Colafemmina, G.; Angelico, R.; Ambrosone, L. and Ceglie, A. “Materiale adsorbente contenente tensioattivo cationico, sua preparazione ed uso per la rimozione di metalli da soluzioni acquose”, Italian Patent 2006, n. 7490.

Venditti, F.; Ceglie, A.; Palazzo, G.; Colafemmina, G. and Lopez, F. “Removal of chromate from water by a new CTAB–silica gelatin composite”, Journal of Colloid and Interfaces Science, 310, 353-361 (2007).

Ditaranto, N.; Cioffi, N.; Sabbatini, L.; Palazzo, G. and Lopez, F. “XPS characterization of microstructured composites for Cr(VI) removal from polluted environment”, ISA 2010, La Chimica e l’Industria 2010, 92-94 (Ottobre 2010).

Venditti, F.; Cuomo, F.; Ceglie, A.; Ambrosone, L. and Lopez, F. “Effects of sulfate ions and slightly acidic pH conditions on Cr(VI) adsorption onto Silica Gelatin composite”, Journal of Hazardous Material, 173, 552-557 (2010).

2A – Calcium and barium hydroxide nanoparticles for the consolidation of wall paintings

P. Baglioni, N. Toccafondi, L. Dei, R. Giorgi

Aims

Consolidation of wall paintings with compatible inorganic materials.

Results

Criteria for conservation treatments, such as compatibility, minimal intervention or reversibility, have found only in the last years some practical applications with the emerging of new techniques based on nanotechnologies. Nanotechnology is based on the recognition that particles of size below 100 nm form nanostructures with new behaviour and properties.

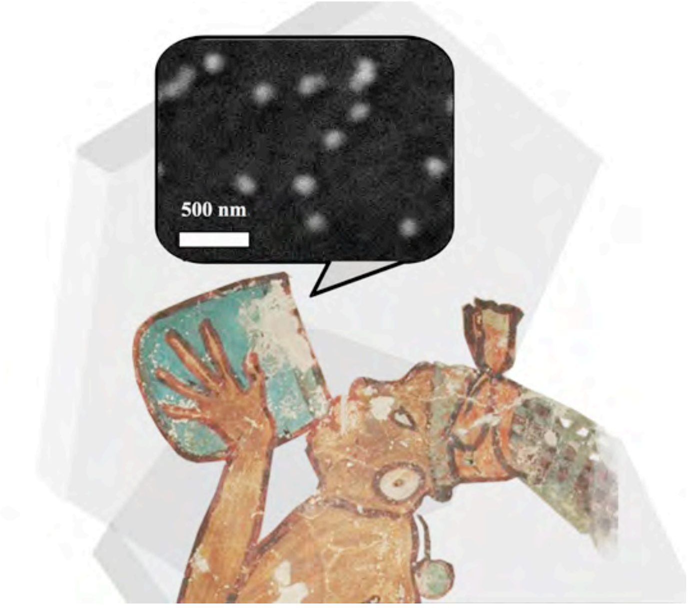
After the 1966 Florence flood, the research group in Florence was one of the first Academic Institutions that applied a rigorous scientific approach to the investigation of Cultural Heritage conservation. In 1969 a new method for *in situ* wall paintings consolidation was proposed by Enzo Ferroni. The method, today known as “barium or Ferroni-Dini method”, inverts the chemical reactions that produce the degradation of wall paintings, stabilizing the structure of the mortar and regenerating the binder of the painted layer, that is calcium carbonate. The method is based on the application of cellulose compress soaked with ammonium carbonate and barium hydroxide solutions. The consolidation is achieved due to two different chemical processes: the formation of fresh portlandite or calcium hydroxide, $Ca(OH)_2$, through the action of barium hydroxide on calcium carbonate, and the slow and gradual formation of barium carbonate, $BaCO_3$. The new slaked lime ($Ca(OH)_2$), formed *in situ*, acts as fresh binder, providing new setting of the mortar.

Consolidation of stones and mural painted surfaces by inorganic treatments is meant to provide the right content of carbonate binder to confer long-term preservation to the works of art. The evolution of Ferroni-Dini is based on calcium hydroxide, which is the best binder for limestone and wall paintings. In fact, the physico-chemical compatibility between the substrate and the restoration materials can be completely achieved by using calcium hydroxide, i.e. the 'original' binder used by artists. Kinetically stable dispersions of nanoparticles, synthesized trough homogeneous and heterogeneous phase reactions, can be obtained in short-chain aliphatic alcohols. The dispersions of nanoparticles are similar to an extremely concentrated solution of lime water (up to 30% volume fraction), well above the physico-chemical limit imposed by the solubility of calcium hydroxide in water.

Recently, new formulations based on barium hydroxide nanoparticles, alone or in combination with calcium hydroxide, have been successfully used for consolidation of degraded wall paintings, even in presence of large amount of salts.

These methodologies are currently used for the consolidation of wall paintings in Italy and other countries, including Mexico (for the conservation of mesoamerican paintings in Calakmul, Tlatelolco, Mayapan, Cacaxtla, and Cholula), Sweden, Israel, and Denmark.

CTS company (Italy) is now distributing in several countries this nanomaterial, whose tradename is “Nanorestore®”, produced at the CSGI laboratory. Nanorestore is the first chemical product based on nanotechnology, made available specifically to the conservator community.



La Antigua Ciudad Maya de Calakmul, Mexico: wall paintings have been restored by using $Ca(OH)_2$ nanoparticle dispersions

References

Baglioni, P. and Giorgi, R. "Inorganic nanoparticles for works of art conservation, in Inorganic Nanoparticles: Synthesis, Applications, and Perspectives", Series: Nanomaterials and their Applications; Editors: C. Altavilla & E. Ciliberto, CRC Press – Taylor & Francis Group: London (2010).

Giorgi, R.; Ambrosi, M.; Toccafondi, N. and Baglioni, P. "Nanoparticles for Cultural Heritage Conservation: Calcium and Barium Hydroxide Nanoparticles for Wall Painting Consolidation", Chemistry – A European Journal (Chem. Eur. J.), 16, 9374-9382 (2010).

Baglioni P.; Giorgi R. and Dei L. "Soft condensed matter for the conservation of cultural heritage", Compte Rendus Chimie, XX, 1-9, *article in press* (2008).

Baglioni, P. and Giorgi, R. "Soft and Hard nanomaterials for restoration and conservation of cultural heritage", Soft Matter, 2, 293-303 (2006).

Giorgi, R.; Chelazzi, D.; Carrasco, R.; Colon, M.; Desprat, A. and Baglioni, P. "The Maya site of Calakmul: "in situ" preservation of wall paintings and limestone by using nanotechnologies", The Object in Context: Crossing Conservation Boundaries, Munich IIC Congress 2006: proceedings, Edited by David Saunders, Joyce H. Townsend and Sally Woodcock, 162-169 (2006).

2A – Nanotechnology for the deacidification of books and manuscripts

R. Giorgi, G. Poggi, N. Toccafondi, P. Baglioni

Aims

Nanoparticles dispersions to preserve books and manuscripts

Results

Deacidification of cellulose-based materials is universally known as a major conservation issue for the large number of items to be treated (books in libraries, newspapers, textiles, wood, and so on). It is well known that acid catalyzes the hydrolysis of cellulose, leading to depolymerization. As a consequence, the physical and mechanical properties of the cellulose polymer are compromised. For paper, this process produces brittleness and fragility, so that many ancient books and documents could be lost, if not properly treated. In the past years many methods for paper deacidification have been developed, as the Wei T'o and the Bookkeeper. New methods based on the application of magnesium and of calcium hydroxide nanoparticles dispersed in a nonaqueous solvent are under investigation at CSGI. Nanoparticles, due to their tiny dimensions, penetrate into the network of the cellulose fibers, and adhere to them. Part of the hydroxide immediately reacts *in-situ* with the acidity, through solid-state reaction, providing deacidification. The hydroxide excess, due to the high reactivity of nanoparticles, is quickly converted into magnesium carbonate by the carbon dioxide present in the environment. In this way, an alkaline buffer is created in order to withstand the forthcoming acidity that can develop inside the fibers (for example, due to pollution). Calcium hydroxide nanoparticles could be used as well, but the smaller size of magnesium hydroxide particles involves a better penetration and faster carbonation inside the cellulose substrate. At this moment, research efforts are focused on synthesis routes that allow smaller size of the particles. Hydrolysis and oxidation usually act in a synergistic way by creating the so-called *spiraling effect* that can be detrimental for the preservation of paper. For that, also an antioxidant treatment is required. A strong interest in the coupling of these two treatments is growing in the field of manuscripts and inked paper conservation.

For that reason, an innovative approach was followed during the last two year: a single-step pH-controlled deacidification was used to inhibit the concomitant degradation induced by hydrolysis and oxidation of cellulose-based objects because it was showed that around neutrality the oxidation reactions induced by metal ions from the inks, proceed at a much slower pace.

In particular, the effects of innovative calcium and magnesium hydroxide nanoparticles dispersions, specifically designed for the application on gall inks containing paper, were evaluated on artificially aged reference systems.

Metal gall inks have been the most common writing fluids in Europe from the Middle Ages to the first half of the 20th century. The characteristics that made gall inks' fortune are their durability and their richness in color. Unfortunately, metal gall inks can produce severe degradation of cellulose as the perforation of the inked areas or a general loss of the typical mechanical properties of paper, i.e. elasticity and tensile strength. Both oxidation and hydrolysis reactions are catalyzed by these fluids.

The model inks used were prepared according to an adapted recipe by Petrus Caneparius reported in the *De Atramentis Cujuscunque Generis* treatise (A.D. 1619) and applied by brush on Whatman Filter Paper disks. After the application of different conservation treatments, including innovative calcium and magnesium hydroxide nanoparticles, inked samples were aged in a sealed box at 90°C and 80% RH for 48 hours.

In order to evaluate the treatments efficacy, viscosimetric determinations of Degree of Polymerization (DP) were performed. For each sample 60 mg of paper were extracted on 4mL of cold water and, after one hour, the pH was measured with a digital pH-meter Crison Basic 20. At the end of the aging cycle, a pH-controlled deacidification with nanoparticles was demonstrated to be sufficient to achieve a complete conservation treatment that simultaneously inhibit metal-catalyzed oxidation and acid-catalyzed hydrolysis of cellulose.

Further study on the benefits of the deacidification of inked cellulosic objects are needed; in particular, the application of nanoparticles dispersions on old manuscripts and inked paper, may prove that these systems can be used by libraries and conservation institutes in order to extend the useful life of their collections.

References

Poggi, G.; Giorgi, R.; Toccafondi, N.; Katzur, V. and Baglioni, P. “Hydroxide Nanoparticles for Deacidification and Concomitant Inhibition of Iron-Gall Ink Corrosion of Paper”, Langmuir, 26, 19084-19090 (2010).

Baglioni, P. and Giorgi, R. “Soft and Hard nanomaterials for restoration and conservation of cultural heritage”, Soft Matter, 2, 293-303 (2006).

Giorgi, R.; Bozzi, C.; Dei, L.; Gabbiani, C.; Ninham, B.W. and Baglioni, P. “Nanoparticles of $Mg(OH)_2$: synthesis and application to paper conservation”, Langmuir, 21, 8495-8501 (2005).

Chelazzi, D.; Giorgi, R.; Dei, L. and Baglioni, P. “Nanotecnologie per la conservazione del patrimonio culturale”, La Chimica e l’Industria, 87 (10), 78-82 (2005).

Giorgi, R.; Dei, L.; Ceccato, M.; Schettino, C.V. and Baglioni, P. “Nanotechnologies for conservation of Cultural Heritage: paper and canvas deacidification”, Langmuir, 18, 8198-8203 (2002).

Giorgi, R.; Dei, L.; Schettino, C. and Baglioni, P. “A new method for paper deacidification based on calcium hydroxide dispersed in non-aqueous media”, Preprint of the IIC Baltimore Congress 2002, Works of Art on Paper, Books, Documents and Photographs: Techniques and Conservation, P. Smith Ed., 69 (2002).

2A – Microemulsions and micellar solution for the cleaning of wall paintings

P. Baglioni, M. Baglioni, D. Berti, E. Carretti, L. Dei, R. Giorgi

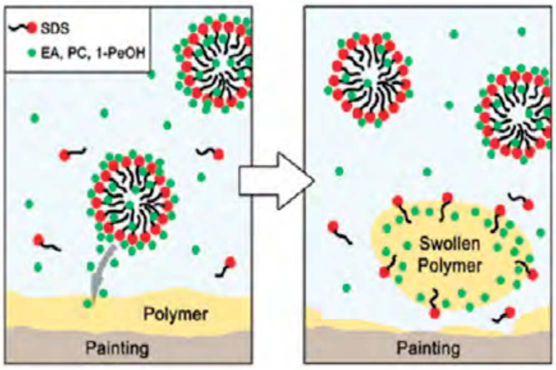
Aims

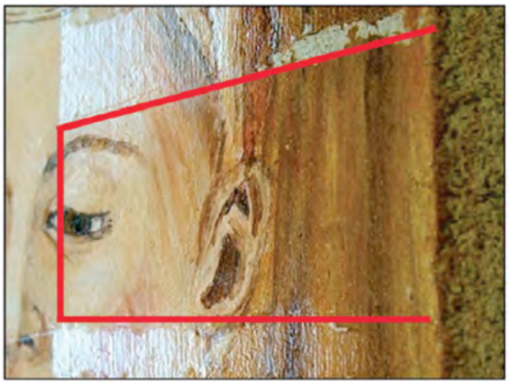
Surfactant-based systems to remove synthetic polymers from painted surfaces.

Results

Nanotechnology has recently provided new formulations for the cleaning of paintings that can replace the traditional methods based on organic solvents. These last are very often environmentally unsafe and usually not specific for the selective removal of degraded resins (polymers) or grime. Moreover, their application results in the undesired spreading of the dissolved materials within the porous structure of the artwork. Since the beginning of the 1990s, CSGI has been investigating the potential application of microemulsions and micellar solutions for the cleaning of artworks surfaces.

Past restoration treatments, based on the use of synthetic polymers, proved detrimental due to the polymers degradation. In fact, they are unstable in many environmental conditions: drastic temperature and relative humidity changes, mechanical abrasion by dust and wind, rain and water condensation, light and pollution, all promote degradation. The final effect is the oxidation of polymer end-groups or side-groups, the chemical breakdown of polymer chain (chain-scission), and cross-linking reactions. All these processes lead to the loss of pigments adhesion, yellowing of polymers, decrease of polymer solubility and loss of treatment reversibility. The only way for removing them has been limited for years to the usage of mixtures of toxic solvents.





Cleaning procedures, when improperly performed, may be aggressive and invasive for the original materials. Micelle solutions, microemulsions and gels offer new tools for the cleaning of surfaces.

The first example of microemulsion application for cleaning organic contaminants (bee wax spots) on fresco paints was performed on Masaccio, Lippi, and Masolino masterpieces in Florence (Brancacci chapel). In the last year we reported on the search of new nano-structured systems (microemulsions and micellar solutions) formulated to face new conservative challenges, like the removal of vinyl/acrylic copolymers from mesoamerican wall paintings in archeological sites in Mexico. Recently, these systems have been used in several restoration interventions for the removal of vinyl and acrylic polymers from large areas of painted surfaces. Microemulsions and micellar solution developed at the CSGI Center were used in the Sacristy of San Salvador Church in Venice (60 m^2), for the cleaning of the mural paintings in the Conegliano (near Venice) Cathedral Façade (250 m^2) and also on the mural paintings of the Old Sacristy of Santa Maria della Scala in Siena (90 m^2).

Wall paintings in the San Salvador Church in Venice: before (A) and after (B) cleaning with an o/w microemulsion.

References

Baglioni, M.; Rengstl, D.; Berti, D.; Bonini, M.; Giorgi, R. and Baglioni, P. "Removal of acrylic coatings from works of art by means of nanofluids: understanding the mechanism at the nanoscale", Nanoscale, 2, 1723-1732 (2010).
Giorgi, R.; Baglioni, M.; Berti, D. and Baglioni, P. "New methodologies for the conservation of cultural heritage: micellar solutions, microemulsions and hydroxide nanoparticles", Accounts of Chemical Research, 43, 695-704 (2010).
Baglioni, P.; Giorgi, R. and Dei, L. "Soft condensed matter for the conservation of cultural heritage", Compte Rendus Chimie, 12, 61-69 (2009).
Giorgi R.; Chelazzi D.; Carretti E.; Falletta E. and Baglioni P. "Microemulsions for the cleaning of wall paintings", Proceedings of the 15th Triennal Conference ICOM Committee for Conservation, New Delhi, September 22-26, 2008, vol.I, p. 527-533.
Carretti E.; Giorgi R.; Berti D. and Baglioni P. "Oil-in-Water Nanocontainers as Low Environmental Impact Cleaning Tools for Works of Art: Two Case Studies", Langmuir, 23, 6396-6403 (2007).

2A – Deacidification of waterlogged wood: the Vasa shipwreck case studies

P. Baglioni, D. Chelazzi, R. Giorgi, G. Poggi

Aims

Calcium and magnesium hydroxide to protect wood from acidity.

Results

The promising results obtained in the deacidification of paper and books suggested that magnesium and calcium hydroxide nanoparticles could be used also for wood. Wood is a more complex system than paper. In fact, it shows a three-dimensional structure due to the arrangement of cells and contains also lignin and hemicellulose as a major component. This involves that small particles must be used in order to get a good penetration into the substrate. Moreover, the interaction of the nanoparticles (as well as the carrier solvent) with the different chemical wood components must be carefully taken into account.

Vasa shipwreck at Swedish Maritime Museum in Stockholm

The Vasa wood shows particular features that made it a unique case in archaeological wood preservation. The warship sank during its maiden voyage in 1628, in the Stockholm port, and was recovered only in 1961. In order to avoid the shrinkage of the structure, PEG aqueous solutions were sprayed on the wood for seventeen years after the recovering. Inside the wood sulfuric acid and sulfates, responsible for low pH values, are present; moreover, iron, resulting from the corrosion of bolts, is found in both of its most common oxidation states. For these reasons, both hydrolys and oxidation corrision phenomena are currently active inside the wood.

In order to preserve this artwork, the inhibition of both deterioration processes is needed. Environmental conditions, i.e. pH, are of outmost importance and, for this reason, to develop an efficient conservation treatment specifically designed for the warship, pH role must be always considered. During the past 5 years, interesting results in the deacidification of small portion of the wood from *Vasa*, both oak and pine, were achieved. The experimental work carried out in the past year can be considered an improvement of the previous research and it is mainly based on the acquired knowledge. Our aim was the development of a novel approach that can make possible the treatment of large portion of wood, as, for example, a statue from the hull's decoration. In order to plan this kind of intervention, the effective costs (in terms of material and time) must be considered. It's worth noting that, even though cost may be lowered, a long-term stabilization of the wood must be still provided.

For this reason, calcium and magnesium hydroxide nanoparticles dispersions, especially designed for the application on wood samples from the *Vasa* were prepared and applied to large wood samples from the Vasa. PH measurments and thermogravimentric measurements were carried out on deacidified pinewood sample, at variable depths, in order to evaluate the effectivness of the applied treatments.

From the experimental data, it can be concluded that the removal of PEG, although is a time-consuming and chancy intervention, is necessary for the penetration of the neutralizing dispersion. Moreover, among the applied deacidification treatment, the better penetration was achieved with magnesium hydroxide dispersion whose particles are smaller than the ones of the calcium hydroxide formulation. Nevertheless, high pH values were recorded on the deacidified wood and a double-step treatment was necessary in order to remove the PEG and increase the penetration and the distribution of the neutralizing agent within the wood cells. Even though promising results were obtained with the innovative systems, it should be concluded that a dispersion that meets both the requirements of high production rate (with low cost) and good performance (penetration and neutralization) has yet to be developed.

References

Giorgi, R.; Chelazzi, D. and Baglioni, P. "Nanoscience contribution to preservation of acidic shipwrecks", Proceedings of the 10th ICOM-CC conference on Wet Organic Archaeological Materials - WOAM 2007, Amsterdam on September 10-15 2007, Editors: K. Straetkvern, D.J. Huisman, RACM: Amersfoort, 525-538 (2009).

Chelazzi, D.; Giorgi, R. and Baglioni, P. "Nanotechnology for Vasa Wood De-Acidification", Macromolecular Symposia (Special Issue: Macromolecules in Cultural Heritage, Issue Edited by F. Cappitelli, Y. Shashoua, E. Vassallo.) 238 (1), 30-36 (2006).

Chelazzi, D.; Giorgi, R. and Baglioni, P. "Nanotechnologies for the conservation of waterlogged wood: the Vasa case studies", Heritage, Weathering and Conservation conference (HWC-2006): proceedings, edited by R.Fort, M.Alvarez de Buergo, M.Gomez-Heras & C.Vazquez-Calvo, Taylor & Francis/A.A.Balkema Publishers, London, 797-802 (2006).

Giorgi, R.; Chelazzi, D. and Baglioni, P. "Conservation of acid waterlogged shipwrecks: nanotechnologies for de-acidification", Applied Physics A: Materials Science & Processing (Special issue: Materials Science and Cultural Heritage, Guest Editor(s): M.-C. Corbeil, M. Stuke, M. Menu, G. Padeletti), 83 (4), 567-571 (2006).

Giorgi, R.; Chelazzi, D. and Baglioni, P. "Nanoparticles of calcium hydroxide for wood conservation. The deacidification of the Vasa warship", Langmuir, 21, 10743-10748 (2005).

2A – Chemical gel for the restoration of canvas paintings

P. Baglioni, D. Chelazzi, R. Giorgi, G. Pizzorusso, M. Bonini, E. Fratini (CSGI, University of Florence).

Aims

Removal of resins used during relining in canvas consolidation.
Formulation of magnetic-responsive chemical gel.

Results

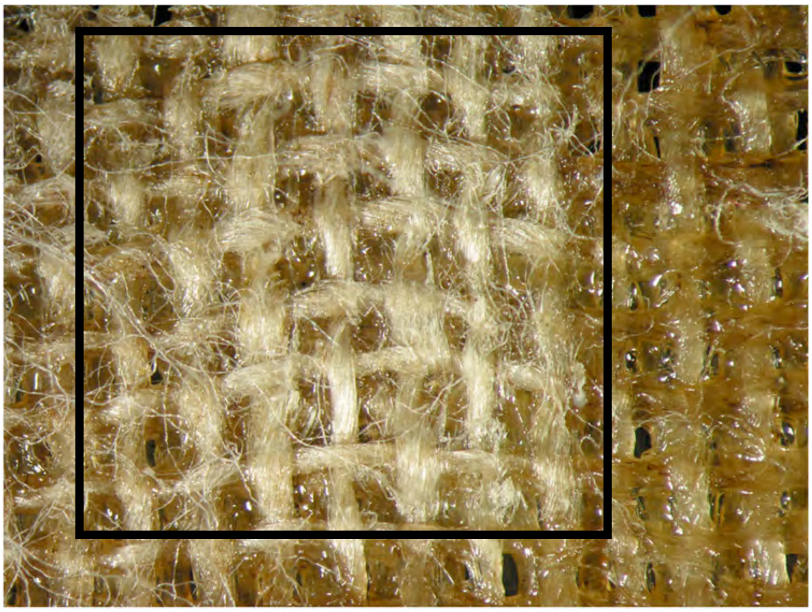
The most common cleaning method in restoration of canvas paintings is based on the usage of physical gels (called solvent gels) containing large amounts of pure solvent. This method, in spite of its high cleaning capacity, presents some drawbacks for both the object and the operator. First of all the solvent could penetrate through the surface and solubilize the painting's binder; a second issue is due to the fact that most of the commonly used solvents are toxic. After the application, it is necessary to remove the solvent gel; in order to do that, restorers use swabs soaked with white spirit, and it has been shown that after this operation some gel residues can be found on the substrate.

This project is focused on two main points: to avoid the use of pure free solvent and to substitute physical gels with chemical gels. In this way, solubilization of painting's binder and the presence of gel residues can be avoided.

Physical gel systems have been extensively used for the cleaning of artwork surfaces, especially canvas and wood paintings. Physical gels consist of a structural network, based on weak forces like hydrogen bonding, Van der Waals and dipole-dipole interactions. Due to this nature they can be easily applied, for example by gentle brushing, also over large surfaces. Unfortunately, they have the great disadvantage of leaving residues on the surface of the artwork and usually they are sticky. In order to avoid these drawbacks, different gelators were also investigated in order to obtain gels that could be loaded with microemulsions.

Besides traditional gelators as cellulose derivatives, functionalized magnetic nanoparticles can be chemically attached to a polymer matrix to form chemical magnetic responsive gel, acting as a permanent hydrogel. These gels can be magnetically manipulated to eliminate the residues left on the surface. The unique properties of the magnetic responsive chemical hydrogel have been screened in order to tune the system response to physical stress (the magnetic field generated by a permanent magnet) and to optimize the cleaning properties of the oil in water/microemulsion the gel was loaded with. Our work was focused on the optimization of the hydrogel properties in order to obtain an "easy-to-load" reversible system for the incorporation of the detergent system.

The gel matrix consists of acrylamide/N,N'-bisacrylamide network polymerized in the presence of CoFe2O4 magnetic nanoparticles. As far as the problem with residues is concerned, a specific maleic anidride functionalized polyethylene-glycol cross-linker has been synthesized. Due to its chemical nature it allows the chemical bonding of the polymer chains from the cross-linker to the nanoparticles' surface (through the carboxylic groups) and to the gel network (through the double bond that may participate in the polymerization process). Using this approach, being nanoparticles chemically linked to the gel network, possible residues left on the surfaces are avoided.



Removal of viniyacetate-acrylate co-polymer from linen canvas by using a chemical gel soaked with o/w microemulsion

References

Chevalier, A.; Chelazzi, D.; Baglioni, P.; Giorgi, R.; Carretti, E.; Stuke, M.; Menu, M. and Duchamp, R. “Extraction d’adhésifs de rentoilage en peinture de chevalet: nouvelle approche”, Proceedings of the 15th Triennal Conference ICOM Committee for Conservation, New Delhi, September 22-26, vol.II, p. 581-589 (2008).
Bonini, M.; Lenz, S.; Falletta, E.; Ridi, F.; Carretti, E.; Fratini, E.; Wiedenmann, A. and Baglioni, P. “Acrylamide-based magnetic nanosponges: an approach to nanocomposite materials”, Langmuir, 24, 12644-12650 (2008).
Bonini, M.; Lenz, S.; Giorgi, R. and Baglioni, P. “Nanomagnetic Sponges for the Cleaning of Works of Art”, Langmuir 23, 8681-8685 (2007).
Giorgi, R.; Chelazzi, D.; Carretti, E.; Falletta, E. and Baglioni, P. “Microemulsions for the cleaning of wall paintings”, Proceedings of the 15th Triennal Conference ICOM Committee for Conservation, New Delhi, September 22-26, vol. I, p. 527-533 (2008).

2A – Study of the technique in Mesoamerican mural painting: characterization of binders and their behavior.

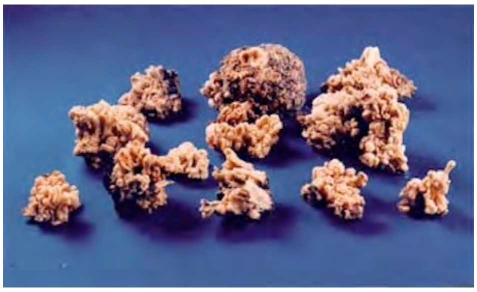
L. Bernini, R. Giorgi, F. Ridi, P. Baglioni (CSGI, University of Florence).

Aims

Characterization of Mesoamerican painting techniques, pigments, dyes and mortars were carried out, and deterioration causes of the paintings were investigated. Special attention was dedicated to the behavior of polysaccharide binders. Water-gum interactions were studied through thermal analysis.

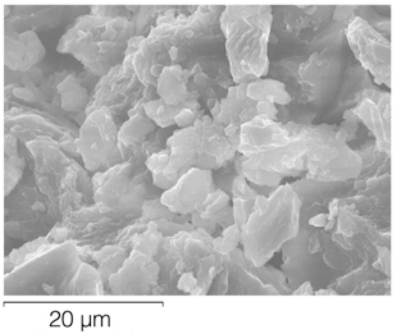
Results

The painting techniques used by Mesoamerican people to create *murales* (mural paintings of the pre-Columbian era) are partially unknown. Knowledge of these techniques was deepened. Samples of wall paintings were collected in several archaeological sites in central Mexico. Analyses were performed using FTIR spectroscopy to identify the main compounds (soluble salts, organic binders, clays used as dyer supporting material, etc.), XRD to characterize inorganic pigments (i.e. ochre and FeO_x), Optical Microscopy and SEM-EDS for morphological and elemental analysis of cross-sections. Ochre and hematite were found in painted layers, but in some cases organic dyes were probably used, since no trace was found of elements that could provide color. Analyses allowed identifying maya blue, an organic blue dye absorbed on the clay palygorskite, and it was also supposed that there could be other colors with similar composition.

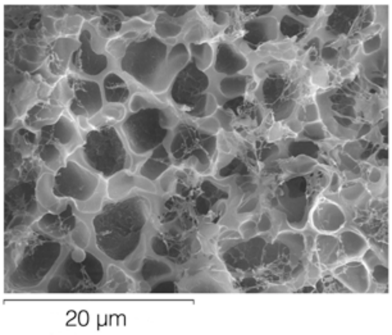


Literature reports that painters of this area used natural exudates extracted from plants as binders for pigments and dyes. Exudate gums have a polymeric structure and polysaccharide composition. The most common is the *goma de nopal*, but also *goma de mesquite* and *orquidea* extracts had a large diffusion. Ten natural gums were selected as a reference set of materials, in order to create a database to be used for an easier identification of the binders extracted from wall paintings samples. It was hypothesized that the excellent conservation state of the paintings in extreme environmental conditions due to tropical climate (very high humidity and temperatures) could be explained by the specific interaction between gums and water, in a similar way to the protective effect of trehalose on biological structures. GC-MS was used to characterize the composition of gums and to detect the presence of polysaccharides in painting samples. Different kinds of monomers where detected in the gums, and their presence was detected also in painting samples.

The glass transition temperature of gums and the percentage of bound water were measured by thermal analysis (DSC and DTG). DSC analysis was carried out on the pristine, lyophilized and hydrated samples. The glass transitions were determined with heating scans in the 20-140ºC temperature range. Values of glass transition temperatures are estimated at 120ºC ca. In order to measure the bound water content, the samples were cooled down to -90ºC and then heated again to room temperature. It was demonstrated that, when the samples are hydrated, they bound part of the water that is not capable to freeze and melt again. DTG analysis was also performed to estimate the amount of water in the pristine and in the samples hydrated at high relative humidity, in order to simulate the tropical climatic conditions. Total amount of water in pristine samples is estimated in 10% w/w ca. The morphology of dry and hydrated samples was also investigated with SEM in order to identify the role of the water on the gel structure (figure).



Opuntia as pristine



Opuntia-water 50% w/w (lyophilization was performed before SEM analysis)

References

Sahagun, F.B. “Historia general de la Nueva España” Ed. Porrua, Mexico (1975).

Magaloni Kerpel, D. “Metodología para el análisis de la técnica pictórica mural prehispánica: el Templo Rojo de Cacaxtla”, INAH colección científica 1994.

Peña, A.; Capella, S. and González, C. “Characterization and Identification of the Mucilage Extracted from orchid Bulbs (Bletia Campanulata) by High Temperature Capillare Gas Chromatography (Ht-CGC)”, J. High Resol. Chromatogr., 18 (1995).

McCrystal, C.; Ford, J. and Rajabi-Siahboomi, A.R. “A study on the interaction of water and cellulose ethers using differential scanning calorimetry” Thermochimica Acta, 294, 91-98 ELSEVIER (1997).

2A – Ionic liquid/Brij 30/nonane microemulsions: Characterization and applications

M. C. Arroyo, P. Baglioni, D. Berti, E. Fratini, R. Giorgi (CSGI, Dep. Chemistry, Univ. Florence, Italy)

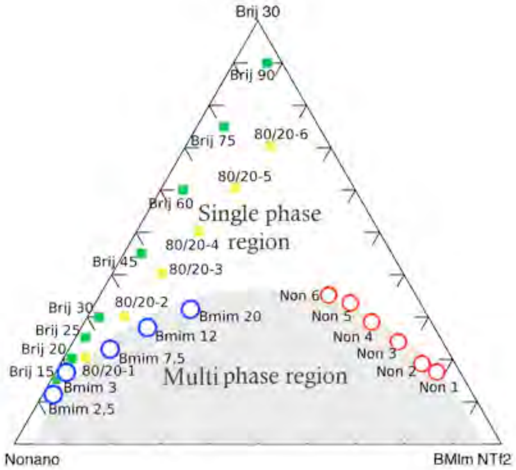
Aims

Phase behavior and microstructure of ionic liquid-brij30-nonane ternary system. Reverse water-less microemulsions as novel cleaning agents for water sensitive artworks. Ionic liquid (IL) based microemulsions as templating systems for the production of gold nanoparticles.

Results

Waterless microemulsions composed of low-viscosity bis(trifluoromethylsulfonyl) imide-based, room-temperature ionic liquids, surfactant Brij 30, and nonane have been prepared and characterized by phase behavior, dynamic light scattering (DLS), and Small-Angle X-Ray Scattering (SAXS).

The ternary phase diagram of the 1-butyl 3-methylimidazolium bistrifluoromethyl sulfonyl imide (Bmim NTf2) at 25 ºC was determined by direct observation of the transition from turbidity to transparency.



The single phase microemulsion region is heterogeneous on the microscopic scale: ordered microstructures such as IL-in-nonane (IL/O) or nonane-in-IL (O/IL) microdroplets can form at high nonane or IL content. These are separated by highly structured bicontinuous microemulsions. Results obtained by SAXS are in excellent agreement with values derived from DLS analysis. It was observed that the size of reverse microemulsion droplets initially increased with increasing Brij 30 and IL molar fractions, but under further addition of these components the size of droplets decreased remarkably. It was hypothesized that the number of microemulsion droplets had increased. SAXS data fit a model of polydisperse cylinders, the cylinder length decreasing with increasing surfactant concentration. High IL-fraction microemulsions were fitted to the Teubner-Strey model. Results confirm the presence of highly structured bicontinuos microemulsions. Greater IL and surfactant concentrations determine more ordered systems.

Ionic liquid microemulsions are increasingly studied in many different chemical application areas since they combine the unique features of ILs and microemulsions. In this research project the reverse IL/O microemulsions are being investigated as templating systems for the production of gold nanoparticles from tetrachloroaurate(III), $HAuCl_4$, by UV-photoactivation technique. Formation of gold nanoparticles was monitored using UV-Vis absorption spectroscopy. Nanoparticles were characterized by DLS and SAXS and compared with colloidal gold synthesized using water-in-oil (W/O) microemulsions as templating system. W/O synthesized nanoparticles are spherical in shape while synthesis in IL/O microemulsions gives cylindrical-shaped and less polydispersed gold nanoparticles.

These reverse microemulsions are also being tested as novel cleaning agents for water sensitive artwork, for the removal of aged polymeric materials applied in past restorations as consolidants or protective coatings. Microemulsions solve the problem of using large amounts of pure solvents, which are very often environmentally unsafe and not specific for the selective removal of degraded resins or grime. Moreover the presence of water could be dangerous for delicate, vulnerable and water-sensitive artworks. In fact cellulosic materials (such as paper, canvas and wood), and painting layers tend to absorb water that induces swelling, deformation and mechanical stress. Preliminary tests showed that IL-based microemulsions are effective for the removal of several polymers, such as Mowilith DMC2, Mowilith DM5, Plexisol, Paraloid and BEVA. In order to characterize results of cleaning tests, it will be necessary to carry out an accurate laboratory study on model samples. Extraction capability and selectivity of the cleaning tools, as well as the potential release of residues, are being investigated through visual and photographic observation, Scanning Electron Microscope (SEM) and micro-reflectance Fourier Transform Infrared Spectroscopy (FT-IR) techniques.

References

Greaves, T.L. and Drummond, C.J. “Ionic liquids as amphiphile self-assembly media”, Chem. Soc. Rev. 37, 1709-1726, (2008).

Qiu, Z. and Texter, J. “Ionic liquids in microemulsions”, Curr. Opin. Colloid Interface Sci 13, 252-262, (2008).

Gayet, F.; El Kalamouni, C.; Lavedan, P.; Marty, J.D.; Brûlet, A.; Lauth-de Viguerie, N. “Ionic liquid/oil microemulsions as chemical nanoreactors”, Langmuir 25(17), 9741-9750 (2009).

Atkin, R. and Warr, G.G. “Phase behavior and microstructure of microemulsions with a room-temperature ionic liquid as the polar phase”, J. Phys. Chem. B 111, 9309-9316 (2007).

Pal, A. “Photochemical synthesis of gold nanoparticles via controlled nucleation using a bioactive molecule”, Materials Letters 58, 529-534 (2004).

2A – Surfactant for environmental remediation

L. Ambrosone, A. Ceglie, G. Bufalo (ISPESL, Naples)

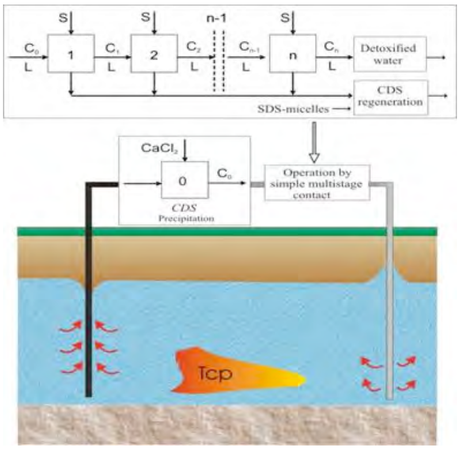
Aims

The Environmental Remediation Project focused on characterization, monitoring, and modelling of subsurface environments, with a particular emphasis on contaminant remediation and water resources. The project is both basic and applied, and includes studies that span a wide range of spatial scales (molecular studies to full-scale field investigations) and of environmental conditions, utilizing expertise in various fields.

Results

Groundwater pollution is the loss of water quality due to waste products or others substances which alter the chemical and microbiological water properties. Traditional *pump-and-treat* techniques are very expensive and in the recent years considerable attention has been addressed towards the development of alternative technologies, such as *surfactant-enhanced aquifer remediation*. In this research project the micellar solubilization of 2,4,5 trichlorophenol was spectrophotometrically investigated and the results were used as a model of chlorinated contaminant.

A novel surfactant-based adsorbent material able to solubilize pollutants in SDS-micelles was obtained[1,2]. By means of this material the excess of the pollutant can be easily removed with a precipitation process. The adsorptive efficiency of this novel material was tested through a cocurrent multistage process and its performance was compared with those of most common adsorbents such as activated carbon and silica gel. The experimental results are used to outline a new design to detoxify groundwater[2] (see figure).



References

Ambrosone, L. and Ceglie, A. “Gel stabili”, Italian Patent 2003 n. 4454.

Venditti, F.; Angelico, R.; Ceglie, A. and Ambrosone L. “Novel Surfactant-Based Adsorbent Material of Groundwater Remediation”, Environment Science Technology, 41, 6836-684 (2007).

2A – Nanoparticles for biodeterioration control

F. Bellissima, M. Bonini, E. Fratini, R. Giorgi, P. Baglioni, P.Canton (Università Ca'Foscari, Venezia)

Aims

The aim of the work is the design and preparation of nanosystems able to protect the surface of manufactured lithoic materials from the proliferation of bacteria, fungi and lichenes. Current procedures for the treatment of the biological deterioration of the cultural heritage materials involve the use of biocides, but they fail in the long-term protection and present toxicity-related problems. Our purpose is to confer the materials long-term anti-microbial properties, with no harm for the environment, through the coating of the surfaces with nanoparticle-based dispersions that would inhibit the growth of biodeteriogens.

Results

We prepared nanostructured titanium dioxide, TiO_2, and we studied the effects of the reaction solvent on the structure and the physico-chemical properties of the particles.

The structural analysis was performed using small angle X-ray scattering (SAXS) and the fitting results (Figure 1) revealed primary particles with radius in the 3-5 nm range. This was confirmed by high-resolution transmission electron microscopy (HR-TEM), also used to investigate the crystalline structure of the particles. All the samples consisted of the anatase phase, as confirmed by X-ray diffraction pattern (XRD, Figure 2), and the bigger nanocrystals appeared to be elongated along one preferential direction (Figure 3).

The particle surface was modified by chemically bonding different silanes in order to enable the particles to graft to the lithoid materials, either through physical or chemical interaction. The surface functionalization was confirmed by infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA) and HR-TEM (Figure 4).

The antimicrobial activity of TiO_2 nanoperticles is a consequence of the photo-production of reactive oxygen species (ROS), inducing damages on the cell membrane of the microorganisms. The photocatalytic properties of the colloidal dispersions were evaluated through a model photoreaction based on the UV degradation of an organic dye, methylene blue (MB). Both the naked and the functionalized nanoparticles proved to be photocatalitically active (Figure 5). Tests of the antimicrobial properties of functionalized TiO_2 nanoparticles against *Bacillus subtilis* are now in progress.

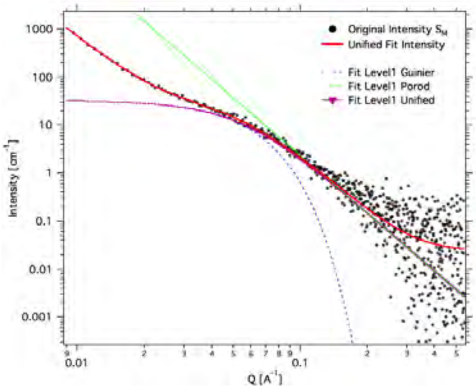


Figure 1. SAXS fitting result on TiO_2 nanoperticles obtained from pure methanol as solvent.

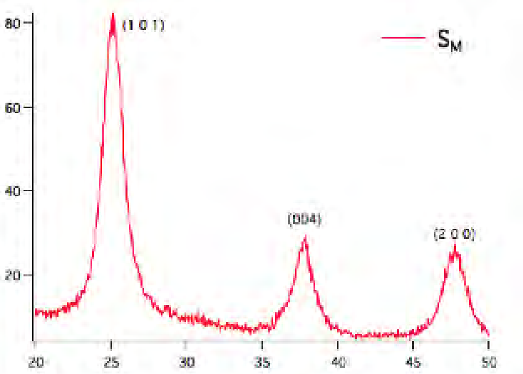


Figure 2. XRD diffraction pattern relative to the sample obtained from pure methanol as solvent.

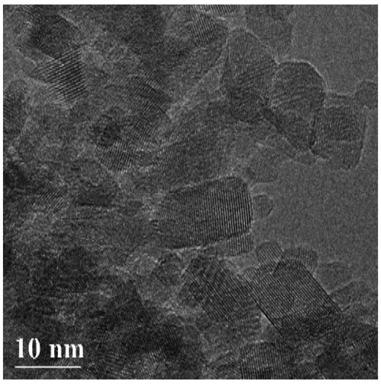


Figure 3. HR-TEM image of naked TiO_2 nanoparticles.

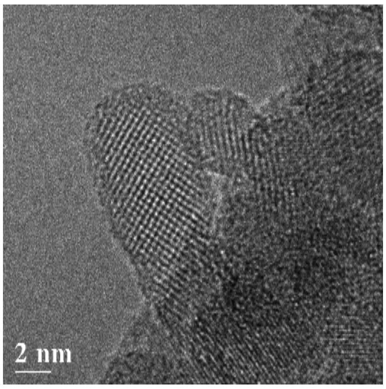


Figure 4. HR-TEM image of silane functionalized TiO_2 nanoparticles.

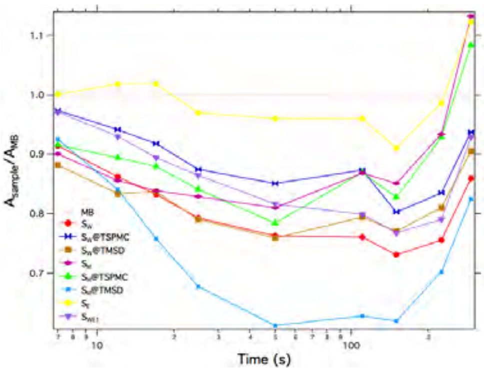


Figure 5. Absorbance of the samples MB/TiO_2 (as –prepared from different solbent mixture and silane functionalized) normalized for the absorbance ob MB at λ=657 nm as a function of the irradiation time.

References

Liao, J.; Shi, L.; Yuan, S.; Zhao, Y. and Fang, J. "Solvothermal synthesis of TiO_2 nanocrystal colloids from peroxotitanate complex solution and their photocatalytic activities", J. Phys. Chem. C, 113, 18778-18783 (2009).

2A – Polyvinyl alcohol highly viscoelastic dispersions: a new class of cleaning tools for works of art

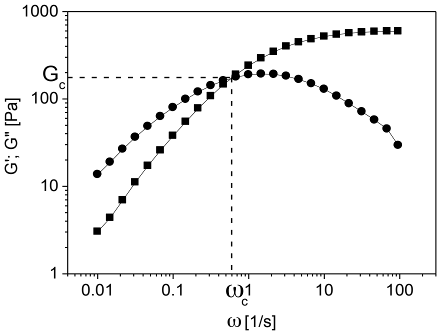
E. Carretti, I. Natali, L. Dei, P. Baglioni

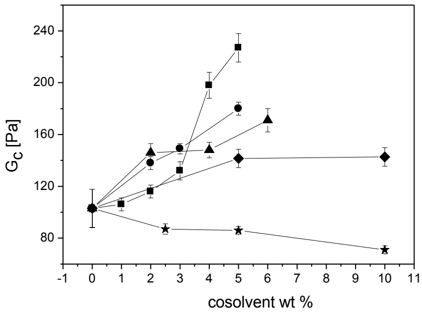
Aims

The main objective of this project was to develop and characterize a new class of cleaning tools for works of art that minimize both the use of organic liquid solvents and the presence of residues after the cleaning action. The ability of poly (vinyl alcohol) (PVA) aqueous dispersions cross-linked with borate ions to give highly viscoelastic systems, in the presence of some of the most largely used organic solvents usually employed during the cleaning of paintings, has been largely explored.

Results

It has been observed that the PVA-borate systems do provide selective, surface-controlled cleaning action as well as facile and benign removal from a painting surface. Their very high elasticity allows them to be peeled from a surface without introducing a strong lateral force. By so doing, residues left on the painted surface from the patina and from the cleaning tool are expected to be minimized and the mechanical action and repeated washings usually necessary for the complete removal of traditional gels can be avoided. Moreover, this elasticity can be easily modulated by changing the ratio of PVA to borate or their total concentration.



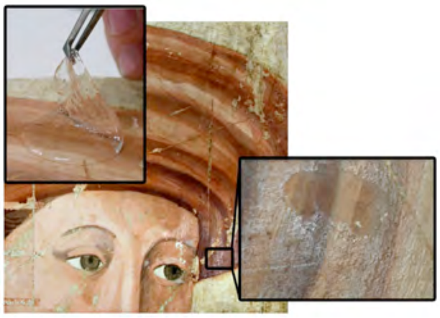


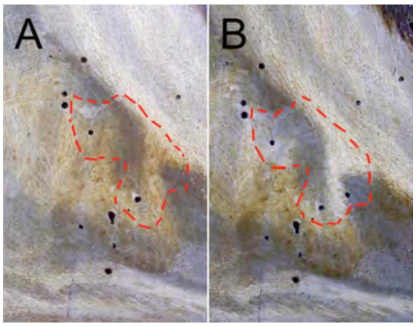
In order to evaluate the behaviour of these new polymeric dispersions when they are in contact with the painted surfaces and during their removal once they have carried out their function, the rheological properties have been explored as a function of both the organic co-solvent concentration and chemical nature. Frequency sweep curves collected for samples containing different amount of organic co-solvents indicated that at low frequencies the viscous modulus G″ is higher than the elastic modulus G′, while at high frequencies G′ > G″. The presence of a crossover between the G′ and the G″ curves indicates that the mechanical behaviour of these systems is characteristic of high viscosity polymer solution rather than true gels.

However, the crossover coordinates G_c and ω_c are typical of each system and are useful to understand if and how the presence and the concentration of co-solvent influences the mechanical properties. For all the co-solvents studied, apart from propylene carbonate (★), G_c increases with the amount of the added co-solvent; the order of change magnitude induced is: cyclohexanone (■) > 1-pentanol (▲)> 2-butanol (•) > 1-propanol (♦).

This trend is in agreement with the expected increase in the degree of crosslinking and indicates that increasing the amount of co-solvent, the solid-like behaviour, the elastic character of these systems are exalted; the higher the elastic character of the cleaning agent, the easier is its removal.

Furthermore, the ability to load wider range of organic solvents into the cleaning agent increases their ability to swell or soften/solubilize several different forms of deteriorated coatings and varnishes (as well as other hydrophobic substances) as demonstrated in several cleaning tests performed in laboratory as well as onto artistic surfaces (Santo Stefano by Ludovico Cardi detto il Cigoli, Incoronazione della Vergine by Neri di Bicci and others). These systems require no after-washing to remove residues, their cleaning action is easily controlled, and they can be removed in one piece by peeling.





Recently, we have found that the weight fraction and range of organic liquids within the aqueous liquids of borate gels can be increased significantly by employing poly(vinyl alcohol-*co*vinyl acetate)s (PVAc-VA) as the cogellants. Preliminary cleaning tests have been conducted on a fragment of a 19th century Italian wooden frame. The top layer of shellac varnish was removed selectively and gently by applying a piece of (PVAc-VA(ca. 40% vinyl alcohol)-borate and 80/20 (w/w) ethanol/water as liquid). After 15 min, the polymeric dispersion was lifted with a spatula, and the surface was dabbed with a soft tissue to remove residual liquid. Fluorescence and visual analyses of the surface before and after cleaning indicate that all of the shellac was removed while the silver leaf remained intact.

References

Carretti, E.; Grassi, S.; Cossalter., M; Natali, I; Caminati, G.; Weiss, R.G.; Baglioni, P. and Dei, L. “Poly(vinyl alcohol)-borax hydro/cosolvent gels. Viscoelastic properties, solubilizing power, and application to art conservation”, Langmuir, 25, 8656-8662 (2009).

Carretti, E.; Natali, I.; Matarrese, C.; Bracco, P.; Weiss, R.G.; Baglioni, P. and Dei, L. “A new family of viscoelastic polymeric dispersions for cleaning easel paintings”, Journal of Cultural Heritage, 11, 373-380 (2010).

Carretti, E.; Bonini, M.; Dei, L.; H. Berrie, B.; Angelova, L.V.; Baglioni, P. and Weiss, R.G. “New Frontiers in Materials Science for Art Conservation. Responsive Gels and Beyond”, Accounts of Chemical Research 43, 751-760 (2010).

2A – Silver nanoparticles on fabrics: synthesis and antimicrobial effect

E. Falletta, M. Bonini, E. Fratini, P. Lo Nostro, P. Baglioni,
A. Lo Nostro[1], G. Pesavento[1], P. Canton[2]
[1]: Dept. Public Health, Univ. of Florence
[2]: Dept. PhysicalChemistry, University of Venice Ca' Foscari

Aims

Clusters of polyacrylate-templated Silver nanoparticles can be used to transfer the antimicrobial properties of Ag to different fabrics.

Results

Silver-poly(acrylate) clusters have been synthesized in water by reduction of $AgNO_3$ in the presence of poly(acrylates) of different molecular weights through two different methods, $NaBH_4$ reduction and UV exposure. The structure of the clusters and the effect of the synthesis parameters on the size and polydispersity of the particles were evaluated by means of small-angle X-ray scattering (SAXS). Fitting results reveal the presence of a bimodal distribution of spherical nanoparticles, showing that both the reduction method and the polymer chain length play key roles in determining the final size of the particles and the overall size of the clusters. This is confirmed by High-resolution transmission electron microscopy (HR-TEM), as shown in the example of the effect of the reduction method on the nanoparticle size and shape given in Figure 1.

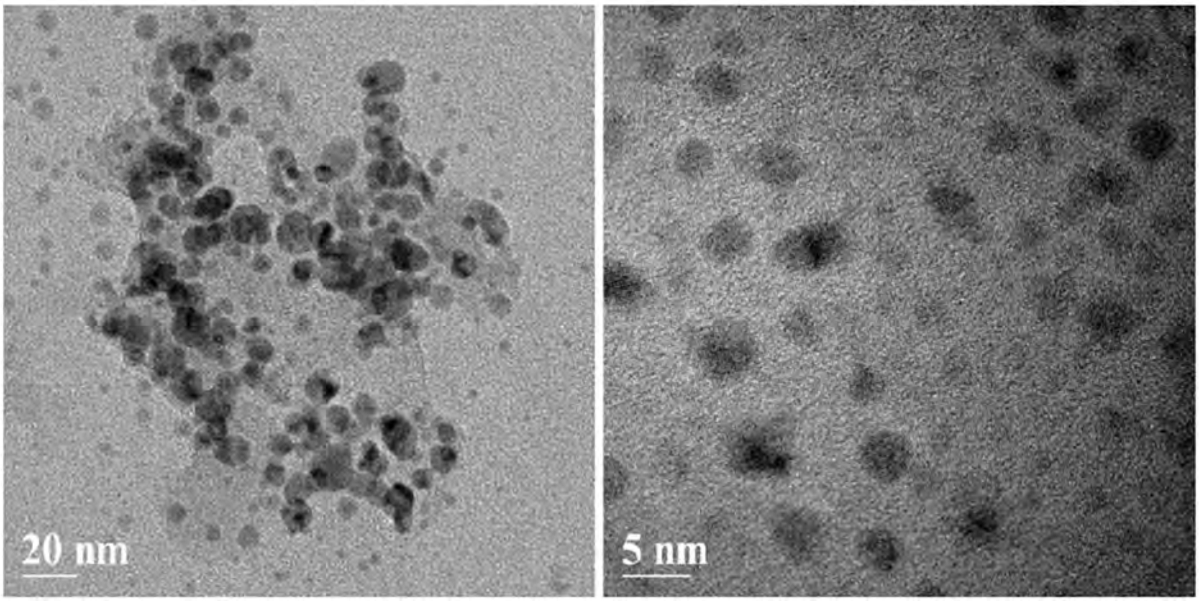


Figure 1. HR-TEM images of two Silver nanoparticle dispersions prepared in the same conditions, except for the reduction method: by UV radiation (on the *left*) and with $NaBH_4$ (on the *right*).

Nanoparticle dispersions were then used to functionalize cotton, wool, and polyester fabrics. Samples were first conditioned at constant relative humidity (RH 33%) and temperature (20 °C). They were then soaked for 15 min at room temperature in the Ag nanoparticles dispersion under magnetic stirring, squeezed to remove the excess dispersion, rinsed, and dried in an oven at 130 °C for 15 min at atmospheric pressure (dry heat). The antimicrobial activity of treated samples has been tested according to a standard procedure (agar plate diffusion test/CEN/TC 248 WG 13) against four different strains: Staphylococcus aureus, Staphylococcus epidermidis, Pseudomonas aeruginosa, and Candida albicans. The results for Ag-treated cotton samples are shown in Figure 2. The treated textiles exhibit antimicrobial activity depending on both the strain and the fabric material.

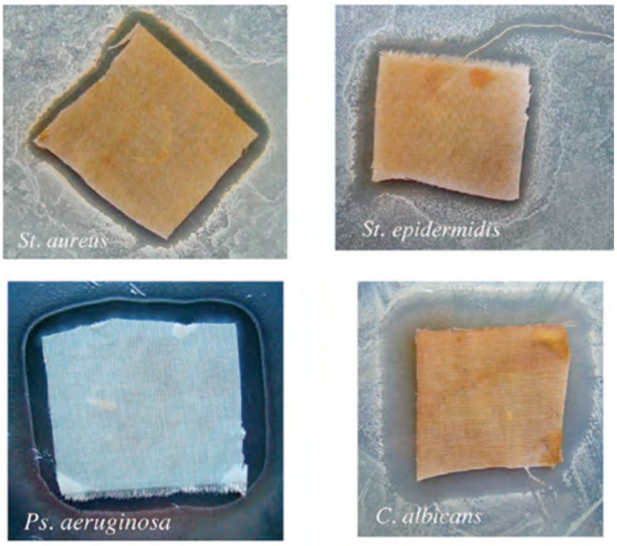


Figure 2. Effect of Ag-treated cotton samples towards the growth of the investigated strains.

References

Falletta, E.; Bonini, M.; Fratini, E.; Lo Nostro, A.; Pesavento, G.; Becheri, A.; Lo Nostro, P.; Canton, P. and Baglioni, P. “Silver Nanoclusters with Acrylates as Templating Agents: a SAXS study”, J. Phys. Chem. C 112, 11758 (2008).

Falletta, E.; Bonini, M.; Fratini, E.; Lo Nostro, A.; Becheri, A.; Lo Nostro, P. and Baglioni, P. “Poly(acrylic) acid-coated Silver Nanoparticles for Antibacterial Textile Finishing”, Nanotech 2007 (Santa Clara, CA).

2A – Surface functionalization of textiles

P. Lo Nostro, M. Bonini, L. Tattini, E. Falletta, P. Baglioni

Aims

Modification of the surface of textile materials

Results

Modification of the surface of textile materials, mainly wool and cellulosic fabrics (cotton and Tencel®), was obtained through:

- grafting of a cyclodextrin derivative in order to endow the surface with empty hosting cavities that can be used for uptake/release of fragrances, insect repellents (such as DEET), antimicrobials, etc. (Figure 1)
- deposition of metal oxide nanoparticles (PZT, ZnO and TiO_2) or solar filters for anti-UV shield and comfort upgrade (Figure 2)
- flame retardancy through surface reaction of cellulosic fibers with ammonium sulfammate and urea water solutions

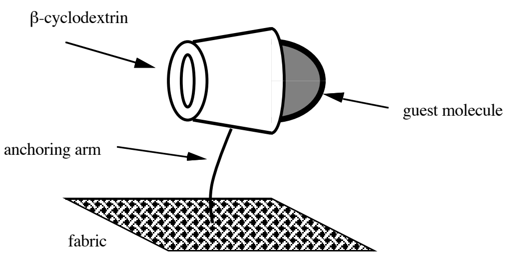


Figure 1

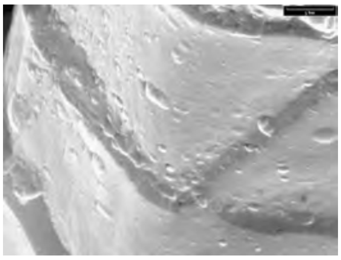


Figure 2

The formation of stable inclusion compounds at the fabrics' surface was tested with several techniques: UV-VIS spectrophotometry (with integrating sphere), back-extraction with organic solvents, calorimetry, aroma testing and insect repellency tests (in collaboration with the Italian National Institute of Health, Rome). Figures 3 and 4 show a specimen of Tencel® treated with monochlorotriazinyl-b-cyclodextrin and then with DEET, a common insect repellent.

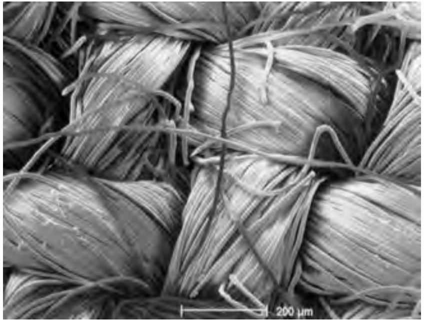


Figure 3

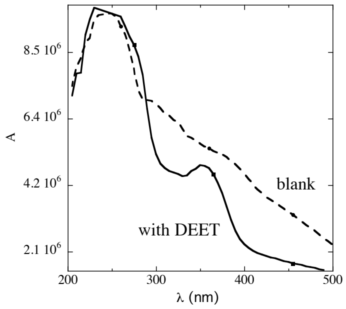
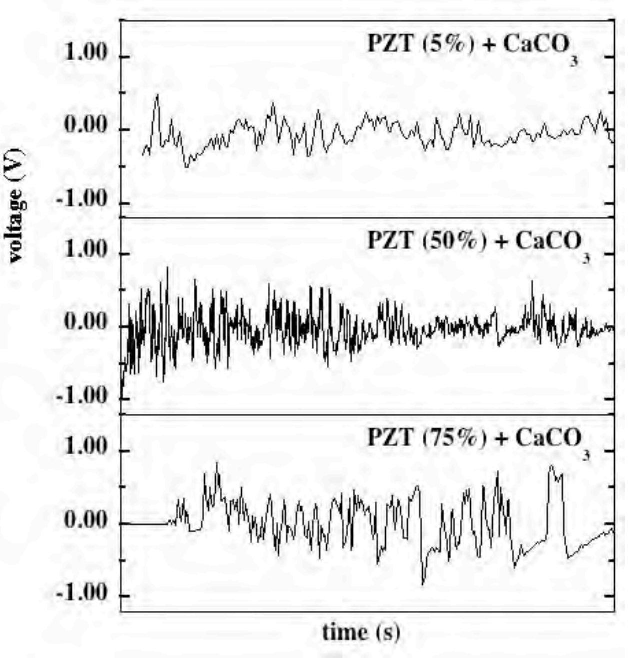


Figure 4

The synthesis of PZT nanoparticles with piezoelectric effect (Figure 5) was carried out for application in geotextiles.



References

Tattini, L.; Lo Nostro, P.; Ravalli, A.; Stirner, M. and Baglioni, P. "Piezoelectric PZT nanodevices from a hybrid ligand burning method", J. Nanoparticle Res. (2010) Available Online. DOI 10.1007/s11051-010-9930-5.

Scalia, S.; Tursilli, R.; Bianchi, A.; Lo Nostro, P.; Bocci, E.; Ridi, F. and Baglioni, P. "Incorporation of the sunscreen agent, octyl methoxycinnamate in a cellulosic fabric grafted with b-cyclodextrin", Int. J. Pharm. 308, 155 (2006).

Romi, R.; Lo Nostro, P.; Bocci, E.; Ridi, F. and Baglioni, P. "Bioengineering of a Cellulosic Fabric for Insecticide Delivery via Grafted Cyclodextrin", Biotechnology Progr. 21, 1724 (2005).

Lo Nostro, P.; Fratoni, L.; Ridi, F. and Baglioni, P. "Surface Treatments on Tencel® fabric: grafting with b-cyclodextrin", J. Appl. Pol. Sci. 88, 706 (2003).

Lo Nostro, P.; Fratoni, L. and Baglioni, P. "Modification of a Cellulosic Fabric with b-Cyclodextrin for Textile Finishing applications", J. Incl. Phen. Macrocyclic Chem. 44, 423 (2003).

Becheri, A.; Dürr, M.; Lo Nostro, P. and Baglioni, P. "Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers", J. Nanoparticle Res. 10, 679 (2008).

Falletta, E.; Bonini, M.; Fratini, E.; Lo Nostro, A.; Pesavento, G.; Becheri, A.; Lo Nostro, P.; Canton, P. and Baglioni, P. "Clusters of Poly(acrylates) and Silver Nanoparticles: Structure and Applications for Antimicrobial Fabrics", J. Phys. Chem. C 112, 11758 (2008).

2A – Dynamics of chromophoric dissolved organic matter and dissolved organic carbon in lakes

L. Bracchini, A.M. Dattilo, A. Tognazzi, S.A. Loiselle, C. Rossi

Aims

Study the temporal and spatial dynamics of chromophoric dissolved organic matter (CDOM) and dissolved organic carbon in lakes. The effect of solar radiation as well as the release of CDOM of alga derived matter and the effect of bacterial activity were studied

Results

The results from the present study indicate that (i) CDOM in the hypolimnion undergoes little modification through the year (if compared with changes occurred in the epilimnion) and winter CDOM optical properties are similar throughout the water column; (ii) the relative composition of CDOM changes from “humic-like” to “protein-like”, that is well described by the spectral slope calculated using 270-400 nm wavelength interval (Figure 1), (iii) solar UV attenuation coefficients are better correlated to CDOM absorption and Chlorophyll a concentrations than DOC concentrations. Moreover in the epilimnion, Chlorophyll a and pheopigment concentrations shows positive linear relationships with both absorption and fluorescence of CDOM. This suggest that phytoplankton contribute, together with the long term solar UV exposition, to the observed seasonal changes of the CDOM optical properties.

Salto Lake represents an interesting system where the loss in aromaticity was not followed by loss of carbon content of DOM. This promote an uncoupling between CDOM and DOC measurements (Figure 2). Multiple factors lead to an uncoupling of DOC and CDOM. Summer time conditions lead to a net loss of CDOM in the epilimnion, likely connected to processes that promote CDOM photodegradation and/or production of less (or non) chromophoric DOM. Regardless of the dominating mechanisms the results supports the idea that production of non chromophoric DOM may influence the DOC measured in the epilimnion more than CDOM photodegradation.

Finally, also the timing and duration of the physical stratification of the lake may have direct impact on CDOM/DOC dynamics. Changes in the characteristics of the stratification of the water masses (linked to climate and local changes) would have important consequences on the lake carbon budget as well as solar UV radiative transfer in the water column.

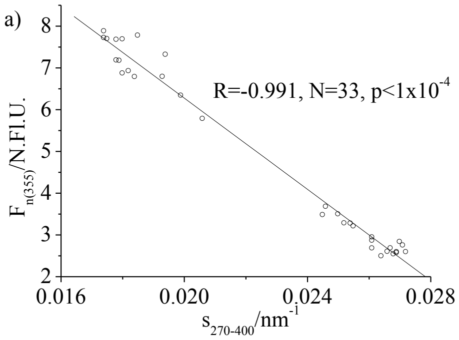


Figure 1. relationship between spectral slope ($s_{270-400}$) and Fluorescence of humic like CDOM.

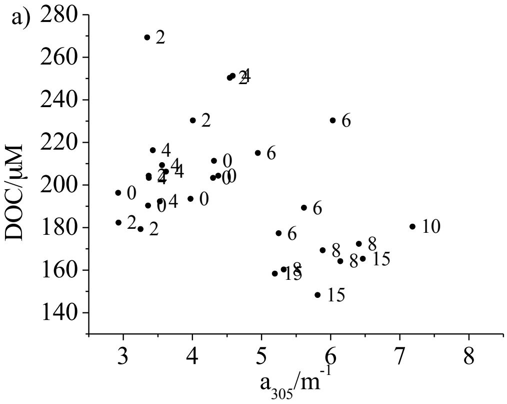


Figure 2. Uncoupling between CDOM absorption and DOC concentrations.

References

Bracchini, L.; Loiselle, S.A.; Dattilo, A.M.; Mazzuoli, S.; Cózar, A. and Rossi, C. "The spatial distribution of the optical properties in the UV and Visible in an aquatic ecosystem", Photochemistry and Photobiology 80, 139-149 (2004).

Bracchini, L.; Loiselle, S.A.; Dattilo, A.M. and Rossi, C. "The optical properties of chromophoric dissolved organic matter in the Central-Eastern Mediterranean Basin", Aquatic Sciences 72, 485-498 (2010).

2A – Interaction study of indigo carmine with albumin and dextran by NMR Relaxation

C. Bonechi, S. Martini, C. Rossi

Aims

In this work, the interaction processes between a dye and two different macromolecular models were studied with the aim to obtain physical-chemistry information about the dyeing of textiles. Two macromolecules, albumin and dextran, were chosen in order to simulate wool and cotton fibers during the coloration procedure in water. Proton NMR selective and non-selective spin-lattice relaxation rate measurements were used to monitor the strength of the overall complexation behaviour of indigo carmine towards albumin or dextran. The *affinity index*, a quantitative parameter related to the strength of the ligand-macromolecule interaction, was determined from selective spin-lattice relaxation rate enhancements due to the bound ligand molar fraction. Moreover, this approach allowed the calculation of the equilibrium constant of the complex formation (K) between the dye and macromolecular models.

NMR data suggested a higher indigo carmine-albumin complex thermodynamic stability with respect to the indigo carmine-dextran adduct. These results indicate a stronger persistence of the dyeing process in wool with respect to cotton fibers.

The approach we propose in this work, able to easily compare the ability of a dye to interact with different fiber constituents, may represent a contribution for understanding the efficiency of industrial processes of dyeing textile.

Results

The interaction of albumin (BSA) and dextran (DX) with indigo carmine was investigated via nuclear magnetic resonance (NMR) spectroscopy using proton selective (R_1^{SE}) and non-selective (R_1^{NS})spin-lattice relaxation rate measurements.

For the indigocarmine-BSA interaction study, the first evidence was that, in the absence of albumin, R_1^{NS} was bigger than R_1^{SE}. This result permits to confirm that indigo carmine (without protein) show fast reorientational motions in solution. These dynamical conditions allow the interaction processes to be investigated through the analysis of the selective and non-selective spin–lattice relaxation rates of the ligands.

The second evidence was that with the increase of albumin concentration R_1^{NS} values remained constant while R_1^{SE} increased. This enhancement reveal the existence of a large contribution from the bound ligand fraction to the observed relaxation rate, which suggests the presence of an interaction between the colorant and BSA.

In order to evaluate the strength of the interaction between the ligand, indigo carmine, and BSA, the normalized affinity index $\left[A^N\right]_L^T$ was calculated and its $\left[A^N\right]_L^T$ value was found to be (16497.0 ± 80.8) $\mathrm{mol^{-1}.dm^3}$. In order to study the interaction processes between the indigo carmine and a different macromolecule, dextran, the experimental approach proposed above was used. The experimental data show that the condition $R_1^{NS} > R_1^{SE}$ was respected in the absence of dextran. The normalized affinity index value was found to be (1121.8 ± 85.7) $\mathrm{mol^{-1}\ dm^3}$. The comparison between the affinity indexes calculated for the two dye-macromolecule systems (Figure 1), indicate that indigo carmine has a stronger affinity for BSA with respect to DX. $\left[A^N\right]_L^T$ of indigo-BSA system was 15 times the indigo-DX affinity index.

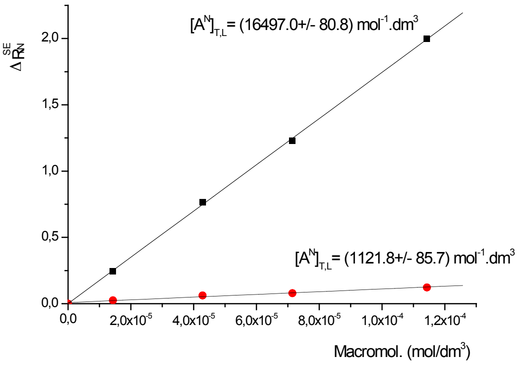


Figure 1

This behaviour is in agreement with other studies concerning the investigation of the interaction of cotton and wool with dye. It is clear, in fact, that the structure of the dye plays a key role in affecting their recognition processes with proteins and polysaccharides. In particular, indigo carmine interacts mainly via hydrophobic interactions, which are stronger for albumin, with respect to dextran. The analysis of the thermodynamics of complex formation constitutes an important step in order to deeply understand the properties of dye-macromolecule adducts, in terms of complex stability. In order to calculate the values of the complexation equilibrium constant (K), selective relaxation rates of indigo carmine were measured at different concentrations in the presence of a constant amount of BSA and DX. These experimental data allowed the calculation of the equilibrium constants associated to the complex formation, which were found to be: (1500.6 ± 156.0) mol^{-1} dm^3 and (121.0 ± 15.0) mol^{-1} dm^3 for indigo carmine-BSA and for indigo carmine-DX, respectively. These results show that indigo was able to form more stable complexes with BSA compared to DX, confirming its higher affinity towards the plasma protein with respect to DX. Data obtained in this work demonstrate that indigo carmine, one of the most used dye, show very different affinity towards albumin (used to simulate wool fiber) and dextran (used to reproduce cotton environment), quantified by the calculation of the affinity indexes and equilibrium constants of dye-macromolecule systems. These results can be interpreted in terms of diverse persistence of indigo carmine in wool and cotton fibers, as well as different efficiency of the dyeing processes.

References

Hulme, A.N.; Ferreira, E.S.B.; McNab, H. and Quye, A. "The natural constituents of historical textile dyes", Chem. Soc. Rev. 33, 329-336 (2004).

Martini, S.; Consumi, M.; Bonechi, C.; Rossi, C. and Magnani, A. "Fibrinogen catecholamines interaction as observed by NMR and FT-IR", Biomacromolecules 8, 2689-2696 (2007).

Komboonchoo, S. and Bechtold, T. "Natural dyeing of wool and hair with indigo carmine (C.I. Natural Blue 2), a renewable resource based blue dye", J. Cleaner Prod. 17, 1487-1493 (2009).

Nath, R.K.; Singh, Th. C.; Dasgupta, S.; Mitra, A. and Panda, A.K. "Interaction of cationic dye/surfactants with *Klebsiella* K18 capsular polysaccharides: Physico-chemical studies", Materials Science and Engineering C 30, 549-554 (2010).

2A – The controlling factors of productivity in African Great Lakes

S. Loiselle, A.M. Dattilo, L. Bracchini, A. Cozar, A. Tognazzi, C. Rossi

Aims

The UNISI research unit has been examining the spatial and seasonal variations in primary production and phytoplankton biomass in the African Great Lakes. These intra and interannual modifications can have a strong spatial heterogeneity due to complex links between hydrodynamics and local ecological factors. Seasonal cycles of light availability and nutrients can vary geographically, controlling the phytoplankton blooms. Using an integrated approach it is possible to analyse spatial variations in primary productivity. The resulting hypothesis is then confronted with satellite measurements of surface biomass concentrations to link forcing functions with biomass and estimate how changing climate patterns may effect ecosystem functioning.

Results

The patterns of abundance of algal biomass in aquatic ecosystems depend upon on the supply of resources (both nutrients and solar irradiance) as well as upon dominant loss processes (such as grazing and sedimentation). We develop an ecosystem specific approach for determining the algal biomass carrying capacity under light limiting conditions. The model is based on the relationship between the total solar energy available and the energy stored (algal biomass) within the ecosystem at steady state. We applied this model to describe real conditions in two disparate algal communities; the phytoplankton community in Lake Victoria, East Africa and the nanophytoplankton biomass of Lake Tanganyka.

Aquatic autotrophs have nutritional and energetic requirements that are necessary for their photosynthetic carbon fixation and growth. However, the upper limits of growth in light limiting conditions remain poorly understood with respect to nutrient-controlled capacities. This bias has partly arisen due to the complexity in modelling light availability in aquatic environments. The main challenges are the spatio-temporal variability of light within the water column, the competition for light with abiotic components and the negative feedback of algal auto-shading. *Lake Victoria, Africa*. Lake Victoria, the second largest lake in the world, represents a unique reservoir of tropical biodiversity as well as a fundamental resource for the 30 million persons living within its catchment. Beginning in the past century, increasing human activity has led to changes in the distribution and bio-availability of the nutrient pools in the watershed, airshed and lakes. Because of the extensive nature of Lake Victoria, the impact of the climate factors may be highly differentiated in space (Plisnier et al. 2000). A series of calibrated SeaWiFS images acquired from NASA archive was used to identify the lake regions sharing a similar temporal co-variation in chlorophyll-*a* concentration. A single value decomposition analysis (SVD) was applied to a matrix of 680 lake sections (9×9 km^2) for 150 scenes, covering biweekly the period from August 1997 to March 2004. Gaps in the biweekly-averaged scenes were previously filled through a kriging spatial interpolation. It was found that Lake Victoria can be mainly divided into three large regions; north, south, and an intermediate section. Other four small inshore regions (Murchinson Gulf, Winam Gulf, Sese Islands and Bumburi Channel) were also found to co-vary independently. The study period covered different El-Niño (1997-98 and 2002-03) and La-Niña (1998-99) events. To examine the possible influence of these global climate events on the interannual variability of lake production cycles, the temporal series of each lake region were subsequently decomposed into seasonal and trend components following an ARIMA-model based method. Lake Victoria showed a regular seasonal variability in phytoplankton biomass (Fig. 1). An appropriate average seasonal series of surface meteorology was used to determine the climate influence on the spatial heterogeneity of the seasonal chlorophyll-*a* cycles. Regional differences in the stratification-mixing cycle of the lake were analyzed from lake surface energy budgets. Results show that the mixing phase determined in the north lake initiates with the maximal heat loses during July-August throughout the lake. However wind forcing is significantly stronger in south, where southeasterly monsoons enter the lake. A lengthy mixing reduces the exposition of the phytoplankton cells to the solar irradiance. The manifestation of this disturbed condition on the productivity of Lake Victoria is regulated by climate anomalies teleconnected to El-Niño phenomenon. Results show that El-Niño explained 71% of the variability in phytoplankton biomass over the last seven years (1997-2004). *Lake Tanganyika*. The spatial and seasonal variations in phytoplankton concentrations can be pronounced in large lakes and this is particularly true in Lake Tanganyika. In the present work, spatial and temporal variations of surface chlorophyll-a concentrations for the whole of Lake Tanganyika have been determined using a seven-year time-series (1997-2004) of satellite observed measurements. Statistical analysis was used to define regions with similar temporal co-variation of phytoplankton biomass and to extrapolate their bloom seasonality. The different phytoplankton cycle of each Lake region provides information on the relationship between climate and productivity. A shift in the phytoplankton seasonality was observed at the end of 2000, showing the high sensitivity of the Lake to regional climate patterns.

References

Bergamino, N.; Horion, S.; Stenuite, S.; Cornet, Y.; Loiselle, S.A.; Plisnier, P.-D. and Descy, J-P. “Spatio-temporal dynamics of phytoplankton and primary production in Lake Tanganyika using a MODIS based bio-optical time series”, Remote Sensing of Environment 114, 772-780 (2010).

Loiselle, S. A.; Bracchini, L.; Dattilo, A.M.; Ricci, M.; Tognazzi, A.; Cozar A. and Rossi, C. “The optical characterization of chromophoric dissolved organic matter using the wavelength distribution of absorption spectral slopes”, Limnology and Oceanography 54, 590-597 (2009).

Bracchini, L.; Dattilo, A.M.; Hull, V.; Loiselle, S.A.; Tognazzi, A. and Rossi, C. “Modelling Upwelling Irradiance using Secchi disk depth in lake ecosystems”, Journal of Limnology 68, 83-91 (2009).

Loiselle, S.A.; Azza, N.; Cózar, A.; Bracchini, L.; Tognazzi, A.; Dattilo, A. M. and Rossi, C. “Variability in factors causing light attenuation in Lake Victoria”, Freshwater Biology 53, 535-545 (2008).

2B – New doped materials for technological applications

V. Massarotti, D. Capsoni, M. Bini, S. Ferrari, P. Mustarelli[*]*,*
M.C. Mozzati[#]*, P. Galinetto*[#]
([*]*Università di Pavia, Dip. di Chimica Fisica "M. Rolla";*
[#]*Università di Pavia, Dip. di Fisica "A. Volta")*

Aims

Characterization and optimization of the physico-chemical properties of materials with technological applications to put into evidence the relationship between properties, synthesis method and doping.

Results

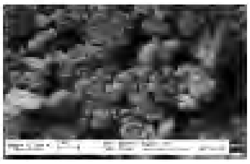
We investigated in detail a series of undoped and doped compounds that find application in the electrochemical devices.

We demonstrated that the Cr doping of the $Li_4Ti_5O_{12}$ anode material strongly affects both the local and average structural properties. The combined use of structural and spectroscopic techniques clearly suggests that Cr ions occupy the octahedral site of the spinel lattice substituting both Ti^{4+} and Li^+ ions; this Cr distribution in the cationic framework gives rise to two distinct EPR signals, corresponding to opposite axial distortion of the relative octahedral environment. Defect models, involving oxygen or cation vacancies are proposed to explain the gain in conductivity observed for Cr doped samples with respect to the undoped ones.

Among the cathode materials for lithium-ion batteries, we investigated the $LiFePO_4$ compound, which is very promising for large-scale application, due to its thermal stability, no toxicity, low cost, and being environmentally benign. Our results put into evidence how the electrochemical features strongly depend on the synthesis route, the carbon coating and the particle size of pure and Mn doped $LiFePO_4$. We demonstrated that the sol-gel route seems to be more promising than the solid state one to prepare an impurity free cathode material. By solid state route some impurity phases such as $Li_4P_2O_7$, Li_3PO_4, $Fe_2P_2O_7$, $Li_3Fe_2(PO_4)_3$, FeO and Fe_3O_4 are detected by X-Ray diffraction and EPR techniques, micro-Raman spectroscopy and magnetization measurements. For what concerns the doped material, we clearly demonstrated that the Mn ions successfully insert into the cationic framework of the $LiFePO_4$ olivine structure. Mn ions, in the +2 oxidation state, preferentially substitute the Fe^{2+} ions, while small quantities of dopant are present on the Li^+ site; this last substitution is responsible for the slight cell parameters expansion with increasing the Mn amount. The influence of carbon coating and particle morphology (rounded particles or platelet–like shaped particles grown in the (020) crystallographic orientation) on the electrochemical behaviour of $LiFePO_4$ has been investigated on a series of undoped samples prepared by hydrothermal synthesis. Our results demonstrate that carbon coated platelet-like (020) oriented $LiFePO_4$ particles (Figure 1), obtained by hydrothermal synthesis and glucose addition as carbon source, give improved discharge cycling performances for low C rates (C/20 –C/5). In the high C rates range (C – 5C) better results are instead obtained on the samples prepared by hydrothermal synthesis and glucose addition but ball-milled, too; in this case carbon coated rounded not-oriented particles are obtained (Figure 2).

Figure 1

Figure 2



We recently studied the Mn doped $LiTi_2(PO_4)_3$ compound, a NASICON type material that can find application as an intercalation electrode material for lithium batteries as well as a solid lithium electrolyte for sensors and other electrochemical devices. Conventional X-Ray and Neutron ToF powder diffraction data demonstrate that the Mn ions, present in the +2, +3, and +4 oxidation state, distribute on different crystallographic sites. In particular, the Mn^{2+}, present on the 6b lithium crystallographic site, is responsible for the lower conductivity of the doped samples and prevails as a conductivity limiting factor on the porosity-sinterization effects. The sol-gel synthesis seems more appropriate for the samples preparation, because it allows to obtain impurity free samples at lower sintering temperature and with a lower amount of Mn^{+2} ions on the lithium sites with respect to the solid state one.

For what concerns the Mn doped $Li_3V_2(PO_4)_3$ cathode material, we demonstrated that a solubility limit is reached for the Mn insertion [$x = 0.124$ in $Li_3V_{2-x}Mn_x(PO_4)_3$] in the NASICON type structure for the samples obtained via sol-gel synthesis. This insertion plays a favourable role on the electrochemical performances of the material. For the samples prepared via solid-state synthesis, obtained at higher sintering temperature, the improvement in the charge-discharge performances with respect to the undoped $Li_3V_2(PO_4)_3$ compound is likely due to the segregation of the $LiMnPO_4$ phase (about 8 wt%) and to the formation of highly aggregated particles, as observed by SEM images.

2B – MANUDIRECT – Direct ultraprecision manufacturing

P. Matteazzi, A. Colella

Aims

This project is funded by the European Commission 6thFramework Programme, under priority 3: Nanotechnology and nanosciences, knowledge-based multifunctional materials and new production processes and devices (NMP).

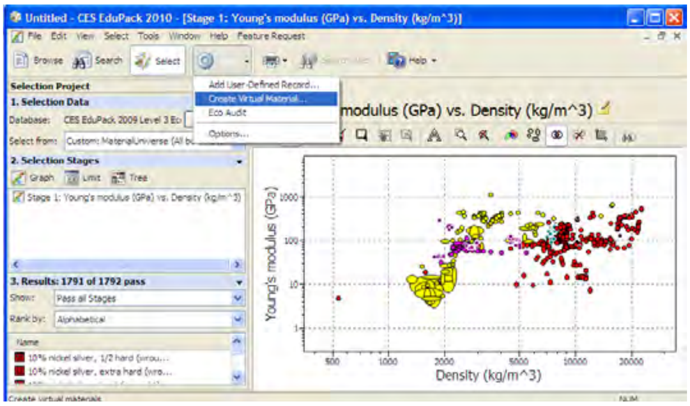
The first level objective of the project is to provide the manufacturing industry with an entirely new platform for manufacturing, by the way of high productivity-high resolution direct, one step, laser sintering using metals and ceramic materials, that includes:

1) several powders grades developed for the technology, integrated in the micro/nanoscale;
2) highly localized powder and laser fluxes;
3) high productivity combined with spatial resolutions in the scale of 50 μm;
4) new methodologies for integrated materials and components design;

The impact of the project and its success is horizontal to many sectors and vertical in engineering methodologies. Virtual engineering concepts and design will be translated into products without the need of prototyping steps. But the impact is much wider, because it open the way to direct macroscale fabrication.

Results

The virtual design software system is based on a set of tools, developed within the project: material property modelling; a web-based database system; a set of design and manufacturing methodologies (Fig. 1). It exhibits the flexibility to allow new material and process models to be incorporated as required and it is capable of handling nano-phase materials).



Database: CES EduPack 2009 Level 3 Ec

Select from: Custom: MaterialUniverse (All b

Stage 1: Young's modulus (GPa) vs. Density (kg/m^3)

Show: Pass all Stages

Rank by: Alphabetical

10% nickel silver, 1/2 hard (wrou...

10% nickel silver, extra hard (wro...

Figure 1. CES selector Virtual material/composite synthesizer

The core of the Manudirect direct laser sintering micro manufacturing platform (Fig. 2) is the sintering chamber, containing the laser and optical head. The powder feeders are hosted on the top chamber of the machine. The system can be equipped up to six powder feeders that allow the machine to realize a part with six different materials, in a single production batch, or a part with 3 materials having two different powders sizes. According to the material or materials combination selection, the sintering process strategies are defined by the system, to achieve the best results in terms of shape resolutions and final mechanical properties. The laser sintering process works in a controlled argon atmosphere and the powder load and unload operations can be done during the production, without interrupting the process activities.

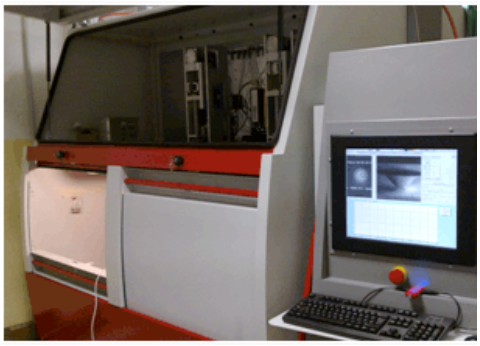


Figure 2. Manudirect industrial platform

Ten systems of nanophased powders for direct manufacturing were developed using high energy ball milling technology.

The platform is equipped with automatic measurement system to perform quality inspection/control of the realized part, in order to identify any deviation from the part CAD mechanical drawing. At present stage the manufacturing of metal components, selected by end users as case studies, is running with encouraging results in terms of spatial resolution, accuracy and density. The first testing phase aimed to evaluate the capabilities of the laser-sintered nanomaterials and to test their suitability for use in their target application.

A set of samples with more complex geometries have been realized, as prototypes of the case studies selected by end users: a grid with four parallel walls, a 12-edge ring, blade shapes (Fig. 3, anticlockwise).

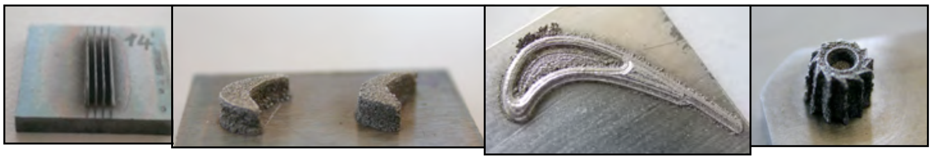


Figure 3. Realized geometries

References

Czerner, S.; Stippler, P.; Ostendorf, A. and Matteazzi, P. "MICRO-LASER SINTERING (MICROLS) FOR RAPID PROTOTYPING OF METAL-CERAMICS", Proceeding of the 2nd Pacific International Conference on Application of Lasers and Optics 2006, edited by Milan Brand and Erol Harvey.

Matteazzi, P.; Czerner, S.; Becker, H.; Stippler, P. and Ostendorf, A. "High Resolution Laser Sintering Using Agglomerated Nanophased Powders", ISNM2005, Cyprus November 3-5, 2005.

Nachum, S.; Fleck, N.A.; Ashby, M.F.; Colella, A. and Matteazzi, P. "The microstructural basis for the mechanical properties and electrical resistivity of nanocrystalline Cu-Al2O3", J. Mat. Sci. and Eng. A., 527, 20 (2010). Submitted.

Tagarielli, V.L.; Fleck, N.A.; Colella, A. and Matteazzi, P. "Mechanical properties and deformation mechanisms of nanocrystalline Fe/Cu 60/40 composites", Journal Of Materials Science, 46, 2, 385-393 (2009).

2C – Expression and purification of the recombinant mustard trypsin inhibitor 2 (MTI2) in Escherichia coli

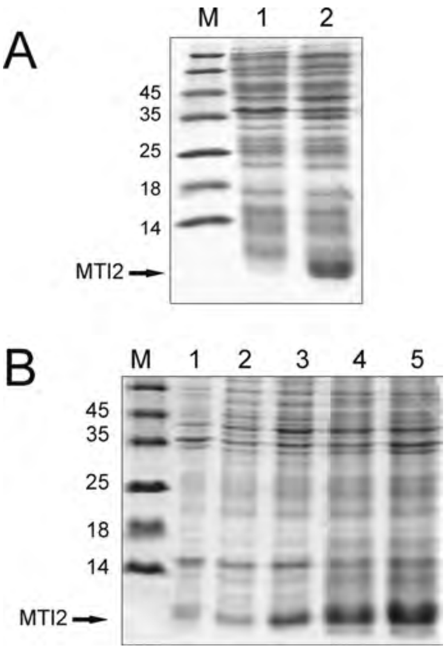
A. Stefan, L. Ugolini, E. Martelli, S. Palmieri, A. Hochkoeppler

Aims

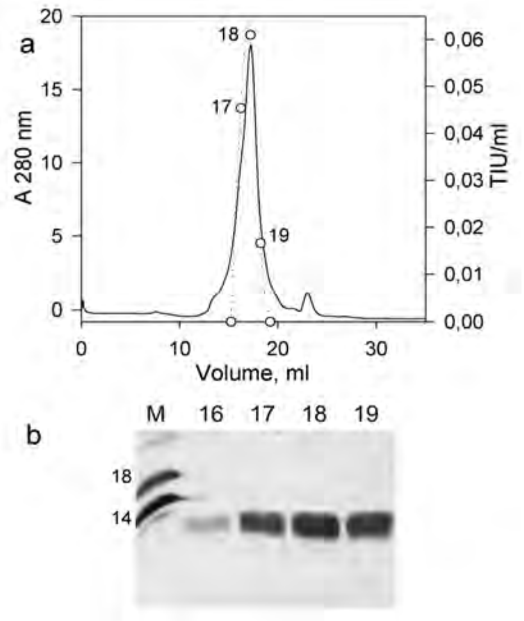
This study describes a specific procedure for the production and purification of the mustard trypsin inhibitor 2 (MTI2) using a prokaryotic system.

Results

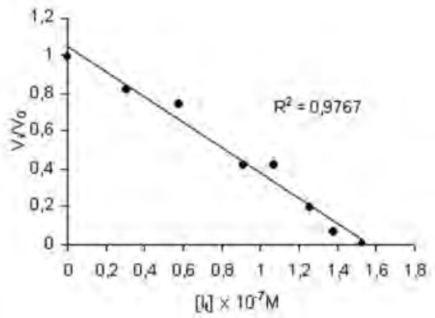
MTI2 is a serine proteinase inhibitor isolated from ripe seeds of *Sinapis alba*. This protein belongs to the plant inhibitors (PIs) groups and it acts increasing plant defences against the proteolytic enzymes of many insects (especially Lepidopteran). In recent years, the recombinant MTI2 has been produced using the yeast *Pichia pastoris*. Here we propose an alternative and efficient procedure for the production of this protein. In particular, the synthetic *mti2* gene was cloned into the pET9a vector and overexpressed in *Escherichia coli*. Different parameters were studied in order to optimise the yield and recovery of the recombinant protein from the insoluble fraction of protein extracts. Independently of these variables, the recombinant protein was always expressed and clearly visible in SDS-PAGE (15 %). Moreover, most of the recombinant MTI-2 was not soluble but detectable inside the insoluble fraction (Fig. 1A). In order to solubilise the protein from the cellular pellet and to optimize its recovery, different conditions were assayed (Fig. 1B).



The extracted protein was refolded by dialysis, then isolated by ion-exchange chromatography on a MONO Q column at pH 8 followed by a gel filtration chromatography on a Superose 12 column (see figure). Fractions were collected on the basis of the inhibitory activity found against trypsin and analysed on SDS-PAGE:



The inhibitory activity of recombinant MTI2 was finally determined against trypsin in a spectrophotometric assay using N-a-benzoyl-L-arginine-*p*-nitroanilide (Ba*p*NA) as substrate. The value of K_i for the recombinant MTI2 results lower than 1.57 x 10^{-9} M.



References

Menegatti, E.; Palmieri, S. and Walde, P. “Isolation and characterization of a trypsin inhibitor from white mustard (*Sinapis alba* L.)”, J Agric Food Chem 33, 784-789, (1985).

Volpicella, M.; Shipper, M.A. and Jongsma, M.A. “Characterization of recombinant mustard trypsin inhibitor 2 (MTI2) expressed in *Picha pastoris”*, FEBS Lett 468, 137-141, (2000).

2C – Proteolysis controls the assembly of Escherichia coli DNA polymerase III catalytic core

D. Bressanin, A. Stefan, F. Dal Piaz, S. Cianchetta, L. Reggiani, A. Hochkoeppler

Aims

This study shows that proteolysis is a key regulatory step in the assembly of *Escherichia coli* DNA polymerase III.

Results

Escherichia coli expresses 5 distinct DNA polymerases, among which DNA polymerase III is responsible for genome replication. This enzyme is composed of 10 subunits, of which DnaE and DnaQ (also denoted as α and ε) bear DNA extension and proofreading activities, respectively. Despite a wealth of data concerning the properties of DNA polymerase III in vitro, little information is available on the assembly in vivo of this complex enzyme. The catalytic core of *E. coli* DNA polymerase III (DNA Pol-III) is composed of three different subunits, i.e. α, ε, and θ, respectively coded by *dnaE*, *dnaQ* and *holE* genes.

To analyse ε stability and competence in association with DNA Pol-III, we over-expressed in *E. coli* full-length DnaQ or specific variants of this protein featuring truncations at the C-terminus (see figure); the sensitivity to proteolysis and the association state of these different forms of DnaQ was also studied.

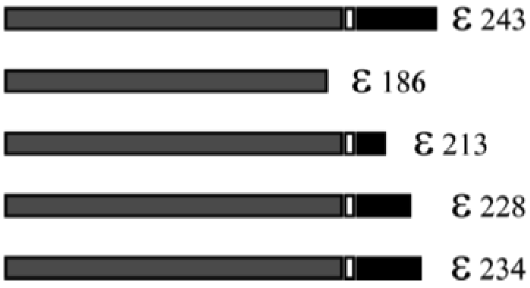
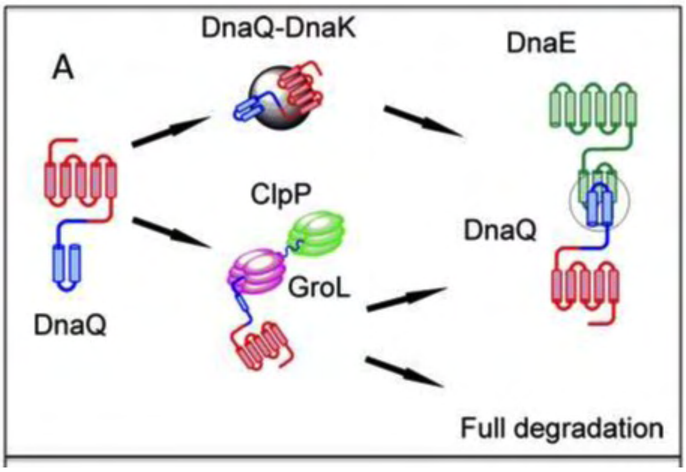


Fig. Full-length DnaQ and truncated forms

In order to characterize each DnaQ variant in monomeric and in associated form(s), protein extracts were subjected to gel filtration, activity determination (using thymidine 5'-monophosphate p-nitrophenyl ester as substrate), and western blotting. The observed proofreading activities suggest that truncation of DnaQ C-terminus confers stability to this protein, and that association with DNA Pol-III holoenzyme mainly depends on the C-terminal region between residues 186 and 213.

We propose that the proofreading subunit represents the limiting factor for a correct assembly of DNA Pol-III. In particular, we suggest the following model of the dependence on proteolysis of DNA Pol-III assembly in vivo. Full-length DnaQ is depicted as red-blue group of cylinders. Two helices of DnaE proposed as determinants of binding to DnaQ are represented in green.



According to our model, the C-terminal region of epsilon constitutes a complex target for the regulation of DNA Pol-III assembly in vivo. Further investigations could identify other molecular factors involved into this frame. For example, the construction of site-specific mutants or N-C-terminal chimerae of DnaQ will help to deepen our understanding of the assembly of bacterial genome-replicating enzymes.

References

McHenry, C.S. and Crow, W. “DNA Polymerase III of *Escherichia coli*. Purification and identification of subunits”, J. Biol. Chem. 254, 1748-1753 (1979).
Foster, P.L. and Marinus, M.G. “Levels of epsilon, an essential replication subunit of *Escherichia coli* DNA polymerase III, are controlled by heat shock proteins”, J. Bacteriol. 174, 7509-7516 (1992).

2C – Shine-Dalgarno sequence enhances the efficiency of lacZ repression by artificial anti-lac antisense RNAs in Escherichia coli

A. Stefan, F. Schwarz, D. Bressanin, A. Hochkoeppler

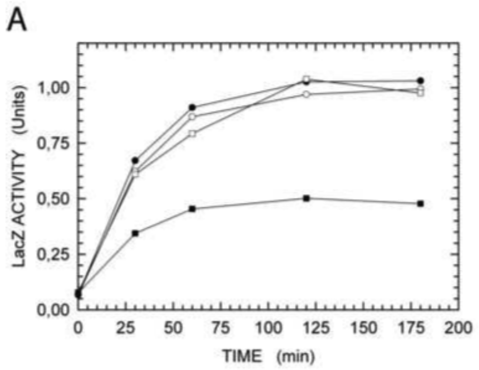
Aims

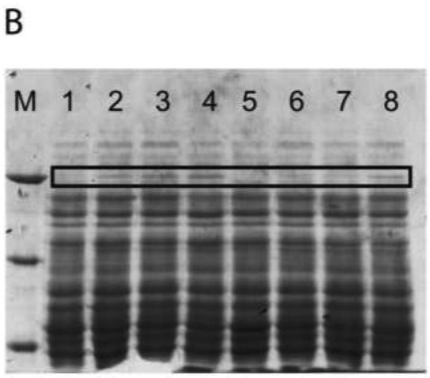
The present work deals with the relevance of the Shine-Dalgarno sequence to the silencing capability of antisense RNAs and reports further insights into the mechanism of action(s) exerted by artificial asRNAs in *E. coli*.

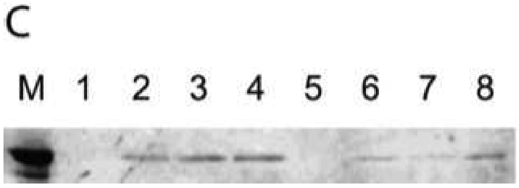
Results

In recent years, considerable efforts have been made to develop a robust strategy for the silencing of prokaryotic genes. The factors affecting antisense stability *in vivo* and, hence, silencing are crucial in order to design an efficient asRNA.

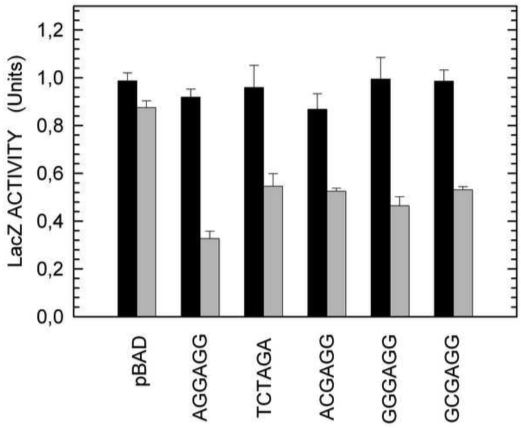
Here, silencing of the *lacZ* gene in *Escherichia coli* was attempted by means of the expression of antisense RNAs (asRNAs) *in vivo*. In particular, a short fragment of *lacZ* was cloned into the pBAD expression vector, in reverse orientation. This construct (pBAD-Zcal1) was used to transform *E. coli* cells, and the antisense transcription was induced simply by adding arabinose to the culture medium. We demonstrated that the Zcal1 asRNA effectively silenced *lacZ* using β-galactosidase activity determinations (Fig.A), SDS-PAGE (Fig. B) and western blotting. Because the concentration of the *lac* messenger was always high in cells that expressed Zcal1, we hypothesize that this antisense acts by inhibiting messenger translation. Similar analyses, performed with a series of site-specific Zcal1 mutants, showed that the Shine-Dalgarno sequence, which is conferred by the pBAD vector, is an essential requisite for silencing competence. Indeed, the presence of the intact Shine-Dalgarno sequence positively affects asRNA stability and, hence, silencing effectiveness.







To evaluate the relation between antisense stability and silencing competence, we investigated the influence of the RBS, conferred by the pBAD vector, on the silencing effectiveness of asRNAs. In particular, we have mutated the AGGAGG hexamer present in Zcal1 to create different antisense variants. In order to estimate their stability, we analyzed the overall decay of the different asRNAs. Therefore, integrity of the RBS primary structure appears strictly necessary to confer stability to asRNAs. Finally, to investigate the influence of the RBS on silencing effectiveness by asRNAs, we have compared the action of all the Zcal antisense constructs. Zcal1 reduced LacZ activity by approximately two-thirds, in agreement with our previous observations. All the other asRNA variants featured silencing, but they were less efficient than Zcal1:



References

Stefan, A.; Reggiani, L.; Cianchetta, S.; Radeghieri, A.; Gonzalez Vara y Rodriguez, A. and Hochkoeppler, A. “Silencing of the gene coding for the ε subunit of DNA polymerase III slows down the growth rate of *Escherichia coli* populations”, FEBS Lett., 546, 295-299 (2003).

2C – Ordered Mesoporous Materials. Part 3: Biodiesel synthesis and phenolic compounds oxidation

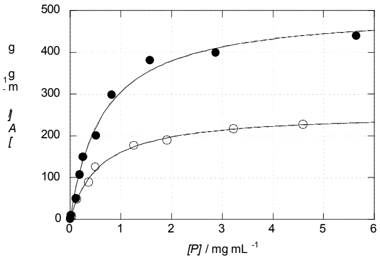
A. Salis, M.S. Bhattacharyya, M. Pisano, E. Sanjust, V. Solinas, M. Monduzzi

Aims

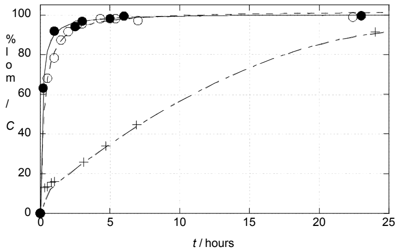
Lipase and laccase immobilization on ordered mesoporous materials. Chemical modification of support surface. Biocatalytic synthesis of biodiesel. Oxidation of phenolic compounds.

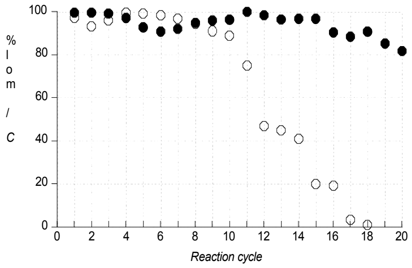
Results

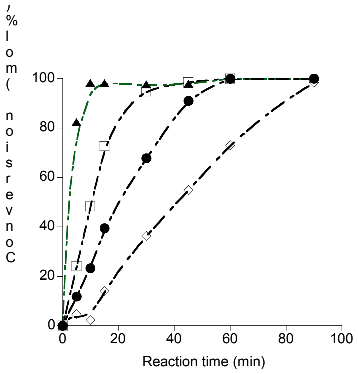
Applied biocatalysis technology makes use of enzymes to perform chemical reactions of potential industrial or environmental interest. Their ability to efficiently catalyze reactions under mild conditions – i.e. low temperature and atmospheric pressure – makes enzymes promising candidates for the development of environmentally friendly green chemistry processes. In the present project we have immobilized two enzymes (lipase from *Pseudomonas fluorescens* and Laccase from *Pleurotus sajor caju*) on SBA-15 mesoporous silica. Two active and stable biocatalysts were obtained.



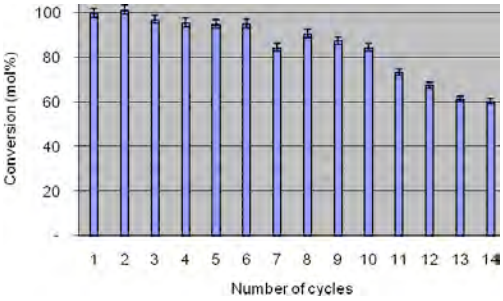
XRD, TEM, and N_2 physisorption were used to monitor the effect of surface functionalization on the structural and textural features of the SBA-15 silica support. Lipase immobilization on chemically modified surface, and unmodified surface of SBA-15 mesoporous silica was successfully achieved. The enzyme loading strongly depends on the type of enzyme-support interaction, the maximal loading of the chemisorbed lipase being about twice that of the physisorbed (502 and 256 $mg_{protein}/g_{dry\ support}$ respectively). The resulting biocatalysts, regardless of the different loading, were tested with a hydrolytic catalytic assay. It was found that, despite of the lower loading, the physically immobilized lipase is more active than that chemically immobilized. Both biocatalysts were also found to be active in a green process for biodiesel production, leading to almost full conversion of sunflower oil and ethanol into the corresponding ethyl esters after about 7 hours at 30°C, atmospheric pressure, and in solvent-free conditions. Recycling experiments showed that the chemically immobilized lipase was still active after twenty reaction cycles whereas the physically immobilized lipase lost its activity after the tenth cycle.







The immobilisation process Laccase on functionalized SBA-15 reached the equilibrium after about 100 minutes. In order to study the effect of loading (*L*) on activity of the immobilised laccase, the adsorption isotherm was built and the activity of the corresponding immobilised biocatalysts was determined. The activity of the immobilised preparations reached a maximum at $L = 217$ kU g_{SBA-15}^{-1}, whereas higher loadings gave rise to a less efficient biocatalyst. The immobilised laccase was used for the oxidation of a mixture of four phenolic compounds (protocatechuic acid, ferulic acid, sinapic acid, and caffeic acid) chosen among those present in olive mill wastewaters (OMWs). These compounds determine the phytotoxicity of OMWs. Different reaction rates were observed for the oxidation of the examined phenolic compounds. The biocatalyst was recycled, and a conversion of 84 mol% at the 10th reuse and of about 60 mol% after the 14th was obtained. In conclusion, lipase and the laccase immobilization on SBA-15 result in potential useful biocatalysts for biodiesel production and bioremediation of OMWs.



References

Salis, A.; Pisano; M., Monduzzi; M., Solinas, V. and Sanjust, E. “Laccase from Pleurotus sajour caju on functionalised mesoporous silica: immobilisation and use for the oxidation of phenolic compounds”, J. Molec. Catal. B: Enzym., 58, 175-180, (2009).

Salis A.; Bhattacharyya M.S.; Monduzzi M. and Solinas V. “Role of the support surface on the loading and the activity of *Pseudomonas fluorescens* lipase used for biodiesel synthesis”, J. Molec. Catal. B: Enzym., 57, 262-269, (2009).

Salis, A.; Casula, M.F.; Bhattacharyya, M.S.; Pinna, M.; Solinas, V. and Monduzzi, M. “Physical and Chemical Lipase Adsorption on SBA-15. Effect of Different Interactions on Enzyme Loading and Catalytic Performance”, ChemCatChem, 2, 322-329, (2010).

Salis, A.; Nicolò M.; Guglielmino, S. and Solinas, V. “Biodiesel from microalgae in Microbiology of Hydrocarbons, oils, lipids and derived compounds”, Ed. Timmis, K., Springer Berlin Heidelberg, 2827-2839, (2010). ISBN: 978-3-540-77584-3

2C – Bioprocess of rhamnolipid synthesis from glycerol, byproduct of biodiesel production

M.G. Cambria [1], C. Frezza [1], A. Ballistreri [2], G. Impallomeni [3], S. Guglielmino [1]
([1]Laboratorio M&NBit, Dipartimento Scienze della Vita, Università di Messina; [2]Dipartimento di Scienze Chimiche, Università di Catania; [3]Istituto di Chimica e Tecnologia dei Polimeri, CNR, Catania)

In recent years, great attention has been put in biofuels production, because of the possibility to use them as substitutes of fossil fuels.

Biodiesel is a biofuel commonly produced by the transesterification of the vegetable oils or animal fat feedstocks. A byproduct of the transesterification process is glycerol, that finds many different applications (food and drink, pharmaceuticals, personal care, polymers and explosives). Recent analyses show that, by replacing 2% of fossil diesel with biodiesel, 325.000 tons per year crude glycerol would be produced.

Considering the increasing interest in biofuels, and in biodiesel specifically, the related glycerol massive production could have important commercial perspectives.

In this study, we evaluated the possibility to perform a bioconversion process for the production of high-added value products, such as biosurfactants, by using glycerol as a low-cost substrate.

Among biosurfactants, the rhamnolipids represent in this context an important category of products, also for their activities in medical field (antifungal and antibacterial activity, useful, for example, for prosthetic surfaces treatment).

In this work, we present the development of a batch process for biosurfactant production by *Pseudomonas aeruginosa*, which is able to produce mono- and di-rhamnolipids mixtures.

About 120 *P. aeruginosa* strains were selected and subjected to screening on solid medium; the strain *P. aeruginosa* L05, one of the best rhamnolipid producers, was chosen.

Growth conditions and production optimization were performed by modulating several nutritional parameters, particularly C/N, C/Mg and C/Fe ratios.

Rhamnolipids were twice extracted with ethyl ether and were analyzed through 1 and 2D NMR spectroscopy, which showed the presence of dirhamnolipids and a minor amount of monorhamnolipids.

This work showed the possibility to produce rhamnolipids by an industrial waste feedstock, coupling the disposal of glycerol with the production of high- added value biomolecules.

2C – Polyelectrolyte Multilayer Films containing Silver Nanoparticles as antibacterial and antiadhesive coatings

L. Grasso [1], S. Carnazza [1], I. Pisagatti [2], S. Spadaro [2], F. Barreca [2], A. Cascio [2], G. Currò [2], F. Neri [3], S. Guglielmino [1]
([1] Laboratorio M&NBit, Dipartimento Scienze della Vita, Università di Messina; [2] Advanced and Nano Materials Research s.r.l., Messina; [3] Dipartimento di Fisica della Materia e Ingegneria elettronica, Università di Messina)

In recent years, the peculiar properties of nanosized particles (NPs) of noble metals, particularly silver (Ag), have aroused much interest in several sectors, such as microelectronics, catalysis, optoelectronics, magnetics and, for their antibacterial activity, also in biomedical field. Although the mechanism of Ag effects on the killing of bacteria is not completely clear, its multilevel antimicrobial mode has been well known: soluble Ag ions inhibit the pathogens' respiratory enzymes and electron transport components. The fabrication of composite thin films containing Ag nanoparticles is aimed to obtain stable antimicrobial coatings. A frequently utilized method to create composite thin films containing Ag-NPs involves fabricating organic thin films via layer-by-layer (LbL) assembly of polyelectrolytes. The immobilization of the polyelectrolytes occurs via electrostatic and/or hydrophobic interaction and results in a film in which parameters like size, shape and distribution of NPs can be finely tuned. Moreover, the use of polyelectrolytes as poly(methacrylic acid) (PMA) for the reduction of Ag has already been widely studied and presents the advantage to act as reducing agent so as stabilizing agent.

In this work, we present a simple method to create a LbL assembled multilayer structure produced by sequential dipping, in which the composite film is constructed by electrostatic attraction between positively charged poly(dimethyldiallylammonium chloride) (PDDA) and negatively charged colloidal solution of Ag-NPs capped with PMA. The Ag-NPs with controlled size distribution were prepared starting from silver nitrate and PMA sodium salt in aqueous solution and using UV irradiation to induce the Ag^+ reduction and polymer cross-linking. The multilayer Ag-NP assembled structures were characterized by UV-vis, AFM and SEM analyses. The antibacterial and antiadhesive activities were assessed against different bacterial strains, as representative of predominant infecting bacteria on biomedical devices, by a comparison of the number of viable cells (colony forming unit, CFU) and adherent cells (direct microscopic observation) after bacterial suspension being in contact with the different substrates according ASTM E2149-01 Standard Test Method. Data showed both complete viability inhibition and adhesion prevention on 4-layers film with a surface plasmon resonance of Ag-NPs of only 0.056. It is likely that viability inhibition is caused by the silver ions (Ag^+) released from the matrix, with the nanoparticles capped in the LbL film providing a stable reservoir of Ag over the time. The proposed preparation method for the LbL system is simple, faster than others and intrinsically free of any toxic agent, so it could be applied both in medical and in food related industry processes, even on a large scale. Because of its demonstrated antimicrobial properties, it may be applied for example in functionalization of medical devices, such as indwelling catheters, useful in reducing the risk of infectious complications.

2C – New perspectives in bacterial retention study

L. Grasso, S. Carnazza, S. Guglielmino
(Laboratorio M&NBit, Dipartimento Scienze della Vita,
Università di Messina)

It is known that bacterial adhesion to surface, so far described in terms of DLVO theory that by now is outdated, is accompanied by a bacterial dependent change in electric potential due to charge transfer between bacteria and surface. Although it is known that the charge transfer is involved in cell-surface interaction in the early phase of adhesion, it is not yet clear whether it is a dynamic event in time. Some authors have proposed a new approach to manage bacterial adhesion in several sectors, such as in medical and in food related industry processes, by changing the extent of charge transfer during the adhesion process.

The aim of this work is to analyze the parameters involved in bacterial retention on a abiotic surface in equal ion strength condition. In particular, we evaluated fluctuating high shear-off forces, such as those determined by washing and dewetting processes, thus alternating stages of hydration and dehydration, and their dependence on both the ionic strength of the medium and the cell viability and metabolism. To this purpose, cells or the surface were pre-incubated in the different media in order to assess bacterial resistance to these shear-off forces, as an indirect indicator of their retention strength.

Since the bacterial surface charge is strain dependent, a model strain was chosen, i.e. *Staphylococcus epidermidis* ATCC 12228, lacking the *ica* operon, not producing the polysaccharide intercellular adhesin involved in cell-to-cell interactions and thus unable to form biofilm, in order to assess only the effect of electrostatic interactions on retention.

Data clearly show that pretreatment of cells or surface with the different buffer solutions implies a diverse charge transfer resulting in a modified retention; in particular, different patterns were observed depending on the buffer used, as a result of the different cell detachment in response to shear-off forces, i.e. of the specific retention strength. In addition, it was found that the charge transfer is a dynamic event in time, which varies throughout the kinetics of adhesion, and that cellular retention is closely linked to cell viability.

2C – "Phage-displayed" peptides application to recognize L. monocytogenes in dairy products

M. La Lia, M. Caratozzolo, C. Caglioti, G. Gioffrè, S. Guglielmino
(Laboratorio M&NBit, Dipartimento Scienze della Vita, Università di Messina)

Among microorganisms that are responsible for food-borne infections, *Listeria monocytogenes* represents an important risk factor for human health. *L. monocytogenes* causes purulent meningitis, septicemia and meningoencephalitis, and a high percentage of
cases represented by fetal perinatal infections that occur during the last period of pregnancy in women with vaginal *L. monocytoges*. Moreover recently an increase of listeriosis cases and more frequent isolation of the microorganism in natural foods such as milk, soft cheeses, fresh and frozen meat, fruit and vegetable products were observed.

The most common systems used for *L. monocytogenes* detection are based on cultivation, use of monoclonal antibodies, DNA probes, PCR and Real Time PCR to extended response times. However, all these techniques require either a long time period for response or are not compatible with chemico-physical properties of considered food matrices.

The aim of this work was to develop a new system to capture quickly *L. monocytogenes* in food matrices and discriminate *L. monocytogenes* from other Listeria strains, such as *L. grayi*, *L. innocua*, *L. ivanovi*, *L. seeligeri* and *L. welshimeri* providing the immediate control of foodstuffs prior to distribution. The detection technique used peptides selected by "phage
display" from M13 random libraries of 9 amino acids that were able to selectively bind *L. monocytogenes*. Among the selected oligopeptides, two peptides, called LI5 and LI6, showed the greater reactivity versus *L. monocytogenes*. Therefore we have functionalized the surface of polystyrene 96 wells plates by coating of precipitated phage clones LI5 and LI6; bacterial samples were added to be tested, and finally the bond was highlighted by the addition of anti-Listeria polyclonal HRP antibody. The ELISA reactivity of LI5 and LI6 versus 71 Listeria strains isolated from dairy products was tested. Specificity of the system was further confirmed by coating bacterial cells and testing the phage clones bond by the anti-M13 monoclonal HRP antibody.

2C – Research of serotype-specific epitopes of Group B Coxsackievirus for development of new diagnostics

M. Puliafico, F. Bianco, S. Carnazza, S. Guglielmino
(Laboratorio M&NBit, Dipartimento Scienze della Vita, Università di Messina)

Coxsackievirus are human enteroviruses of *Picornaviridae* family, divided into group A and group B based on their pathogenicity in mice. Both groups can cause nonspecific febrile illnesses, rashes, upper respiratory tract disease, and aseptic meningitis; however, there is a specificity of disease associated to the Group. In general, group A Coxsackieviruses tend to infect the skin and mucous membranes, causing herpangina, acute hemorrhagic conjunctivitis and hand-foot-and-mouth disease; whereas, group B coxsackieviruses tend to infect the heart, pleura, pancreas, and liver, causing pleurodynia, myocarditis, pericarditis, and hepatitis.

Enterovirus infections are diagnosed mainly via serological tests such as ELISA and from cell culture, but establishing an association between a Coxsackievirus and a particular disease in a patient is nowadays difficult, especially because of the common serological features often leading to cross-reactivity among different Coxsackie serotypes. Moreover, confirmatory testing and typing are costly in both time and economic order and false positives are very frequent.

The aim of this work was the implementation of more sensitive and especially specific diagnostic systems for Group B Coxsackievirus by the use of serotype-specific epitopes selected by phage-display technology. The proposed systems, in fact, ensuring the selective and specific recognition of each serotype, should overcome the main obstacle encountered by the serological diagnostic systems currently available, represented by cross-reactivity among serotypes of group B.

The work proposed the use of phage display for the selection of peptides from phage libraries based on M13 filamentous phage engineered to express the capsid protein VIII in the form of random peptide fusion protein. Phage were selected by using as binding target neutralizing monoclonal antibodies specific for each serotype of Group B Coxsackievirus (B1-B3-B4-B5). The reactivity of selected phage against each serotype was confirmed by immunoscreening and ELISA. Furthermore, the specificity of the clones was tested for possible cross-reactivity with monoclonal antibodies directed to other serotypes. Then the serological response of specific phage identified for each serotype was tested against a collection of sera from patients positive for Group B Coxsackievirus. The peptide sequences identified can be used for the development of new diagnostic systems, based on a modified principle of ELISA, with a high specificity of response and more convenient than the conventional systems, since not requiring structures qualified either for the cultivation of mammalian cells or for the safe handling of hazardous biological agents.

2C – High quality oil for biodiesel production and biomass yields from a microalga Coccomyxa sp. by autotrophic growth

M.S. Nicolò [1], G. Columbro [1], S. La Porta[1], N. Cicero [2], G. Dugo [2], S.P.P. Guglielmino [1]
([1]Dip. di Scienze della Vita,Università di Messina; [2] Dip. di Scienze degli Alimenti e dell'Ambiente,Università di Messina)

The aim of this study was to obtain high quality oil for biodiesel production and biomass yields from an isolated oligotrophic strain of genus Coccomyxa. Common media for microalgae, as BG11 and Zarrouk's, have been used to investigate on Coccomyxa nutritional requirements. To optimise biomass yields and growth rate, a new growth medium has been formulated. The results showed that cell density significantly increased under several nutritional conditions, especially with increased amounts of phosphate and magnesium sources; moreover, urea has been used as nitrogen source, because biomass yields were higher than those obtained using either nitrate or ammonium chloride. Fatty acid composition, evaluated in stationary phase, revealed that 72.29% was represented by saturated and mono-unsaturated fatty acids, mostly oleic (42.43%) and palmitic (18.86) acids. Polyunsaturated acids were mostly represented by linoleic acid (21.87%).

Data strongly indicate that, due to absence of fatty acids with more than four double bonds, Coccomyxa oil is a very good substrate for transesterification and consequent biodiesel production. A specific growth medium for Coccomyxa is then proposed.

2C – Biodegradable Plastics from Brassica Carinata Oil and from Very Long Chain Fatty Acids: Synthesis and Characterization

A. Ballistreri [1], G. Impallomeni [2], G.M. Carnemolla [1], S.P.P. Guglielmino [3], M. Nicolò [3], M.G. Cambria [3]
([1]Dipartimento di Scienze Chimiche, Università di Catania;
[2]Istituto di Chimica e Tecnologia dei Polimeri, CNR di Catania;
[3]Dipartimento di Scienza della Vita, Università di Messina)

Very long chain fatty acids (VLCFA), longer than C20, were employed for the production of medium chain length poly(3-hydroxyalkanoates) (mcl-PHA) by Pseudomonas aeruginosa. In order to keep the production costs low, Brassica carinata oil (erucic acid content 35 - 48%) was employed as the intact triglyceride containing VLCFA. As free fatty acids erucic acid (C22:1) and nervonic acid (C24:1) were employed. Weight average molecular weight, determined by GPC, varied from 56000 for PHA from B. carinata oil to about 120000 for those from erucic and nervonic acids. Monomeric units composition was obtained by GC analysis while the structural characterization was performed by 1H- and 13C-NMR. The 3-hydroxyacids making up the repeating units of such polymers were saturated and unsaturated, with a higher content of the latter in the case of PHAs obtained from B. carinata oil. ESI MS of partially pyrolysed samples allowed the identification of oligomers up to heptamers and statistical analysis of the ion intensity in the mass spectra showed that these PHAs are random copolymers. The PHAs from erucic and nervonic acids were partially crystalline, with rubbery characteristics and a melting point (Tm) of 50°C, while the increase of unsaturation degree in the repeating units of PHA from B. carinata oil afforded a totally amorphous
material, with a glass transition temperature (Tg) of -47°C.

2C – Influence of ion strength and viability in bacterial self-assembly pattern on abiotic surface: preliminary models

M. Caratozzolo [1], M. Frasca [2], L. Grasso [1], S. Guglielmino [1], L. Fortuna [2]
([1]Dept Life Science "Marcello Malpighi", Univ. Messina,
[2]Dept Electrical Electronics and System Engineering, Univ. Catania)

Bacterial colonization is a very complex process influenced by several factors such as material surface, characteristics of cell surface and environmental factors. Many researchers focused on chemical properties of surface like hydrophobicity, hydrophilicity, roughness, steric hindrance and the existence of a "conditioning layer" at the surface. Among these factors there are the electrostatic forces generated by a net charge distribution on both the biomaterial surface and the bacterial wall. The acid–base interactions may assume an important role involving electric charge transfer or sharing as in ionic or covalent bonds, or hydrogen bonds which may occur when the bacterial wall approaches the polymeric substrate. Bacterial surface characteristics are very relevant as well as substratum features. Indeed, bacteria have outside chemical macro-molecules that interact against or in synergy with surface. The purpose of the work reported in this article was to model cell colonization and how cell distribution and local cell density influenced this phenomenon. To this aim we studied *Staphylococcus epidermidis* surface colonization of a abiotic surface (boro-silicate glass) using both alive and dead cells. A cell suspension, with bacteria coming from exponential or stationary phase in saline buffer (PBS), physiological solution, and Trizma buffer and deionised water with a concentration of approximately 5 x 10^8 cells/ml was prepared and transferred to a Petri dish containing a surface of boro-silicate glass. For experiment using dead cells, bacteria were killed by 4 % formaldehyde for a hour, washed by each buffer solution and then added to four buffer (5 x 10^8 cells/ml). The bacterial cells were allowed to adhere onto the polymers for a given time after which unattached cells were removed by dipping the samples in sterile ultra-pure water. The adhered bacteria were stained with the fluorochrome acridine orange and observed by a Leica DMRE epifluorescence microscope. In H_2O alive bacteria coming from exponential phase showed a little adhesion with little clusters whereas in PBS e physiological buffer bacteria formed a self-organized fractal pattern on the surface; finally in Trizma buffer bacteria formed a beginning pattern with branch structure. In H_2O alive bacteria coming from stationary phase showed a little adhesion whereas in PBS, physiological solution and Trizma buffer bacteria adhered and formed a fractal pattern. When used dead cells in H_2O bacteria showed a little adhesion whereas in PBS, physiological solution and Trizma buffer bacteria covered whole surface. When used dead cells coming from exponential phase in H_2O bacteria showed a little adhesion, whereas in PBS, physiological and Tris buffer bacteria covered the whole surface. Then experimental images showed that when bacteria were alive formed a fractal pattern of adhesion and this pattern was organized and maintained through the time. The data suggested that pattern formation was influenced by both abiotic and bacterial surface charges which, in turn, were influenced by buffer solutions. These charges were generated by ions exiting in PBS an physiological buffer as sodium, potassium and phosphate, whereas hydrogen ions in Trizma where a complex molecule take or leave hydrogen ions. However the main role during pattern formation was played by bacterial physiological state. These data supported the hypothesis that characteristic fractal pattern observed was determined by "mobility", or bacterial active capability to move along, determined pattern maintenance. The obtained images were analysed for a quantitative evaluation of adhering cell number onto the surface in terms of integrated density. Using microscopic images experimental captured, we designed an agent-based model where adhesion, aggregation and motility phenomena were described by mass-diffusion equations, in order to reproduce observed behaviour in experimental images. Our approach is similar to the ``generic modelling" introduced in Kozlovsky et al 1999, where the biological behaviour of bacterial growth is modelled and explained by generic features and basic principles elicited from biological considerations and experimental observations. In particular, several generic models can be grouped into the category of discrete generic models (BenJacob 1995, Kessler and Levine 1993). These models share the idea of modelling micro-organisms with discrete moving entities and to describe the time evolution of nutrients or chemicals with reaction-diffusion equations. We focus on the surface and propose a model based on discrete entities which represent bacteria on it. The simulator sofware NetLOGO was used to design this model. The agents move in the space and therefore interact with a time-variant neighborhood. Let us first consider the motion of each bacterium. We assume that each bacterium can be assimilated to a random walker. Let us indicate with $\mathbf{x}_i$ its position and with v_i its velocity. The second part of the model focuses on the density-dependent rule for bacterial adhesion. For each time instant, we sequentially process each agent of the system. For each of them, let us indicate with ϱ the density of agents in a given neighbourhood of it. In particular, for each agent and each time instant, we take into account three different radii and, thus, three different values of ϱ (ϱ_1, ϱ_2, and ϱ_3).We, then, compare ϱ_1, ϱ_2, and ϱ_3 with fixed thresholds and, if these values are greater than the given thresholds, the bacterium adheres to the surface; otherwise all the bacteria in the given radius will move following equations:

$$\begin{aligned} x_i(t+\Delta t) &= x_i(t) + v_i(t)\Delta t; \\ \vartheta_i(t+\Delta t) &= \xi_i \end{aligned} \qquad (1)$$

where $v_i(t) = ve^{j\vartheta_i(t)}$ and $\xi_i \in [-\pi, \pi]$.

These diffusion equations used whether an individual or group or mix approach; individual approach considered dead bacteria, group approach considered alive interacting bacteria while mix approach considered both dead and alive cells in a bacterial population. The preliminary phase of our simulations consists of a phase in which bacteria move and aggregate in small communities. Starting from this condition we then let bacteria/agents evolve until a steady-state condition is reached. We investigated the behaviour with respect to several different parameters and in particular with respect to the density of bacteria on the surface. Figure 1 shows several simulation frames at different times and with respect to different values of the density. For each density value the last frame shown in Figure 1 represents the steady-state condition obtained. It is interesting to note that each of these three conditions has been observed under different experimental conditions.

2C – PHA synthesis by Pseudomonas aeruginosa ATCC 27853 in magnesium and nitrogen starvation

Caterina Frezza [1], *Annamaria Ferreri* [1], *Giuseppe Impallomeni* [3], *Alberto Ballistreri* [2], *Giovanni M. Carnemolla* [2], *Salvatore P.P. Guglielmino* [1].
([1]Dipartimento di Scienze della Vita, Università di Messina, [2] *Dipartimento di Scienze Chimiche, Università di Catania,* [3] *Istituto di Chimica e Tecnologia dei Polimeri, Consiglio Nazionale delle Ricerche, Catania)*

Polyhydroxyalkanoates (PHAs) are useful biodegradable polymers, which can be used in place of synthetic plastics for a wide range of applications.
It is known that PHAs are microbial storage compounds, synthesised when metabolism is unbalanced due to depletion of nutrients, such as phosphate, nitrogen and magnesium.
In this study, we evaluated the incidence of nutrient deprivation on PHAs biosynthesis, specifically nitrogen hunger and magnesium or nitrogen starvation.
The ability of *Pseudomonas aeruginosa* ATCC 27853 to synthesize PHAs from related carbon sources, as saturated fatty acids with a number of carbon atoms ranging from seven to twenty, and glucose, as unrelated carbon source, has been investigated.
PHAs composition was determined by gas chromatography of methanolyzed samples and C13 nuclear magnetic resonance.
PHA synthases *phaC1* and *phaC2* gene expression was analyzed by reverse transcriptase polymerase chain reaction (RT-PCR), by using specifically designed primers.
Qualitative analysis showed that no PHA was detected with 6-7-17-19 carbon atoms fatty acids both in nitrogen hunger and in magnesium starvation; under the last nutritional condition, no PHA production was displayed also when 18- and 20 carbon atoms related sources were employed. On the contrary, under nitrogen starvation, PHA was produced with any of the carbon sources used.
Quantitative analysis showed that, with higher carbon atoms related sources and with glucose, PHA was produced only under nitrogen starvation, whereas under nitrogen hunger, low PHA yield was obtained. On the other hand, under magnesium starvation, increased PHA yields were recovered using fatty acids from 8 to 16 carbon atoms.
RT-PCR analysis showed that *phaC1* is constitutively expressed when related and unrelated carbon sources were employed, whereas *phaC2* was induced only with related carbon sources.
These data showed that nutrient starvation affects differently the PHAs production as function of the supplied carbon source.

2C – Conformational epitopes on monoclonal mouse anti-Yersinia pestis F1 antigen YPF19 identified by peptide phage display and molecular modeling

M. Puliafico, S. Carnazza, F. Bianco, S. Guglielmino.
(Department of Life Sciences, University of Messina)

The identification of *Yersinia pestis* as a potential bioterrorism agent and the emergence of antibiotic resistant strains have highlighted the need for improved vaccines and treatments for plague. Fraction 1 capsular antigen (F1), identified as one of *Y. pestis* major antigens, is a plasmid encoded, proteinaceous capsule, synthesized in large quantities by the pathogen, with antiphagocytic properties. It is highly immunogenic and has been indirectly associated with eliciting a protective immune response in humans, as evidenced by detection of high levels of anti-F1 antibody in F1-immunized volunteers. The F1 antigen immunodominant epitope has been studied, but the conformational epitopes involved in immunoresponse are not yet well defined. To this aim, in this study, we used the monoclonal antibody YPF19 to identify the Ab epitopes of F1 antigen by screening phage-displayed random peptide libraries. YPF19 has high affinity towards purified F1 antigen from *Y. pestis* vaccine strain EV76, while not cross-reacting with *Y. pseudotuberculosis* and *Y. enterocolitica*. Four rounds of selection were used to screen each of four different phage libraries, containing respectively random nonapeptides, dodecapeptides, cysteine-constrained nonapeptides and dodecapeptides. ELISA and Immunoscreening were used to test selectivity and specificity of the selected phage clones. Five reactive phagotopes were isolated from a dodecapeptide library, and three different sequences were identified. By ELISA one of the three phagotopes resulted highly reactive. The sequences of the selected peptides were aligned individually with the sequence of F1 antigen, and the regions of F1 antigen containing similar chemo-physical properties were identified, using Clustal W. They were also mapped to a homology model of the F1 antigen three-dimensional structure, by 3D-Molecule Viewer. The data obtained suggest the presence of a discontinuous epitopic structure between aa 80-130, recognized by YPF19.

2C – ToF-SIMS Imaging of Surface Self-Organized Fractal Patterns of Bacteria

[1]N. Tuccitto,[1]G. Marletta, [1]A. Licciardello, [2]M. Caratozzolo, [2]L. Grasso, [2]S. Guglielmino
([1]Dipartimento di Scienze Chimiche, Università di Catania,
[2]Dipartimento di Scienze della Vita, Università di Messina)

Bacterial colonization is a very complex process influenced by several factors such as material surface properties, characteristics of the cells and environmental factors. Many researchers focused on the chemical properties of the surface, such as hydrophobicity, hydrophilicity, roughness, steric hindrance and the existence of a "conditioning layer" at the surface. Another important issue to be taken into account is the presence of surface charges both on the biomaterial surface and on the bacteria wall. In a previous study some of us showed that bacteria can form self-organized fractal patterns, depending of surface characteristics and environmental conditions during the colonization process. The purpose of this work is to elucidate the influence of ionic charges on the *Staphylococcus epidermidis* ATCC 12228 adhesion. To this aim four different conditions for bacterial culture have been tested, differing each other in terms of ionic composition and ionic strength, namely saline phosphate buffer (PBS), physiological solution, TRIS buffer, and deionised water. Bacteria were allowed to colonize a silicon (with native oxide) surface. Optical microscopy showed a different organization of adhered bacteria, related to the different conditions. In particular in PBS buffer and in physiological solution bacteria form a self-organized fractal pattern on the surface, in TRIS buffer they form a pattern with branched structure whereas in deionised H2O poor adhesion is observed with a few clusters on the surface. In order to gain information on the effect of the incubation solution on the resulting pattern, a ToF-SIMS imaging study of the bacteria patterns on the surface has been carried out. Both elemental and molecular chemical maps from differently cultured specimens were obtained. It will be shown that the surface distribution of salts, most probably excreted by the bacteria, is strictly related to their surface organisation.

2C – Physico-Chemical Properties of Pharmaceutical Systems

G. Bruni, V. Berbenni, C. Milanese, A. Girella, A. Marini

Aims

The research activity in the pharmaceutical field proposes developing methods for the resolution of problems related to the preformulation phase of active principles. The topics of interest are: polymorphism and stability of drugs in the solid state, host-guest systems, drug-excipient compatibility, crystallinity degree and phase diagrams characterization. In particular, in the years 2009-2010 the efforts have been directed towards the physico-chemical characterization of the solid state of pharmaceutical compounds with special care to the detection of different solid forms and to their relative stability and inter-conversion.

Results

The thermodynamic properties of an antidepressant drug, developed by GlaxoSmithKline with the code GW597599, were studied from room temperature to 200 °C. When slowly heating a “fresh” sample the following phenomena occur: melting of a form (F1, ~ 170 °C), crystallization of a structurally different form (F2), melting of F2 (~180 °C). In no circumstances the direct transition from F1 to F2 can be observed. On the other hand, F2 reverts to F1 upon cooling below ~130 °C. A glassy phase is formed upon cooling from above 180 °C, as confirmed by X-ray analysis and the appearance of a glass transition when reheating. The “reversible” and “non reversible” contributions to the measured enthalpies were estimated with temperature modulated DSC measurements, resulting into a consistent description of thermodynamics of the forms, their melting and their kinetics of transformation.
As part of a systematic study undertaken to find and optimize a general method of detecting the drug-excipient interactions, the compatibility of haloperidol with several excipients (PVP, magnesium stearate and α-lactose) in binary and ternary mixtures, both as prepared and ball-milled, has been assessed by thermal methods, electron microscopy, IR spectroscopy and X-ray diffraction. The DSC has proven to be, among the selected analytical techniques, the most sensitive and specific in assessing the compatibility. A strong interaction has been observed between PVP and haloperidol. It is favoured by the mechanical stress and is more evident in the composition 20:80 (drug:excipient, w/w). On the contrary, α-lactose and magnesium stearate were found to be compatible with the drug.
Part of the research activity fell within a scientific collaboration between the University of Pavia and the pharmaceutical factory A.M.S.A. (Como, Italy). The research topic has been the physico-chemical characterization of polymorphs of nateglinide (named B, H and S), an antidiabetic agent. It has been established that S polymorph can crystallize from the melt obtained from both B and H samples or also following an isothermal treatment of both forms at temperatures lower than the relevant melting points. Our analyses have allowed to evaluate the relative stability of the three polymorphs through the construction of the energy vs. temperature diagram. In particular, S polymorph, the highest-melting form, has resulted to be the only

stable form. Furthermore, it has been verified that the product obtained during the final steps of the nateglinide synthesis is the hemihydrate form which melts at about 86 °C provided that the adopted experimental conditions hinder the removal of the crystallization water. Otherwise, if the crystallization water is removed, the hemihydrate transforms to a new anhydrous polymorph that melts at 102.8 °C. The anhydrous polymorph, if stored at room temperature and humidity, gradually changes to H polymorph while, if stored in water vapour saturated atmosphere, it gets back water and reverts to the hemihydrate form. On the contrary, both an isothermal treatment at 80 °C and melt cooling bring to the B polymorph.

A method for the quantification of the polymorphic purity of nateglinide, in mixtures formed by polymorphs H and B, has been devised. In order to achieve this goal, binary systems of known composition have been prepared and the melting peaks of both polymorphs have been recorded by differential scanning calorimetry. Experiments have determined that the method of preparation of the mixtures has to be carefully evaluated. Indeed it has been shown that grinding the samples induces transition from B to H form. Furthermore, it could be observed that the enrichment of the binary mixture with H form is caused by heating. Therefore, after having prepared the mixture without grinding stage, we proposed a method to evaluate the content of H polymorph in mixture with the B one from the melting peak of B.

Commercial (C) and re-crystallized (Re) polycrystalline samples of carprofen, a non-steroidal anti-inflammatory drug, were studied by thermal, spectroscopic and structural techniques: sample Re, stable at room temperature, is a single polymorphic form of carprofen (polymorph I) that undergoes an isostructural polymorphic transformation by heating (HT-Re, polymorph II). Polymorph II remains then metastable at ambient conditions. Sample C is instead a mixture of polymorph I and II. The thermodynamic relationships between the two polymorphs were determined through the construction of an energy/temperature diagram.

References

Bruni, G.; Milanese, C.; Berbenni, V.; Sartor, F.; Villa, M. and Marini, A. “Crystalline and Amorphous Phases of a New Drug”, J. Therm. Anal. Cal. 102, 297-303, (2010).

Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A. and Marini, A. “Drug-excipient compatibility studies in binary and ternary mixtures by physico-chemical techniques”, J. Therm. Anal. Cal. 102, 193-201 (2010).

Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Viganò, E.; Lanfranconi, S. and Marini, A. “Thermodynamic relationships between nateglinide polymorphs”, J. Pharm. Biomed. Anal. 50, 764-770 (2009).

Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Lanfranconi, S. and Marini, A. “New solid modifications of nateglinide”, J. Pharm. Biomed. Anal. 51, 1054-1059 (2010).

Bruni, G.; Berbenni, V.; Milanese, C.; Girella, A.; Cardini, A.; Lanfranconi, S. and Marini, A. “Determination of the nateglinide polymorphic purity through DSC”, submitted for publication, J. Pharm. Biomed. Anal. 54, 1196-1199 (2011).

Bruni, G.; Gozzo, F.; Capsoni, D.; Bini, M.; Macchi, P.; Simoncic, P.; Berbenni, V.; Milanese, C.; Girella, A.; Ferrari, S. and Marini, A. “Thermal, spectroscopic and ab-initio structural characterization of carprofen polymorphs”, J. Pharm. Sci. 100, 2321-2332 (2011).

2C – BIoprocessing for Sustainable production of COLoured textiles (BISCOL)

R. Pogni, S. Giansanti, M.L. Parisi, A. Martorana, A. Bonucci, D. Spinelli, M.C. Baratto, R. Basosi

Aims

Development of a new dyeing process based on the ecological optimisation of the overall dyeing process cycle, for European textile SMEs which will become more competitive and innovative .

Results

BISCOL is a project co-funded by European Commission in the framework of CIP Eco-innovation “First Application and market replication projects”, led by the University of Siena (coordinator: prof. R. Pogni).

Eco-innovation covers a wide range of green products, services and processes that can turn environmental challenges into business opportunities. BISCOL is one of the 45 projects selected from among over 200 proposals submitted by the call deadline. Ranging from Innovative materials for easy sorting and recycling to advanced production methods that save water and other resources, the selected projects are set to strengthen Europe’s competitive edge while improving its environmental standing.

BISCOL shall run for 36 months from September 1st, 2010. It is involved in the program area “*Green Business*: Clean Production”, in the sector “Finishing of textile”. The textile and clothing industry is one of the world most global industries, and constitutes an important source of income and employment of many EU countries. Dyeing process represents one of the most important step of the textile production chain since it is responsible for the fashionable and aesthetic effect of the final products. Its local environmental impact is mainly due to the extensive use of fresh-water used in dyeing process and then discharged: on average the effluent volume covers 90-95% of the water used. Of the 700,000 tons of dyes annually produced world-wide, about 10 to 15% is disposed off in effluents.

The objective of the European project BISCOL is to propose a new dyeing process as global alternative for the bioconversion of raw materials into competitive eco-viable final products through the optimization of:

- textile pre-treatments, aiming to increase dyeability of textiles versus bio-dyes:
- synthesis of bio-dyes, using new safe and environmental friendly routes (enzymatic processes, Fig. 1);
- synthesis of new auxiliaries at lower environmental impact
- optimisation of dyeing process, reducing energy demand (e.g. lowering temperature and time of treatments).

All steps will be assisted by Life Cycle Assessment, to embed environmental constrains in each step of the process preventing environmental impacts linked to the whole process, and by toxicological tests.

New Bio-dyeing processes will have a beneficial impact on the following environmental issues:

- Climate change: reduction of greenhouse gas;
- Soil and stream pollution: reduction of amount of waste and hazardous waste;
- Sustainable production and consumption: reduction of raw materials and extra chemicals;
- Protection of water resources;
- Reduction of toxicity of new dye and auxiliaries.

Transition from the traditional industry with well known, resource intensive chemistry having little innovation with low number of relevant patents, to modern bio-process industry based on high level of knowledge and patents and less requirements for resources, will enhance competitiveness of target SMEs.

It is expected that the new dyeing process will lead to a concrete evolution of the traditional colour industries towards high tech SMEs, which will become more competitive, more innovative and develop sustainable processes.

Figure 1. Bioreactor used for the synthesis of new bio-dyes

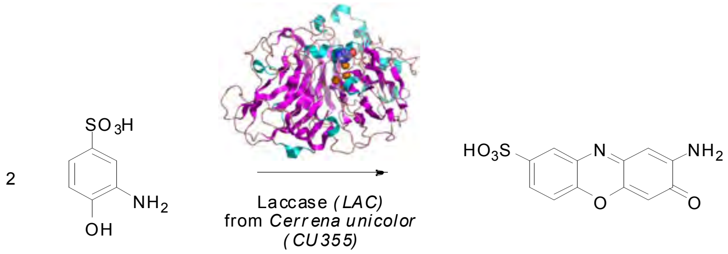


Figure 2. Enzymatic synthesis of phenoxazine dye Sophied Orange 25

References

Forte, S.; Polak, J.; Valensin, D.; Taddei, M.; Basosi, R.; Vanhulle, S.; Jarosz-Wilkolazka, A. and Pogni, R. “Synthesis and structural characterization of a novel phenoxazinone dye by use of a fungal laccase”, J. Mol. Cat. B: Enzymatic 63, 116-120 (2010).

Bruyneel, F.; Basosi, R.; Bols, C.M.; Enaud, E.; Hercher, C.; Jager I.J.; Marchand-Brynaert, J.; Pogni, R.; Polak, J.; Jarosz Wilkolaska, A. and Vanhulle, S. 12/498, 666 (2009).

Bruyneel, F.; Basosi, R.; Bols, C.M.; Enaud, E.; Hercher, C.; Jager, I.J.; Marchand-Brynaert, J.; Pogni, R.; Polak, J.; Jarosz Wilkolaska, A. and Vanhulle, S. PCT PCT/EP2009/058640 (2009).

Bruyneel, F.; Basosi, R.; Bols, C.M.; Enaud, E.; Hercher, C.; Jager, I.J.; Marchand-Brynaert, J.; Pogni, R.; Polak, J.; Jarosz Wilkolaska, A. and Vanhulle, S. US Patent 61/078670 (2008).

2C – Renewable energies from agriculture

*D. Spinelli *, S. Jez, E. Busi, R. Pogni, R. Basosi*

Aims

In 2009, the new Directive 2009/28/EC aimed to establish an overall binding target of a 20% share of renewable energy sources in energy consumption and a 10% binding minimum target for biofuels in transports to be achieved by each Member State, as well as binding national targets by 2020 in line with the overall EU target of 20%. Italian target for the share of energy from renewable sources in final consumption of energy in 2020 is 17%. The development and use of biofuels (like biodiesel, crude oil etc.) in the transport system represents an opportunity to achieve the Italian target.

Results

An environmental impacts analysis for a pilot production line of biodiesel from sunflower on local scale1,2,3 has been attempted. All the steps of the production row (agricultural phase, extraction, transesterification and final use) are entirely closed in a small area in Italy: the Province of Siena (Tuscany). Then biodiesel was used in mixture 25% with Diesel in the local transport system of Siena.

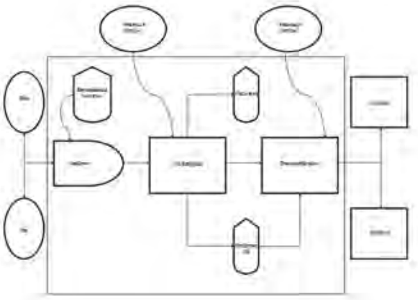


Figure 1. System diagram of a biodiesel production line from sunflower

Environmental Impact Indicators have been provided by Material Flow Accounting4 (MFA), Embodied Energy Analysis5 (EEA) and Emergy Accounting5 (EA). The major impacts and uses of resources of biodiesel production are due to the production of mineral nitrogen fertilizers and diesel fuel. Biodiesel is a renewable fuel for 58.8% in term of oil equivalent and carbon dioxide saving. Because of the use as fuel was in mixture 25% with Diesel, the CO2 emission savings was estimated for about 15% respect to the use of Diesel as fuel for public transport. A comparative Life Cycle Assessment6 (LCA) analysis for the pilot biodiesel production line compared with normal diesel production showed environmental advantages of the local scale biodiesel production.

The most widespread nitrogen mineral fertilizers are ammonium nitrate and urea. Therefore a comparative environmental impacts analysis of the production systems have been used to evaluate their indirect effects due to the use in the agricultural phase7. Ammonium Nitrate production showed an high impact on human health and for the ecosystem quality and its less impact on resources consumption was due to the less fossil fuels consumption than in the Urea production. Hence the use of Urea fertilizer would give a high contribute to energy consumption and thus also on agricultural phase of the biodiesel production line from sunflower. Technological improvements in the Ammonium Nitrate production could also be introduced in order to reduce emissions of reactive chemical substances in the environment.

Environmental benefits have also been evaluated for a pilot production line of sunflower oil for the use as direct energy source instead of diesel fuel8. All approaches reveal that the agricultural phase is the critical step in the whole production line from the point of view of environmental impact. A comparative Life Cycle Assessment analysis for the sunflower oil production line from conventional farming with organic farming showed environmental advantages of this one. The production of sunflower oil from sunflower seeds produced from organic farming reduce the amount of fossil fuels consumption in respect to those from conventional farming. Furthermore use of vegetable oils instead of diesel oil as energy sources in internal combustion engines appear to be a potential way to decrease CO2 emissions.

In general the aim of the study represents an opportunity to reduce dependence of petroleum in the transport sector and of a major diffusion of renewable energies for a sustainable development of the province of Siena.

References

Spinelli, D.; Bardi, L. and Basosi, R. "Energy and Environmental analysis of nitrogen fertilizers", Energy Policy, submitted (2011).

Spinelli, D.; Jez, S. and Basosi, R. "Integrated Environmental Assessment of a sunflower production line", Process Biochemistry, submitted (2011).

Spinelli, D.; Jez, S.; Pogni, R. and Basosi, R. "Environmetal and Life Cycle Analysis of a biodiesel production line from sunflower in the province of Siena (Italy)", Biomass and Bioenergy, accepted (2011).

Basosi R.; Federici, M. and Verdesca, D. "Thermodynamic and Economic Analysis of Biomass Energy Recovering Processes. Siena Case Study", World Renewable Energy Congress IX, 19-25 Agosto 2006 Firenze, Elsevier, Oxford, UK (2006).

Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A. and Tonon, S. "Biodiesel as alternative fuel:Experimental analysis and energetic evaluations", Energy, 29, 2195-2211 (2004).

Wuppertal Institute, www.wupperinst.org/Pojekte/mipsonline/download/MIWerte (2003).

Goedkoop, M. and Priensma, R. "A damage oriented method for Life Cycle Assessment", The Eco-Indicator 99, Methodology report, Third edition, Pre Consultants, BB Amersfoort (2001).

Brown, M.T. and Herendeen, R.A. "Embodied energy analysis and EMERGY analysis: a comparative view", Ecological Indicators, 19, 219-35 (1996).

* Recipient of a contribution to the PhD grant from CSGI.

2C – Structural and Dynamic Studies of Metal Complexes with Ligands of Biological Interest

M.C. Baratto, A. Martorana, M. L. Parisi, E. Busi, R. Basosi

Aims

The aim of this project is an EPR approach aided by computational studies to investigate metal-complexes with biological applications in solution, in order to determine a structural and dynamic characterisation.

Results

This research project proposes to increase the knowledge of the structures in solution, of the stability and in general of the physico-chemical properties of metal chelates with peptides, alpha-hydroxyacids and synthetic ligands with biological activity. In order to obtain structural and geometric information of the metal center, an EPR approach aided by computational studies, was carried out. In this context one topic focused on Cu(II)-complexes with alpha-hydroxyacids, owing to their important role in enzymatic processes and considering their actual and potential uses in animal and human nutrition and in pharmacology. EPR spectra recorded at different pH values and variable temperatures allowed to determine different species distribution in solution and obtain the magnetic properties of the analyzed systems. For the same compounds with diamagnetic metals (Zn^{2+}) theoretical and computational analysis was performed by means of DFT calculations to gain a deeper insight and a straightforward confirmation of the experimental data. Furthermore, the second topic concerns the nuclease activity of copper complexes having ligand containing phenolato donors. Such type of complexes is efficient in hydrolytic cleavage, oxidative cleavage and photolytic cleavage of DNA. The PhimpH ligand having two imines and one phenolato donors and its modifications have been synthesized and their Cu(II) complexes have been spectroscopically characterized. The binding mode of ligands towards Cu(II) was supported by EPR which allows to determine information on the coordination sphere of the metal centre. SOD and nuclease activity, DNA interaction studies have been related to the geometrical and structural information obtained by the spectroscopic approach. The third topic concerns the study of Cu(II) coordination to peptide fragments encompasing residues 45-55 of alpha synuclein (aS), including systems containing the inherited mutations E46K and A53T, as model peptides of the His-50 site. It has been recently shown that aS, as other proteins associated with neurodegeneration (Ab, Prion Protein, etc.), is a copper binding protein. Moreover it has been reported that metal binding strongly modulates aS aggregation and oligomerization. of the protein. Three different aS copper binding domain have been proposed: (i) the N-terminal residues that represent the minimal copper binding domain; (ii) the His-50 imidazole and (iii) the Asp and Glu residues within the acidic C-terminal domain. The spectroscopic characterization of copper binding to aS has been investigated by different methods defining at physiological pH a 3N1O Cu(II) binding mode both in the wild and mutated peptides. The estimation of K_d and the analysis of copper competition effects revealed that His-50 behaves as an independent copper binding site, showing a metal affinity 1-2 order of magnitude smaller than aS_{1-15} systems. Since copper interaction to aS was proven to accelerate protein aggregation and oligomerization, the delineation of the Cu(II)- aS binding is vital for understanding the related metal toxicity. In fact the His-50 residues was shown to be essential for the copper dependent formation of toxic oligomers but not for the general aggregation of the protein.

Moreover, programs implementing the linear combination of single simulations were used, allowing the interpretation of EPR spectra without modifying experimental conditions. The simulation of multiple-species isotropic EPR spectra via linear combination of single simulations is a useful tool to correctly interpret all the spectra components. The advantages of the simulation of multiple species EPR spectra were preliminary tested in a spin trap study on hyaluronan degradation mechanism, where the spectra were easier to be analyzed.

References

Busi, E.; Travagli, E.; Zanardi, I.; Gabbrielli, I. and Basosi, R. “Simulation of EPR spectra as a tool for interpreting the degradation pathway of hyaluronan”, Applied Magnetic Resonance 37, 325-337 (2010).

Ghosh, K.; Kumar, P.; Tyagi, N.; Singh, U.P.; Aggarwal, V. and Baratto, M.C. “Synthesis and reactivity studies on new copper(II) complexes: DNA binding, generation of phenoxyl radical, SOD and nuclease activities”, E. J. Med. Chem., 45, 3770-3779 (2010).

Valensin, D.; Camponeschi, F.; Luczkowski, M.; Baratto, M.C.; Remelli M.; Valensin, G. and Kozlowski K. “The role of His-50 of a-Synuclein in binding Cu(II): pH dependence, speciation, thermodynamics and structures”, Metallomics, *accepted*, (2010), DOI:10.1039/c0mt00068.

Predieri, G.; Beltrami, D.; Pattacini, R.; Parisi, M.L.; Sinicropi, A.; Valensin, D. and Basosi R. “Structural studies in solution and in the solid state on the zinc chelate of 2-hydroxy-(4-methylthio) butanoic acid, an effective mineral supplement in animal feeding”, Inorganica Chimica Acta 362, 1115-1121 (2009).

2C – Structure-Activity Relationship Studies on Enzymes of Biotechnological Interest

R. Pogni, M.C. Baratto, S. Giansanti, A.T. Martinez, R. Basosi

Aims

Structure-activity relationship studies of new natural and synthetic enzymes (Peroxidases, Oxidoreductases, Mono-Di-Oxygenases) to clarify the catalytic mechanism.

Results

Lignin-degrading peroxidases, a group of biotechnologically interesting enzymes, oxidize high redox potential aromatics via an exposed protein radical. Direct detection of a protein radical in a ligninolytic peroxidase was obtained in Pleurotus eryngii and Bjerkandera adusta VP by low temperature EPR of its Compound-I. Then, the presence of a protein radical in Compound II has been confirmed, so an extension of the basic catalytic cycle of VP was proposed by including two forms (A and B) of both Compound-I (VPI) and Compound-II (VPII) (Fig. 1).

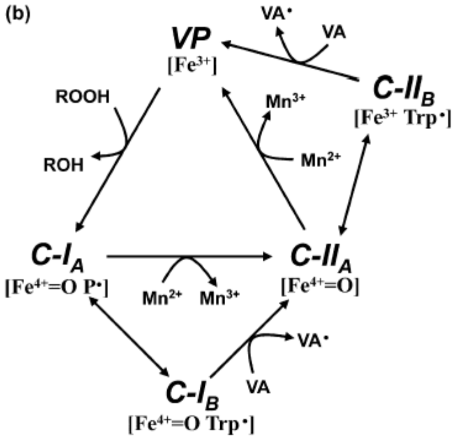


Figure 1. Extended cycle including also compounds IB (C-IB, containing Fe^{4+}-oxo and Trp radical) and IIB (C-IIB, containing Fe^{3+} and Trp radical) involved in oxidation of veratryl alcohol (VA) and other high redox potential aromatic compounds (C-IB and C-IIB are in equilibrium with C- IA and C-IIA respectively, which correspond to the classical compound I and II (other low redox potential aromatic compounds are probably oxidized by both the A and B forms).

The resting state and peroxide-activated forms of the native enzyme and the variants obtained by Trp164 site directed mutagenesis (W164Y, W164S, W164H) were analyzed by EPR to detect the presence and nature of radicals.

Finally, a new type of LiP, recently found in the white-rot basidiomycete Trametes cervina, has been characterized. Its first molecular characterization showed that T. cervina LiP lacks the conserved catalytic tryptophan, and contains one tyrosine residue (Tyr-181) at a position where tyrosine residues were never found in other LiP and VP sequences. Low-temperature EPR of the peroxide-activated T. cervina LiP* successfully detected a protein radical at Tyr-181. These results provide the first structure-function information on the only ligninolytic peroxidase described to date that has a catalytic tyrosine.

A supramolecular approach to prepare an artificial peroxidase soluble in aqueous solution has been developed. The catalytic mechanism of the synthetic system has been studied by UV-Vis and EPR spectroscopies and the Compound I intermediate has been shown. This system affords a simple way to access non-covalent peroxidase mimetic system and we expect that such approach could be the basis for developing new and more efficient mimetic peroxidase systems effective both in homogeneous and heterogeneous environments.

References

Miki, Y.; Rodríguez, F.; Pogni, R.; Ruiz-Dueñas, F.J.; Martínez, M.J.; Basosi, R.; Romero, A. and Martínez, A.T. "Crystallographic, kinetic, and spectroscopic study of the first lignin peroxidase presenting a catalytic tyrosine", J. Biol. Chem., submitted (2011).

Ruiz-Duenas, F.J.; Pogni, R.; Morales, M.; Giansanti, S.; Mate, M.J.; Romero, A.; Martinez, M.J.; Basosi, R. and Martinez A.T. "Protein Radicals in Fungal Versatile Peroxidase - Catalytic tryptophan radical in both compound I and compound II and studies on W164Y, W164H and W164S variants", J. Biol. Chem., 284, 7986-7994 (2009).

Castriciano, M.A.; Romeo, A.; Baratto, M.C.; Pogni, R. and Monsù Scolaro L. "Supramolecular Mimetic Peroxidase Based on Hemin and PAMAM Dendrimers", Chemical Communications, 6 , 688-690 (2008).

2C – Casein-divalent ions interaction: a solvent exchange study

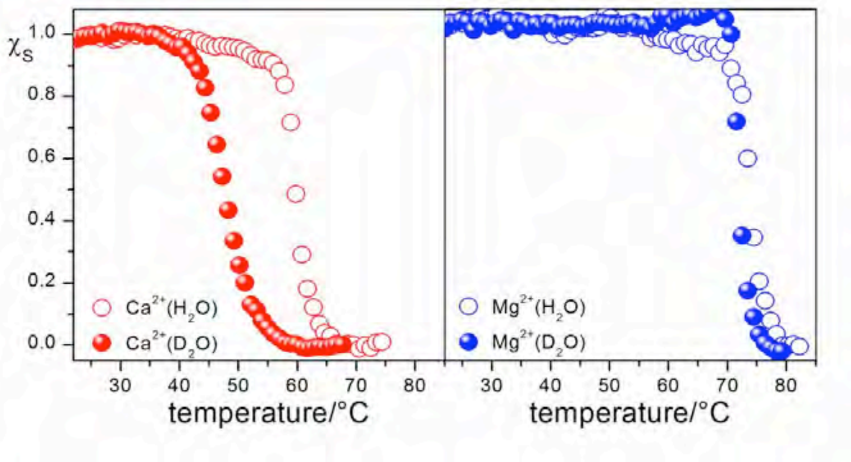
F. Lopez, F. Cuomo, A. Ceglie

Aims

This study was undertaken to analyze the specific interaction phenomena between caseinate molecules and divalent ions. The main target of this project is to distinguish different type of binding process between proteins and ions by means of solvent exchange.

Results

The intrinsic fluorescence of casein was used to detect the precipitation of caseinate solution upon exposure to interactions with calcium and magnesium ions. The specific precipitation temperatures TP were calculated by following the molar fractions of the soluble protein in H_2O and D_2O as a function of the temperature. T-scan experiments indicated that in the presence of calcium ions the TP values were significantly lower in D_2O than in H_2O. In contrast, TP values were not different in the two solvents when magnesium ions were added. Remarkably, deuterium oxide was used to demonstrate differences of the two divalent cations affinities for proteins and thus the presence of two distinct binding sites for calcium and magnesium. The characteristics of the precipitation process observed in the presence of both calcium and magnesium ions suggest the existence of cooperative processes.



References

Cuomo, F.; Ceglie, A. and Lopez, F. "Temperature dependence of Calcium and Magnesium induced caseinate precipitation in H_2O and D_2O", Food Chemistry 126, 8-14 (2011).

2C – Stability and nanostructure of food emulsions and veiled extra virgin olive oil

M. Mosca, L. Ambrosone, A. Ceglie

Aims

Determination of the parameters which affect the oxidative stability of veiled olive oils and other olive oil-based food emulsions. The formulation of novel olive oil-based functional foods.

Results

Among vegetable oils, in the last years olive oil has become widely spread due to the increased demand for healthy foods.

Olive oil is the main vegetable oil consumed in the Mediterranean countries and there is a continuous sales increase in other countries. Then a strong international competition has arisen and financial survival depends on the capability of each enterprise to keep or expand its market introducing new products or to increase the value of traditional products. In this way, it becomes crucial to produce olive oil that can retain full activity of its healthy beneficial components, such as antioxidants, for the longest possible period. Such components have to be transferred from olives to the final product in a proper way and kept in dispersion within the oil. This can be achieved avoiding or minimizing the decanting step in order to have the traditional "veiled" extra virgin olive oil. The peculiarity of veiled olive oils is their unique nanostructure that affects their nutritional and technological properties. In the aqueous dispersed phase, in fact, some endogenous antioxidant may partition so affecting the shelf life of the product. The main problem to overcome is to obtain a stable product that can guarantee the presence of antioxidants throughout its shelf life. Olive oil is a natural food characterized by the presence of an enormous number of compounds so that the above aims can be achieved only by comparison with suitable reference systems.

The research project has been carried out through several stages as follows:

1) experimental determination of the correlation between susceptibility to oxidation of veiled olive oils and the surface area to unit volume of dispersed phase[1];

2) study of the role of the dispersed phase in the processes of oxidative degradation of olive oils [2,3], analysis of the amphiphilic nature of hydroperoxides and their ability to lower the interfacial tension between water and oil;

3) analysis of a model ternary system (Glycerol trioleate-Sodium oleate-water) to study the oxidation mechanism of heterogeneous systems[4];

4) determination of the impact of edible surfactants on the oxidation of veiled olive oils and their use to produce more stable products[5];

5) use of the model system as carrier of antioxidant to set up new functional foods[6,7].

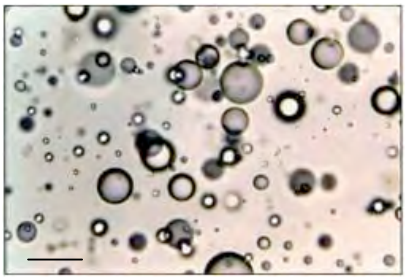


Figure1. Microphotograph of a water-in-olive oil emulsion. Bar = 5 μm.

References

Ambrosone, L.; Angelico, R.; Cinelli, G.; Di Lorenzo, V. and Ceglie, A. "The Role of Water in the Oxidation Process of Extra Virgin Olive Oils", JAOCS, 79, 577-581 (2002).

Ambrosone, L.; Cinelli, G.; Mosca, M. and Ceglie, A. "Susceptibility of water-emulsified extra virgin olive oils to oxidation", JAOCS, 83, 165-170 (2006).

Ambrosone, L.; Mosca, M. and Ceglie, A. "Oxidation of water emulsified olive oils", Food Hydrocolloids, 20, 1080-1086 (2006).

Mosca, M.; Murgia, S.; Ceglie, A.; Monduzzi, M. and Ambrosone, L. "Biocompatible Lipid-based Liquid Crystals and Emulsions", J. Phys. Chem. B, 110, 25994-26000 (2006).

Ambrosone, L.; Mosca, M. and Ceglie, A. "Impact of edible surfactants on oxidation of olive oil in water-in-oil emulsions", Food Hydrocolloids, 21, 1163-1171 (2007).

Mosca, M.; Ceglie, A. and Ambrosone, L. "Biocompatible Water-in-Oil Emulsions as a model to study Ascorbic Acid effect on lipid Oxidation", J. Phys. Chem. B, 112, 4635-4641 (2008).

Mosca, M.; Ceglie, A. and Ambrosone, L. "Antioxidant dispersions in emulsified olive oils", Food Res. Int., 41, 201-207 (2008).

2C – The role of the interface in the radical induced oxidation in emulsions and liposomes

M. Mosca, L. Ambrosone, A. Ceglie

Aims

Study the role of interfaces in the determining lipid oxidation pathways in heterogeneous systems.

Results

Lipid peroxidation plays a central role in determining the stability and shelf life of foods but also in normal functioning and in the onset of important diseases. The products of oxidation are known to be responsible of severe pathological events such as tumorigenesis, liver disease, atherosclerosis. For these reasons it is important to have a thorough knowledge of the mechanisms of oxidation in complex heterogeneous systems. The interfaces role in the oxidation reaction is important because chain reactions taking place in compartimentalized systems can follow kinetics and mechanisms quite different than those observed in homogeneous solution. The lipophilic 2,2'-azobis(2,4-dimethylvaleronitrile) (AMVN) was used to study the oxidation reaction in a model W/Olive oil emulsion system. This radical species decomposes thermally with a calculated dissociation constant, k_d, in olive oil at 40° C equal to 2.5×10^{-4} min^{-1}. Oxidation data gathered as hydropheroxides concentration measured by a fluorimetric method, showed that in presence of a large interface and a radical initiator, the oxidation reaction is accelerated in W/Olive oil emulsions with respect to whole oil. The mediation of the interface can be observed by the addition of saturated solution of Ascorbic Acid in dispersion in the oil, because it brings about a strong reduction of the oxidation rate even in the presence of the highest AMVN quantity. In liposomes, lipid hydroperoxides, the main intermediates of the peroxidative reaction, accumulate in the bilayer and induce changes in the structure and biophysical organization of membrane lipid components. Liposomes were oxidized by using a hydrophilic radical initiator, the (2,2-azobis(2-amidinopropane) hydrochloride, AAPH. The oxidation of liposomes, monitored by following the absorbance of the primary products of oxidation at 234 nm, was shown to be dependent on the composition of the liposomal bilayer and so on its biophysical properties. In addition, size and z-potential measurements gathered in the time course of the peroxidation reaction, revealed that oxidation induced a modification of the superficial characteristics of the membrane bilayer so as to change its charge at the shear plane (z-potential). This behavior was shared by all liposomal preparation independent of the composition. The rigidity induced by cholesterol makes the membrane more resistant to radical attack from an external aqueous phase and this in turn delays the start of the oxidation reaction. The decrease of z-potential of the liposomal particles induced by the oxidation process may be an important clue to understand the mechanisms involved in the etiology of important diseases.

References

Mosca, M.; Ceglie, A. and Ambrosone, L. "Lipid oxidation in water-in-olive oil emulsion initiated by a lipophilic radical source", J. Phys. Chem. B, 114, 3550-3558 (2010).

Mosca, M.; Ceglie, A. and Ambrosone, L. "Effect of membrane composition on lipid oxidation in liposomes", Chem. Phys. Lipids, in press (2011).

2C – Model systems for saccharide-based biosensor

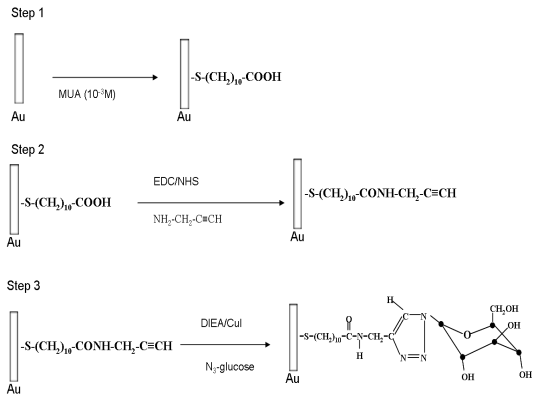
G. Leone, M. Consumi, A. Tognazzi, A. Magnani.

Aims

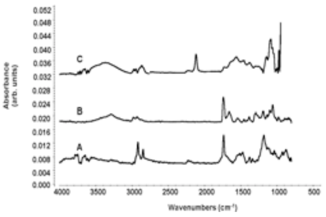
In their infection strategy, microorganisms often use sugar-binding proteins which present submicromolar affinity toward monosaccharides. In vivo, these interactions are extremely complex processes and consequently the identification and the analysis of each single process is extremely difficult. Consequently, the aim of this research is the development a simple model system which can represent a starting point for the realisation of biosensor.

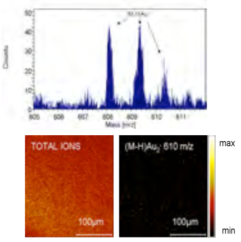
Results

The biosensor model system based on the immobilisation of a monosaccharide onto gold substrate is realised by a "three-steps procedure" which involves SAM and click-chemistry methodologies as shown in scheme A.

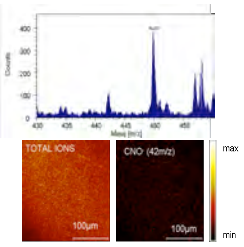


Each step of modification can be characterised by reflection absorption infrared spectroscopy (RAIRS) and time of flight secondary ion mass spectrometry (ToF-SIMS).

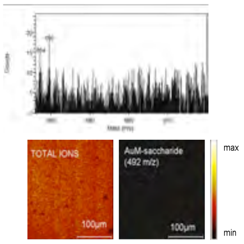




STEP 1

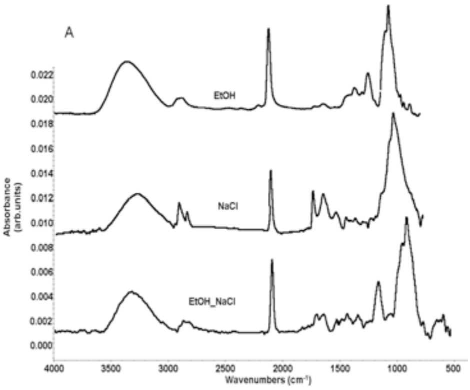


STEP 2



STEP3

Sample incubation in EtOH or Sodium Chloride solutions over a period of 30 days do not affect the stability of the monolayer.



The proposed procedure appears to be useful for the realisation of homogeneous surfaces containing the glucose receptor covalently bound to the substrate without extensive modification. Consequently, the realised systems, due to the glucose moiety accessibility can be proposed for the preparation of model systems of biosensors. The validation of this methodology allows us to modify our model system into a more specific system changing the glucose residue with a more specific saccharide or oligosaccharide moiety which directly interacts with specific cells or bacteria.

References

Leone, G.; Consumi, M.; Tognazzi, A. and Magnani, A. "Realisation and chemical characterisation of a model system for saccharide-based biosensor", Thin Solid Films 519, 462-470 (2010).

2C – Increasing photostability and water-solubility of carotenoids: synthesis and characterization of β-carotene-humic acid complexes

S. Martini, C. D'Addario, C. Bonechi, G. Leone, A. Tognazzi,
M. Consumi, A. Magnani, C. Rossi

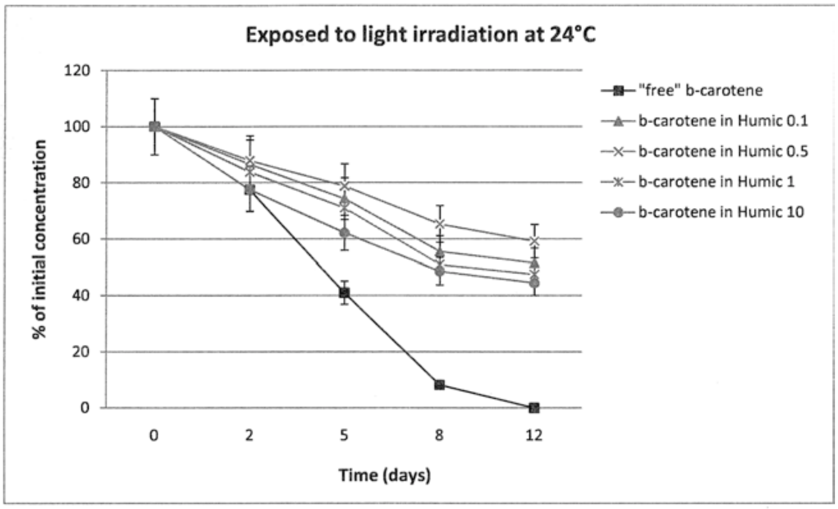
Aims

Carotenoids are a group of phytochemicals that are recognized as playing an important role in the prevention of several degenerative diseases due to their antioxidant activity. The low water-solubility and poor photostability of b -carotene, a potentially important dietary antioxidant, prompted us to investigate b-carotene complexes able to increase its water solubility as well as its photostability in aqueous solution. In this work we have used humic acid in order to synthesize β-carotene-humic acid complexes in different ratios.

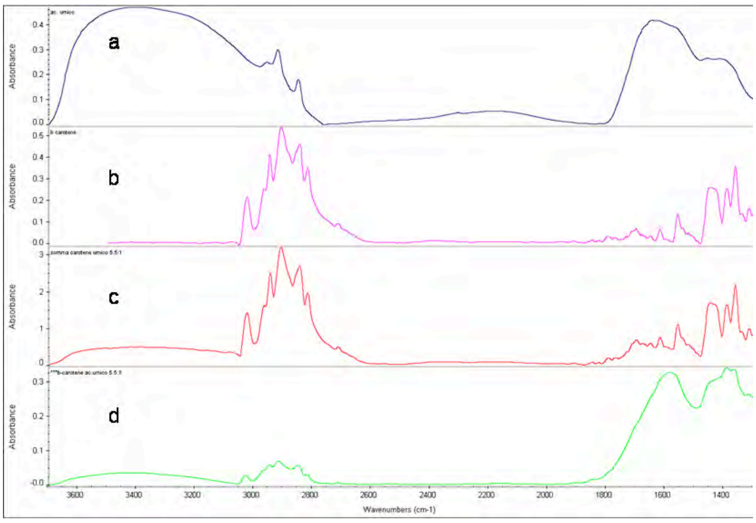
Results

Complexes were characterised by FT-IR and DSC. β-carotene determination were performed by HPLC and antioxidant activity of β-carotene, humic acid and the complexes were determined by the TEAC method. The formulation β-carotene-humic acid 2:1 showed the highest photo-stability and water solubility. The antioxidant activity of the complexes was about 20 times lower than "free" β-carotene, suggesting a decreased chemical reactivity of the carotenoid in the complex.

The percentage of β-carotene measured in solutions of the synthesised complexes exposed to light irradiation in relation to time at 24°C was determined. The results indicate that "free" β-carotene underwent complete degradation after about 12 days, while after the same period, the amount of β-carotene complexed to humic acid was about the 60% of the initial concentration for Humic 0.5, 50% for Humic 0.1 and 45% for Humic 10 and Humic 1.



The interaction between β-carotene and humic acid was studied by infrared spectroscopy with the aim of determining the HA moieties responsible for the β-carotene “binding”. By considering the highly conjugated structure of β-carotene and the presence in the HA molecule of aromatic characteristics, a π–π interaction can be hypothesised.



We showed that complexation of β -carotene with humic acids was able to increase its water solubility and photostability, and to affect the antioxidant activity of β-carotene after inclusion in HAs.

References

Martini, S.; D’Addario, C.; Bonechi, C.; Leone, G.; Tognazzi, A.; Consumi, M.; Magnani, A.; Rossi, C. “Increasing photostability and water-solubility of carotenoids: synthesis and characterization of β-carotene-humic acid complexes”, J. Photchem. Photobiol. 101(3), 355-361 (2010).

2C – Antibacterial activity of plant extracts towards cagA positive and cagA negative Helicobacter pylori clinical isolates

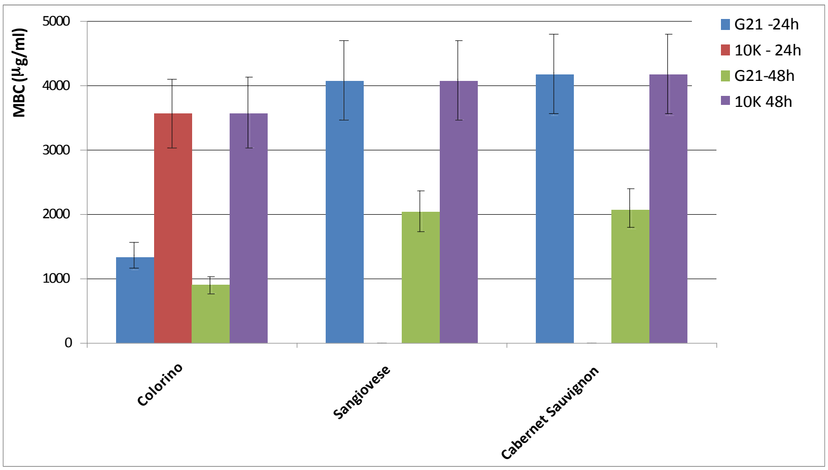
S. Martini, C. Bonechi, N. Figura (Dept. of Internal Medicine, Univ. of Siena, Italy), C. Rossi

Aims

There is considerable interest in alternative/adjuvant approaches for the eradication of *Helicobacter pylori* using biologically active compounds, especially antioxidants from plants. The aims of the present research field, were the determination of the antioxidant and antimicrobial activities of plant extracts as well as isolated compounds against *H. pylori cagA* negative and *cagA* positive clinical isolates by the determination of the minimum bactericidal concentration (MBC).

Results

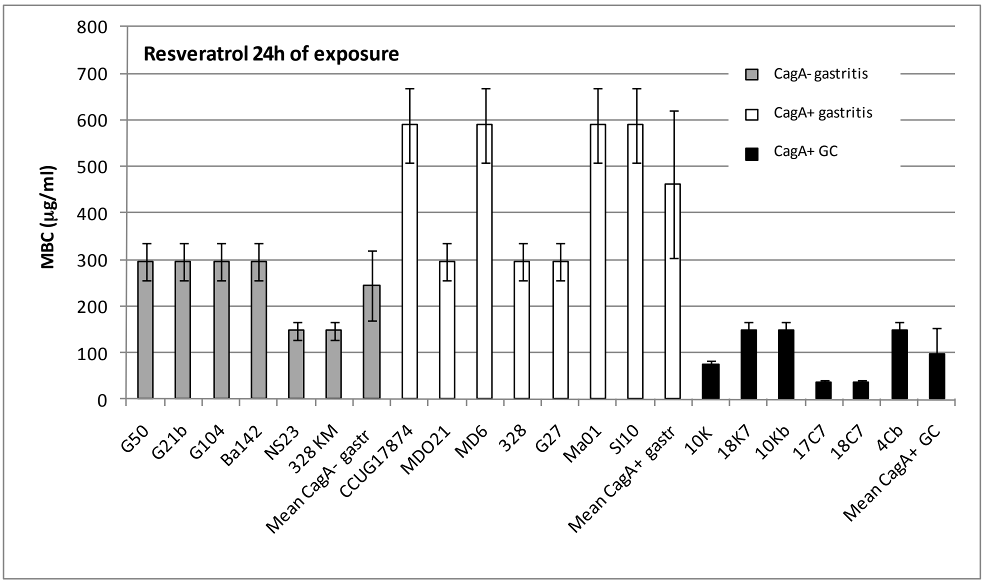
We tested the antibacterial activity of different grape cultivar (Colorino, Sangiovese and Cabernet Sauvignon) by the evaluation of MBC values of the respective polyphenolic extracts. After 24h of incubation, Colorino extract showed the highest antibacterial activity against G21 strain (CagA-) with respect to Sangiovese and Carbernet Sauvignon. Regarding the CagA positive strain (10K), after 24h, only the Colorino grape showed antimicrobial activity. In fact, Sangiovese and Cabernet Sauvignon grape extracts did not exerted any anti-*H. pylori* activity. After 48h of incubation, all the extracts showed antibacterial activity against both the *H. pylori* strains. In particular, for the CagA negative strain, we observed a general decrease in the MBC values, with respect to the 24h experiments. Colorino gave the lowest MBC value as observed for the results obtained after 24h of incubation. Regarding the CagA positive strain, Colorino gave the same MBC as after 24h, while Sangiovese and Cabernet Sauvignon, which did not demonstrate any anti-*H. pylori* activity after 24h, showed a bactericidal activity.



Remarkably, the more pathogenic strain (10K) was less susceptible to the grape extracts known to exert a powerful antioxidant activity. This phenomenon may help explain why patients with gastric carcinoma are more likely to be infected by organisms encoding the CagA protein.

However, this observation cannot be transferred simply to all the *cagA*$^{+}$ organisms, since the various clinical isolates are very heterogeneous from a genomic point of view. Nevertheless, given that *cagA* is also a marker for the presence of a pathogenicity island (PAI) in the bacterial chromosome, it can be assumed that strains possessing *cagA* may show a different behaviour towards chemotherapeutics.

We tested the anti-*H. pylori* activity of *trans*-resveratrol against CagA^{-} and CagA^{+} strains.



We found an increased susceptibility to resveratrol of strains isolated from gastric cancer cases with respect to strains isolated from patients without gastric cancer. Our hypothesis for this behaviour is that one target of the antibacterial action of resveratrol may be one or more F-type ATPases, which normally protect the bacteria from low pH levels by maintain a proton gradient across membranes.

References

Martini, S.; D'Addario, C.; Braconi, D.; Bernardini, G.; Bonechi, C.; Figura, N.; Santucci, A. and Rossi C. "Antibacterial activity of grape extracts towards cagA positive and cagA negative *Helicobacter pylori* clinical isolates", J. Chemother., 21(5), 507-513 (2009).

Martini, S.; D'Addario, C.; Colacevich, A.; Focardi, S.; Borghini, F.; Figura, N.; Santucci, A. and Rossi, C. "Antimicrobial activity against Helicobacter pylori strains and antioxidant properties of blackberry leaves (*Rubus ulmifolius*) and isolated compounds", Int. J. Antimic. Agents 34 (1), 50-59 (2009).

2C – Substitutes of human vitreous

G. Leone, M. Consumi, M. Aggravi, A. Donati, S. Lamponi, A. Magnani.

Aims

The surgical treatment of various complicated retinal detachments requires the availability of a vitreous substitute, either temporary or permanent, ideally to be injectable into the vitreous cavity at the time of surgery. Actually, silicone oil is the most commonly used temporary vitreous substitute. However, the ability of the eye to tolerate this foreign material has been repeatedly questioned.

This research concerns the development of a new poly(vinyl-alcohol) (PVA) based hydrogel as potential vitreous substitute.

Results

The natural vitreous body in the vertebrate eye has viscoelastic properties. Based on the assumption that any materials to substitute the vitreous should also be viscoelastic, hydrogel with very high water content is obtained by crosslinking PVA with STMP.

The rheological analysis in terms of G' G", loss tangent and creep behaviour points out that PVA_cr8 behaves significantly better than the commercial silicon oil, comparing them with porcine vitreous (Table 1 and Fig 1 and Fig 2)

Table 1. Storage and loss moduli of fully hydrated (NaCl 0.9%) PVA_cr8 at 5 Hz compared with bovine vitreous, porcine vitreous and a commercial silicon oil.

	G' (Pa)	G"(Pa)
Bovine Vitreous *	7±2	2.2±0.6
Porcine Vitreous *	2.8±0.9	0.7±0.4
Commercial silicon oil	0.0013±0.0005	14±2
PVA_cr8	3.9±0.1	2.8±0.1

*: average steady-state moduli

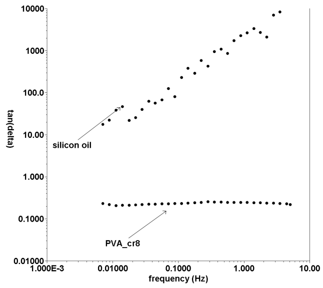


Figure 1. Phase shift tangent: The lower the loss tangent the higher the resilience. A material with high resilience may perform better mechanically in a vitreous cavity.

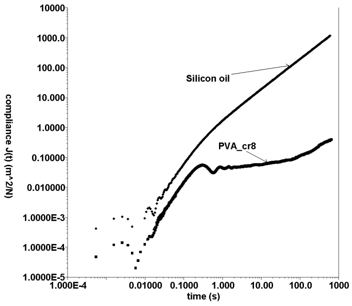
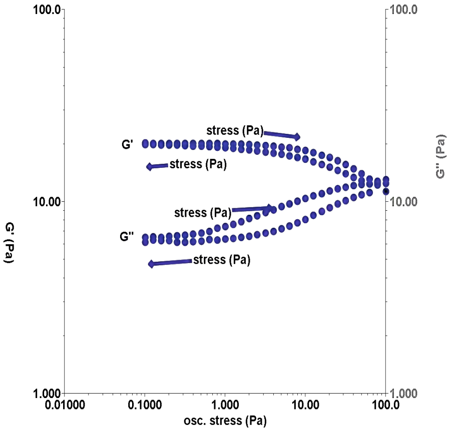


Figure 2. shear creep analysis: Hydrogels show prominent instantaneous elastic responses followed by substantial retarded elastic responses during the time under constant shear stress. Silicon oil shows no instantaneous or retarded elastic response.

Thixotropy permits to foresee the injectability of hydrogel. PVA_cr8 shows a thixotropic behaviour. In fact, a perfect overlapping of both G' and G" is recorded in the loop test.



The rheological analysis, the water content determination (96±1%), the light transmittance measurements (94±3%) and the cytotoxicity test point out that the PVA_cr8 is able to fulfil the requirements for a good vitreous substitute. These preliminary results suggest that an application as vitreous substitute can be foreseen for PVA_cr8 hydrogel.

References

Leone, G.; Consumi, M.; Aggravi, M.; Donati, A.; Lamponi, S. and Magnani, A. "PVA/STMP based hydrogels as potential substitutes of human vitreous", J Mater Sci: Mater Med 21:2491-2500 (2010).

2C – In vivo NMR study of yeast fermentative metabolism in the presence of Ferric iron

M. Ricci, S. Martini, C. Bonechi, C. Rossi

Aims

Mathematical modelling analysis of experimental data, obtained with *in vivo* NMR spectroscopy and ^{13}C labelled substrates, allowed to describe how the fermentative metabolism in *Saccharomyces cerevisiae*, taken as eukaryotic cell model, is influenced by stress factors.

Experiments on cellular cultures subject to increasing concentrations of ferric ions were conducted in order to study the effect of oxidative stress on the dynamics of the fermentative process. The developed mathematical model was able to simulate the cellular activity, the metabolic yield and the main metabolic fluxes occurring during fermentation and to describe how these are modulated by the presence of ferric ions.

Results

Data show that the dynamics of glucose degradation and ethanol production were slightly decreased by the presence of ferric chloride, while both the ethanol yield and the time of fermentation remained almost unchanged. Indeed, close to the end of fermentation the error bars somewhat overlap. This indicates that the final ethanol yield was not significantly affected by iron, while glucose concentration approaches the zero value in about 40 hours during all the three experiments.

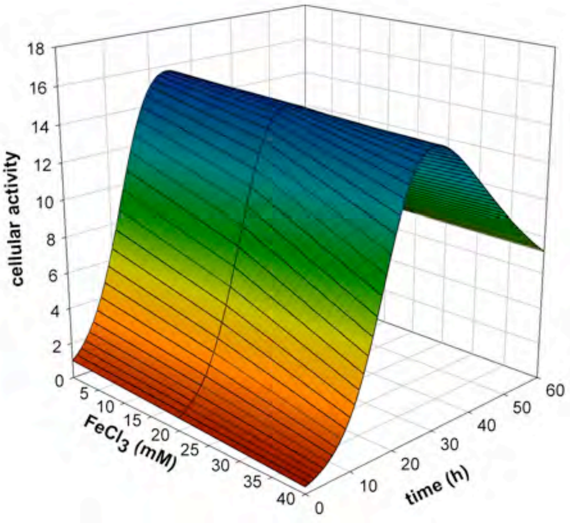


Figure 1. D surface of simulated cellular activity versus time and $FeCl_3$ concentration

We consider the fermentative route as the main catabolic pathway for glucose, in our experimental conditions, although glucose enters in many metabolic pathways (and it is converted, for example, into ethanol, CO_2, glycerol, and biomass).

The experimental yield can be derived from experimental data by plotting the ethanol time course vs the metabolized glucose time course. A linear dependence is evident and the slope of each line, calculated by linear regression, represents the experimental metabolic yield (EMY).

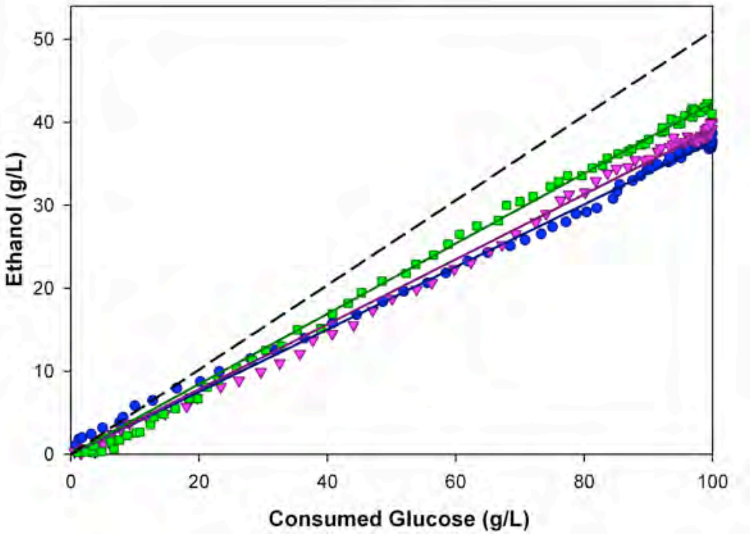


Figure 2. Endogenous ethanol vs metabolised glucose during glucose fermentation in *Saccharomyces cerevisiae* K310 in the presence of $FeCl_3$: blue (☐)= 0 mM, pink(☐) = 20 mM, green (☐) =40 mM. The slope of each line was calculated by linear regression. The theoretical maximum yield (0.511) is also reported (dashed line).

The combined use of mathematical modelling and *in-vivo* ^{13}C NMR spectroscopy revealed as a powerful tool for *in-vivo* investigation of metabolism and its modulation in response to increasing ferric chloride concentration in the fermentation medium of a wild-type strain of *Saccharomyces cerevisiae*.

The schematization obtainable by the developed compartmental model highlights the principal biochemical processes of glucose metabolism in yeast, i.e. the glucose metabolization and products formation and their modulation in function of the ferric iron concentration.

More in particular, the model highlights that the presence of ferric ions in the range 0 mM – 40 mM causes the modulation of the dynamics of the fermentative metabolism in *Saccharomyces cerevisiae* K310 during the first stages, but it doesn’t affect in a significant manner the final ethanol yield. This is explained in terms of a reduced metabolic activity at the beginning of fermentation that is function of ferric iron concentration.

References

Ricci, M.; Martini, S.; Bonechi, Braconi, D.; Santucci, A.; Rossi, C. “*In vivo* NMR study of yeast fermentative metabolism in the presence of Ferric iron”, J. Biosci. (2011). In press.

2C – Structural and dynamic NMR studies of oligopeptides mimicking nur77 binding site

M. Aggravi, S. Butini, G. Campiani, A. Casagni, A. Donati, R. Noschese

Aims

Structural investigation on an oligopeptide (PEP2) and its cyclic homologue synthesized on the template of the aminoacidic sequence of the Nur77 binding site.

Results

PEP2 primary structure is reported in **Fig.1**. The two Nur77 binding domains (a poly-proline domain and a "LxxLL" domain), are here linked together by a proline.

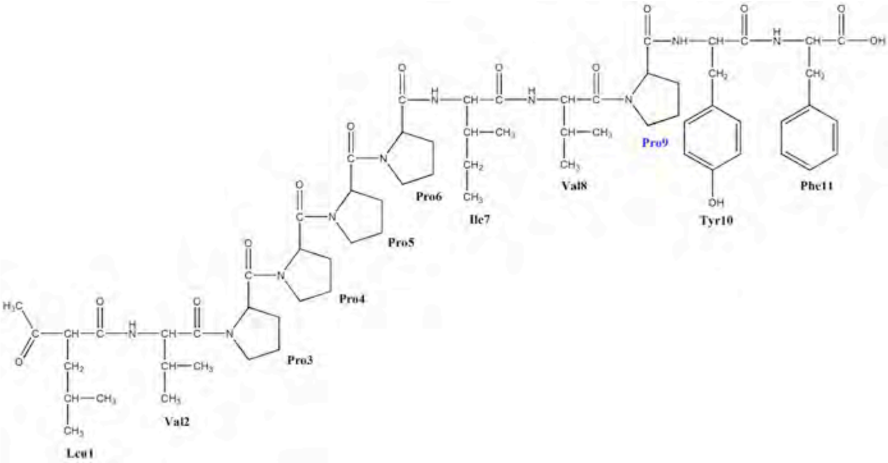


Fig.1

In order to determine the favourite spatial conformation of PEP2, 1D- and 2D-experiment were driven at different temperatures using a 600MHz Bruker spectrometer.

First, the PEP2 sequence was completely assigned by using COSY, NOESY and TOCSY spectra. Then, all the significant restraints were collected, i.e. dihedral angles and NOE distances. The dihedral angles Φ were calculated from the measurements of $^3J_{NH\alpha}$ in ^{1}H experiments. used as were Only the inter-residue interactions (sequential and medium-range) were used as NOE distance contraints.

The structure determination of PEP2 through computational optimization was the further step. Using AMBER software, conformational space of the peptide was sampled through 30 cycles of restrained simulated annealing and the resulting structures were then subjected to energy minimizations. Simulated annealing was performed following this protocol: temperature was increased from 0K to 600K in 40ps and maintained as such for 55ps to surmount torsional barriers, then it was linearly reduced to 0K in 5ps.

Most of the obtained structures (**Fig.2**) totally complied with experimental restraints.

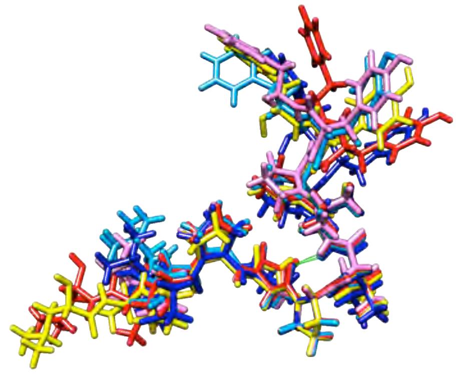


Fig.2

As shown in **Fig.2**, the central portion including the poly-proline domain is well retained in all the structures, while terminal residues are much more flexible. This fact was also supported by experimental data. In fact, NOESY spectra showed phase-reversed peaks for the phenylalanine (**Fig.3**), indicating that this residue has an higher degree of freedom.

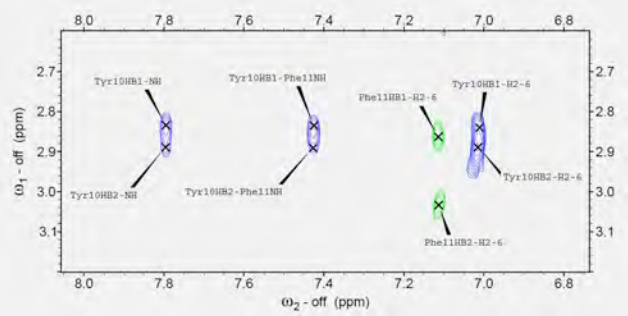


Fig.3

Moreover, it is interesting to note that an H-bond, linking the amidic proton of Phe11 and the carbonyl oxygen of Pro9, was found in one structure of this ensemble.
Moreover a stable H-bond was predicted between Val8 and Pro5 in all the structures of the ensemble. This last H-bond was very similar to the one found in Nur77 (Val587-Pro584). This additional H-bond probably explains the slow-exchange NH proton of Phe11 observable in ^{1}H experiments acquired at high temperature.

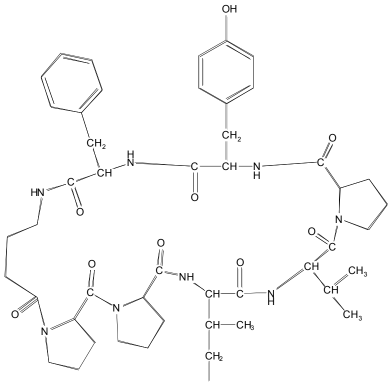


Fig.4

All the members of this family satisfactorily superposed to Nur77 binding domains (RMSD between peptidic backbones in is 1.326 Å), suggesting that PEP2 can act like a peptidomimetic of the natural human protein.
However, to try to overcome the flexibility of the structure on the terminal residues, a new peptide was synthetized. It's a cyclic peptide which retains the key aminoacidic sequence of PEP2 and blocks the two main domains in a particular conformation. This cyclic peptide (PEPcyc) is shown in **Fig.4**. For this molecule 2D-NMR experiments have been performed to confirm the structure, assign all the resonances and collect experimental restraints.
MD calculations will be performed to obtain the structures compatible with NMR data,. Our aim is to establish the degree of similarity between PEPcyc and the Nur77 binding site, in order to understand if cyclic peptide can be regarded as a lead compound to develop a new class of protein-based anticancer drugs.

References

Ferlini, C.; Cicchillitti, L.; Raspaglio, G.; Bartollino, S.; Cimitian, S.; Bertucci, C.; Mozzetti, S.; Gallo, D.; Persico, M.; Fattorusso, C.; Campiani, G. and Scambia, G. "Paclitaxel directly binds to Bcl-2 and functionally mimics activity of Nur77", Cancer Res. 69 (17), 6906-14 (2009).
Lin, B.; Kolluri, S.K.; Lin, F.; Liu, W.; Han, Y.; Cao, X.; Dawson, M.I.; Reed, J.C. and Zhang, X. "Conversion of Bcl-2 from Protector to Killer by Interaction with Nuclear Orphan Receptor Nur77/TR3", Cell, 116, 527-540 (2004).

2C – Interaction between vine pesticides and serum albumin studied by nuclear spin relaxation data

S. Martini, C. Bonechi, C. Rossi

Aims

Pesticides are chemicals usually used in agriculture to prevent possible diseases to crops, such as grapes, caused by parasites. Even if most of the pesticides are degraded during the wine process, residual levels remain in the final product. The aim of this work was the investigation of the interaction between three of the most used fungicides belonging to the chemical classes mentioned above (myclobutanil, triadimenol, and pyrimethanil) and serum albumin (BSA) by nuclear spin relaxation analysis.

Results

In order to evaluate the existence of pesticides-BSA interactions, proton spin-lattice relaxation rates of pyrimethanil, myclobutanil, and triadimenol solutions in the absence and in the presence of BSA have been measured. Data show that the presence of the protein did not affect the non-selective relaxation rate, nevertheless an increase in the selective relaxation rate with increasing BSA concentration within the three systems was observed. It can be noted that BSA influenced selective relaxation rate values to different extent depending of the fungicide within the system under study. This result suggests the existence of binding processes between the three pesticides and BSA. R_{1N}^{SE} enhancements (ΔR_{1N}^{SE}), caused by the presence of molecular interactions, can be quantified in relation to protein concentration. ΔR_{1N}^{SE} dependence of BSA content is always linear in this kind of systems and the slope of the straight line provides a useful index, the affinity index, $\left[A_I^N\right]_L^T$, which is related to the strength of the overall interaction processes (specific and non-specific binding) occurring between the pesticides and the protein. . The plot reported in Figure 2 shows the experimental values of ΔR_{1N}^{SE} vs. BSA concentration together with data fitting and affinity index calculation for the three systems under investigation. The results indicate that myclobutanil had the highest affinity for BSA ($\left[A_I^N\right]_L^T$= 73676 mol^{-1} dm^3), whereas pyrimethanil and triadimenol showed lower affinity for the protein giving affinity indexes of 33458 mol^{-1} dm^3 and 20813 mol^{-1} dm^3, respectively. In particular, the affinity of myclobutanil for BSA was about three and a half times that of triadimenol.

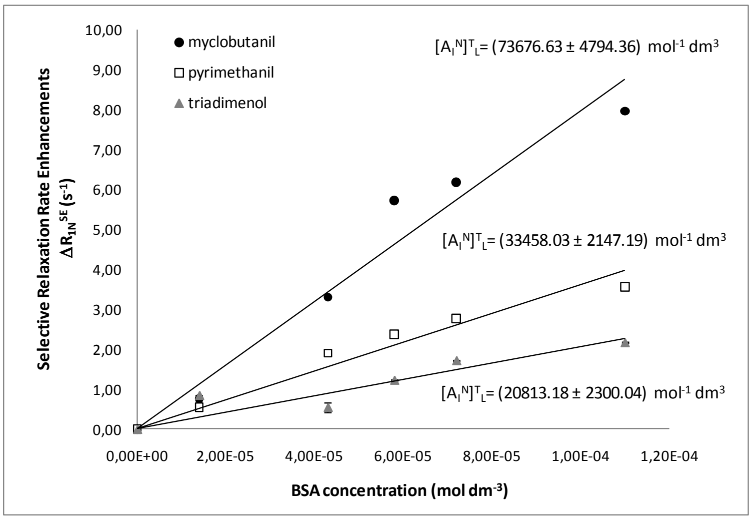


Figure 1. Experimental values of ΔR_{1N}^{SE} vs. BSA concentration together with data fitting and affinity index calculation.

Equilibrium constant values for pesticide-BSA complexes were: myclobutanil (494.43±0.54) mol^{-1} dm^3, pyrimethanil (315.37±0.76) mol^{-1} dm^3, and triadimenol (46.73±0.77) mol^{-1} dm^3. The data highlighted that myclobutanil-BSA was the most stable complex, and confirmed the weakness of pyrimethanil-BSA interaction process, in agreement with affinity index results.

References

Martini, S.; Bonechi, C. and Rossi, C. "Interaction between vine pesticides and bovine serum albumin studied by nuclear spin relaxation data", J. Agric. Food Chem. 58 (19), 10705-10709 (2010).

2C – In vitro biocompatibility of new PVA-based hydrogels as vitreous body substitutes

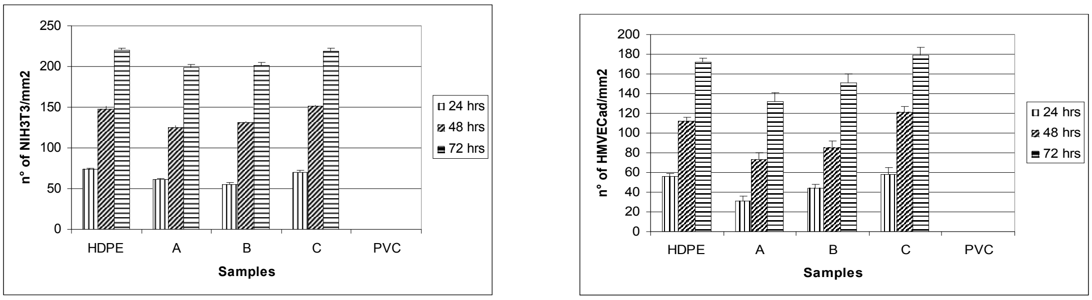
S. Lamponi, G. Leone, M. Consumi, G. Greco, A. Magnani

Aims

The aim of the present study was the evaluation of the in vitro biocompatibility of three new hydrogels (STMP/PVA 1:4, 1:6 and 1:8) in terms of their interaction with cultures of mouse fibroblasts NIH3T3 and primary Human Microvascular Endothelial Cells adult (HMVECad). Moreover, the adhesion and proliferation of human lens cells to the most promising hydrogel in terms of cell compatibility, i.e. the 1:8 STMP/PVA, was studied. At last, the biocompatibility of sheared STMP/PVA 1:8 was also tested.

Results

For the evaluation of the SMTP/PVA hydrogels cytotoxicity, mouse fibroblasts NIH3T3 were chosen and for the evaluation of cytocompatibility endothelial cells. Not confluent adhered cells were incubated with 10 mg of each swollen sample up to confluence was reached. Samples were analysed at intervals of 24 hours and results are reported in Figure 1. All the tested samples (STMP/PVA 1:4, STMP/PVA 1:6, STMP/PVA 1:8 were not cytotoxic for neither mouse fibroblast 3T3 nor HMVECad and they did not interfere with cell growth. In fact, the number of adhered cells/mm^2 in contact with the hydrogels was not statistically different in comparison to the negative control (high density polyethylene).



a) b)

Figure 1. Number of a) adhered NIH3T3 and b) HMVECad in contact with the three different hydrogels as a function of incubation time evaluated by optical microscopy cell count. Data are means ± standard error of five counts for each sample tested in triplicate. No value is statistically different versus Control (HDPE). A: STMP/PVA 1:4; B: STMP/PVA 1:6; C: STMP/PVA 1:8.

Mouse fibroblasts NIH3T3 and primary endothelial cells HMVECad proliferation and viability in contact with the hydrogels was evaluated over three days at intervals of 24 hours by WST-1 assay. The results obtained demonstrated that the mitochondrial activity of fibroblasts and endothelial cells after 24, 48 and 72 hrs of contact with the three different substrates, showed the same characteristics. No impairment of the mitochondrial function or sign of cytotoxicity was found in the cell lines.

SEM morphology of NIH3T3 and HMVECad in contact with the three different hydrogels was evaluated by SEM analysis after 72 hrs of culture. SEM analysis demonstrated that morphology of both NIH3T3 and HMVECad was maintained when the STMP/PVA hydrogels were present. In the presence of the specimens, as well as of the negative control, NIH3T3 showed an excellent spreading and their density increased with increasing the PVA content in the hydrogel (i.e. from 1:4 to 1:8).

As the STMP/PVA 1:8 resulted the most biocompatible hydrogel it was selected for being tested with human lens cells. Human anterior chamber was put directly on hydrogel surface in order to investigate its bio-specific adhesiveness. The results are shown in Fig. 2. No cells were found attached and spread on the surface of the hydrogel demonstrating the low adhesion properties of this specimen also towards specific human lens cells. Moreover, as observed for fibroblasts and endothelial cells, once removed the specimens from the bottom of the wells multidish (after 30 days of culture), no cells were found adhered to the polystyrene plate due to the structure of the hydrogel which does not allow the cells to cross it.

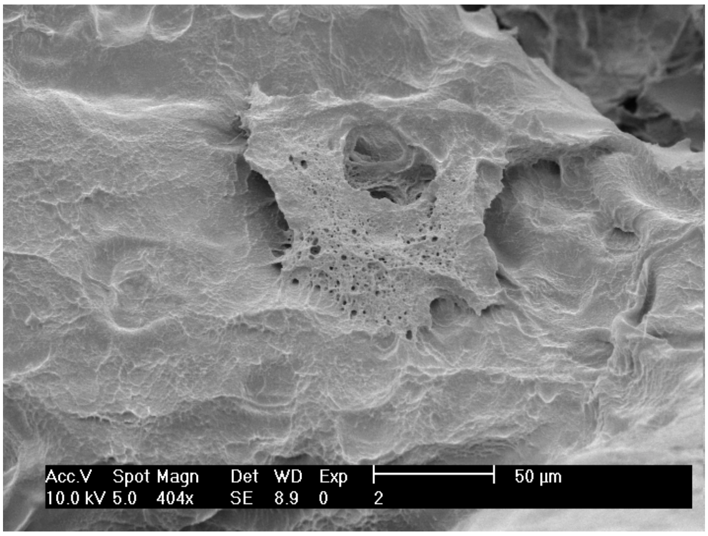


Figure 2. SEM images of hydrogel samples after 30 days of culture with human anterior chamber.

In conclusion, all the STMP/PVA hydrogels properties, i.e. high cell compatibility and inhibition of cell adhesion on the surface, make them suitable as vitreous substitutes. Among them, the 1:8 sample, showing the best behaviour in terms of biocompatibily, is the most suitable candidate for such an application.

References

Lamponi, S.; Leone, G.; Consumi, M.; Greco, G. and Magnani, A. “In vitro biocompatibility of new PVA-based hydrogels as vitreous body substitutes”, J Biomat Sci. Pol Ed. (2011). In press.

Leone, G.; Consumi, M.; Aggravi, M.; Donati, A.; Lamponi, S. and Magnani, A. “PVA/STMP based hydrogels as potential substitutes of human vitreous”, J Mat Sci: Mat Med 21, 2491-2500 (2010).

2C – Microbial synthesis and structural characterization of biodegradable polyesters from fatty acids with odd number of carbon atoms

Alberto Ballistreri [1], Giuseppe Impallomeni [2], Giovanni M. Carnemolla [1], Salvatore P.P. Guglielmino [3], Marco Nicolò [3], Maria G. Cambria [3]
([1]Dipartimento di Scienze Chimiche,Università di Catania, [2]Istituto di Chimica e Tecnologia dei Polimeri, Consiglio Nazionale delle Ricerche,[3]Dipartimento di Scienze della Vita , Università di Messina)

Considering the great scientific interest toward Pseudomonas aeruginosa in the field of genetic engineering1, we undertook a systematic study on the synthesis and characterization of poly(3-hydroxyalkanoates) (PHAs) potentially producible by P. aeruginosa2. The aim of the present study was to extend the investigations on the capability of P. aeruginosa to grow and synthesize PHAs from longer C-odd fatty acids from heptadecanoic to eneicosanoic by changing microelements limiting conditions in the fermentation step. The PHAs obtained were characterized by GC, GPC, DSC, 1H and 13C-NMR. The variation in their physical properties were explored systematically in comparison to those obtained from even-carbon sources. ESI MS of partial pyrolyzed samples allowed the identification of oligomers up to heptamers and statistical analysis showed that these PHAs are random copolyesters.

References

Ren, Q.; Sierro, N.; Witholt, B. and Kessler, B.J. Bacteriol., 182, 2978-2981 (2000).
Barbuzzi, T.; Giuffrida, M.; Impallomeni, G.; Carnazza, S.; Ferreri, A.; Guglielmino, S.P.P. and Ballistreri, A. Biomacromolecules, 5, 2469-2478 (2004).

Author Index

A

Aggravi M. · 32, 33, 56, 261, 262, 265, 270
Al Kayal T. · 35, 43, 49, 50, 158, 159
Almgren M. · 154, 155
Altieri S. · 14, 27, 28, 32, 148, 149
Ambrosi M. · 7, 13, 26, 27, 49, 152, 153, 175, 187
Ambrosone L. · 6, 7, 12, 25, 39, 44, 49, 120, 121, 127, 185, 200, 251, 252, 253, 254
Angelico R. · 6, 7, 12, 25, 39, 120, 121, 126, 127, 185, 200, 252
Angius R. · 8, 20, 104, 105, 106, 107
Arroyo M.C. · 39, 198

B

Baglioni M. · 190
Baglioni P. · 3, 6, 7, 13, 14, 26, 27, 28, 34, 35, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 52, 53, 54, 56, 91, 92, 93, 94, 95, 96, 97, 98, 144, 145, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 174, 175, 186, 188, 190, 192, 194, 196, 198, 201, 203, 204, 205, 206, 207, 208
Ballistreri A. · 20, 26, 31, 40, 43, 46, 57, 227, 234, 237, 271
Banchelli M. · 13, 26, 40, 42, 46, 47, 103, 144, 145, 157
Baratto M.C. · 24, 40, 50, 53, 173, 182, 183, 242, 246, 247, 248, 249
Barone V. · 10, 11, 22, 23, 24, 37, 38, 41, 42, 43, 46, 57, 77, 78, 114, 115
Barreca F. · 48, 228
Barse B. · 19, 45, 164, 165
Basosi R. · 11, 12, 24, 25, 36, 37, 40, 42, 43, 45, 46, 47, 50, 53, 54, 55, 56, 58, 79, 80, 116, 117, 166, 167, 168, 169, 170, 171, 172, 173, 182, 183, 242, 243, 244, 245, 246, 247, 248, 249
Bausi F. · 61, 97
Bellissima F. · 41, 61, 201
Berbenni V. · 9, 19, 21, 22, 24, 33, 34, 42, 43, 51, 75, 76, 240, 241
Bernini C. · 166, 172
Bernini L. · 196
Berti D. · 8, 13, 14, 26, 27, 35, 39, 40, 41, 42, 43, 44, 46, 47, 49, 50, 52, 103, 104, 105, 144, 145, 156, 157, 158, 159, 190, 191, 198
Bhattacharyya M.S. · 8, 20, 48, 55, 73, 74, 164, 165, 225, 226
Bianco F. · 54, 63, 232, 238
Biczysko M. · 10, 11, 22, 23, 24, 41, 42, 43, 77
Bilanicova D. · 174, 175
Bini M. · 9, 22, 33, 34, 42, 43, 44, 46, 50, 103, 215, 241
Bloino J. · 10, 11, 22, 23, 24, 37, 41, 42, 43, 114, 115
Bonechi C. · 14, 19, 32, 37, 43, 45, 50, 64, 65, 124, 125, 160, 161, 211, 212, 257, 258, 259, 260, 263, 264, 267, 268
Bonini M. · 6, 7, 26, 28, 35, 39, 41, 49, 52, 54, 56, 154, 155, 158, 159, 191, 194, 195, 201, 204, 205, 206, 207, 208
Bonucci A. · 47, 64, 116, 242
Bortolussi S. · 14, 27, 28, 32, 148, 149
Boscagli C. · 61, 85
Boström M. · 14, 19, 20, 34, 164, 165
Bracchini L. · 19, 32, 33, 37, 56, 176, 178, 179, 180, 181, 209, 210, 213, 214
Bravi M. · 36, 37, 43, 64, 79, 80
Bressanin D. · 8, 19, 43, 59, 221, 223
Bruni G. · 9, 19, 21, 22, 24, 33, 34, 42, 43, 44, 46, 51, 53, 55, 58, 75, 76, 240, 241
Bufalo G. · 44, 200
Busi E. · 24, 36, 43, 53, 58, 244, 246, 247
Butini S. · 33, 43, 265

C

Cacelli I. · 10, 11, 23, 24, 37, 41, 43, 114, 115
Caglioti C. · 48, 231
Cambria M.G. · 20, 40, 43, 227, 234, 271
Caminati G. · 13, 14, 26, 35, 40, 42, 43, 44, 45, 46, 47, 49, 50, 62, 83, 85, 89, 144, 145, 146, 204
Campiani G. · 43, 265, 266
Canton P. · 22, 35, 48, 54, 201, 206, 208
Capsoni D. · 9, 22, 33, 34, 42, 43, 44, 46, 48, 50, 54, 215, 241
Caratozzolo M. · 8, 12, 20, 26, 31, 44, 48, 57, 63, 231, 235, 239
Carnazza S. · 8, 20, 26, 31, 33, 44, 48, 54, 57, 228, 230, 232, 238, 271
Carnemolla G.M. · 20, 40, 46, 234, 237, 271
Carnerup A.M. · 9, 20, 106, 107
Carnimeo I. · 41, 57, 77
Carretti E. · 6, 13, 26, 27, 35, 44, 48, 52, 53, 153, 190, 191, 195, 203, 204
Casagni A. · 265
Cascio A. · 48, 228
Cavaciocchi L. · 44, 61, 85
Cavigli P. · 44, 45, 61, 83
Ceglie A. · 6, 7, 12, 25, 36, 45, 49, 52, 120, 121, 122, 126, 127, 128, 129, 184, 185, 200, 250, 251, 252, 253, 254
Chelazzi D. · 13, 187, 189, 191, 192, 193, 194, 195
Cianchetta S. · 8, 43, 221, 224
Ciani L. · 14, 18, 27, 44, 45, 46, 148, 149, 160
Cicero N. · 17, 53, 233
Colella A. · 11, 12, 24, 45, 50, 51, 52, 87, 217, 218
Columbro G. · 53, 233
Consumi M. · 32, 33, 37, 45, 48, 124, 125, 212, 255, 256, 257, 258, 261, 262, 269, 270
Cozar A. · 19, 33, 179, 181, 213, 214
Cugia F. · 20, 45, 71, 72
Cuomo F. · 12, 25, 36, 45, 49, 122, 123, 128, 129, 185, 250
Currò G. · 48, 228

D

Dal Piaz F. · 8, 43, 221
Daniele C. · 168
Dattilo A.M. · 19, 32, 33, 37, 56, 176, 178, 179, 180, 181, 209, 210, 213, 214
Dei L. · 6, 7, 13, 26, 35, 44, 52, 53, 98, 153, 186, 187, 189, 190, 191, 203, 204
Del Buffa S. · 61, 93, 94
Diaz G. · 20, 106, 107
Donati A. · 24, 28, 32, 43, 56, 65, 167, 261, 262, 265, 270
Doppiu S. · 51, 75
Dugo G. · 53, 233

E

Enzo S. · 6, 9, 39, 48, 52, 75, 186

F

Falchi A.M. · 20, 52, 106, 107
Falletta E. · 35, 191, 195, 205, 206, 207, 208
Faraone A. · 14, 27, 46, 91, 92, 95, 96, 151
Ferrari S. · 9, 14, 22, 27, 28, 32, 33, 34, 42, 43, 44, 46, 48, 50, 54, 63, 149, 215, 241
Ferreri A. · 46, 237, 271
Ferretti A. · 10, 11, 23, 37, 41, 43, 61, 114, 115
Figura N. · 19, 32, 37, 50, 160, 161, 259, 260
Fortuna L. · 8, 44, 235
Frasca M. · 8, 44, 235
Fratini E. · 6, 7, 13, 14, 26, 27, 35, 39, 41, 44, 46, 49, 52, 53, 54, 91, 92, 93, 94, 95, 96, 98, 150, 151, 152, 153, 155, 175, 194, 195, 198, 201, 205, 206, 208
Frezza C. · 43, 46, 63, 227, 237
Fulini P. · 12, 46, 64, 168

G

Galinetto P. · 9, 22, 46, 50, 215
Gambinossi F. · 13, 26, 35, 40, 42, 43, 44, 45, 46, 47, 61, 83, 85, 89, 144, 145, 146
Garlaschelli D. · 24, 54, 170, 171
Ghezzi M. · 13, 14, 61, 83
Giacca M. · 20, 106, 107
Giannuzzi G. · 79
Giansanti S. · 11, 24, 36, 47, 56, 64, 173, 182, 183, 242, 248, 249
Gioffrè G. · 48, 231
Giorgi R. · 6, 13, 26, 28, 32, 39, 41, 42, 48, 52, 53, 54, 153, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 198, 201
Girella A. · 9, 21, 22, 24, 33, 34, 42, 43, 47, 51, 52, 53, 55, 56, 75, 76, 240, 241
Giustini L. · 154
Giustini M. · 12, 13, 14, 48, 49, 53, 61, 118, 119, 130, 131, 153, 155
Graniglia N. · 168, 169
Grasso L. · 8, 20, 25, 26, 31, 44, 48, 57, 63, 228, 230, 235, 239
Greco G. · 32, 33, 37, 48, 124, 125, 269, 270
Guglielmino S. · 8, 19, 20, 26, 31, 33, 40, 43, 44, 46, 48, 53, 54, 57, 226, 227, 228, 230, 231, 232, 233, 234, 235, 237, 238, 239, 271

H

Hiwale P. · 20, 48, 52, 73, 74
Hochkoeppler A. · 7, 8, 19, 37, 43, 45, 56, 219, 221, 223, 224

I

Impallomeni G. · 20, 40, 43, 46, 227, 234, 237, 271

J

Jez S. · 36, 56, 168, 244, 245

K

Karlsson[1] G. · 154
Kiros Y. · 8, 33, 55, 58, 69

L

La Lia M. · 48, 63, 231
La Porta S. · 53, 233
Lampis S. · 8, 20, 36, 48, 52, 104, 105, 106, 107, 108, 109
Lamponi S. · 19, 32, 33, 37, 40, 41, 46, 48, 64, 124, 125, 160, 261, 262, 269, 270
Leone G. · 19, 32, 33, 37, 48, 56, 57, 64, 65, 124, 125, 255, 256, 257, 258, 261, 262, 269, 270
Li Destri G. · 25, 48, 55, 60, 140, 142
Licciardello A. · 12, 13, 18, 19, 20, 25, 26, 31, 47, 48, 55, 56, 57, 82, 99, 100, 101, 102, 139, 162, 163, 239
Lindman B. · 25, 45, 122, 123
Liu Y. · 7, 14, 27, 37, 46, 82, 150, 151, 266
Lo Nostro A. · 205
Lo Nostro P. · 6, 7, 13, 14, 26, 27, 34, 48, 49, 53, 56, 152, 153, 154, 155, 174, 175, 205, 206, 207, 208
Loiselle S.A. · 19, 32, 33, 37, 64, 176, 178, 179, 180, 181, 209, 210, 213, 214
Lopez F. · 7, 12, 16, 18, 25, 29, 30, 35, 36, 45, 49, 118, 119, 122, 123, 128, 129, 130, 131, 184, 185, 250
Losito I. · 12, 25, 39, 126, 127

M

Magnani A. · 32, 33, 37, 45, 48, 56, 57, 65, 124, 125, 212, 255, 256, 257, 258, 261, 262, 269, 270
Mallardi A. · 12, 25, 53, 118, 119, 130, 131

Mamusa M. · 8, 36, 52, 59, 108, 109
Mangiapia G. · 8, 9, 20, 21, 45, 58, 110, 111, 112, 113
Mano M. · 20, 106, 107
Mariani S. · 65, 103
Marini A. · 8, 9, 10, 19, 21, 22, 24, 33, 34, 42, 43, 47, 50, 51, 52, 53, 55, 56, 75, 76, 240, 241
Marletta G. · 3, 8, 12, 20, 25, 26, 31, 44, 48, 49, 50, 51, 54, 55, 56, 57, 60, 81, 100, 101, 102, 132, 134, 136, 138, 139, 140, 142, 239
Martelli E. · 8, 56, 219
Martina M.R. · 49, 50, 62, 89, 146
Martinez A.T. · 11, 24, 28, 36, 42, 47, 54, 55, 56, 248, 249
Martini G. · 13, 14, 19, 27, 32, 33, 37, 43, 45, 50, 57, 148, 160, 161, 211, 212, 257, 258, 259, 260, 263, 264, 267, 268
Martorana A. · 24, 40, 50, 182, 242, 246
Massarotti V. · 9, 22, 33, 34, 42, 44, 46, 50, 215
Matteazzi P. · 6, 11, 21, 24, 45, 50, 51, 52, 87, 217, 218
Mazzini V. · 152
Medda L. · 19, 20, 48, 73, 74, 164, 165
Messina G.M.L. · 12, 25, 50, 51, 60, 63, 132, 134, 136, 227, 228, 230, 231, 232, 233, 234, 235, 237, 238, 239, 271
Miguel M.G. · 25, 45, 122, 123
Milanese C. · 8, 9, 19, 21, 22, 24, 33, 34, 42, 43, 45, 47, 50, 51, 52, 53, 55, 56, 58, 75, 76, 240, 241
Minunni M. · 103
Monduzzi M. · 8, 12, 19, 20, 36, 45, 46, 48, 52, 55, 71, 72, 73, 74, 104, 105, 106, 107, 108, 109, 164, 165, 174, 175, 225, 226, 252
Monti S. · 11, 15, 17, 22, 23, 29, 30, 31, 37, 38, 41, 43, 114, 115
Montis C. · 52, 62, 156
Mosca M. · 25, 52, 251, 252, 253, 254
Mozzati M.C. · 9, 22, 42, 44, 46, 50, 215
Mula G. · 20, 71, 72
Mulas G. · 9, 33, 34, 43, 47, 51, 52, 56, 75, 76
Müller A. · 91
Murgia S. · 8, 12, 20, 36, 46, 48, 52, 104, 105, 106, 107, 108, 109, 252
Mustarelli P. · 9, 22, 42, 44, 48, 50, 54, 215

N

Napolitano E. · 10, 23, 43, 51, 75
Nappini S. · 28, 35, 52, 62, 158, 159
Natali I. · 13, 26, 44, 52, 53, 62, 203, 204
Nelli P. · 8, 9, 33, 53, 55, 58, 65, 69
Neri F. · 35, 48, 204, 228
Nicolò M.S. · 19, 20, 40, 53, 226, 233, 234, 271
Ninham B.W. · 6, 8, 13, 14, 19, 20, 27, 34, 49, 53, 55, 152, 153, 155, 164, 165, 174, 175, 189
Nordèn B. · 28, 35, 52, 158, 159
Noschese R. · 265

O

Oliviero Rossi C. · 120, 121
Olivucci M. · 11, 24, 55, 56, 166, 167
Olsson U. · 25, 120, 121
Ortona O. · 9, 21, 45, 57, 110, 111, 112

P

Paduano L. · 8, 9, 20, 21, 45, 57, 58, 110, 111, 112, 113
Palazzo G. · 6, 7, 8, 12, 25, 36, 39, 45, 52, 53, 108, 109, 118, 119, 120, 121, 130, 131, 185
Palmieri S. · 8, 56, 62, 219, 220
Palmisano F. · 12, 25, 39, 126, 127
Panza L. · 14, 44, 148, 149
Parisi M.L. · 12, 24, 36, 37, 43, 53, 54, 56, 65, 79, 80, 166, 167, 242, 246, 247
Parsons D.F. · 14, 17, 19, 20, 34, 55, 164, 165
Pedone A. · 15, 17, 21, 22, 23, 29, 37, 38, 41, 114, 115
Peruzzi N. · 27, 28, 49, 53, 62, 174, 175
Pesavento G. · 175, 206, 208
Pesenti R. · 58, 59, 69
Picciolo F. · 170
Piludu M. · 20, 48, 73, 74
Pinna M.C. · 174, 175, 226
Piras M. · 20, 48, 73, 74
Pisagatti I. · 48, 228
Pisano M. · 8, 225, 226
Pistolesi S. · 11, 53, 62, 116, 117, 167
Pizzorusso G. · 13, 52, 53, 54, 62, 194
Poggi G. · 26, 188, 189, 192
Pogni R. · 11, 24, 25, 36, 40, 42, 47, 50, 53, 54, 55, 56, 116, 117, 167, 169, 172, 173, 182, 183, 242, 243, 244, 245, 248, 249
Porcar L. · 27, 150, 151
Prampolini G. · 10, 11, 22, 23, 24, 37, 38, 41, 43, 77, 114, 115
Puliafico M. · 54, 232, 238
Punzo F. · 25, 48, 140, 142

R

Ranieri G.A. · 12, 120
Reggiani L. · 8, 43, 221, 224
Ricci M. · 19, 32, 33, 34, 37, 178, 179, 181, 214, 263, 264
Ridi F. · 14, 35, 49, 54, 93, 94, 97, 98, 153, 155, 158, 195, 196, 208
Ristori S. · 14, 18, 19, 27, 28, 32, 35, 43, 44, 45, 50, 148, 149, 160
Rossi C. · 14, 19, 24, 25, 32, 33, 37, 43, 45, 46, 50, 56, 57, 62, 64, 65, 120, 121, 124, 125, 154, 155, 160, 161, 167, 175, 176, 178, 179, 180, 181, 209, 210, 211, 212, 213, 214, 257, 258, 259, 260, 263, 264, 267, 268
Rossi O. · 120, 121
Ruzzenenti F. · 12, 24, 54, 65, 170, 171

S

Salis A. · 8, 19, 20, 45, 48, 55, 71, 72, 73, 74, 164, 165, 174, 175, 225, 226
Salvi P. · 8, 9, 19, 33, 53, 55, 58, 69
Sanjust E. · 8, 20, 48, 104, 105, 225, 226

Sapuppo D. · 55, 162
Sartorio R. · 8, 9, 21, 45, 57, 110, 111, 112
Scarano S. · 103
Schmidt J. · 20, 106, 107
Schwarz F. · 19, 223
Setzu S. · 20, 71, 72
Sinicropi A. · 11, 12, 24, 25, 36, 40, 42, 50, 54, 55, 56, 79, 166, 167, 172, 173, 183, 247
Solinas V. · 8, 19, 20, 55, 225, 226
Spadaro S. · 228
Spampinato V. · 25, 55, 56, 57, 99, 101, 102, 162
Spinelli D. · 12, 36, 53, 56, 242, 244, 245
Stefan A. · 6, 7, 8, 19, 37, 43, 45, 56, 219, 221, 223, 224
Steri D. · 20, 48, 73, 74

T

Taddei M. · 24, 79, 183, 243
Talmon Y. · 20, 52, 106, 107
Tattini L. · 14, 27, 49, 56, 63, 207, 208
Toccafondi N. · 26, 186, 187, 188, 189
Tognazzi A. · 19, 32, 33, 37, 56, 57, 176, 178, 179, 180, 181, 209, 213, 214, 255, 256, 257, 258
Torrisi V. · 12, 13, 18, 19, 25, 26, 31, 54, 56, 57, 81, 82, 100, 101, 102, 138, 139, 163
Trabalzini L. · 11, 53, 116, 117
Trani F. · 10, 12, 22, 37, 41, 57, 77, 78, 131
Tuccitto N. · 12, 18, 19, 20, 25, 26, 31, 55, 56, 57, 82, 99, 100, 101, 102, 139, 162, 163, 239

U

Ugolini L. · 8, 56, 219

V

Venditti F. · 7, 13, 18, 25, 49, 184, 185, 200
Venturoli G. · 53, 118, 119, 130, 131
Vestri A. · 103
Villa M. · 8, 9, 19, 22, 33, 53, 55, 58, 59, 69, 241
Vitiello G. · 9, 21, 45, 58, 110, 111, 112

Z

Zangari G. · 8, 9, 19, 33, 53, 69
Zappalà G. · 55, 60, 99, 162
Zucca P. · 8, 20, 48, 104, 105