Chimica Fisica

FIS-KN-01 Colloidal nanocrystals: Synthesis, properties, assembly

L. Manna

Italian Institute of Technology, via Morego 30, 16163, Genova (Italy)

Fabrication Current efforts and success of nanoscale science and technology are related to the fabrication of functional materials and devices in which the individual units and their spatial arrangement are engineered down to the nanometer level. One promising way of achieving this goal is by assembling of colloidal inorganic nanocrystals as the novel building blocks of matter. This trend has been stimulated by significant advancement in the wet-chemical syntheses of robust and easily processable nanocrystals in a wide range of sizes and shapes. The increase in the degree of structural complexity of solution-grown nanostructures appears to be one of the directions towards which nanoscience will increasingly orient. Recently, several groups have indeed devised innovative syntheses of nanocrystals through which they have been able to group inorganic materials with different properties in the same particle. These approaches are paving the way to the development of nanosized objects able to perform multiple technological tasks.

The talk will highlight the recent advances in the synthesis of colloidal nanocrystals, with emphasis on the strategies developed at IIT (Genova) for the fabrication of colloidal nanocrystals, as well as on their properties and their assembly.

FIS-KN-02 Antibodies and SERS for Targeting and Imaging with Functionalized Gold Nanoparticles

Moreno Meneghetti,[a] Vincenzo Amendola,[a] Marina Gobbo,[a] Alessia Scarsi,[a] Lucio Litti,[a] Anita Boscaini,[b] Giulio Fracasso[b] and Marco Colombatti[b]

[a] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35100, Padova (Italy)
[b] Department of Pathology, Section of Immunology, University of Verona, Policlinico GB. Rossi, P.le La Scuro 10, 37100 Verova (Italy)
moreno.meneghetti@unipd.it

Gold nanoparticles are biocompatible nanostructures which are under scrutiny for applications in nanomendicine. We synthesized gold nanoparticles by a laser ablation methodology (LASIS) which does not need any stabilizing agent for the colloidal solutions [1]. The free surface of the nanoparticles, with diameters of about 20 nm, is easily functionalized with molecules for the surface enhanced Raman scattering (SERS) [2] and with antibodies.

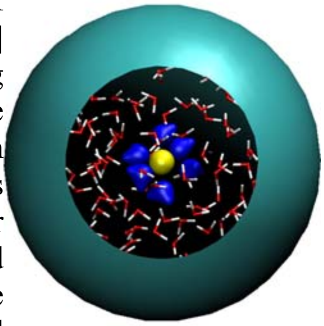
We obtained nanostructured materials with innovative antibodies for antigens like PSMA and PSCA which allow efficient targeting of prostate cancer cells. Strong SERS signals are registered for targeted cells among others which do not express the recognized antigens. In vivo experiments show that strong SERS signals are observed in cancer tissues. The results show that the gold nanomaterials we obtained are stable also in vivo and allow efficient targeting of prostate cancer cells. Preliminary results with doxorubicine loading the gold nanomaterials for drug delivery will be also reported.

[1] V. Amendola and M. Meneghetti J. Mater Chem. 17, **2007**, 4705; S. Salmaso, P. Caliceti, V. Amendola, M. Meneghetti, J. Pall Magnusson, G. Pasparakisc and C. Alexander. J. Mater Chem. 19, **2009**, 1608; V. Amendola and M. Meneghetti, J. Phys. Chem. C, 113, **2009**, 4277.
[2] V. Amendola, M. Meneghetti, S. Fiameni, S. Polizzi, G. Fracasso,
A. Boscaini and M. Colombatti, Analyt. Meth., DOI: 10.1039/c0ay00660b, **2011.**

FIS-KN-03 Time-dependent Modeling of Complex Systems in the Soft Condensed Matter

Giuseppe Brancato

Italian Institute of Technology, IIT@NEST
Center for Nanotechnology Innovation
Piazza San Silvestro 12, I-56127 Pisa. *E-mail: giuseppe.brancato@iit.it*



In this presentation, we report on recent developments of the General Liquid Optimized Boundary (GLOB) [1,2] model, an effective computational approach for simulating the time evolution of complex molecular systems in the soft condensed matter at different levels of theory, from purely quantum-mechanics to hybrid QM/MM methods and classical force fields. Moreover, we describe our progress in the modeling of static and time-resolved spectroscopic observables through some illustrative examples [3], ranging from ions in solution to optical and magnetic probes. In this context, a special focus will be put on the description, at molecular level, of the role of the dynamics in the modulation of different spectroscopic parameters.

[1] Brancato, G.; Rega, N.; Barone, V. J. Chem. Phys. **2008**, 128, 144501.

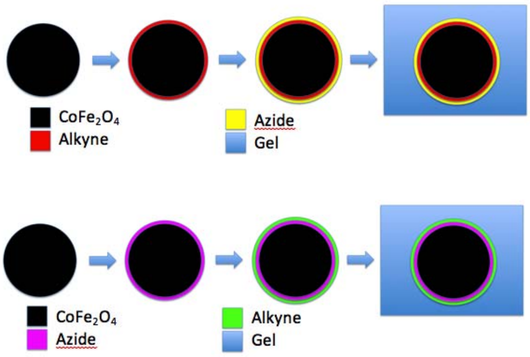
[2] Brancato, G.; Rega, N.; Barone, V. Chem. Phys. Lett. **2009**, 483, 177.

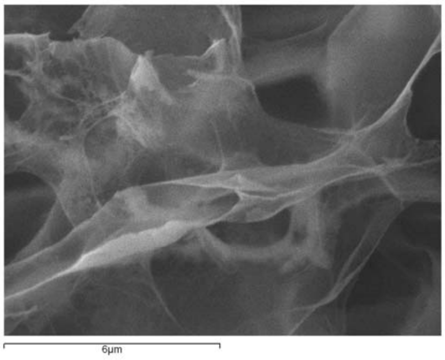
[3] Brancato, G.; Rega, N. *Computational spectroscopy by classical time-dependent approaches*, Chapter in *COMPUTATIONAL STRATEGIES FOR SPECTROSCOPY: From Small Molecules To Nano Systems*, V. Barone editor, Wiley and Sons, New York, ISBN: 978-0-470-47017-6.

FIS-OR-01 Magnetic Nanoparticles and click-chemistry: towards functional nanocomposite materials

Ilaria Meazzini, Massimo Bonini, Francesca Ridi, Piero Baglioni

CSGI & Dipartimento di Chimica "Ugo Schiff" dell'Università degli Studi di Firenze, Via della Lastruccia 13, 50019, Sesto F.no (FI), Italy
massimo.bonini@unifi.it





The preparation of nanocomposite materials through the assembly of nanosized building blocks has already been proven as an effective route for the preparation of functional materials.[1,2] In this contribution we describe a versatile approach for the embedding of inorganic nanoparticles within a gel matrix based on click-chemistry.

The nanoparticles, *i.e.* $CoFe_2O_4$ particles with size around 10 nm, are first synthesized via a modified Massart approach.[3] Their surface is then functionalized by reaction with an organic molecule including a carboxylic functionality. Functionalized nanoparticles are then reacted via click-chemistry (Huisgen 1,3-dipolar cycloaddiction between an alkyne and an azide group[4]) to make them polymerizable.

Surface functionalized nanoparticles were finally embedded within the an acrylamide-based hydrogel network through their radical co-polymerization with acrilamide and *N*,*N'*-methylenebisacrylamide.

These results represent an example of the bottom-up approach to the preparation of functional nanocomposites through the surface functionalization *via* Click Chemistry of magnetic nanoparticles.

[1] M. Bonini, S. Lenz, E. Falletta, F. Ridi, E. Carretti, E. Fratini, A. Wiedenmann, P. Baglioni, *Langmuir*, **2008**, *24*, 12644-12650.
[2] M. Bonini, S. Lenz, R. Giorgi, P. Baglioni, *Langmuir*, **2007**, *23*, 8681-8685.
[3] M. Bonini, A. Wiedenmann, P. Baglioni, *J. Phys. Chem. B*, **2004**, *108*, 14901-14906.
[4] R. Huisgen, *Proc. Chem. Soc.,* **1961**, 357-369.

FIS-OR-02 NIR-emitting mono- and bimodal PbS NC superlattices

<u>M. Corricelli</u>,[a,b] F. Enrichi,[c] D. Altamura,[d] L. De Caro,[d] C. Giannini,[d] A. Falqui,[e] A. Agostiano,[a,b] M. Striccoli,[a] M. L. Curri[a]

[a] Istituto IPCF-CNR c/o Dip. Chimica, Università di Bari; [b] Dip. Chimica, Università di Bari; [c] CIVEN, Marghera (VE); [d] Istituto IC-CNR, Bari; [e] Fondazione IIT, Genova; *lucia.curri@ba.ipcf.cnr.it*

Recently, increasing attention has been focussed on inorganic nanocrystal (NC) shape- and size-dependent properties, which are crucial for both fundamental studies and their high impact in many technologic fields[1].

Here, we report on the fabrication of superlattices of PbS NCs, characterized by a narrow monomodal size distribution (MSD) or a bimodal size distribution (BSD). In the case of PbS NCs with a MSD, the influence of fundamental parameters, such as NC concentration, dispersing solvent and substrate, on the superlattice formation, was studied.[2] PbS NCs with a BSD were successfully organized in different geometries, as a function of the size ratio of the two PbS NC families. In order to elucidate the spatial arrangement of the NCs and the crystalline structure of the assembly, the fabricated superlattices were investigated by means of structural techniques (small and wide angle XRD and TEM) and theoretical simulations of the XRD patterns.[3] The size-dependent absorption and emission spectroscopic properties of PbS NCs, were intensively investigated. The comparison between the emission features of the PbS NCs in solution and organized in thin film, suggest the occurrence of a FRET energy transfer between the close-packed NCs, only when geometric and energy constrains are fulfilled.

The hierarchical organization of nano-objects has a very high potential for the fabrication of functional "solids", materials in which collective properties (e.g. electromagnetic properties) mainly arise from the controlled interaction among building blocks, such as metamaterials.

This work has been partially supported by the 7th FP EU funded project METACHEM (Grant CP-FP 228762-2).

[1] J. J. Urban, D. V. Talapin, E. V. Shevchenko and C. B. Murray; *J. Am. Chem. Soc.,* 128, **2006**, 3248.

[2] M. Corricelli, D. Altamura, Li. De Caro, A. Guagliardi, A. Falqui, A. Genovese, A. Agostiano, C. Giannini, M. Striccoli and M. L. Curri; *CrystEngComm*, 13, **2011**, 3988.

[3] D. Altamura, M. Corricelli, L. De Caro, A. Guagliardi, A. Falqui, A. Genovese, A. Y. Nikulin, M. L. Curri, M. Striccoli, and C. Giannini; *Cryst. Growth Des.*, 10, **2010**, 3770.

FIS-OR-03 Electron and dielectric properties of TiO_2 nanotubes

Anna M. Ferrari

Dipartimento di Chimica IFM, Università di Torino and NIS -Nanostructured Interfaces and
Surfaces - Centre of Excellence, http://www.nis.unito.it, Via P. Giuria 7, 10125 Torino, Italy

Due to the spatial confinement , oxide nanosheets are characterized by peculiar chemical and physical properties. They grow on appropriate metal substrate or self assembly as nanotubes, nanorods or nanowires. In particular TiO_2 nanotubes have attracted a lot of attentions in the last decade because of their unique chemical and physical properties.[1] One of the most interesting applications is connected to the preparation of dye sensitized solar cells where the one dimensional structures of the tubes are expected to significantly improve the electron transport properties, whereas the high surface area optimize the number of sensitizers anchored to the oxide.[2] The performances of the device however are related to the size, length, thickness and structure of the titania tubes.

Although theoretical calculations can play a major role in providing information on the atomic scale, because of the size of the systems involved, only a handful of computational studies of TiO_2 nanotubes appeared in the literature. In this work TiO_2 nanotubes constructed from anatase TiO_2 layers were investigated with DFT methods and by employing the periodic CRYSTAL09 code.[3] Dependence of electronic and dielectric properties on size and morphology of the tubes has been investigated in the 20-60 Å range.[4]

---

[1] D.V. Bavykin, J.M. Friedrich, F.C. Walsh; Adv. Mater. 18 (2006) 2807

[2] P. Roy, D. Kim, K. Lee, E. Spiecker, P. Scmuki, Nanoscale 2 (2010) 45

[3] R. Dovesi, V. R. Saunders, R. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, and M. Llunell, CRYSTAL09 (CRYSTAL09 User's Manual. University of Torino, Torino, 2009).

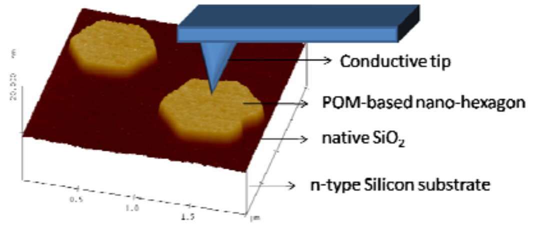
[4] D. Szieberth, A.M. Ferrari, Y. Noel, M. Ferrabone Nanoscale 2 (2010) 81

FIS-OR-04 Capacitive effects in silicon-supported polyoxometalate-based nanocrystals

Chiara Musumeci,[a] Mali Husby Rosnes,[b] Filippo Giannazzo,[c] Leroy Cronin[b,*] and Bruno Pignataro[d,*]

[a]Superlab-Consorzio Catania Ricerche, S.le Primosole 50, 95121 Catania, Italy. [b]Department of Chemistry, WestCHEM, University of Glasgow, Glasgow, G12 8QQ, United Kingdom, *Lee.Cronin@glasgow.ac.uk*
[c]CNR-IMM, Strada VIII, 5, Zona Industriale, 95121, Catania, Italy.
[d]Dipartimento di Chimica "S. Cannizzaro", Università di Palermo, V.le delle Scienze -90128 Palermo, Italy, *bruno.pignataro@unipa.it*

Polyoxometalates (POMs) are complex metal oxide molecules, which have attracted growing interest, due to their wide potential redox, photochemical and catalytic properties. The potentiality for these compounds to be applied in functional devices has shown the need of investigating their assembly and organization in the solid state and on solid substrates. On this respect, we recently showed the possibility to form at solid surfaces a large landscape of supramolecular architectures by employing derivatized POMs under both static and dynamic self-assembly conditions. [1,2] By using Langmuir-Blodgett, here we show that the symmetric C9-alkenes derivatized Mn-Anderson clusters give in combination with dioctadecyldimethylammonium (DMDOA) counter-ions well-defined 2D hexagonal nanostructures at silicon surfaces. Such an organization derives by a nucleation and growth process involving the hopping of DMDOA on top of C9-Mn-Anderson upon barrier compression. We report on the hexagonal nanostructures as effective nanodielectrics, their nanoscale capacitive properties having been measured by scanning capacitance microscopy. Noteworthy, the dielectric properties of these nanoscale structures can be modulated upon the applied bias to the scanning tip. These findings open fascinating perspectives that these novel supramolecular assembly may give in emerging scientific and technological fields including their application as smart materials in plastic and/or hybrid (organic-inorganic) electronics.



[1] M.H. Rosnes, C. Musumeci, C.P. Pradeep, J.S. Mathieson, D.L. Long, B. Pignataro, R. Cogdell, L. Cronin, *J. Am. Chem. Soc. (Communication)*, 132 **2010** 15490.
[2] C. Musumeci, A. Luzio, C.P. Pradeep, H.N. Miras, M.H. Rosnes, Y.F. Song, D.L. Long, L. Cronin, B. Pignataro, *J. Phys. Chem. C 115* **2011** 4446.

FIS-OR-05 Nanoparticles for Cultural Heritage Conservation: calcium and barium hydroxide nanoparticles for wall paintings consolidation

Rodorico Giorgi[a], **Moira Ambrosi** [a], **Nicola Toccafondi**[a], **Piero Baglioni**[a]

[a] CSGI and Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy; mail: *giorgi@csgi.unifi.it*

Nanotechnology provides new materials with the ideal characteristics for the consolidation and protection of wall paintings. In particular, calcium and barium hydroxide nanoparticles offer a versatile and highly efficient toolset to face the main degradation processes altering wall paintings. Clear example of the efficacy and potentiality of nanotechnology is represented by the rescue, in situ, of Maya wall paintings in the archaeological area in Calakmul (Mexico).

The paint layer is at the interface between the wall and the surrounding environment and it is strongly susceptible to degradation due to the mechanical stresses following salt crystallization.

The effects of this process are usually strongly amplified if any protective coating, possibly applied in previous restoration treatments, is present. Polymers, mainly acrylic and vynil resins, have been widely used to consolidate wall paintings and to confer to the painted layer protection and hydrorepellency [1]. The use of inorganic materials, which are compatible with wall paintings, minimizes the aforementioned risks and prevents from unexpected side effects. Inorganic consolidants are highly chemically stable and preserve the wall painting porosity ensuring long-lasting consolidation effects.

Lime ensures the highest physico-chemical compatibility with the work of art and it should be preferred when degradation results from loss of calcium carbonate [2,3]. The presence of sulfate salts as a contaminant can inhibit the consolidation effects. Innovative formulations based on calcium and barium hydroxide nanoparticles overcome these limitations thank to their synergistic action, which confers to the paintings a stable consolidation.

This contribution reports on the preparation of barium hydroxide nanoparticles, and the formulation of nonaqueous dispersions for their application on wall paintings.

Note: This work has been partly supported by the project *TemArt*; *Programma Operativo Regionale - Regione Toscana*, co-financed by *Fondo Europeo di Sviluppo Regionale* (*POR CreO FESR 2007-2013*).

[1] R. Giorgi, M. Baglioni, D. Berti, P. Baglioni, *Accounts of Chemical Research*, **2010**, 43, 695–704.

[2] M. Ambrosi, L. Dei, R. Giorgi, C. Neto, P. Baglioni, *Langmuir*, **2001***, 17,* 4251–4255.

[3] Baglioni, P., Giorgi, R., *Soft Matter*, **2006**, 2, 293-303.

FIS-OR-06 Development and Characterization of Nano-Fluids for the Cleaning of Wall Paintings

Michele Baglioni[a] , Debora Berti[a], Rodorico Giorgi[a], Piero Baglioni[a]

[a] CSGI and Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy; mail: *baglioni_m@csgi.unifi.it*

Synthetic polymers have been often used in conservation of wall paintings. Polymers are highly harmful for the original material of these artworks [1]. We have proposed the use of alternative methodologies for conservation and formulated innovative cleaning nanostructured systems to remove previously applied polymer films and grime from painted surfaces [2, 3]. In particular, a novel "micellar system", which was named "EAPC", composed of water, SDS, 1-pentanol, propylene carbonate, and ethyl acetate has been recently developed [4, 5]. EAPC was found to be particularly effective in polymer removal. The nanostructure of this system was thoroughly investigate by means of several scattering techniques (QELS, SAXS and SANS) and compared to that one of a xylene-in-water microemulsion. The interaction process that takes place between the nanostructured fluids and a different detergency mechanism from a classical was found. Micellar aggregates act as solvent nano-containers and interact with the polymer film leading to its swelling and the detachment from the surface. After the removal process, the micelles become smaller due to depletion of the organic solvents. These findings represent an important step in opening up new perspectives in the design and formulation of new cleaning systems specifically tailored for intervention on particular conservation issues.

Note: This work has been partly supported by the project *TemArt*; *Programma Operativo Regionale - Regione Toscana*, co-financed by *Fondo Europeo di Sviluppo Regionale* (*POR CreO FESR 2007-2013*).

[1] E. Carretti, L. Dei, *Progress in Organic Coatings*, **2004**, 49, 282-289.
[2] E. Carretti, L. Dei, P. Baglioni, *Langmuir*, **2003**, 19, pp. 7867-7872.
[3] E. Carretti, R. Giorgi, D. Berti, P. Baglioni, *Langmuir*, **2007**, 23, 6396-6403.
[4] R. Giorgi, M. Baglioni, D. Berti, P. Baglioni, *Accounts of Chemical Research*, **2010**, 43, 6, 695-704.
[5] M. Baglioni, D. Rengstl, D. Berti, M. Bonini, R. Giorgi, P. Baglioni, *Nanoscale*, **2010**, 2, 9, 1723-1732.

FIS-OR-07 Hydrophobic CdSe@ZnS nanocrystals loaded liposomes and their interactions with RC membrane protein

V. De Leo,[a] F. Milano,[b] G. Graziano,[a] R. Comparelli,[b] A. Falqui,[c] M. Striccoli,[b] and L. Catucci[a,b]

[a]Dipartimento di Chimica dell'Università di Bari, Via Orabona 4, 70126 Bari, Italy
[b]IPCF-CNR, Via Orabona 4, 70126 Bari, Italy
[c]Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
f.milano@ba.ipcf.cnr.it

A versatile and rapid method to encapsulate CdSe@ZnS nanocrystals (NCs) in the lipid bilayer of liposomes has been developed. NC surface has been suitably engineered to improve the hydrophobic interaction between NC capping ligand and the lipid alkyl chain. NC-loaded liposomes of various composition were realized by the Micelles to Vesicles Transition (MVT) method [1]. Several NC-loaded liposomes were prepared as a function of NC capping layer, NC concentration, detergent and lipid mixture composition. The properties and the stability of the system have been characterized from the optical (UV–Vis-NIR and emission spectroscopy) and morphological (RT-TEM, Cryo-TEM and DLS analysis) point of view, in order to investigate the optimal experimental conditions for NC-liposome formation. The experimental conditions were tailored to allow the construction of a vesicular hybrid system containing both CdSe@ZnS NCs and reaction centre (RC) protein of *Rhodobacter sphaeroides* [2]. Absorption spectra suggest that the protein scaffold of RC remained structurally intact in the presence of NCs even after one week. Charge recombination kinetics of RC have confirmed that even at the functional level the protein was not damaged by the NCs.

The obtained results are promising and the proposed method could be extended to any type of hydrophobic nanoparticles (metallic, semiconductor, magnetic), lipids and membrane proteins. On the one hand this technique could extend the study of interactions between nanoparticles and proteins to the important class of integral membrane proteins, on the other hand it can be employed to easily produce a non-specific labeling in reconstituted systems and in natural cell membranes using fusogenic techniques.

[1] P. Walde, in: H.S. Nalwa (Ed.) *Encyclopedia of nanoscience and nanotechnology*, American Scientific Publishers, **2003**, 1.
[2] A. Verméglio, P. Joliot, *Trends in Microbiology, 7*, **1999**, 435.

FIS-OR-08 Lattice measurements in metallic nanoparticles by means of HRTEM images.

Patrizia Canton[a], **Andrea Pietropolli Charmet**[a]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Universita' Ca' Foscari Venezia, Via Torino 155/b 30170 Venezia-Mestre e Calle Larga S.Marta 2137, Venezia
e-mail:cantonpa@unive.it

In the frame of structural characterization of nanostructures by means of HRTEM (High Resolution Transmission Electron Microscopy) technique, several authors have highlighted the importance of quantifying the errors related to the measurements of lattice spacing. This point is particularly crucial in the case of smaller nanoparticles (<10 nm) in which the effect due to the high surface/volume ratio can give misleading results in the determination of interatomic distances. In this context the method developed by de Ruijter [1] appears a promising approach to achieve the requested sub-pixel resolution in order to quantify properly the atomic distances. To this purpose we implemented a software program to be employed in the study of lattice parameters of nanometer structures. Simulated images of thermodynamic-stable morphology of metal nanoparticles were used as test cases to check for the surface strain effect [2] in the determination of atomic distances. Some experimental HRTEM images of nanoparticles were then analyzed and the lattice parameters consequently determined and compared with those tabulated for the bulk structures (Figure 1).

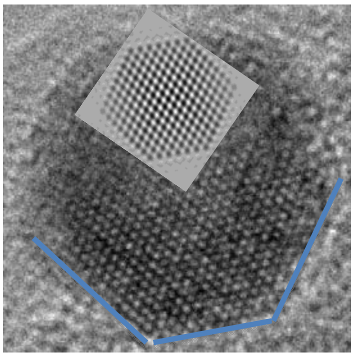


Figure 1: Image simulation of Au cubooctahedral in [101] Zone Axis and experimental HRTEM image of Au nanoparticle.

[1] W. J. de Ruijter , *J. of Computer-Assisted Microscopy*, Vol. 6, No. 4, **1994**, 195-212.
[2] S. –C.Y. Tsen, P. A. Crozier, J. Liu, *Ultramicroscopy*, Vol. 98, **2003**, 63-72.

FIS-OR-09 Role of base-pairing in the synthesis of nucleolipids obtained through alkylation of Cytidine and Guanosine monophosphates by n-dodecyl-epoxide.

R. Angelico[a], **I. Losito**[b,c], **B. Introna**[b], **F. Cuomo**[a], **A. Ceglie**[a], **F. Palmisano**[b,c]
[a]**CSGI** c/o Dept.Food Technology, UNIMOL, Via De Sanctis, 86100, Campobasso, Italy
[b]Dipartimento di Chimica, UNIBA "Aldo Moro", Via E. Orabona 4, 70126 Bari, Italia
[c]Centro Interdipartimentale **SMART**, UNIBA "Aldo Moro", Via E. Orabona 4,70126 Bari, Italia
E-mail: angelico@unimol.it

We recently demonstrated that aqueous colloidal solutions provided suitable environments to investigate the role played by the molecular interaction between complementary nucleobases Adenine-Uracil (A-U) in the synthesis of the respective amphiphilic nucleolipids [1,2,3]. Several types of ribonucleotide mono-phosphates XMP (X=A, U) were hydrophobically modified through a S_N2-type reaction by the water insoluble n-Dodecyl-Epoxide (DE) as alkylating agent, which was dispersed at r.t. in aqueous micellar solutions formulated with the cationic surfactant Cetyl-Trimethyl-Ammonium-Bromide (CTAB). The presence of a charged interface acted as a catalytic locus where both reactants, DE and XMP, were able to meet and react. In the present communication the reaction between DE and CMP/GMP [i.e. nucleotides bearing two further complementary bases (C,G)], present as single reactants or as equimolar mixture, is discussed. In particular, HPLC-ESI-MS using a 3D-ion trap spectrometer as the detector, operated in negative polarity, has been used for a MS and MS/MS characterization of the two nucleotide alkylated by-products. The reaction evolution was monitored at different times and the signals related to the m/z ratios of $[M-H]^-$ ions for nucleolipids of CMP and GMP (i.e. structures derivatized by hydroxyl-dodecyl moieties) were detected in the LC-ESI-MS traces after 40 days. In particular, mono and bi-alkylated species could be observed for both nucleotides, whereas tri-alkylated derivatives were also detected in the case of CMP. Similarly to nucleolipids obtained from AMP and UMP [2], the first alkylation involved either a phosphate OH or one of the nucleophilic sites on the Cytosine or Guanine nucleobases (primary NH_2, OH arising from keto-enolic tautomerization); however, mono-alkylation on the nucleobase was favored in the case of GMP.

Alkylation on both types of sites was obtained for bi-alkylated products, whereas ribose OH groups appeared to be also involved when tri-alkylated CMP were considered. Quantitative estimates, as obtained from extracted ion chromatograms, provided further interesting information, first on single nucleotide systems. Indeed, bi-alkylated species were found to be predominant in the case of GMP, whereas a comparable incidence of tri-alkylated species was observed for CMP. Moreover, the peak areas for residual XMP suggested that alkylation proceeds faster in the case of GMP. The described features were confirmed when the mixed-nucleotide system C+G was investigated, yet a much faster alkylation could be hypothesized for both nucleotides in this case. In fact, no significant signal was detected after 40 days of reaction for residual unreacted CMP and even that related to GMP was quite weak. Moreover, mono-alkylated species were found to be significantly less abundant in mixed systems, compared to single nucleotide ones. Time-resolved zeta-(ζ)-potential measurements performed on the aqueous aggregate dispersions indirectly confirmed the enhanced production of the fraction of the correspondent bi-chained XMP nucleolipids for the system C+G, compared to the germane samples C and G. An involvement of C-G base-pairing might be invoked to explain these original experimental features in terms of molecular recognition effect.

[1] R. Angelico, A. Ceglie, F. Cuomo, *Colloids Surf. B: Biointerfaces*, *70*, **2009**, 68.
[2] I. Losito, R. Angelico, A. Ceglie, S. Diomede, F. Palmisano, *J. Mass Spectr.*, *44*, **2009**, 1053.
[3] R. Angelico, L. Ambrosone, A. Ceglie, I. Losito, G. De Zio, F. Palmisano, *Phys. Chem. Chem. Phys.*, *12*, **2010**, 7977.

FIS-OR-10 Self-Assembly of helical peptide foldamers

M. Caruso[a], **E. Gatto**[a], **E. Placidi**[b], **A. Palleschi**[a], **G.Bocchinfuso**[a], **S. Raniolo**[a], **F. Formaggio**[c], **C. Toniolo**[c] **and M. Venanzi**[a]

[a] Dip.Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, via della Ricerca Scientifica, 00133, Roma;
[b] Dip. Fisica and CNR, Università di Roma Tor Vergata, via della Ricerca Scientifica, 00133, Roma;
[c] ICB, Padova Unit, CNR, Dip.Chimica, Università di Padova, Via Marzolo 1.
mario.caruso@uniroma2.it

Many neurodegenerative diseases have been associated with the early stages of amyloid aggregation, triggered by the formation of small β-sheet aggregates that grow to micrometric fibrils through a slow self-assembly process. Experimental evidences indicate that peptide aggregation is mainly driven by hydrophobic interactions, with aromatic residues playing a specific role.

We carried out optical spectroscopy, microscopy with nanometric resolution and computational studies on aggregates formed by Z-Aib$_n$N oligopeptides, with n= 6, 12 and 15. Aib (α-aminoisobutiric acid) is a conformationally-constrained amino acid characterized by the gem-dimethyl substitution on the C^{α} atom. From structural studies in solution and in the crystal state, homo-Aib polypeptides have been shown to populate 3_{10}- or α-helical structures depending on the length of the peptide chain. A naphthyl (N) chromophore was inserted at the C-terminus of the peptide chain to study the influence of aromatic groups on the aggregation properties of the peptides investigated by applying optical spectroscopy techniques. UV-Vis absorption and fluorescence experiments revealed the formation of J- and H-aggregates in water/methanol solutions only for Aib$_{12}$N and Aib$_{15}$N.

Atomic Force Microscopy (AFM) has been employed to analyze the morphology of the aggregates and to establish the mechanical stress resistance of peptide fibrils. To obtain the Young's modulus we used force spectroscopy measurements on for fibrils and the values, 11 ± 1 MPa, 6.7 ± 0.6 MPa, 6.6 ± 0.6 MPa and 15 ± 1 MPa, confirms that a low packing it's a general feature of amyloidal fibrils. The observed variation in the Young's modulus indicates that fibrils produced under identical conditions might exhibit different mechanical properties while the values along the single fibril doesn't vary significantly; same internal packing environments indicate structural homogeneity along the fibril.

Molecular dynamics simulations (MD) revealed the presence of different aggregated species, the morphology of which is determined by the length of the peptide chain and the specific arrangement of aromatic groups.

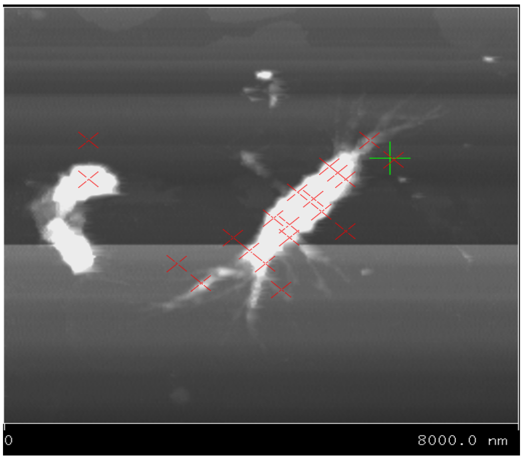


Figura 1 One of the fibrils that were used in force spectroscopy experiments

FIS-OR-11 Peptide-mediated confinement of liposomes in nanopores

G.M.L. Messina[1], R. Lettieri[2], M. Venanzi[2], F.Formaggio[3], C.Toniolo[3] and G.Marletta[1]

[1]Laboratory for Molecular Surface and Nanotechnology (LAMSUN) – Dept. of Chemical Sciences – University of Catania and CSGI – Catania - Italy
[2] Dept. of Chemical Sciences and Technologies- University of Rome Tor Vergata – Rome - Italy
[3] Dept. of Chemistry – University of Padova – Padova – Italy
gmarletta@unict.it

In view of the relevance of nanostructured surfaces for biomedical applications, including sensing, spatially resolved surface-cell interactions, drug delivery, etc.., the idea of confining biofunctional compounds in nanosized structures is gaining more and more interest. Accordingly, in this communication we present a versatile approach to nanostructurate polymeric films, in order to achieve the selective confinement of a multipurpose biological platform, consisting in suitable liposome formulation, driven by an antibacterial peptide anchored within the surface nanostructures.

In particular, in this contribution we demonstrate the use of monodisperse inorganic nanospheres, forming an ordered colloidal crystal on gold surfaces, as a templating system to nanostructurate a poly(methylmethacrylate) (PMMA) ultra-thin film (thickness <30 nm). The nanoparticle array embedded within the PMMA film is then selectively removed giving rise to the formation of hybrid nanopore arrays, having polymeric walls and gold bottom.

Trichogin GA IV, an antimicrobial peptide functionalized at the N-terminus by a thiol-group, was shown to be selectively chemisorbed within the obtained nanopores, due to the interaction of its thiol termination with the nanopore-paving gold . The Trichogin GA IV strong affinity for the liposome structures is then exploited to drive the selective confinement of phospholipid bilayers within the functionalized nanopores. It is found that liposomes are efficiently included within the trichogin-functionalised pores, and that only the liposomes in direct contact with trichogin remain firmly attached within the pores.

The formation of a peptide self-assembled monolayer covalently linked to the gold surface inside the pores, as well as the immobilization of liposome bilayers was demonstrated by using cyclic voltammetry (CV), Atomic Force Microscopy (AFM), Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) and X-ray Photoelectron Spectroscopy (XPS), obtaining information on the peptide/liposome interaction as well as on the best suited conditions of liposome immobilization.

FIS-OR-12 Characterization of vesicles formed by lipopolysaccharides: from the molecular structure to the aggregate architecture

E. Vaselli[1], **G.D'Errico**[1], **A. Silipo**[2], **A. Molinaro**[2], **R. Lanzetta**[2], **A. Radulescu**[3], **L. Paduano**[1], **G. Mangiapia**[1]

[1] CSGI and Department of Chemistry – University of Naples "Federico II"
[2] Department of Organic Chemistry – University of Naples "Federico II"
[3] Jülich Centre for Neutron Science, Lichtenbergstrasse 1, D-85747 Garching bei München (Germany)
E-mail: mangiapia.gaetano@alice.it

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. [1] 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. Recent studies have revealed that presumably the physical characteristics of these molecules are correlated to their biological activity. [2-3] Here we present a structural study on the architecture and the conformation assumed by LPSs in the lipid membrane. Particularly, we try to connect their self-aggregation behavior to the molecular structure. The investigation has been performed using an experimental strategy which has been proved to be extremely informative on vesicle aqueous suspension and combines dynamic light scattering (DLS) to estimate vesicle dimension, small angle neutron scattering (SANS) to analyze the aggregate morphology and to estimate the thickness of the lipid bilayer and electron paramagnetic resonance (EPR) to investigate the dynamics of the lipid hydrophobic tail in the bilayer.

References

[1] A. Silipo, C. De Castro, R. Lanzetta, M. Parrilli, and A. Molinaro, Lipopolysaccharides *in Prokaryotic Cell Wall Compounds; Structure and Biochemistry*, ed. H. König, H. Claus and A. Varma, Springer, Heidelberg, 2010.

[2] G. D'Errico, A. Silipo, G. Mangiapia, A. Molinaro, L. Paduano, and R. Lanzetta, *PCCP*, 11, **2009,** 2314

[3] G. D'Errico, A. Silipo, G. Mangiapia, G. Vitiello, A. Radulescu, A. Molinaro, R. Lanzetta, and L. Paduano, *PCCP*, 12, **2010,** 13574

FIS-OR-13 On the common role played by the pre-TM domain of different viral fusion glycoproteins in the infective process.

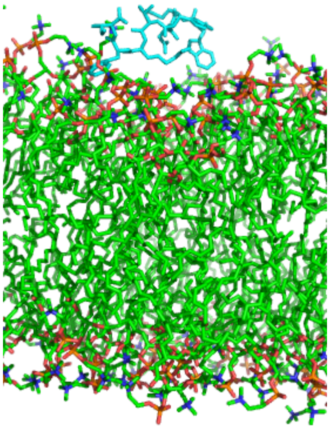
Gerardino D'Errico,[a,b] **Giuseppe Vitiello,**[a,b] **Elena Busi,**[b,c] **Anna M. D'Ursi,**[d] **Stefania Galdiero,**[e,f] **Antonello Merlino,**[a,f] **Delia Picone,**[a] **Luigi Paduano**[a,b]

[a] Dipartimento di Chimica "Paolo Corradini" dell'Università di Napoli "Federico II", Monte Sant'Angelo, 80126, Napoli, Italy
[b] CSGI, Consorzio interuniv. per lo sviluppo dei Sistemi a Grande Interfase
[c] Dipartimento di Chimica dell'Università di Siena, Italy
[d] Dipartimento di Scienze Farmaceutiche dell'Università di Salerno, Fisciano, Italy
[e] Dip. di Scienze Biologiche dell'Università di Napoli "Federico II", Italy
[f] Istituto di Biostrutture e bioimmagini, CNR, Napoli, Italy
gerardino.derrico@unina.it

Enveloped viruses require fusion between the viral envelope and the target membrane for entry into the cell. This process is controlled by one or more viral fusion glycoproteins that undergo conformational changes favouring the necessary micro- and mesoscopic lipid re-arrangements. Several membranotropic regions of the fusion proteins cooperate, according to a concerted mechanism, to accomplish the membranes fusion.

We investigated the interaction between peptides deriving from the pre-transmembrane (pre-TM) domain of fusion proteins of different viruses (*i.e.*, HIV, FIV [1], herpes simplex [2] and hepatitis C [3] viruses) and biomimetic lipid bilayers. This comparative study combines experimental results from EPR, Neutron Reflectivity, CD, Fluorescence Spectroscopy and MD simulations.

Despite the little homology between these peptides, the results show that all of them adsorb on the membrane surface with very limited penetration. Lipid packing perturbation due to this interaction propagates along the acyl chains. This originates a marked asymmetry among the bilayer leaflets, definitely favouring a local curvature change. Thus, we suggest that the pre-TM domain role in the viral infection pathway is the destabilization of the target cell membrane, which allows its fusion with the viral envelope.



[1] G. D'Errico, G. Vitiello, A. M. D'Ursi and D. Marsh *Eur. Biophys. J. 38*, **2009**, 873.
[2] S. Galdiero, A. Falanga, G. Vitiello, M. Vitiello, C. Pedone, G. D'Errico, M. Galdiero Biochim. *Biophys. Acta Biomembranes 1798*, **2010**, 579.
[3] R. Spadaccini, G. D'Errico, V. D'Alessio, E. Notomista, A. Bianchi, M. Merola, D. Picone Biochim. *Biophys. Acta Biomembranes 1798*, **2010**, 344.

FIS-OR-14 On the origin of infrared spectral changes upon protein folding/unfolding

I. Daidone [a], **L. Polzi-Zanetti** [b], **M. Aschi** [a] **and A. Amadei** [c]

[a] Dipartimento di Chimica Ingegneria Chimica e Materiali, University of L'Aquila, via Vetoio (Coppito 1), 67010 L'Aquila, Italy

[b] Dipartimento di Chimica, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185 Rome, Italy

[c] Dipartimento di Scienze e Tecnologie Chimiche, University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133 Rome, Italy

E-mail: daidone@caspur.it

While the amide I absorption pattern of folded structural elements is rather well understood, the physical origin of the spectroscopic behaviours of unfolded states is much less understood, despite differences in the amide I bands of folded and unfolded states having become a crucial spectral feature to follow protein and peptide folding kinetics in time-resolved and temperature dependent IR spectroscopies. Here, we study by means of a theoretical-computational method, the Perturbed Matrix Method (PMM) [1-3], the IR spectra in the amide I region of two β-hairpin peptides. The main feature of the method is that the IR behavior can be accurately reproduced not only for folded states but also for the very heterogeneous unfolded states, whose IR spectrum is commonly difficult to be computed due to their high conformational flexibility. The computed spectra result to be in good agreement with the experimental ones, thus providing an explanation of the physical origin underlying the differences of the unfolded- and folded-state spectra.

[1] I. Daidone, M. Aschi, L. Zanetti-Polzi, A. Di Nola and A. Amadei. *Chem. Phys. Lett.* 2010, 488:213-218.
[2] A. Amadei, I. Daidone, A. Di Nola and M. Aschi. *Curr. Opin. Struct. Biol.* 2010, 20:155-161.
[3] A. Amadei, I. Daidone, L. Zanetti-Polzi and M. Aschi. *Theor. Chem. Acc.* 2011, 129:31-43.

FIS-OR-15 Bio-membranes integrated into organic thin-film transistors for biophysical studies

D. Angione[1], S. Cotrone[1], M. Magliulo[1], A. Mallardi[2], G. Scamarcio[3], L. Torsi[1]*, G. Palazzo[1]*

[1] Dip. Chimica, Università di Bari, Via Orabona, 4, I-70126 Bari, Italy.
[2] Ist. per i Processi Chimico-Fisici, CNR, Via Orabona, 4, I-70126 Bari, Italy.
[3] Dip. Fisica - Università degli Studi di Bari, Via Orabona, 4, I-70126 Bari, Italy.

* *corresponding authors e-mail: palazzo@chimica.uniba.it*; *torsi@chimica.uniba.it*

Membrane and proteins integration into an organic thin-film transistor (OTFT) structure will be presented. The proposed architecture allows the direct interfacing between membranes and an OTFT channel retaining both the electronic properties and the biological functionality. Though also enzymes and antibodies have been successfully integrated, the present contribution will focus on the response of phospholipid bilayer (also embedding membrane proteins) integrated into OTFTs.

The response of these OTFT depends on the properties of the integrated biological membrane and thus opens a new way of probing the events involving membranes. The biological membranes are deeply involved in crucial cellular functions such as adhesion, trafficking, recognition, and signalling. Probably the most familiar form of cellular signaling is the synaptic transmission, the central event of the whole nerve transmission. Anaesthetics are drugs and chemicals that strongly hinder the synaptic transmission. We have found that lipid bilayer integrating OTFTs tested against volatile-anesthetics (concentration 1-5%) reveal drug-induced membrane changes [1, 2]. The responses to anesthetics obtained with OTFTs integrating either lipid bilayer or membrane proteins will be discussed and it will be shown how the results of the present study challenges the anesthetic mechanisms model relying on the so far provided evidence that clinically relevant doses (2.4 %) do not alter lipid bilayers overall-structure, significantly.

These examples show how the proposed bio-electronic platform, besides resulting in extremely performing biosensors, can open to insights into phenomena, such as cell-signaling and recognition, involving weak membrane interfacial modifications.

[1] L. Torsi, et al. European Patent. EP 10425146.7 Submitted May 2010.
[2] M.D. Angione et al. submitted.

FIS-OR-16 NANOCLAYS AND BIOPOLYMERS IN AQUEOUS SOLUTION AND IN SOLID STATE. INTERACTIONS AND STRUCTURE

G. Cavallaro, R. De Lisi, G. Lazzara, S. Milioto

Department of Chemistry "S. Cannizzaro", University of Palermo, Viale delle Scienze Pad. 17, Parco D'Orleans II, 90128 Palermo, Italy, *g.lazzara@unipa.it*

Over the last years several biopolymers have been investigated because their combination with other compounds may form new composite materials with potential technological applications environmental friendly and available at low cost. In this work, we studied modified cellulose and pectins as biopolymer and nanoclays with different morphologies to prepare nanocomposites materials.

The two clays are: halloysite nanotubes, characterized by a cylindrical-like shape and laponite RD with a disk-like shape. Their affinity towards biopolymeric matrices was studied in both the aqueous and the solid state from the physicochemical view-point in dependence of the composition of both the polymer and the filler.

The nanoclay-biopolymer interactions in water were evidenced by calorimetry (ITC, DSC) and light scattering. Efforts have been devoted in modelling the enthalpy data providing the key thermodynamic properties.

The nanocomposites (prepared by means of the casting method) were imaged by SEM and the different morphologies were correlated to the thermal degradation behaviour, optical transparency, wettability, mechanical properties and dielectric response.

FIS-OR-17 Towards a “surface science model for biology”: glycine adsorption on nanohydroxyapatite with well defined surfaces

Albert Rimola,[a,b] Yuriy Sakhno,[a] Marco Lelli,[c] Salvatore Coluccia,[a] Piero Ugliengo,[a] Gianmario Martra[a]

[a]Dipartimento di Chimica IFM & NIS Center of Excellence, Università di Torino, Via P. Giuria 7, 10125, Torino, Italy.
[b]Department de Química, Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain.
[c]Dipartimento di Chimica “G. Ciamician”, Università di Bologna, Via Selmi 2, 40126, Bologna, Italy
gianmario.martra@unito.it

Hydroxyapatite (HA), [$Ca_{10}(PO_4)_6(OH)_2$], the natural major inorganic constituent of bone and teeth in the form of nano-crystals, is usually a system of choice to study protein/biocompatible-surface interactions. The study of these interactions is crucial not only for the development of new biomaterials and to understand biomineralization processes but also for several technological and biomedical applications such as biodevices and drug delivery systems. Nonetheless, despite the great efforts in investigating protein/HA systems, atomistic information on the actual contact occurring at the interface is rather scarce. Suitable to this target is the adoption of a “surface science model” approach, based on the interplay among the preparation of materials with well defined surface features, spectroscopic and accurate quantum mechanical techniques. This approach has been very fruitful to obtain a deep knowledge on surface molecular events relevant for heterogeneous catalysis, hence successfully developing a well-established “surface science model for catalysis”. In that respect, it is worth pointing out that for the model to be successful, extended non-defective crystalline faces grown out of a single crystal are usually employed, together with ultra high vacuum conditions. At variance with this approach, here we worked at standard conditions and focused on the possibility to employ nanometric HA particles with well defined surfaces, because in bone tissues, HA is present as nanoparticles embedded in a collagen matrix, to form a highly organized composite material and not as a bulk extended crystal.

These HA nanoparticles were used to investigate the adsorption of non-ionic HOOC-CH_2-NH_2 glycine (Gly) vapours by means of IR measurements. The adoption of a single aminoacid, as the basic molecular brick of proteins, has allowed to supplement the experimental measurements with modelling techniques (Figure 1) based on first principle quantum mechanical methods which have been successfully adopted in the past by some of us. Details and relevant literature are in ref [1].

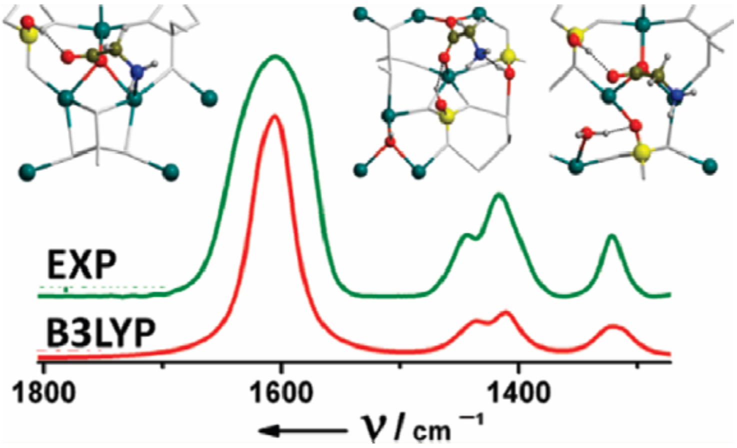


Figure 1.

[1] A. Rimola, Yu. Sakhno, L. Bertinetti, M. Lelli, G. Martra, and P. Ugliengo, *J. Phys. Chem. Lett.*, *2*, **2011**, 1390.

FIS-OR-18 Playing with Peptides: How to Build Supramolecular Peptide Nanostructures by Exploiting Aromatic and Helix-Helix Macrodipole Interactions

E. Gatto[a], A. Porchetta[a], M. Caruso[a], F. Casiero[a], F. Formaggio[b], C. Toniolo[b], M. Scarselli[c], M. De Crescenzi[c], M. Venanzi[a]

[a]Department of Chemical Sciences and Technologies, University of Rome “Tor Vergata”, 00133 Rome, Italy; [b]ICB, Padova Unit, CNR, Department of Chemistry, University of Padova, 35131 Padova, Italy; [c]Department of Physics, University of Rome “Tor Vergata”, 00133 Rome, Italy

emanuela.gatto@uniroma2.it

Biomolecules have been extensively investigated as possible components of nanoscaled electronic circuits. In particular, hybrid materials obtained by functionalizing metals with biomolecules have been recently synthesized, paving the way for the fast-growing field of bionanoelectronics.

In this work mono- and bi-component peptide-based self-assembled monolayers (SAMs) have been immobilized on gold surfaces and studied by electrochemical and spectroscopic techniques [1]. The peptides investigated comprised almost exclusively *Cα*-tetrasubstituted α-amino acids. These non-coded residues, because of their unique conformational properties, forced the peptide backbone to attain helical conformations, which promote the formation of stable SAMs on gold surfaces.

Blocking experiments performed in ferricyanide solution gave basic information on the stability and packing density of the peptide layers on the electro active surface, while fluorescence experiments performed by using spatially sensitive fluorescent probes, gave information about the possible formation, in the bicomponent SAMs, of raft domains, i.e. segregated single-component regions.

The photocurrent generation properties of these mono- and bi-component peptide-based SAMs were studied by electrochemical and spectroscopic techniques. In fact, all the SAMs investigated were composed of peptides derivatized with chromophores strongly absorbing in the UV region to enhance the efficiency of the photocurrent generation.

The composition of the bi-component SAMs on the surface have been analyzed by a combination of electrochemical and spectroscopic techniques. Interestingly, the surface composition is quite different from the solution stoichiometry used for SAM preparation.

[1]. Emanuela Gatto, Mario Caruso, Alessandro Porchetta, Claudio Toniolo, Fernando Formaggio, Marco Crisma and Mariano Venanzi, *Modulating photocurrent generation through bicomponent peptide monolayers on gold surfaces: antenna and junction effects,* J. Peptide Science, 2011, 17, 124-131.

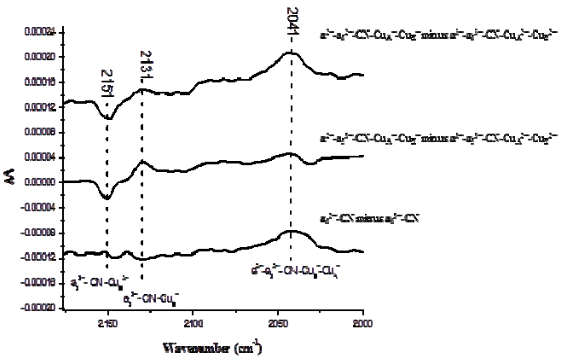
FIS-OR-19 Resolution of the Redox IR signatures of the Metal Centers of Bovine Cytochrome c Oxidase by Controlled Electrochemistry of Specific Ligated Forms

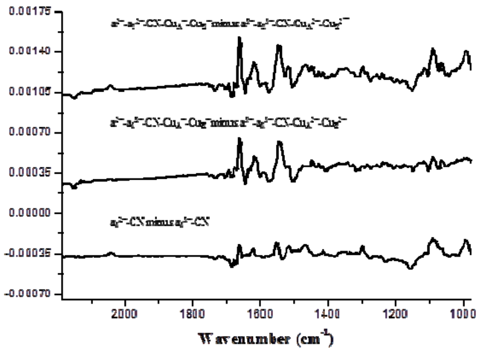
[a-b] **S. Bettini**; [b]**A. Maréchal**; [a]**L. Valli**; [a]**P. R. Rich.**

[a]Glynn Laboratory of Bioenergetics, Institue of Structural and Molecular Biology, University College London, Gower Street, London, U.K. WC1E 6BT;
[b]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, 73100 Lecce, Italy.
simonabettini@unisalento.it

Attenuated Total Reflection (ATR) Fourier transform infrared (FTIR) spectroscopy in the mid-IR range (4000-900 cm^{-1}) is a powerful analytical tool that is increasingly being applied to biological macromolecules, such as proteins. However because of the vast number of IR-active normal modes of a typical protein, interpretation of IR data at the atomic level is usually only feasible when recorded as difference spectra between two defined states in which localized changes are induced. An ATR system has been developed in which electron transfer protein substates can be controlled automatically via a conventional three-electrode potentiostat whilst recording UV/visible changes with a fibre optic reflection probe [1, 2].

Electrochemically-induced ATR-FTIR difference spectroscopy was performed on samples of bovine cytochrome c oxidase (CcO) that had been deposited as thin films on the surface of a silicon microprism. CcO is the terminal enzyme of the mitochondrial and many bacterial respiratory chains. It catalyzes the reduction of molecular oxygen to water and couples energy released to generate a protonmotive force used for ATP synthesis. Four redox active metal centers are present: heme a, Cu$_A$, heme a$_3$, Cu$_B$. Heme a and Cu$_A$ mediate electron transfer from cytochrome c to the heme a$_3$/Cu$_B$ oxygen reducing binuclear center (BNC). A variety of ligands can also bind to the BNC is specific redox states. For example, CO binds to the reduced binuclear center and raises the redox potentials of both heme a3 and CuB. Cyanide (CN) binds most strongly to oxidized heme a$_3$ and lowers its midpoint potential .[3-4]





These ligands were used in combination with controlled electrochemistry to separate the IR redox spectra of haem a$_3$ alone, Cu$_B$ alone and haem a/Cu$_A$.

[1] D. Marshall; N. Fisher; L. Grigic; V. Zickermann; U. Brandt; R. T. Shannon; J. Hirst; R. Lawrence and P. R. Rich, Biochemistry, 2006, 45, 5458-5467;
[2] P. R. Rich and J. Breton, Biochemistry, 2002, 41, 967-973;
[3] A. J. Moody and Rich P. R., Biochem. Biophys. Acta, 1990, 1015, 205-215;
[4] S. Yoshikawa; M. Mochizuki; X.J. Zhao and W. S. Caughey, J. Biol. Chem., 1995, 270, 4270-4279.

FIS-OR-20 Drug interactions with cation transport ATPases investigated on solid supported membranes

Francesco Tadini-Buoninsegni, Gianluca Bartolommei, Maria Rosa Moncelli

BioElectroLab - Department of Chemistry "Ugo Schiff", University of Florence,
Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
francesco.tadini@unifi.it

The solid supported membrane (SSM) represents an experimental model of a lipid bilayer membrane, and is extensively used to investigate charge movements in electrically active membrane transporters [1]. Proteoliposomes or native membranes (vesicles or fragments) incorporating the transport protein can be adsorbed on a SSM and activated by a substrate concentration jump. The substrate jump induces charge displacement within the transport protein, resulting in a current transient which can be detected in the external circuit [1,2]. Therefore, the SSM serves two purposes at once, i.e. offering an adhesive surface to the adsorbed membrane entities and functioning as a transducer of a biosensor system.

BioElectroLab has a wide expertise in the study of charge transfer in cation transport ATPases through the SSM technique [2]. Our attention has recently been focused on the inhibition of ion pumps by molecules of potential pharmacological interest [3] and xenobiotics [4]. Molecules like thapsigargin and cyclopiazonic acid belong to high (nanoM) affinity inhibitors of the Ca-ATPase, whereas curcumin and clotrimazole are medium (microM) affinity inhibitors of both Ca-ATPase and Na,K-ATPase. Moreover, the toxic heavy metal Pb^{2+}, that poses a major public health problem, is able to inhibit Na,K-ATPase activity in the low micromolar range.

By combining biochemical and electrical measurements, we have compared systematically the effects of various compounds demonstrating different degrees of potency and specificity. From our results we may conclude that the inhibition mechanism involves stabilization of intermediate states of the ATPase cycle, whereby progress and completion of the enzymatic cycle are impeded.

The financial support of Ente Cassa di Risparmio di Firenze and M.I.U.R. (PRIN Project) is gratefully acknowledged.

[1] P.Schulz, J.J.Garcia-Celma, and K.Fendler, *Methods*, *46*, **2008**, 97.

[2] F.Tadini-Buoninsegni, G..Bartolommei, M.R.Moncelli, and K.Fendler, *Arch.Biochem.Biophys.*, *476*, **2008**, 75.

[3] F.Tadini-Buoninsegni, G.Bartolommei, M.R.Moncelli, D.M.Tal., D.Lewis, and G.Inesi, *Mol.Pharmacol.*, *73*, **2008**, 1134.

[4] E.Gramigni, F.Tadini-Buoninsegni, G.Bartolommei, G..Santini, G..Chelazzi, and M.R.Moncelli, *Chem.Res.Toxicol.*, *22*, **2009**, 1699.

FIS-OR-21 First-principles modeling of cathode materials for solid oxide fuel cell applications

Michele Pavone,[a,‡] **A. M. Ritzmann**,[b] **A. B. Muñoz-García**,[a] **Emily A. Carter**[a,c]

Departments of [a]Mechanical and Aerospace Engineering, [b]Chemical and Biological Engineering, [c]Program in Applied and Computational Mathematics and Gerhard R. Andlinger Center for Energy and the Environment, Princeton University
mpavone@princeton.edu - michele.pavone@unina.it

The development of efficient cathode materials for solid oxide fuel cells (SOFCs) has been based largely on perovskite-type transition metal oxides ABO_3 (A= La, Sr; B = Cr, Mn, Co, Fe, Ni). The key factors contributing to the usefulness of these materials are: high-temperature stability, the ability to catalyze the oxygen reduction reaction (ORR) at reasonable rates and high enough electronic conductivity. To reduce the SOFC operating temperature and retain good overall performance, significant efforts have been devoted to finding cathode materials that present the characteristics of a mixed ionic electronic conductor (MIEC) [1]. However, a more fundamental understanding of the underlying processes occurring at the cathode surface, within the cathode bulk material, and at the cathode/electrolyte interface, is needed to improve these materials further.

To this aim, we performed a systematic study of $LaMO_3$ (M = Cr, Mn, Fe, and Co) materials based on *ab initio* density functional theory + U (DFT+U) [2]. From the analysis of our results and available experimental data [3], we derived rational design principles that can be easily implemented for new and more effective cathode materials for SOFC applications. Based upon these design principles, we will discuss the role of the presence of alloying elements, at A and B sites, as well as the effects of the element ratio on the following properties: (a) the crystal and electronic structures; (b) the tendency to form oxygen vacancies necessary for bulk oxygen transport and (c) the surface chemistry toward ORR catalysis. In particular, we will present the results for the most exploited SOFC cathode, $La_{1-x}Sr_xMnO_3$ (LSM) [4], and, for comparison, for two promising materials recently proposed for symmetric SOFC applications, namely $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) [5] and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO) [6] materials.

[1] C. Sun, R. Hui, J. Roller, *J. Solid State Electrochem. 14*, **2010**, 1125
[2] N. J. Mosey, P. Liao, E. A. Carter, *J. Chem. Phys. 129,* **2008**, 14103
[3] T. Ishihara, *Perovskite Oxide for Solid Oxide Fuel Cells*, Springer **2009**
[4] S. P. Jiang, *J. Mater. Sci. 43*, **2008**, 6799
[5] X. Yang, J. T. S. Irvine, *J. Mater. Chem. 18*, **2008**, 2349
[6] Q. Liu, X. Dong, G. Xiao, F. Zhao, F. Chen, *Adv. Mater. 22*, **2010**, 5478

[‡] Permanent address: Dipartimento di Chimica, Universita` di Napoli Federico II

FIS-OR-22 General-purpose approaches for computational spectroscopy studies of complex molecular systems

Julien Bloino, **Malgorzata Biczysko, Vincenzo Barone**

Scuola Normale Superiore, piazza dei Cavalieri 7, 56126 Pisa, Italy

Spectroscopy represents a tool of choice for the characterization of all kinds of molecular systems. Among its many applications, we can cite the determination of the structure, dynamics or the photochemical properties, of utmost importance in the conception of photovoltaic cells, for instance. However, the interpretation of most experimental spectra is difficult due to their inherent complexity caused by the thermal or environmental effects, but also intrinsic properties of the system itself. In this matter, computational spectroscopy has shown to be a valuable tool to help unravel the various contributions to the spectrum, allowing for a better understanding of the underlying phenomena.

Several computational tools, covering a large panel of spectroscopies, in particular those of vibrational and electronic origin, have been developed and coded. However, the most advanced ones are often made available in the form of independent programs, which may be difficult to deploy and use for a non-expert as well as to interact with other programs needed to compute required input data. One of the key challenges, necessary for a broader adoption of advanced theoretical models is the integration in single packages, able to perform the complete task from the determination of the structure to the final output of the spectrum of interest, and simple interfaces to use them.

In this context, we present general-purpose modules for the simulation of the line-shapes for vibrational spectroscopy (e.g. infrared) at the anharmonic level and vibrationally-resolved electronic spectroscopy (one-photon, electronic circular dichroism). The theoretical models used aim at providing a computational support for the realistic IR-UV-vis experimental spectra of complex systems, including their environment, and are less focused on highly accurate predictions for small molecular systems or studies of peculiar features. Various computational strategies exploiting the localized nature of spectroscopic phenomena are available at both levels, allowing to handle larger systems, which may be too cumbersome to treat in their entirety, with limited impact on the accuracy. Those approaches represent a great improvement with respect to the methods still commonly used in such cases (harmonic approximation, vertical electronic transitions) and contribute to the better understanding of experimental spectra of large molecular systems routinely studied nowadays.

References:

1. J. Bloino, M. Biczysko, F. Santoro, V. Barone, *General Approach to Compute Vibrationally Resolved One-Photon Electronic Spectra*, J. Chem. Theory Comput. 6, 1256-1274 (2010)
2. V. Barone, J. Bloino, M. Biczysko, F. Santoro, *Fully Integrated Approach to Compute Vibrationally Resolved Optical Spectra: From Small Molecules to Macrosystems*, J. Chem. Theory Comput. 5, 540-554 (2009)
3. J. Bloino, M. Biczysko, O. Crescenzi, V. Barone, *Integrated computational approach to vibrationally resolved electronic spectra: Anisole as a test case*, J. Phys. Chem. 128, 244105 (2008)
4. V. Barone, J. Bloino, C.A. Guido, F. Lipparini, *A fully automated implementation of VPT2 Infrared intensities*, Chem. Phys. Lett. 496, 157-161 (2010)
5. V. Barone, M. Biczysko, J. Bloino, M. Borkowska-Panek, I. Carnimeo, P. Panek, *Toward anharmonic computations of vibrational spectra for large molecular systems*, Int. J. Quantum Chem., *accepted*

FIS-OR-23 Rotational spectroscopy for astrophysical investigations

Cristina Puzzarini,[a]

[a]Dipartimento di Chimica “G. Ciamician”dell’Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy,
cristina.puzzarini@unibo.it

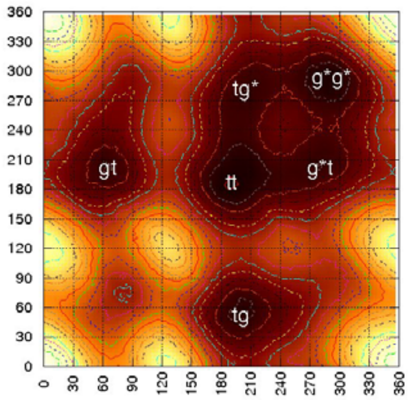
Among the various spectroscopic research fields, the investigation of the phenomena that allow to understand the chemistry of the interstellar medium plays a particularly relevant role. The need of laboratory, experimental as well as computational, investigations in this field is due to the fact that astronomical observations require the knowledge of the spectroscopic parameters involved. For the sake of giving an example, we mention that the recent Herschel, SOFIA and ALMA missions require the accurate knowledge of the transition frequencies in the submillimeter-wave range up to the infrared frequency region for a huge number of molecules, for those of relevance, the so-called “flowers”, as well as for the disturbing species, the so-called “weeds”. The need of the knowledge of the spectroscopic parameters has then led to the set up of various databases, that are continuously updated and enlarged.

Among the various spectroscopic techniques, thanks to its intrinsic high resolution, rotational spectroscopy is a powerful tool for studying the chemistry and physics of the atmosphere and interstellar medium. In the present contribution, the reseach lines of the LMSB (Laboratory of Millimeter-wave Spectroscopy of Bologna) in the field of astrophysical investigations are prersented. The focus is on the accuracy of the retrieved transition frequencies of neutral as well as ionic species and on line-broadening investigations.

FIS-OR-24 How Does Tacticity Affect the Solution Behaviour of Poly(N-isopropyl acrylamide)? A Molecular Dynamics and Metadynamics Simulation Study

Emmanuel Autieri[ç], Ester Chiessi[§], Alice Lonardi[§], Marcello Sega[ç]

[§]Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica I, 00133 Rome, Italy
[ç]Department of Physics, University of Trento, via Sommarive 14, 38123 Trento, Italy
ester.chiessi@uniroma2.it



Conformational free energy map of the PNIPAAm syndiotactic dyad in water at 293 K.

The peculiar thermal phase behavior of poly(N-isopropyl acrylamide) (PNIPAAm) in aqueous media caught the attention of physicists and chemists in the last two decades, leading to both elegant chemical physics investigations and smart soft matter devices. The discovery of a new procedure for the stereocontrolled radical polymerization of acrylamides [1] allowed to test the water phase behavior of stereoregular PNIPAAm's, showing a strong influence of the polymer tacticity [2,3]. The purpose of this study is highlight the factors determining the PNIPAAM tacticity-dependent differences of its solution properties, tackling the problem both form a structural and dynamic point of view with a double simulation approach. The conformational free energy behavior as a function of backbone conformation was obtained by metadynamics simulations. The structural characteristics, the intramolecular and water hydrogen bonding and the torsional dynamics were explored by molecular dynamics simulations. The investigation, extended to all stereoisomers of PNIPAAm trimer, representing syndiotactic, isotactic and atactic sequences, showed that the experimentally observed lower hydrophilicity of isotactic poly(N-isopropyl acrylamide), in comparison with the syndiotactic one, is related to a lower conformational entropy. Simulation results were critically compared with available experimental data on solution properties and reactivity of poly(N-isopropyl acrylamide) [4].

[1] Isobe, Y.; Fujioka, D.; Habaue, S.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 7180.
[2] Hirano, T.; Okumura, Y.; Kitajima, H.; Seno, M.; Sato, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4450.
[3] Katsumoto, Y.; Kubosaki, N. *Macromolecules* **2008**, *41*, 5955.
[4] Autieri, E.; Chiessi, E,; Lonardi, A.; Paradossi, G.; Sega, Marcello *J. Phys. Chem. B.* **2011**, ASAP Article.

FIS-OR-25 Structural and Dynamic Features of Thermoresponsive Microgels around the Volume Phase Transition Temperature

<u>Gaio Paradossi</u>, Shivkumar V. Ghugare

Dipartimento di Scienze e Tecnologie Chimiche, Via della Ricerca Scientifica, Università di Roma Tor Vergata, 00133 Rome, Italy
paradossi@stc.uniroma2.it

Sustained drug delivery requires the use of multi-functional devices with enhanced properties, including responsivity to external stimuli (such as temperature, pH, ionic strength), ability to target specific receptors, enhanced bioadhesion to cells and biocompatibility. Microgels represent one such multifunctional suitable as drug delivery and switchable microdevices. The fabrication of a stable colloidal aqueous suspension of biocompatible microgel spheres is based, for instance, on a poly(vinyl alcohol)/poly(methacrylate-co-*N*-isopropylacrylamide) network [1]. These microgel spheres undergo an entropy driven volume phase transition around physiological temperature, this process being driven by the incorporation of NiPAAm residues in the network. In this study the microgel was loaded with the anti cancer drug, doxorubicin. Upon microgel de-swelling, a marked increase in the amount of doxorubicin released was noted. Sieving and size exclusion effects were studied by laser scanning confocal microscopy with microgel particles exposed to fluorescent probes with different molecular weights (Figure 1). In this contribution we focus on some fundamental issues regarding modifications of the network structure at a nanoscopic level and of the diffusive behavior of water associated with the polymer network around the volume phase transition temperature (VPTT) [2]. Observations carried out at room temperature and at 40 °C (i.e. below and above the VPTT), provided an evaluation of the variation of the average pore size (from 5 nm to 3 nm). The diffusive behaviour of water molecules closely associated to the polymer network around the VPTT was investigated quasi-elastic neutron scattering. Nanostructured changes around VPTT of the microgel particles was probed in direct and reciprocal space, i.e. small angle neutron scattering (SANS) (Figure 2) and scanning transmission X-ray microscopy (STXM), respectively. A transition of the microgel interface from brush-like to smooth surface was evidenced by a power law change from 2 to 4 (Porod's law).

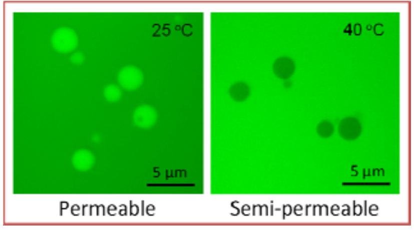


Figure1. Confocal microscopy/size exclusion experiment at 25 and 40°C

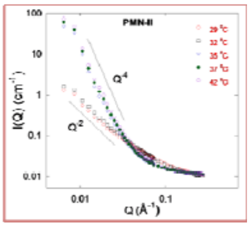


Figure 2. SANS on PMNII microgel around the VPTT

[1] S. V. Ghugare, P. Mozetic and G. Paradossi, *Biomacromolecules*, *10,* **2009**, 1589.
[2] S. V. Ghugare, E. Chiessi, M. T. F. Telling, A. Deriu, Y. Gerelli, J. Wüttke and G. Paradossi *J. Phys. Chem. B*, *114*, **2010**, 10285.
[3] S.V. Ghugare, E. Chiessi, R. Fink, Y. Gerelli, A. Scotti, A. Deriu, G. Carrot and G. Paradossi, *Macromolecules*, **2011,** DOI: 10.1021/ma200979

FIS-OR-26 Tuning the Aerosol-OT surfactant film curvature in water through the 1-butyl-3-methylimidazolium BF_4^-/Br^- ionic liquids

Sergio Murgia,[a] **Gerardo Palazzo,**[b] **Marianna Mamusa,**[a] **Sandrina Lampis**[a] **and Maura Monduzzi**[a]

[a] Dipartimento di Scienze Chimiche dell'Università di Cagliari, CNBS e CSGI, s.s. 554 bivio Sestu, 09042 Monserrato (CA), Italy.
[b] Dipartimento di Chimica dell'Università di Bari e CSGI, via Orabona 4, 70126 Bari, Italy.
E-mail: murgias@unica.it

Through a detailed analysis conducted basically via SAXRD and NMR PGSTE techniques, it is here shown that the curvature of the micellar aggregates originated by the sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT, NaAOT) in water can be severely altered when a polar ionic liquid, namely the 1-butyl-3-methylimidazolium tetrafluoborate ($bmimBF_4$), is added to the binary system. Although the whole phase diagram is investigated, here the focus is mainly on the isotropic micellar region. Data reveals that the ionic liquid is strongly adsorbed at the interface and that the overall processes can be described as a co-micellization of AOT^- and $bmim^+$ involving roughly two cations for each anion. Concerning the micellar phase, such an adsorbtion induces a huge modification of the interfacial geometry that results in the occurrence of discrete spherical micelles having positive curvature, as evidenced from the self-diffusion experiments.[1] Remarkably, the micellar phase nanostructure can be tuned by the simple substitution of the ionic liquid's counter-ion. Indeed, when bromide instead of tetrafluoroborate is used as the imidazolium counter-ion the nanostructure changes from discrete to bicontinuous.[2] This finding can be accounted for suggesting a decreasing of the NaAOT effective surfactant packing parameter, although the effect in the presence of Br^- is less pronounced. Data modeling shows the same degree of interfacial adsorption for the $bmim^+$ cation in both systems, regardless of the particular counterion used – either BF_4^- or Br^-. Thus, the remarkable differences between the two systems investigated appear to be mainly due to a specific counterion effect. This result highlights once again the ions specificity, which is found ubiquitously in chemistry and biology.

[1] S. Murgia, G. Palazzo, M. Mamusa, S. Lampis, and M. Monduzzi, *J.Phys.Chem.B*, *113*, **2009**, 9216.
[2] S. Murgia, G. Palazzo, M. Mamusa, S. Lampis, and M. Monduzzi, *Phys.Chem.Chem.Phys.*, *13*, **2011**, 9238.

FIS-OR-27 Inside Complex Sol-Gel Materials: a Detailed Investigation of Organic-Inorganic Hybrid Coatings Through Solid-State NMR

S. Borsacchi,[a] **F. Martini,**[a] **M. Toselli,**[b] **F. Pilati**[c], **M. Geppi**[a]

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, Pisa, Italy.
[b] Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, via Terracini 28, Bologna, Italy.
[c] Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, via Vignolese 905, Modena, Italy.

silvi@ns.dcci.unipi.it

The sol-gel approach is one of the most convenient way for preparing organic-inorganic nanostructured hybrid materials thanks to the mild chemistry involved and the possibility of obtaining a wide variety of molecular structures and morphologies. The detailed knowledge of the phase and molecular properties of these materials is a very important task, especially for clarifying their complex relationships with preparation conditions and final macroscopic properties. Solid-state NMR (SSNMR) is an extremely powerful technique for the detailed characterization of structural and dynamic properties of complex hybrid materials, on very large spatial (0.1-100 nm) and time (s-ps) scales [1,2]. Here we present an extensive SSNMR study of a set of polyethylene-*b*-poly(ethylene glycol)/poly(4- hydroxystyrene)/silica hybrid coatings, obtained via sol-gel, exhibiting good barrier properties against oxygen diffusion [3]. By exploiting a variety of nuclei available (^{1}H, ^{13}C, ^{29}Si) and a large set of experiments (high-resolution quantitative and selective 1D spectra, 2D Double Quantum and HETCOR spectra), including the most recent technological advances (^{1}H ultra-fast MAS spectra @60 kHz, courtesy of Agilent), we could characterize in detail the chemical structure of the inorganic domains, the phase, dynamic and conformational properties of the organic components, as well as obtain important evidences of the interfacial interactions among the different components. These properties resulted to be strongly dependent on samples composition and showed interesting correlations with the barrier performances.

[1] M.Geppi, S.Borsacchi, G.Mollica, C.A.Veracini *Appl. Spectrosc. Rev.*, *44*, **2009**, 1.
[2] M.Geppi, S.Borsacchi, G.Mollica "Solid-state NMR of organic/inorganic multicomponent materials" in *Encyclopedia of Magnetic Resonance*, R.K.Harris and R.E.Wasylishen, eds-in-chief.; J. Wiley & Sons, **2008**.
[3] M.Toselli, F.Pilati, M.Marini, F.Doghieri, M.G.De Angelis, M.Minelli, *Eur. Polym. J.*, *44*, **2008**; 3256.

FIS-OR-28 LIBS application to the recovery of precious metals from scrap and waste materials

S.Legnaioli[a], **G.Lorenzetti**[a], **L.Pardini**[a], **V.Palleschi**[a], **G.Carelli**[b], **R.Grassi**[b], **F.Sorrentino**[b], **F.Francesconi**[b], **M.Francesconi**[b], **P.Marsili**[b] **and R.Borgogni**[c]

[a]Institute of Chemistry of Organometallic Compounds of CNR, UOS of PISA – Via G. Moruzzi 1 56124 Pisa, Italy
[b]Marwan Technology s.r.l. – Via del Borghetto 34, Pisa, Italy
[c]Cabro S.p.A., Via Setteponti 141, Arezzo, Italy
s.legnaioli@pi.iccom.cnr.it

The LIBS technique was applied to the measure of traces of precious metals in scrap and waste materials, in view of their recovery. Using MODI' (Mobile Dual-Pulse Instrument) several certified samples were analyzed with the purpose of determining the trueness of the method and the detection limits for Gold, Silver, Platinum, Palladium and Rhodium quantitative analysis in copper-based alloys. In this communication, the results of the study are presented and discussed. The possibility of improving the performances of LIBS on this kind of materials through internal standardization, self-absorption correction and calibration-free analysis is also discussed.

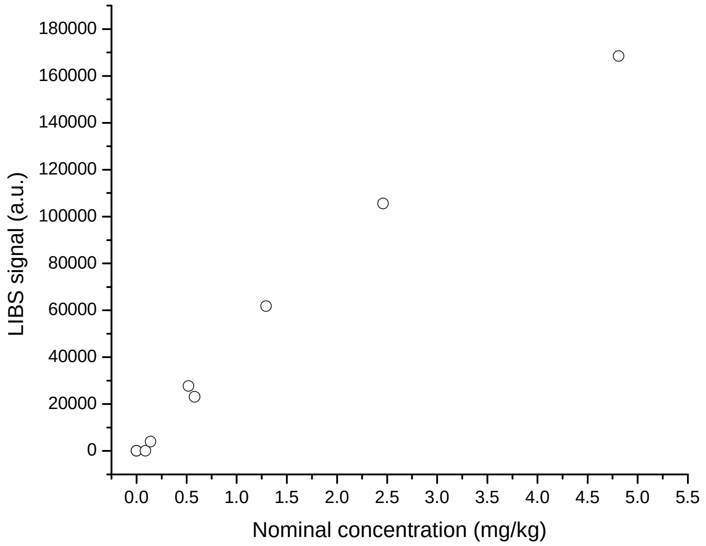


Fig.1 – Calibration curve for Rhodium

FIS-OR-29 Carbon Nanotube Saturable Absorbers For Ultrafast Pulsed Lasers

Stefania Ferrari,[a] **Antonio Agnesi**,[b] **Federico Pirzio**,[b] **Giancarlo Reali**,[b] **Marcella Bini**,[a] **Doretta Capsoni**,[a] **Vincenzo Massarotti**,[a]

[a] Dip. di Chimica – Sezione di Chimica Fisica dell'Università di Pavia, Viale Taramelli 16, 27100 Pavia, Italia
[b] Dip. di Elettronica dell'Università di Pavia, Via Ferrata 1, 27100 Pavia, Italia
stefania.ferrari@unipv.it

Single walled carbon nanotubes (SWCNTs), thanks to their unique physical and chemical properties, have been actively researched to realize efficient non linear components for optical systems, such as passively pulsed lasers [1]. In particular, broad spectral operating wavelength and easy tunability, possibility to realize both transmission- and reflection-type absorbers on a wide variety of substrates, very fast recovery time, low saturation fluence and absence of two-photon absorption are favourable intrinsic properties that make these devices very attractive for passive mode-locking of ultrafast lasers.
A very well known problem concerning the fabrication of SWCNTs films, is their tendency to form clusters, that can cause the interweaving of nanotubes, then showing inferior mode-locking performances. Regarding this, a crucial role is played by the preparation method, in particular the dispersion with ultra-sonication and the successive deposition of the films.

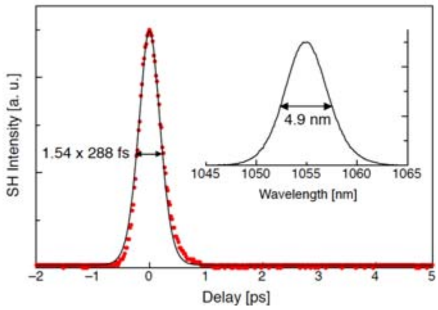


Figure 1

In this work, we present the results of the preparation of a SWCNTs film deposited on a quartz substrate by slow solvent evaporation method. The purified semiconductors nanotubes result well dispersed and homogeneously distributed on the surface of the substrate as verified by Raman spectroscopy and optical response. The film was tested in a Nd:glass based femtosecond laser. 288-fs-long, very stable mode-locked pulse trains at a central output wavelength of 1055 nm were obtained with an average output power of about 20 mW. Both the spectrum and the pulses autocorrelation trace are shown in Figure 1.

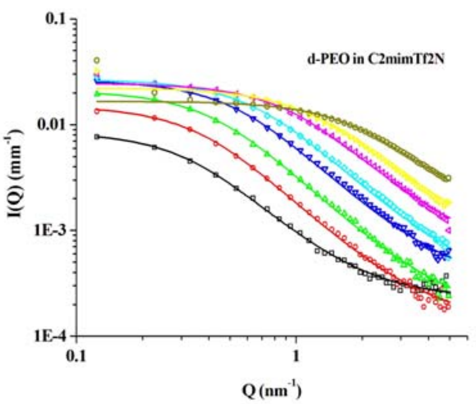
[1] J. Wang, Y. Chen, and W. J. Blau, *J .Mater. Chem., 19,* **2009**, 7425.
[2] Y.-C. Chen, N. R. Raravikar, L. S. Schadler, P. M. Ajayan, Y.-P. Zhao, T.-M. Lu, G.-C. Wang, and X.-C. Zhang, *Appl. Phys. Lett., 81,* **2002**, 975.

FIS-OR-30 Structural properties of binary poly(ethylene-oxide)/room temperature ionic liquids mixtures: an experimental and computational study.

Alessandro Triolo[a] **and Ruggero Caminiti**[b]

[a] Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, Roma
[b] Dipartimento di Chimica, Università di Roma “Sapienza”, Roma
triolo@ism.cnr.it

Poly (ethylene oxide) is one of the few polymers that are soluble in room temperature ionic liquids. These mixtures can find several applications such as polymer electrolytes or separation media.
A few years ago, we highlighted the good solvent nature of RTILs towards PEO, using SANS technique [1], and Ribeiro simulated the morphology and dynamics of PEO-rich mixtures [2]. Recently the activities of Watanabe’s [3], Rogers’s [4] and Lodge’s [5] groups focused on the phase diagram of PEO-RTIL binary mixtures, detecting the existence of a Lower Critical Solution Temperature for these systems and screening the role of RTIL’s chemical details on this complex behavior.



SAXS data from PEO solutions in C2mimTf2N, as a function of polymer concentration.

Here we show recently obtained results from both Small Angle X-ray and Neutron Scattering from PEO-RTILs mixtures at ambient temperature, as a function of polymer concentration, for a variety of RTILs. We screened the role of the RTIL’s alkyl chain length, methylation of position 2 in the RTIL imidazolium ring and other chemical details of the RTIL on the morphology of the macromolecule, extracting information as interesting as its average size, the persistence length and chain rigidity.
These results have been complemented with MD simulation study of oligo (ethylene oxide) dissolved in C2mimTf2N and C2C1mimTf2N, in order to explore the role of hydrogen bonding on microscopic organization in such mixtures.

[1] Triolo et al., JPCB 110, 1513 (2006)
[2] Ribeiro et al., JCP 124, 184902 (2006)
[3] Watanabe et al., Chem. Comm. 4939 (2008)
[4] Rogers et al., PCCP 11, 1096 (2009)
[5] Lodge et al., JPC-Letters 1, 1962 (2010)

FIS-OR-31 Microfluidic devices for chemical reactions: fabrication and characterization with computational modeling and fluorescence experiments.

N. Rossetto, I. Fortunati, E. Collini, R. Signorini, C. Ferrante, M. Montagna, S. Carlotto, A. Polimeno.

Dipartimento di Scienze Chimiche e UdR INSTM dell'Università di Padova, Via Marzolo 1, 35131 Padova, Italy.

Recently microfluidic has been proposed for chemical synthesis with the purpose to have a better control on reactions that involve either highly toxic or highly unstable species. This control can be achieved through a programmed mixing of the reagents and a microscopic modulation of other physical parameters (such as: temperature, oxygen content of the solvents etc.).

In particular we have focused our interest on the characterization of controlled mixing of reagents in microfluidic devices through in-silico simulations and fluorescence experiments.

Microfluidic devices in polydimethylsiloxane (PDMS) are realized through replica molding technique of a silicon master. The master itself is realized by means of one- and two-photon induced laser photopolymerization of a commercial photoresist: SU8. With this technique we can build 3D structures with resolution of 1μm in the x-y plane and 8-10 μm on the z axis perpendicular to the x-y plane.

The motion and mixing of fluids in the channels of the microfluidic device is simulated via a Navier-Stokes finite-element approach, coupled to convection-diffusion equations. Time and frequency resolved fluorescence techniques are used to experimentally evaluate parameters such as concentration of chemical species and laminar flow speed. The results of these experiments are compared with the data of the numerical simulations.

Finally we will present our preliminary results on: (i) the investigation of fluorescence quenching of the fluorescein dye in water by controlled mixing with a potassium iodide solution and (ii) tetrakis(4sulphonatophenyl)porphyrin aggregate formation in acidified water.

FIS-OR-32 Charge-assisted hydrogen bonds and weak intermolecular interactions as tools to fabricate complex supramolecular architectures

Angiolina Comotti
Department of Materials Science, University of Milano Bicocca, Via R. Cozzi 53, Milan, Italy.
E-mail: angiolina.comotti@mater.unimib.it

Molecular self-assembled crystalline materials are promising in several fields, including gas adsorption, catalysis, selective recognition and modulation of functions of active molecules, although the rational design of synthetic supramolecular architectures based on well-defined structure-directing forces and hydrogen bonding is still a challenge. We present a supramolecular cage assembled through 72 hydrogen bonds which is constructed from two kinds of hexagonal molecular tiles (Figure 1) forming a truncated octahedron, one of the thirteen Archimedean polyhedra[1]. The framework resembles those of sodalite and zeolite A and displays an extraordinary ability to encapsulate a wide range of differently charged species, ranging from transition metal complexes to nanoclusters not observed otherwise. The thermodynamic stability of the octahedral cage is explained by the presence of an extended network of charge-assisted $N\text{-}H^+\ldots{}^-O\text{-}S$ hydrogen bonds.

By the exploitation of the same kind of interactions, orientation of polyconjugated guest molecules is obtained in tunable host cavities[2]. Through judicious selection of intermolecular interactions, the framework architectures can be controlled systematically in a manner that enables the regulation of the guest orientation and aggregation. The effects of the distinct packing motifs is manifested as bathochromic shifts in the absorption and emission spectra of the guests. This behavior is supported by ab initio TDDFT calculations that reproduce the bathochromic shifts associated with the effects of guest-guest and guest-host interactions, combined with conformational constraints imposed on the guest molecules by the rigid host framework.

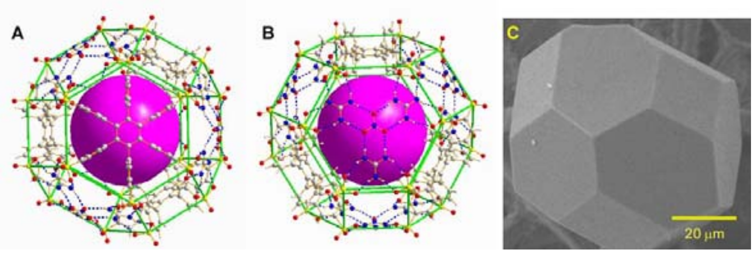


Figure 1. The quasi-truncated octahedron *q*-TO (left) and scanning electron microscopy image of a crystal (right), illustrating the hexagonal and square faces that reflect the symmetry of the *q*-TO.

Interestingly, through CH···π interactions, the molecular recognition of specific blocks of triblock copolymers by a host molecule enables the formation of hierarchical periodic structures [3]. The formation of the supramolecular architectures is followed by *in situ* synchrotron X-ray diffraction while the specific CH···π intermolecular interactions are highlighted by fast-^{1}H MAS NMR and GIAO HF ab initio calculations.

Moreover, weak intermolecular interactions play a key role in modulating the dynamics of molecular rotors in amphidynamic materials. Indeed, the precise engineering of highly-organized porous silica scaffolds supporting organic elements enables the fabrication of fast molecular rotors ($k>10^8$ Hz) entirely exposed to the guest molecules which act as regulators [4].

[1] Y. Liu, C. Hu, A. Comotti, and M. D. W. Ward, *Science,* **2011**, ASAP.
[2] A. Soegiarto, A. Comotti, and M. D. Ward, *J. Am. Chem. Soc., 132*, **2010,** 14603.
[3] S. Bracco, A. Comotti, L. Ferretti, and P. Sozzani, *J. Am. Chem. Soc,. 133,* **2011**, 8982.
[4] A. Comotti, S. Bracco, M. Beretta, P. Valsesia, and P. Sozzani, *Angew. Chemie Int. Ed., 49*, **2010**, 1760.

FIS-OR-33 Protective effect of the mesoporous host towards the photo oxidation of fluorescent guests: a UV-Vis spectroscopy study

Ivana Miletto,[a] **Annalisa Massa,**[b,c] **Giuseppe Caputo,**[c] **Elena Ugazio,**[b] **Maria Eugenia Carlotti,**[b] **and Salvatore Coluccia**[a]

[a] Dipartimento di Chimica I.F.M. dell'Università degli Studi di Torino, Via Quarello 11a, Torino, Italy
[b] Dipartimento di Scienza e Tecnologia del farmaco dell'Università degli Studi di Torino, Via P. Giuria 9, Torino, Italy
[c] Cyanine Technologies S.p.A., Torino, Italy
ivana.miletto@unito.it

In recent years, mesostructured silica nanoparticles variously functionalized have been studied and tested for a wide range of biological, biomedical and technological applications. In several studies organic or inorganic fluorophores have been hosted in mesostructured materials in order to obtain a new class of hybrids with improved performances in term of brightness, quantum yield, photostability, etc. [1,2]. Fluorescent hybrid organic-inorganic mesoporous nanoparticles can be prepared by physical adsorption or grafting of indocyanine dyes within the channels of MCM-41 nanoparticles. Previous experiments showed that this kind of architecture provides the highest stability and signal intensity upon specific thermal treatments, if compared to the correspondent indocyanine dye in solution and other kinds of nanoparticles [3].

In this contribution the sensitivity of fluorescent hybrid organic-inorganic nanoparticles to the photo oxidation was tested under different experimental conditions and compared to the performances of the correspondent indocyanine dye in solution. Photodegradation experiments were performed under simulated solar illumination and the optical performances of the samples after irradiation were evaluated by UV-Vis absorption and emission spectroscopy, augmented by fluorescence lifetime measurements. The effect of different parameters, such as the absence or the presence of oxygen and TiO_2 and pH, on the photodegradation was investigated.

The results demonstrated a beneficial effect of the silica matrix on the photostability of the embedded indocyanine dyes, showing an increased stability both in presence and in absence of TiO_2 as well as in alkaline conditions. Interestingly, the analysis of the fluorescence lifetimes data allowed us to highlight a selective degradation of the indocyanine molecules located on the external surface of the silica nanoparticles, with respect to the molecules hosted within the pores.

[1] E. Gianotti E, et al. *ACS Appl Mater Interfaces* 1(3), **2009**, 678.
[2] E. Bottinelli, et al. *J. Fluoresc.* 21 (3), **2011**, 901.
[3] L. Mortati et al. *J. Fluoresc.* 21 (3), **2011**, 929-936

FIS-OR-34 Autoinhibition of angiogenins: insights from the X-ray structure of RNase 2 from Atlantic salmon

Antonello Merlino[a,b*], **Irene Russo Krauss**[a], **Carla Carluccio**[a], **Elio Pizzo**[c], **Giuseppe D'Alessio**[c], **Lelio Mazzarella**[a,b], **Filomena Sica**[a,b]

[a]Dipartimento di Chimica 'Paolo Corradini' dell'Università di Napoli 'Federico II', Complesso Universitario di Monte Sant'Angelo, Via Cinthia, I-80126, Naples, Italy
[b]Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, I-80134 Naples, Italy
[c]Dipartimento di Biologia Strutturale e Funzionale dell'Università di Napoli 'Federico II', Complesso Universitario di Monte Sant'Angelo, Via cyntia, I-80126, Naples, Italy
antonello.merlino@unina.it

Recently, the superfamily of animal, extracellular, pyrimidine-specific RNases, often called the RNase A superfamily, has been shown to include not only tetrapod enzymes, but also fish enzymes [1]. In particular, five RNases from zebrafish (*Danio rerio*) [1-3] and two from the Atlantic salmon (*Salmo salar*) [4] have been reported to have a very low RNase activity and to be endowed, like RNase 5 (human angiogenin), with powerful angiogenic activity. We have determined the X-ray structure of two zebrafish RNases [3]. In these proteins, like in human angiogenin, the putative binding subsite B1 of the pyrimidine base is partially obstructed by the side chain of Glu located in the C-terminal segment of the protein, and this structural feature well account for their low catalytic activity.

More recently, the crystal structure of RNase-2 from *Salmo salar* (Ss2) has been also determined. Surprisingly, within an essentially unmodified RNase folding, the enzyme presents an extensive reorganization of the active site region with respect to other pancreatic RNases. In particular, although it has the highest catalytic activity among fish RNases, it presents an active site fully obstructed by a peptide segment at C-terminal region (CTR), and with the two catalytic histidines in direct contact. Thus the enzyme appears to be auto-inhibited in a completely different manner compared to the other angiogenins. Comparison of the structure of Ss2 with those of RNase complexes with substrate analogs suggests that Ss2 could adopt two distinct conformations: a closed form with the CTR blocking the substrate binding cleft (observed in the crystal structure) and an open conformation, where the CTR swings out forming an open cleft with the active site exposed. Overall, these data provide novel structural insights into the mechanism that modulates RNase activity of angiogenins.

[1] E. Pizzo, P. Buonanno, A. Di Maro, S. Ponticelli, S. De Falco, N. Quarto, M.V. Cubellis and G. D'Alessio, *J Biol Chem, 281*, **2006**, 27454.
[2] S. Cho and J. Zhang, *Mol Biol Evol, 24*, **2007**, 1259.
[3] E. Pizzo, A. Merlino, M. Turano, I. Russo Krauss, F. Coscia, A. Zanfardino, M. Varcamonti, A. Furia, C. Giancola, L. Mazzarella, F. Sica, G. D'Alessio, *Biochem J., 433(2)*, **2010**, 345
[4] E. Pizzo, M. Varcamonti, A. Di Maro, A. Zanfardino, C. Giancola, G. D'Alessio, *FEBS J, 275*, **2008**, 1283.

FIS-OR-35 Clusters Fingerprint in Lysozyme Protein Solutions

E. Fratini,[a] **Y. Liu**,[b] **L. Porcar**,[c] **P. Baglioni**[a]

[a]Department of Chemistry and CSGI, University of Florence, via della Lastruccia 3, 50019, Florence, Italy
[b]NIST Center for Neutron Research, 100 Bureau Drive, Gaithersburg , MD, US
[c]ILL, B. P. 156, 38042, Grenoble, France
fratini@csgi.unifi.it

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.

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. Moreover contrary to literature conclusions, at relatively low concentrations, there is evidence that 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.

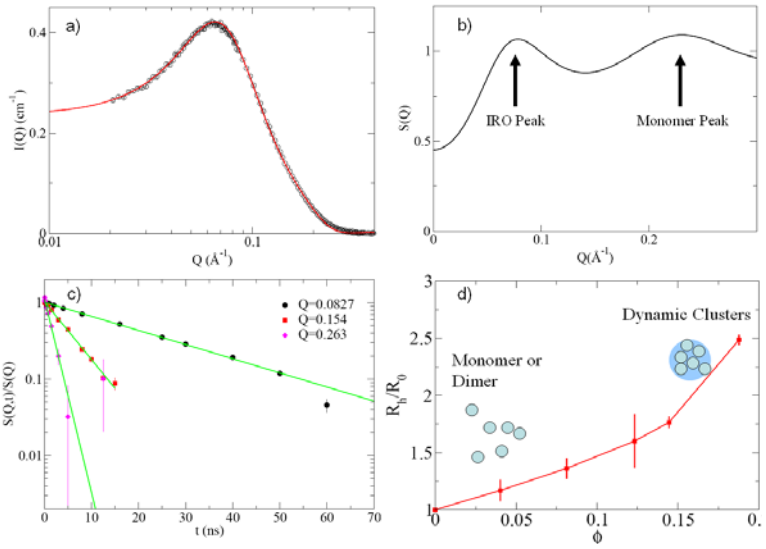


Figure 1. a) Fitting curve (solid line) together with the experimental points of 5 wt% lysozyme solution measured by SANS, **b)** Extracted inter-particle structure factor, S(Q), for the 5 wt% sample, **c)** *S(Q,t)/S(Q) vs t* in the Q

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 (IRO) structure governed by a short-range attraction and a long-range repulsion.

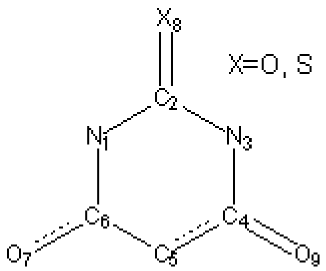
[1] L. Porcar, P. Falus, W.R. Chen, A. Faraone, E. Fratini, K.L. Hong, P. Baglioni, Y. Liu, *J. Phys. Chem. Letters*, *1,* **2010**,126-129.
[2] Y. Liu, L. Porcar, J. Chen, W.R. Chen, P. Falus, A. Faraone, E. Fratini, K. Hong, P. Baglioni, *J. Phys. Chem. B*, in press, DOI:10.1021/jp109333c.

FIS-OR-36 Soft X-ray photoelectron-photoabsorption spectroscopy and electronic structure of barbituric and 2-thiobarbituric acid.

Assimo Maris,[a] **Sonia Melandri**,[a] **Luca Evangelisti**,[a] **Vitaly Feyer**,[b] **Kevin Charles Prince**,[b] **Marcello Coreno.**[c]

[a] Dipartimento di Chimica Ciamician dell'Università di Bologna, Via Selmi 2, I-40126, Bologna, Italy.
[b] Sincrotrone Trieste S.C.p.A., s.s. 14 km 163.5 in Area Science Park, I-34012 Basovizza (Trieste), Italy
[c] CNR-IMIP, Montelibretti (Rome), I-00016 Italy
Corresponding author: assimo.maris@unibo.it

We present a combined experimental and theoretical investigation of the electronic spectra of barbituric acid (BA) and 2-thiobarbituric acid (TBA) molecules in the vapour phase. The valence band photoemission and the core level (O, N, C 1s and S 2p) photoemission and photoabsorption spectra have been measured in the vapour phase using synchrotron light and then assigned with the support of quantum chemical calculations. First the valence band binding energies have been calculated using the Koopman's approximation at the B3LYP/6-311++G** level, then the outer valence behaviour has been better approximated with electron propagator calculations (OVGF and P3 approximations), available in the G09 software package. [1] The core ionized states and core-to-excited states transitions were solved within the Hartree-Fock approximation by explicitly taking into account the core hole, using the GSCF3 code developed by prof. N. Kosugi. [2] The calculations were run for both the tri-keto and the hydroxy-di-keto form, where the enolization of one of the two equivalent keto groups is produced by proton transfer from the methylene group, which is more acidic than the NH groups. In agreement with previous *ab initio* [3, 4] and gas-phase electron diffraction [5] works, only the tri-keto tautomers have been detected.



[1] Gaussian 09, Revision A.02, M. J. Frisch *et al.*, Gaussian, Inc., Wallingford CT, 2009.
[2] N. Kosugi, and H. Kuroda, *Chem. Phys. Lett.* 74, **1980**, 490. N. Kosugi, and H. Kuroda, *Chem. Phys. Lett.*, 94, **1983**, 377. N. Kosugi, *Theor. Chim. Acta*, 72, **1987**, 149.
[3] F. Zuccarello, G. Buemi, C. Gandolfo and A. Contino, *Spectrochim Acta A*, 59, **2003**, 139-151.
[4] E. Méndez, M. F. Cerdá, J. S. Gancheff, J. Torres, C. Kremer, J. Castiglioni, M. Kieninger, and O. N. Ventura, *J. Phys. Chem. C*, 111, **2007**, 3369-3383
[5] O. V. Dorofeeva, I. I. Marochkin, N. M. Karasev, I. F. Shishkov and H. Oberhammer, *Structural Chemistry*, 22, **2011**, 419-425

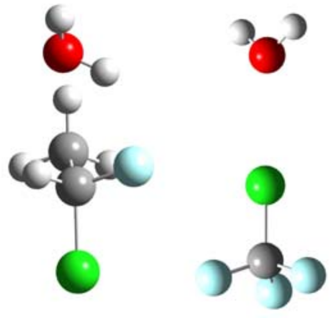
FIS-OR-37 Complexes of water with freons: an interim perspective by microwave spectroscopy

Luca Evangelisti,[a] **Gang Feng**,[a] **Laura B. Favero**,[b] **Walther Caminati**.[a]

[a] Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, I-40126, Bologna, Italy.
[b] Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, via Gobetti 101, I-40129, Bologna, Italy.

Corresponding author: luca.evangelisti6@unibo.it

In recent years very importance have been purchased by CFCs. Their impact in atmosphere arises both the role in ozone reduction and greenhouse effect. Because the abundance of atmospheric water, the information of intermolecular interaction between CFCs and water will be helpful in understanding the behavior and impact of CFCs in atmosphere. In fact its internal dynamics contribute to determine the properties of these systems. [1] In freons, all data suggest O-H···Hg (Hg = F, Cl) to be a weak interaction but different behaviors are observed and it is quite difficult to rationalize them. We measured the molecular beam Fourier transform microwave spectra of six isotopologues of the 1:1 adducts of CH_3CHClF with water and five isotopologues of CF_3Cl with water (see the Figure). In the first case [2] the water prefers to form an O-H···F rather than an O-H···Cl hydrogen bond. This is exactly the contrary of what observed in the chlorofluoromethane-water adduct, where a O-H···Cl link was formed.[3] In the second case [4] the interaction between the subunits occurs via C-Cl···O(H_2O) halogen bond. For both complexes, besides the rotational constants, the quadrupole coupling constants of the chlorine atom and structure information have been determined. In addition, information on the internal dynamics has been obtained. Ab initio calculation (MP2 level of electron correlation and 6-311++G** basis set) have been carried out in order to obtain information about the structure and relative stability.



[1] L. Evangelisti and W. Caminati, *Phys. Chem. Chem. Phys. 12*, **2010**, 14433.
[2] G. Feng, L. Evangelisti, L.B. Favero, J.U. Grabow, Z. Xia, and W. Caminati, *Phys. Chem. Chem. Phys.* **2011**, DOI: 10.1039/C1CP20751B.
[3] W. Caminati, S. Melandri, A. Maris and P. Ottaviani, *Angew. Chem. Int. Ed. 45*, **2006**, 2438.
[4] L. Evangelisti, G. Feng, P. Ècija, E.J. Cocinero, F. Castaño and W. Caminati, *Angew. Chem. Int. Ed., accepted*.

FIS-OR-38 Detailed Characterization of the Dynamics of Organic Molecules in the Solid State: a Multi-Technique NMR Approach

Elisa Carignani, Silvia Borsacchi, Marco Geppi

Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
v. Risorgimento 35, 56126 Pisa (Italy)

mg@dcci.unipi.it

The molecular dynamics of a solid drug strongly affects its pharmaceutical properties and other important characteristics, such as solid state reactions and degradations. Moreover, it plays an important role in drug-excipient interactions, in turn significantly affecting the drug release properties.

Solid State Nuclear Magnetic Resonance (SSNMR) is one of the most powerful techniques to investigate molecular dynamics of organic molecules, since it offers several approaches to study motions over a wide range of frequencies [1]. In order to monitor the widest possible range of frequencies and to get the most detailed information about individual motional processes, a variety of techniques must be applied and the results simultaneously analyzed. In our approach we combined: ^{13}C and ^{1}H longitudinal relaxation times (T_1) to investigate fast motional processes, with characteristic frequencies (ν_C) of the order of MHz; ^{13}C and ^{1}H longitudinal relaxation times in rotating frame ($T_{1\rho}$), ^{1}H T_1 dispersion curves, and ^{13}C line shape analysis (both arising from chemical shift anisotropy and MAS spectra) to investigate the intermediate motional regime (ν_C of the order of kHz), while insights about the slow motional regime (ν_C of the order of 1 kHz or less) could be obtained from exchange effects occurring in ^{13}C high-resolution spectra. In particular, this approach was applied to the characterization of the dynamic properties of two forms of ibuprofen, acid (IBU-A) and sodium salt (IBU-S), which, from a preliminary previous work [2], were found to exhibit different dynamic behaviour, in spite of their very similar chemical structure. The combined analysis of all the data allowed the identification and the detailed characterization, in terms of correlation times and activation energies, of all the reorientational and interconformational motions, such as the π-flip of the phenyl rings, the reorientation of methyl groups and aliphatic chains, as well as the π-flip of the dimeric structure formed by the acidic groups in IBU-A [3, 4].

[1] M.Geppi, G.Mollica, S.Borsacchi, C.A.Veracini, *Appl. Spectrosc. Rev.*, *43*, **2008**, 202.
[2] M.Geppi, S.Guccione, G.Mollica, R.Pignatello, C.A.Veracini, *Pharm. Res.*, *22*, **2005**, 1544.
[3] E.Carignani, S.Borsacchi, M.Geppi, *Chem. Phys. Chem.*, *12*, **2011**, 974.
[4] E.Carignani, S.Borsacchi, M.Geppi, *J. Phys. Chem. A*, submitted.

FIS-OR-39 Proton transfer in homo- and hetero-dimers of carboxylic acids: Precise information from the rotational spectra.

Gang Feng,[a] Laura B. Favero,[b] Assimo Maris,[a] Annalisa Vigorito,[a] Luca Evangelisti,[a] Patricia Écija,[c] Emilio J. Cocinero,[c] Fernando Castaño,[c] Walther Caminati[a]

[a] Department of Chemistry, University of Bologna, Via Selmi 2, I-40126, Bologna, Italy.
[b] Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, Via Gobetti 101, I-40129 Bologna, Italy.
[c] Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Apartado 644, E-48080 Bilbao, (Spain)

E-mail: walther.caminati@unibo.it

Tunneling effects have been measured in the pulsed jet Fourier transform microwave spectra of two isotopologues of the benzoic acid-formic acid bi-molecule and of four isotopologues of the dimer of acrylic acid. The dimer of acrylic acid can exist in two forms, depending on the *entgegen* or *zusammen* orientations of the two allyl groups. The latter one (*zusammen*) has a permanent value of the μ_b dipole moment component, which allowed to measure its pulsed jet Fourier transform microwave (MW) spectrum (see Figure 1). From the tunneling splittings originated by the concerted proton transfer of the two carboxylic hydrogens, measured for the various isotopologues of the two bi-molecule, we could size the barrier and the dynamics of the proton transfer.

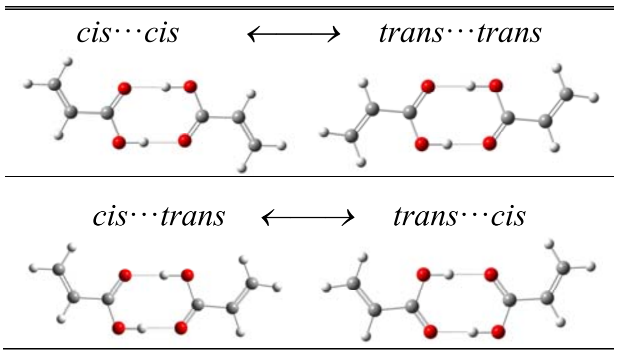


Figure 1. Homo-conformational dimers of AA (s-cis···s-cis, s-trans···s-trans) are non-polar, while hetero-conformational dimers

By applying a suitable flexible model to the experimental tunnelling splittings it has been possible to determine the barrier to the double proton exchange; In addition, from the ratios between the tunnelling splittings measured for the various H/D species, we could estimate the dynamics of the skeletal structural relaxation.

FIS-PO-01 The strange world of polyprotic inorganic acids

Emiliano Fratini,[a] Antonio Faraone,[b,c] Achim Müller,[d] Piero Baglioni[a]

[a]Department of Chemistry and CSGI, University of Florence, via della Lastruccia 3, 50019, Florence, Italy
[b]NIST Center for Neutron Research, 100 Bureau Drive, Gaithersburg, , MD, US
[c]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, US
[d]Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany
baglioni@csgi.unifi.it

Recent results on polyprotic inorganic acids, $\{Mo_{72}X_{30}(H_2O)_{91}\}$~$150H_2O$ (X=Fe, Cr, V , see fig.1 right) are presented, with emphasis on water dynamics and self-assemblies properties.

The dynamics of the crystal water in the voids between the well-defined and arrayed nanocages is significantly slower than that of bulk water at the same temperature. Our data show a non-Debye relaxation behavior originating from a distribution of relaxation times, probably related to the different local environments experienced by the water molecules. In the investigated range the temperature dependence of the relaxation time can be described in terms of an Arrhenius law (E_a=47.3 kJ/mol), indicating that the dynamics is triggered by breaking of the bonds connecting the crystal water molecules with the hydrophilic nanocage surfaces. Interestingly, in the case of $\{Mo_{72}Cr_{30}\}$ it was possible to decouple the dynamics of the in-cage water from the total while the presence of V in $\{Mo_{72}V_{30}\}$ allowed the monitoring of the dynamics of the inorganic cage itself.[2]

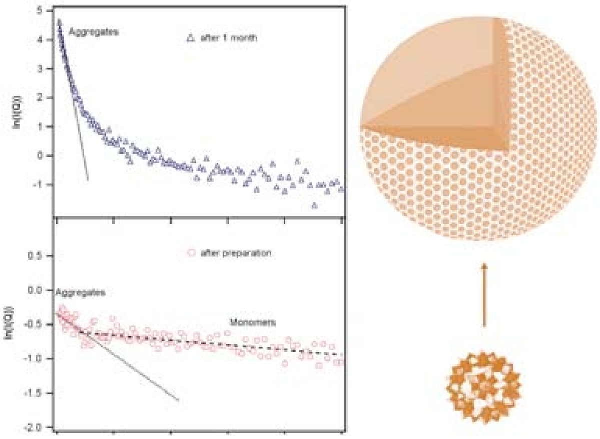


Figure 1. Left) 1-month evolution of the SAXS pattern **Right)** Sketch of the monomer to "blackberry" transition.

Small angle X-ray scattering on freshly prepared aqueous solution evidences the presence of hollow nanostructructures 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.[3] 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.

[1] A. Faraone, E. Fratini, A.M. Todea, B. Krebs, A. Muller, P. Baglioni, *Journal of Physical Chemistry C, 113,* **2009**, 8635-8644.
[2] A. Faraone, E. Fratini, A. Muller, P. Baglioni, manuscript in preparation.
[3] E. Fratini, A. Faraone, A.M. Todea, P. Baglioni, *Inorganica Chimica Acta, 363,* **2010**, 4234-4239.

FIS-PO-02 Bis-Histidyl coordination in tetrameric hemoglobins: Cold-adapted fish hemoglobins *versus* human hemoglobin

A. Balsamo,[1] **A. Merlino**,[1,2] **L. Tutino**,[3] **E. Parrilli**,[3] **L. Mazzarella**, [1,2] **A. Vergara**[1,2]

[1]Department of Chemistry 'Paolo Corradini', University of Naples, Naples, Italy
[2] Institute of Biostructures and Bioimaging, CNR, Naples, Italy
[3]Department of Organic Chemistry and Biochemistry, University of Naples, Naples, Italy
**avergara@unina.it*

All tetrameric hemoglobins from the Antarctic fish, included *Trematomus bernacchii*, HbTb, in its ferric state promptly, and distinctively from all the other tetrameric hemoglobins, form a mixture of aquo-met at the α subunits and bis-histidyl adduct (hemichrome) at the β subunits [1,2]. The role of the tertiary and quaternary structure in the hemichrome formation in HbTb is still unknown. Here we report the cloning, expression, purification, spectroscopic and computational characterization of the β-chain of HbTb (Tbβ), along with a novel crystallographic determination of the ferric β-chain of human Hb (β_4-HbA). As β_4-HbA [3,4, Tbβ self assembles to form a β_4 homotetramer, but, differently from β_4-HbA, Tbβ forms quantitatively a reversible bis-histidyl adduct in the ferric state. Indeed, the herein presented crystal structure of the ferric β_4-HbA hosts an aquo-met coordination in all the four independent chains, and not hemichrome. A molecular dynamics study on the isolated β-subunit of HbTb indicates that the ability to form hemichrome is an intrinsic feature of Tbβ chain, probably due to the higher flexibility of this chain with respect to that HbA. Differently from HbTb $\alpha_2\beta_2$ heterotetramer [5,6], Tbβ forms a bis-histidyl adduct also in the ferrous state (hemochrome). On the basis of these experimental, crystallographic and computational results, the effect of the quaternary assembly on the stability of the ferrous and ferric endogenous hexa-coordination is presented.

We acknowledge PNRA and PRIN for financial support

[1] A. Merlino, L. Vitagliano, B. Howes, C.Verde, G. di Prisco, G. Smulevich, F. Sica, and A. Vergara, *Biopolymers*, **2009**, 91, 1117.

[2] A.Vergara, M. Franzese, A. Merlino, L.Vitagliano, G. di Prisco, C.Verde, H.C. Lee, J. Peisach, and L. Mazzarella, *Biophys. J.* **2007**, 93, 2822.

[3] E.A. Rachmilewitz, J. Peisach, and W.E. Blumberg, *J. Biol. Chem.* **1971**, 246, 3356.

[4] K. Shikama, Chem. Rev. **1998**, 98, 1357.

[5] A. Vergara, L. Vitagliano, A. Merlino, F. Sica, K. Marino, C. Verde, G. di Prisco, and L. Mazzarella, *J. Biol. Chem.* **2010**, 285, 32568.

[6] L. Mazzarella, A. Vergara, L. Vitagliano, A. Merlino, G. Bonomi, S. Scala, C. Verde, and G. di Prisco, *Proteins* **2006**, 65, 490.

FIS-PO-03 Insights on the homocoupling reaction of 4-methylamino benzoic acid mediated by *Trametes versicolor* laccase

M. C. Baratto, A. Martorana, C. Bernini, D. Valensin, A. Sinicropi, R. Pogni and R. Basosi

Dipartimento di Chimica, Università di Siena, Via A. De Gasperi 2, 53100 Siena, Italia
baratto@unisi.it

Studies on eco-friendly oxidation processes represent an important alternative in the synthetic reactions. The potential benefits of utilizing enzymes in industrial processes arise from their activity under mild conditions of temperature, pH and pressure, compared to inorganic catalysts [1]. Enzyme-catalysed oxidations in the presence of air as co-substrate, such as laccases work, are low cost reactions that use non-toxic reagents in aqueous solutions. These enzymes belong to the multicopper oxidases which are able to catalyze the one-electron oxidation of a wide variety of organic compounds, including mono-, di- and polyphenols, aminophenols, methoxyphenols, aromatic amines with the concomitant four-electron reduction of oxygen to water [2,3]. In recent years the coupling activity of the laccase-precursor system has been widely used in the synthesis of novel compounds and materials [4]. In this work we investigate the synthetic reaction starting from the precursor molecule 4-methylamino benzoic acid catalysed by the *Trametes versicolor* laccase. The study concerns a multidisciplinary research approach, where a variety of spectroscopic measurements (EPR, NMR, UV-Vis) combined with Density Functional Theory (DFT) calculations have been applied to understand the reaction mechanism. The attempt was to synthesize a new azo-dye. The biocatalytic reaction gave as the main final product a polymer containing a secondary amine function with a single N-N bond. This represents a novel example of the homocoupling reaction mediated by laccase [5].

[1] S. Ncanana, S. Burton, *J. Mol. Cat. B: Enzymatic*, 2007, 44, 66-71
[2] S. Burton, *Curr. Org. Chem.*, 2003, 7, 1317
[3] B. Brogioni, D. Biglino, A. Sinicropi, E.J. Reijerse, P. Giardina, G. Sannia, W. Lubitz, R. Basosi, R. Pogni, *PCCP*, 2008, 10, 7284
[4] S. Forte, J. Polak, D. Valensin, M. Taddei, R. Basosi, S. Vanhulle, A. J. Wilkolazka, R. Pogni, *J. Mol. Cat. B: Enzymatic*, 2010, 63, 116
[5] A. Mikolasch, F. Schauer, *Appl. Microbiol Biotechnol*, 2009, 82, 605

This work has been supported by CSGI (Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase), the BISCOL European Project (ECO/09/256112) and the CINECA (for granted calculation time).

FIS-PO-04 Dynamics of methane accumulation in the Hearth atmosphere.

<u>Guido Barone</u>[a], **Elena Chianese**[b], **Angelo Riccio**[c]

[a]Department of Chemistry, University of Naples Federico II, Via Cintia, Monte S. Angelo, 80126 Naples, Italy*:*
[b]Department of Environmental Sciences "Parthenope" University, Centro Direz. Isola C4, 80134, Naples Italy
[c]Department of Applied Sciences, "Parthenope" University, Centro Direz. Isola C4, 80134, Naples Italy.
E-mail: guido.barone@unina.it

During the last century the methane content of the atmosphere, increased as never occurred in the last 800,000 years. Note that methane is much more effective (25 times) than CO_2 [1]. The increasing concentration of methane in the atmosphere, indeed, could influence the future of the climate by means of non linear positive and dangerous feedback, with the risk of the achievement of a no-return threshold, beyond which the Global Warming (GW) become out of human control. This is made easier promoted by the increasing of the same GW on the dynamics of emission processes from the natural sources (destabilization of hydrates, stimulation of metabolic production by plants and animals, etc.) and by the leaks of gas during the extraction and management activities. The methane concentration in the atmosphere is 780 at the end of 19° Century. At present it achieved 1787 ppbv at 2008 [2]. Conspicuous emissions of methane were recently observed from the Arctic and were attributed to the anaerobic decomposition of organic sediments on the deep of marshes due to the fusion of permafrost [3]**.** Also unexpected methane flows were observed during the 2010 year from the Central and Eastern Siberian Seas [4]**. T**he decomposition of the methane hydrates in this case seems more convincing [5]. The residence times of each Green House gas affect differently the Radiation Forcing (RF) power, then the GW. The methane concentration in the atmosphere is regulated by the dynamical interplay between sources and sinks. The lifetime of CH_4 is mainly limited by the reactions with the (OH) radicals and is estimated 9.6 years. A recent detailed analysis of the contributions to the GW due to the methane emissions from the Arctic has been published [6]. The conclusions are impressive as it is forecast an increase of the RF of 0.6 Wm^{-2} on a Time Horizon of 50 years for the methane increase alone,

[1] United States Environmental Protection Agency [U.S. EPA], **2010**.
[2] Dlugokencky, E. J. & Bruhwiler, L. (2009). *Geophys. Res. Lett.*, 36. **2009**
[3] Walter, K. M.; Smith, L. C. & Chapin III, F. S.. *Phil. Trans. R. Soc.*, 365, **2007**,1657-1676.
[4] Shakhova, N.; Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D. & Gustafsson, O. *Science,* 327, **2010.** 1246-1250.
[5] Barone, G. & Chianese, E. *ChemSusChem*, 2, **2009**, 992-1008.
[6]Isaksen, I.S.A., Gauss M., Myhre G., Walter Antony K.M., Ruppel C. *Global Biogeochem. Cycles,* 25, **2011,** 1-11.

FIS-PO-05 Plant oil bodies as nano/microcarriers to deliver natural polyphenols for anti-cancer therapy

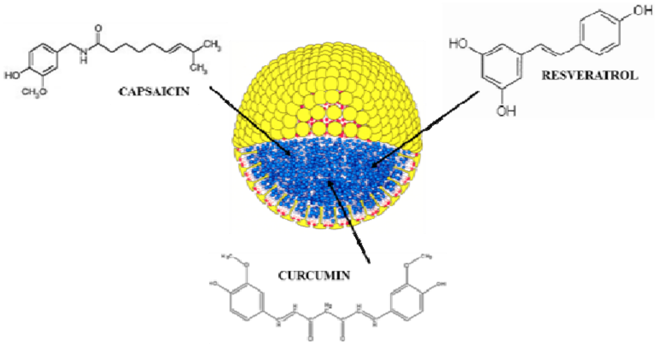
[a]S. Bettini; [b]D. Vergara; [c]S. Bonsegna; [b]M. Maffia; [c]A. Santino; [a]L. Valli.

[a]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, 73100 Lecce, Italy;
[b]Laboratory of General Physiology, Department of Biological and Environmental Science and Technology, University of Salento, S.P. 6, Lecce – Monteroni, 73100 Lecce, Italy;
[c]Institute of Sciences of Food Production CNR Unit of Lecce, Via Monteroni, 73100 Lecce, Italy.
simona.bettini@unisalento.it

Oil bodies (OBs) are specialized organelles ubiquitously detected in plant oil seeds, that serve as lipid storage compartments. OBs consist of a hydrophobic core of triacylglycerol (TAGs), surrounded by a monolayer of phospholipids (PLs) with some specific embedded proteins, including oleosins and some minor proteins, i.e. caleosin and steroleosin. The diameter of OBs range from 0.5 to 2 μm [1-2]. In order to demonstrate that OBs could have potential applications as micro\nano carriers to deliver hydrophobic drugs, we developed an easy method to reconstitute OBs, of similar shape to the natural ones, starting from their natural constituents and some structural proteins[3].

The aim of this work was to efficiently encapsulate into reconstituted OBs a series of polyphenols, with well-known anti-cancer properties, but with poor intestinal absorption. We first verified the effects of some different polyphenols on the vitality of ovarian cancer cell lines.

This allowed us to identify some natural compounds with promising anti-proliferative/pro-apoptotic activities. Selected polyphenols were then efficiently encapsulated either singly or in pairs into artificial oil bodies and were used to monitor their uptake into the ovarian cancer cell lines.



Our results indicated that OBs could act as novel carriers to deliver hydrophobic bioactive compounds and that the therapeutic effects of encapsulated natural polyphenols are similar or even stronger than those of the free drug.

[1] N.J. Roberts; R.W. Scott; J.T.C. Tzen *Open. Biotechnol. J.* **2008**, 2, 13-21;
[2] F. Capuano; F. Beaudoin; J.A. Napier; P. R. Shewry *Biotechnol. Adv.* **2007**, 25, 203-206;
[3] S. Bonsegna; S. Bettini, R. Pagano, A. Zacheo, V. Vergaro, G. Giovinazzo, G.Caminati; S. Leporatti; L. Valli; A. Santino *Appl. Biochem. Biotechnol.* **2011**, 163, 792-802.

FIS-PO-06 Sensitization of nanostructured electrodes with colloidal CdSe nanocrystals towards nanocrystal based solar cells

Binetti E.[a], Ingrosso C.[b], Tamborra M.[c], Panniello A.[c], Tena-Zaera R.[d], Agostiano A.[a,c], Curri M.L.[c], Striccoli M.[c]

[a] University "Aldo Moro" of Bari, Via Orabona 4, 70126 Bari, Italy.
[b] CNR-IMM, Strada Prov. Lecce-Monteroni km 1,200, 73100 Lecce, Italy
[c] CNR-IPCF, Dept. of Chemistry, Via Orabona 4, 70126 Bari, Italy
[d] New Materials Department, CIDETEC, Centre for Electrochemical Technologies, Paseo Miramon 196, Donostia-San Sebastian 20009, Spain
E-mail: e.binetti@ba.ipcf.cnr.it

In the last years, a growing interest has been addressed to innovative and economic solar cells. Among this class of devices, the most promising are the photoelectrochemical cells, also called sensitized solar cells, whose main part is a photoactive anode which provide to absorb light and transport photogenerated electrons. Such an electrode is made of a conductive and transparent substrate, covered with a thin-film of a wide-gap semiconductor, such as TiO_2 or ZnO, sensitized with a low-gap dye material, such as small molecules, metal-complexes or semiconductor nanocrystals. The use of semiconductor NCs in lieu of widely-used photosensitive dyes can provide an enhancement of the conversion efficiency in solar cells, due to the large NC extinction coefficients, the multiple exciton generation phenomenon[1] and their intrinsic stability.
Here, colloidal CdSe NCs, 5.5 nm in diameter, were used to sensitize two kinds of nanostructured electrodes, made respectively of TiO_2 nanoparticles, deposited by means of a doctor-blade technique, and ZnO nanowires electrochemically grown on ZnO thin-film[2]. CdSe NCs were synthesized as reported by Peng et al.[1], in presence of a mixture of three long-chain capping agents, which allowed an high control on NC size and shape, and make NCs dispersible in organic solvents. Two different strategies were tested for the electrode sensitization, namely the direct absorption and the linker-mediated absorption. In the last method, pristine CdSe capping agents were replaced with cysteine molecules, which are short chain three-functional organic ligand, able to link NCs to the ZnO electrode and allow an effective charge transfer between NCs and oxide. Sensitized electrodes were characterized by means of steady-state absorption and PL spectroscopy, confocal microscopy and scanning electron microscopy (SEM) investigations. A promising electrode sensitization degree has been obtained.

1. Peng et al., Nature 2000, 404 (6773), 59-61.
2. Tena-Zaera, R. et a., J. Phys. Chem. C 2007, 111 (45), 16706-16711.

This work has been partially supported by the EU 7th Framework Programme ORION project (229036).

FIS-PO-07 Characterization of the self-assembly of 8-armed amphiphilic star block copolymers in water by NMR spectroscopy

Sytze J. Buwalda,[a] Lucia Calucci,[b] Pieter J. Dijkstra,[a] Claudia Forte[b]

[a] Department of Polymer Chemistry and Biomaterials, Faculty of Science and Technology, MIRA Institute for Biomedical Technology and Technical Medicine, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.
[b] Istituto di Chimica dei Composti OrganoMetallici, CNR-Consiglio Nazionale delle Ricerche, Area della Ricerca di Pisa, via G. Moruzzi 1, 56124, Pisa, Italy.
lucia.calucci@pi.iccom.cnr.it

Self-assembly of amphiphilic block copolymers in water has been exploited to prepare physically cross-linked hydrogels of interest for biomedical applications. Indeed, at low concentration micellar aggregates form by association of the hydrophobic copolymer blocks, while at high concentration inter-micellar hydrophobic interactions give rise to networks. In recent years 8-armed star block copolymers, having poly(ethylene glicol) (PEG) as the hydrophilic polymer in the inner part, and hydrophobic polyesters, such as poly(lactide) (PLA), poly(ε-caprolactone) (PCL), and poly(trimethylene carbonate) (PTMC), as the outer chains have been extensively investigated, thanks to their ability to yield physically cross-linked hydrogels at much lower concentration compared with linear di- and triblock copolymers. It has been found that the hydrogel mechanical properties and stability to degradation are strongly dependent on the interactions governing self-assembly, in turn influenced by the degree of polymerization, the hydrophobicity, and the stereochemistry of the hydrophobic blocks. Therefore, a molecular-level investigation of the structural and dynamic properties of the polymeric components in water is of fundamental importance for the comprehension of self-assembly for these systems. In this respect, the application of suitable Nuclear Magnetic Resonance (NMR) techniques in solution and in the solid state reveals valuable. In this work representative examples of applications of NMR experiments to the investigation of the self-assembly of 8-armed PEG-PLA and PEG-PTMC copolymers are presented [1-4].

[1] L. Calucci, C. Forte, S.J. Buwalda, P.J. Dijkstra, J. Feijen, *Langmuir,* 26, **2010**, 12890.
[2] S.J. Buwalda, L.B. Perez, S. Teixeira, L. Calucci, C. Forte, J. Feijen, P.J. Dijkstra, *Biomacromolecules*, DOI: 10.1021/bm200515h.
[3] S.J. Buwalda, L. Calucci, C. Forte, P.J. Dijkstra, J. Feijen, *Soft Matter*, submitted.
[4] L. Calucci, C. Forte, S.J. Buwalda, P.J. Dijkstra, *Macromolecules*, submitted.

FIS-PO-08 Factors determining the superior performance of lipid/DNA/protammine nanoparticles over Lipoplexes

Giulio Caracciolo,[a] Anna Laura Capriotti,[b] Aldo Laganà,[b] Daniela Pozzi,[a] Michelle A. Digman,[c] E. Gratton[c]

[a] Dipartimento di Medicina Molecolare della Sapienza Università di Roma, Viale Regina Elena, 324, 00161, Rome, Italy
[b] Dipartimento di Chimica della Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy
[c]Laboratory for Fluorescence Dynamics, Department of Biomedical Engineering, University of California, Irvine, 3120 Natural Sciences 2, Irvine, California 92697-2715, United States

giulio.caracciolo@uniroma1.it

The utility of using a protammine/DNA complex coated by a lipid envelope made of cationic 1,2-dioleoyl-3-trimethylammonium propane (DOTAP) for transfecting CHO (Chinese hamster ovary cells), HEK293 (human embryonic kidney cells), NIH 3T3 (mouse embryonal cells) and A17 (murine cancer cells) cells was examined. The widely used DOTAP/DNA lipoplex was employed as a reference. In all the tested cell lines lipid/protamine/DNA (LPD) nanoparticles were more efficient in transfecting cells than lipoplexes even though the lipid composition of the lipid envelope was the same in both devices. Physical-chemical properties were found to control the ability of nanocarriers to release DNA upon interaction with cellular membranes. LPD complexes easily release their DNA payload, while lipoplexes remain largely intact, and accumulate at the cell nucleus. Collectively, these data explain why LPD nanoparticles do often exhibit superior performances compared to lipoplexes in trasfecting cells and represent a promising class of nanocarriers for gene delivery.

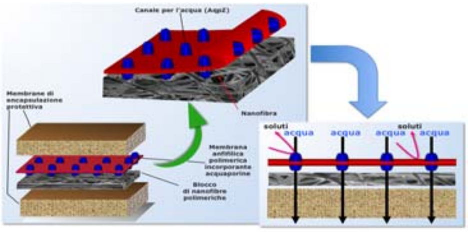
FIS-PO-09 A novel bionanotechnological approach for water filtration

G. Calamita,[a,b] A. Camposeo,[a,c] S. Casilli,[a] G. Farinola,[a,d] S. Girardo,[a] G. Iacobellis,[a] M. Pellegrini-Calace,[a] D. Pisignano,[a,c,e] L. Valli[a,e]
serena.casilli@unisalento.it

[a]Rete di Laboratori Pubblici di Ricerca della Regione Puglia, WAFITECH; [b]Dipartimento di Fisiologia Generale ed Ambientale, Università di Bari *Aldo Moro*, Campus Universitario, Via Amendola 165/A, 70126, Bari, Italy; [d]Dipartimento di Chimica, Università di Bari *Aldo Moro*, Campus Universitario, Via E. Orabona n.4, 70125, Bari, Italy; [c] National Nanotechnology Laboratory-Istituto Nanoscienze-CNR, Via per Arnesano 16, 73100, Lecce, Italy; [e]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via per Arnesano, Edificio La Stecca, 73100, Lecce, Italy.

Le acquaporine (AQP) sono canali di natura proteica che mediano il flusso di acqua attraverso le membrane biologiche. Sotto l'azione di gradienti osmotici, ogni singolo poro formato da AQP può trasportare miliardi di molecole di acqua per secondo. Tale straordinaria peculiarità rende le AQP uniche in natura offrendo notevolissime potenzialità di tipo applicativo. Ciò ci ha suggerito la progettazione e realizzazione di membrane biomimetiche incorporanti AQP, con applicazioni basate sulla filtrazione dell'acqua, come la dissalazione dell'acqua a scopi potabili, il trattamento e riciclo di acque reflue, la produzione di acqua ultrapura, la dialisi ed il *drug delivery* e la produzione di energia ecosostenibile da gradienti di salinità.

Il primo stadio della ricerca è stato la preparazione su larga scala di AQP ricombinanti e, successivamente, di membrane artificiali. Quindi, per l'incorporazione funzionale delle AQP in membrane selettive, resistenti ed economiche sono stati progettati, sintetizzati e caratterizzati nuovi copolimeri [ad es., polimetil ossiazolina(block)PDMS (block)polimetil ossiazolina]. Questi copolimeri sono stati trasferiti via tecnica di Langmuir-Blodgett sia attraverso co-deposizione sia attraverso l'utilizzazione diretta di proteoliposomi su supporti solidi con una struttura composta da un substrato in vetro, un film sottile di polimetilmetacrilato (PMMA) sul quale sono depositate nanofibre di PMMA, realizzate per elettrospinning.



FIS-PO-10 Surface features and interfacial behaviour towards proteins of engineered silica nanoparticles

Catalano F., Alberto G., Coluccia S., Martra G.

Department of IPM Chemistry and NIS Centre of Excellence, University of Torino,
Via Giuria 7, 10125, Turin, Italy,
salvatore.coluccia@unito.it

Silica based/coated nanoparticels (NPs) are an emerging tool in nanobiotechnology. Among the various preparation methods, polymerization in microemulsion of reverse micelles results in spherical NPs highly homogeneous in size, with relevant advantages in behaviour homogeneity in both cell-free and cell tests and applications. Most part of the performances of such NPs in biological media are ruled by their surface/interface features, that have been the subject of this work. The converging use of different methodologies (HR-TEM, Z-potential, Dynamic Light Scattering, FT-IR, BET, TGA) made allowance to establish that NPs (50±2 nm in size; monodispersed in water) exhibit a structured, highly hydroxylated surface, where all silanols are engaged in H-bonding with neighbour –OH. Such a rich hydroxyl layer appeared poorly active towards Bovine Serum Albumin (BSA) adsorption (ca. 50% of the theoretical side-on momolayer), producing a thin, incomplete corona around the silica core. Moreover, by *in situ* FT-IR ATR and UV-Circular Dichroism, it was found that adsorbed BSA underwent severe modifications in terms of both tertiary and secondary structure.

FIS-PO-11 Nanostructured semiconductors in photocatalytic processes for protection of stone materials

V. Margiotta,[a] F. Petronella,[a] A. Pagliarulo,[a] A. Licciulli[c,] A. Rocca[d,] D. Diso[d], A.Calia [e], M. Lettieri [e], D.Colangiuli [e], A. Agostiano,[a,b] M. Lucia Curri,[b] R. Comparelli[b]

[a]Università degli Studi di Bari – Dipartimento di Chimica, Via Orabona 4, 70126, Bari, Italy
[b]CNR-IPCF, c/o Dipartimento di Chimica, Via Orabona 4, 70126, Bari, Italy
[c] Università degli Studi del Salento, via per Arnesano 73100 Lecce
[d] Salentec srl, Via dell'Esercito 8, 73020 Cavallino, Le, Italy
[e] CNR-IBAM, Prov.le Lecce Monteroni, 73100 Lecce
r.comparelli@ba.ipcf.cnr.it

Under UV irradiation TiO_2 exhibits photocatalytic activity leading to the degradation of a wide range of organic pollutants resulting in self-cleaning effect.[1] Owing to their high surface to volume ratio nanostructured TiO_2 catalysts exhibit a photoactivity higher than their bulk counterpart. Moreover, the possibility to tune the band gap and the redox potential as a function of size and shape, is expected to improve the interface charge transfer enhancing their photocatalytic activity.[2]

The application of TiO_2 coatings on stone has been investigated in order to provide surface protection and self-cleaning properties. Several synthetic approaches (namely hot injection, sol-gel and hydrothermal nanophase crystallisation) were used to synthesise colloidal TiO_2 nanocrystal differing in size, shape and surface chemistry. The obtained nanocrystals (NCs) were characterized from optical and morphological point of view and subsequently deposited onto two different kinds of stone (calcarenite and limestone, as example of porous and compact stone, respectively) without any post-deposition thermal curing.

A morphological and physical characterisation was carried out both on coated and uncoated stone, in order to elucidate the TiO_2 NC film distribution, and evaluate possible colour change, water absorption phenomena as well as water vapour permeability of the investigated materials.

The self-cleaning properties of the coated surfaces were evaluated under solar irradiation (radiating source: Solar Light Simulator) using an organic dye as target compound.

The obtained results suggest that the nanocrystalline TiO_2 coating seems good candidate for environmental protection of stone materials.

[1] A. Fujishima, X. Zhang, D.A. Tryk, *Surf. Sci. Rep.,* 63, **2008**, 515.
[2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.,* 95 **1995**, 69.

FIS-PO-12 Bio-conjugation of Semiconductor Nanocrystals in PEG-Modified Phospholipid Micelles for bio-medical application

Nicoletta Depalo,[1,2] Pasquale Carrieri,[2] Roberto Comparelli,[1] Marinella Striccoli,[1] Angela Agostiano,[1,2] Luca Bertinetti,[3] Claudia Innocenti,[4] Claudio Sangregorio,[5] M. Lucia Curri[1]

[1] IPCF-CNR Bari division Via Orabona 4 Bari, 70126 (Italy)
[2] Department of Chemistry-University of Bari, Via Orabona 4, Bari, 70126 (Italy)
[3]Dipartimento di Chimica IFM e NIS Center of Excellence, Università degli studi di Torino, V. Giuria 7, 10125 Torino (Italy)
[4]Dipartimento di Chimica, Università di Firenze and INSTM, via della Lastruccia 3, I-50019 Sesto Fiorentino (Italy)
[5]CNR-ISTM via C. Golgi 19, I-20133 Milano (Italy)
n.depalo@ba.ipcf.cnr.it

The design of artificial bioconjugated nanocrystals (NCs) remains an attractive and important research area for bio-imaging, bio-labeling, and bio-sensing applications. Recent advance in colloidal synthesis have opened the possibility of producing hydrophobic NCs with very elaborated shapes and with different composition.[1] Despite its success in obtaining an excellent control on size, shape and crystallinity, the colloidal synthetic approach typically produces NCs with hydrophobic surfaces. Therefore, their surface chemistry has to be conveniently manipulated to promote their water solubility and to provide a conjugation moiety for a targeting ligand. In this work, organic capped NCs, namely magnetic or photoactive oxides (Iron Oxide and TiO_2, respectively) and binary asymmetric nanocrystals formed by a spherical γ-Fe_2O_3 magnetic domain epitaxially grown onto a lateral facet of a rodlike anatase TiO_2 (BNCs), have been incorporated into water dispersible block copolymer micelles composed of polyethylene glycol modified phospholipids (PEG lipids).[2] The obtained water soluble NC including PEG lipid micelles have been successfully covalently bound to BSA. Each step has been thoroughly monitored by using optical, structural and electrophoretic techniques. DLS measurements have proved that the obtained NC/micelles and BSA/NC conjugates, with a hydrodynamic diameter smaller than 100 nm, are homogeneously dispersed and sufficiently stable in aqueous solution. The magnetic characteristics of the Iron Oxide NCs and BNCs, before and after incorporation in PEG lipid micelles and subsequently to the bio-conjugation, are mostly retained. The proposed approach to achieve water soluble anisotropic BNCs and their bioconjugates could have a large potential in catalysis and biomedicine, and offers key functional building blocks for biosensor applications.

[1] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem Rev., 105*, **2005**, 1025.
[2] N. Depalo, P. Carrieri, R. Comparelli, M. Striccoli, A. Agostiano, L. Bertinetti, C. Innocenti, C. Sangregorio, M. L. Curri, *Langmuir*, *27*, **2011**, 6962.

FIS-PO-13 Formation of ROS by Photosyntentic Pigment/Cyclodextrin Inclusion Complexes

A. Agostiano[a, b], B. M. Cellamare[a], P. Fini[b] and P. Cosma[a, b]

[a] Dipartimento di Chimica, Università degli Studi "Aldo Moro" di Bari, via Orabona 4, I-70126 Bari, Italy
[a] Istituto per i Processi Chimico Fisici CNR, sez. Bari, via Orabona 4, I-70126 Bari, Italy
agostiano@chimica.uniba.it

Photodynamic therapy (PDT) is a treating modality of malignant tumours and hyperproliferative diseases. It is based on the use of photosensitizer (PS), herein the chlorophyll a, and a light having appropriate wavelength. The interaction of the PS with the light produce ROS, reactive oxygen species, a powerful oxidizing agents that cause critical damage to the tissue.

In order to solubilize in aqueous solution chlorophyll a and to obtain it as monomer, we have used cyclodextrins, carriers which are able to interact with the pigment and form the inclusion complex.

The aim of this work is to examine which type of ROS are formed in the system using specific molecules, named primary acceptor, that react selectively with the reactive species. In fact the changes of the absorption and the emission spectra of this molecules after the illumination of the PS provide information on the specific ROS formation. Uric acid, 9,10-diphenilanthracene and singlet oxygen sensor green have been used as primary acceptors in order to verify the formation of the $^1O_2$. Moreover 2,7-dichlorofluorescin and ferricytochrome c have been used to detect the formation of the hydrogen peroxide and superoxide radical anion that reduces Fe^{3+} of the ferricytchrome to Fe^{2+}, respectively.

FIS-PO-14 Investigation of laser-induced degradation mechanism by micro-Raman spectroscopy and thermal analysis of some pigments and alteration products

Giorgio A. Costa[a], M. Maddalena Carnasciali[a,b], Enrico Franceschi[a,b], Marina Rui[a], Serena Campodonico[a,b], Federico Locardi[a], Dion Nole[a].
[a]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genoa, Italy;
[b] INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Via G. Giusti 9, 50121 Florence, Italy. *Email: costa@chimica.unige.it*

In order to contribute to the improvement of restoration and conservation science of artworks belonging to the Cultural Heritage, this paper allows to investigate the possible degradation induced during micro-Raman analysis owing to the use of laser.

Recently Raman microscopy has been widely developed and applied as a suitable methodology for the identification of pigments, corrosion and alteration products, minerals and other substances in the field of archaeometry and diagnostic analysis.

Anyway, in some cases this technique results micro destructive for some substances or compounds because it can induce thermally phase transitions or decomposition processes. With the aim of evaluate those chemical physical alterations we first identified them through simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC) on standard samples, commercial or prepared *ad hoc* in laboratory, such as copper carbonates, lead oxides [1][2], iron oxides and hydroxides [3][4] and others[5]. Then we tested in which conditions they occur using a micro-Raman spectrometer with a 632.8 nm laser.

Coupling these two techniques it is possible to define the potential applicability of micro-Raman spectroscopy as non destructive method and also avoid ambiguous identifications of compounds.

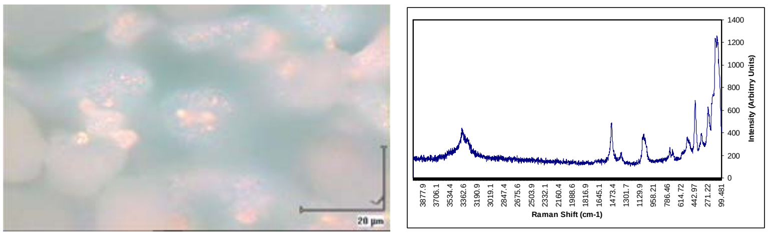


Fig. 2. OM Commercial Malachite 50x (copper carbonate) and micro Raman spectrum at 25% of power.

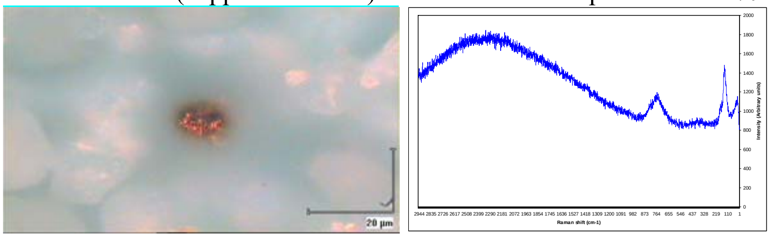


Fig. 3. OM Commercial malachite deterioration after a micro Raman analysis at 50% of power and its spectrum.

[1] K. Gavrichev, A. Bolshakov, D. Kondakov, A. Khoroshilov and S. Denisov, *J. Thermal Analysis and Calorimetry, 92*, **2008**, 857-863.

[2] L. Burgio, R. J. H. Clark and S. Firth, *Analyst*, 126, **2001**, 222–227

[3] D. L. A. de Faria, S. Venancio Silva and M. T. de Oliveira, *J. Raman Spectroscopy, 28*, **1997**, 873-878.

[4] A. Perardi, A. Zoppi and E. Castellucci, *J. Cultural Heritage, 1*, **2000**, S269-S272.

[5] A. De Santis, E. Mattei and C. Pelosi, *J. Raman Spectroscopy,* 38, **2007**, 1368–1378

FIS-PO-15 CdSe nanocrystals – conjugated polymers based nanocomposite for photovoltaic applications: effect of surface chemistry on morphological and spectroscopic properties

A. E. Di Mauro,[1,2] M. Toscanini,[3] S. Destri,[3] A. Agostiano,[1,2] M. L. Curri,[2] M. Striccoli[2]

[1]Università degli Studi di Bari – Dip. Di Chimica,Via Orabona 4, Bari, 70126, Italy
[2]CNR-IPCF-Sez.Bari, c/o Dip. Chimica, Via Orabona 4, Bari; 70126, Italy
[3]ISMAC-CNR –Sez.Milano, Via Bassini 15, Milano, 20133, Italy

Photovoltaic devices based on conjugated organic polymers are promising alternatives to conventional silicon-based technology thanks to their flexibility and low costs. More recently, blend of conjugated polymers and nanocrystals (NCs) of inorganic semiconductors have been investigated for the production of "hybrid solar cells", where NCs, acting as good electron acceptors from polymers, offer high electron mobility or improved spectral coverage, enhancing device efficiency. It is fundamental in the above device to obtain a homogeneous dispersion of NCs in the polymer matrix, to create a high interfacial surface area between the two materials. Self-assembly of rod-coil block copolymer is a potentially elegant path to improve nanosegregation of the blend.
Here we report the preparation and the characterization of nanocomposite materials consisting of semiconducting CdSe NCs and the rod fragment: poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT). The rod polymer has been obtained via two different policondensation reactions, namely Stille and Suzuki. The best results in terms of molecular weight control have been obtained by using the Suzuki pathway. The CdSe NCs have been synthesized via a colloidal chemistry reaction, by using trioctylphosphine oxide (TOPO) as coordinating agent. Hybrid materials have been obtained by mixing an appropriate amount of Cdse NCs chloroform solution with PCPDTBT solution. Thin films of the nanocomposite have been fabricated by spin coating on silicon or glass. In order to modify the interfacial transfer reactions the pristine TOPO ligand has been replaced with pyridine (Py). The surface chemistry of NCs has been investigated by means of ATR-FTIR spectroscopy. Atomic force microscopy (AFM) images of the nanocomposite films clearly demonstrate that Py-treated NCs provide more homogeneous and well-dispersed polymer composites compared with TOPO–capped CdSe NCs. The optical properties of the composite materials have been investigated by means of UV-visible spectroscopy, steady-state and time-resolved photoluminescence spectroscopy. The next step is then to prepare a nanocomposite material, based on rod-coil di-block copolymer having PCPDTBT as functional block.

The support of the EC-funded project ORION (Contract no. NMP-CP-IP 229036-2) is gratefully acknowledged.

FIS-PO-16 Vibrational analysis of trans N-methyl-acetamide in aqueous solution from ab-initio molecular dynamics

Greta Donati[a], **Giuseppe Brancato**[b], **Alessio Petrone**[a], **Vincenzo Barone**[c], **Nadia Rega**[a]

[a]Dipartimento di Chimica "Paolo Corradini", Università di Napoli "Federico II"
[b]Italian Institute of Technology, IIT@NEST, Pisa
[c]Scuola Normale Superiore, Pisa
g.donati@studenti.unina.it, nadia.rega@unina.it

The knowledge of the proteins secondary structure has in the vibrational spectroscopy a valid instrument, structural motifs can be identified by characteristic changes in position and shape of IR or Raman bands, in particular the amide bands (Amide I, Amide II and Amide III) are often used as structural probes.

The basic theoretical approaches to study vibrational spectroscopy are provided by quantum-mechanics (e.g. perturbative approach of the anharmonic treatment [1]), that allows for sophisticated studies of IR and related properties.

Nowadays, we are able to obtain a complementary solution of the vibrational problem by the ab-initio molecular dynamics [2] [3]. Indeed, through the study of the time evolution of the system and the statistical analysis of molecular dynamics trajectories [2] [3] [4] it is feasible to account for finite temperature effects and for the explicit solute-solvent interactions.

We have performed our study on a molecular compound often used to simulate the backbone of proteins: trans N-methyl-acetamide (NMA) in aqueous solution [5] [6] [7]. By the analysis of the obtained trajectories, we have analyzed NMA in water, and then we have extracted NMA clusters to investigate in an accurate way the interactions of the solute with the environment. We have noticed that clusters with three water molecules are representative of the specific interactions involved in the Amide modes solvatochromic shift.

In this way it is possible to reproduce the characteristic amide mode (Amide I, Amide II, Amide III) and to obtain a detailed knowledge of the factors characterizing IR spectroscopy of NMA and the coupling with the solvent of these peculiar modes of peptides.

[1] V.Barone, J.Chem.Phys., 122, 2005, 014108.
[2] A.Strachan, J.Chem.Phys., 120, 2004, 1, 1.
[3] N.Rega, Theor.Chem.Acc., 116, 2006, 347 .
[4] M.MArtinez, M.P. Gaigeot, D.Borgis, and R.Vuilleumier, J.Chem.Phys., 125, 2006, 114106.
[5] M.P.Gaigeot, R.Vuilleumier, M.Sprik, and D.Borgis, J.Chem.Theory.Comput., 1, 2005, 722.
[6] K.Kwac, and M.Cho, J.Chem.Phys., 119, 2003, 4, 2247.
[7] K.Kwac, and M.Cho, J.Chem.Phys., 119, 2001, 4, 2256.

FIS-PO-17 Immobilization of photosynthetic materials onto quartz by a Layer-by-Layer procedure for applications in the detection of herbicides

A. Ventrella,[a] **L. Catucci,**[a, b] **T. Placido,**[a, b] **F. Longobardi,**[a] **A. Agostiano**[a, b, c]

[a]Dip. di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70126 Bari, Italy,
[b]IPCF- CNR, sez. Bari, Via Orabona 4, 70126 Bari, Italy
[c]INSTM, Via G. Giusti 9, 50121 Firenze, Italy
a.ventrella@ba.ipcf.cnr.it

In this work, the Layer-by-Layer (LbL) technique was employed to modify quartz substrates with photosynthetic materials (PMs). In particular, the biomaterials were obtained from the thylakoid membranes of spinach leaves. For performing the LbL, poly(ethyleneimine) (PEI) was used as positively charged polyelectrolyte to be alternated to the biocomponents, so obtaining an increasing number of PEI/PM layers. Due to the optical transparency of quartz, it was possible to analyze the optical properties of the photosynthetic materials, naturally rich in pigments, even after their deposition. The bio-modified substrates were characterized by UV-Vis absorbance and/or fluorescence emission techniques, and the morphological aspects were evaluated by Atomic Force Microscopy. The electron transfer efficiencies of the photosynthetic materials before and after the immobilizations were studied by assays in solution. The multilayers obtained were found to be interestingly able to give electron transfer and the optical signals were found to be proportional to the number of deposited layers until a plateau level. The responses of the multilayers were tested in the presence of a target herbicide at different concentrations, evidencing that the electron transfer activity of the immobilized PMs can be used to detect terbutryn at concentrations higher than 10^{-7}M. Such results are very remarkable, since they open up possibilities to employ LbL multilayers based on PMs to produce biomaterials applicable to energy transduction and environmental fields.

FIS-PO-18 On the Cl···N halogen bond: a microwave spectroscopy study of $CF_3Cl···NH_3$ complex

Gang Feng,[a] **Luca Evangelisti**,[a] **Nicola Gasparini**,[a] **Walther Caminati.**[a]

[a] Department of Chemistry, University of Bologna, Via Selmi 2, I-40126, Bologna, Italy.

E-mail: gang.feng2@unibo.it

The CF_3Cl-NH_3 complex was studied by using pulsed jet Fourier transform microwave spectroscopy.[1] The conformer formed via Cl···N halogen bond was observed. MP2/6-311++G (d, p) level calculation suggested four stable conformers. The global minimum has a conformation formed via a Cl···N halogen bond interaction. The structure and relative stability of these conformers are shown in Figure 1.

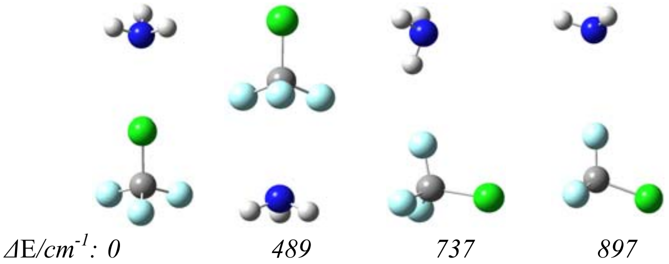


Figure 1. Four stable conformers and their relative energy obtained at MP2/6-311++G (d, p) level calculations.

We investigated first the spectra of the ^{15}N enriched isotopologues, which have simpler spectra respect to those of the ^{14}N isotopologues, because, according to the nuclear spin quantum numbers [$I(^{15}N) = 1/2$, $I(^{14}N) = 1$], is free from quadrupole hyperfine structures. Then, ^{14}N and full deuterated ammonia isotopologues were studied.

Rotational, centrifugal distortion and quadrupole (^{35}Cl, ^{37}Cl, ^{14}N) coupling constants have been precisely obtained. From the experimental rotational constants, the r_0 structure of the complex was evaluated, which gives a 3.083 Å length of the Cl···N halogen bond. The force constant, $k_s = 6.3$ Nm^{-1} has been obtained, which corresponds to a harmonic stretching frequency of 86 cm^{-1}. The dissociation energy of the complex is 11.0 $kJmol^{-1}$. This value is quite similar to the dissociation energy values of weak hydrogen bonds (O-H···F, O-H···Cl, CH···N).

[1] G. Feng, L. Evangelisti, N. Gasparini and W. Caminati, *submitted*.

FIS-PO-19 Do intermolecular interactions affect the relaxation dynamics of dimers of quadrupolar dyes?

E. Collini[a], T. Margola[a], E. Garbin[a], R. Bozio[a], C. Ferrante[a], A. Abbotto[b], N. Manfredi[b].

[a]Dipartimento di Scienze Chimiche e UdR INSTM dell'Università di Padova, Via Marzolo 1, 35131 Padova, Italy.
[b]Dipartimento di Scienza dei Materiali & INSTM dell'Università di Milano-Bicocca, Via Cozzi 53, 20125 Milano, Italy.

Fluorescence experiment on dimers of the quadrupolar dye 2,5-Bis[1-(4-N-methylpyridinium)ethen- 2-yl)]-N-methylpyrrole ditriflate (PEPEP) connected by C3 and C6 saturated alkyl chains revealed a striking decrease of fluorescence quantum yield only for the C3 linked dimer.[1]

To shed further light on the origin of such behavior, time resolved fluorescence and transient absorption experiments in the fs and ps time range will be presented.

Time-resolved fluorescence experiments show a marked decrease of the lifetime of the emitting state going from PEPEP monomer to the C3-dimer, confirming the behavior revealed by the FQY experiments. More detailed information on the global decay mechanisms in the PEPEP monomer and dimer can be gained through transient absorption experiments with polarized laser light. Transient absorption spectra recorded with VV polarization for pump and probe beams of PEPEP and its dimer are remarkably similar up to 50 ps, whereas on longer timescales they reflect the same behavior already observed with time-resolved fluorescence experiments.

Preliminary data on anisotropy decay at selected wavelengths seem to confirm the presence of an ultrafast energy transfer process between the two moieties forming the dimer.

We are deeply thankful to Prof. A. Painelli for insightful discussion on the properties of these molecular systems.

[1] C. Sissa *et al.*, *J. Phys. Chem. B, 114*, **2010**, 882.

FIS-PO-20 Anti-site defects formation in $LiFePO_4$ cathode material prepared by microwave-assisted hydrothermal synthesis

S. Ferrari,[a] **M. Bini,**[a] **D. Capsoni,**[a] **V. Massarotti,**[a] **P. Mustarelli,**[a] **G. Spina,**[b] **C. Leonelli,**[c] **A. Rizzuti,**[d] **F. Del Giallo,**[e] **M. Lantieri**[e]

[a]Dipartimento di Chimica – Sez. Chimica Fisica – dell'Università di Pavia, Viale Taramelli 16, 27100, Pavia, Italy
[b]Dipartimento di Fisica e Astronomia dell'Università di Firenze, Via Sansone 1, 50019, Sesto Fiorentino (FI), Italy
[c]Dipartimento di Ingegneria dei Materiali e dell'Ambiente dell'Università di Modena e Reggio Emilia, Via Vignolese 905, 41125, Modena, Italy
[d]Dipartimento di Ingegneria delle Acque e di Chimica del Politecnico di Bari, Via Orabona 4, 70125, Bari, Italy
[e]Istituto dei Sistemi Complessi - CNR, Via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy
stefania.ferrari@unipv.it

Among the cathode materials for lithium-ion batteries, $LiFePO_4$ is indeed the most promising for large-scale applications; its olivine structure presents suitable thermal stability, no toxicity and low cost [1]. Numerous low temperature synthetic routes have been recently used in order to have control on size and shape of $LiFePO_4$ particles and to reach optimized morphologies, promising for the electrochemical applications [2]. In all these cases intrinsic defects are formed and can be removed only after annealing for long time at high temperature. Our study deals with the preparation of crystalline $LiFePO_4$ by an innovative procedure based on the simultaneous application of microwave and hydrothermal processes, in order to overcome the limitations of the hydrothermal method alone, that makes use of low operating temperature, but requires long reaction times and can produce olivine with a non-homogeneous particles dimension and shape. The combined use of spectroscopic and structural techniques allowed a detailed study of the local order of olivine. The results obtained by the Mössbauer spectroscopy, combined with the overall and local structural evidences obtained by the Rietveld refinement and PDF analysis of synchrotron radiation X-Ray diffraction data allowed to characterize the defectivity of $LiFePO_4$. The PDF analysis, applied for the first time to the $LiFePO_4$ structure, shows that the anti-site defect and the symmetry lowering resulted more probable, and Mössbauer spectroscopy confirmed these findings. In particular, a few percent of anti-site defect has been determined and also the presence of a small amount of Fe^{3+} on regular octahedral sites has been revealed.

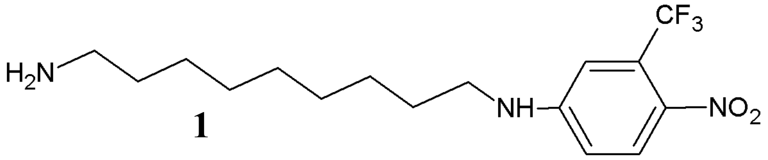
[1] M. S. Whittingam, *Chem. Rev.*, *104*, **2004**, 4271.
[2] S. Ferrari, R. L. Lavall, D. Capsoni, E. Quartarone, A. Magistris, P. Mustarelli and P. Canton, *J. Phys. Chem. C*, *114*, **2010**, 12598.

FIS-PO-21 Light-controlled nitric oxide delivery from Langmuir-Schafer films

G. Giancane[a], **S. Sortino**[b], **E. Vittorino**[b], **L. Valli**[a]

[a] Department of Innovation Engineering, University of Salento, Italy, Via per Arnesano, I-73100 Lecce
[b] Laboratory of Photochemistry, Department of Drug Sciences, University of Catania, Italy, Viale Andrea Doria 6, I-95125 Catania
gabriele.giancane@unisalento.it

Nitric oxide (NO) plays a crucial role in the bioregulation of a wide range of pathophysio- and physiological processes such as vasodilatation, neurotransmission, hormone secretion, macrophage induced cytotoxicity [1], anticancer process [2]. This multifaceted role of NO has prompt many researchers to develop compounds which can serve to deliver NO. The main problem associated with NO donors is the precise spatiotemporal control of the nitric oxide released. In this context, light seems to be an ideal external on/off trigger to regulate, with a high control, the NO dosage. The compound **1** used in this work is reported in figure and acts as the NO photo-deliverer which can be transferred by means of Langmuir-Schaefer (LS) technique. Due to the presence of the -CF_3 substituent, the nitro group is placed almost perpendicular to aromatic plane, and this twisted conformation is crucial for NO photorelease. As we reported in other works [3], LS method ensures the transfer of an efficient solid film; on the contrary, other deposition techniques, such as spin coating or casting, quench the nitric oxide emission. Silver nanoparticles (AgNPs), used for their well-known antibacterial properties, were dissolved in the aqueous subphase and the interaction among **1** and the hydrosoluble Ag nanoparticles allowed to transfer, by the LS method, a multilayered film of **1**/AgNPs. The increase of NO concentration after an appropriate light stimulus and the transfer of nitric oxide to myoglobin was observed after the illumination of the LS film.



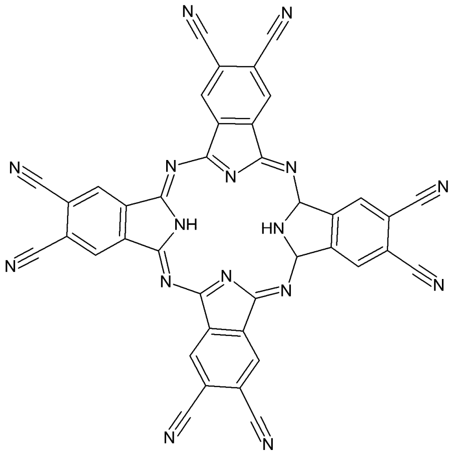
1

[1] E. Culotta, D. E. Koshland, *Science*, *258*, **1992**, 1862
[2] W. Xu, L. Z. Liu, M. Loizidou, M. Ahmed, I. G. Charles, *Cell Res.*, *12*, **2002**, 311
[3] S. Sortino, G. Giancane, V. Valli, *J. Mat. Chem.*, *18*, **2008**, 2437

FIS-PO-22 Effect of the molecular packing on the efficiency of an organic solar cell: a comparison between Langmuir-Blodgett and spin coating photovoltaic devices

G. Giancane[a], **L. Valli**[a]
[a] Department of Engineering for Innovation, University of Salento, Italy, Via per Arnesano, I-73100 Lecce
gabriele.giancane@unisalento.it

An important parameter that strongly influences the performances of an organic solar cell is the percolation path of the free carriers [1]. A not uniform matrix, as well as a long percolation path, provides traps for the free electrons and holes and, of course, a deterioration of the solar device efficiency. In order to optimize the charge collection, many researchers suggested both the use of highly anisotropic materials, such as nanotubes and quantum wires [2, 3], and very expensive deposition techniques. In this work, Langmuir-Blodgett technique, one of the most elegant and well-suited approaches that allows accurate control of both packing and molecular orientation, was used to deposit a dyad of a functionalized phthalocyanine (Pc) (see figure) and the [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). Absorption spectra in the UV-Visible range carried out at different polarization angles of incident light, showed a high oriented LB film of the co-spread Pc/PCBM dyad. On the contrary, dichroic ratio calculated for the spin-coated film is about 1. The device realized with 10 LB layers of the dyad showed a rapid photoresponse and a J_{sc} of 48 μA cm^{-2} was recorded; spin coated solar cell exhibited a short circuit current of 0.9 μA cm^{-2}. Short circuit current is an important parameter closely linked to the percolation path.



[1] S. W. Tong, C. F. Zhang, C. Y. Jiang, Q. D. Ling, E. T. Kang, D. S. H. Chan, C. Zhu, *Appl. Phys. Lett.*, *93*, **2008**, 043304.

[2] G. Giancane, A. Ruland, V. Sgobba, D. Manno, A. Serra, G. M. Farinola, O. H. Omar, D. M. Guldi, L. Valli, *Adv. Funct. Mater.*, *20*, **2010**, 2481.

[3] A. A. Damitha T. Adikaari, D. M. Nanditha M. Dissanayake, S. Ravi P. Silva, *Quantum Electron.*, *16*, **2010**, 1595.

FIS-PO-23 FTIR studies on paper mache composition of "Madonna delle Alcantarine" statue

<u>G. Giancane</u>[1], E. Imperio[1], L. Miotto[2], L. Valli[1]

[1]Dipartimento di Ingegneria dell'Innovazione, Complesso Ecotekne, edificio "La Stecca", Via per Monteroni, 73100, Lecce, Italy
[2]Centro Restauro Materiale Cartaceo, Via Roberto Caracciolo 6, 73100 Lecce, Italy
gabriele.giancane@unisalento.it

Today's science and technology development has led to many different kinds of approaches in the study of Cultural Heritage. New non-destructive methodologies have been employed for the physical and chemical analysis of several valuable remains. The goal of this work was to lead to a wider knowledge of technical processes used in the production of paper mache statues by baroque artists in Salento. Objects of the investigation were few samples from one of the five little angel heads of the *Madonna delle Alcantarine* composition statue. Each specimen represented a particular paper mache layer. The analysis was carried out using a FTIR Spectrometer in the region of MIR. As it is well-known, IR spectroscopy is a technique sensitive to the presence of chemical functional groups, thus the analysis allowed to identify different kinds of paper[1]. In addition, some comparison permitted to underline the presence of glue made of vegetable between the layers. In particular, we were able to establish that he adhesive material was extracted by wheat bran [2].

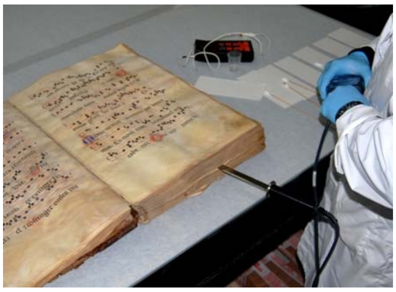
[1] Infrared spectra of crystalline polysaccharides, C.Y Liang., *Marchessault R.H.*, 1959.
[2] Chimica dei supporti cartacei, P.F.Calvini, *Università Ca' Foscari*, Venezia, 2007.

FIS-PO-24 ATR infrared characterisation of the components of a XV century *Responsorium Graduale*

G. Giancane[a], **D. Bramato**[a], **G. De Felippis**[b], **L. Valli**[a]

[a] Department of Engineering for Innovation, University of Salento, Italy, Via per Arnesano, I-73100 Lecce
[b] Laboratorio di Legatoria, Restauro e Conservazione di Beni Archivistici e Librari Codex, Via Vecchia Lecce, 73010 Guagnano (Le)
gabriele.giancane@unisalento.it

An ancient religious book, more in detail a *Responsorium Graduale* [1], damaged during the earthquake that upset L'Aquila in April 2009, was examined and restored. During every step of restoring procedure, the specimens were analyzed by means of infrared spectroscopy. All the acquisitions proposed in this work are completely not destructive.



The *Graduale* is constituted by a cover realized in parchment and it was revealed that this cover was tanned with a particular procedure, typical of medieval period. Strings used for giving a more rigid structure to the spine was obtained probably from hemp [2], then they was treated by starch, according to a typical procedure adopted during XV century. Then a wooden axe is used to give rigidity to the book structure. Another interesting result was obtained comparing the tanning method used for the parchments and the cover of the book with the strings used to bind the book sheets. The binding strings need to be flexible and the infrared analysis clearly shows that the so-called "Chamois" tanning was employed by the ancient craftsmen to obtain this result.

Finally, we compared the adhesive used for realizing the book with the one employed for repairing some inner pages. Infrared analysis showed strong differences between the glues: a cellulosic one [3] was used for "restoring" the book, on the contrary a proteic glue was employed for binding the wooden part with parchment sheets.

[1] M. Gitton, Iniziazione alla liturgia romana, Qiqajon, 2008, Bose
[2] J. Greenfield, ABC of Bookbinding: an illustrated glossary of terms for collectors and conservators, Oak Knoll Press and Plough Press, 1998, New Castle
[3] M. R. Derrick, D. Stulik, J. M. Landry, Infrared Spectroscopy in Conservation Science, Getty Conservation Institute, 1999, Los Angeles

FIS-PO-25 Interaction of azatrux with human telomeric G-quadruplex under molecular crowding conditions: biophysical and molecular modeling studies

Luigi Petraccone,[a] **Iolanda Fotticchia,**[a] **Annunziata Cummaro,**[a] **Bruno Pagano,**[b] **Luca Ginnari-Satriani,**[c] **Shozeb Haider,**[d] **Antonio Randazzo,**[e] **Ettore Novellino,**[f] **Stephen Neidle,**[g] **Concetta Giancola,**[a]

[a]Dipartimento di Chimica "P. Corradini", Università di Napoli "Federico II", via Cintia, 4, I-80126 Napoli, Italy. [b]Dipartimento di Scienze Farmaceutiche, Università di Salerno, Via Ponte Don Melillo, 84084, Fisciano (SA), Italy. [c]Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale A. Moro 5, 00185 Roma, Italy. [d]Centre for Cancer Research and Cell Biology, Queen's University Belfast, 97 Lisburn Road, Belfast BT9 7BL, U.K. [e]Dipartimento di Chimica delle Sostanze Naturali, Università di Napoli "Federico II", Via D. Montesano 49, 80131 Napoli, Italy. [f]Dipartimento di Chimica Farmaceutica e Tossicologica, Università di Napoli "Federico II", Via D. Montesano 49, 80131 Napoli, Italy. [g]Cancer Research UK Biomolecular Structure Group, The School of Pharmacy, University of London, 29-39 Brunswick Square, London WC1N 1AX, U.K.
giancola@unina.it

Human telomeric G-quadruplex structures are known to be promising targets for an anticancer therapy [1]. Knowledge of the structures formed by human telomeric G-quadruplexes under physiological conditions is crucial for structure-based drug design of potent and selective small-molecule ligands. It has been reported that human telomeric DNA quadruplexes can be highly polymorphic and can fold into a variety of different conformations [2]. However, there is increasing evidence that crowding solution conditions can significantly stabilize the parallel G-quadruplex topology over others [3]. Since molecular crowding is reflecting the nuclear environment in eukaryotic cells, it is appropriate to study the binding properties of new ligands with the parallel G-quadruplex fold. The present study has employed a combination of spectroscopic, calorimetric and computational methods to explore the binding of the three side-chain triazatruxene derivative, termed azatrux [4], to a human telomeric G-quadruplex, under conditions of molecular crowding. The binding of azatrux to the tetramolecular $[d(TGGGGT)]_4$ parallel quadruplex in the presence and absence of crowding conditions, was also characterized. The selectivity of azatrux for the human telomeric G-quadruplex relative to another biologically relevant G-quadruplex and to duplex DNA was also evaluated. The data indicates that azatrux binds in an end-stacking mode to the parallel G-quadruplex scaffold and shows that azatrux has good selectivity for the human telomeric G-quadruplex over the other investigated DNA structures.

[1] B. Pagano and C. Giancola, *Curr.Cancer Drug Targets, 7*, **2007**, 520.
[2] J. Dai, M. Carver and D. Yang, *Biochimie*, *90*, **2008**, 1172.
[3] L. Martino, B. Pagano, I. Fotticchia, S. Neidle and C. Giancola, *J.Phys.Chem.B.*, *113*, **2009**, 14779.
[4] L. Ginnari-Satriani, V. Casagrande, A. Bianco, G. Ortaggi and M. Franceschin, *Org.Biomol.Chem., 7*, **2009**, 2513.

FIS-PO-26 Reversible binding of metal ions onto bacterial layers revealed by protonation-induced ATR-FTIR difference spectroscopy

Livia Giotta[a], Disma Mastrogiacomo[b], Francesca Italiano[c], Francesco Milano[c], Angela Agostiano[c], Krisztina Nagy[b,d], Ludovico Valli[b] , Massimo Trotta[c]

[a] Dipartimento di Scienza dei Materiali, Università del Salento, S.P. Lecce-Monteroni, 73100 Lecce, Italy
[b] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, S.P. Lecce-Monteroni, 73100 Lecce, Italy
[c] Istituto per i Processi Chimico-Fisici, CNR, Sezione di Bari, Via Orabona 4, 70126 Bari, Italy
[d] Institute of Biophysics, Biological Research Center of Hungarian Academy of Sciences, H-6726 Szeged, Hungary
E-mail: livia.giotta@unisalento.it

The ability of microorganisms to adhere to abiotic surfaces and the potentialities of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy have been exploited in order to study protonation and heavy metal binding events onto bacterial surfaces. This work represents the first attempt to apply on bacteria the recently developed method known as perfusion-induced ATR-FTIR difference spectroscopy [1]. Such technique allows measurement of even slight changes in the infrared spectrum of the sample, deposited as a thin layer on an ATR crystal, while an aqueous solution is perfused over its surface. Solutions at different pH have been used for inducing protonation/deprotonation of functional groups lying on the surface of *Rhodobacter sphaeroides* cells, chosen as a model system. The interaction of Ni^{2+} with surface protonable groups of this microorganism has been investigated with a double-difference approach exploiting competition between nickel cations and protons. Protonation-induced difference spectra of simple model compounds have been acquired in order to guide band assignment in bacterial spectra, thus allowing identification of major components involved in proton uptake and metal binding. The data collected reveal that carboxylate moieties on the bacterial surface of *R. sphaeroides* play a role in extracellular biosorption of Ni^{2+}, establishing with this ion relatively weak coordinative bonds.

[1] P.R. Rich, M. Iwaki, *Molecular Biosystems* **2007,** 3, 398-407.

FIS-PO-27 Rotational spectrum and dynamics of tetrahydrofuran-krypton

Qian Gou,[a] Gang Feng,[a] Luca Evangelisti,[a] Marianna Marchini,[a] Assimo Maris,[a] Biagio Velino,[b] Walther Caminati.[a]

[a]Dipartimento di Chimica “G. Ciamician” dell’Università di Bologna, via selmi 2, I-40126, Bologna, Italy.
[b]Dipartimento di Chimica Fisica e Inorganica dell’ Università di Bologna, Viale Risorgimento 4, I-40136 Bolongna, Italy.

E-mail responsabile presentazione: gouqian33@gmail.com

Due to the higher polarizability of Kr with respect to Ar, a higher dissociation energy interaction is expected for complexes containing Kr. However it is not true for 2,5-dihydrofuran(2,5-DHF)[1-3]. It could be interesting to investigate this comparison in the case of other five-membered heterocyclic molecule, especially with different aromaticity or double bonds.

Tetrahydrofuran (THF), a fully aliphatic member of the furan series, is not a planar molecule like 2,5DHF in the gas phase but exhibits pseudorotation. Here, the rotational spectrum of THF-Kr complex has been investigated by molecular beams Fourier transform microwave spectroscopy. The spectra of normal and ^{86}Kr species showed that the Kr atom is located nearly over the oxygen atom, almost perpendicularly to the COC plane (see Figure 1). Each rotational transition is split into two component lines due to the residual pseudorotational effects of the ring in the complex, according to the observed Coriolis coupling term between the tunnelling states. The splitting between the two vibrational sublevels has been calculated to be 87.462(2) MHz. The dissociation energy, as obtained from centrifugal distortion effects, is 3.73 kJ mol^{-1}, higher than that of its corresponding argon complex[4].

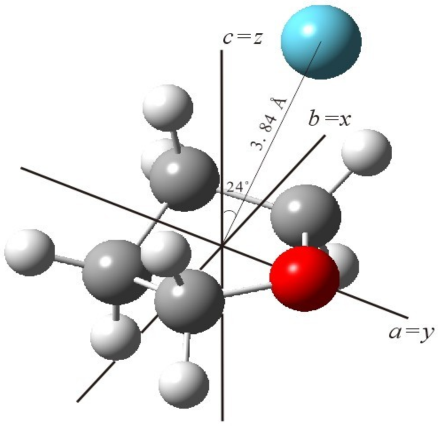


Figure 1. Sketch of THF-Kr in the principle axis system of THF.

[1] J.L. Alonso, F.J. Lorenzo, J.C. Lopez, A. Lesarri, S. Mata, and H. Dreizler. *Chem Phys. 218*, **1997**, 267.
[2] W. Caminati, P.G. Favero, S. Melandri, and J. Makarewicz. *Mol Phys. 91*, **1997**, 663.
[3] B. Velino, S. Melandri, A. Maris, P.G. Favero, and W. Caminati. *Mol Phys. 98*, **2000**, 1919.
[4] S. Melandri, J.C. Lopez, P.G. Favero, W. Caminati, and J.L. Alonso. *Chem Phys. 239*, **1998**, 229.

FIS-PO-28 Characterization of the Geographical and Botanical Origin of Italian Cherries by Nuclear Magnetic Resonance and Isotope Ratio Analysis

Longobardi F.[1*], Bianco A.[1], Casiello G.[1], Mazzilli V.[1], Ventrella A.[1], Catucci L.[1], Agostiano A.[1], Sacco D.[1], Sacco A.[1], Cafagna I.[2], Gallo V.[2], Mastrorilli P.[2]

[1]Department of Chemistry, via Orabona 4, Campus, University of Bari, 70126, Bari, Italy
[2]Dipartimento di Ingegneria delle Acque e di Chimica, via Orabona 4, Politecnico di Bari, Bari, Italy
[*]*longobardi@chimica.uniba.it*

In this study, the Isotope Ratio Mass Spectrometry (IRMS) and the Nuclear Magnetic Resonance Spectroscopy (NMR) were used in combination with multivariate statistical techniques for the characterization of Italian cherries of different geographical (Emilia Romagna and Puglia) and varietal (Bigarreau, Ferrovia, Giorgia) origin. In particular, the Discriminant Function Analysis (DFA) was performed on the NMR spectra and isotopic composition data to determine discriminant functions useful in predicting the geographical and variety origin of unknown samples. The statistical analysis conducted on NMR data showed a prediction ability (estimated by the "leave-more-out " procedure) equal to 94.3% for the geographical discrimination identifying malic acid and tyrosine among the most important compounds for this discrimination. The statistical treatment of IRMS data showed a predictive ability of 83.0%. All these results demonstrated the goodness of the models obtained, especially considering that these were constructed from a dataset in which the variability, in addition to their geographical origin, is linked to many other factors such as the degree of ripeness and varietal origin of cherries. In addition, applying DFA to the entire dataset (NMR and IRMS data) very good results were obtained in prediction (98.9%), demonstrating the validity of a synergic approach. Finally, for each of the two growing Italian regions, the NMR and IRMS results have been used for the discrimination of the botanical origin among the three cultivars obtaining a prediction percentage equal to 100.0% and 98.9% for Emilian and Apulian samples, respectively. However, these latter results require further validation using a larger number of samples.

Regione Puglia is gratefully acknowledged for financial support ("Apulian Food Fingerprint" project, n. 68, Reti di Laboratorio Pubblici).

FIS-PO-29 Targeting RGD-recognizing integrins: aggregation behavior of a novel class of amphiphilic RGD integrin binders.

E. Vaselli[1], G.D'Errico[1], R. Sartorio[1], G. Vitiello[1], F. Zanardi[2], L. Manzoni[3], L. Paduano[1], G. Mangiapia[1]

[1] CSGI and Department of Chemistry – University of Naples "Federico II"
[2]Department of Pharmacy – University of Parma
[3] CNR – Institute of Molecular Science and Technologies – Milan
E-mail: mangiapia.gaetano@alice.it

Receptors that are uniquely expressed or markedly overexpressed in tumors have been the potential targets for cancer therapy and diagnosis. Vascular integrins such as alphaVbeta3 and alphaVbeta5 have become major biological indicators for treating cancer since they are expressed on invasive tumors such as late-stage glioblastomas, breast and prostate tumors, malignant melanomas, ovarian carcinomas, as well as the new-born blood vessels. [1-2] In this domain, low-molecular weight RGD-based integrin antagonists displaying high alphaVbeta3 and alphaVbeta5 binding affinity and selectivity constitute privileged molecules, since they would serve as "tumor targeting navigator systems", while selectively killing angiogenic tumor endothelial cells.

Here we present preliminary results concerning the aggregation behavior of a novel class of amphiphilic integrin binders carrying the RGD peptidic sequence. This class includes molecules capable to be potentially used both for therapeutic and diagnostic purposes. Concerning this latter point of view, Fe/Au based nanoparticles have been synthesized for a potential use for Magnetic Resonance Imaging applications.

References

[1] S. Urman, K. Gaus, Y. Yang, U. Strijowski, N. Sewald, S. De Pol, and O. Reiser, *Angewandte Chemie,* 46, **2007,** 3976.

[2] F. Zanardi, P. Burreddu, G. Rassu, L. Auzzas, L. Battistini, C. Curti, A. Sartori, G. Nicastro, G. Menchi, N. Cini, A. Bottoncetti, S. Raspanti, and G. Casiraghi, *J. Med. Chem.* 51, **2008,** 1771

FIS-PO-30 Incorporation of lycopene into lipid vesicles for pharmacological applications

Disma Mastrogiacomo[a], Marialuisa Di Carolo[a], Livia Giotta[b], Francesco Milano[c], Marcello Lenucci[d], Leonardo Rescio[e], Giuseppe Dalessandro[d], Ludovico Valli[a]

[a] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, S.P. Lecce-Monteroni, 73100 Lecce, Italy
[b] Dipartimento di Scienza dei Materiali, Università del Salento, S.P. Lecce-Monteroni, 73100 Lecce, Italy
[c] Istituto per i Processi Chimico-Fisici, CNR, Sezione di Bari, Via Orabona 4, 70126 Bari, Italy
[d] Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, S.P. Lecce-Monteroni, 73100 Lecce, Italy
[e] Lio Farmaceutici s.r.l. Zona Industriale, SP 362 – Km 17,650 – 73013 Galatina (LE), Italy
E-mail: disma.mastrogiacomo@unisalento.it

Lycopene is one of the most powerful carotenoids able to quench singlet oxygen. This high antioxidant activity has received wide attention for possible pharmacological applications. However, being highly hydrophobic, its incorporation in drug delivery systems represents an important issue in order to obtain active and stable preparations.

A natural and solvent-free oleoresin containing lycopene dissolved in a highly unsaturated vegetable oil [1] has been integrated into lipid vesicles in order to obtain liposomial dispersions suitable for pharmaceutical preparations. Size exclusion chromatography has been employed for vesicles preparation using both zwitterionic and negatively charged phospholipids. Elution profiles were followed by visible and infrared spectroscopy revealing the successful incorporation of lycopene into the lipid bilayer. The final preparations for which a complete carotenoid incorporation was achieved contained about 1 mM of phospholipids and 2 μM lycopene. Negatively charged phospholipids proved to effectively prevent the coalescence of liposomes leading to highly stable disperse systems. Finally the antioxidant activity of lipid-embedded lycopene was assessed by following the kinetics of degradation of chlorophyll *a*, a natural hydrophobic pigment, highly sensitive to light and oxygen. A 36% reduction of the degradation kinetic constant was observed when lycopene was present in chlorophyll containing liposomes.

[1] M.S. Lenucci, A. Caccioppola, M. Durante, L. Serrone, L. Rescio, G. Piro,G. Dalessandro. *J. Sci. Food Agric.* **2010**, 90, 1709-18.

FIS-PO-31 THERMOGRAVIMETRIC STUDIES OF ARCHAEOLOGICAL WOODS

G. Cavallaro, D.I. Donato, G. Lazzara, S. Milioto

Department of Chemistry "S. Cannizzaro", University of Palermo, Viale delle Scienze Pad. 17, Parco D'Orleans II, 90128 Palermo, Italy, *milioto@unipa.it*

Within the cultural heritage field, the wood assumes a relevant importance because of its presence in several art-works. In particular, the waterlogged woods represent a complex matter because they undergo to serious damages if dried being that the loss of water shrinks and deforms the material. Therefore, proper methodologies for their conservation and preservation are required. For a correct conservation process, a deep knowledge of the waterlogged wood state is required, that needs several techniques.

In this report, we will highlight some aspects dealing with archaeological waterlogged woods (*Pinus pinaster* and *Fagus sylvatica L.*) from the ship Chrétienne C, (II century, BC), discovered over the coast of Provence (France) and the sound woods of the same taxa. Thermogravimetry (TGA) has been revealed a proper and suitable technique for this purpose. In particular, TGA enabled us: 1) to define a new protocol to rapidly calculate the Maximum Water Content parameter, which is related to the wood degradation state; 2) to monitor the efficiency of the consolidants as well as to discriminate the consolidants when present in mixtures; and 3) to evaluate the activation energy, which is distinctive parameter for the archaeological woods.

FIS-PO-32 Surface properties of anatase nanocrystals investigated by CO adsorption: a combined experimental and ab initio study

Lorenzo Mino, Anna Maria Ferrari, Giuseppe Spoto, Silvia Bordiga, Adriano Zecchina

Department of Inorganic, Physical and Materials Chemistry and NIS Centre of Excellence, University of Turin, via P. Giuria 7, 10125 Torino, Italy

E-mail address: lorenzo.mino@unito.it

Titanium dioxide is one of the most important metal oxides because of its applications as white pigment, as important component in solar cells and as photocatalyst [1]. In the last two applications the relevant phenomena are occurring at the surface of anatase nanoparticles, which are generally considered to be more active than rutile ones [2]. Therefore it is relevant for both technological and fundamental motivations to study the structure of the different surfaces terminating the anatase nanocrystals.

In our work we performed periodic DFT calculations of the structure of (101), (100), (001) and (112) anatase faces and of the vibrational properties of CO adsorbed on them at two coverages in order to assign the main features of FTIR spectra of CO adsorbed at 60K on highly dehydroxylated anatase nanocrystals. CO is a weak Lewis and its stretching frequency is related to the electrophilicity of the surface Lewis acid sites: the greater is the electrophilicity of the metal cation, the higher is the blueshift with respect to the value in gas phase [3]. The study of the CO behaviour on different TiO_2 materials can highlight the correlation between surface structure and chemical reactivity.

Our contribution shows that the combination of spectroscopic and computational approaches is of extreme utility for the elucidation of the Lewis acid properties of Ti sites present on the different surfaces and on their influence on the stretching frequencies of adsorbed CO, for the explanation of the coverage dependent effect of dipole-dipole interaction and for the determination of the average nanoparticle morphology. This study highlights that the close comparison of experimental and computational results forms the safest basis for the cross validation of the two approaches [4].

[1] A. Fujishima, X. T. Zhang, D. A. Tryk, *Surf. Sci. Rep.*, *63*, **2008,** 515-582.
[2] U. Diebold, *Surf. Sci. Rep.*, *48*, **2003,** 53-229.
[3] K. I. Hadjiivanov, D. G. Klissurski, *Chem. Soc. Rev.*, *25*, **1996,** 61-69.
[4] L. Mino, A. M. Ferrari□, V. Lacivita, G. Spoto, S. Bordiga, A. Zecchina, *J. Phys. Chem. C, 115*, **2011**, 7694-7700.

FIS-PO-33 Protein-protein interactions in the complex ERK2-KIM peptide and identification of putative high affinity mutant KIM peptides: a computational investigation

A. Arrigoni[c], **L. De Gioia**[a], **U. Cosentino**[b], **R. Brambilla**[c], **G. Moro**[a]

[a] Dipartimento di Biotecnologie e Bioscienze, Università di Milano-Bicocca; piazza della Scienza 2, 20126 Milano, Italy
[b] Dipartimento di Scienze dell'Ambiente e del territorio, Università di Milano-Bicocca; piazza della Scienza 1, 20126 Milano, Italy
[c] Dipartimento di Biologia Molecolare e Genomica Funzionale, Fondazione S. Raffaele del Monte Tabor, via Olgettina 60, 20132 Milano, Italy
arrigonialberto86@gmail.com

MAP kinases have a central role in determining the transduction of a great number of stimuli, such as neurotrasmitters, hormones, cellular stress and cytokines. Any deregulation capable of influencing the normal activity of this pathway can potentially lead to a wide variety of diseases, including Alzheimer's disease, Parkinson's disease, and various types of cancers. The catalytic activity of MAP kinases is mainly regulated by phosphorylation: protein kinases and phosphatases interact with the MAP kinases via a conserved region (KIM), which constitutes a pivotal determinant for the formation of a stable complex.

In the present work, we devised a computational procedure based on molecular dynamics simulations (MD) and free energy perturbation (FEP) in order to select mutant KIM peptides which can putatively bind ERK2 with higher affinity than the wild type.

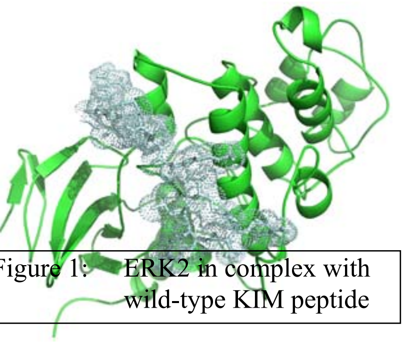


Figure 1: ERK2 in complex with wild-type KIM peptide

Our approach features an initial set of MD simulations of the mutant peptides in complex with ERK2, followed by an analysis of the persistence of the electrostatic and hydrophobic interactions at the complex interface during the simulations. This provided a qualitative insight which led us to the identification of promising mutant peptides to be subsequently energetically evaluated through FEP simulations. These putative high affinity mutant peptides could be used to prevent other interacting protein partners from binding ERK2, therefore modulating its catalytic activity and function during the cell cycle.

[5] S.Liu, J.P.Sun, B.Zhou, Z.Y.Zhang, *Proc. Natl. Acad. Sci.*, 103, **2006**, 5326.
[6] T.Tanoue, M.Adachi, T.Moriguchi, E.Nishida, *Nat. Cell. Biol.*, 2, **2000**, 110.
[7] B.Zhou, L.Wu, K.Shen, J.Zhang, D.S.Lawrence, Z.Y.Zhang, *J. Biol. Chem.*, 276, **2001**, 6506.
E.K.Kim, E.J.Choi, *Biochim. Biophys. Acta*, 1802, **2010**, 396.

FIS-PO-34 WAVELET ANALYSIS OF MOLECULAR DYNAMICS DATA

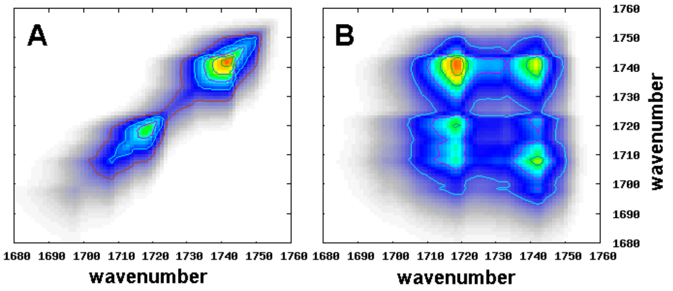
F. Muniz-Miranda [1], **M. Pagliai** [2], **G. Cardini** [2], **R. Righini** [1,2], **V. Schettino** [1,2]

[1] European Laboratory for Non-Linear Spectroscopy (LENS), University of Florence, via Nello Carrara 1, 50019, Sesto Fiorentino (Firenze), Italy
[2] Department of Chemistry, University of Florence, via della Lastruccia 3, 50019, Sesto Fiorentino (Firenze), Italy
francesco.munizmiranda@unifi.it

Time resolved IR experiments provide new relevant insights regarding the structure and dynamic behaviour of complex molecular systems. However, to elucidate accurately the spectral features, often new *in silico* experiments are required. Car-Parrinello Molecular Dynamics (CPMD) simulation data contain in principle most of structural and dynamic information revealed by 2D IR experiments. In order to extract this information from the simulations for a straightforward comparison with the experiments, the development of computational tools to analyze CPMD trajectories becomes therefore particularly useful.

The Wavelet Transform (WT) is a mathematical "tool" that performs time-frequency analysis. With WT it is possibile to correlate directly structural and spectoscopic properties, corroborating the usual standard interpretation of experimental spectra.

As case studies, we have tested different WT-based methods on molecular systems whose dynamics is driven by Hydrogen Bonds formation and breaking. The computed vibrational spectra have been calculated from time-resolved bond-lengths and the dynamic effects of the Hydrogen Bonding onto the vibrational modes have been probed with WT. Cases of Chemical Exchange and Inhomogenous Broadening have been elucidated and correlated with the strength and stability of the Hydrogen Bonds.



C=O *stretching region of* Methyl Acetate *in* MeOH*;*
A) *delay time* = 0 ps *;* **B**) *delay time* = 20 ps

Moreover, using the time-localization features of WT, bidimensional frequency correlation plots have been generated (see figure) multiplying frequency spectra obtained at different delay times. When Chemical Exchange occurs due to the Hydrogen Bonding, specific cross peaks appear in the 2D wavelet spectrogram.

FIS-PO-35 Preparation and structural characterization of graphene and vinyl ester/graphene composites.

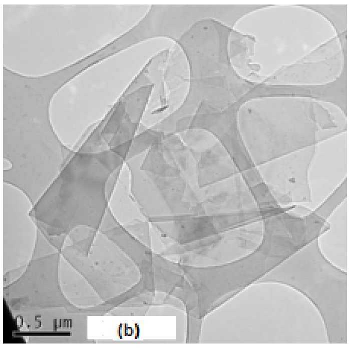
G. Nasillo,[a,b] M. L. Saladino,[a] G. De Bellis,[c,d] A. Tamburrano,[c,d] M.S. Sarto,[c,d] E. Caponetti[a,b]

[a] Dipartimento di Chimica "S. Cannizzaro" dell'Università degli Studi di Palermo, Parco D'Orleans II, Viale delle Scienze - Pad. 17, 90128, Palermo, Italy
[b] Centro Grandi Apparecchiature – UniNetLab dell'Università degli Studi di Palermo, via Filippo Marini 14, 90128, Palermo, Italy
[c] Centro Ricerca Nanotecnologie applicate all'Ingegneria della Sapienza - CNIS, Sapienza Università di Roma, via Eudossiana 18, 00184 Roma
[d] Dipartimento di Ingegneria Astronautica, Elettrica, Energetica della Sapienza Università di Roma, via Eudossiana 18, 00184 Roma
giorgio.nasillo@unipa.it

Graphene, one of the allotropes of elemental carbon with a planar monolayer of carbon atoms arranged into a two-dimensional honey-comb lattice, has demonstrated a variety of intriguing properties as new material for future electronic and composite industry [1-2].

The aim of the current research is the preparation and the characterization of graphene and new composite using vinyl-ester resins as matrix.

The preparation of graphene was carried out by thermal treatment of commercial Graphite Intercalation Compounds (GICs) [3]. After the thermal treatment, expanded graphite (also known as worm-like or accordion-like in this phase) was dispersed in a proper solvent and sonicated obtaining Graphite Nano Platelets (GNPs) thick films, having an average thickness of about 200 μm.



TEM micrograph of GNPs flakes.

Structural and morphological characterization of graphene and their composites have been made by means of X-Ray Diffraction, Small Angle X-Ray Scattering, and Electron Microscopy. Results show that, by choosing appropriate conditions (temperature, solvent, sonication time, etc..), the GICs flakes expand their volume producing high quantities few layers graphene sheets.

The electrical investigations show that the measured dc resistance of different thick films decreases as function of the GNP expansion temperature

[1] Y. Zhang, Y. Tan, H. Stormer and P. Kim, *Nature*, **2005**, 438, 201.
[2] C. Lee, X. Wei, J. Kysar and J. Hone, *Science*, **2008**, 321, 385.
[3] G. De Bellis, A. Tamburrano, A. Dinescu, M.L. Santarelli and M.S. Sarto, *Carbon*, **2011**, DOI: 10.1016/j.carbon.2011.06.008.

FIS-PO-36 Innovative hybrid materials based on colloidal nanocrystals in imidazolium ionic liquids

A. Panniello,[1] E. Binetti,[1,2] L. Triggiani,[2] M.L. Curri,[1] R. Tommasi,[1,3] A. Agostiano,[1,2] M. Striccoli[1]
[1]CNR-IPCF Div. Bari, c/o Chemistry Department, via Orabona 4, 70126 Bari, Italy
[2]Chemistry Dept., University of Bari, via Orabona 4, 70126 Bari, Italy
[3]Dept. of Medical Biochemistry, Biology, and Physics, University of Bari, P.zza G. Cesare 11, 70124 Bari, Italy.
a.agostiano@ba.ipcf.cnr.it

In the last decades, Room Temperature Ionic Liquids (RTILs) have attracted the interest of scientific community, and are being considered a novel, promising class of materials for a variety of technological applications.[1] ILs are a class of substances, exclusively composed of ions, typically organic cations and different kinds of anions (i.e. halides, phosphates, imides), which have shown unique physico-chemical properties differing from aqueous ionic solutions and high temperature molten salts. ILs are characterized by a negligible vapor pressure, good thermal and electrochemical stabilities, low flammability, good solvent capabilities for many organic and inorganic compounds.[2] Thanks to these peculiar properties and the enormous potential RTILs offer in fields such as sensors, energy storage and information technologies, such kind of compounds is replacing conventional volatile organic solvents as green solvents in numerous chemical and industrial applications. Moreover, RTILs are also exploited as non-molecular solvents in various synthetic protocols for the preparation of numerous metallic, oxide and semiconductor nanoparticles.[3]

One of the most largely investigated class of ILs, is based on 1-alkyl-3-methyl imidazolium cation. In such imidazolium based ILs, a well defined organization has been found in both the solid and liquid phase.[4] The whole physico-chemical and original structural properties of such a class of materials can be exploited as templating and structure directing agents in the preparation of innovative hybrids and at the same time can convey their intrinsic functionalities, i.e. high ionic conductivity and electroactivity.

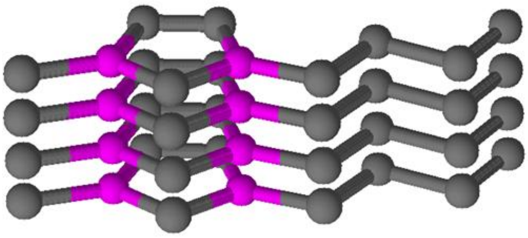


Figure 1. Imidazolium IL structural properties: π-π interactions between cation rings

In the growing field of hybrid materials, the combination of imidazolium based ILs and colloidal nanocrystals (NCs) in a unique nanocomposite is still almost unexplored, although can offer an enormous potential towards the design and the development of original components for advanced electrochemical devices, namely batteries and new generation solar cells. Here, we report on the incorporation of organic capped semiconductor and oxide NCs in different imidazole based ILs. Spectroscopic investigation has been carried out on the various prepared NC-IL composites and the variation of the alkyl chain length as well as the different nature of the inorganic anion on the properties of the prepared composites and the effect of the solvent have been extensively probed. Unexpectedly, time-resolved fluorescence measurements reveal the possible interaction between the different moieties, namely energy transfer or electron transfer, depending on the type of the involved NC. Such a result improves the knowledge on the dynamics involved in the hybrid formation, bringing a potential development in material science towards the fabrication of highly innovative next generation solar cells and electrochemical devices.

[1] J. F. Wishart and J. E. W. Castner, *J. Phys. Chem. B*, *111*, **2007**, 4639.
[2] N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, *37*, **2008**, 123.
[3] M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem. Int. Ed.*, *43*, **2004**, 4988.
[4] J. Dupont and P. A. Z. Suarez, *Phys. Chem. Chem. Phys.*,*8*, **2006**, 2441.

FIS-PO-37 Investigating dynamical systems on a mesoscopic scale with cellular automata

Federico G. Pazzona, Alberto Pintus, Andrea Gabrieli, Pierfranco Demontis, Giuseppe B. Suffritti

Università degli Studi di Sassari, Dipartimento di Chimica, via Vienna 2 – 07100 Sassari, Italy
fpazzona@uniss.it

A well parametrized Molecular Dynamics (MD) simulation can offer a realistic picture of the dynamical (non-reactive) processes in a molecular system. Analogously, molecular Monte Carlo (MC) simulations can provide its static equilibrium properties with quite good accuracy. Even though they are much cheaper than quantum mechanical models, still their level of microscopic detail is pretty high. This making them quite costly, especially if for example one wishes to simulate a rare-event phenomenon, for which really lenghty runs are required in order statistically meaningful data to be collected.

Lattice-gas models (most of them probabilistic) are often referred to when dealing on coarse-graining of molecular simulations. Not only do they represent inalienable tools for the investigation of the very foundations of statistical mechanics, but also their discrete, highly simplified configuration space offers an attractive alternative in the approach to the simulations on the mesoscale. Within the landscape of discrete models, cellular automata (CA) represent one of the most interesting objects at all [1]. Evolving in time as micro-worlds inspired by biological systems, they possess the really attractive feature of *synchronicity* (that the MD technique does possess as well, whereas MC approaches, on-lattice or off-lattice, do not), which makes them well suited to the study of collective dynamical properties, and they are *exact in the evolution*, due to the absence of round-off errors. Problem is, whereas nowadays MD/MC can be (and in fact they are) often used as brutal integrators/samplers to study a variety of systems, CA require to be set up *ad-hoc* for almost any problem one wishes to investigate. We show how progresses are being made by our group in using CA to study problems of adsorption/diffusion in zeolites [2].

[1] B. Chopard and M. Droz, *Cellular Automata Modeling of Physical Systems*, Cambridge University Press: Cambridge, England, 1998.
[2] F. G. Pazzona, P. Demontis, and G. B. Suffritti, *J. Chem. Phys., 131*, **2011**, 234703 and 234704.

FIS-PO-38 Fabrication and Characterization of Au Nanorod based Layer by Layer Architecture towards Biosensors

T. Placido,[a,b] **R. Comparelli,**[a] **E. Fanizza,**[b] **P. Cosma,**[a,b] **M. Striccoli,**[a] **M. L. Curri,**[a] **A. Agostiano**[a,b]

[a] CNR-IPCF Istituto per i Processi Chimici e Fisici, Sez. Bari, c/o Dip. Chimica Via Orabona 4, 70126 - Bari, Italy
[b] Università degli Studi di Bari – Dip. Chimica, Via Orabona 4, 70126 - Bari, Italy
t.placido@ba.ipcf.cnr.it

Metal nanoparticles have attracted great research interest in recent years because of their unique optical, electrical, and magnetic properties very appealing for electroanalysis and the construction of electrochemical sensors.[1] A key challenge in molecular bioelectronics is to improve the efficiency of long-range charge transfer. Gold nanoparticles allow the conductive materials to come into a close proximity of the active process and provide bioelectrocatalytic activity that can be utilized in biosensor devices.[2] The direct electron transfer of redox proteins has been realized and applied on various electrodes modified by gold nanoparticles, setting up biosensors based on their electrocatalytic activity.[3]

Layer-by-layer (LbL) assembly can build composite film multilayers containing different molecules or/and metal nanoparticles by simple wet chemistry.[4]

We report on the preparation and characterization of nanostructured film based on Au nanorods (NRs) obtained by using layer-by-layer (LBL) assembling, by exploiting electrostatic interaction among metal nanoparticles and polyelectrolyte. Multilayer films have been fabricated by using LBL assembly of poly(sodium styrenesulfonate) (PSS) and positively charged Au NRs onto polyelectrolyte-modified substrate. The effect of factors like substrate, initial polyelectrolyte anchoring layer, number of layers has been also spectroscopically and morphologically investigated. Finally, hybrid structures, based on Au NR and cytochrome *c*, have been assembled in order to create an effective interface between the red-ox protein and Au NRs deposited onto ITO electrode. The multilayered structures have been investigated by means of UV-vis absorbance spectrum, Atomic Force Microscopy (AFM) and Cyclic Voltammetry, ultimately defining spectroscopic properties, morphology and electrochemical behaviour of the obtained nanostructured architectures

[1] C. Daniel et al. Chem. Rev. 104 (2004) 293-346.
[2] A.N. Shipway et al., Chemphyschem, 1, (2000) 18-52
[3] P.S. Jensen et al., J. Phys. Chem. C, 111 (2007) 6124-6132
[4] G. Decher, Science 277 (1997) 1232-1237.

FIS-PO-39 Crystallographic, kinetic, and spectroscopic study of the first ligninolytic peroxidase presenting a catalytic tyrosine

Rebecca Pogni[§], Yuta Miki[‡], Fabiola R. Calviño[‡], Stefania Giansanti[§], Francisco J. Ruiz-Dueñas[‡2], María Jesús Martínez[‡], Riccardo Basosi[§], Antonio Romero[‡] and Angel T. Martínez[‡]

[§]Department of Chemistry, University of Siena, I-53100 Siena, Italy and [‡]Centro de Investigaciones Biológicas, CSIC, Ramiro de Maeztu 9, E-28040 Madrid, Spain,
rebecca.pogni@unisi.it

Trametes cervina lignin peroxidase ($^{\text{LiP}}$) is a unique enzyme lacking the catalytic tryptophan strictly conserved in all other LiP and versatile peroxidases (more than 30 sequences available to date)[1,2]. Recombinant *T. cervina* LiP and site-directed variants were investigated by crystallographic, kinetic, and spectroscopic techniques. The crystal structure showed three substrate oxidation site candidates involving His-170, Asp-146 and Tyr-181. Steady-state kinetics for oxidation of veratryl alcohol (the typical LiP substrate) by variants at the above three residues revealed a crucial role of Tyr-181 in LiP activity. Detailed spectroscopic and kinetic investigations, including low-temperature EPR, showed that the porphyrin radical in the two-electron activated *T. cervina* LiP is unstable and rapidly receives one electron from Tyr-181, forming a protein radical with a catalytic function. The crystal structure revealed a partially-exposed location of Tyr-181, compatible with its catalytic role, and several neighbor residues probably contributing to catalysis (Fig. 1). This is the first structure-function study of the only ligninolytic peroxidase described to date that has a catalytic tyrosine [3].

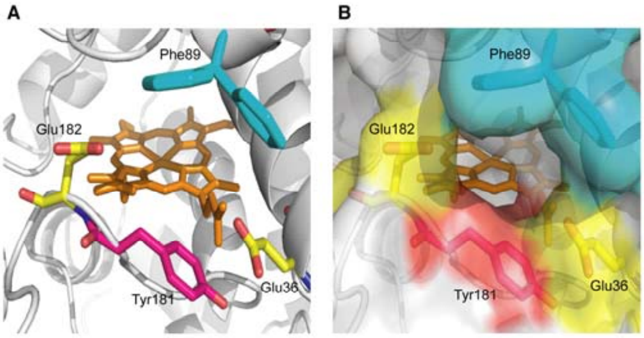


Figure 1

References

[1] W. A. Doyle, W. Blodig, N.C. Veitch, K. Piontek, and A.T. Smith, (1998) *Biochemistry* 37**, 1998**, 15097

[2] R. Pogni, M.C. Baratto, C. Teutloff, S. Giansanti, F.J. Ruiz-Dueñas, T. Choinowski, K. Piontek, A.T. Martínez, F. Lendzian, and R. Basosi, *J. Biol. Chem.* 281, **2006**, 9517

[3] M. Yuta, F.R. Calvino, R. Pogni, S. Giansanti, F.J. Ruiz-Duenas, M.J. Martinez, R. Basosi, A. Romero, and A.T. Martinez, *J. Biol. Chem.* 286, **2011**, 15525

FIS-PO-40 Nanoparticle-plasma protein interactions: confirmation by nanoLC-MS/MS of existence of hybrid structures in cationic liposome/DNA complexes

Daniela Pozzi,[a] Giulio Caracciolo,[a] Giuseppe Caruso,[b] Francesco Di Pascasio,[b] Patrizia Foglia,[b] Aldo Laganà[b], Heinz Amenitsch[c]

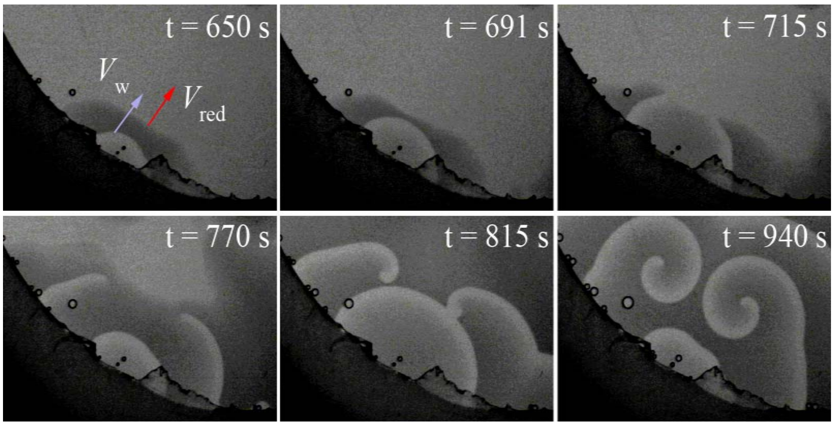
[a] Dipartimento di Medicina Molecolare della Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy
[b] Dipartimento di Chimica della Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy
[c]Institute of Biophysics and Nanosystems Research, Austrian Academy of Sciences, Schmiedelstrasse 6, A-8042 Graz, Austria
daniela.pozzi@uniroma1.it

The self-assembling of cationic liposomes (CLs) and DNA can give rise to a variety of nanostructures and morphologies. Multilamellar complexes are made of DNA intercalated between opposing lipid bilayers, while clusters formed by intact vesicles may exist as ‘beads-on-a-string’ (i.e. CLs attached to a string of DNA). Precise knowledge of the structure and morphology of complexes is relevant in many biological important processes such as gene delivery. Here dynamic light scattering, zeta potential, synchrotron small angle X-ray scattering and one-dimensional polyacrylamide gel electrophoresis were performed to investigate the equilibrium structure, morphology and interactions with plasma proteins of lipoplexes made of the cationic lipid (3β-[N-(N’,N’-dimethylaminoethane)-carbamoyl])-cholesterol (DC-Chol), the zwitterionic lipid dioleoylphosphatidylethanolamine (DOPE) and DNA. Results show that DC-Chol–DOPE/DNA complexes are multilamellar systems with DNA protected by cationic lipids. On the other hand, the ‘protein corona’ associated to lipoplexes after interaction with human plasma was found to be much richer in basic immunoglobulins gamma proteins (Ig-Gs) than that of pure lipid vesicles in the absence of DNA. According to the most recent evidences reported in the literature, this finding would suggest the existence of hybrid structures made of multilamellar complexes either stuck together by DNA or coexisting with DNA-loaded intact vesicles. Because surface properties of lipoplexes may determine their interaction with cells and tissues, these results may be important for predicting biological responses in vivo.

FIS-PO-41 Spontaneous spirals formation in excitable media

<u>Federico Rossi</u>[1*], **Rosario Varsalona**[2], **Nadia Marchettini**[1], **Maria Liria Turco Liveri**[2]

[1] Department of Chemistry, University of Siena, Via della Diana 2a 53100, Italy
[2] Department of Chemistry, University of Palermo, Viale delle Scienze Pad. 17, 90128 Palermo Italy
[*] *f.rossi@unisi.it*



The transition from planar fronts, trigger waves or solitary pulses to spirals in excitable media attracted an increasing interest in the past few decades, mainly because of its relevance for biological and medical applications[1,2]. In this contribute we describe a new and convenient method for spirals generation starting from symmetric wavefronts. By using the micelle-forming zwitterionic surfactant *N*-tetradecyl- *N,N*-dimethylamine oxide in a Belousov-Zhabotinsky solution[3,4], it is possible to control to a large extent the domains where spirals can be spontaneously generated. The mechanism responsible for the wavefront break up lies on the interaction of the propagating waves with the unexcitable regions formed by the interaction of the micelles with some of the Belousov-Zhabotinsky key intermediates (see figure).

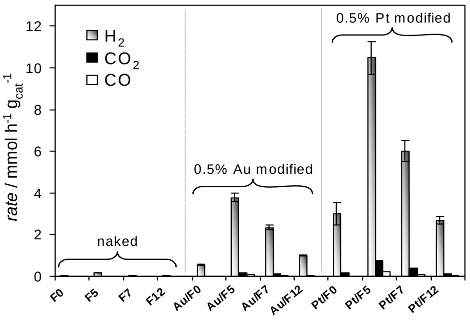
[1] A.V. Panfilov, *Chaos,* 8, **1998**, 57.
[2] T.K. Shajahan, A.R. Nayak, R. Pandit, *PLoS ONE,* 4, **2009**, e4738.
[3] F. Rossi, R. Varsalona, M.L.T. Liveri, *Chem. Phys. Lett.* 463, **2008**, 378-382.
[4] F. Rossi, M.L. Turco Liveri, *Colloids Surf. A-Physicochem. Eng. Asp.,* 351, **2009**, 60 - 64.

FIS-PO-42 Photocatalytic Hydrogen Production from Aqueous Solutions on Noble Metal-Modified and/or Doped TiO_2

Marco Altomare,[a] Gian Luca Chiarello,[a,b] Maria Vittoria Dozzi,[a] Alessia Saccomanni,[a] Elena Selli[a]

[a] Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy
[b] Institut für Technische Chemie und Polymerchemie, Karlsruher Institut für Technologie, Engesserstr. 20, 76131 Karlsruhe, Germany
E-mail. elena.selli@unimi.it

The photocatalytic production of hydrogen from water/methanol solutions was studied on titanium dioxide and on a series of NH_4F-doped TiO_2 photocatalysts prepared by sol-gel synthesis, varying the dopant-loading from 0% up to 12%. The photocatalysts were tested both naked and after deposition of gold and platinum nanoparticles, performed either by the reverse micelles method [1] or by photoreduction of metal precursors. Pt-modified undoped titania with 0-2 wt.% metal loadings was also investigated. The photocatalytic runs were carried out in a recirculation apparatus with the photocatalyst bed continuously fed with methanol/water vapor, employing a xenon lamp as irradiation source. Methanol underwent oxidation up to CO and CO_2; formaldehyde and formic acid were identified as oxidation intermediates [2,3].



For all of the investigated TiO_2 samples, the rate of H_2 production greatly increased upon Au and Pt nanoparticles deposition, because of their ability to enhance the separation of photoproduced electron-hole pairs. In particular Pt was a better co-catalyst than Au, in agreement with their work function values [2]. No significant increase in the H_2 production rate was attained with Pt loadings higher than 0.75% up to 2%.

Doping of TiO_2 enhanced the hydrogen production rate, with an identical bell-shaped trend with increasing the dopant content for the naked, Au- and Pt-modified titania series, with the 5% NH_4F-doped sample always being the best photocatalyst within each series. Thus, the structural properties of bulk doped titania ensure a more effective separation of photoproduced charge carriers. Indeed, doping followed by annealing at 700°C led to the formation of highly crystalline pure anatase [3], which is more photoactive than rutile. In contrast, over-doping led a decrease of the hydrogen production rate, possibly due to an excess of structure defects.

[1] G.L. Chiarello, A. Di Paola, L. Palmisano, E. Selli, *Photochem. Photobiol. Sci.*, *10*, **2011**, 355.
[2] G.L. Chiarello, M.H. Aguirre, E. Selli, *J. Catal.*, *273*, **2010**, 182.
[3] G.L. Chiarello, D. Ferri, E. Selli, *J. Catal.*, *273*, **2011**, 182.
[4] M.V. Dozzi, S. Livraghi, E. Giamello, E. Selli, *Photochem. Photobiol. Sci.*, *10*, **2011**, 343.

FIS-PO-43 The first X-Ray structure of a cold-adapted glutathione synthetase

Antonello Merlino[a,b], **Irene Russo Krauss**[a], **Andrea Pica**[a], **Alessandro Vergara**[a,b], **Antonella Albino**[c], **Mariorosario Masullo**[c], **Emmanuele De Vendittis**[c], **Filomena Sica** [a,b*]

[a]Dipartimento di Chimica 'Paolo Corradini' dell'Università di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cinthia, I-80126, Naples, Italy
[b]Istituto di Biostrutture e Bioimmagini, CNR, Via Mezzocannone 16, I-80134 Naples, Italy

[c]Dipartimento di Biochimica e Biotecnologie Mediche, Università di Napoli Federico II, Via Pansini 5, I-80131 Naples, Italy

**filosica@unina.it*

Glutathione (GSH) is the major antioxidant molecule in most living organisms. Besides its protective role in contrasting oxidative free radical species and in the removal of toxic metals, GSH is involved in redox homeostasis and cell signaling; furthermore, it is essential to maintain cellular proteins in their reduced state and acts as a post-translational regulator of protein function. The synthesis of GSH from its constituent amino acids involves two ATP-requiring enzymatic steps catalyzed by glutamate cysteine ligase (GshA) and glutathione synthetase (GshB), respectively. Its biosynthetic route has been described in details for a variety of organisms; however, nothing is known about this process ***in psychrophilic*** microorganisms. In particular, although various GshBs have been purified and sequenced, none of these enzymes belong to an organism living at low temperatures. Very recently, a recombinant form of GshB from the cold-adapted bacterium *Pseudoalteromonas haloplanktis* (*Ph*GshB) has been purified. The activity of *Ph*GshB was assayed through a direct method, measuring the release of inorganic phosphate from radiolabelled ATP. *Ph*GshB is active at 10°C and its activity significantly increases with temperature, at least up to 30°C; the K_m for ATP ranges between 0.14 and 0.25 mM in the 10 – 30°C interval.

The crystal structure of *Ph*GshB has been determined and refined at 2.3 Å resolution. Structural information is combined with a characterization of the thermal stability of the enzyme performed by circular dichroism and fluorescence measurements. A comparison between our data and those obtained for the closely related GshB from the mesophilic *Escherichia coli* [1-3], sharing 69% identity with *Ph*GshB, is presented in the attempt to understand the mechanisms of cold-adaptation of the psychrophilic enzyme.

[1] H. Yamaguchi, H. Kato, Y. Hata, T. Nishioka, A. Kimura, J. Oda, Y. Katsube, *J Mol Biol., 229(4)*, **1993,** 1083.
[2] T. Hara, H. Kato, Y. Katsube, J. Oda, *Biochemistry, 35(37)*, **1996**, 11967.
[3] K. Matsuda, K. Mizuguchi, T. Nishioka, H. Kato, N. Go, J. Oda, *Protein Eng., 9(12)*, **1996**, 1083.

FIS-PO-44 QM/MM characterization of redox-active Trp radicals in LiP and LiP-like systems

Adalgisa Sinicropi, **Caterina Bernini, Rebecca Pogni, Riccardo Basosi**

Department of Chemistry, University of Siena, 53100 Siena, Italy
sinicropi@unisi.it

Lignin Peroxidase (LiP) plays a central role in the biodegradation of the plant cell wall constituent lignin and is able to catalyze the oxidation of a variety of high redox potential compounds [1]. Spin-trapping, peptide mapping, site-directed mutagenesis and protein crystallography have been used to demonstrate that a surface oxidation site (Trp 171) in LiP is involved in the electron transfer to the heme cofactor via a long range electron transfer mechanism activated by H_2O_2 (Figure 1A). However, no direct evidence for the formation of the Trp171 radical intermediate has been reported to date. An additional intriguing finding is that Trp171 is stereospecifically hydroxylated at its C□-atom as result of an autocatalytic self-oxidation that takes place during the first turnover cycles [1,2].

Recently, site-directed mutagenesis has been used to manipulate the microenvironment of Trp171 site in LiP (E250Q+E168Q, Figure 1B), allowing the detection by EPR spectroscopy of the Trp171 radical species [3]. The same engineering-based approach has been also applied to introduce the catalytic Trp and its acidic environment into Coprinus cinereus Peroxidase (CiP), that has similar protein fold but lacks oxidation activity. A Trp radical in the resulting CiP triple variant (D178W+R257E+R271D, Figure 1C) was identified and characterized by multifrequency EPR spectroscopy (9 and 285 GHz) [3].

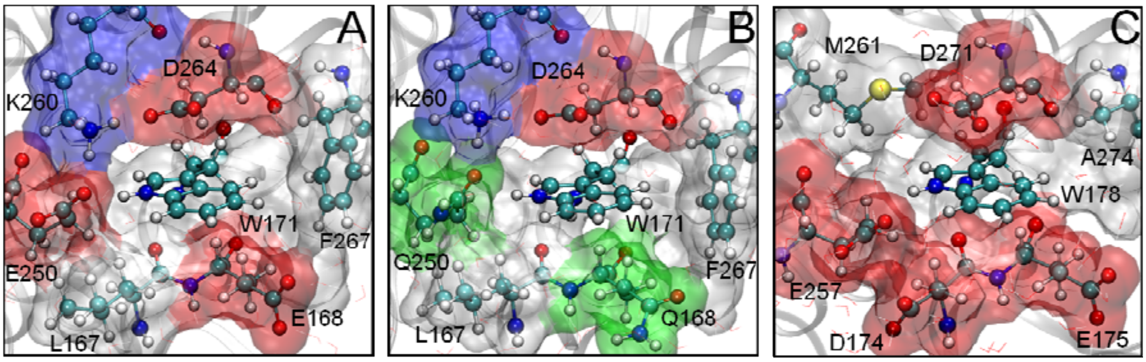


Figure 1

In the light of the newly available EPR experimental data we performed a QM/MM computational study in order to characterize Trp radicals in the protein matrix of these LiP-like systems (Figure 1). In particular, the inclusion in the calculation of all the electrostatic and steric interactions within a QM/MM (DFT/CHARMM) strategy, already applied successfully to the study of Trp and Tyr radical intermediates in a Versatile Peroxidase and in its W164Y mutant [4], allowed a direct comparison between experimental and computed data. Differences in electronic and geometrical structure of Trp radicals among these enzymes are discussed, with the aim of understanding the different behaviour of LiP in comparison to that of LiP and CiP mutants.

[1] W. Blodig, A. T. Smith, W. A. Doyle, K. Piontek, *J. Mol. Biol.*, *305*, **2001**, 851.
[2] W. Blodig, A. T. Smith, K. Winterhalter, K. Piontek, *Arch. Biochem. Biophys.*, *370*, **1999**, 86.
[3] A. T. Smith, W. A. Doyle, P. Dorlet and A. Ivancich, *PNAS*, *106*, **2009**, 16084.
[4] C. Bernini, R. Pogni, F. J. Ruiz-Duenãs, A. T. Martínez, R. Basosi and A. Sinicropi, *Phys. Chem. Chem. Phys.*, *13*, **2011**, 5078.

FIS-PO-45 Aggregation properties, inclusion in membrane models and LB film formation of porphyrin scaffolds functionalized by glucosilated steroid units

R. Lettieri,[1] D. Monti,[1] Pavel Drasar[2] and M. Venanzi[1]

[1] Department of Chemical Sciences and Technologies, University of Rome “Tor Vergata”, 00133 Rome, Italy; [2] Institute of Organic Chemistry and Biochemistry, AS CR, Praha, Czech Republik.
venanzi@uniroma2.it

New glucosylated steroid modified porphyrins, differing from the number and type of ring substitutions, have been taken in consideration as chiral recognition elements in organized environments (Figure 1). The aggregation properties in solution, the formation of porphyrin films on hydrophilic surfaces and the inclusion in biological membrane models like liposomes or supported lipid bi-layers have been investigated by optical spectroscopy (UV-Vis absorption, steady-state and time-resolved fluorescence spectroscopy, circular dichroism). The aggregation of porphyrin derivatives in DMSO/H_2O (40/60 v/v) gives rise to the broadening of the Soret band and a strong hypochromic shift. Such effects can be ascribed to the formation of J-type supramolecular structures. Circular Dichroism studies revealed the chiral nature of the formed supramolecular species.

Porphyrin multilayers are built up through Langmuir-Blodgett deposition on quartz supports. The behavior of each system at the air/water interface was characterized by recording compression isotherms.

Several experiments were also carried out to investigate the interaction between the synthesized porphyrin derivatives and a membrane model represented by unilamellar 1-palmitoyl,2-oleoyl-sn-glycero-3-phosphocholine (POPC) liposomes. The partition between the aqueous and lipid phase and the inclusion of the above porphyrins in a lipid bilayer have been investigated by fluorescence anisotropy and fluorescence quenching measurements. The results indicate that, while the bi-substituted derivative is most likely located at the outer surface of the liposome, the monosubstituted porphyrin is able to insert the hydrophobic part into the bi-layer, exposing the hydrophilic group to the aqueous solution, out of the vesicle.

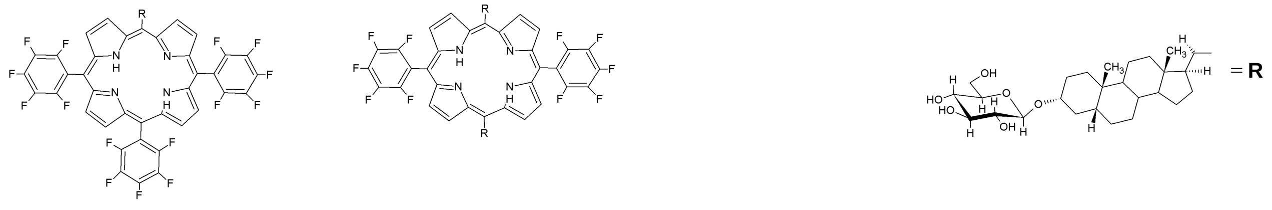


Figure. 1 – Molecular scheme of the functionalized porphyrin investigated

FIS-PO-46 Polyelectrolyte multilayer as a platform for nanocrystal uniform and patterned assembly

E. Fanizza,[1,2] M. Altomare,[1,2] T. Del Sole,[1,2] A. E. Di Mauro,[1,2] M. Corricelli,[1,2] N. Depalo,[1,2] R. Comparelli,[1] A. Agostiano,[1,2] M. Striccoli,[1] M. L. Curri [1]

[1]CNR-IPCF-Sez.Bari, c/o Dip. Chimica, Via Orabona 4, Bari; 70126, Italy
[2]Università degli Studi di Bari – Dip. Di Chimica,Via Orabona 4, Bari, 70126, Italy
m.corricelli@ba.ipcf.cnr.it

Fabrication of nanoparticle (NP) film allows to transfer onto solid surface the peculiar size dependent properties of nano-sized materials, thus opening access not only to fundamental understanding of new phenomena and characteristics of such nanostructured materials but also to their technological exploitation in devices, such as biochips and sensors.Proper design of substrate and particle surface chemistry defines the driving force directing the assembly of stable particle layer, namely electrostatic interaction, covalent bonding, host guest and, in general supramolecular, interaction.Here the fabrication of uniform and patterned nanocrystal (NC) assemblies was thoroughly investigated. A layer by layer strategy was used to prepare polyelectrolyte functionalized substrates as platform for electrostatically driven NC assembly. Substrate surface charge and morphology were tailored by carefully choosing the suitable deposition condition, substrate treatment as well as post deposition procedures, in order to properly template an effective and uniform NC assembly. In particular water soluble luminescent (CdSe)ZnS and CdS NCs were selected as functional materials, being also a valuable model material for a prompt monitoring of the assembling process. Tuning particle surface chemistry by the implementation of suitable surface engineering, such as ligand- exchange reaction, growth of hydrophilic silica shell and formation of hydrophilic inclusion complex, offered a variety of NPs with specific surface functional groups soluble in aqueous solution and with a good colloidal stability in defined pH-range. The specific interaction between substrate chemistry and NP surface charge was extensively investigated, and found crucial for ultimately direct particle assembly. Finally, particular microcontact printing combined to wet chemistry strategies is demonstrated to be a straightforward approach to fabricate discrete structures where particle positioning is carefully directed and controlled.

Fanizza E., Malaquin L. , Kraus T. , Wolf H., Striccoli M., Micali N., Taurino A., Agostiano A., Curri M. L. *Langmuir*, **2010**, *26*, 14294–14300
Depalo N., Comparelli R., Striccoli M., Curri M.L., Fini P., Giotta L., Agostiano A. *J.. Phys. Chem. B*, **2006**, *110*, 17388–17399
Feld Z., Varga I., Blomberg E. *Langmuir* **2010,** *26*, 17048-17057
Park J., Hammond P.T., *Adv. Mater.* **2004**, *26*, 520-525

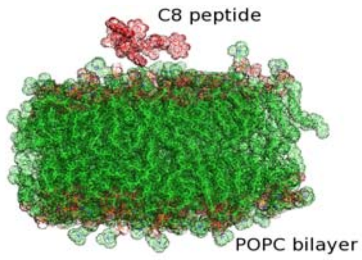
FIS-PO-47 Lipid composition regulates the biomembranes micro-structural properties and modulates the interaction with a peptide deriving from the viral glycoprotein gp36.

Giuseppe Vitiello[a,b], Giovanna Fragneto[c], Anna Maria D'Ursi[d], Luigi Paduano[a,b] and Gerardino D'Errico[a,b]

[a] Dipartimento di Chimica, Università di Napoli "Federico II", Napoli, Italy.
[b] CSGI, Firenze, Italy.
[c] Institut Laue-Langevin, Grenoble, France.
[d] Dipartimento di Scienze Farmaceutiche, Università di Salerno, Fisciano, Italy.
giuseppe.vitiello@unina.it

Lipid–protein interactions play a key role in a wide variety of cellular processes. Lipids can affect protein structure and dynamics either via physicochemical characteristics of the membrane, such as elasticity, curvature, surface charge, hydration and the formation of domains, or by specific interactions involving the chemical structure, conformation and dynamics of the lipid head groups and acyl chains. Consequently, much attention has been paid to the lipid composition of biomembranes, which includes a rich diversity of phospholipids, sterols and glycolipids, on influencing several membrane processes.

In this work, we have performed a study on the effect of the cholesterol, at different concentrations (from 0% to 30% wt/wt), and sphingomyelin presence on the micro-structural properties of palmitoyl-oleoyl phosphatidylcholine (POPC) bilayers. The investigation has been carried out by a combined experimental approach, performing Neutron Reflectivity (NR) and Electron Paramagnetic Resonance (EPR) experiments on supported lipid bilayers and liposomes, respectively. We also focusing on the role of lipid composition on the interaction with a peptide (Ac-Trp-Glu-Asp-Trp-Val-Gly-Trp-Ile-NH_2), named C8 and deriving from the membrane-proximal external region (MPER) of the glycoprotein gp36 of Feline Immunodeficiency Virus (FIV).



We observed that C8 peptide adsorbs on the POPC bilayer surface, perturbing the lipid packing and chain motion in the membrane[1, 2]. The addition of cholesterol and sphyngomelin produces significant changes on the POPC bilayer micro-structure, influencing the subsequent interaction with the C8 peptide.

References

[1] G. D'Errico, G. Vitiello, A.M. D'Ursi, D. Marsh, *Eur. Biophys. J.*, *38*, **2009**, 873-882.

[2] A. Merlino, G.Vitiello, M. Grimaldi, F. Sica, E. Busi, R. Basosi, A.M. D'Ursi, G. Fragneto, L. Paduano, G. D'Errico, *submitted*, **2011**.