Società Chimica Italiana

Programma del XXVI Congresso Nazionale della Società Chimica Italiana

Centro Congressi Hotel Ariston
Paestum (SA), 10-14 settembre 2017

- Divisione di Chimica Fisica

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Sommario

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Delegato di Divisione

- Riccardo Zanasi, Università degli Studi di Salerno

Programma Scientifico

Divisione di Chimica Fisica

Lunedì 11 Settembre 2017

	Sala Vivaldi - Hotel Savoy
Photoactive Materials	
Chairperson: Elena Selli	
9:00 - 9:15	FIS OR01: A. Truppi, F. Petronella, T. Placido, C. Giannini, T. Sibillano, A. Agostiano, M. L. Curri, R. Comparelli *TiO_2/Au NRs photocatalysts for photodegradation of water pollutants under UV and visible light*
9:15 - 9:30	FIS OR02: F. Ortica, M. Frigoli, A. Zangarelli, D. Pannacci *Photochromism of N-phenyl-carbazole benzopyrans*
9:30 - 9:45	FIS OR03: A. Panniello, A. E. Di Mauro, E. Fanizza, M. L. Curri, M. Striccoli *Hydrophobic carbon dots with intense phololuminescence towards single white emitting materials*
New Composite Materials	
Chairperson: Moreno Meneghetti	
9:45 - 10:00	FIS OR04: F. Cesano, S. Cravanzola, F. Gaziano, D. Scarano *Graphene-like domains on MoS_2/TiO_2 systems, via acetylene polymerization: in-situ synthesis and characterization*
10:00 - 10:15	FIS OR05: C. Ingrosso, M. Corricelli, G. V. Bianco, V. Pifferi, P. Guffanti, A. Testolin, F. Bettazzi, F. Petronella, R. Comparelli, A. Agostiano, M. Striccoli, I. Palchetti, L. Falciola, G. Bruno, M. L. Curri *Colloidal Nanocrystal Surface Decorated Graphene based Hybrid Materials for Sensors*
10:15 - 10:30	FIS OR06: C. Sartorio, V. Campisciano, C. Chiappara, S. Cataldo, M. Gruttadauria, F. Giacalone, B. Pignataro *Enhanced power-conversion efficiency in organic solar cells incorporating polymeric compatibilizers*
10:30 - 11:00	Coffee Break
Models & Experiments	
Chairperson: Giovanni Marletta	
11:00 - 11:30	FIS KN01: P. Ugliengo, A. Rimola, M. Sodupe M. Fabbiani, G. Martra *Amide Bond Formation by Condensation between Unactivated Reagents at Silica Surfaces: Rôle in Prebiotic Chemistry*
11:30 - 11:45	FIS OR07: A. Painelli, S. Sanyal, F. Terenziani, S. Pati, C. Sissa *Molecular Aggregates: a Fresh Perspective*
11:45 - 12:00	FIS OR08: F. Sessa, V. Migliorati, A. Serva, P. D'Angelo *On the Zn^{2+} ion speciation in challenging ionic media: a molecular dynamics and X-ray absorption spectroscopy study*
Materials for Biotechnological Applications 1	
Chairperson: Patrizia Canton	
12:00 - 12:15	FIS OR09: F. Vischio, N. Depalo, I. Arduino, S. Villa, F. Canepa, E. Fanizza, S. H. Lee, B. C. Lee, R. M. Iacobazzi, V. Laquintana, A. Lapedota, A. Cutrignelli, M. P. Scavo, M. Striccoli, A. Agostiano, M. L. Curri, N. Denora *Magnetic Solid Lipid Nanoparticles for Magnetically Targeted Delivery of Sorafenib for Treatment of Hepatocellular Carcinoma*
12:15 - 12:30	FIS OR10: A. De Santis, I. R. Krauss, L. Paduano, G. D'Errico

	Micro-structural characterization of model membranes containing DHA
12:30 - 12:45	FIS OR11: G. Valente, N. Depalo, E. Fanizza, R. M. Iacobazzi, N. Denora, V. Laquintana, L. Zaccaro, A. Del Gatto, I. De Paola, M. Saviano, P. D. Howes, C. Spicer, M. M. Stevens, M. Striccoli, A. Agostiano, L. M. Curri *Nanoparticles encapsulation in micellar systems for biomedical applications*
12:45 - 13:00	FIS OR12: R. Gelli, L. Mati, F. Ridi, P. Baglioni *Effect of cellulose ethers on the formation and properties of magnesium phosphate-based cements for biomedical applications*

13:00 - 14:00	Intervallo Pranzo – Lunch Break

	Sala Paestum B
14:00 - 15:00	*Poster Session 1 (FIS PO01 - FIS PO16)*
Molecular and Supramolecular Systems	
Chairperson: Gerardino D'Errico	
15:00 - 15:15	FIS OR13: G. De Filpo, P. Formoso, S. Manfredi, A. I. Mashin, F. P. Nicoletta *Bifunctional polymer-dispersed liquid crystals*
15:15 - 15:30	FIS OR14: J. Cautela, J. J. Crassous, N. V. Pavel, L. Galantini *Supracolloidal association of microgels and supramolecular tubules of bile salt derivatives*
15:30 - 15:45	FIS OR15: P. Sassi, B. Gironi, A. Lapini, M. Paolantoni, A. Morresi, P. Foggia *The lipid bilayer of model membranes: news from the inside*
Physical Studies of Materials and Molecules	
Chairperson: Gianmario Martra	
15:45 - 16:00	FIS OR16: V. Domenici, A. Resetic, J. Milavec, B. Zupancic, B. Zalar *Physical-chemical study of a new shape-memory material based on liquid crystalline elastomers*
16:00 - 16:15	FIS OR17: G. Cavallaro, V. Bertolino, G. Lazzara, F. Parisi, S. Milioto, M. Gradzielski *Hybrid nanostructures based on halloysite nanotubes and sustainable polymers*
16:15 - 16:30	FIS OR18: G. Monaco, F. Aquino, R. Zanasi, W. Herrebout, A. Massa *Absolute Configuration Assignment of two Hybrid Isoindolinone-phthalide Molecules by Vibrational Circular Dichroism*
16:30 - 17:00	Coffee Break
Chemistry of Materials and Surfaces	
Chairperson: Ludovico Valli	
17:00 - 17:15	FIS OR19: E. Groppo, A. Piovano, G. Martino, M. D'Amore, C. Barzan, S. Bordiga *Can we speak of "ancillary ligands" also in heterogeneous catalysis? Selected examples in olefin polymerization catalysts*
17:15 - 17:30	FIS OR20: E. Fanizza, F. Cascella, A. Panniello, L. Triggiani, N. Depalo, C. Giannini, D. Altamura, A. Agostiano, M. L. Curri, M. Striccoli *Synthesis and post preparative shape control of cesium lead bromide colloidal nanocrystals*
17:30 - 17:45	FIS OR21: M. L. Saladino, F. Armetta, D. Hreniak, L. Marciniak, W. Stręk, C. Giordano, E. Caponetti *Non conventional based Ce:YAG nanocomposites*
Materials for Biotechnological Applications 2	
Chairperson: Concetta Giancola	
17:45 - 18:00	FIS OR22: F. Ridi, R. Gelli, L. Gigli, M. Scudero, M. Bonini, P. Baglioni *Synthesis and characterization of immunologically relevant calcium and magnesium phosphate amorphous nanostructures and strategies for their stabilisation*

18:00 - 18:15	FIS OR23: E. Gatto, R. Lettieri, A. Colella, F. Leonelli, L. Giansanti, L. Stella, M. Venanzi *Physico-chemical characterization of smart lipid biointerfaces for the detection of a tumor biomarker*
18:15 - 18:30	FIS OR24: I. Miletto, L. Invernizzi, C. Gionco, M. C. Paganini, E. Giamello, L. Marchese, E. Gianotti *Luminescent* $ZrO_2{:}Ln^{3+}@SiO_2$ *Nanosystems Conjugated with Rose Bengal as Efficient Nanoplatform for Theranostic Applications*
18:30 - 20:00	Assemblea della divisione di Chimica Fisica ***Sala Olimpia – Hotel Ariston***

Martedì 12 Settembre 2017

Sala Verdi - Hotel Savoy	
Materials	
Chairpersons: Debora Berti, Gianmario Martra	
9:00 - 9:15	FIS OR25: A. Girlando, N. Castagnetti, M. Masino *Phenomenology of the Neutral-Ionic Valence Instability in Mixed Stack Charge Transfer Crystals*
9:15 - 9:30	FIS OR26: M. Fabbiani, G. Tabacchi, E. Fois, G. Martra *The effect of temperature in the formic acid - formate system on* TiO_2 *(101) surfaces*
9:30 - 9:45	FIS OR27: M. Tonelli, R. Moscatelli, M. Sebastiani, F. Martini, L. Calucci, M. Geppi, S. Borsacchi, F. Ridi *Interaction of phosphate-based additives with* MgO/SiO_2 *cements*
9:45 - 10:00	FIS OR28: L. Triggiani, C. N. Dibenedetto, G. Tartaro, A. Loiudice, T. Sibillano, C. Giannini, G. Bruno, R. Brescia, R. Buonsanti, A. Agostiano, M. Striccoli, E. Fanizza *Composition and architecture engineering of colloidal* TiO_2 *nanocrystals for the enhancement of sunlight conversion ability*
10:00 - 10:15	FIS OR29: Y. Miele, A. F. Taylor, T. Bánsági Jr, L. Izzo, F. Rossi *Coupling of nonlinear chemical reactions with pH-responsive polymers*
10:15 - 10:30	FIS OR30: J. Gubitosa, V. Rizzi, P. Fini, A. Petrella, F. Fanelli, A. Agostiano, M. Perrone, I. Arduino, A. Lopedota, P. Cosma *Green synthesis of gold nanoparticles using Punica Granatum Juice for cosmetic applications*
10:30 - 11:00	Coffee Break
Materials	
Chairpersons: Alberto Girlando, Gerardino D'Errico	
11:00 - 11:15	FIS OR31: M. Bonini, A. Gabbani, S. Del Buffa, F. Ridi, P. Baglioni, R. Bordes, K. Holmberg *Adsorption of Amino Acids and Glutamic Acid-Based Surfactants on Imogolite Clays*
11:15 - 11:30	FIS OR32: M. Corno, I. Miletto, E. Gianotti, M. Cossi, L. Marchese *Organic-inorganic hybrid materials as heterogenous catalysts for pharma industry*
11:30 - 11:45	FIS OR33: L. Ambrosone, G. Bufalo, F. Cuomo, F. Lopez *Coupling of sieving and thermogravimetric analyzes for studying the activation energy distribution function of complex reactions*
11:45 - 12:00	FIS OR34: M. Baglioni, C. Montis, F. Brandi, T. Guaragnon, I. Meazzini, P. Baglioni, D. Berti *Dewetting of acrylic polymeric films induced by water/propylene carbonate/surfactant mixtures - Implications for cultural heritage conservation*

12:00 - 12:15	FIS OR35: V. Rizzi, M. A. Ricci, E. Altamura, P. Fini, S. Sortino, A. Fraix, P. Semeraro, L. De Cola, E. A. Prasetyanto, P. Cosma *Supramolecular Self-Assembly of Chlorophyll A and Mesoporous Silica Nanoparticles in Water Medium*
12:15 - 12:30	FIS OR36: R. Camerini, D. Chelazzi, R. Giorgi, P. Baglioni *Silica-based composites for the consolidation of earthen materials*
12:30 - 12:45	FIS OR37: B. Di Napoli, P. Conflitti, C. Mazzuca, M. Venanzi, M. De Zotti, F. Formaggio, A. Palleschi *Langmuir-Blodgett and MD characterization of peptides at the air/water interface*
12:45 - 13:00	FIS OR38: L. Litti, A. Ramundo, V. Amendola, M. Meneghetti *Detection and Quantification of Anticancer Drugs with Surface Enhanced Raman Spectroscopy*

13:00 - 14:00	Intervallo Pranzo

Sala Paestum B	
14:00 - 15:00	*Poster Session 2 (FIS PO17 - FIS PO33)*

Mercoledì 13 Settembre 2017

Sala Paestum B	
14:00 - 15:00	*Poster Session 3 (FIS PO34 - FIS PO51)*
Sala Vivaldi - Hotel Savoy	
Environmental Physical Chemistry	
Chairpersons: Maria Lucia Curri, Riccardo Zanasi	
15:00 - 15:15	FIS OR39: A. Tursi, N. De Vietro, A. Beneduci, F. Chidichimo, F. Fracassi, G. Chidichimo *Effective remediation of highly polluted water by petroleum hydrocarbons with functionalized cellulose fiber*
15:15 - 15:30	FIS OR40: S. Salvestrini *A comparison between the Langmuir rate equation and the pseudo-first and pseudo-second order models for adsorption processes*
15:30 - 15:45	FIS OR41: F. Venditti, F. Cuomo, L. Ambrosone, A. Ceglie, G. Cinelli, F. Lopez *Microstructured composite for Cr (VI) removal from polluted environment*
15:45 - 16:00	FIS OR42: F. Lopez, F. Cuomo, F. Venditti, L. Ambrosone, A. Ceglie *Olive mill wastewaters phenol photocatalytic degradation by visible light activated carbon doped titanium*
16:00 - 16:15	FIS OR43: P. Semeraro, J. A. Gabaldón, P. Fini, J. A. Pellicer, V. Rizzi, A. Longo, E. Núñez, P. Cosma *Removal of an azo textile dye from wastewater using cyclodextrin-epichlorohydrin polymers*
16:15 - 16:30	FIS OR44: R. Angelico, C. Colombo, G. Palumbo, G. Ventruti *Arsenic Adsorption on Iron Oxides and its Environmental Impact*
16:30 - 17:00	Coffee Break
Physical Chemistry of Biological Systems	
Chairpersons: Concetta Giancola, Maria Rosaria Tinè	

17:00 - 17:15	FIS OR45: F. Tadini-Buoninsegni *Electrophysiological measurements on a solid supported membrane to investigate the transport activity of sarcoplasmic reticulum* Ca^{2+}*-ATPase*
17:15 - 17:30	FIS OR46: F. Sciubba, M. Delfini, M. E. Di Cocco, F. Ferraris *Protein-ligand interaction: a NMR study*
17:30 - 17:45	FIS OR47: C. Satriano, P. Di Pietro, N. Caporarello, C. D. Anfuso, G. Lupo, A. Magrì, D. La Mendola *Immobilisation of neurotrophin peptides on gold nanoparticles by direct and lipid-mediated interaction: a new multipotential therapeutic nanoplatform for CNS disorders*
17:45 - 18:00	FIS OR48: V. De Leo, F. Milano, R. Comparelli, E. De Giglio, A. Trapani, S. Di Gioia, M. Conese, M. Mattioli-Belmonte, A. Agostiano, L. Catucci *Small liposomes for drug delivery*
18:00 - 18:15	FIS OR49: G. Arrabito, F. Cavaleri, A. Porchetta, F. Ricci, V. Vetri, M. Leone, B. Pignataro *Molecular Confinement in Femtoliter Scale Aqueous Compartments*
18:15 - 18:30	FIS OR50: S. Rapino, L. Bartolini, C. Albonetti, A. Soldà, G. Valenti, F. Valle, P. G. Pelicci, F. Paolucci, F. Zerbetto *The Influence of Chemical Microenvironment on Living Cell Shape*

Joined Sessions

Lunedì 11 Settembre 2017

Sala Afrodite - Hotel Ariston	
SessioneABC+ANA+FIS: La trasversalità della chimica per i Beni Culturali	
Chairperson: Lucia Toniolo	
9:00 - 9:25	ABC/ANA/FIS KN01: Rocco Mazzeo *Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces*
9:25 - 9:40	FIS OR65: C. Berlangieri, E. Carretti, G. Poggi, S. Murgia, M. Monduzzi, L. Dei, P. Baglioni *Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces*
9:40 - 9:55	FIS OR66: P. Ferrari, A. Mirabile, M. Trabace, L. Montalbano, R. Giorgi, P. Baglioni *Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks*
9:55 - 10:10	FIS OR67: N. Bonelli, R. Mastrangelo, C. Montis, P. Tempesti, P. Baglioni *Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network*
10:10 - 10:25	FIS OR68: G. Poggi, R. Giorgi, P. Baglioni *Nanocomposites for the consolidation and deacidification of cellulose-based artifacts*
10:30 - 11:00	Coffee Break
Chairperson: Elisabetta Zendri	
11:00 - 11:25	ABC/ANA/FIS KN02: Erika Ribechini *GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century*
11:25 - 11:40	ABC/ANA/FIS OR05: Francesca Di Turo

	FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach
11:40 - 11:55	ABC/ANA/FIS OR06: Antonella Casoli *I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra*
11:55 - 12:10	ABC/ANA/FIS OR07: Elettra Barberis *Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects*
12:10 - 12:25	ABC/ANA/FIS OR08: Giuseppe Egidio De Benedetto *Provenance of bitumen from different Apulian Bronze Age settlements through a biomarker based approach*
12:25 - 12:40	ABC/ANA/FIS OR09: Marzia Fantauzzi *From XAES signals to depth-profile reconstruction: the case of copper and copper alloys*
12:40 - 12:55	ABC/ANA/FIS OR10: Marco Orlandi *Integrated approach for the chemical characterization of archaeological woods*
Sala Diana - Hotel Ariston	
Sessione: Sistemi Biologici - Fisica	
Chairpersons: Carla Isernia, Concetta Giancola	
11:00 - 11:50	CSB PL2: Maria Rosaria Tinè *Calorimetry and Thermoanalytical Techniques in the Study of Proteins*
11:50 - 12:05	FIS OR69: R. Oliva, A. Grimaldi, P. Del Vecchio, V. Cafaro, K. Pane, E. Notomista, L. Petraccone *Biophysical studies of membrane perturbation induced by the antimicrobial peptide GKY20*
12:05 - 12:20	CSB OR3: Alessandro D'Urso *Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation*
12.20 - 12.35	FIS OR70: A. Del Giudice, C. Dicko, L. Galantini, N. V. Pavel *The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite*
12.35 - 12.50	CSB OR4: Jussara Amato *Identification and characterization of DNA G-quadruplex interacting proteins*

Martedì 12 Settembre 2017

Sala Vivaldi - Hotel Savoy	
Sessione Congiunta: Fisica - Elettrochimica - Enerchem	
Chairpersons: Moreno Meneghetti, Alessandro Minguzzi	
9:00 - 9:30	ELE KN01: Riccardo Ruffo *Negative Electrode Materials for Sodium Ion Batteries*
9:30 - 9:45	FIS OR51: F. Lamberti, L. Litti, M. De Bastiani, R. Sorrentino, M. Gandini, M. Meneghetti, A. Petrozza *High-Quality, Ligands-Free, Mixed-Halide Perovskite Nanocrystals Ink for Optoelectronic applications*
9:45 - 10:00	ELE OR20: M. Musiani, E. Verlato, S. Barison, S. Cimino, L. Lisi, G. Mancino, F. Paolucci *Electrochemical preparation of nanostructured* CeO_2*-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol*
10:00 - 10:15	FIS OR52: S. Binetti, A. Le Donne, M. Acciarri, S. Marchionna *New Earth-Abundant Thin Film Solar Cells Based on* Cu_2MnSnS_4

10:15 - 10:30	ELE OR21: C. Durante, G. Daniel, G. Mattiacci, G. A. Rizzi, A. Gennaro *Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction*
10:30 - 11:00	Coffee Break
Sessione Congiunta: Elettrochimica - Fisica - Enerchem	
Chairpersons: Simona Binetti, Claudio Gerbaldi	
11:00 - 11:15	FIS OR53: P. Mustarelli, F. Invernizzi, M. Patrini, K. Vezzù, V. Di Noto *Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters*
11:15 - 11:30	FIS OR54: G. L. Chiarello, M. Bernareggi, M. Pedroni, M. Magni, S. M. Pietralunga, E. Vassallo, E. Selli *A Bilayer WO_3 n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting*
11:30 - 11:45	ELE OR22: F. Bella, F. Colò, L. Zolin, D. Pugliese, A. M. Stephan, C. Gerbaldi *Lignocellulosic Materials for Electrochemical Energy Storage and Conversion*
11:45 - 12:00	FIS OR55: S. Brutti, S. Panero, A. Paolone, P. Reale *Hydrides as High Capacity Anodes in Lithium Cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project*
12:00 - 12:15	ELE OR23: F. Bertasi, V. Di Noto - *Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes*
12:15 - 12:30	FIS OR56: S. La Gatta, F. Milano, R. Ragni, A. Agostiano, G. M. Farinola, M. Trotta *Bio-hybrid Complexes in Artificial Photosynthesis*
12:30 - 12:45	ELE OR24: A. Minguzzi, M. Fracchia, A. Visibile, A. Naldoni, F. Malara, C. Locatelli, A. Vertova, P. Ghigna, S. Rondinini *Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting*
12:45 - 13:00	FIS OR57: A. Beneduci, A. L. Capodilupo, G. A. Corrente, E. Fabiano, V. Maltese, S. Cospito, G. Ciccarella, G. Chidichimo, G. Gigli *Electronic Coupling in H-Shaped Tetra-Arylamine Mixed-Valence Compounds*
13:00 - 14:00	Intervallo Pranzo

Mercoledì 13 Settembre 2017

Sala Puccini - Hotel Savoy	
Sessione Congiunta: Fisica - Teorica	
Chairperson: Michele Pavone	
15:00 - 15:40	TEO KN01: C. Cappelli *A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions*
15:40 - 16:00	TEO OR01: R. Dovesi, S. Salustro, F. Gentile , Y. Noel *Hydrogen defects in diamond. A quantum mechanical approach*
16:00 - 16:15	FIS OR58: L. Zamirri, M. Corno, A. Rimola, P. Ugliengo *Forsterite surfaces as models of interstellar core dust grains: computational study of carbon monoxide adsorption*
16:15 - 16:30	FIS OR59: M. Mattia, D. E. Claudio, D. Luca, P. Cristina, S. Lorenzo *Prebiotic Molecules in Interstellar Space: Aminoacetonitrile and C-Cyanomethanimine*
16:30 - 17:00	Coffee Break
Chairperson: Ludovico Valli	
17:00 - 17:15	FIS OR60: M. V. La Rocca, L. Izzo, S. Losio, M. Mella *Should we introduce pre-equilibria into Markov models for homogeneously catalyzed copolymerization?*

17:15 - 17:30	FIS OR61: F. Di Maiolo, C. Pieroni, A. Painelli *Intramolecular Energy Transfer in Real Time*
17:30 - 17:45	TEO OR02: E. Bodo, A. Le Donne *Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations*
17:45 - 18:00	TEO OR03: N. Tasinato, L. Spada, C. Puzzarini,V. Barone *Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer*
18:00 - 18:15	FIS OR62: A. Mariani, R. Caminiti, L. Gontrani *A spotlight on the complex hierarchical structure of some ionic liquid-molecular liquid binary mixtures*
18:15 - 18:30	FIS OR63: O. Russina, R. Caminiti *Fluorous mesoscopic domains in room temperature ionic liquids*
18:30 - 18:45	FIS OR64: E. Fois, R. Arletti, L. Gigli, G. Vezzalini, S. Quartieri, G. Tabacchi *Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure*

Keynote

- FIS KN01: Piero Ugliengo, Università degli Studi di Torino
- ELE KN01: Riccardo Ruffo, Università degli Studi di Milano Bicocca
- TEO KN01: Chiara Cappelli, Scuola Normale Superiore, Pisa
- ABC/ANA/FIS-KN01: Rocco Mazzeo, Università di Bologna
- ABC/ANA/FIS-KN02: Erika Ribechini, Università di Pisa

Amide Bond Formation by Condensation between Unactivated Reagents at Silica Surfaces: Rôle in Prebiotic Chemistry

P. Ugliengo[a], *A. Rimola*[b], *M. Sodupe*[b] *M. Fabbiani*[c], *G. Martra*[a]

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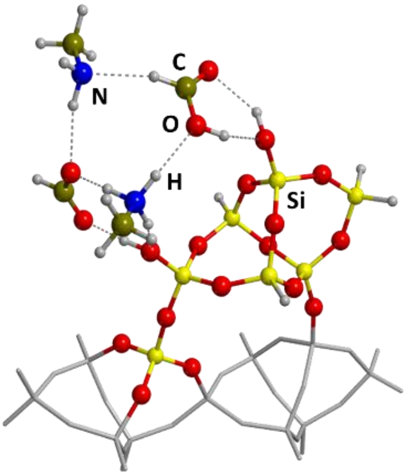
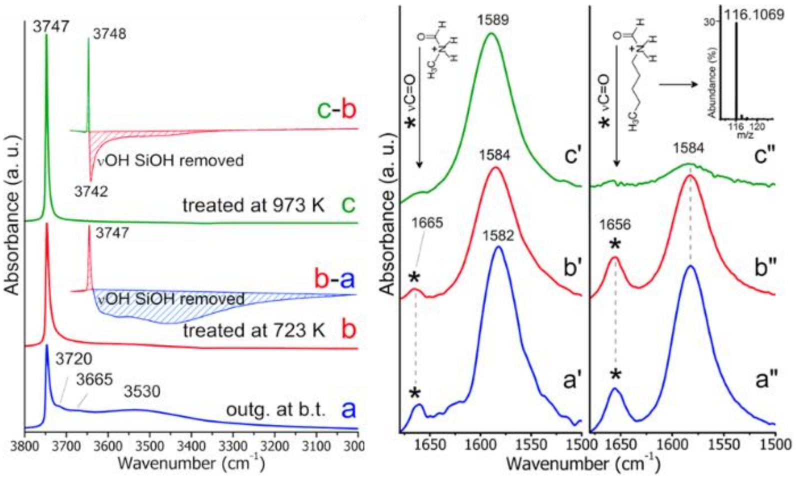
The role of mineral surfaces in promoting the formation of peptides in the prebiotic era by condensation reaction of aminoacids has long been established (1). We contributed to the field through experiment (2) and simulation (3), focusing on common oxides, as potential helpers in the formation of small glycine oligopetides. Here, we propose the mechanism of the amide bond formation between non-activated carboxylic acids and amines (simpler analogous of aminoacids), hosted at the surface of amorphous silica. We elucidate the mechanism by a combined use of molecular simulation through quantum mechanical calculations based on density functional theory (B3LYP-D3/6-311++G(d,p)) and experimental infrared spectroscopic measurements. Experiments based on infrared spectroscopy carried out on carefully thermal treated silica samples, identified very weakly interacting SiOH surface group pairs, as key sites for hosting and activating, ionic and neutral pairs of the reactants, whose simultaneous presence is crucial for the amide bond formation. The atomistic view provided by DFT modelling revealed the catalytic site envisaging pairs of surface silanol (Si-OH) groups ca. 5 Å apart (see figure). The proposed mechanism on dry silica resembles that operative in the ribosome for the peptide bond formation (4), in which the Si-OH groups at silica play the role of water in the biological system.





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Negative Electrode Materials for Sodium Ion Batteries

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The world annual consumption of energy is in the range of 100 TWh whose largest part of this energy is supplied by fossil fuels or nuclear plants. Both these technologies are nowadays considered as not sustainable; however the global energy demand is still increasing. In this dim picture, renewable energy supplied by sun, wind, earth crust heat, and sea represent a viable and environmental friendly alternative which is leading to the investigation, development, and commercialization of new technology such as solar cells, wind mills, heat pumps, etc. The full exploitation of the energy produced by these primary sources, which are intrinsically intermittent, represents another technological issue which is currently approached by the design of better energy distribution grids and the large use of energy storage devices. Moreover, an important part of the total energy consumption is related to the automotive field, where fossil fuels still play a predominant role. Just in the last few years the automotive market is showing an exponential growing interest in electrical power units to feed hybrid or full electrical vehicles.

Electrochemical energy storage units are currently used in high or low tech portable devices. The most demanding high tech tools require the use of high energy density system, such as lithium ion batteries. Smart grid developers or automotive engineers are looking with growing interest at the development of better batteries with higher performances, however, the figure of merits depends on the specific applications. Few years ago, due to the large use of lithium, several investigators are questioning about its availability and possible material shortness. There are several answers to this issue: the design of better lithium based systems (lithium air, lithium sulfur), the lithium recycling, actually non-convenient, or the development of lithium free battery technology.

Aim of the present contribution will be the description of the current researches performed at the Material Science Department of the University of Milano Bicocca on materials for sodium ion secondary battery, focusing in particular on the negative electrode. Usually, research efforts in this field are directed towards the production of optimized phases by a trial and error procedure focused on the electrochemical performances rather than a full understanding of the mechanism beyond the electrochemical reaction. In our case, however, the scope is to elucidate the structure properties correlations by combining SEM, TEM, XRPD, and Raman measurements with the electrochemical behaviour in half cells vs. metallic sodium. Several phases, representative of different reaction classes have been investigated: conversion oxides (Co_3O_4, Fe_2O_3), intercalation or pseudo-capacitive oxides (TiO_2), and carbons, which show different reaction mechanism depending on their properties. Specific morphologies were designed to optimize the sodium uptake/release from the electrolyte addressing preparation routes towards proper particle size and shape.

A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions

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The computational modeling of molecular spectra of aqueous solutions is particulary challenging. In fact, it requires at the same time an accurate modeling of the response of the solute to the external radiation field and a reliable account of the effects of the surrounding environment, which can hugely modify the solute's spectral features as a result of specific/directional interactions (1).

A recently developed Quantum-Mechanical (QM)/polarizable molecular mechanics (MM)/polarizable continuum model (PCM) (2) embedding approach has shown extraordinary capabilities, yielding calculated spectra in excellent agreement with experiments.

An overview of the the theoretical fundamentals of this methods, which combines a fluctuating charge (FQ) approach to the MM polarization with the PCM is given, and specific issues related to the calculation of spectral responses (3) are discussed in the context of selected applications (4).

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Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces

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In the last decades, many research efforts have been devoted to the development of advanced non-invasive approaches for the examination of cultural heritage. However, up to now, too few attentions has been paid on the potentialities of the Macro Mid-Infrared total reflection (MA-FTIR) mapping analysis. Indeed, the infrared reflectance spectroscopy single point investigation has been largely applied in analytical studies of artworks due to its advantage of characterizing both organic and inorganic materials. On the other hand, the possibility to simultaneously obtained information on molecular composition and spatial distribution of constituents is of crucial importance for properly addressing conservation issues.

To this aim, the present research work was focused on the application of an advanced MA-FTIR mapping system for the study of altered bronze surfaces. Moreover, an *ad hoc* multivariate approach has been proposed for the interpretation of data.

A bronze sculpture exposed in the atmosphere deteriorates with time, developing a greenish/blackish layer mainly constituted of corrosion products. The formation of these corrosion products implies complex chemical, electrochemical and physical processes that strongly depend on the constituents of the surrounding environment. In addition, different acrylic resins, synthetic waxes and organic inhibitors may be commonly applied for short-term protection of outdoor bronze sculptures.

To the Authors knowledge for the first time Mid FTIR macro mapping analysis was performed on metal patinas, allowing the location of corrosion products and old coatings, and describing their interactions. The performances of the approach have been initially evaluated on standard bronze samples characterized by the presence of a green basic hydroxysulfate (brochantite) treated with different organic materials. Subsequently, the exceptional case of study of the bronze sculptures of the Neptune Fountain (Bologna, 16th century) has been investigated.

The instrument acquired hyperspectral cubes by scanning the metal surface without any contact, recording sequential total reflection single-point spectra. The big dimension of the data cubes obtained, as well as, the deformation of IR bands induced by specular reflection phenomena, may serious hampering the correct interpretation of the spectral features. Thus, a chemometric method, based on the use of the brushing procedure, was proposed to extract all the useful information embedded in a complex hypercube.

The high specificity of MA-FTIR mapping revealed important outcomes on the state of conservation of the monumental statue. In particular, it was possible to clearly describe well preserved areas in which wax and incralac resulted to be still present, describing their distribution and identifying zones affected by a more aggressive corrosion process.

GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century

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The aim of this work is focused on the identification of the organic residues from ceramic vessels recovered from a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

Comunicazioni Orali

TiO2/Au NRs photocatalysts for photodegradation of water pollutants under UV and visible light

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In the quest to solve environmental remediation and solar energy conversion issues, plasmonic heterostructures composed of noble metals in combination with semiconductors have been attracting tremendous attention (1,2). In particular anisotropic metal nanoparticles are very appealing for photocatalytic applications (1,3). Owing to their tuneable longitudinal plasmon band and their anisotropic shape cylindrical Au nanorods (Au NRs) are among the most studied plasmonic NPs. However, it must be pointed out that the role played by gold nanoparticles in the overall photoactivation mechanism is different according the photoactivation wavelength. Under UV irradiation titania is activated and photo-generated electrons, sink in NPs of noble metal, hindering the recombination of charge carriers (e^-/h^+),which results in an increase of the photocatalytic activity. While, under visible light irradiation titania cannot be activated (band-gap: 3–3.2 eV), and thus light must be absorbed by plasmonic NPs. Two possible mechanisms of titania activation by plasmonic NPs under visible light irradiation have been recently proposed, i.e. charge and energy transfer (4).
The present work focuses on the synthesis of TiO_2/Au NRs hybrid nanocomposites exploiting pre-synthetized Au NRs as nucleation seeds for the growth of anatase TiO_2 nanoparticles according to co-precipitation procedure followed by calcination at different temperatures. The final goal of this work is to obtain a visible light active plasmonic photocatalyst on a gram scale exploiting a user friendly and easy scalable procedure. Photocatalytic experiments were performed under UV irradiation in order to test the degradation of a target compound (methylene blue) in aqueous solution using TiO_2 P25 Evonik as a reference material. Moreover, the photocatalytic removal of the antibiotic Nalidixid acid upon visible light irradiation was investigated. TiO_2/AuNRs calcined at 450°C presented a photoactivity up to 2.5 times higher than TiO_2P25 Evonik under UV light. Interestingly, after 15 min of visible irradiation TiO_2/AuNRs 450°C based nanocomposite has achieved a 20% degradation while NA degradation achieved by other TiO_2/AuNRs samples, unmodified TiO_2 nanoparticles and TiO_2 P25 Evonik was negligible. HPLC-MS analyses further confirmed that NA degradation reaction occurred only in presence of TiO_2/AuNRs 450°C sample. Furthermore, the photoreduction of CO_2 was evaluated for all the samples under study under UV-visible irradiation. In particular, TiO_2/Au NRs 450°C catalysed the formation of CH_3COOH in high yield 113 $\mu mol \cdot g^{-1}$ cat. The obtained results point out the promising photoactivity of TiO_2/AuNRs samples in the visible range and their potential viability for water remediation and artificial photosynthesis.

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Photochromism of N-phenyl-carbazole benzopyrans

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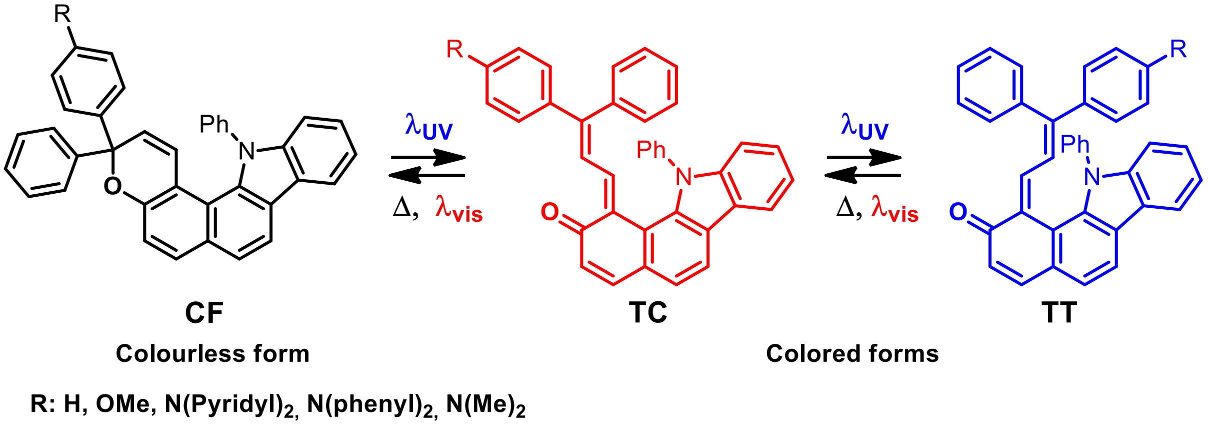
In this study, which is part of a wider investigation carried out in our laboratories on photochromic systems belonging to the chromenes class (1,2), we report on the synthesis and the photochromic behaviour of a series of benzopyrans bearing a N-phenyl carbazole moiety (Scheme 1). Unlike most chromenes, these molecules exhibit a significant conversion percentage to the transoid-*trans* coloured isomer (TT), as high as 70% in the case of the unsubstituted compound. This feature, along with the long-lasting thermal stability in the dark of the TT isomer, which can be completely bleached back to the starting material by visible light, suggests the possible use of these compounds as P-type photochromic systems (3) in optical memories and photoswitchable devices.



Scheme 1. Simplified photochromic mechanism of N-phenyl-carbazole benzopyrans.

Various information which shed light on the mechanism of the photochromic reaction have been obtained. The combination of spectral, kinetic and HPLC data allowed the quantitative absorption spectra of the closed colorless form (CF), the transoid-cis (TC) and the transoid-trans (TT) coloured isomers to be measured, along with the quantum yields for the UV photocolouration and visible photobleaching processes. The effect of the substituent located on the phenyl ring linked to the sp3 carbon atom of the pyran ring on the thermal stability of the TT isomer, the spectral features and the kinetic profiles has been investigated.

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Hydrophobic Carbon Dots with intense phololuminescence towards single white emitting materials

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Carbon dots (C-dots) draw increasing attention as new emitting nanomaterials in different applications, including optoelectronics, bioimaging and biosensing, thanks to their high quantum yield (QY), biocompatibility, low toxicity and cost effective sources (1), compared to inorganic Cd based quantum dots. C-dots are all organic, carbonaceous materials, less than 10 nm in size, with a bright and multi-colored emission that typically depends on the excitation wavelength. Although the origin of C-dot photoluminescence (PL) properties is still a debated topic, two main contributions to their radiative emission, one arising from the intrinsic core, consisting of sp^2 carbogenic domains, and the second involving surface states, i.e. emission traps, surface defects, functional groups connected with C-dots surface, were proposed (2). Moreover, when the synthesis of C-dots is performed by means of hydrothermal methods in the presence of amines, high emitting molecular fluorophores can be formed by the condensation reaction and the concomitant loss of water in the synthetic medium between the carboxylic moiety of the carbonaceous precursor and the amine group (3). In this work, the synthesis of oil-soluble C-dots has been investigated (4) by systematically controlling the reaction conditions, in order to assess the role of the preparative conditions on the optical and morphological properties of the nanoparticles. In particular, the carbonization conditions, temperature and time, and surface passivation have been studied. We have demonstrated that, besides the fundamental role of the amine-containing passivating agents in improving the PL emission of C-dots, *via* the formation of molecular fluorophores alongside the carbonization process, also the reaction temperature is decisive in addressing the optical properties of C-dots. Indeed, in specific reaction conditions, additional UV-vis absorption and fluorescence signals appear, whose occurrence has been assigned to further multiple excited states emitting at low energies and/or to the aggregation of intermediate molecular species. Such C-dots, when excited in the blue region, show high intensity white emission, thus resulting potential candidate for the fabrication of all-organic and bio-compatible colloidal white emitting single nano-objects. The white emission appears retained also when the nanoparticles are processed in solid films by incorporation in a PMMA host matrix (QY=23%). In addition, the colour point of the suspension and of the polymeric films still stays in the white colour region of the 1931 CIE diagram after several months, thus proving the colour stability of the nanoparticles.

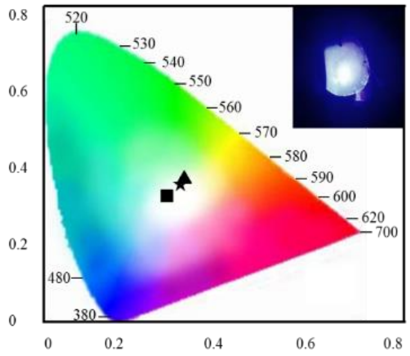

Fig. 1 1931 CIE diagram of the C-dot /PMMA film showing white emission when excited in the blue region (400, ★405 and ■ 410 nm▲). The inset shows the white emission of the C-dot /PMMA film illuminated with a monochromatic radiation of 405 nm.

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Graphene-like domains on MoS2/ TiO2 systems, via acetylene polymerization: in-situ synthesis and characterization

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Carbon–based materials with different dimensionality, including graphene, graphene oxide and graphite nanoplatelets have attracted an increasing attention due to their unique electrical conductivity, structural regularity, chemical inertness, biocompatibility, mechanical and thermal stability (1,2). Actually, carbon nanomaterials are ideal templates and supports for the interaction and growth of organic and/or inorganic structures, according to the properties required by the final carbon-based nanocomposite. On the basis of the literature concerning the *in situ* synthesis of carbon nanostructures on the surface of TiO_2, via acetylene (C_2H_2) polymerization (3) and according to the bottom-up approach, our aim was to obtain graphene-based structures grown at the surface of MoS_2 (a layered metal dichalcogenide), via C_2H_2 polymerization, to be compared with RGO (reduced graphene oxide)/MoS_2 hybrid nanostructures, previously obtained via top down method (exfoliation) (4).

It is relevant to underline that a metal oxide support is crucial for the dilution of dark MoS_2 samples. Among the different oxides, TiO_2 particles, due to the relatively narrow size distribution and to the good crystallinity, are known to limit the heterogeneity of the supported species. Following this line, the role of MoS_2 in MoS_2/TiO_2 system in affecting C_2H_2 polymerization is highlighted, as compared to pure TiO_2. Morphology, structure, optical and vibrational properties of the obtained materials, for each step of the synthesis procedure, have been investigated by means of high-resolution TEM, X-ray diffraction, Raman, UV-vis and FTIR spectroscopies.

HRTEM images provide a simple tool to highlight the effectiveness of the sulfidation process, thus showing 1L, 2L, and few-layer MoS_2 nanosheets anchored to the surface of TiO_2 nanoparticles. In-situ FTIR spectroscopy investigation gives information on the nature of the polymeric species, showing that the formation of both polyenic and aromatic systems can be taken into account, being their formation plausibly promoted by both Ti and Mo catalytic sites (Fig. 1).

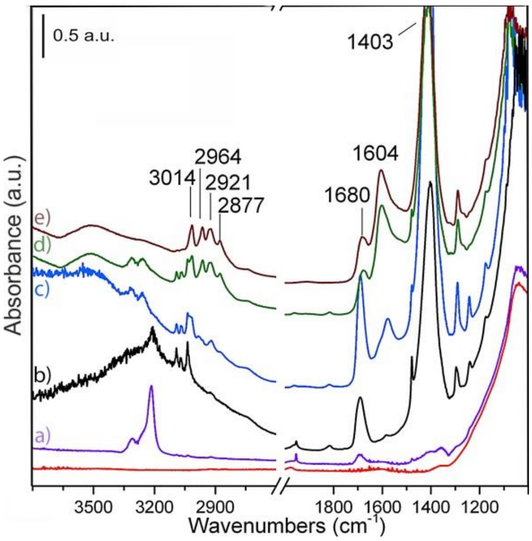

Fig.1. FTIR spectra of C_2H_2 (120 Torr) adsorbed on MoS_2/TiO_2 at 298K (0-30’ a-c) and at 423K (d,e).

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Colloidal Nanocrystal Surface Decorated Graphene based Hybrid Materials for Sensors

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Graphene is an extraordinary structural material for (bio)sensors, solar cells, supercapacitors, batteries and photocatalytic devices, due to its excellent thermal and electrical conductivity, high surface area, mechanical strength and light transparency from visible to infrared (1). The reactivity of graphene as a two-dimensional platform offers the possibility to implement a large variety of strategies of hybridization, including molecular decoration approaches with (bio)molecules or nanostructured compounds, finally resulting in novel functional nanocomposites. Such hybrid materials exhibit novel functionalities and improved pristine properties, further extending the technological applications of graphene. Colloidal nanocrystals (NCs), prepared by means of solution-based colloidal chemistry routes, are particularly suitable for the chemical decoration of graphene. The surface chemistry of these nano-objects can be engineered by playing with the coordinated surfactant molecules that allow their anchoring to graphene. In this way, the original size- and shape-dependent properties of the NCs can be ingeniously combined the unique functionalities of graphene, finally merging in a novel composite material promising for advanced device applications (2). Here, the preparation and characterization of hybrid materials based on graphene and semiconductor NCs (i.e. PbS, TiO_2) or Au nanoparticles (NPs) are presented. Nanocomposites based on CVD grown graphene and colloidal NCs were prepared by exposing graphene films to solutions of 1-pyrene butyric acid (PBA) surface coated semiconductor NCs (PbS, TiO_2), obtained by a capping exchange procedure onto pre-synthesized NCs (3,4) (see Figure 1 A). As an alternative, composites formed of Reduced Graphene Oxide (RGO), surface modified by a functional pyrene and then decorated by semiconducting NCs or Au NPs grown by using *in-situ* colloidal routes, were prepared. The sensing characteristics of the hybrid nanocomposites have been preliminarily tested and result promising for the materials integration in photodetectors and in electroanalytical sensors for detection of DNA or neurotransmitter molecules (see Figure 1 B).

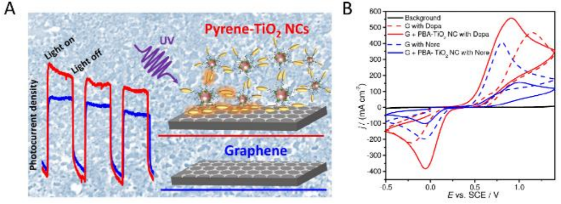

Figure 1. A) (On the left) Sketch of photocurrent density response of graphene decorated with PBA-TiO_2 NCs. (On the right) Sketch of the PBA-TiO_2 NCs anchored to graphene with scheme of the chemical immobilization by the pyrene linker capping NC surface, B) CVs of 1 mM dopamine (Dopa) and norepinephrine (Nore) registered at 0.1 V s^{-1} in 0.1 M aqueous $NaClO_4$ on ITO electrodes modified with graphene (G) and with PBA-TiO_2 NC functionalized G.

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Enhanced power-conversion efficiency in organic solar cells incorporating polymeric compatibilizers

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Organic Solar Cells (OSCs) have attracted considerable interest because of their flexibility, lightness, and potential for low-cost and simplicity of the manufacturing processes. Devices based on the P3HT:PCBM thin film heterojunctions are among the most studied, providing power conversion efficiency (PCE) of 3-6% and 0.1-3.1% in bulk (BHJ) and planar (PHJ) heterojunctions, respectively (1,2). Although encouraging progress has been made, performances are not yet suitable for large-scale implementation. Many effort has been spent on the development of low band-gap polymers, fullerene derivatives, and additives for obtaining improved performance and controlled morphology of the heterojunctions (3-4). However, the development of most semiconducting polymers or copolymers involves complicated multistep synthetic procedures that affect the yield and the cost of final materials. In the present work, three polymers based on polythiophene and C_{60} units have been designed, easily synthesized, characterized, and employed as compatibilizers in P3HT:PCBM devices.

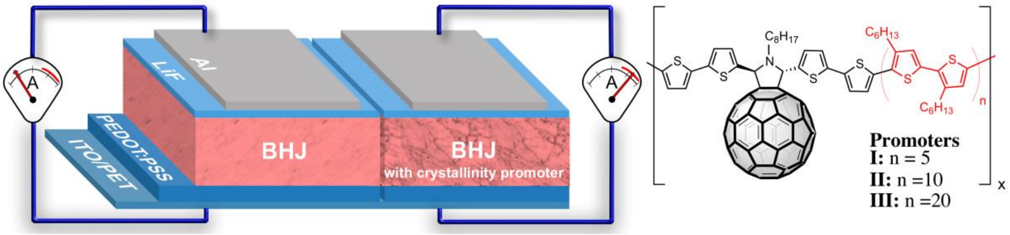

Figure 1 Schematic representation of devices with and without compatibilizer (left) and its chemical structure (right).

The effect of the thienyl spacer length between C_{60} monomers on optoelectronic properties, morphology, and structure of heterojunction has been examined using several techniques (NMR, FTIR, XPS, DSC and AFM). We observed that small quantities of these systems can play a critical role in tuning the device morphology by enhancing crystallinity along with charge transport of the thin film heterojunction. In addition, a good matching in the energy levels was observed, so that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of these systems form a cascade energy band structure. What above allows for up to a 3-fold enhancement of PCE by adding small amount (about 2%) of compatibilizer. By our approach, we obtained the highest short-circuit current density (~ 16 mA/cm^2) and PCE (~ 4.5%) values ever reported for P3HT:PCBM solar cells on plastic/flexible substrates, thus giving new perspectives to applications of flexible photovoltaics.

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Molecular aggregates: a fresh perspective

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The exciton model for molecular aggregates relies on two major approximations: the neglect of molecular polarizability and the dipolar description of intermolecular interactions. Both approximations are bound to fail in aggregates of organic dyes for NLO applications (1).

Here we discuss aggregates of quadrupolar dyes, a class of conjugated molecules characterized by the presence of electron donor (D) and acceptor (A) groups in structures D-A-D or A-D-A, described by essential state models, and parametrized against TD-DFT calculations on dimeric units. The proposed model predicts sizable excitonic effects in 2-photon absorption spectra and explains the experimental observation of non-fluorescent J-aggregates (2).

We also address linear aggregates of D-A polar dyes (specifically 4-Dimethylamino-4′-nitrostilbene, DANS) molecules aligned into carbon-nanotubes (CNT). In a recent paper (3) the amplified β-response observed for DANS@CNT that was ascribed to ~70 aligned dyes (3). Essential state models, parametrized according to the calculated geometry of DANS dimers in CNT (Fig. 1), demonstrate that the molecular polarizability leads to a superlinear amplification of the response that reduces the required number of aligned dyes to ~10, while quite naturally explaining the large red-shift of the HyperRayleigh scattering signal with respect to the linear absorption peak.

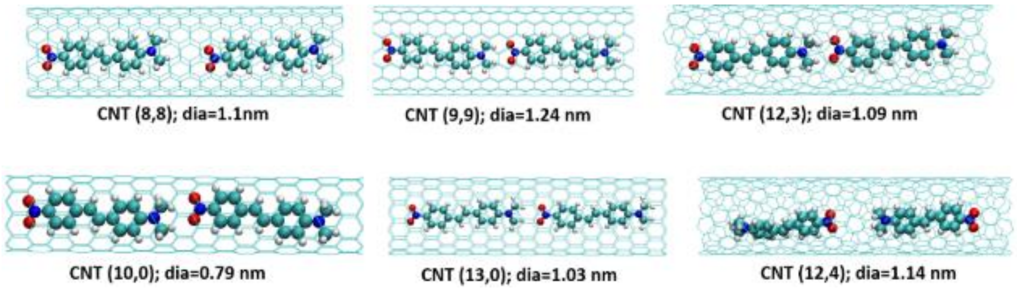
CNT (8,8); dia=1.1nm
CNT (9,9); dia=1.24 nm
CNT (12,3); dia=1.09 nm
CNT (10,0); dia=0.79 nm
CNT (13,0); dia=1.03 nm
CNT (12,4); dia=1.14 nm

Fig. 1 DANS dimers in CNT (DFT optimized geometry).

Acknowledgements
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On the Zn2+ ion speciation in challenging ionic media: a molecular dynamics and X-ray absorption spectroscopy study

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Ranging from analytical chemistry to electrochemistry, Ionic Liquids (ILs) are interesting compounds that have seen a wide array of applications, including their use as replacement for organic solvents, lubricants, reaction media and transport media. Due to their low volatility and non-flammability, as well as their high chemical and thermal stability, ILs are safer and more environmental-friendly than the commonly used solvents. Furthermore, the capability to tune their chemico-physical properties with slight changes in the composition makes them appealing from the point of view of efficiency.(1) Among the many applications in which ILs have been employed as solvents, an interesting one is Zn deposition for Zn-air batteries.(2,3) While many studies have been reported on this subject, obtaining reliable structural data and identify species in IL solutions is still a challenging task. Indeed, information on the solvation properties of Zn(II) salts in ILs and on how these properties are influenced by the choice of the IL cation and anion is still lacking.

Here, four solutions of zinc bis(trifluoromethanesulfonyl)imide ($Zn(Tf_2N)_2$) in Tf_2N based ILs were studied by combining molecular dynamics (MD) and X-ray absorption spectroscopy (XAS) in order to shed light on the influence that the IL organic cation has on the structural properties of Zn-Tf_2N solvation complexes. The MD-XAS approach has been already proven a valuable tool for the study of IL solutions: the high selectivity and versatility of the XAS technique allows one to obtain reliable data on liquid samples, while MD simulations provide a dynamic atomistic description of the systems.(4,5) We found the Zn^{2+} ion coordinated in a typical octahedral fashion, with the IL cation having no influence on the short range arrangement of atoms around the metal up to 3.5 Å. Conversely, the choice of the organic cation has a significant impact on the speciation of the metal ion (see Figure 1) and on the dynamic properties of the Zn-Tf_2N solvation complexes.

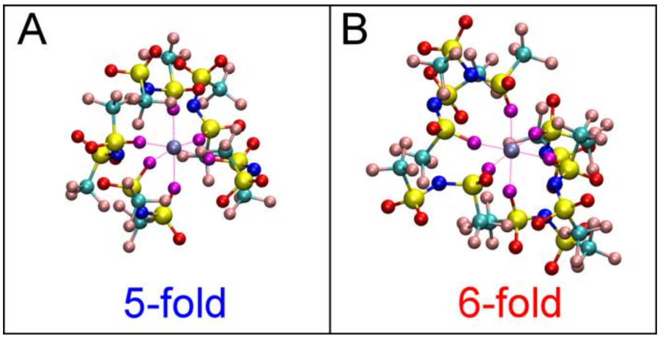

Figure 1: Pictorial example of the structural arrangement of Tf_2N^- anions around a Zn^{2+} cation in the 5-fold (A) and 6-fold (B) solvation complexes.

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Magnetic Solid Lipid Nanoparticles for Magnetically Targeted Delivery of Sorafenib for Treatment of Hepatocellular Carcinoma

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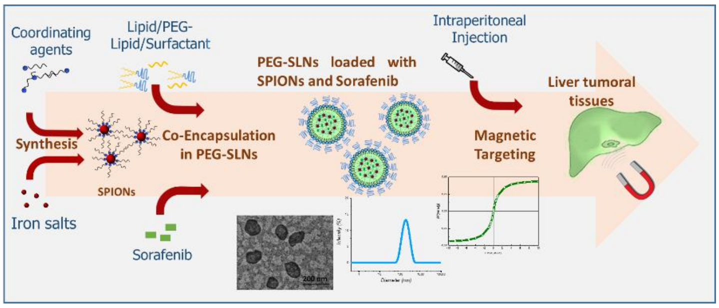
Sorafenib is an orally active multikinase inhibitor and it is only anticancer drug that has proved to significantly prolong the survival time in patients with advanced hepatocellular carcinoma (HCC), when not candidates for potentially curative treatment or transarterial chemoembolization. However, sorafenib is characterized by severe toxic side effects limiting the possible therapeutic response (1,2). Nanoparticle (NP) based approaches offer a valuable alternative for cancer drug delivery, functioning as a carrier for entry through fenestrations in tumor vasculature, thus allowing direct cell access and ensuring the accumulation of high concentrations of drug to the targeted cancer cell, with a concomitant reduced toxicity of normal tissue. In this contest, superparamagnetic iron oxide NPs (SPIONs) are very attractive for delivery of therapeutic agents as they have been reported to enhance the drug delivery to specific locations in the body through the application of an external magnetic field (3,4). Here, solid lipid NPs (SLN) containing sorafenib and SPIONs have been prepared by a hot homogenization technique using cetyl palmitate as lipid matrix and polyethylene glycol modified phospholipids (PEG lipids), in order to achieve a PEG-based anti-fouling coating on SLN surface. These nanoformulations, thoroughly investigated by means of complementary techniques, have finally resulted effective drug delivery magnetic nanovectors with good stability in aqueous medium and high drug encapsulation efficiency (% EE>90%). In addition, the relaxometric characterization has proven that the magnetic SLN loaded with sorafenib are also very efficient contrast agents, with a great potential in magnetic resonance imaging (MRI) technique. The proposed magnetic SLNs loaded with sorafenib represent promising candidates for image guided and magnetic targeting of sorafenib to liver towards an efficacious treatment of HCC.



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Micro-structural characterization of model membranes containing DHA

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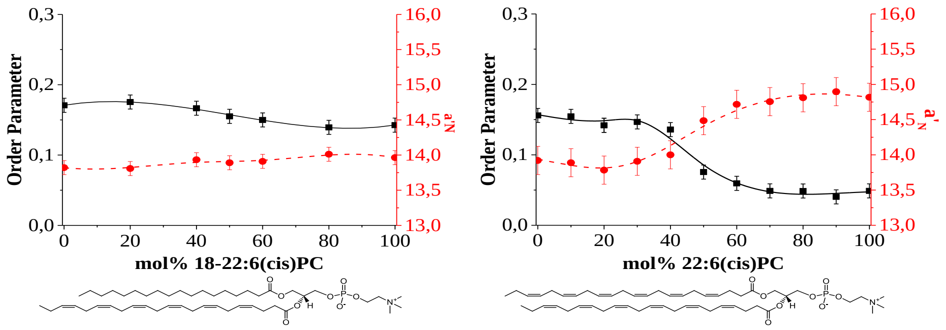
DocosaHexaenoic Acid (DHA) is the longest and most unsaturated fatty acid present in cell membranes, playing a pivotal role in the prevention of cardiovascular diseases and cancer and exerting a strong neuroprotective effect (1). Among other hypotheses, mainly based on their radical-scavenging and anti-inflammatory action (2) it has been proposed that omega-3 fatty acids, to which DHA belongs, once converted to lipids could alter the structure of biological membranes, whose involvement in major biological processes, such as signaling and protein trafficking, is reported. However, how one molecule can be associated to many different beneficial effects is still unclear.

Lipid diversity regulates a wealth of biomembranes processes, because those molecules can tune the physicochemical characteristics of the lipid bilayer, such as elasticity, curvature, surface charge, hydration and the formation of domains by specific interactions involving the chemical structure, conformation and dynamics of the lipid head groups and acyl chains. For instance, it has been shown that certain lipids can promote nonlamellar phase formation, such as inverted hexagonal and cubic phases, as well as favor insertion of proteins into the membrane. These lipids, including sphigolipids and lysolipids, are defined non-bilayer lipids. Moreover, both theoretical and experimental data provide clear indications that, at least transiently, non-lamellar structural intermediates must exist *in vivo (*3).

With the aim to understand the functional role of DHA, we characterized the microstructure of different phospholipid systems containing this fatty acid. A variety of physico-chemical techniques such as Electron Spin Resonance (ESR) spectroscopy with the spin-labelling approach and Neutron Reflectivity (NR) were used to achieve our aims.

ESR results indicates clearly that the di-polyunsaturated phospholipid is able to induce dramatic variation in the fluidity of the bilayer, described by the order parameter, in association with higher hyperfine coupling constant values, index of the polarity experienced by the spin label (Figure 1). These significant changes in the biomembranes micro-structure supports the hypothesis that the phospholipids di-polyunsaturated behaves as a nonbilayer lipid, playing a key role as a morphological element to support the dynamic organization of cellular membrane systems.



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Nanoparticles encapsulation in micellar systems for biomedical applications

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Increasing interest has been devoted to colloidal inorganic nanoparticles (NPs) in the last decades in order to improve their properties and implement their use in nanomedicine.

As synthesized colloidal inorganic NPs require a proper functionalization in order to be further used in combination with biologically relevant structures for biomedical applications. Among the most common functionalization techniques, the exploitation of the hydrophobic interactions between NPs capping ligands and hydrophobic tails of amphiphilic molecules represents a prompt, versatile and reproducible method. Micelles forming amphiphilic molecules are able to encapsulate NPs in the hydrophobic core preserving their properties, enabling their dispersion in aqueous media and providing, at the same time, suitable functionalities at their surface serving as anchor points for the bioconjugation with peptides, DNA, drugs, proteins *etc*.

Several systems based on micelles forming molecules have been reported able to encapsulate NPs, here the results recently obtained on the phospholipids functionalization of multifunctional anisotropic Fe_3O_4-TiO_2 heterostructured NPs have demonstrated the success of the technique for achieving peptide bioconjugates, potentially effective for theranostic applications (1).

Another class of materials, namely amphiphilic peptides (APs) have been found able to self-assemble in several supramolecular structures (micelles, fibers, vesicles, *etc.*) and have been used as delivery carriers for drugs, RNA and DNA molecules (2).

Here, APs have been synthesized with hydrophilic backbones and functional groups and hydrophobic acyl chains, as advanced and highly customizable encapsulation agents for emitting NPs (QDs). The comprehensive spectroscopic and morphological investigation of the functionalized QDs has elucidated the role played by the different APs features in the functionalization procedure. Finally, the conjugation of the prepared APs capped QDs with DNA to achieve exceptional probes envisages a great potential for biomolecular detection and imaging applications.

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Effect of cellulose ethers on the formation and properties of magnesium phosphate-based cements for biomedical applications

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In the field of injectable materials for bone regeneration, magnesium phosphate-based cements (MPCs) represent an underexplored area of research, which is nowadays getting more attention thanks to their attractive features that, in some cases, make it possible to overcome the traditional drawbacks associated to the deeply investigated calcium phosphate cements. MPCs are reported to display an effective combination of mechanical properties, fast setting and resorption rate, while maintaining a good biocompatibility (1). Polymeric additives are commonly employed in calcium phosphate-based cements to improve paste cohesiveness, injectability and rheological properties (2); however, to the best of our knowledge, only few reports investigated the effect of polymers on MPCs. Moreover, little attention is devoted so far to understand why a specific additive works and how the molecular structure and properties of the polymer affect the final properties of the paste.

The present contribution deals with the investigation of the effect of three different biocompatible cellulose ethers (carboxymethyl cellulose, hydroxypropyl cellulose and (hydroxypropyl)methyl cellulose) on the formation and properties of magnesium phosphate-based cements. The pastes were prepared by mixing $Mg_3(PO_4)_2$ with a solution of $(NH_4)_2HPO_4$. First, the powder to liquid ratio and the concentration of the phosphate solution were optimized to obtain a good conversion degree to the final product (struvite, $MgNH_4PO_4 \cdot 6H_2O$), as investigated by X-rays Diffraction experiments. Then, we incorporated into the mixture different percentages of polymeric additives (5% wt and 10% wt) and we investigated their effect on both the formation and final properties of the material. We observed the morphology by means of Scanning Electron Microscopy, while the effect of the celluloses on the crystallinity of the formed mineral phases was explored using X-ray Diffraction. We employed Differential Scanning Calorimetry to investigate the amount of free and confined water in these systems and to get information about the porosity. The microstructure and the porosity were also evaluated by means of nitrogen adsorption measurements. The setting reaction of the pastes at physiological temperature was monitored using calorimetry, while the setting time was determined with the Gillmore needle test. Given the potential of the obtained materials as injectable bone cements, we tested their injectability at different setting times, using a custom-made apparatus. We then investigated the stability in a physiological medium at 37 °C and studied the dissolution behaviour up to 28 days, as well as the modifications in the morphology and in the crystallinity of the cements. We believe that this study represents a step forward in the field of MPCs and in the understanding of the effect that polymeric additives display on this kind of materials.

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Bifunctional polymer-dispersed liquid crystals

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Reverse mode polymer-dispersed liquid crystals (PDLCs) are transparent films in their OFF state (no applied electric field) and become opaque in their ON state. The addition of a photo-chromic compound allows a colour change of films, when they are UV irradiated. The aim of this work was the preparation and characterisation of bifunctional materials, able to change their transparency by application of an electric field and colour under UV irradiation. In particular, the performance of PDLCs doped with different spiro(indolo)-oxazine molecules was investigated. Both the electro-optical and photo-chromic response of these systems were evaluated and compared (1).

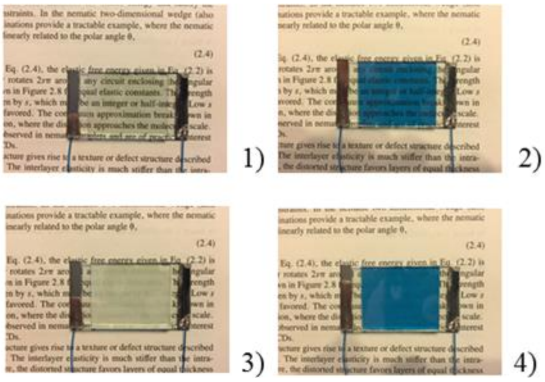

Figure 1. The four independent states of a photo-chromic reverse mode PDLC: 1) Transparent and uncoloured (no electric field and no UV irradiation); 2) Transparent and coloured (no electric field, but in the presence of UV irradiation); 3) Opaque and uncoloured (if the electric field is turned on, but no UV irradiation); 4) Opaque and coloured (if both the electric field and UV irradiation are present).

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Supracolloidal association of microgels and supramolecular tubules of bile salt derivatives

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The aggregation of colloid-sized particles is a fascinating subject, widely employed in chemistry, physics, and biology. The formation of supracolloidal nanostructures represents nowadays an intriguing approach for building novel artificial nanomaterials and devices (1). However, a fine control over the interactions of colloidal particles is fundamental to approach complex structures. This control is particularly crucial when involving systems of particles of different shapes, where specific interactions can be exploited to provide complex supracolloidal geometries with expanded application potential. With this background, we studied the supracolloidal aggregation of spherical microgels and supramolecular surfactant tubes. The interactions were controlled by changing charge of the particles and parameters like electrolyte concentration and temperature. We used cationic or anionic microgels and catanionic surfactant tubes with tunable charge, formed by mixtures of anionic and cationic derivatives of bile salts (2). The charge of the tubes was tuned by controlling the anionic/cationic derivative molar ratio. A structure of triangular rolled layer were observed for the catanionic mixtures, with the edges of the layer designing spirals along the tubular structure. Tubes with a smooth surface were instead provided by the pure anionic derivative solutions. We demonstrated that specific interactions of the microgels occur with the edges of the layers that form the tubular structures. By properly choosing the tube type and adjusting the interaction conditions, virus like particles, microgel decorated tubules or clusters of tubes interconnected by microgels were formed (Figure 1a, b and c, respectively). Extended forms of these clusters provided the basic framework of low density hybrid gels.

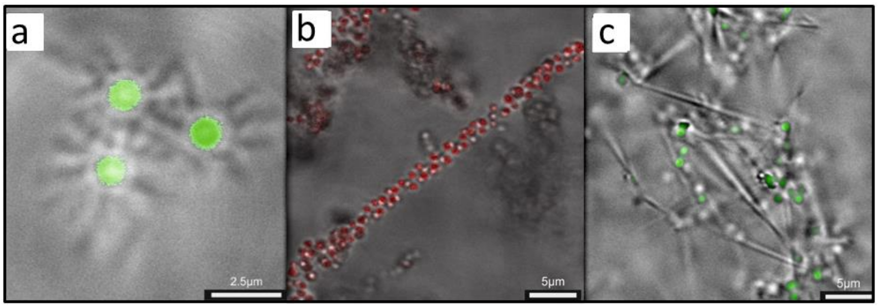

Figure 1 Virus like particles with a microgel core and a corona of tubes (a), microgel decorated tubes (b), clusters of tubes interconnected by microgels (c).

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The lipid bilayer of model membranes: news from the inside

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The solubility of small molecules into a lipid bilayer is central to many biological and biotechnological processes. Lieb and Stein (1) proposed that small molecules dissolve and diffuse by "hopping" between empty voids and molecular dynamics studies have shown that the largest voids are located in the center of the membrane (2), that they increase by increasing temperature and unsaturations in the acyl chains (3), decrease by adding cholesterol (4), and that it depends on lipid composition (5). Unfortunately, this description can hardly find an experimental confirmation and the diffusion and permeation routes at the atomic level are still not completely understood.

In the present study we use IR spectroscopy, both stationary and time resolved, to characterize the properties of cholesterol loaded POPC liposomes. To this extent we use a vibrational probe, hexacarbonyl tungsten $W(CO)_6$, to follow the solubility of a small hydrophobic molecule inside the membrane at different temperatures and solvent composition (DMSO/water solutions at different DMSO mole fraction), and to follow the dynamics of fat acid hydrophobic tails in the picosecond time domain.

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Physical-chemical study of a new shape-memory material based on liquid crystalline elastomers

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In this work, we present a new type of soft-soft composite material based on liquid crystalline elastomers, namely Polymer-Dispersed Liquid Crystal Elastomers (PDLCEs) [1]. PDLCEs are made of isotropic polymer, or elastomer matrix, filled with oriented liquid crystal elastomer (LCE) microparticles as colloidal inclusions. The relative composition of the two soft components as well as the liquid crystalline properties of the LCE microparticles allow for a fine-tuning of the final thermo-actuator properties of the PDLCEs [2]. Respect to previous LCE-based composites, characterized by mono-dimensional and uniaxial actuation [3,4], we are able to obtain different actuation geometries and shapes (*Figure 1*).

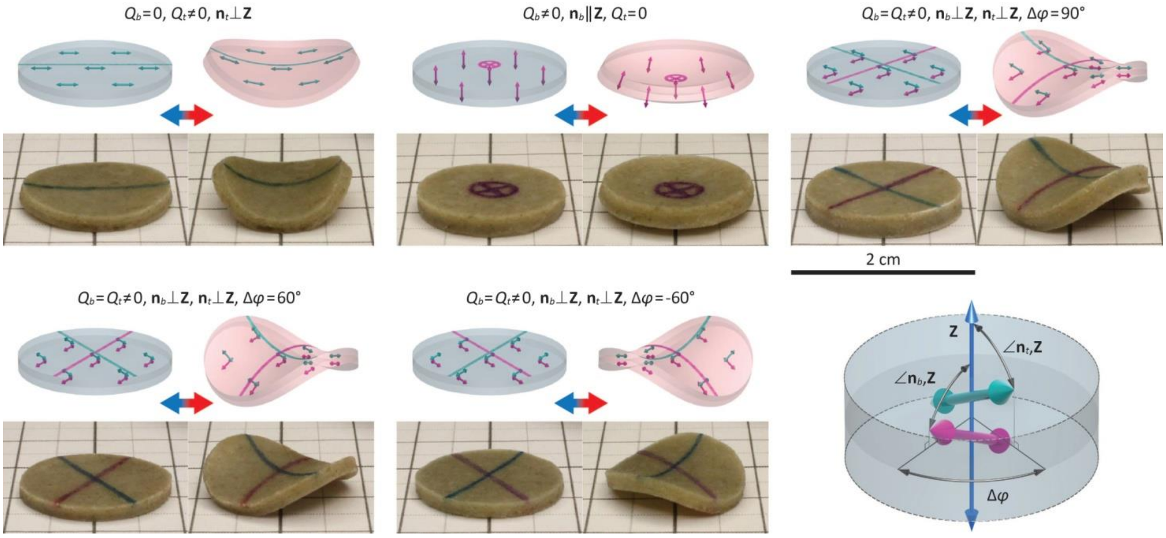

Figure 1. Different thermomechanical actuation modes obtained in bilayer PDLCE disks realized by a suitable choice of PDLCE orientational order Q_b and Q_t, orientation of $\boldsymbol{n_b}$ and $\boldsymbol{n_t}$ with respect to the surface normal **Z**, and azimuthal angle $\Delta\varphi$ between $\boldsymbol{n_b}$ and $\boldsymbol{n_t}$.(*b*=bottom, cyan; *t*=top, magenta).

The peculiar physical properties of the new PDLCEs is related to their orientational properties, namely the LCE microparticles orientational order (***S***), the overall PDLCE orientational order (***Q***) and the distribution functions of the mesophase director (**n**). ^{2}H NMR spectroscopy [5,6] of PDLCEs, prepared under different conditions with ^{2}H-selectively labelled LCE microparticles, provided a clear understanding of all these aspects. A magnetic alignment model was proposed and then validated by means of thermo-mechanical, thermo-elastic and ^{2}H NMR measurements [1,2].

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Hybrid nanostructures based on halloysite nanotubes and sustainable polymers

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This work addressed the critical technical challenges in design of functional nanostructures based on halloysite nanotubes (HNTs) and sustainable polymers (both ionic and non-ionic). Chemically, HNTs are composed of gibbsite octahedral sheet (Al−OH) groups on the inner surface and siloxane (Si−O−Si) groups on the external surface. This different chemistry determines a positively charged lumen and a negatively charged shell in the 2−8 pH range. Consequently, the adsorption of ionic biopolymers onto the HNTs surfaces can be controlled by the specific electrostatic interactions as highlighted by the ζ-potential experiments. The thermodynamics of the adsorption process was investigated by isothermal titration calorimetry (ITC), which evidenced that the polymer/HNTs interactions are enthalpy driven (1). The entropic contribution for the polymer adsorption is always negative, demonstrating the loss of configuration freedom for the polymer in the adsorbed state (1). According to the ITC data, non-ionic Hydroxylpropylcellulose is the most efficient polymer in retarding the HNTs sedimentation because of the steric interactions. As a general feature, cationic chitosan is efficient in stabilizing HNT dispersions under acidic pH, whereas anionic pectin is recommended for the same purpose at basic pH values (1). The dynamic behavior of the polymers adsorbed onto the HNTs surfaces was studied by the Fluorescence Correlation Spectroscopy (FCS). To this purpose, the biopolymers were fluorescently labelled with fluorescein derivatives. We observed that the mobility of the polymers is reduced as a consequence of their adsorption onto HNTs surfaces. Structural insights about the polymers adsorbed onto the HNTs surfaces were obtained through Small Angle Neutron Scattering (SANS) and Electric Birefringence (EBR) measurements, which showed that the rotational mobility of the nanotubes decreases in the hybrid systems. The strongest effect was estimated for cationic chitosan that is wrapped onto the HNTs external surface. The studies of the biopolymer/HNTs aqueous dispersions were correlated to the mesoscopic properties of the corresponding bionanocomposite films, which were prepared through the casting method in water. The thermal stabilization of anionic biopolymers can be ascribed to its confinement into the HNTs lumen (2). For both cellulose ethers and chitosan the HNTs addition did not affect the tensile properties, while the presence of HNTs into alginate matrix determined an increase of the elastic modulus. Dynamic mechanical analysis evidenced that the glass transition of the polymers is reduced as consequence of the specific interactions with the HNTs surfaces (2). Mechanical and thermal characteristics of the bionanocomposites were successfully related to their morphology and wettability. In conclusion, this work provides a valuable platform for the development of smart composite nanomaterials with interesting technological properties that can be controlled by the specific biopolymer/HNTs interactions.

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Absolute Configuration Assignment of two Hybrid Isoindolinone-phthalide Molecules by Vibrational Circular Dichroism

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Vibrational Circular Dichroism (VCD) is more and more used as a sensitive technique to determine the absolute configuration (AC); the many signed signals typical of the mid infra-red region of the spectrum offer a sound basis to discriminate between stereochemical models. Despite the richness of the data, in presence of many low-energy conformers and/or more than one stereocenter, either visual comparison of computed and calculated spectra for all possible diastereomers or use of standard indicators of agreement can be non-straightforward. An ad hoc quantitative indicator of agreement, the similarity index (1), has been advantageously used for that task (2).

We have used VCD spectrsocopy for the AC assignment of the recently synthesized (+)-**1** and (+)-**2**, which are heterocyclic hybrids isoindolinone-phthalide (3), and we have determined their absolute configurations as (*S*,*R*). The study has offered the occasion to compare experimental and computed spectra according to a new similarity index, which can encompass the experience acquired in recent years on the limitations of quantum-chemical calculations (4).

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Can we speak of "ancillary ligands" also in heterogeneous catalysis? Selected examples in olefin polymerization catalysts

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The role of the ancillary ligands is well known in homogeneous catalysis. Small variations in the composition, geometry and flexibility of the ligands could lead to important changes on the active site functionality, on the catalytic performances and on the selectivity. Paradigmatic examples can be found in the field of olefin polymerization catalysis. For example, homogeneous nickel catalysts can give almost exclusively ethylene oligomers (e.g. Keim's Ni ylides), but also tailored polyolefins (e.g. Brookart's Ni-diimine and Grubbs' Ni-iminophenolate), depending on the type of the ancillary ligand. Similarly, the molecular architecture of single-site metallocene–based catalysts can be tuned to produce selectively isotactic, syndiotactic, hemiisotactic or stereoblock polypropylenes.

Much less explored, if not often neglected, is the role of the ancillary ligands in heterogeneous catalysis. In this contribution, we will show that also for heterogeneous ethylene polymerization catalysts it is possible to speak about "ancillary ligands", and that they take an important part in the definition of the properties of the active sites, in many cases displaying a flexible and dynamic behavior very much similar to that found in homogeneous catalysts. The selected examples will cover the two main categories of industrially employed heterogeneous catalysts for olefin polymerization, i.e. the $MgCl_2/TiCl_4$ Ziegler-Natta catalysts and the Cr-based Phillips catalysts, investigated by means of advanced spectroscopic methods. Depending on the system, the "ancillary ligands" can be added as external components (e.g. the so-called electron donors in Ziegler-Natta catalysis), can be formed "in situ" in the presence of the monomer (e.g. oxygenated by-products during the reduction of the Phillips catalyst), or can be even present as a part of the support (e.g. the siloxane bridges at the surface of the Phillips catalyst). In all the cases, they contribute in creating the three-dimensional (nano-sized) environment around the active sites, acting in a concerted way during the ethylene polymerization.

Synthesis and post preparative shape control of Cesium Lead Bromide colloidal nanocrystals

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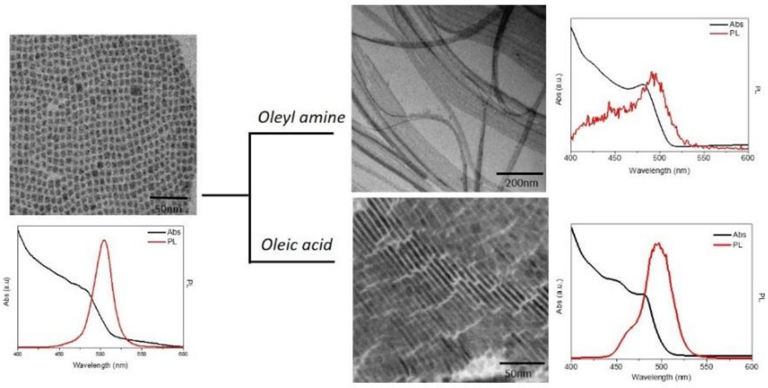
All-inorganic lead halide perovskite materials have attracted significant attention in the context of photovoltaic and other optoelectronic applications, and recently, efforts have been devoted to the fabrication of colloidally stable versions of these materials.(1) Cesium Lead Bromide ($CsPbBr_3$) colloidal nanocrystals (NCs), in particular, exhibits bright, size and shape-tunable photoluminescence in the blue-green region of the visible spectrum, that is usually not easily accessible with conventional quantum dots. While compositional band gap engineering and size tunability of the band-gap energies have been investigated by anion exchange, the role of the ligands in post-synthetic treatments at room temperature is still a critical issue towards the application of this class of material for devices fabrication. It is worth to note that surfactants assist the shape and size regulation during the synthetic step, provide the better stability and help to maintain the optical properties of the final colloidal forms. The ionic nature of the $CsPbBr_3$ NCs and labile interaction of the ligands with the colloidal NC surface suggest a crucial role of surface chemistry on the as prepared NCs. In this regard, this work investigates the shape regulation of the $CsPbBr_3$ NCs played by the ligand composition in a post synthetic treatments based on simply addition of freshly oleylamine and oleic acid to the as prepared NCs. Optical, morphological and structural characterization have been performed in order to depict the ligand role in the colloidal stabilization. This analysis will provide an insight in the surface chemistry and solution processability of this new and widespread investigated class of material, which will be also useful to predict its behavior for future applications in multicomponent complex systems for device fabrication.



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Non conventional based Ce: YAG nanocomposites

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The interesting technological applications of Yttrium Aluminum Garnet (YAG, Y3Al5O12), whose cubic structure is in the space group Ia-3d, doped with lanthanides ions, in inorganic electroluminescence displays, X-ray scintillators, lasers, and white light LED are nowadays well consolidated. Notwithstanding, the interest of researchers is still growing because the optical properties of nanocrystals are expected to be dependent on the properties of doping agent and on the synthesis route that may influence particle size and its distribution and morphology.

The aim of this work is to prepare Ce:YAG nanoparticles with well-defined morphology, reduced sizes and hindered aggregation, simplifying at the same time the reaction conditions in order to scale up the synthesis. Innovative methodologies of preparation such us Urea glass Route, synthesis in microemulsion and solvothermal method in autoclave have been used.

Some nonconventional nanocomposites have been obtained combining the better nanoparticles with polymetylmetacrylate (PMMA), filter paper, cotton wool and glass wool.

Structure, morphology and optical properties have been thus investigated.

Figure. (From left to right) Nanoparticles dispersed in a solvent, Ce:YAG composites in glass wool, filter paper and cotton wool.

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Synthesis and characterization of immunologically relevant calcium and magnesium phosphate amorphous nanostructures and strategies for their stabilisation

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Some recent investigations showed that calcium and phosphate ions are secreted from the distal small intestine of humans and other mammals into the lumen, leading to the formation of amorphous magnesium-substituted calcium phosphate nanostructures, which are able to trap macromolecules in the lumen (such as bacterial peptidoglycans) and transport them to immune cells of the intestinal tissue. (1) This sampling process of luminal content is recognized to be a form of local immunosensing and surveillance (2) and it is now confirmed that at least part of this process is mediated by this endogenous amorphous nanomineral. (1) The stability of amorphous magnesium and calcium phosphate (AMCP) towards its crystallization is dramatically affected by the pH and by the composition of the solution in which it forms or it is dispersed in. (3)

In this study, we focused on the preparation and the characterization of AMCP particles, readapting a protocol from the literature. (4) We systematically investigated the parameters affecting AMCP stability against crystallization to brushite. We explored the effect of pH, ionic strength, Mg^{2+} concentration and the presence of small organic molecules commonly found in the gut lumen. The presence of amorphous and/or crystalline phases was assessed by means of infrared spectroscopy and X-ray powder diffraction. The amount of adsorbed organic molecules was evaluated by thermogravimetry, while scanning electron microscopy was used to investigate the morphology of the nanostructures.

We identified a synthetic protocol producing amorphous nanostructures with improved stability against crystallization, *i.e.* stable for several days. We investigated the structural evolution of these particles once freeze-dried and redispersed in buffer solutions, finding that the spontaneous transition of AMCP into brushite (which normally takes place within few minutes) can be slowed down with the addition of organic additives. These protective strategies against crystallization are relevant to tailor a drug or food additive formulation containing AMCP, for the improvement of the immune system functionality. To this aim, the study of the interactions of AMCP with the gut microbiota is currently ongoing.

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Physico-chemical characterization of smart lipid biointerfaces for the detection of a tumor biomarker

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Supported lipid membranes represent an elegant way to design smart fluid biointerfaces able to mimic the physico-chemical properties of biological membranes. Furthermore, being accessible to a wide variety of surface-specific physico-chemical and analytical techniques, they provide smart biointerfaces to be optimized for specific biotechnological applications (1), such as the design of chemical and biomedical sensors. In this contribution, we describe a new lipid-based sensor for the detection of the thymidine phosphorylase (TP) enzyme, one of the most known biological markers of solid tumors. This enzyme promotes tumor growth and metastasis and is overexpressed in the presence of cancers, so that also its blood levels increase (2). To achieve this goal, a TP target analyte, i.e. the pyrimidine analogue 5-fluorouracil (5-FU) (3) has been properly functionalized with a chain consisting of six (derivative **1**) or seven (derivative **2**) units of glycol, linked to an alkyl moiety of 12 carbon atoms, in order to be inserted into gold supported lipid membranes. The TP affinity towards derivatives (**1**) and (**2**) has been firstly evaluated in solution by fluorescence measurements, then the derivatives have been inserted into a lipid bilayer linked to a gold surface. The supported lipid biointerfaces have been characterized by ellipsometry, AFM and electrochemical techniques (4). The TP interaction with the substrate has been quantitatively evaluated by quartz crystal microbalance, following the oscillation frequency of the QCM crystal, making this system a very promising sensor for the detection of TP concentration in blood.

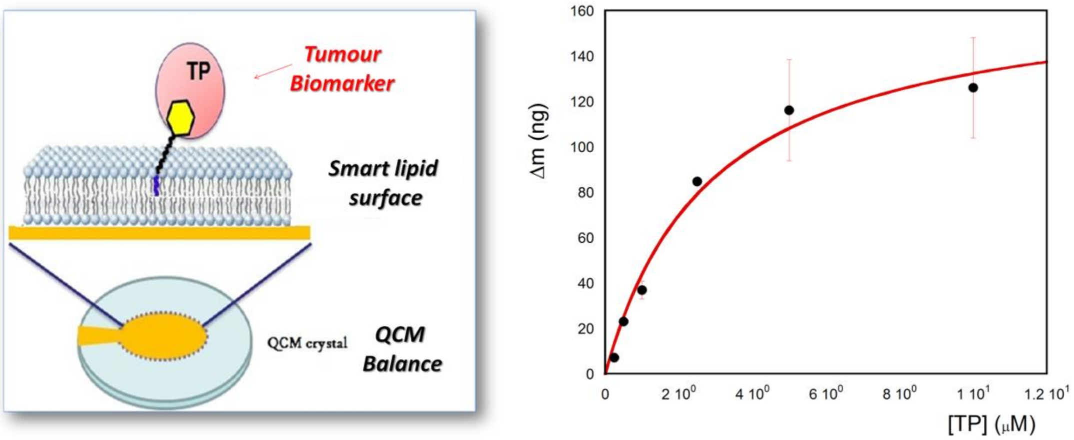

Figure. Left: scheme of the gravimetric sensor. Right: gravimetric quantification of the TP in buffer solution with the designed lipid surface.

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Luminescent ZrO_2:Ln^{3+}@SiO_2 Nanosystems conjugated with Rose Bengal as Efficient Nanoplatform for Theranostic Applications

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Nanocarriers as theranostic agents are of great interest in modern nanomedicine, and several kinds of nanomaterials with interesting chemical and physical properties have been developed and tested, showing encouraging results *in vitro* and *in vivo* (1-3). Zirconium oxide, or zirconia (ZrO_2) is a metal oxide which is extensively used, in the bulk form, in many different application fields, such as thermal barrier coatings, dental and bone prostheses, gas sensors, optical devices and catalysts (4,5). Conversely, it is a relatively new material for theranostic applications, with many promising features: it is biocompatible, chemically inert, with good mechanical and thermal properties (4). The doping of ZrO_2 matrix with Vis and/or NIR luminescent rare earth ions allow the preparation of intrinsically luminescent nanosystems which can be further functionalized for the introduction of therapeutic and targeting moieties. In this contribution, the preparation and characterization of silica coated ZrO_2 nanoparticles doped with Vis and NIR luminescent rare earth ions (hereafter ZrO_2:RE, where RE= Er, Pr, Yb) are discussed. ZrO_2:RE samples were prepared via a hydrothermal process starting from a 1.0 M aqueous solution containing the stoichiometric ratio of $ZrOCl_2 \cdot 8H_2O$ and the RE precursor ($Er(NO_3)_3 \cdot 5H_2O$; $Pr(NO_3)_3 \cdot 6H_2O$; $Yb(NO_3)_3 \cdot 5H_2O$). For each RE dopant, samples of different concentrations, namely 0.5%, 1% and 5% molar, were prepared. Structural and morphological properties were investigated by X-ray powder diffraction, Dynamic Light Scattering and electron microscopies. Absorption and emission UV-Vis-NIR electronic spectroscopies were used to select the best samples in term of photoluminescence performances. A direct correlation between the dopant concentration, ZrO_2 crystalline phase and photoluminescence performances was evidenced, thus allowing the selection of the lowest dopant concentration samples as the best candidates as bioimaging probes. Both non-porous and mesoporous amino-functionalized silica shell was deposed on the selected samples, thus creating anchoring groups for the covalent immobilization of Rose Bengal, a well know photosensitizer for photodynamic therapy. Photodynamic activity was assessed by evaluating $^1O_2$ generation efficiency by a chemical method, evidencing that the photosensitizer maintains its activity upon immobilization on the silica shell. NIR luminescent ZrO_2:RE nanosystems are particularly interesting because they can be potentially used in up-conversion modality, with the possibility of using NIR light to trigger, by up-conversion, the photodynamic activity of visible-absorbing photosensitizers.

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Phenomenology of the Neutral-Ionic Valence Instability in Mixed Stack Charge Transfer Crystals

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Organic charge-transfer (CT) crystals constitute an important class of functional materials, characterized by the directional CT interaction between π-electron Donor (D) and Acceptor (A) molecules, with the formation of one-dimensional ...DADAD… mixed stacks (*ms*). Among the many different and often unique phenomena displayed by this class of crystals, Neutral-Ionic phase transition (NIT) occupies a special place, as it implies a *collective* electron transfer along the stack, involving charge, spin and phonon degree of freedom. NIT can be induced by pressure (1), temperature (2), or even light (3). We present an updated and extensive summary of the phenomenology of the few temperature induced NIT, with emphasis on the spectroscopic signatures of the transition.

NIT are characterized by a valence instability (variation of the degree of CT ρ, with the Neutral-Ionic borderline at ρ ~ 0.5), driven by the 3D Madelung energy, and by a Peierls instability (stack dimerization δ), driven by the 1D electron-lattice phonon interaction. The competition between these two instabilities, respectively first- and second-order, is what makes NIT such a complex and intriguing phenomenon. In the first part of the talk we shall show how properly interpreted single crystals infrared and Raman spectra can provide detailed and reliable information on the evolution of both valence and dimerization instability, inclusive of the detection of the low-frequency soft mode accompanying the Peierls instability (4).

In the second part of the talk we shall present a comprehensive phase space exploration of *ms* CT crystals (Figure 1), showing that the Neutral-Ionic borderline may be crossed at ambient conditions by chemical substitution. This kind of studies have been prompted by the possible exploitation of *ms* CT crystals as ambipolar semicondutors, or as ferroelectrics. We shall also show how a general understanding of the phase diagram can be gained through a modified Hubbard model properly parametrized through simple first principle calculations (5). However, the understanding of the detailed mechanism of NIT and the explanation for the rarity of its occurrence requires consideration of the weak inter-molecular forces determining the packing of the stacks inside the crystals.

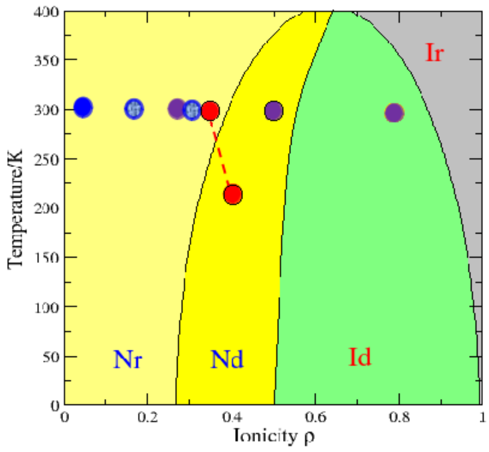

Figure 1: Empirical ρ vs. T phase diagram of ms CT crystals

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The effect of temperature in the formic acid - formate system on TiO_2 (101) surfaces

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The interaction between simple organic molecules and TiO_2 nanoparticles has received much attention because of its relevance for applications in innovative technologies (1). Among the organic adsorbates, formic acid HCOOH has been the subject of many studies as it represents the smallest organic acid and because of the anchoring capacities of the carboxylic group. Moreover, the interest of HCOOH on top of TiO_2 has gathered momentum because of recent reports on solvent-free amide bond formation obtained by dosing gas phase amines on top of {101} anatase surfaces previously treated with HCOOH (2). In spite of its relevance, the actual HCOOH state on {101} anatase facets is yet poorly understood. First-principles modelling investigations on HCOOH@TiO_2{101} predict, on clean surfaces, a molecularly monodentate adsorption geometry (3). On the other hand, IR studies clearly indicate that HCOOH dissociates on anatase forming a monodentate formiate on not defective {101} facets and a minority of bidendate species associated to defective sites. Moreover, the fate of the proton derived from formic acid deprotonation is unclear as well, indeed after $HCOO^-$ adsorption in IRRAS spectroscopic experiments, no surface OH stretching signal was detected (4). Thus, the picture emerging from modeling seems to be different from that indicated by experiments.

Here we show that the two pictures are only in apparent contradiction and that the keyword capable of settling the question is Temperature. Indeed, the above mentioned modeling studies are mainly energy minimization, resulting in 0 K structures. When considered IR experiments one needs to account for at the least 300 K. In our modeling approach, the HCOOH adsorption problem is considered with both regimes, namely geometry optimizations (0 K) and finite temperature (300 K) molecular dynamics simulations, carried out within the same first-principles theoretical framework focusing on a regular clean and not defective {101} anatase slab model. Four different structures were found carboxyl proton is actually shared between the formate and the surface moieties.

For the adsorption of HCOOH on our slab model: two molecularly adsorbed and two dissociated. The two molecularly adsorbed structures, nearly degenerate, were the most stable ones. On the other hand, the finite temperature simulations, performed with either DCOOD or HCOOH, revealed that the acid proton shuttles between a TiO_2 surface oxygen and the carboxylic oxygen (Figure 1). The fast interconversion (at the femtosecond-scale) between the dissociated and the non-dissociated formic acid moiety was found to have consequences on the IR signal as well. The fingerprint of the spectroscopic behavior of the system was obtained by linear response approaches using appropriate autocorrelation functions, resulting in the absence of a well-defined and localized signal due to the O-H stretchings involving carboxyl proton shared between the formate and the surface moieties.

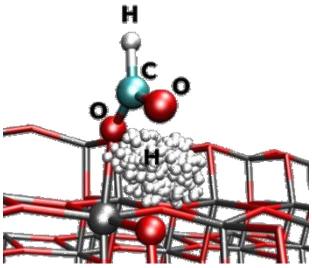

Figure 1. Schematic drawing of the sharing of the carboxyl proton between HCOOH and

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Interaction of phosphate-based additives with MgO/SiO2 cements

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In the last decade, research efforts on the investigation of MgO/SiO_2 cements have significantly grown because they are one of the most promising materials for the encapsulation of radioactive waste (1-4). In the presence of water, MgO/SiO_2 mixtures hydrate and form a binder phase, M-S-H (magnesium silicate hydrate), a colloidal gel analogue to calcium silicate hydrate (C-S-H), present in traditional cements. Even if research interest in MgO-based cement is growing, only one additive (sodium hexametaphosphate, HMP) has been used so far with this kind of cement, while in CaO-based cement many additives are commonly used to modulate the performances to specific applications. In fact, it has been recently reported that HMP in MgO-based cements increases the fluidity of the pastes, which is essential for practical applications, but its action mechanism is still unknown (5-7). In this study, we investigated the mechanism of interaction of different phosphate-based salts (i.e. sodium orthophosphate (OP), sodium trimetaphosphate (TMP), and HMP) with MgO-based cements, in order to understand the changes induced by the phosphate presence on the hydration reaction and on the M-S-H structure. The effect of the investigated additives on M-S-H has been studied by comparing data obtained in samples with and without additives with a multi-technique approach. In particular, the kinetics of hydration of the studied pastes was monitored by means of differential scanning calorimetry, while the hydrated phases formed during the reaction were characterized by thermogravimetric analysis, infrared spectroscopy, X-ray diffraction and solid state NMR. The morphology and topography of the pastes were studied by scanning electron microscopy and atomic force microscopy. Moreover, we performed a characterization of the mechanical properties by statistical nanoindentation and Vickers micro-indentation. The results evidenced that phosphate salts influence the hydration reaction, which is more efficient especially in the presence of OP, which enhances M-S-H precipitation even more than the currently used HMP.

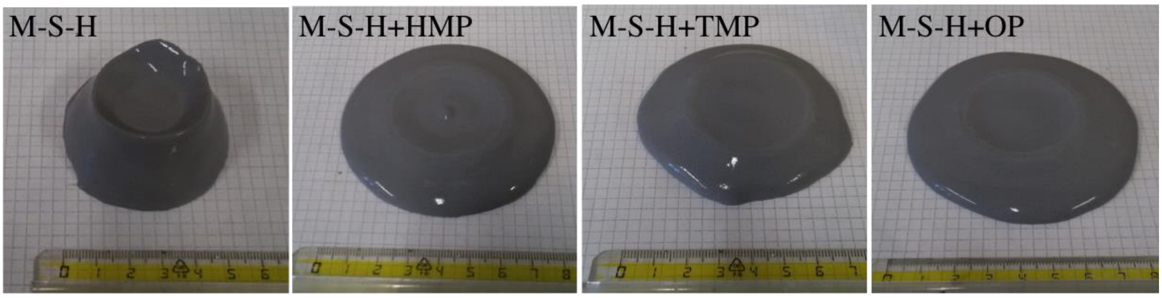

Figure 1. Mini-slump test results.

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Composition and architecture engineering of colloidal TiO_2 nanocrystals for the enhancement of sunlight conversion ability

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Nanometric titanium dioxide (TiO_2) has an acknowledged important role as an environmentally friendly and clean photocatalyst, due to its unique properties, such as the strategic position of the band edges on the electrochemical potential scale, energy band structure, high chemical and thermal stability, to name but a few (1).

However, there are still some disadvantages in using TiO_2 nanocrystals (NCs) for solar light conversion that limit their practical applications. The most crucial one arises from the intrinsic wide energy gaps of TiO_2 phases (3.2 eV for anatase, 3.0 eV for rutile), confining the material photoactivity to the sole ultraviolet region of the solar spectrum (2).

The extension of TiO_2 NCs photoactivity in a wider spectral range has been investigated over the last decade in many ways. Among them, colloidal chemistry offers a plethora of tools for engineering the properties and performance of nanomaterials. We explored two strategies for this purpose, taking advantage of the versatility and the potentiality of colloidal methods.

Firstly, we developed a synthetic strategy based on an alcoholytic route (3) to synthesize pure anatase, highly crystalline TiO_2 NCs, with average size of 9 nm and narrow size distribution.

In the first approach proposed to enhance the sensitivity towards solar light, we fine-tuned the synthetic protocol to rationally manipulate the NC chemical composition (doping). We achieved the incorporation of iron in place of titanium ions up to 20%, retaining size, shape, and crystalline phase of the pristine NCs, demonstrating that it induces enhanced visible light absorption, but simultaneously also worsens the overall material performances.

In a second approach, we sensitized TiO_2 NCs towards visible light by the epitaxial seeded-growth of small lead sulfide nanoparticles (PbS NPs) onto the surface of previously prepared TiO_2 NCs. These PbS/TiO_2 heterostructures indeed show higher absorption both in the visible and near-infrared ranges, thanks to the peculiar size-dependent optical properties of PbS domains (4).

We present structural, morphologic, and spectroscopic investigations supporting the light-harvesting enhancement, but also evidencing opposite outcomes in the two model systems as for the overall performances in visible light conversion ability.

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Coupling of nonlinear chemical reactions with pH-responsive polymers

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Chemical reactions with nonlinear kinetics can give rise to a remarkable set of spatiotemporal phenomena like periodic oscillations, traveling waves and stationary patterns. Despite initial skepticism, much progress has been made in the past three decades in characterizing, designing and modeling these phenomena (1). Nowadays, the main goal is to drag nonlinear reactions out of a purely theoretical context and start exploring the potential applications from catalysis to drug delivery systems and others yet to be imagined. One way to achieve this purpose is to develop biocompatible batch oscillators that oscillate for an extended period in a closed system without a continuous flow of fresh reactants. Among all the families of oscillators, the pH-based ones offer the greatest promise for practical applications because of the ubiquity of hydrogen ion in biological and chemical processes (2). In an attempt to design a biocompatible batch pH oscillator, a couple of years ago, our research group recovered the well-known urea-urease reaction (3,4,5). This reaction, that involves the hydrolysis of urea in ammonia and carbon dioxide, occurs in numerous cellular systems and is used, for example, by bacteria H. pylori in order to raise the local pH (6). By taking advantage of the bell-shaped reaction rate as a function of the pH, this reaction can show autocatalysis with a sharp increase in the pH. In order to obtain pH oscillations, the autocatalytic reaction must be properly combined with a negative feedback (e.g. transport of protons) that restores the initial conditions. The strategy we used to achieve this condition was the encapsulation of the enzyme in 1-palmitoyl-2-oleoylphosphatidylcholine (POPC) lipid membranes, where the differential diffusion of the inhibitor (proton or weak acid) and the activator (urea) were ensured by the different permeability of the membrane to the two species (5). Our results showed that the lipid vesicles are permeable to the species involved in the enzymatic reaction: urea, ammonia, and acids; moreover, by varying the initial concentrations we found several experimental conditions yielding the autocatalysis, however oscillations have not been observed yet. The next step in order to develop a pH oscillator is to couple the urea-urease reaction with pH-sensitive polymers that show swelling-deswelling behavior according to the pH of the solution. pH-sensitive polymers can be obtained through the synthesis of A(BC)n block polymers with linear (n=1) and branched (n=2) architectures where A is the hydrophilic block made of monomethoxypoly(ethylene glycol) (mPEG), while BC is a copolymeric random chain formed by the hydrophobic methyl methacrylate (MMA) and the pH sensitive monomer 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (7,8). The polymers will be used in the form of gels or polymersomes.

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Green synthesis of gold nanoparticles using Punica Granatum Juice for cosmetic applications

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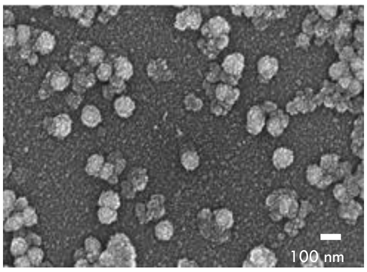

Figure 1: SEM image of AuNPs

The green synthesis of gold Nanoparticles (AuNPs) using *Punica Granatum* Juice (PGJ) was the aim of the present work. $HAuCl_4$ and PGJ, without further purification, were used to induce the formation of AuNPs in water medium. (1) Organic solvents or auxiliary capping agents were avoided enabling the environmental friendly synthesis of AuNPs. More specifically, by using appropriate amounts of PGJ and mild conditions of work, interesting results were obtained. Spherical AuNPs with a mean size of 130 ± 20 nm were observed through SEM images (Figure 1) and carefully characterized using several complementary techniques, i.e. UV-Vis spectroscopy, XPS analyses, DLS and Zeta Potential investigations. Changing in pH values, volume of solutions and temperature values were adopted for affecting the formation and the features of AuNPs. Interesting applications could be suggested. A chitosan or like-structures shell around AuNPs, enriched with PGJ active agents, were proposed to modulate their release presenting a novel formulation with antioxidant, skin lightening and anti-aging properties, especially inhibiting UV-induced pigmentation (see Figure 2). Additionally, the obtained AuNPs could be potentially used as agents to enhance the sun protection factor (SPF) of commercial sunscreens formulations as an alternative to traditionally used nanostructured TiO_2 and ZnO that suffer from side effects such as irritation, percutaneous absorption, photomutagenicity and immunoreaction.(2,3)

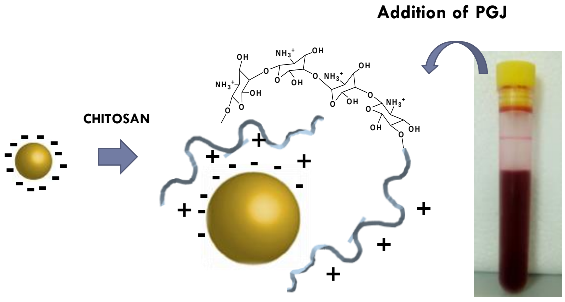

Figure 2: Illustration of AuNPs and chitosan enriched with PGJ

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Adsorption of Amino Acids and Glutamic Acid-Based Surfactants on Imogolite Clays

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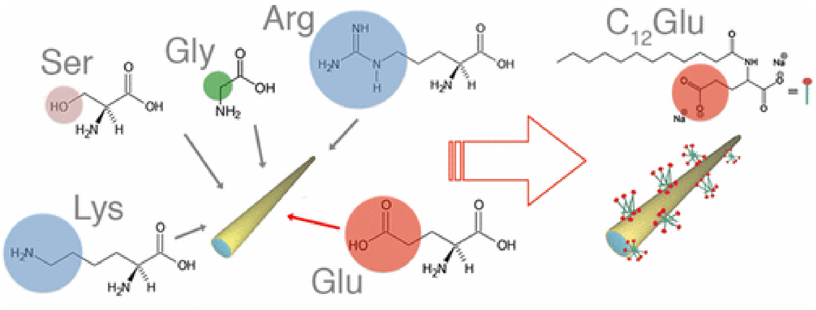
Aluminum oxide surfaces are of utmost interest in different biotech applications, in particular for their use as adjuvants (i.e., booster of the immune response against infectious agents in vaccines production). (1) In this framework, imogolite clays combine the chemical flexibility of an exposed alumina surface with 1D nanostructure. (2) This work reports on the interaction between amino acids and imogolite, using turbidimetry, ζ-potential measurements, and Fourier transform infrared spectroscopy as main characterization tools. (3) Amino acids with different side chain functional groups were investigated, showing that glutamic acid (Glu) has the strongest affinity for the imogolite surface. This was exploited to prepare a composite material made of a synthetic surfactant bearing a Glu polar head and a hydrophobic C_{12} alkyl tail, adsorbed onto the surface of imogolite. The adsorption of a model drug (rhodamine B isothiocyanate) by the hybrid was evaluated both in water and in physiological saline conditions. The findings of this paper suggest that the combination between the glutamate headgroup and imogolite represents a promising platform for the fabrication of hybrid nanostructures with tailored functionalities.



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Organic-inorganic hybrid materials as heterogenous catalysts for pharma industry

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Developing efficient heterogeneous catalysts for pharmaceutical industrial processes in the C-C coupling reactions is a current major challenge for material scientists, organic chemists, industrial engineers and other researchers. Recently, multifunctional organic-inorganic hybrid materials have become an attractive alternative class of catalysts, for applications in cascade, asymmetric, multi-step reactions. The idea of designing hybrid materials is originated by the observation of the success of nature developing enzymes in living organisms. Indeed, selectivity is a crucial factor for the survival of the species.

Organic-inorganic hybrid materials combine the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules or macromolecules (flexibility and functionality) and offer a wide class of new heterogeneous catalysis maximizing the chemical efficiency. Beside the different synthetic strategies to produce hybrid catalysts, the covalent interactions among organic and inorganic units to synthesize class II hybrids allow to obtain more robust and stable functional solids. (1) Nevertheless, the family of Class II hybrid materials could suffer of low conversions and low selectivity because of a non-regular distribution of the different active centers.

In this context, also thanks to the recent evolutions in High Performance Computing (HPC) architectures, theoretical methods can be successfully applied to provide structural information and interface properties at an atomistic level to both guide and interpret experimental synthesis and measurements (2,3).

In this contribution, a preliminary study on the role of theoretical approaches to the synthesis and characterization of innovative porous organic-inorganic materials, with several active sites, will be reported. The joint use of experimental and computational techniques will be also highlighted to deeply understand the structure-properties relationship of the hybrid catalysts.

The present research activity is part of the HORIZON2020 European Project MULTI2HYCAT 'Multi-site organic-inorganic hybrid catalysts for multi-step chemical processes' (Grant Agreement n. 720783).

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Coupling of sieving and thermogravimetric analyzes for studying the activation energy distribution function of complex reactions

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Kinetic parameters of the decomposition of hazardous chemicals can be used for the estimation of the advanced kinetic approach of the thermal behaviour also under adiabatic conditions occurring, e.g. in batch reactors in case of cooling failure. In the present study, a method for analyzing the kinetics of thermal degradation of complex compounds is suggested. Results of thermogravimetric analysis, under nitrogen atmosphere, of ground soft wheat and ground maize have been investigated (1). The thermogravimetric curves reveal two well-distinct jumps of mass loss: volatilization region and decomposition region. We assimilate the global degradation process as a solid state reaction whose kinetics are analyzed separately in each region. By means of a sieving analysis different size fractions of the material are separated and studied (2). A quasi-Newton fitting algorithm is used to obtain the grain size distribution as best fit to experimental data. The individual fractions are thermogravimetrically analyzed for deriving the functional relationship between activation energy of the degradation reactions and the particle size. Such functional relationship turns out to be crucial to evaluate the moments of the activation energy distribution, which is unknown, in terms of the distribution calculated by sieve analysis. From the knowledge of moments the reaction conversion is reconstructed. The comparison with the experimental data reveals that the method reproduces the experimental conversion with an accuracy of 5−10% in the volatilization region and of 3−5% in the decomposition region.

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Dewetting of acrylic polymeric films induced by water/propylene carbonate/surfactant mixtures - Implications for cultural heritage conservation

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The removal of hydrophobic polymer films from surfaces is one of the top priorities of modern conservation science. Nanostructured fluids containing water, a good solvent for the polymer, either immiscible or partially miscible with water, and surfactants have been used in the last decade to achieve controlled removal.[1–6] The dewetting of the polymer film is often an essential step to achieve efficient removal;[7] however, the role of the surfactant throughout the process is yet to be fully understood. We report on the dewetting of a methacrylate/acrylate copolymer film induced by a ternary mixture of water, propylene carbonate (PC) and $C_{9-11}E_6$, a nonionic alcohol ethoxylate surfactant. The fluid microstructure was characterized through Small Angle X-Ray Scattering and the interaction between the film and water, water/PC and water/PC/$C_{9-11}E_6$ was monitored through confocal laser-scanning microscopy (CLSM) and analyzed both from a thermodynamic and a kinetic point of view. The surfactant presence is a prerequisite to induce dewetting of μm-thick films at room temperature, but it is not a thermodynamic driver. The amphiphile lowers the interfacial energy between the phases, favors the loss of adhesion of the polymer on glass, decreasing, in turn, the activation energy barrier, which can be overcome by the thermal fluctuations of polymer film stability, initiating the dewetting process.

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Supramolecular Self-Assembly of Chlorophyll A and Mesoporous Silica Nanoparticles in Water Medium

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Novel photosensitizing system based on mesoporous silica nanoparticles and Chlorophyll *a* (Chl) as a photoactive agent for possible applications in antimicrobial photodynamic therapy (PDT) is presented in this work. The supramolecular system enhanced the solubility of Chl in water medium maintaining the monomeric form of the pigment, important feature for the photodynamic action of Chl. (1) Indeed, under these conditions, the pigment absorbed the visible light inducing the formation of reactive oxygen species (ROS). Silica nanoparticles with different pore sizes were used. Moreover, the functionalization of nanoparticles with amino groups was obtained. The supramolecular system was characterized by means of spectroscopic, diffraction techniques and microscopic imaging methods including time-resolved absorption spectroscopy. Chl showed a strong affinity toward functionalized nanoparticles with amino groups. Indeed, the ζ potential value of nanoparticles occurred to decreased after the insertion of Chl, shielding the positive charge of particles. Nanosecond laser flash photolysis technique provides evidence for the population of the excited triplet state of Chl showing the important precursor of ROS. Among them, the photogeneration of singlet oxygen was demonstrated.

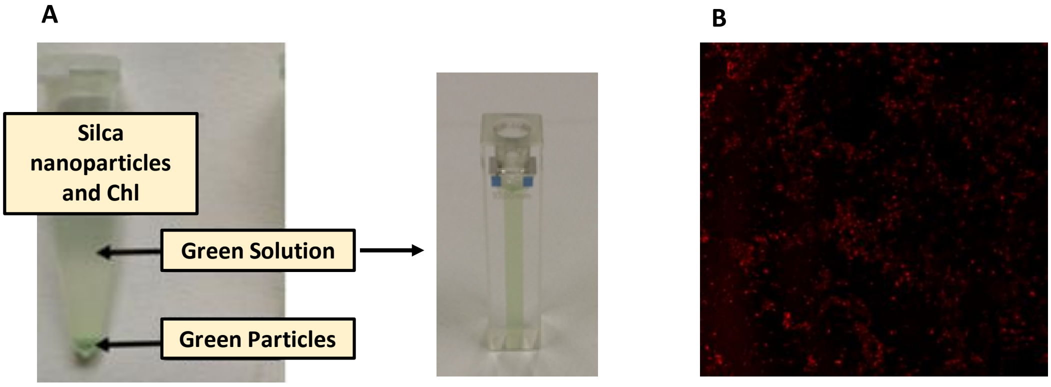

Figure 1. (A) Camera Pictures of Silica Nanoparticles in presence of Chl; **(B)** The fluorescence image of the supramolecular assembly: Chl and Nanoparticles

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Silica-based composites for the consolidation of earthen materials

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Earthen materials are largely used in the architecture of many areas of the world, but the lack of well-established processing techniques and recipes make their conservation challenging. The object of this research is to develop a compatible and long-lasting consolidating treatment for adobe bricks, unbaked mixtures of soil and water, often added with organic matter and/or lime. We are experimenting the formulation and application of a silica-based system, where the combination with a cellulosic derivative and nano-lime aims at obtaining greater effectiveness and compatibility with the substrate.

Mesoporous silica nanoparticles were prepared following a synthesis (1) selected to obtain adequate particle size and porosity (250 nm uniform spheres with 300-600 m^2/g BET surface area were observed with SEM, DLS and porosimetry). Various amounts of *Klucel*®-G (hydroxypropyl cellulose ethanol solution) and *NanorestorePlus*® ($Ca(OH)_2$ nanoparticles ethanol dispersion) were added to the silica aqueous dispersion and kept under stirring to maximize the interaction. Components proportions were chosen according to common restoration applications and in order to minimize the aqueous content. The systems obtained were characterized by DLS, Z Potential, turbidimetry, TGA, FT-IR and SEM-EDS.

Turbidimetric tests confirmed the expected stabilizing effect of hydroxypropyl cellulose on silica, while almost instantaneous flocculation occurs in $Ca(OH)_2$-silica systems, in accordance with surface charge measures. Interestingly, the ternary system maintains a significant stability over several days. FT-IR analyses pointed out an intensification of the stretching band at 965 cm^{-1}, characteristic of calcium silicate hydrate (2,3), in all the systems containing silica and $Ca(OH)_2$ nanoparticles. The hypothesis of the formation of a cementing phase is supported by SEM observations of similar structures. Further analyses are underway. Following these first results, one of the ternary formulations was selected for preliminary application tests on adobe samples from Mexico.

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Langmuir-Blodgett and MD characterization of peptides at the air/water interface

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Molecular monolayers at the air-water interface and on both hard and soft surfaces are deeply studied and well characterized topics. However, a detailed characterization of the behavior of peptides at the air-water interface, in terms of the influence of the peptide concentration on its conformations and on the final film structure is a less examined matter, even if the formation of peptide monolayers is a common established experimental procedure.

In this regard, we studied two different peptides at the air-water interface, namely Trichogin GA IV and Z-(Aib)$_9$-O*t*Bu. The primary structure of Trichogin GA IV is *n*-Oct-Aib-Gly-Leu-Aib-Gly-Gly-Leu-Aib-Gly-Ile-Lol, where Aib is α-aminoisobutyric acid, *n*-Oct is *n*-octanoyl and Lol is leucinol, while, in the homopeptide Z-(Aib)$_9$-O*t*Bu, Z is a benzyloxycarbonyl group, and O*t*Bu is a *tert*-butoxy group. The two peptides differ in hydrophobicity and in the main conformation adopted in solution; Trichogin, indeed, is amphiphilic and can adopt a mixed 3_{10}/α-helical conformation (1), whilst, the homopeptide Z-(Aib)$_9$-O*t*Bu is hydrophobic and tends to prefer right- or left-helical conformations (2).

To study the molecular arrangement at the interface, in terms of conformation and aggregation propensity, we used both experimental and theoretical approaches. The compression isotherms obtained with the Langmuir-Blodgett technique have been used for obtaining data regarding changes in the aggregated structures as a function of peptide concentration. To reproduce the formation of the monomolecular films of these peptides, we ran several molecular dynamic (MD) simulations, at different peptide concentrations, in order to investigate the influence of the aggregation on the peptide conformational behaviour and film formation.

All these results made us able to characterize the process leading to the formation of the monomolecular films of these peptides and their 3D-structures, also highlighting the conformational changes induced by the increasing concentration and molecular interactions under aggregative conditions.

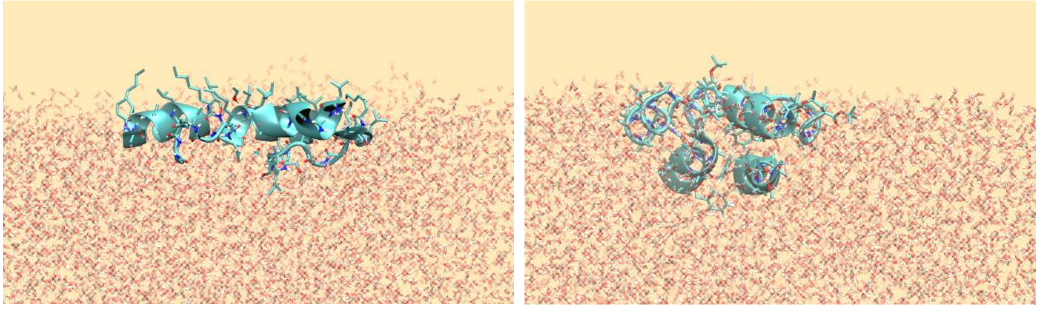

Figure 1. Aggregates of six peptides for Trichogin GA IV (*left*) and Z-(Aib)$_9$-OtBu (*right*)

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Detection and Quantification of Anticancer Drugs with Surface Enhanced Raman Spectroscopy

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Ultrasensitive detection of low-quantity drugs is important for personalized therapeutic approaches in several diseases and, in particular, for cancer treatment. In this field, surface-enhanced Raman scattering (SERS) can be very useful for its ability to precisely identify analytes from their unique vibrational spectra, with very high sensitivity.

Nevertheless, choice of plasmonic substrates for such complex biological samples plays a critical role on the application of this techniques. Zanchi at al. reported a roughened gold surface for the detection of Apomorphine.(1) Calibration curves were also presented for aqueous solutions and the detection was also proved using human blood plasma. Due to the vibrational nature or Raman spectroscopy, signals obtained by complex samples could be usually not trivial to interpret. So, multivariate analysis could often help, as reported by Fornasaro at al. that used Partial Least Square Regression (PLSR) to build calibration curves for Methotrexate in simulated and in real plasma samples. (2)

A further look insight the optical properties of analytes, SERS substrates and the acquisition wavelength could be useful to better understand the relative efficiencies of some setups over others. Our group recently reported a study on five different clinically relevant anticancer drugs over detection and quantification with SERS. (3) The species were Doxorubicin, Paclitaxel, Sunitinib, Irinotecan and it’s active metabolite, SN-38. As plasmonic substrate we used Klarite, a commercially available SERS active surface. Our results clearly showed that the quality of the signal arising from these molecules are closely related to their extinction characteristics, taking fixed the substrate and the excitation wavelength. Of course, this also reflect on the quality of calibration curves, that were done for Sunitinib, Irinotecan and SN-38 at detection limits of 20–70 ng, which is below the threshold for applications in cancer therapy. Principal Component Analysis was also used to discriminate between pure spectra of Irinotecan and SN-38 and a mixture of these two, that was not trivial to obtain without multivariate approach due to the similarity of these molecules.

We also present our newest results on a different approach for quantification using SERS. That is using colloidal solution instead of surfaces and, most important, a covalent, specific recognition of the analyte Erlotinib with our functionalized gold nanoparticles. Our method was found able to quantify the drug up to 20 ng/mL into 150 µL of sample. Calibration curves were obtained in hydro-alcoholic solution, using a competition strategy to overcome the low signals of Erlotinib. Firsts results on simulated plasma samples could open interesting perspectives on this method as a point-of-care tool.

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Effective remediation of highly polluted water by petroleum hydrocarbons with functionalized cellulose fiber

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One of the major environmental problem that needs to be resolved today is the remediation of water bodies such as seabed, lakes and aquifers polluted by hydrophobic organic compounds (HOCs) including BTEX, PCBs, PAHs and some pesticides due to their high toxicity, mutagenicity and carcinogenicity (1). This work gives a first example of remediation, at laboratory level, of water polluted by petroleum hydrocarbons by means of surface functionalized cellulose fiber, extracted from Spanish Broom. In order to transform the hydrophilic character of cellulose surface into the hydrophobic one, therefore to improve its affinity for hydrocarbons, the surface was functionalized with two different methods: in one case, cellulose was allowed to react with 4,4'-methylenebis(phenyl isocyanate) (4,4' MDI) in a home-made reactor. In the other case, the low pressure plasma technique was used to superficially graft with fluorinated groups. The functionalized cellulose was chemically characterized by FT-IR, SEM, XPS and WCA. Batch experiments were performed in order to study the kinetics and thermodynamics of the adsorption process as a function of the initial Total Hydrocarbon concentration and the mass of adsorbent. The kinetics data show that the equilibrium adsorption capacity is reached within an hour, with removal efficiencies as high as 99%. The kinetics of the sorption process can be very well fitted by a pseudo second order model. Moreover, the thermodynamic of adsorption follows a Langmuir isotherm model from which maximum adsorption capacities larger than 200 mg/g can be fitted for the functionalized fiber. Finally, a method for regenerating the cellulose fiber for multiple reuse is discussed.

In conclusion, this work shows a remarkable effectiveness of functionalized cellulose fiber filters for water remediation from petroleum hydrocarbons pollution, since its adsorption capacity is one of the highest ever reported in the literature, showing much higher values than the natural substrates studied so far for such use (2).

Fig.1 Spanish Broom

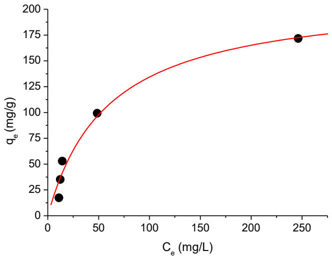

Fig.2 Hydrocarbons adsorption isotherm at 20 °C for the functionalized fiber and fitting with the Langmuir model

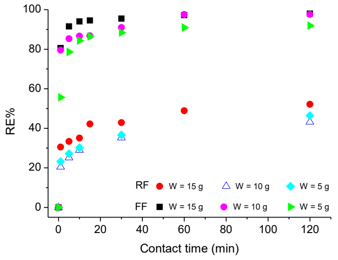

Fig.3 Removal efficiency of SB Functionalized Fiber (FF) and Raw Fiber (RF) for total hydrocarbons from water

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A comparison between the Langmuir rate equation and the pseudo-first and pseudo-second order models for adsorption processes

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The objective of this study is to discuss the applicability of the Langmuir, pseudo-first order (PFO) and pseudo-second order (PSO) models in estimating the kinetic and thermodynamic adsorption parameters. The integrated Langmuir equation depends on five parameters with a direct physical significance, namely the initial solute concentration, the adsorbent dosage, the microscopic adsorption rate constant, the adsorption amount at the equilibrium and the maximum adsorption capacity of the adsorbent. The PFO and PSO models are of common use for describing adsorption kinetics, although both are derived empirically (1,2). An analysis of the factorized form of the differential Langmuir equation shows that the Langmuir kinetics regularly coincides with the PFO model with very low or very high input of solute per mass of adsorbent. By contrast, the PSO model approximates the Langmuir kinetics only when the adsorbent is near saturation and, at the same time, the input of solute per mass of adsorbent is close to the maximum adsorption capacity. The optimal initial solute concentration and adsorbent dosage are determined for approximating the Langmuir kinetics. A graphical method is proposed for assessing the PFO and PSO models as substitutes for the Langmuir equation and estimating the adsorption parameters.

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Microstructured composite for Cr (VI) removal from polluted environment

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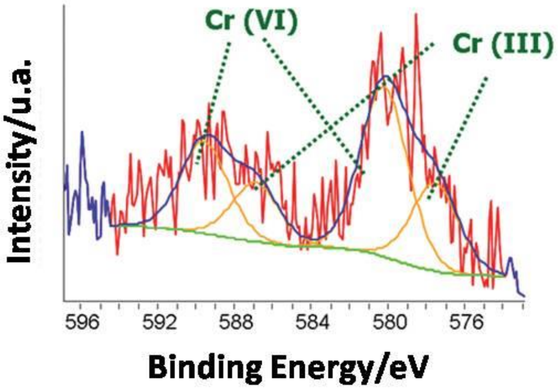
A microstructured composite able to remove hexavalent chromium Cr(VI) from aqueous solutions obtained by adding the silica precursor tetraethoxysilane (TEOS) to the hexadecyltrimethylammonium bromide (CTAB) microemulsion-based gel is here presented (1,2). SEM and NMR analysis showed that this material is made by an interconnected network of gelatin, silicate and surfactant molecules in which water molecules manifest a high mobility. Analyses of the elemental content in the CTAB-silica gelatin composite suggest that the adsorption of chromium takes also places in the internal areas. Remarkably, this composite containing the adsorbed hexavalent chromium left in water for 30 days undergoes a change in colour from yellow to green. This evidence is an indication of the reduction in situ of Cr(VI). X-ray Photoelectron Spectroscopy has been used to characterize the composite materials. Surface analyses performed at different times revealed chromium chemical speciation changes as a function of the pollutant-material interaction time (3). Moreover, the removal of chromate was assessed also through evaluation of the adsorption kinetics of chromate ions on the composite under equilibrium conditions in the presence of sulfate ions and at a slightly acidic pH condition (pH 5.8) (4,5). These findings demonstrated a high specificity of the CTAB–silica gelatin composite for chromium, and highlight the possibility of using this matrix for efficient removal and in situ conversion of chromium from industrial wastewater without the need to eliminate contaminant sulfate ions.



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Olive mill wastewaters phenol photocatalytic degradation by visible light activated carbon doped titanium

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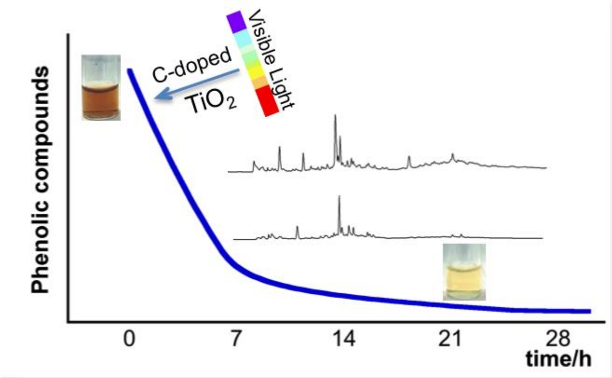
Carbon doped titanium dioxide (CDT) was tested as catalyst for photodegradation of phenolic compounds. Caffeic acid and olive mill wastewater (OMW) phenolic compounds were removed under visible light (1). The cleaning effectiveness of this catalyst towards the polluted wastewater from olive oil industry was demonstrated by means of HPLC and UV-visible spectroscopy combined with phenol compound determination. The photodegradation activity was tested on systems having different initial concentration of phenols and in the presence of different amounts of CDT (2). By introducing a suitable parameter, namely the ratio between the amount of catalyst and the amount of total phenols Ti/TPh, it was demonstrated that the proposed degradation method could be scaled up without losing its effectiveness (3). The OMW decolorization occurring in the presence of CDT particles under visible light radiation is marked enough to be directly appreciated with the naked eye. The decolorization is strongly associated with the removal of phenols. In fact, while bleaching the solutions, CDT successfully removed 70% of the phenols in 24 hours. HPLC analysis demonstrates that CDT was effective in degrading the higher part of the phenols of OMW.
It was found that the whole photodegradation process is governed by a synergic mechanism in which adsorption and photodegradation are involved.



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Removal of an azo textile dye from wastewater using cyclodextrin-epichlorohydrin polymers

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Textile industries and clothing manufacturing release large amounts of dyes in effluents generating high amount of polluted wastewater (1). Indeed, dyes discharged in water are molecules stable to light irradiation, heat and oxidation agents which influence the photosynthetic activity of aquatic species inhibiting their growth (2). Moreover, azo dyes are toxic, carcinogenic and mutagenic both to some aquatic species and to human beings due to the reduction of the azo groups and the consequential formation of aromatic amines in the wastewater (3). Therefore, the removal of dyes from industrial effluents is a fundamental questions and appropriate treatments of wastewater should be done to decrease the environmental impact. Among all the processes developed for the removal of dyes from industrial effluents, adsorption is one of the most effective and cheap methods which industries employ to reduce hazardous pollutants present in the effluent. In this study, cyclodextrins-epichlorohydrin (CDs/EPI) polymers were used as adsorbent materials to remove a textile dye, Direct Blue 78 (DB78), from aqueous solutions. Since in a recent paper (4), we already demonstrated the ability of some commercial cyclodextrins to encapsulate, in their inner cavity, some azo direct dyes, in this work the adsorption process of DB78 on CDs/EPI polymers was performed and the effect of different variables, such as contact time, adsorbent dosage, initial dye concentration, pH of initial solution and temperature were considered and discussed. The equilibrium isotherms and the adsorption kinetics were analyzed using opportune mathematic models. Results of adsorption showed the good adsorption properties towards azo DB78 of β- and γ-CD EPI polymers. The dye removal efficiency was about 99% with β-CD/EPI polymer and about 98% with γ-CD/EPI polymer. This adsorption method allows indeed to obtain very clean water after 2 hours of treatment with polymers permitting the feasible reuse of water in further industrial processes. Moreover, the chemical-physical characteristics of adsorbent polymers were observed by means of different techniques (FTIR-ATR, DSC, TGA and FESEM). The proposed adsorption mechanism involved several kinds of interactions such as physical adsorption in the polymer network, hydrogen bonding and formation of inclusion complex due to the presence of CD molecules through host–guest interactions.

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Arsenic Adsorption on Iron Oxides and its Environmental Impact

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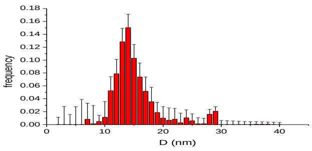
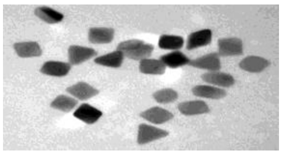
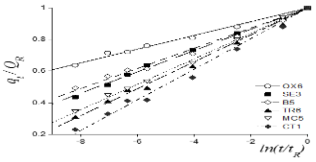
Arsenic occurs naturally in water in many parts of the world. Natural processes, including soil erosion, mineral leaching, and weathering, are responsible for introducing arsenic into surface water. Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs, and ponds), groundwater (aquifers), and rainwater. These sources are very variable in terms of arsenic risk, among which groundwater has high concentration of arsenic (1). Minerals such as iron oxyhydroxide and oxides phases probably play a key and complex role in controlling the mobility and fate of arsenic in groundwater (2). Crystal morphology and surface area often depend on synthesis conditions and several methods are available to enable a range of oxides with specific characteristics to be produced. In this study, laboratory batch experiments were carried out to study the adsorption of arsenic on two of major iron oxide minerals, namely, hematite α-Fe_2O_3 and magnetite Fe_3O_4. To simulate the role played by inorganic and organic ions commonly found in soils in the alteration of crystal morphology of natural hematite, several experimental protocols were applied to synthetize α-Fe_2O_3 through hydrothermal methods in the presence of Al, Mg, Si and oxalic, citric and tartaric acids. Previous investigations demonstrated that the adsorption efficiency of phosphate anions onto hematite nanocrystals could be affected by different crystal shapes induced in α-Fe_2O_3 synthetized in the presence of the aforementioned chemical species, without modifying the structure (isomorphous substitution) (3). Therefore, we explored the adsorption properties of hematite prepared in different experimental conditions to verify their capacity in the immobilization of arsenate anion and investigate its environmental impact. A parallel investigation was carried out by using magnetite nanocrystals as adsorbent for arsenate. We proposed a slight modification of its preparative procedure based on the partial oxidation of a Fe(II) salt solution with KNO_3 under alkaline conditions at 80°C under inert atmosphere of N_2 (4). For both hematite and magnetite adsorbents, kinetic tests were carried out to characterize the mechanism of arsenate adsorption process, by evaluating also the effect of pH. Finally, X-ray diffractograms, FTIR absorption spectra, Atomic Force Microscopy and electron micrographs were included in the present study to link the iron oxide crystal morphology to the arsenate adsorption properties. Overall, these findings improve our knowledge in modeling arsenic adsorption to common soil minerals and provide elucidation of the role played by iron oxides in soil decontamination.







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Electrophysiological measurements on a solid supported membrane to investigate the transport activity of sarcoplasmic reticulum Ca^{2+}-ATPase

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P-type ATPases are a large and varied family of membrane proteins that are involved in many transport processes in virtually all living organisms (1). These membrane proteins couple the energy provided by ATP hydrolysis to the active transport of various ions across biological membranes. Sarcoplasmic reticulum (SR) Ca^{2+}-ATPase promotes muscle relaxation by pumping Ca^{2+} ions from the cytoplasm into the SR lumen. The activity of SR Ca^{2+}-ATPase is regulated by two small membrane proteins, phospholamban (PLN) and sarcolipin (SLN). PLN is primarily expressed in cardiac muscle, whereas SLN expression predominates in skeletal muscle. The molecular mechanisms of PLN and SLN regulation are not fully understood. Solid supported membranes (SSM) have been employed for the functional characterisation of P-type ATPases (2). The SSM, consisting of a hybrid alkanethiol/phospholipid bilayer supported by a gold electrode, is a convenient model system for a biological membrane. Proteoliposomes or native membranes (vesicles or fragments) incorporating the ATPase are adsorbed on the SSM surface and are subjected to a rapid substrate concentration jump. The substrate concentration jump activates the ATPase and the charge displacement concomitant with the transport activity of the enzyme is recorded as a current transient via capacitive coupling (3). Charge transfer in P-type ATPases was investigated by SSM-based electrophysiological measurements in order to gain insights into the ion transport mechanism. In the case of SR Ca^{2+}-ATPase, the SSM technique provided useful information for a detailed characterization of the enzyme's transport cycle, especially as concerns Ca^{2+} binding mechanism, Ca^{2+}/H^{+} exchange and competitive Mg^{2+} binding (4,5). In a typical SSM experiment, SR vesicles containing the Ca^{2+}-ATPase are adsorbed on the SSM and exposed to a concentration jump of a suitable substrate, e.g., ATP. The ATP-induced current transient is related to an electrogenic event corresponding to the translocation and release of bound Ca^{2+} upon phosphorylation by ATP within the first transport cycle (2,4). Recently, SSM-based current measurements were performed to investigate the effects of PLN and SLN on Ca^{2+} translocation by SR Ca^{2+}-ATPase. We observed that PLN altered ATP-dependent Ca^{2+} translocation within the first enzyme cycle, while SLN did not. These measurements indicate that PLN can establish an inhibitory interaction with multiple conformational states of the ATPase. The results are discussed in terms of the recently published crystal structures of SR Ca^{2+}-ATPase bound to PLN and SLN.

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Protein-ligand interaction: a NMR study

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Proteins perform numerous tasks within living organisms, some act as structural support for cells and tissues, others are transporters of non-soluble molecules in water and others, such as lysozyme, are involved in defensive mechanisms against bacterial attacks. The growing ease of obtaining proteins in substantial quantities and purity, by means of increasingly sophisticated bio-engineering techniques (1), may lead to their use in pharmaceutical formulations as drug delivery mechanisms or in food as preservatives (2). However, given the chemical nature of these macromolecules, they are vulnerable to oxidative attacks that would lead to their denaturing resulting in loss of activity. Moreover, some of these, such as lysozyme, once denatured, can give rise to aggregation leading to the onset of amyloidogenic diseases such as Alzheimer's disease and transmissible spongiform encephalopathies. The proteins that cause these diseases have no common characteristics in their native state, but once converted into amyloid fibrils they have many analogies (3). The factors that induce the formation of aggregates remain obscure; a hypothesis is the malfunctioning of mechanisms that govern the folding of proteins and the elimination of erroneously folded ones, or even oxidative stress phenomena caused by a malfunction of superoxide dismutase mutation.

Therefore, it is vital to be able to prevent the oxidation of these enzymes in order to maintain their activity unaltered before they can be used on a large scale. The aim of this study is to investigate, through Nuclear Magnetic Resonance, the interaction between a protein with potential industrial applications (lysozyme), with a molecule with known antioxidant potential, the catechin, which has no compatibility issues with the human body being a substance naturally occurring in numerous foods of natural origin. Subsequently, in order to verify the protective effect of catechin on the protein, the effect of an oxidizing system on lysozyme was assessed both in the absence and the presence of catechin. Finally, in order to estimate the magnitude of such protection, a comparison with another known antioxidant system, the ascorbic acid (4), has been carried out.

The study begins with the chemico-physical characterization of the molecules employing advanced spectroscopic techniques such as ^{1}H-^{1}H COSY, TOCSY, NOESY and ^{1}H-^{13}C HSQC and HMBC bidimensional experiments as well DOSY. These experiments aim to evaluate the spatial structure and arrangement of isolated molecules, as well as evaluate their translational mobility. The study proceeds with the evaluation of the interaction based on the variation of the ligand self-diffusion coefficient, is continued by determining the binding constant by acquiring spectra at different concentration ratios and finally identifying the interaction site on the protein.

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Immobilisation of neurotrophin peptides on gold nanoparticles by direct and lipid-mediated interaction: a new multipotential therapeutic nanoplatform for CNS disorders

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Neurotrophins are essential proteins for the developing and maintenance of neural functions as well as promising drugs in neurodegenerative disorders. Current limits in their effective clinical applications can be overwhelmed by the combined use of peptidomimetic and nanomedicine approaches. Indeed, neurotrophin-mimicking peptides may allow minimising the adverse side effects of the whole protein drug. Moreover, the immobilisation of such peptides on nanomaterials may offer additional advantages, including protection against degradation, enhanced permeability of barrier membranes and intrinsic therapeutic properties of the nanoparticles (e.g., anti-angiogenic and plasmonic features of gold nanoparticles, AuNPs). In the present paper we scrutinize the functionalisation of spherical AuNPs of 12 nm of diameter by peptides owing to the N-terminal domains of nerve growth factor and brain derived neurotrophic factor, NGF1-14 and BDNF1-12, respectively. The hybrid gold-peptide nanobiointerface was investigated, both in the direct physisorption and in the lipid bilayer-mediated adsorption processes, by a multitechnique study that included UV-visible and X-ray photoelectron spectroscopies, dynamic light scattering, zeta potential analyses and atomic force microscopy. Both peptide- and lipid-dependant features were identified, in order to have a modulation in the nanoparticles peptide coverage as well as in the cellular uptake of NGF and BDNF peptides, as investigated by confocal microscopy. The promising potentialities in the capability to cross the blood brain barrier were demonstrated.

Small liposomes for drug delivery

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Micelle to vesicle transition (MVT) method was applied to the realization of small unilamellar liposomes (<100 nm) useful for different types of applications in the field of drug and bioactive molecule delivery. In particular, mucus-penetrating liposomes for pulmonary delivery of beclomethasone dipropionate (BDP), a known anti-inflammatory drug, were realized. We also decorated vesicles with hydrophilic polymers, capable of giving mucus-penetrating properties to the liposomes. Indeed, some pathologies such as lung diseases result often in the overproduction of mucus that forms a barrier for drugs. The method allows obtaining liposomes always below 100 nm and with good yields of drug encapsulation. Liposomes featured a constant low release of the drug over a period of 48h. In vitro assays showed that liposomes with a hydrophilic cover were well tolerated by pulmonary cells. In vivo experiments on mice also showed a good tolerability of BDP-loaded liposomes. The same strategy was successfully adopted to incorporate natural antioxidants, such as curcumin, aiming to obtain formulations of potential nutraceutical and pharmaceutical interest (1). Finally, the possibility of assembly liposomes on Titanium to develop advanced implant surface was exploited in view of possible strategy to local delivery of bioactive molecules. The opportunity of engineering the surface of implantable materials in order to increase the biocompatibility to host tissues, providing at the same time a surface-mediated drug delivery, is a very attractive solution to limit inflammation and to promote new bone formation in the prosthetic application field (2).

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Molecular Confinement in Femtoliter scale aqueous Compartments

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Molecular confinement is known to lead to acceleration of molecular dynamics along with surface interaction. Nature employs confinement in molecularly crowded, heterogeneous and, specialized femtoliter (fL) compartments inside living cells for spontaneously achieving higher reaction efficiency and spatial-programming of composite, multi-step biochemical processes (1). We here show the facile production of aqueous fL droplets for studying molecular confinement on a biochip. We prepare fL aqueous droplets in oil drops on solid substrates by a "field-free"- no external electric fields and electrolytes (2) - piezoelectric inkjet printing in which a novel actuating waveform is employed by picoliter sized nozzles (Fig 1.a). The droplets form an almost-regular circular pattern at the border of mineral oil drops (3), (Fig 1.b) and Alexa 647 molecules, at 10-0.01 µM concentrations, form ring patterns at the surfactant/oil interface (Fig.1c) as predicted by numerical adsorption general models (4). At the single droplet level, we show that molecular confinement leads to modify solute-solvent and solvent driven solute-solute interactions. Confinement effects are tested by using Fluorescence lifetime imaging which reveals different characteristic lifetimes of specific molecules in confined volumes with respect to macroscopic solutions. The same method using the signal of a molecular rotor- i.e. 9-(2-Carboxy-2-cyanovinyl)julolidine - did not reveal changes in solution viscosity due to confinement. We exploit the possibility of analyzing molecules "in action" in fL volume solutions to study the behavior of molecular machines in confined environments. At these volume scales, by employing a model DNA beacon machine, we highlight that DNA-machines/ target interaction is favored in confined conditions with respect to microliter/macroscopic volumes.

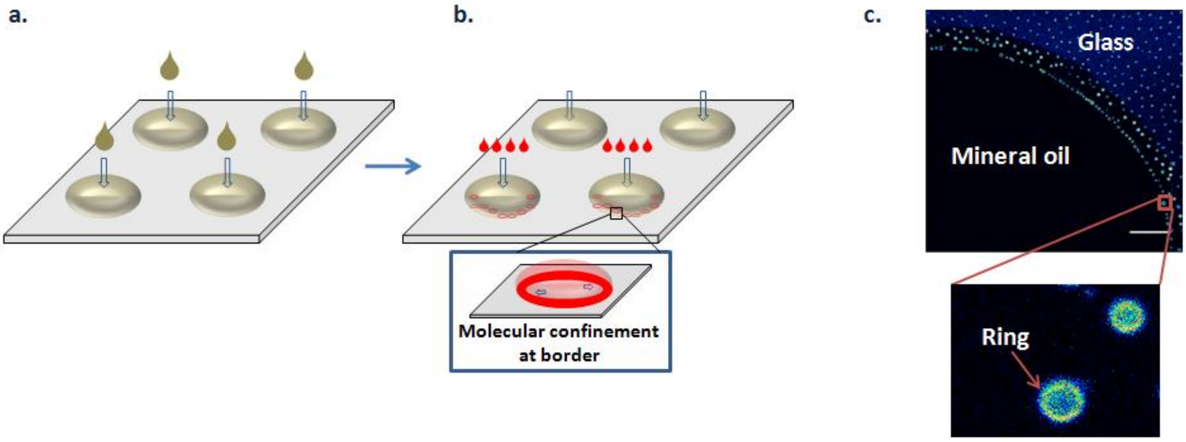

Figure 1. (a-b) Scheme of fL aqueous droplets injection inside mineral oil nanoliter scale droplets. (c) Fluorescence confocal images show the molecular confinement at the border of the droplets (Alexa 647 dye, 10 µM).

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The Influence of Chemical Microenvironment on Living Cell Shape

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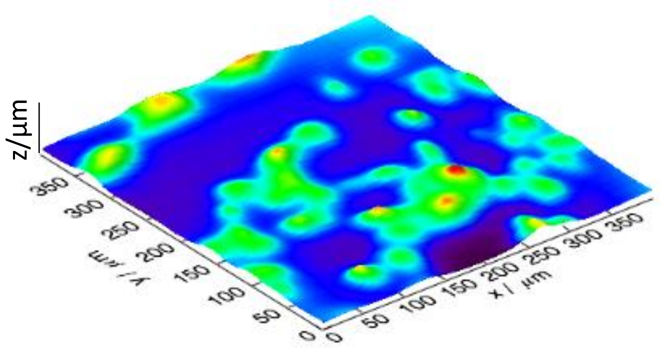
The shape and morphology of cells are related to their health status. Diseases, senescence, and the presence of toxic compounds cause morphological changes. Mechanical forces involved in the interaction with the cell microenvironment influence adhesiveness and morphology. Variations of morphology and motility are present in all cancer cells and are involved in metastasis. Cells adhesion to solid substrates is a multistep and complex process. It involves surface receptors, signaling elements and cytoskeleton. When a cell attaches to a solid substrate, it spreads over the surface. The degree of adhesion can be expressed in terms of shape parameters. Cells sense the physical-chemistry of their microenvironment and modulate their cell shape. We employed 2D nanomaterials, such as organic monolayers with a high surface coverage >95% [1] as culturing surfaces/environment for normal and cancer cells.

We used Scanning Electrochemical Microscopy (SECM) to study the local reactivity [2] and conductivity [3] of the surfaces. Using SECM, fluorescence microscopy and AFM we correlated the local physical chemical characteristics of the environments with the cancer and normal cellular shapes.The investigation of the interactions of living cells with 2D environments can gain fundamental knowledge on the type of environment that retards or accelerates diseases and degeneration and can determine the chemical forces that drive cell recruitment on a bioactive surface. The influence of micro-shaped chemical micro-environments on cell biology was investigated and will be presented as well.



Scanning Electrochemical Image of MCF10A cells growth on a pentacene monolayer

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High-Quality, Ligands-Free, Mixed-Halide Perovskite nanocrystals Ink for Optoelectronic applications

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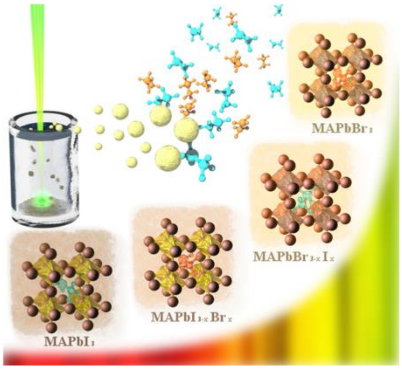
It is now well established that the primary optoelectronic properties of perovskite-halides – such as their tunable direct bandgap, high absorption coefficient, low exciton binding energy, and balanced ambipolar carrier transport – meet many of the requirements for a high-efficiency solar energy conversion technology(1). But in spite of the huge research effort, yet they are far from the market.
Given the simple processability of perovskite-halides, typically from solutions at relatively low temperatures, a non-negligible level of unintentional structural and chemical defects at temperatures relevant for device operation are currently limiting the devices efficiencies and causing instability - i.e. hysteretic behaviours (2) and formation of metastable phases upon photoexcitation which hampers the band-gap tunability (3) - and low reproducibility, especially in view of large area deposition.
In more established semiconductors, such as Si for example, the understanding and control of defects has been a cornerstone of their successful development in devices. Defects thus remain one of the interesting material characteristics in solution processable perovskites that underpin limitations in device operation and influence further progress towards reaching the highest possible power conversion efficiencies. So far, high quality colloidal nanocrystal of perovskites (not necessarily quantum confined) have been demonstrated. However, they all need bulky and insulating organic ligands to remain in suspension, thus hampering the fabrication of conductive thin films.



We demonstrate, for the first time, the synthesis of ligand free metal-halide pervskite nano-crystal inks by Laser Ablation Synthesis in Solution (LASiS).[4] This methodology, simple and easy to use for large scale materials production, allows to produce nano-crystals solutions to print conductive thin films electrically and photo-stable. In fact, we show that such films do not present any hysteretic behavior under polarization, typical in presence of ion migration and permit monotonic tunability of the band gap across the visible spectrum, in absorption and emission, without the formation of sub-band gap emissive phases upon photo-excitation.

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New Earth-abundant thin film solar cells based on Cu_2MnSnS_4

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As it is well known, in the last decade much attention has been focused on I_2-II-IV-VI_4 thin films as an attractive possibility for the synthesis of In and Ga free chalcogenides which may allow terawatt range photovoltaic (PV) applications. A new alternative to copper zinc tin sulfide/selenide belonging to this class of materials is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements which shows an important advantage with respect to copper zinc tin sulfide/selenide. As a matter of fact, not only the abundance in the Earth's crust of Mn is two order of magnitude higher than that of Zn (1100 ppm vs 79 ppm), but the amount of Zn produced in 2015 was 4'600'000 tons lower than that of Mn (13'400'000 Zn tons vs 18'000'000 Mn tons). Therefore, since Mn is definitely cheaper than Zn, optimized CMTS could potentially provide Wp cost definitely lower than copper zinc tin sulfide/selenide, which is crucial for thin film PV applications. CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient ($\alpha=10^4$ cm^{-1}) and direct band gap suitable for PV applications. So far, CMTS was mainly studied as bulk magnetic semiconductor, while, only in the last two years, the present authors (1) and Chen et al. (2) reported on CMTS thin films for PV applications. The latter reported on CMTS layers prepared by direct liquid coating followed by annealing in nitrogen atmosphere and/or post-sulfurization in sulfur vapors, which provided solar cells with 0.49% maximum efficiency. Our work deals instead with CMTS thin films grown by a two-step vacuum process. The metal precursors deposited on Mo-coated soda lime glass (SLG) by thermal evaporation are annealed in sulfur vapors for 1h at 585°C with an initial 1h step at 115°C to enhance the metal intermixing. Of the many possible stoichiometries, Cu-poor/Mn-rich CMTS films with Mn/Sn ratio around 1 were chosen in order to prevent the development of both highly conductive (e.g. $Cu_{2-x}S$) and insulating (e.g. MnS) secondary phases. Several techniques, including Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) , Raman spectroscopy and Photoluminescence have been used to test the quality of CMTS thin films, while CMTS/CdS/iZnO+AZO solar cells were inspected both by External Quantum Efficiency and current density-voltage (J-V) measurements under 1 sun illumination. The beneficial effects of low temperature post-deposition annealing either in air or inert atmosphere between 200 and 275°C on CMTS solar cells were investigated, both in terms of electrical performance and modification of the material properties. In particular, a 40 min 225°C annealing in air lead to the best overall performance: efficiency 0.83%, open-circuit voltage 354 mV, short-circuit current density 5.8 mA/cm2, fill factor 40%. The reasons behind these beneficial modifications of the device parameters were investigated by Raman and PL spectroscopies. Results showed that post-deposition thermal treatments in air between 200 and 275°C generally reduce generally reduces the density of the bulk defect, thus reducing recombination losses and increase the of CdS crystalline quality, while red-shifting its absorption edge.

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Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters

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Energy harvesting of wasted energy is increasingly important for powering wearable electronics in Internet-of-Things world [1]. Here, we reported on innovative nanocomposites made of electrostrictive polymer (thermoplastic polyurethane, TPU), and high-k ceramic filler ($CaCu_3Ti_4O_{12}$, CCTO), which offered outstanding results in recovering energy by human gait. The excellent mechanical properties of TPU allowed up to 50 vol% of filler into the composite without loosing film elasticity even for high strains (~30%). CCTO was able to increase of more than one order of magnitude the resistance of the film harvesters with respect to pure TPU, without lowering the dielectric constant and the breakdown voltage. The combined effect of high dielectric strength, high resistance and allowable strain make these composites very promising as energy harvesting actuators.

By means of careful broadband electric spectroscopy coupled with microstructure analysis, we were able to address the mechanisms underlying energy recovery. In particular, long-range charge migration phenomena mainly occurred along conductivity pathways, which are formed at the extended interfaces between the polymer strands and the filler. Our model allowed optimal tailoring of electrostrictive nano-composite actuators.

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A Bilayer WO_3 n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting

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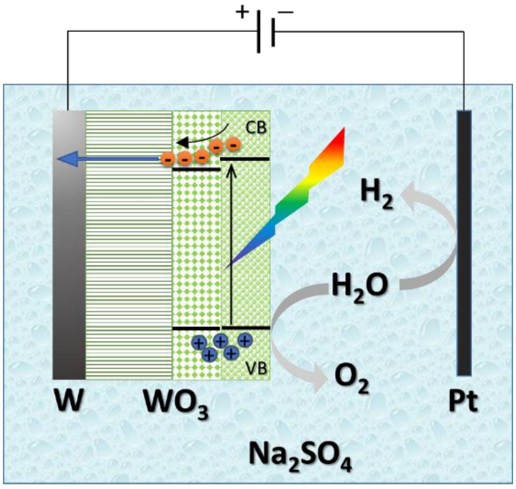
A bilayer WO_3 photoelectrode was prepared by radio frequency (RF) plasma sputtering in reactive 40%O_2/Ar atmosphere by depositing on a tungsten foil two successive WO_3 coatings at two different total gas pressures (3 Pa and 1.7 Pa, respectively), followed by calcination at 600 °C (1). Its photoelectrocatalytic (PEC) activity was evaluated by both Incident Photon-to-Current Efficiency (IPCE) measurements and separate evolution of H_2 and O_2 by water splitting in a two-compartment PEC cell (2), and compared with those of the corresponding single layer grown at constant pressure (1.7 Pa or 3 Pa). FESEM analysis revealed that the photoanodes have a nanostructured porous double layer surmounting a columnar basement (Staffa-like morphology, after the name of the Scottish island). Tauc plot of the single layer revealed that the sample prepared at lower pressure possesses a 0.1 V wider bandgap (2.94 eV) than that prepared at higher pressure (2.82 eV). Both Mott-Schottky analysis and XPS valence band spectra showed that this difference was essentially due to a shift of the conduction flat band (CB) potential. Thus, this work demonstrates that the total pressure during WO_3 deposition by RF diode sputtering affects the position of the CB energy very likely due to the different extent of crystal structure distortion induced by oxygen vacancies (3), in agreement with the crystal field theory (CFT). Lowering the pressure increases the oxygen vacancies, and produces a shift of the CB towards higher energy. The equivalent n-n heterojunction at the interface of the double-layer (see Figure) creates a built-in electric field that facilitates the photopromoted electron transfer toward the lower laying conduction band material, while the columnar innermost layer introduces percolation paths for efficient electron transport toward the conductive tungsten foil. Both phenomena contribute to decrease the interfacial charge transfer resistance (R_{ct}) as measured by impedance spectroscopy and lead to a *ca.* 30% increase in the PEC performance compared to the monolayer and to a 93% faradaic efficiency, which is among the highest reported so far for WO_3 photoanodes. Upon methanol addition an outstanding 4-fold photocurrent density increase up to 6.3 mA cm^{-2} was attained over the bilayer WO_3 photoanode, much larger than the usually observed current doubling effect.



Acknowledgment. This work received financial support from the Regione Lombardia and Cariplo Foundation co-funded "SmartMatLab Centre" project (Grant No. 2013-1766)

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Hydrides as High Capacity Anodes in Lithium Cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project

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Automotive and stationary energy storage are among the most recently-proposed and still unfulfilled applications for lithium ion devices. Higher energy, power and superior safety standards, well beyond the present state of the art, are actually required to extend the Li-ion battery market to these challenging fields, but such a goal can only be achieved by the development of new materials with improved performances. Focusing on the negative electrode materials, alloying and conversion chemistries have been widely explored in the last decade to circumvent the main weakness of the intercalation processes: the limitation in capacity to one or at most two lithium atoms per host formula unit. Among all of the many proposed conversion chemistries, hydrides have been proposed and investigated since 2008. In lithium cells, these materials undergo a conversion reaction that gives metallic nanoparticles surrounded by an amorphous matrix of LiH. Among all of the reported conversion materials, hydrides have outstanding theoretical properties and have been only marginally explored, thus making this class of materials an interesting playground for both fundamental and applied research. In this communication, we illustrate the most relevant results achieved in the frame of the Italian National Research Project FIRB 2010 Futuro in Ricerca "Hydrides as high capacity anodes in lithium cells" and possible future perspectives of research for this class of materials in electrochemical energy storage devices.

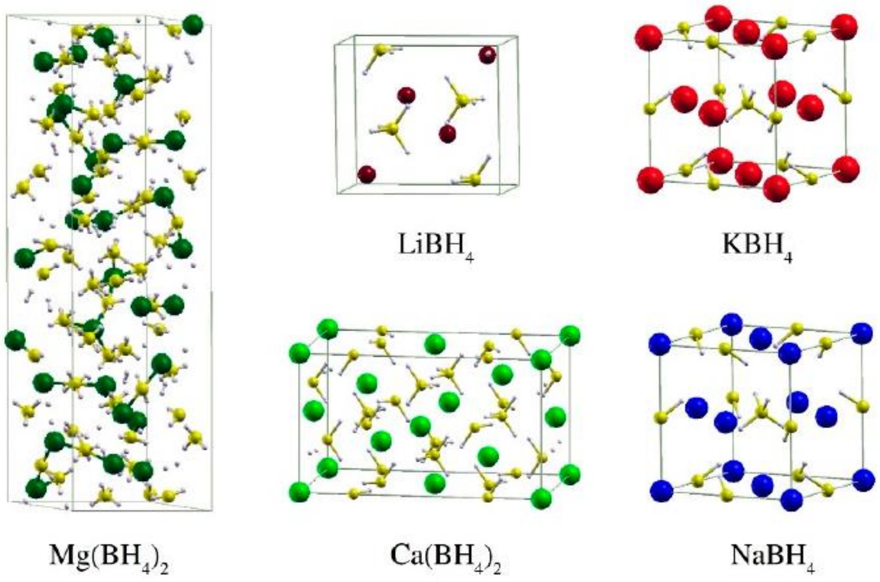

Figure 1. Crystal structures of the borohydrides phases.

Bio-Hybrid Complexes in Artificial Photosynthesis

Simona la Gatta[a], *Francesco Milano*[b], *Roberta Ragni*[a], *Angela Agostiano*[a,b], *Gianluca Maria Farinola*[a] *and Massimo Trotta*[b]

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The sun was born five billion years ago and it is estimated that it will continue to irradiate the same amount of energy for another five billion years. Sun is a renewable energy source, inexhaustible within the humankind life, and, every year, Earth receives an amount of solar energy ten thousand times greater than that the entire planet population uses (1). The ability to convert solar light into chemical energy is the fundamental feature of photosynthetic systems. Photosynthesis is the most important biological process, supplying Earth's biosphere with oxygen and energy for living organisms' metabolism (2). All life on Earth depends on photosynthesis directly or indirectly, and has been deeply investigated by scientists with the aim of reproducing it in the laboratory, mimicking the Nature, and, consequently, producing green energy efficiently, following the artificial photosynthesis way (3). The complexity of the natural photosynthetic systems is difficult to reproduce *in vitro*; however, it is largely related to their living character and can be reduced in a biomimetic environment. In this regard, ideal biomimetic systems must efficiently harvest the sunlight, with the help of suitable antennas, and convert the energy in a stable charge-separated state with a lifetime long enough to allow ancillary chemistry to take place. In the purple, no sulphur photosynthetic bacterium *Rhodobacter sphaeroides R26*, energy from sunlight is harvested by antennas and transferred to reaction center (RC), a most efficient photoconverting transmembrane protein. During the electron transfer process, the RC, upon photon absorption, promotes one electron sitting on the bacteriochlorophylls dimer (D), the electron donor, in its excited state and then it shuttles to the electron acceptors the ubiquinone-10 Q, generating the charge separated state D^+Q^-. In the presence of external electron donors, the oxidized D^+ is reduced again and a second photon impinges a second electron so that the quinone Q, now doubly reduced, is doubly protonated and it is released as quinol. Cytochrome c_2 is the physiological electron donor to the oxidized dimer. Our idea is to build a supramolecular architecture made up of the photosynthetic bacterial reaction center, an artificial light-harvesting antenna, synthesized *ad hoc*, belonging to the class of heptamethine cyanines, with the task of increasing the RC absorption cross section in the visible range, and an electron donor redox protein, the cytochrome c_2. These three components were connected to each other by covalent bonds obtaining a stable bio-hybrid supramolecular complex, easily interfaceable to a semi-conductive surface, with the aim of assembling a sustainable sunlight-to-energy converting device based on proteins. Insert references in brackets as follows: (1) (1,2,3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below:

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Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds

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Organic mixed-valence compounds (MVs) are donor-acceptor compounds that possess an open shell ground state (1). Amongst the MVs particularly interesting are those with arylamines connected through a conjugated bridge. The nature of the bridge as well as that of the substituents on the arylamine moieties, determines the electrooptical properties of such compounds. Specifically, the intervalence charge transfer transition (IVCT) in the near infrared region (NIR), occurring upon photoexcitation of the oxidized monocation species, is heavily affected by the above structural parameters. These compounds can be designed to work as electrochromic materials in smart devices for controlling the solar thermal radiation, as well as for the generation of high charged radical species for high spin magnetic materials (2,3). Here we present organic MVs with an innovative H-shape design, where four redox centres are bridged "vertically" via a dibenzofulvene backbone and "horizontally" via a bis-(dibenzofulvene)-thiophene bridge. They are oxidized to stable high charged radical species, showing IVCT in the NIR, in contrast to the linear systems lacking one dibenzofulvene-bisamine moiety at one end of the thiophene bridge, where band bleaching occurs upon dication formation. Electrochemical, spectroelectrochemical and TD-DFT results, show that the IVCT in high oxidation states of the H-shape MVs is due to the activation of both vertical and horizontal electron transfer pathways (4). The innovative H-shape design may improve the potential electrooptical applications of MVs, highlighting the importance of the coupling between multiple redox centres and paving the way for the development of three-dimensional multicentre mixed valence compounds.

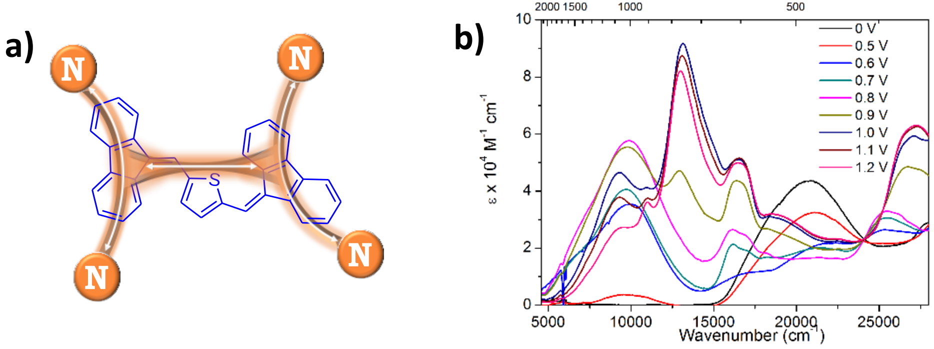

Figure 1. H-shape MVs based on the bis(dibenzofulvene)tiophene bridge a); example of the electrochromic response of an H-shape compound in the Vis-NIR region b).

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Forsterite surfaces as models of interstellar core dust grains: computational study of carbon monoxide adsorption

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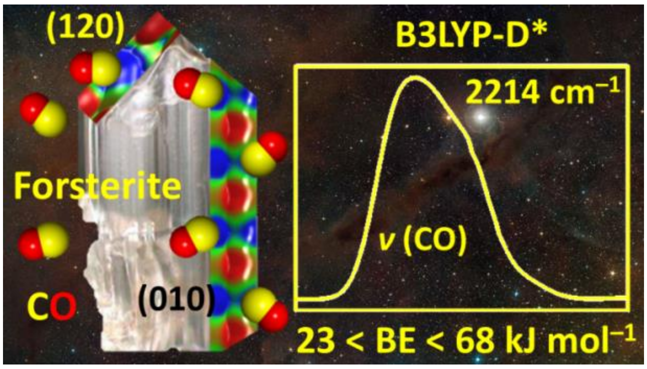
Carbon monoxide (CO) is the second most abundant gas-phase molecule (after hydrogen) of the Interstellar Medium (ISM) (1). In Molecular Clouds (MCs), regions of the ISM where star-forming processes occur, it adsorbs at the surface of grain cores – typically partially crystalline Mg/Fe silicates – or within the icy grain mantle and originate other molecular species through the catalytic power of surface active sites. More than 200 molecular species in the MCs have been observed so far by means of rotational spectroscopic, partly derived from reactions among molecules entrapped at the grains surfaces, while the presence of Mg-silicates has been inferred by IR spectroscopy (1,2,3). Laboratory studies can only partially reproduce the harsh conditions of the ISM (4), thus computational modeling can play a major role in the understanding of the chemical network charactering MCs. In this work, we performed and accurate analysis of the energetic and structural features of CO adsorption on different crystalline forsterite (Fo, Mg_2SiO_4) surfaces by means of DFT techniques. Data indicate that CO exclusively physisorbs on Mg exposed cations of Fo surfaces, with binding energies in the 23-68 kJ mol^{-1} range. Not only simple charge-dipole forces are involved, but also quadrupolar and dispersive ones are responsible of the CO adsorption. We also performed a full thermodynamic treatment of the CO adsorption at the very low temperatures and pressures typical of the MCs together with a full spectroscopic characterization of the CO stretching frequency. We proved the CO stretching frequency value to be extremely sensitive to the local nature of the surface active site of adsorption and showed results at variance with what is known about CO adsorbed on flat oxide surfaces due to the complex electrostatic and structural morphologies of the Fo surfaces. The detailed kinetic analysis of CO desorption at different low temperatures suggested that desorption times are higher than the typical evolution times of the ISM, at least until 100 K when they become comparable. Our computed data could be incorporated in the various astrochemical models of interstellar grains developed so far and thus contribute to improve the description of the complex chemical network occurring at their surfaces.



This work is supported by MIUR and SNS Stars in the Caos PRIN2015 cod. 2015F59J3R.

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Prebiotic Molecules In Interstellar Space: Aminoacetonitrile And C-Cyanomethanimine

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The attempts to detect amino acids in the interstellar medium were so far unsuccessful even for its simplest form, glycine, despite that decades-long efforts have been devoted by many observational studies. From a chemical point of view, it is therefore important to identify the possible precursors of amino acids as well as the astronomical sources where they are abundant. Aminoacetonitrile (NH_2CH_2CN) is one of the possible precursors of glycine in the production process known as Strecker reaction, whose synthetic route is shown below:

$$NH_3 + H_2C{=}O \rightarrow HN{=}CH_2 + H_2O$$
$$HN{=}CH_2 + HCN \rightarrow NH_2CH_2CN$$
$$NH_2CH_2CN + H_2O \rightarrow NH_2CH_2CONH_2$$
$$NH_2CH_2CONH_2 + H_2O \rightarrow NH_2CH_2COOH + NH_3$$

Aminoacetonitrile has been already detected toward the giant molecular cloud Sagittarius B2 (1). Its vibrational ground-state rotational spectrum has been characterized in the laboratory up to 1.3 THz (2). Aminoacetonitrile has a few low-lying (below 400 cm^{-1}) vibrational excited states (3) and rotational transitions within these states may be observed in hot cores and circumstellar shells. In this study (4), the pure rotational transitions in the 3 lowest vibrational states have been assigned and analyzed in the range 80-450 GHz. It was found very important to include Coriolis coupling between the two lowest vibrational fundamentals, while the other one resulted unperturbed. The spectral data of these vibrational excited states are essential for future observations of the molecule in relatively high kinetic temperature conditions.

Another molecule of astrochemical interest is the dimerization product of hydrogen cyanide, C-Cyanomethanimine (HN=CHCN), that is thought to play an important role as intermediate in the prebiotic formation of purines and proteins. In fact, hydrogen cyanide tends to polymerize, giving biologically important molecules such as adenine (pentamer of HCN) (5). C-Cyanomethanimine exists in two isomeric forms, *Z* and *E*. Although the (*E*)-C-cyanomethanimine is about 210 cm^{-1} less stable than the (*Z*)-C-Cyanomethanimine (6), the former has been detected through radio-astronomical observation (7) in the star-forming region (Sgr)B2(N), while no detection for the latter has been claimed so far. For its astrophysical interest and because its rotational spectrum has been investigated only below 100 GHz, the study of this molecule is being extended to higher frequency (millimeter and sub-millimeter wave regions) in order to facilitate astronomical detection. The sextic centrifugal distortion constants for both isomers of C-Cyanomethanimine were evaluated by means of highly accurate *ab initio* calculations (8). Therefore, the assignment of the rotational spectrum above 200 GHz can rely on accurate predictions.

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Should we introduce pre-equilibria into Markov models for homogeneously catalyzed copolymerization?

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Polyolefin elastomers based on ethene and propene are important players in the field of synthetic rubbers and the molecular features that control bulk properties are strictly related to the monomer distributions along the chains (1). Usually, the chemical reactivity of a propagating chain is considered to depend only on the identity of monomer units at the growing end. Two reactivity ratios, r_1 and r_2, were thus defined starting from the kinetic expressions for the uncontrolled radical mechanism in order to describe the radical copolymer micro-structure; mathematical models (e.g. Mayo-Lewis, Fineman-Ross and Kelen-Tudos) derived from such approach have also been exploited to characterize homogeneous catalyzed copolymers despite the latters could present a more complicated mechanism, involving coordination pre-equilibria (2,3).

In this study, we describe a theoretical study of E/P copolymerization by a C_2-symmetric metallocene catalyst, *rac*-Me_2C-Ind_2ZrCl_2 via a synergic DFT/kMC approach offering a robust alternative interpretation of homogeneously catalyzed copolymer process: the mechanism consists of at least two steps, equally important, namely coordination and insertion. If this holds, the application of Markovian models to copolymerization induced by homogeneous catalyst might request extreme care, as they hinge on the mechanism proposed for uncontrolled radical polymerization, which neglects coordination and pre-equilibria.

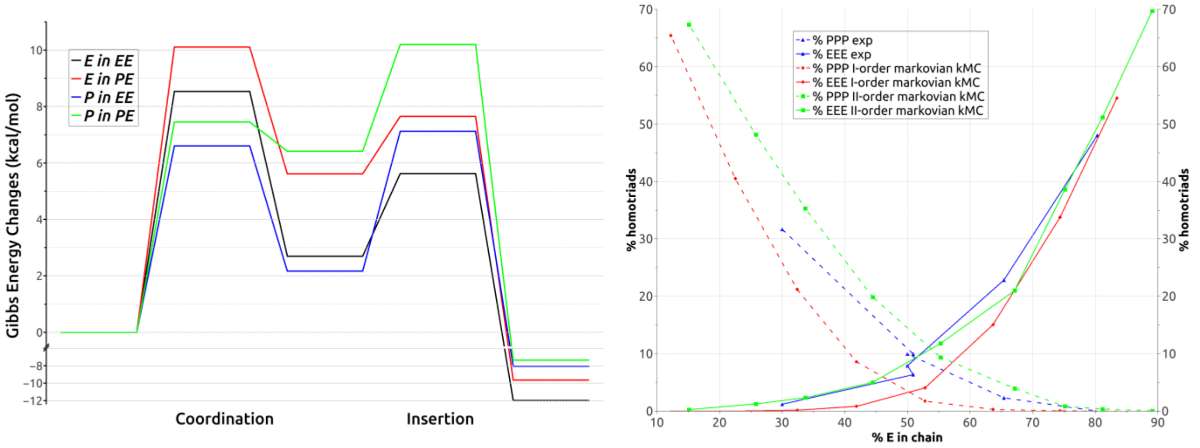

Figure 1. Left, a typical reaction pathway composed of coordination and insertion; right, comparison of experimental and kMC-simulated EEE and PPP triads.

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Intermolecular Energy Transfer in Real Time

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Essential state models (ESM) have been successfully used to describe low-energy optical properties (1,2,3) of different classes of charge-transfer (CT) chromophores, namely dipolar (D-A, where D=donor and A=acceptor of electrons), quadrupolar (D-A-D or A-D-A) and octupolar (A(-D)3 or D(-A)3) chromophores.

Here we introduce a truly dynamical and non-adiabatic model for resonant energy transfer (RET). More precisely, we consider two different dipolar chromophores, an energy donor ($\mathcal{D}$) and an energy acceptor ($\mathcal{A}$), their main resonating structures being used as electronic basis states and introducing the coupling to one effective molecular vibration per chromophore.

By means of a non-adiabatic dynamical calculation also accounting for energy dissipation, we follow in real time the complete $\mathcal{D}$-to-$\mathcal{A}$ energy transfer process (fig.1, panel a). Coherent oscillations of $\mathcal{D}^*$ as induced by an ultrashort light pulse are washed-out in the few hundred femtoseconds by fast intramolecular energy dissipation, while the $\mathcal{D}^*$-to-$\mathcal{A}$ energy transfer process takes place in the following few picoseconds (fig.1, panel b). The whole process is followed through time-dependent fluorescence spectra (fig.1, panel c).

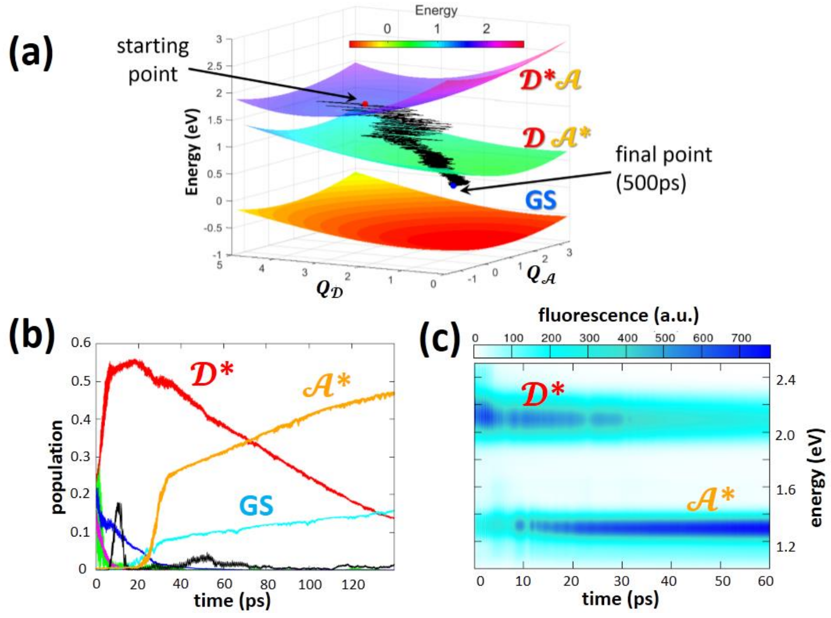

Fig. 1. Energy transfer in real time. Panel a: non-adiabatic $\mathcal{D}\mathcal{A}$ dynamics following impulsive excitation of $\mathcal{D}$; to help the eye, relevant adiabatic energy surfaces are also shown. Panel b: population time-dependence plotted for some relevant $\mathcal{D}\mathcal{A}$ states. Panel c: time-dependent fluorescence spectra for the $\mathcal{D}\mathcal{A}$ system.

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A spotlight on the complex hierarchical structure of some ionic liquid-molecular liquid binary mixtures

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Ionic Liquids (salts with melting point below 373K) are a class of compounds that are being intensively studied because of their peculiar properties (1). Being neat ions in the liquid phase, they exhibit almost zero vapour pressure, high viscosity, high conductivity, wide electrochemical window and low flammability. While it is possible to find a relatively wide literature for these neat chemicals, works on their mixtures are just about 14% of the total and only ~1% concerning structural properties. These mixtures are innovative materials that are recently reported as even more versatile and cheap than pure ILs. The structure of many neat ILs consists of two segregated micro-domains percolating each other: one is polar and the other is non-polar. This organization, often called "sponge like", is at the basis of the characteristic low-q peak in the SAXS patterns (~2-7 nm^{-1}) (2). Adding a second substance into the IL forces some rearrangement in its structure, affecting the domains, for example water enlarges the polar domain, while hexane does so in the apolar. The recent discovery (3) of a more complex structure hierarchy in some ethylammonium nitrate (EAN) + methanol mixtures, opened a new debate on the properties of ILs and the potential applications of such mixtures. A cluster-like organization was suggested then, while almost at the same time Atkin et al. (4) observed the same odd feature in other IL mixtures with longer n-alcohols. They interpreted the "Low q Excess" (LqE) as the fingerprint of self-assembled structures. Recently we have shown that the LqE can be found not only when the co-solvent is amphiphilic (as reported so far), but also when it is highly symmetrical, regardless if the compound is polar or almost apolar. We had the experimental evidence of LqE in EAN+1,4-diaminobutane and EAN+1,2- dimetoxyethane mixtures (5). These molecules cannot self-assembly, thus confuting the hypothesis from Atkin et al.. The results collected using synchrotron radiation together with MD calculations enable us to state that the LqE arise when the mixture is preparing to demix, and is undergoing strong density fluctuations. This appears to be a general behaviour, and not strictly linked to the polar/apolar nature of the co-solvent. Our models are suggesting that some supramolecular structures can be found in the samples showing the LqE. The understanding of the driving force behind this large-scale hierarchical organization could open new landscapes for ionic liquids applications.

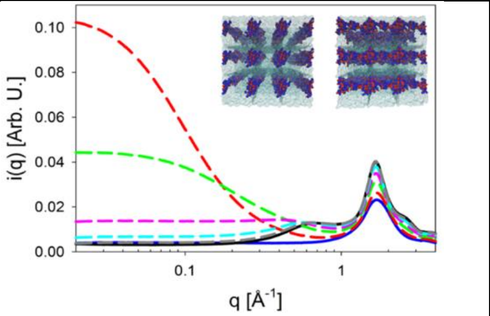

Figure 1: SAXS patterns for ethylammonium nitrate+acetonitrile mixtures. In the inset two snapshots of the simulation box for the mixture with the highest "Low q Excess".

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Fluorous mesoscopic domains in room temperature ionic liquids.

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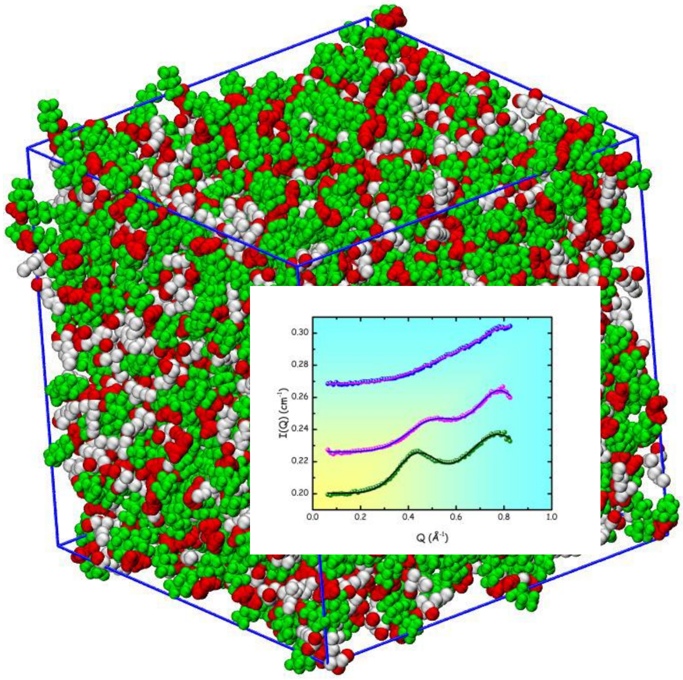
Room temperature ionic liquids (RTILs) are compounds composed solely of ionic species. Recently attention is focusing on the interesting properties of fluorinated RTILs that find application in separation, pharmacology, catalysis etc and show an appealing blending of ionic liquid specific properties and fluorous moieties induced features. Among the relevant properties highlighted in FRTILs, the possibility that fluorous moieties might segregate analogously to their alkyl counterparts in conventional RTILs has been proposed in the past [1–6]. So far however, no direct experimental evidence for such a behavior has been provided.



Simulation box of fluorinated RTILs, highlighting the different alkyl, fluorous and charged moieties. The inset data sets refer to neutron scattering data set collected as a function of the fluorous tail length. [Adapted from Ref. 7 with permission from the PCCP Owner Societies.]

Here we provide the first direct experimental evidence that RTILs bearing a long enough side fluorous chain are characterized by the occurrence of a well-defined mesoscopic organization, consistent with the segregation of the fluorous tails. [7] By exploiting the synergy between x-ray and neutron scattering coupled with state of the art Molecular Dynamics simulations, we will discuss several consistent examples where such a phenomenology has been observed.

We envisage an important role played by these self-aggregating domains of fluorous moieties in determining specific performances in the fields of separation, catalysis and related fields.

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Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure

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Turning disorder into organization is a key issue in science. In particular, supramolecular organization induced by external stimuli has opened new paths for the bottom-up fabrication of nanostructures. By using a combined strategy based on the synergy of X-ray powder diffraction experiments and modeling studies (1), we showed that high pressure - in combination with the shape and space constraints of a hydrophobic all-silica zeolite - separate an ethanol–water liquid mixture into ethanol dimer wires and water tetramer squares (Figure 1).

Separation of ethanol from water was accomplished in an all-silica ferrierite (Si-FER), by using as pressure transmitting medium a mixture of (1:3) ethanol and water in the 0.20 to 1.34 GPa pressure range. The system was studied in situ by high-pressure synchrotron X-ray powder diffraction at BM01 beamline at ESRF and refined via first principles modeling.

Upon separation, the confined supramolecular blocks alternate in a binary two-dimensional architecture that remains stable upon complete pressure release. These results support the combined use of high pressures and porous networks as a viable strategy for driving the organization of molecules or nano-objects towards complex, pre-defined patterns relevant for the realization of novel functional nanocomposites and highlight the need of appropriate modeling for an atomistic level understanding of complex phenomena.

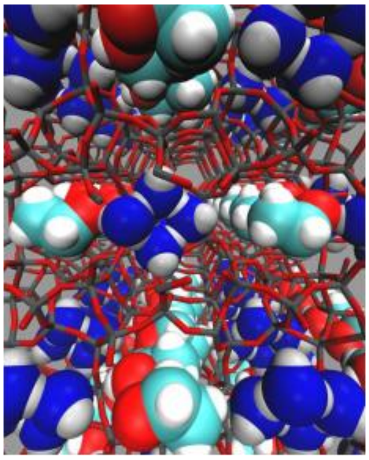

Figure 1.

(1) Arletti, R., Fois, E., Gigli, L., Vezzalini, G., Quartieri, S., Tabacchi, G. (2017) Angew. Chem. Int. Ed. 56, 2105, DOI: 10.1002/anie.201700219

Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces

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The development and characterization of a new family of water based gel-like systems containing hydroxypropyl guar gum (HPG) with borax as crosslinker are presented in this contribution. In the formulation glycerol is introduced as plasticizer, and its role is broadly investigated. The effect of the components on the structure, on the viscoelastic behavior of the system and on the activation energy related to the relaxation process has been investigated by means of rheology, Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS) (1,2). Results indicated that the mechanical properties of the systems can be tuned by varying the amount of each component; ^{11}B-NMR and ^{1}H-NMR measurements highlighted the role of glycerol in the crosslinking mechanism, with the formation of a glycerol-borate complex. The characterization approach is used to identify the best formulation, in the view of a future application in the field of cultural heritage conservation, in particular for the cleaning of surfaces of historical and artistic interest (3). The main goal is to obtain a system adaptable to the roughness typical of surfaces of many artifacts. The best formulation was used for preliminary cleaning tests on a *stucco* artifact deriving from the decorations of *La Fenice* theatre, in Venice. The tests suggest a promising efficacy in selective cleaning of the surface and make these materials particularly interesting in the field of restoration.

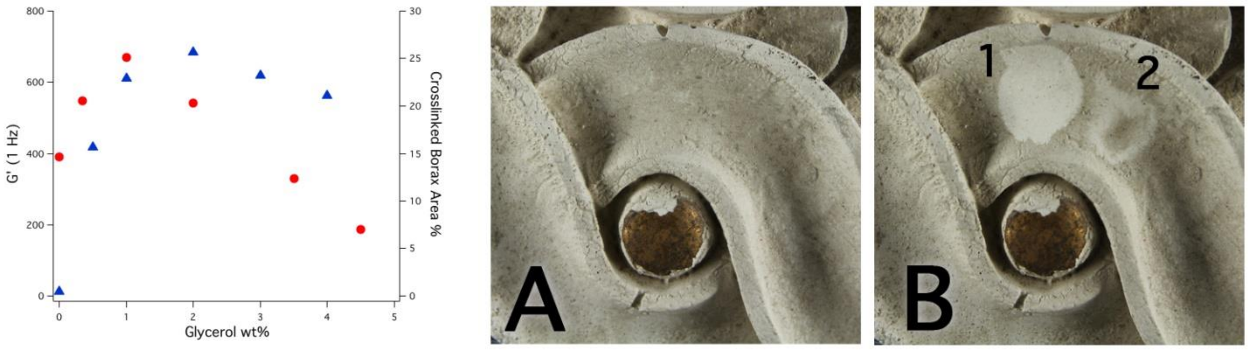

Figure 2: On the left, Storage modulus values at Frequency=1Hz (■) and Crosslinked Borate Area obtained from NMR measurements (▲) are plotted against glycerol concentration. Pictures on the right show the *stucco* surface before (A) and after (B) the cleaning, with the comparison between the the HPG based system (1) and a wet cotton swab (2).

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Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks

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Chemical poly ethyl methacrylate (PEMA) organogels loaded with Diethyl Carbonate (DEC) were synthesized by means of radical polymerization (1, 2). These systems are specifically designed for the removal of degraded Pressure Sensitive Tapes (PSTs) from paper artworks, a very common issue in the field of manuscripts and drawings restoration. DEC, an organic green solvent, shows interesting swelling properties towards PSTs components; besides it is inert to most common inks and dyes, unlike other commonly used cleaning systems such as polar solvents and microemulsions (3).

Several organogels were obtained by changing reaction parameters; on the basis of macroscopic evaluations (e.g. mechanical properties, homogeneity), some systems were chosen for a deep physico-chemical characterization performed by means of different techniques. Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and gravimetric analysis were used to assess solvent content and uptake/release behaviour of gels; rheological analysis permitted the evaluation of their viscoelastic properties; Fourier Transform Infrared Spectroscopy (FT-IR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) allowed to investigate the presence of unwanted residues in the exchange solvents and the effectiveness in the removal of PSTs. The penetration of DEC through the backing layer of PSTs and the swelling of the adhesive was investigated by means of Laser Scanning Confocal Microscopy (LSCM).

Cleaning tests on mock-up samples and real artworks were also successfully performed.

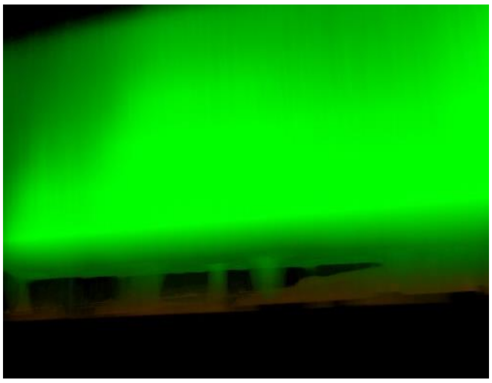

Fig. 1 – Laser Confocal image of a PEMA-DEC gel onto a PST sample: penetration of DEC (in green) through the backing up to the adhesive layer (in red)

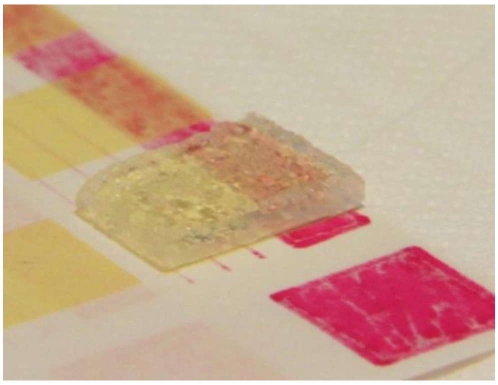

Fig. 2 – Application of a PEMA-DEC organogel for the removal of a Masking Tape from a mock-up sample

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Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network

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Nanosystems and confinement tools for the controlled release of a cleaning agent, e.g., hydrogels and microemulsions, have been used for several years for the treatment of delicate surfaces in art restoration interventions. However, notwithstanding the unprecedented achievements from an applicative point of view, a fundamental comprehension of their interaction mechanism is still lacking. In this study PVA hydrogels, obtained via freeze-thaw processes, are prepared as scaffolds for water-based nanostructured fluids for application in the cleaning of artworks: rheological, thermal, microscopic and scattering techniques showed that, depending on the number of freeze-thaw cycles, the hydrogels exhibit different physicochemical and viscoelastic properties, making them suitable for application in a broad range of cleaning issues. The gels have been loaded with an oil-in-water microemulsion and the diffusion of the microemulsion droplets inside the polymeric network has been investigated through Fluorescence Correlation Spectroscopy (FCS), demonstrating that the microemulsion is permanently kept inside the matrix and can freely diffuse in the network. In addition, we show that, when the gel-microemulsion system is put in contact with a layer of hydrophobic grime, a dynamic interaction between the microemulsion droplets and the underlying layer is established, leading to the solubilization of the hydrophobic molecules inside the droplets in the gel matrix. Thus, for the first time, through FCS, insights about the removal mechanism of hydrophobic grime upon interaction with cleaning agent embedded in the polymeric matrix, are obtained. Some examples of significant case studies treated with these innovative materials will be presented.

Nanocomposites for the consolidation and deacidification of cellulose-based artifacts

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A restoration method designed for the conservation of degraded fibrous-based artifacts should addressed the two main problems concerning these materials. Firstly, a mechanical reinforcement of artifacts is usually needed to ensure that the original material keeps its integrity. Moreover, pH buffering is required to prevent acidic degradation that is inherent to natural materials. (1)

It has been recently shown that these two issues are related. For instance, it takes less than 100 years for acidic compounds to induce a significant loss of mechanical properties in canvases based on natural materials. (2) The same degradation effect of acidic compounds is found in paper-based artworks, drawings and documents. In this regard, several deacidification methods have been proposed and proven efficient in hampering the degradation of cellulose. (3,4,5)

Research efforts have been recently devoted to the development of a nanocomposite material for the consolidation and concomitant pH adjustment of cellulosic works of art and artifacts that is one of the goal within the EU Project NANORESTART.

The use of nanocellulose, in combination with nanoparticles and cellulose derivatives, could ensure the consolidation of fiber-based materials using almost entirely natural materials. The choice of these materials is due to the high compatibility of the proposed treatments with the original fibrous support, which is essential from the conservation point of view.

Considering the high variability of cellulose-based artifacts, several different approaches were followed in order to provide conservators with a wide palette of tools that can be used on different works of art that are in need of both consolidation and deacidification treatments.

Nanocomposite materials were analyzed in order to gain more information about their structure and characteristics. Mechanical tests on not aged and aged reference samples were used to assess the consolidation efficacy of the proposed consolidation treatments before testing on real case studies.

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Biophysical studies of membrane perturbation induced by the antimicrobial peptide GKY20

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The resistance to conventional antibiotics in pathogen organisms (e.g. bacteria) has become a central problem in the international community. Many efforts have been made on the development of new anti-infective agents and among these the most promising are antimicrobial peptides (AMPs). (1,2) AMPs are small, cationic membrane-active peptides that exhibit broad-spectrum activity against bacteria, fungi and even viruses. Despite of their similar physical properties, AMPs share a limited sequence homology and can assume a wide range of secondary structures (e.g. α-helices and β-sheets) upon interaction with membranes whereas they show essentially a disordered structure in solution (1,3,4).

The mechanism by which AMPs interact with membranes strongly depend on the lipid composition of the membrane and on the molecular properties of the peptide (1). Great efforts have been made to elucidate the mechanism of action of AMPs and different models have been suggested (1). However, a peptide adopting solely one of those mechanisms is not common. Further, the molecular mechanism by which the peptide modify the biophysical properties of the membrane is not fully understood.

In this study, we report the physicochemical characterization of the interaction of the antimicrobial peptide GKY20 with model bio-membranes. The recombinant peptide GKY20, modelled on the Gly^{271} to Ile^{290} sequence of the human thrombin, was obtained as described in (5). Liposomes composed by POPC and POPC/POPG lipids were used as model of the eukaryotic plasma membrane and bacterial membrane, respectively. Far-UV circular dichroism (CD) experiments showed that the GKY20 peptide folds from a random-coil structure in solution to a more ordered structure in the presence of lipid bilayers. Steady-state fluorescence measurements revealed that GKY20 binds with higher affinity to the POPC/POPG than POPC liposomes. Further, differential scanning calorimetry (DSC) measurements revealed that GKY20 is able to induce a greater lipid perturbation in the bacterial-mimetic membrane.

The obtained results are consistent with the high antimicrobial activity and low cytotoxicity (6) of GKY20 making this antimicrobial peptide a serious candidate as antibacterial drug for biomedical applications.

Abbrevations:
POPC: *1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine*
POPG: *1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-1'-rac-glycerol*

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The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite

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Human Serum Albumin (HSA), the most abundant protein of body fluids, has a “modular” three-domain structure potentially responding to stress by means of changes of conformation (1). Besides acting as the main carrier protein of the circulation, HSA is also an obvious target of extracellular reactive oxidant species due to its high abundance in plasma. It is for this reason considered the main anti-oxidant defense in blood (2).

This study was aimed at correlating oxidant-induced chemical and structural effects on HSA. The experiments benefited from the use of a multi-technique instrumental platform which combined the simultaneous collection of SAXS, UV-vis absorbance spectra and fluorescence emission on the same sample volume (3).

Despite the chemical modification, the native shape was preserved up to oxidant/HSA molar ratio < 80, above which a structural transition occurred in the critical oxidant/HSA molar ratio range between 80-120. This conformational variation involved the drifting of one of the end-domains from the rest of the protein and corresponded to the loss of one third of the alpha-helix and a net increase of the protein negative charge. The high reproducibility and well-defined nature of this transition suggested that it represents a structural response characteristic of this multi-domain protein that was never observed before (4).

The ability to tolerate high levels of chemical modification in a folded or only partially unfolded state, as well as the stability to aggregation, provides albumin with optimal features as a biological buffer for the local formation of oxidants.

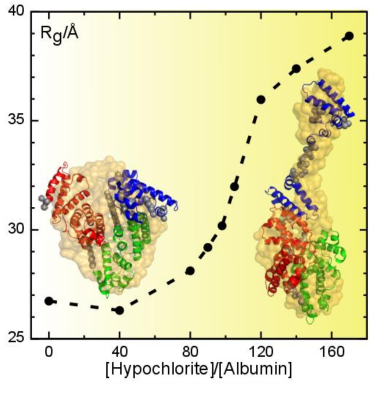

Figure: The variation of the gyration radius of HSA at increasing hypochlorite doses. The low-resolution models obtained by fitting the SAXS experimental profiles of the protein monomer in the native (left) and highly oxidized (right) conditions are also shown.

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Electrochemical preparation of nanostructured CeO_2-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol

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Methanol is a valuable energy feedstock for the future beyond oil and gas, due to its easy storage as a liquid at room temperature, and an excellent fuel for catalytic combustion, a process that is stable in a wide methanol/air operating range, and produces ultra-low NO_x, CO and VOC emissions. Lightweight catalytic burners are often realized using metal foams, due to their outstanding properties in terms of heat and mass transfer coupled with low pressure-drops and thermal resistance. Among the foam materials, Fe-Cr-Al alloy (Fecralloy) have outstanding resistance to high temperatures.

The procedures for depositing firmly anchored, homogeneous catalytic layers onto the foam substrates are often cumbersome and involve many steps. Therefore, there is interest for innovative preparation methods which take advantage of the metallic nature of the foam support, such as electrodeposition and spontaneous deposition through galvanic displacement. Both approaches are capable to form well-dispersed, homogeneously distributed noble metal nano-particles strongly adhering to the substrate (1, 2).

As a part of an ongoing research project, our groups have recently prepared Pt-based structured catalysts for the low-temperature combustion of methanol by electrochemical methods (3). These catalysts consisted of Pt nanoparticles, deposited onto Fecralloy foam supports by pulsed electrodeposition from H_2PtCl_6 aqueous solution, and CeO_2 thin films electrodeposited from a nitrate baths. Reduction of nitrates induced a local pH increase at the foam/electrolyte interface and caused the precipitation of mixtures of $Ce(OH)_3$ and CeO_2 , which were converted to CeO_2 by heating in air. The Pt loading in the catalysts was measured by ICP-MS, while the noble metal surface area was determined by cyclic voltammetry, through the H desorption charge. Although the presence of a CeO_2 film decreased the Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion, without affecting the activation energy of the process. The enhanced catalytic performance of the CeO_2-Pt-Feclalloy catalysts as compared to Pt-Fecralloy was ascribed to the formation of additional active sites along the interface of CeO_2-coated Pt nanoparticles.

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Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction

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The physical amount of platinum existing on the Earth is barely enough to cover the world demand in the next forty years for fuel cell vehicles. Furthermore, the high cost and the low durability of platinum-based catalysts are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR (1,2) In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyze the O_2 reduction to H_2O at overpotentials comparable to that of the most active Pt catalyst (3).

In this paper, nitrogen doped mesoporous carbons containing Fe (Fe@N-MC) were prepared from agarose gel embedding an iron ($FeCl_2$, $FeSO_4$, etc.) and nitrogen (1,10-phenanthroline) precursors. The formation of a hydrogel embedding an iron metalorganic complex, assures an optimal Fe dispersion before pyrolysis. Several types of porogen agents (silica, carbamate, carbonate, etc.) were inserted to induce a hierarchy pore structure in the final pyrolyzed material. After the freeze-drying of the gel, aimed at removing the gelling solvent, the material is subjected to a first thermal treatment at 500 °C, obtaining a crude product, which is further activated at high temperature 900 °C under hydrogen flow. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe−Nx bond at 708.6 eV (Fig. 1a). Beside Fe-Nx not visible from TEM analysis, iron is present as core shell NPs with iron oxide core and carbon shell. The catalytic performances of catalyst ink prepared from Fe@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M $HClO_4$ attesting that O_2 is reduced following an almost $4e^-$ pathway at very positive potentials (0.8 V vs RHE) (Fig. 1b).

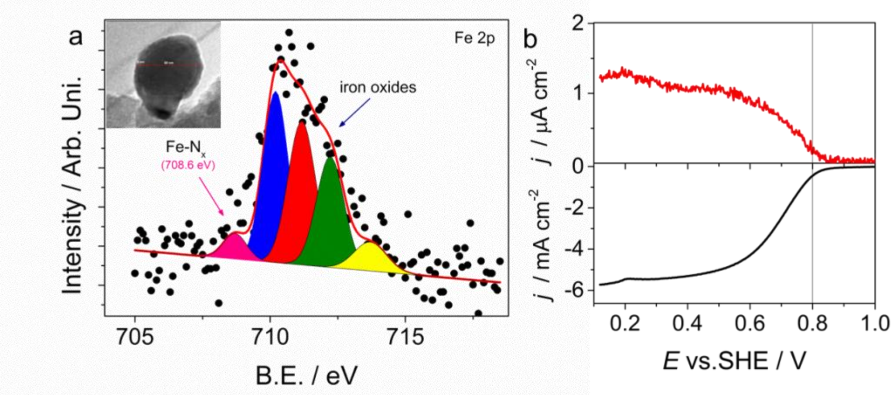

Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals, and Fe NP TEM image. (b) Example of RRDE measurement on Fe@N-MC in 0.1 M $HClO_4$ at 1600 rpm and $\upsilon = 5$ mV/s.

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Lignocellulosic Materials for Electrochemical Energy Storage and Conversion

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In the last 20 years, the Li-ion battery market has rapidly grown thanks to the extensive diffusion of mobile electronics devices. In order to lower the cost and reduce the environmental impact of batteries, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders/separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components (both electrodes and electrolyte). Natural nanoscale-microfibrillated cellulose (NMFC) fibers are readily available; they show stiffness, impressive mechanical robustness, low weight and, furthermore, their preparation process is easy and does not involve chemical reactions.

Here we review the use of paper-making technique for manufacturing:

- Bio-inspired all-paper Li-ion polymer cells, constituted by NMFC-binded paper-electrodes, and NMFC reinforced polymer electrolytes (1). The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process.
- Cellulosic membranes as separators/electrolytes for post-lithium technologies, such as Na-ion and Li-S (2,3), thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future.
- Paper-based flexible electrodes and electrolytes for third generation solar cells (4), useful to lower oil-derived components and typical temperatures used to electrodes processing.

This materials platform is promising not only for the sustainable manufacture of energy devices components, but also for their processability at the end of life. For example, the all-paper lithium cell can be easily re-dispersed in water by simple mechanical stirring, as well as common paper handsheets and battery materials can be recovered using well-known water-based recycling process.

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Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes

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A critical roadblock toward the development of post-lithium-ion batteries is the lack of electrolytes that are safe and electrochemically stable whilst demonstrating good compatibility with the electrode materials (1).

It was recently shown that haloaluminate ionic liquids (ILs) can provide a viable alternative to conventional electrolytes due to their low volatility, negligible flammability and good electrochemical performance (2,3,4).

Following this, an overview on recent advancements on electrolytes for secondary Magnesium batteries is presented with particular reference to imidazolium and pyrrolidinium -based ionic liquids. Insights on the interplay between structure and conductivity of BF_4^-, $Cl^-/AlCl_3$ and I^-/AlI_3 -based systems are given, thus providing an in-depth understanding of the relation between Mg-ion speciation, long-range charge transfer mechanism and electrochemical performance of this very promising class of materials.

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Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting

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Electrochemical in-situ and operando X-ray absorption spectroscopy (XAS) represents one of the most powerful available tools to study the fine structure and the behavior of electrode materials. This serves to better elucidate important reaction mechanisms and to better define structure/activity relations.

This becomes particularly crucial in electrocatalysis, for studying the oxidation state transitions and during the catalytic cycle, in photoelectrochemistry, for highlighting the local structure and the kinetics of charge recombination/transfer at surface defects and/or to study charge transfer among different layers in composite photoelectrodes.

In our recent work, we developed new methods and techniques to carry out operando XAS on electrodes and photoelectrodes with the aim of highlighting: (i) the kinetics of charge transfer across interfaces (1,2), (ii) the role of the (photo)electrode material during the reaction process (3), (iii) the role of the overlayer in composite photoelectrodes (4).

In particular, we developed FEXRAV (5), that consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential and allows to quickly map the variation of the oxidation states of the element under consideration in a desired potential window.

More recently, we carried out the first experiment on pump&probe operando XAS on a photoelectrode (6). In addition, we extended the use of energy dispersive XAS to Ir-based electrocatalysts (7) and improved the use of operando XAS for the steady-state study of photoelectrodes by recording parallel dark/light spectra adopting an innovative procedure (4).

This presentation is devoted to review some of our most significant studies, with a particular emphasis on both photoanode, (α-Fe_2O_3 /IrO_x, α-Fe_2O_3/NiO(OH)) and photocathode (Cu_xO) systems.

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Hydrogen defects in Diamond. A quantum mechanical approach.

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The investigation of native and radiation-induced point-defects in diamond (as well as in other semiconductors) has attracted large theoretical and experimental interest. Diamond is a wide-bandgap material characterized by well-known extreme physical properties (high Young's modulus and thermal conductivity, broad transparency range, high carriers mobility, etc.) with attractive applications in different fields, ranging from microelectromechanical systems to heatsinks, laser windows, particle detectors, etc (1). Hydrogen, with nitrogen, is the most important impurity in diamond. It is included during the growth of natural diamond as well as in chemical vapour deposition (CVD) processes. It is certainly present at the surfaces; a non minor fraction, however, is also thought to be incorporated in the bulk. H atoms are supposed to be involved in several defects combining vacancies and nitrogen aggregates(2). It is identified through its infrared (IR) active modes (stretching and bending), although probably not all hydrogen atoms present in diamond are IR active. The sharp vibrational peaks at 3107 and 1405 cm^{-1} that appear in most natural diamonds (3) have been attributed in the past to various H containing defects. Experimental evidence suggest that H is strongly bonded to a carbon atom, with weak perturbations due to nitrogen atoms (3).

Various H containing defects, in particular VN$_3$H (a vacancy surrounded by three N and one C atom, the latter being saturated with H), have been considered by using a quantum mechanical approach, a local gaussian-type basis set, hybrid functionals, the supercell scheme and the CRYSTAL code (4). The same scheme has recently been used for describing the vacancy (5) and interstitial (6). Various properties (structural, electronic vibrational) have been used for a complete identification of the defect. The Infrared spectra (wavenumbers and intensities, evaluated analytically through the Coupled Perturbed Hartree-Fock method) are generated and compared with experiments.

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Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations.

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Ionic liquids (ILs) are salts made by bulky, sterically mismatched molecular ions that possess a low melting point because the electrostatic interactions are weakened by charge delocalization and lattice formation frustrated by geometric effects. In contrast to traditional organic solvents, ILs possess negligible flammability and volatility and represent a new class of "green" solvents that are inherently safer than conventional solvents. A Protic Ionic Liquid (PIL) is formed through an acid base reaction. When the difference of pKa between the acid and the conjugate acid of the base is large (>10 pKa units) the ensuing liquid is completely ionized. In this case, the acidic proton is transferred quantitatively from the acid to the base during the synthesis reaction and turns out to be strongly bound to the latter. Subsequent proton transfer is therefore not possible. Conduction in these liquids is therefore due to ion drift (Walden mechanism) and inversely proportional to the liquid viscosity. In order to have a larger conductivity one has to find a way to promote the formation of different charge carriers. One possibility is to have proton transfer from one molecular ion to another. Compounds where amino acids in their deprotonated (anionic) form are combined with inorganic cations such as [Ch][Asp] and [Ch][Cys] might have these features. The former has a weak acid terminal, while the latter has a weak basic proton attached to the sulphur atom. We will show evidences of a non-ordinary behavior of these two materials that have been obtained by carefully validated ab-initio and classical molecular dynamics simulations [1].

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Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer

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Spectroscopic techniques provide a wealth of qualitative and quantitative information on the chemical and physical-chemical properties of molecular systems, in a variety of environments. However, the interpretation of experimental data is often a difficult task mainly because the observed spectroscopic properties depend on the subtle interplay of different effects, whose specific impact on the overall behavior is difficult to address. From this point of view, theoretical approaches are invaluable tools for guiding and complementing experiment as well as supporting the interpretation of spectra. For this reason, measurements are increasingly supported by theoretical studies, and computational spectroscopic techniques have become essential tools for understanding spectra in terms of basic physical-chemical process. The widespread use of computational spectroscopy has prompted the development of a virtual multifrequency spectrometer (VMS), which gives access to the latest developments in the field of computational spectroscopy also to non-specialists (1-4). In addition to the computational module (VMS-Comp), which provides the support for a wide range of spectroscopic techniques, it features VMS-Draw. This is a multiplatform graphical user interface (GUI), which offers to the user a powerful integrated environment for processing the outcomes of quantum-chemical calculations and visualizing the relevant information in an intuitive way. In addition, VMS-Draw includes a panel of advanced tools for the comparison of theoretical and experimental spectra, thus assisting their interpretation. In this contribution, we present VMS with particular attention to its newborn rotational spectroscopy module, VMS-Rot. VMS-Rot has been specifically designed for guiding the assignment and interpretation of rotational spectra: from the assignment of the observed transitions to a set of quantum numbers, as well as their fitting with a given model Hamiltonian, to the prediction and simulation of the whole spectrum. Given the general philosophy of VMS and the leading role played by quantum-chemical calculations in modern rotational spectroscopy, unlike other software supporting the analysis of MW spectra, VMS-Rot is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations. VMS-Rot is composed of four closely related modules, namely (i) the computational engine that allows spectroscopic parameters to be computed from first principles; (ii) the fitting-prediction engine that allows the refinement of the spectroscopic parameters, based on the assigned transitions, and the calculation of the simulated spectrum. (iii) the GUI that allows the comparison between theoretical and experimental spectra, aided by a number of advanced features for spectra manipulation and (iv) the assignment tool that takes care of the assignment of the rotational spectrum recorded experimentally by comparison with the simulated one. An overview of the range of applicability of VMS-Rot is given in order to demonstrate how this module of VMS represents a one-pot solution for the analysis of rotational spectra based on the interpretation of experimental measurements supported by quantum chemical simulations.

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Calorimetry and Thermoanalytical Techniques in the Study of Proteins

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Thermal analysis and calorimetry, particularly when combined with other analytical and spectroscopic techniques, offer powerful methods for studying biological macromolecules. Here, we present and discuss the application of calorimetry and thermogravimetric analysis to the study of the conformational behavior of proteins in three cases belonging to very different fields, ranging from the use as binders in tempera paintings, to medical or pharmaceutical applications. The first issue concerns with proteinaceous materials used as paint media in order to disperse and apply pigments. Over the centuries, animal glue, egg and milk or casein have been the most common proteinaceous binders used in tempera technique. The characterization of these paints is complex because of the sample size, the high inorganic content, the degradation phenomena undergone with time, and the simultaneous presence of other organic materials. We used a combined approach (Thermogravimetric Analysis, TGA, Differential Scanning Calorimetry, DSC, Fourier Transform Infrared Spectroscopy, FTIR) to investigate the interaction occurring between selected pigments and ovalbumin, casein, and rabbit glue as well as their changes with ageing. This allowed us to characterize the molecular modifications undergone by proteins as an effect of light ageing, and depending on the pigment, in terms of amino acid side chain oxidations, cross linking/aggregation, hydrolysis, and the formation of stable complexes. We highlighted that in most cases the inorganic pigments interact with proteins by decreasing their thermal stability and their intermolecular β-sheet content, and that ageing induces aggregation. The second issue concerns with some biocompatible nanomaterials suitable to be used in biotechnological and medical applications. We focused our attention on alloysite nanotubes (HNTs) which are considered very promising as nanocarriers, because of their low cost, high availability, biocompatibility, atoxicity, anti-inflammatory properties, and capacity to maintain the biological activity of immobilized enzymes. HNTs can be loaded with a wide range of molecules, from antioxidants to antibiotics, anticancer, and anti-inflammatory drugs and can be used for drug delivery, as tablets and capsule fillers. Therefore, to study their interaction with proteins is important because of the general concern regarding the safety of nanoparticles and the modifications that loaded biological material may undergo with alteration of their biological functions. We studied the interaction between HNTs and some proteins (bovine serum albumin, α-lactalbumin and β–lactoglobulin) loaded into HTNs, by using TGA and FTIR. These techniques enable us to assess the protein conformation and thermal stability, respectively, and to estimate the amount of protein loaded into the HNTs.

Finally, as the third issue, we show here some preliminary results on the use of protein-polymer conjugates in order to improve the properties of therapeutic proteins. It is well known that proteins and peptides exhibit great potentialities as therapeutic agents; however, they also show severe drawbacks (low solubility in water, tendency to agglomerate during storage in solution, short shelf-life, rapid kidney clearance, destruction by proteolytic enzymes, propensity to generate neutralizing antibodies). One of the most promising modification for overcoming these drawbacks is the covalent attachment of synthetic polymers (the most common being PEG) to the protein, to form protein-polymer conjugates with the aim of improving both the stability and the pharmacokinetics properties of the drug. In particular, we present some preliminary results obtained by TGA and DSC measurements on Myoglobin-PEG and myoglobin-polyphosphoesters conjugates. In fact, polyphosphoesters (PPEs) are one of the most promising new classes of polymers in biomedicine.

Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation

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Mature microRNAs (miRNAs) are a class of evolutionally conserved, single-stranded, small (approximately 19−23 nucleotides), endogenously expressed, and non-protein-coding RNAs that act as post-transcriptional regulators of gene expression in a broad range of animals, plants, and viruses.(1,2) The biogenesis of miRNAs is a multiple step process, which complete with the incorporation of the mature miRNA into RNA-induced silencing complex.(3) The RISC complex functions by perfectly or imperfectly matching with its complementary target mRNA, and induces target mRNA degradation or translational inhibition. Thus, alterative expression of miRNAs has been associated with a number of diseases, genetic disorders and tumors progression.(3)

We think that the knowledge of the miRNA structure may give a new insight into miRNA-dependent gene regulation mechanism and be a step forward in the understanding their function and involvement in cancerogenesis. With this aim we characterized the conformation and structures adopted by several endogenous miRNA in physiological conditions. Preliminary data obtained by CD melting experiments, using synthetic miRNA,(4) highlighted the important role played by the structures adopted by miRNA. Indeed the sequences showed a sigmoidal CD melting curves induced a significant inhibition of the luciferase activity for two of the most prominent genes associated to lung cancer, c-MET and Epidermal Growth Factor Receptor (EGFR).

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Identification and characterization of DNA G-quadruplex interacting proteins

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Guanine-rich DNA sequences can form non-canonical structures known as G-quadruplexes (G4s). These peculiar structural arrangements emerged as biologically significant due to compelling evidence that they participate in several biological processes. Experimental evidences imply that G4 DNA structures are, for example, involved in tumorigenic processes, probably with regulatory functions, and that various proteins are involved in the recognition of these structures and modulate their effect on such processes.

The analysis of the G4–protein interaction network can be considered a crucial point to clarify the elusive biological mechanisms in which such relevant DNA structures could be implicated. Some proteins are able to recognize G4 structures and some are also able to unfold them. The discovery of these proteins raises interesting questions regarding the dynamic nature and function of such structures within the genome, especially at telomere, a region of repetitive G-rich sequences at each end of chromosomes. In this frame, we decided to search for proteins able to recognize G4-forming truncations of human telomeric DNA sequence (1). In particular, we employed a chemoproteomic-driven approach, where the molecule of interest is used as a bait to fish out its interactors from nuclear extracts. In particular, we have used different G4 conformations, namely the parallel and the anti-parallel folds. Very interestingly, novel G4-interacting partners were identified, thus suggesting a possible, and so far unknown, role of these proteins. In this communication, the latest results will be presented, including a preliminary structural study of the interaction between the HMGB1 protein and the parallel telomeric G4 structure.

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FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach

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Metal artifacts are among the most common materials in the Cultural Heritage field: alloys have been used in several fields of everyday life and their analysis can prove useful information about the technology of the ancient populations. In particular, coins are important for studying provenance, dating, minting and corrosion processes as well as provenance and stratigraphy of the archaeological sites (1,2).

In this work a set of Roman silver coins, dated back to the Antonini's period, has been analyzed using FIB-FESEM-EDX aiming to establish the used technique for the silvering and discriminating different mints. Recently, this approach was used as a complementary technique for the characterization of bronze coins (3) but this is the first application on Roman silver coins. The aim of this work is to investigate the microstructure and the composition of the alloy with a micro-invasive approach. Commonly to investigate the composition of the metal core are used invasive and destructive techniques, therefore the developing of methods with minimal damage on metal is of a great interest.

The study of Antonini's coins is also important as in that historical period Roman Empire underwent to a severe debasement which influenced coinage, so the surface silvering it is still an open question. Diocletian in the 294 A.D. introduced a complex alloy (Cu-Sn-Pb-Ag) with an Ag-rich surface patina of 2 µm. Some coins of the set show a very fine silvered surface with a core composition entirely made of Cu, whereas others have the composition made of Sn-Cu-Pb with a very low concentration of Ag. This technique has been joined with surface analysis (Raman spectroscopy, SEM mapping, voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS)) for a deeper knowledge of the samples. The results showed the leaching of the Sn and Pb as well as of the Cu that formed several common products on the surface of the coins, *i.e*, Cu_2O, CuO, PbO, SnO. The presence of AgCl has been detected in several coins.

In conclusion, FIB-FESEM-EDX analysis provides information about the composition, structure and thickness of the metal patina as well as the composition and microstructure of the metallic core which in turn reflects the technology of minting. As a result, FIB-FESEM-EDX features yield information for the diagnostic, authentication, technologies and historical context in which the coins were fabricated. Such multi-analytical data allow us the possibility of screening the coins minting, obtaining significant differences between those minted in Roma and those minted in the Gallia.

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I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra

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Konrad Witz, tedesco di origine, ma attivo soprattutto in Svizzera fra il 1431 e il 1445 circa, è, per dirla con le parole dello storico dell'arte Jonathan Jones, "un gigante della pittura medievale che aspetta solo di essere scoperto". Le opere superstiti di questo artista sono davvero poche; fra queste sicuramente le più importanti sono le due tavole dipinte nel 1444 su entrambi i lati per l'altare maggiore della Cattedrale di Ginevra ed ora conservate nel Musée d'art et d'histoire de Genève (1). Il presente studio illustra i risultati della campagna diagnostica condotta, prima dell'intervento di restauro, sui materiali costitutivi, la tecnica esecutiva e lo stato di conservazione di queste opere. Le indagini scientifiche sono state condotte dapprima mediante tecniche strumentali non invasive, successivamente su microcampioni prelevati in modo mirato dopo l'acquisizione dei dati delle analisi preliminari.

Gli obiettivi delle indagini sono così sintetizzati:

- osservazione in situ della superficie delle opere mediante l'impiego di microscopia a bassi ingrandimenti, in luce visibile e UV, per osservare lo stato di conservazione della pellicola pittorica originale e differenziare le parti originali dalle eventuali ridipinture;
- analisi XRF in più punti delle superfici policrome per avere dati preliminari sulla composizione degli elementi chimici e orientare la scelta dei prelievi di campione;
- esame chimico-stratigrafico di campioni di materiale pittorico per documentare la composizione delle stratificazioni dei materiali costitutivi, dalla preparazione fino alle vernici superficiali, e avere così informazioni circa la tecnica esecutiva;
- identificazione delle cariche minerali negli strati preparatori e dei pigmenti nelle stesure pittoriche;
- riconoscimento, mediante test microchimici ed istochimici, delle classi di appartenenza dei leganti organici nelle varie stratificazioni;
- identificazione dei leganti pittorici mediante gascromatografia abbinata alla spettrometria di massa (GC-MS).

Una prima ricognizione delle superfici pittoriche delle quattro opere è stata effettuata mediante l'impiego di uno stereo-microscopio operativo con sorgenti di luce visibile e UV. Successivamente, sono state analizzate le superfici pittoriche mediante uno spettrofotometro portatile a raggi X (XRF). Sui dipinti sono state, inoltre, eseguite indagini radiografiche e riflettografiche all'IR per studiarne lo stato di conservazione e esaminare i dettagliati disegni preparatori. Una volta acquisite in situ tutte queste informazioni sono stati effettuati sedici microprelievi di materiale pittorico in zone ritenute maggiormente significative in relazione alle domande di conoscenza.

I test microanalitici impiegati sono stati finalizzati alla ricerca di sostanze proteiche, composti saponificabili e polisaccaridi. Le analisi rivolte all'identificazione dei leganti organici sono state condotte mediante microspettroscopia infrarossa a trasformate di Fourier e gascromatografia accoppiata alla spettrometria di massa (GC/MS).

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Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects

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During the last years, there has been a growing interest in the identification of proteinaceous material of cultural heritage and archaeological objects. Our group recently developed a new method for the non-invasive analysis of proteins material from precious and ancient artworks. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics (1).

In this research, we will present the application of this method to several historical and archaeological samples. Moreover, we will discuss the analytical performances for the identification and quantification of proteins in complex matrixes.

In particular, we will present the developed protocol and the results obtained from the analysis of several artworks: a polychrome wooden altarpiece from the Maestro of Oropa, a polychrome sandstone capital, a rare polychrome alabaster, several wood medieval and renaissance panels (Pietro Gallo from Alba, Defendente Ferrari, Martino Spanzotti, Jean Bapteur, Gerolamo Giovenone) and a detached fresco from Antoine de Lonhy.

Moreover, through the use of this method we were able to identify the animal origin of an old precious manuscript from Domenico della Rovere (XIV century) as well as the binders from a rare sample of painted leather casket from Parisian manufactory (beginning of XIV century).

The analysis of the bottom of several greek vessels (Pyxis, Krater, Kylix cup and Kantharos) revealed the presence of animal origin proteins.

In conclusion, this study will report the first use of this non-invasive method for the characterization of proteins from ancient objects without the need to transport or sampling the artifacts.

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Comunicazioni Poster

Single Crystal to Single Crystal Transformations In A Cyclic Hexapeptoid

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Cyclic alpha-peptoids are peptido-mimetic compounds which represent interesting building blocks for the design and synthesis of artificial systems at the frontier between materials science and biology (1). Peptoids differ from peptides in the side chains, which are shifted by one position along the peptide backbone to the nitrogen atom to give N-substituted oligoglycine. The lack of the amide proton prevents the formation of NH•••OC hydrogen bonds and weaker interactions, as CH•••OC hydrogen bonds and CH-pi interactions, play a key role. Inter-annular CH•••OC hydrogen bonds can provide face to face or side by side arrangement of macrocycles mimicking beta-sheet secondary structure in proteins (2). In particular, the side chains have a key role in the solid state assembly of peptoid macrocycles promoting the formation of peptoid nanotubes by acting as pillars, extending vertically with respect to the macrocycle planes (3,4). Moreover conformational flexibility of cyclic peptoids can lead to unexpected solid state dynamic properties (5).

Single crystal X-ray diffraction, hot stage microscopy, DSC and TGA helped in exploring the landscape of crystal forms for a cyclic hexapeptoid decorated with four methoxyethyl and two propargyl side chains (compound **1** in Figure 1). Interestingly single crystal to single crystal transformation were detected and characterized by in situ variable temperature single crystal X-ray diffraction.

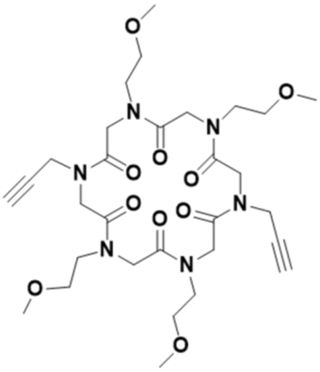

Figure 1

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Hirshfeld Analysis Of The Solid State Assembly Of Cyclic Octapeptoids

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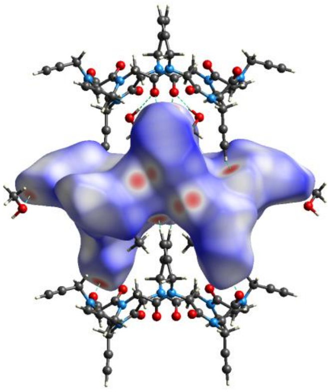
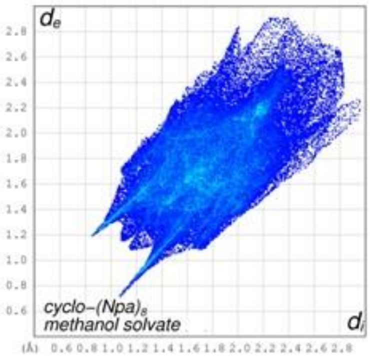
Cyclic peptoids for their biostability and potential diversity seem to be the ideal candidates to evoke biological activities and novel chemical properties (1,2).

Peptoids differ from peptides in the backbone position of the side chains, which are attached to the nitrogen atoms. CH···OC hydrogen bonds play a key role in the solid-state assembly of cyclic α-peptoids: face to face or side by side arrangement of the macrocycles mimick β-sheet secondary structure in proteins (3). In particular side chains may act as pillars, extending vertically with respect to the macrocycle plane, inducing the columnar arrangement of the peptoid macrocycles (3).

The structural diversity of the solid state assembly of cyclic peptoid is accompanied by peculiar host-guest chemistry and sorption properties (4-6). Hirshfeld surface analysis revealed to be extremely useful in fingerprinting the molecular interactions that lead to the solid state molecular assembly with particular reference to the role of the guest molecules (3-5).





In figure as an example it is shown the Hirshfeld surface analysis for the compound cyclo-(Npa)$_8$, *Npa* = *N*-(propargyl)glycine, which crystallizes as methanol solvate. The shortest contacts are depicted as green dotted lines. The Hirshfeld surface mapped with d_{norm} is shown on the left, as viewed along the *c* axis to allow a better view of the closest contacts leading to the formation of a peptoid nanotube, also the closest contacts with methanol molecules are evidenced. The corresponding fingerprint plot is shown on the right.

We will describe in details the results obtained by applying the Hirshfeld surface analysis to a library of cyclic octapeptoids decorated with propargyl and/or methoxyethyl side chains.

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Self-assembly of peptide nanostructures driven by graphene oxide nanoplatforms

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Over the last 20 years, self-assembled peptide nanostructures have been investigated as biomaterials due to their impressive potential to be used in different bio-nanotechnological applications such as sensors, drug delivery systems, bioelectronics, tissue reparation, among others (1,2). Through self-assembly, peptides can give rise to a range of well-defined nanostructures such as nanotubes, nanofibers, nanoparticles, nanotapes, gels and nanorods. In the present work, we investigated both experimentally and theoretically the self-assembly process of the hydrophobic phenylalanine (FF) and its analogous tyrosine (YY) dipeptides, in the presence or not of graphene oxide (GO) nanosheets.

The CD, UV-vis and fluorescence spectroscopies revealed that YY is able to form ordered nanostructures similarly to YY, already at short incubation time (< 2 h) and in ultrapure water. In the presence of GO dispersion, the formation of ordered structures was also found, with a conformational stability) higher than the dipeptides alone at longer incubation time (< 72 h). QM calculations well reproduced the experimental findings pointing to the preeminence of intermolecular instead of intramolecular interactions. Atomic force microscopy showed the peptide-specific ‘decoration’ of GO nanosheets, with FF molecules gathering at the GO edges whereas the YY preferentially collect onto the GO basal plans. Moreover, QCM-D analyses, performed to scrutinise the GO-dipeptide interface interactions, highlighted different viscoelastic responses of the GO-YY and GO-FF adlayers, respectively.

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On the sodium alginate aqueous solutions and nanodispersions flow behavior

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Hydrocolloids are widely used in different industrial fields to perform a number of functions including thickening and gelling of aqueous solutions, stabilizing foams, emulsions dispersions and so on (1).

Sodium alginate, due to its biocompatibility, non toxicity, and biodegradability, is a good candidate for food and biomedical applications (2). An accurate study of the rheological and conductivity behaviors of this polymer could help in the formulation of supramolecular systems that can be used as edible coatings and films to preserve food products (3,4).

In this study, rheological behavior and conductivity of aqueous solutions with different sodium alginate concentrations were evaluated by tuning temperature and polyelectrolyte viscosity. As expected, lower polymer concentrations gave low values of conductivity and viscosity (5).

Two of the polymer aqueous solutions considered were then chosen as continuous phase for the realization of dispersions obtained by adding a surface active agent (Tween 80) and a lipid component, lemongrass essential oil, selected for its antimicrobial activity against pathogenic microorganisms (6).

Viscosity and conductivity were measured on the produced dispersions in order to evaluate how different type energy sources (homogenization and sonication) and the addition of surfactant and lipid phase could affect the dispersion properties. In particular the effect of essential oil amounts on the emulsion properties were evaluated.

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Food-grade nanocarriers for protection and delivery of bioactive compounds

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The encapsulation of active ingredients into nanoemulsions as carrier systems is a novel approach for drug delivery. Nanoemulsions are considered to be more stable than classical emulsions thanks to the smaller droplet size that minimizes the particle aggregation and gravitation separation. These systems are generally employed for encapsulation of hydrophobic bioactive compounds to improve their solubility, chemical stability and oral bioavailability. One of the most important and extensively researched bioactive molecules is the curcumin. It is considered highly effective against colorectal and pancreatic cancer (1) thanks to its ability to interfere with various biochemical pathways (2). These aspects make curcumin an interesting molecule as a bioactive agent in functional foods, supplements, and pharmaceuticals. Nevertheless, the main challenge that currently limits the incorporation of curcumin into commercial products is its low water-solubility, chemical instability, and poor oral bioavailability (3,4). In this study, an oil-in-water nanoemulsion, stabilized by either surfactant (Tween 20) and/or Sodium Caseinate, was proposed to encapsulate curcumin. The stability of the host emulsion system was studied according to time, temperature and pH changes. The characterization of the proposed system was carried out through dynamic light scattering and rheometry measurements in order to investigate on size, stability and viscosity of the preparation. The loading ability of curcumin, detected through molecular spectroscopy, varied with the emulsifier type and concentration.

The outcomes of this study provide useful information on the relationship between the emulsion composition and the bioavailability of an important molecule, like curcumin and other similar molecules.

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Encapsulation and release of hydrophilic and lipophilic molecules from layer by-layer assembled capsules

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Polyelectrolyte capsules produced through layer-by-layer (LbL) method have been assembled by alternatively depositing anionic and cationic polymer layers onto liposomes cores (1-3). High and low molecular weight molecules were entrapped into the liposome core before the polyelectrolyte deposition. The release of the loaded molecules from the nanocapsules was demonstrated.

The combination of dynamic light scattering (DLS), ζ-potential, and transmission electron microscopy (TEM) techniques provided detailed information on the stability, dimensions, charge, and wall thickness of these polyelectrolyte globules. TEM microphotographs demonstrate the presence of nanocapsules with an average diameter of below 300 nm and with a polyelectrolyte wall thickness of about 20-25 nm.

Transport behavior through the multishell wall was detected for the diffusion of the entrapped molecules (4,5) Additionally, it was proven that the proposed nanocapsules appear to be appropriate for prolonged molecule compartmentalization and protection, even for molecules having low molecular weight. The influence of pH and wall thickness on the release properties were also considered. As a whole, vesicle templated polyelectrolyte nanocapsules show great potential as novel controllable drug-delivery devices for biomedical and biotechnological applications

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Supramolecular complexes based on Chlorophyll *a*/Cyclodextrins for Photodynamic Therapy (PDT) applications

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The natural porphyrin Chlorophyll *a* (Chl *a*) has the features of a good photosensitizer for photodynamic therapy (PDT) applications. Indeed, when photoactivated, this molecule is able to induce the production of reactive oxygen species, such as H_2O_2, superoxide radical anion ($^{\bullet}O_2^{-}$) and, in particular, $^1O_2$ (1, 2, 3). Since Chl *a* has a lacking solubility in water and high tendency to aggregate, in this study, it was first included into different cyclodextrins (CDs) to form stable water-soluble supramolecular complexes (4), then the PDT performance of Chl *a*/CDs complexes was evaluated. 2-Hydroxypropyl-β-cyclodextrin (2-HP-β-CD), 2-Hydroxypropyl-γ-cyclodextrin (2-HP-γ-CD), Heptakis(2,6-di-*o*-methyl)-β-cyclodextrin (DIMEB) and Heptakis(2,3,6-tri-*o*-methyl)-β-cyclodextrin (TRIMEB) were used to solubilize the Chl *a* into aqueous environments. The chemical physical properties of Chl *a*/cyclodextrins complexes in cellular medium were studied by means of UV–Vis absorption spectroscopy demonstrating the better aptitude of 2-HP-β-CD and 2-HP-γ-CD than the other CDs to solubilize Chl *a* in cell culture medium in monomeric form.

Consequently, Chl *a*/2-HP-β-CD and Chl *a*/2-HP-γ-CD supramolecular complexes were tested *in vitro* on the human colorectal adenocarcinoma HT-29 cell line to evaluate their photodynamic effects. As shown by MTT tests, both supramolecular complexes exhibited no dark toxicity and a high phototoxicity toward HT-29 cells promoting a high percentage of cell death, after illumination, particularly when high concentration of Chl *a* and long incubation time were used. When the higher dose of the photosensitizer was used ($5\cdot10^{-5}$ M), the relative survival rate was about 10% after 24 hours of incubation, for both studied systems.

Cellular uptake of porphyrin was determined by means of fluorescence measurements and intracellular localization was evaluated by confocal microscopy proving that Chl *a* was localized primarily in lysosomal organelles of HT-29 cells. Moreover, flow cytometric analysis demonstrated that the cell death occurred by necrotic mechanisms.

Therefore, it is possible to affirm that supramolecular complexes based on cyclodextrins not only are promising formulations for loading natural Chl *a*, but also that Chlorophyll *a*/cyclodextrins complexes have great potentials for therapeutic applications.

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Cytotoxicity of red-emitting CdSe@ZnS nanocrystals embedded in Liposomes

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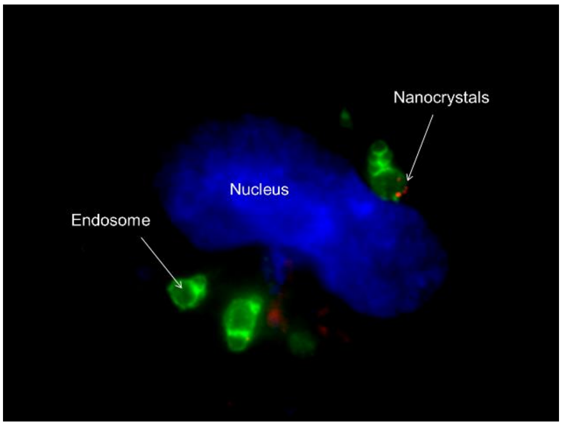

Fluorescent nanocrystals (NCs) are an advantageous alternative to conventional organic fluorescent dyes for bioimaging applications (1) and their toxicological evaluation is currently a primary field of research. In this work, the micelle-to-vesicle transition (MVT) method was applied to the encapsulation of hydrophobic and highly fluorescent CdSe@ZnS NCs into the lipid bilayer of liposomes (2). The obtained aqueous NC−Liposome preserved the spectroscopic characteristics of the pristine NCs. Then, the in vitro toxicological effects on HeLa cells of these red emitting NC-Liposomes were carried out. In addition, we evaluated the effect of the lipid carrier on the cell toxicity by using liposomes of different phospholipid composition. The toxic effects of NCs, evaluated by cells proliferation, cell death study and MTT test on HeLa cells at concentrations up to 20 nM, are negligible compared to those of the lipid carrier, especially when this is constituted by DOTAP, a cationic phospholipid. The obtained data suggest that DOTAP has a dose- and time-dependent toxic effect on HeLa cells, while the addition of PEG to the liposome formulation does not alter significantly the viability of the cells. The ability of NC-Liposomes to penetrate HeLa cells was also assessed by fluorescence and confocal microscopy investigation. Obtained images show that NC-Liposomes are internalized into HeLa cells through the endocytic pathway, enter early endosomes and reach lysosomes in about 1 h. NCs co-localized with endosome vesicles and were positioned at the limiting membrane of these organelles. Experimental results suggest that the system as a whole, hydrophobic NCs and its lipid carrier, should be considered for the development of fully safe biological applications of CdSe@ZnS NCs, providing essential indications to define the optimal conditions to use the proposed system as optical probe for both in vitro and in vivo investigations.

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A photoelectrochemical transduction system based on solubilized photosynthetic reaction center proteins

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The screen-printing technology in electrochemical applications offers the possibility to produce a large number of electrochemical (bio-)assays at low cost. Intrinsic characteristics and reproducibility of screen-printed electrodes make them extremely versatile in the development of a wide range of electrochemical devices (1). In this work we have characterized a miniaturized photoelectrochemical transduction system represented by a screen-printed electrochemical cell dipped in an aqueous electrolyte, containing photosynthetic reaction center (RC) enzymes, extracted from the phototrophic bacterium *Rhodobacter sphaeroides*, and suitable redox mediators.

In vivo, RC enzymes act as photocatalysts promoting the transfer of two electrons from two ferrocytochrome proteins (electron donor) to a ubiquinone molecule (electron acceptor) upon absorption of two photons. Photocurrent generation in RC-based photoelectrochemical cells (PECs) occurs when RC photocycle is sustained by light in the presence of either physiological or synthetic electron donors and acceptors, acting as redox mediators between protein and electrodes (2).

The ability of our device to generate photocurrents under illumination has been assessed and the factors limiting (or enhancing) the photoresponse have been investigated. The efficiency of ferrocenemethanol and decylubiquinone in performing the role of electron donor and acceptor in our PEC has been demonstrated. Moreover, a theoretical model has been proposed, able to describe the chronoamperometry profiles with high accuracy. This model has allowed obtaining, under light and in the dark, the concentration of all involved species as a function of time, both in the bulk and in proximity of working and counter electrodes. The results achieved show that the steady photocurrent is the result of a fine balance between photochemical reaction, reverse chemical reaction and mass transfer processes involving bulk and electrodes/solution interfaces.

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Functional incorporation of bacterial photosynthetic reaction centers in polydopamine nanospheres

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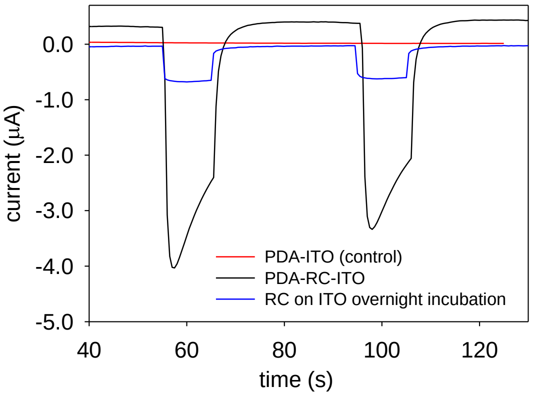
Polydopamine (PDA) nanospheres have recently gained great attention as a new material with the potential to incorporate various molecules meanwhile firmly immobilizing them onto different surfaces (1). The intriguing possibility of incorporating proteins maintaining their biocatalytic activity is currently a “hot” field of investigation with promising perspectives. In this work, we offer a characterization of the behavior of the bacterial photosynthetic reaction center (RC) from *Rhodobacter sphaeroides* incorporated in polydopamine nanospheres either dispersed in solution or immobilized onto ITO-covered glass slides. RC is a membrane-spanning pigment-protein complex that, upon illumination, produces a stable charge-separated state (2). This electron-hole pair can be used, with the help of suitable mediators, to produce photocurrents, making RCs a good model for basic studies of protein activity immobilized in bioactive films (3). Herein, we first report that, upon oxygen-assisted dopamine polymerization in the presence of the protein, RC (a) is incorporated, (b) is capable to generate the charge-separated state, and (c) to produce photocurrents in a properly designed electrochemical setup either when immobilized onto ITO (used as working electrode) and when suspended in solution in the presence of the electron donor ferrocenemethanol (FcnMeOH) and the electron acceptor decylubiquinone (dQ). Upon illumination, RC promotes the reduction of dQ to dQH2 by withdrawing electrons from FcnMeOH. The incorporation of RC into PDA has been carried out either in Tris and in Phosphate buffer at pH 8 at increasing dopamine concentration using an overnight incubation at room temperature. We found that in Tris the complete incorporation of RC occurs at lower dopamine concentration with respect to phosphate. For maximal RC photoactivity when immobilized onto ITO we found that it is important to maximize the RC/PDA ratio, possibly because increasing the PDA matrix decreases the amount of light available for RC excitation and/or the interaction of the mediators with the RC active sites and the electrode surface is unpaired. Moreover, it is possible also to co-incorporate FcnMeOH and dQ in the PDA film, so that the photocurrents can be detected only by using ferrocyanide as electrochemical mediator at the counter electrode.



Photocurrents detected using RC-PDA covered ITO as WE (black trace), bare ITO (red trace) and ITO after overnight incubation with RC (blue trace).

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Photosynthetic Reaction Centers exposed to ultrasounds: effect on structure and function

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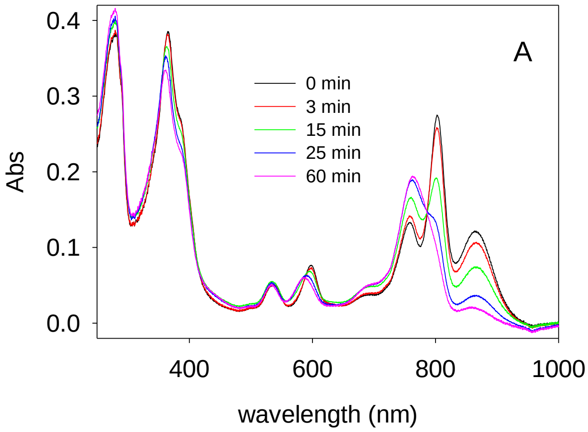

Ultrasounds are used in many industrial, medical and research applications, for example for equipment cleaning, milk homogenization (1), microorganisms and enzymes inactivation (2), liposome preparation, drug delivery (3), liposuction, tumor ablation and kidney stone disruption. Properties and function of proteins are strongly influenced by the interaction with the ultrasonic waves and their bioactivity can be lost because of alteration of protein structure. A systematic study of ultrasounds effect on Integral Membrane Proteins (IMPs), which are responsible for a variety of fundamental biological functions is lacking in literature. We have undertaken this subject using the photosynthetic Reaction Center (RC) of the bacterium *Rhodobacter sphaeroides* as a model for assessing the ultrasound-induced IMP denaturation. Purified RCs were suspended in i) detergent micelles, in ii) detergent-free buffer and iii) reconstituted in liposomes, and then treated with ultrasound at 30 W and 20 kHz at increasing times. The advantage of using RCs is that they have an optical spectrum rich in diagnostic signals that can be used for monitoring the protein integrity. In particular, the bands at 760, 800 and 865 nm are in the ratio 1:2:1 in the native protein, while progressive denaturation results in a decrease of the 865 nm band and increase of the 760 nm one. The optical absorption spectra (shown in the figure for the case of detergent) indicated a progressive and irreversible denaturation in all cases, resulting from the perturbation of the protein scaffold structure, as confirmed by circular dichroism spectra that showed progressive alterations of the RC secondary structure. The functionality of the RC can be assayed with time resolved optical spectroscopy, since after light excitation it forms a charge separated state. The amplitude of the subsequent dark charge recombination signal at 865 nm is diagnostic of protein photoactivity. The lifetime for the loss of RC photoactivity was of 32 min in detergent micelles, ranged from 3.8 to 6.5 min in the different proteoliposomes formulations, and of 5.5 min in detergent-free buffer. Atomic force microscopy revealed the formation of large RC aggregates related to the sonication-induced denaturation, in agreement with the scattering increase observed in solution.

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Targeting DNA G-quadruplex in KRAS oncogene promoter: computational, calorimetric, and spectroscopic studies

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The discovery of G-quadruplex structures in G-rich DNA sequences has shed light on new functions for DNA in biology. G-quadruplexes (G4) are nucleic acid structures formed in relevant genomic regions, as telomeres and oncogene promoters. Recently, cellular studies proved the *in vivo* existence of G4, confirming their key role in living cells (1). A growing body of evidence supports the idea that G4-DNA formed by promoter sequences is involved in the regulation of gene expression.

KRAS is one of the most frequently mutated oncogenes involved in the pathogenesis of different types of cancers, such as colorectal and pancreatic carcinoma. Its promoter contains a nuclease hypersensitive element (NHE) with repetitive guanine residues able to fold in DNA G4 (2). An effective anticancer therapy may be obtained targeting the G4 formed in this oncogene promoter.

We identified a pool of ligands through receptor-based high-throughput virtual screening (HTVS) starting from the recently determined NMR structure (3). A rapid screening of the affinity of the identified ligands was obtained by circular dichroism melting experiments. After this screening, several derivatives of the best ligand were synthesized to improve the affinity for KRAS G4 and the selectivity against DNA double helix.

The affinity, the binding stoichiometry and all the thermodynamic parameters related to the association processes were obtained by means of Isothermal Titration Calorimetry (ITC), Circular Dichroism (CD) and fluorescence (for the ligands containing chromophoric groups). Differential Scanning Calorimetry (DSC) measurements was also utilized to evaluate the quadruplex stabilization upon ligand binding.

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Spectroscopic and biochemical characterization of a new bacterial Tyrosinase from *Streptomyces cyaneofuscatus*

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Streptomycetaceae, a family of Actinobacteria, are Gram-positive soil bacteria and some members are involved in lignin degradation, melanin formation and in the production of antibiotics and secondary metabolites. Tyrosinases are produced by the genus *Streptomyces* spp. and 40% of them produces melanin-like exopigments on tyrosine containing agar media (1,2). Tyrosinase belongs to the Type 3 copper proteins, where two antiferromagnetically coupled copper ions are present (3); the enzyme catalyzes two different reactions: the ortho-hydroxylation of monophenols (cresolase activity) and the oxidation of o-diphenols to o-quinones (cathecolase activity). As typical substrates of tyrosinases are mono- and diphenols, tyrosinase has biotechnological applications: from wastewater treatment to food and material functionalization (4).
In this study, different Actinomycete strains were isolated from Algerian Saharan soil and the Ms1 strain was selected for its capability to produce melanin in various solid media. Chromosomal DNA was purified and a novel tyrosinase encoding sequence was identified and assigned to *Streptomyces cyaneofuscatus* sp. (99.6%). The tyrosinase was isolated and biochemically characterized to test its stability and activity at different pHs, temperatures, in the presence of inhibitors, reducing agents and metals. The tyrosinase was able to oxidize l-DOPA with an optimum activity at 55°C and pH 7 and also in presence of different concentrations of water-miscible organic solvents. The enzyme activity showed a total inhibition effect with cysteine, sodium metabisulphite, ascorbic acid, whereas a limited inhibition effect was observed with EDTA. Furthermore the X-band EPR spectra were recorded to highlight the "half-met" form after activation of the Type 3 copper center through nitrite and ascorbate addition. The EPR spectra were also recorded in presence of inhibitors like the L-mimosine ligand (5,6). Finally, as the enzyme immobilization increases its stability and allows its reusability (7), the tyrosinase was supported on electrospun Nylon 6 nanofibers and tested; the enzyme immobilization efficiency was also calculated.

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Transducing light giant lipid vesicles: towards the preparation of autotrophic protocells

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A challenging goal of the synthetic biology is the synthesis of artificial cells from scratch. This research topic sheds insights both on the emergence of life, i.e. the transition between non-living to living matter, and on the preparation of micro-sized confined bio-reactors designed for accomplishing specific tasks, i.e. *bio-robots*.

Lipid vesicles and emulsion droplets have been extensively used as minimal model cells, also called *protocells,* since they have an aqueous core enclosed by a lipid bilayer boundary. Their size can range from few nanometres to tens of micron (*giant vesicles*) and they can encapsulate biomolecules, like proteins, DNA and RNA, in the inner aqueous solution. Some years ago, the water-in-oil (W/O) emulsion transfer method has been presented(0) as a flexible and robust procedure to prepare Giant Unilamellar Vesicles (GUVs). In recent years, we have used this method for the preparation of GUVs encapsulating enzymatic pathways in the internal aqueous core(0), or for the reconstitution of trans-membrane proteins in the GUV lipid bilayer with a defined and uniform orientation(0). Moreover, different theoretical approaches have been also developed in order to describe the time evolution of a population of reactive GUVs taking into account both intrinsic and extrinsic stochastic effects (4, 5).

In this contribution, an example of protocells able to transduce light energy into chemical energy will be presented and discussed(0). In fact, it has been possible to functionalize the lipid membrane of GUVs inserting in the hydrophobic domain an integral membrane protein: the *Photosynthetic Reaction Center* (RC) retaining its physiological orientation (RC@GUV). Under continuous light irradiation, RC@GUVs are able to convert light energy into a trans-membrane pH gradient that can be exploited, in a near future, for sustaining metabolic pathways, like for instance the conversion of ADP in ATP. This represents a genuine first step forward the preparation of semi-synthetic autotrophic protocells.

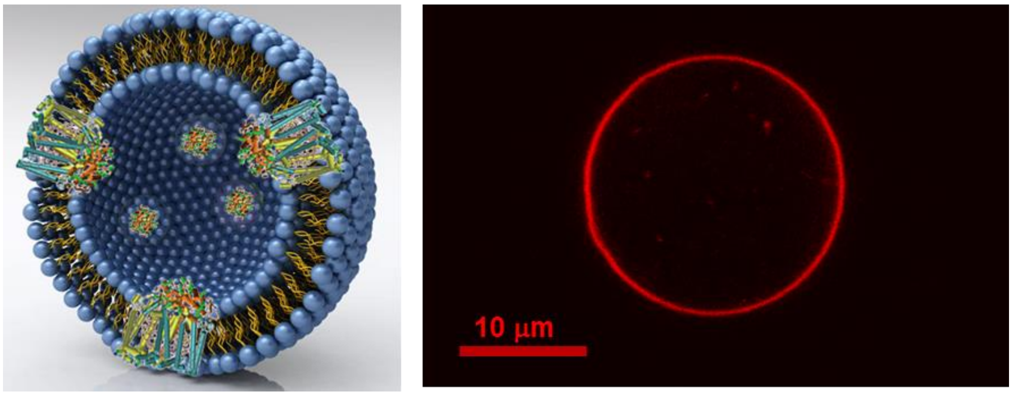

Figure 1. Giant Unilamellar Vesicle with RC reconstituted in the lipid membrane: a sketch of the lipid membrane showing the RC physiological orientation on the left, a confocal microscopy image of a RC@GUV whit RCs fluorescently labelled, on the right.

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Structural and functional characterization of photosynthetic reaction centers in deep eutectic solvents.

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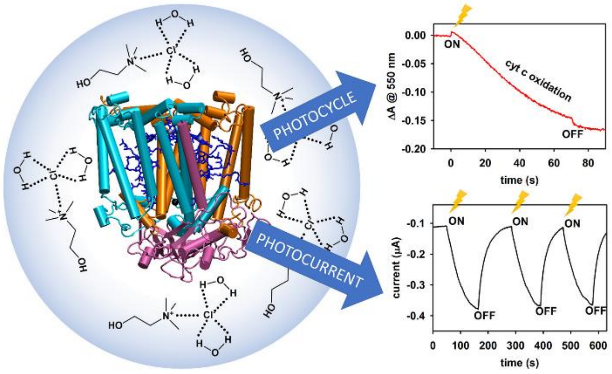

Deep eutectic solvents (DESs) are emerging as a new class of green solvents with the potential to replace organic solvents in many applications both at industrial and academic level (1). In this work, we offer an unprecedented characterization of the behavior of the bacterial photosynthetic reaction center (RC) from *Rhodobacter sphaeroides* in a series of choline-based DESs. RC is a membrane-spanning three-subunit pigment-protein complex that, upon illumination, is capable to produce a stable charge-separated state. Thus, it represents the ideal model for carrying out basic studies of protein-solvent interactions. Herein, we first report that, in many DES mixtures investigated, RC (a) is stable, (b) is capable to generate the charge-separated state, and (c) even to perform its natural photocycle. It proved, indeed, to be effective in reducing quinone molecules to quinol by withdrawing electrons from cytochrome c. As an example of biotechnological application, a photoelectrochemical cell based on DES-dissolved RC has also been designed and successfully employed to generate photocurrents arising from the reduction of the electron-donor ferrocenemethanol.

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Light Transducing Protocells: reconstituting and characterizing the bc1 complex into the membrane of giant lipid vesicles.

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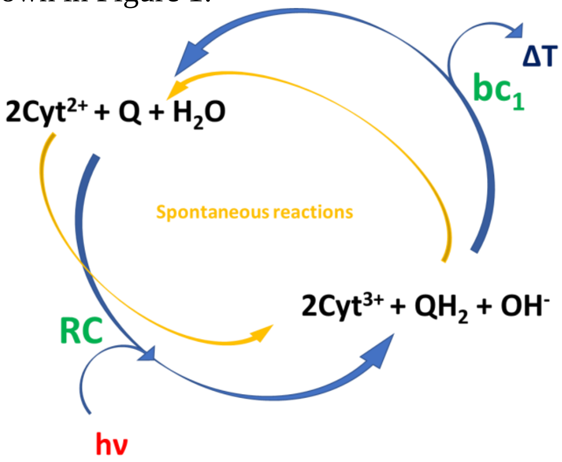
Photosynthesis is responsible for the photochemical conversion of light into the chemical energy that fuels the planet Earth. The photochemical core of this process in all photosynthetic organisms is a transmembrane protein called the reaction center (RC) (1). In purple photosynthetic bacteria a simple version of this photo-enzyme catalyzes the reduction of a quinone molecule, accompanied by the uptake of two protons from the cytoplasm and the oxidation of cyt^{2+} to cyt^{3+} from external medium. In a previous work (2), giant unilamellar vesicles (GUVs) were prepared by the phase transfer method (3) reconstituting in the lipid membrane RCs retaining the physiological orientation at 90%. These synthetic protocells (RC@GUVs) are capable of generating a photo-induced proton gradient 0.061 pH units per min across the membrane under continuous illumination and in presence of an excess of cyt^{2+} and quinone in the external solution. In this contribution, bc1 extracted both from bacteria and mitochondria are reconstituted in giant vesicle membrane (bc1@GUVs) and characterized by studying the enzymatic activity in reducing cyt^{3+} to cyt^{2+} in presence of quinole QH_2. This is a forward step towards the coupling of both RC and bc1 in in the synthetic protocells order to implement the complete photo-cycle, as shown in Figure 1:



This pave the way for the construction of more functional protocells for synthetic biology which can be ultimately harnessed to synthesize ATP(4,5).

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PDMS membranes loaded with TiO_2 NPs: antibacterial activity and self-cleaninproperties

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Poly (dimethyl siloxane) “PDMS” is a highly hydrophobic, thermally and mechanically stable polymer whose features are attributable to its Si-O bonds, which have higher bond strengths and larger bond lengths than average C-C bonds. Therefore, PDMS is widely used in different fields, such as sealants, separating membranes and biomedical devices (1). In order to fit the PDMS synthesis to the electrospinning, a sol-gel route was used to synthesize PDMS elastomer. PDMS hydroxyl terminated prepolymers with two different molecular weights and therefore viscosities (20.000 e 50.000 cSt), TEOS (tetraethyl orthosilicate) as multifunctional cross-linking agent, THF as solvent and HNO_3 as acid catalyst (2) were used. The sol-gel route is essential for the electrospinning process, which guarantees a fibrous structure with microscale to nanoscale dimensions (figure 1). In order to obtain the crosslinked PDMS membranes coupled with TiO_2, a Sn-based catalyst was used (3). TiO_2 was synthesized using titanium tetraisopropoxide, 2-propanol and water (1:2:5, V/V) to get an amorphous gel which was then subjected to two different thermal treatments, that are a solid-state and a hydrothermal synthesis, to get crystalline anatase TiO_2. This coupled system allows to have membrane sheets loaded with NPs TiO_2, combining the high adsorbent capacity and the macroscopic handling of the membrane with the photocatalytic antibacterial and self-cleaning features of TiO_2. The photocatalytic activity of this system can be activated by an UV light source, whose photons have an energy at least equal to the TiO_2 energy gap (3.2 eV for anatase) and the PDMS membrane showed a high resistance to this type of source. For this work, different synthetic conditions were investigated, varying the PDMS prepolymers ratio, the temperature and the time of the polymer synthesis and the electrospinning conditions (voltage, flow, distance from the electrodes). Two different amounts of titania were loaded (5% and 10% w/w) inside the membranes, by suspending the powders or the sol in a THF solution and then electrospraying together with the PDMS membrane. The samples synthesized were characterized by means of rheological measurements and FE-SEM.

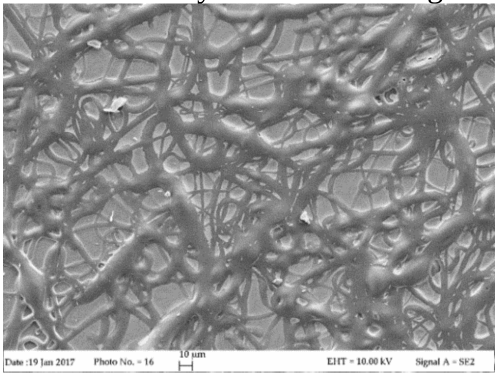

Figure 1. FE-SEM image for a PDMS membrane loaded with 5% w/w TiO_2 (solid-state crystallization)

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Spectroscopic investigations on the effects of hydrophobic silver nanoparticles on peptide conformations

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Protein function is highly dependent on the tridimensional structure of the protein itself; proteins fold into defined structures via a specific pathway to execute their biological function. Since nanomaterials have been widely used in recent years for therapeutical purposes, a deeper knowledge on the effects on protein conformation and folding is fundamental for the development of new therapeutic and diagnostic devices.

Gramicidin A is a linear 15 aminoacid peptide with the ability to adopt single- or double-stranded helical conformations when inserted into phospholipid membranes: the dimerization of two single-stranded helices originates a cation-selective ion channel. Due to its properties, the peptide is an excellent model for membrane proteins and ion channels (1). Silver nanoparticles (AgNPs) are likely among the most used nanomaterials in many consumer applications, mostly because of their well-demonstrated and safe antimicrobial properties (2,3); recent findings on their optical properties (4,5,6) suggest that AgNPs could be a versatile component for therapeutic and diagnostic devices. However limited information are available on the impact of AgNPs on proteins' conformations.

In this work, the effect of silver nanoparticles (AgNPs) on Gramicidin A conformation is presented; in particular, Gramicidin A is inserted into POPC liposomes, to mimic cell membrane. Dodecanethiol-stabilized spherical AgNPs (D-AgNPs) (7) are prepared to have dimensions (5 nm) and an hydrophobic nature compatible with the POPC lipid bilayer.

Tryptophan (Trp) fluorescence, together with Raman signals of Trp residues, were used to probe the position of the peptide inside the bilayer due to their sensitivity to the local environment (8,9). ATR-FTIR spectroscopy was employed to study Gramicidin A conformation: amide I and II vibrational bands are indeed sensitive to secondary structure of peptides and proteins (10). ATR-FTIR spectra revealed the single- and double-stranded conformations of Gramicidin A in the lipid bilayer, and the effects of D-AgNPs addition on peptide conformation.

Our results suggest that D-AgNPs may affect the peptide dimerization and the formation of the ion channel.

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High-Resolution Molecular Spectroscopy Of Open Shell Molecules: Isotopologues Of The Imidogen (^{15}ND) And Amidogen ($^{15}ND_2$) Radicals

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A wide number of studies have been carried out on the imidogen and amidogen radicals, which are thought to be involved in the ion-reaction scheme in which ammonia is produced from N^+. The rotational spectrum of the main isotopologue of the imidogen radical NH has been investigated in the THz region (1), as well as in the Far-Infrared-Region (2). In addition, the less common isotopologues ND and ^{15}NH have been studied by rotational spectroscopy (3,4,5). The interest on this small free radical has increased, since both NH and ND have been detected is several astronomical sources (6,7). However, no data on the rare isotopologue ^{15}ND were available until now. In this work, ^{15}ND radical has been produced by electrical DC discharge of $^{15}ND_3$ and Ar as gas buffer and its pure rotational spectrum has been recorded up to 1.2 THz. The fine and hyperfine structure of the $N = 1 \leftarrow 0$ and $N = 2 \leftarrow 1$ transitions has been assigned and all the measured line frequencies have been analyzed, allowing to determine the rotational constant B, the centrifugal distortion term D and 9 fine and hyperfine parameters. A global analysis including rotational and vibrational data of all the isotopologues of NH radical is in progress (8). While discharging ammonia, the spectrum of another radical, rapidly identified as $^{15}ND_2$, appeared (Fig. 1). In fact, imidogen and amidogen radicals are usually obtained in the same conditions. Although the amidogen radical has been subjected to numerous studies (9,10,11,12,13), no spectroscopic data on $^{15}ND_2$ are reported. In the second part of our work, the rotational spectrum of the $^{15}ND_2$ radical has been observed in selected frequency region between 264 GHz and 1.2 THz. A total number of 164 transitions have been recorded and assigned, whose analysis allowed us to determine with high accuracy the rotational constants A, B and C, some centrifugal distortion terms and 21 fine and hyperfine parameters.

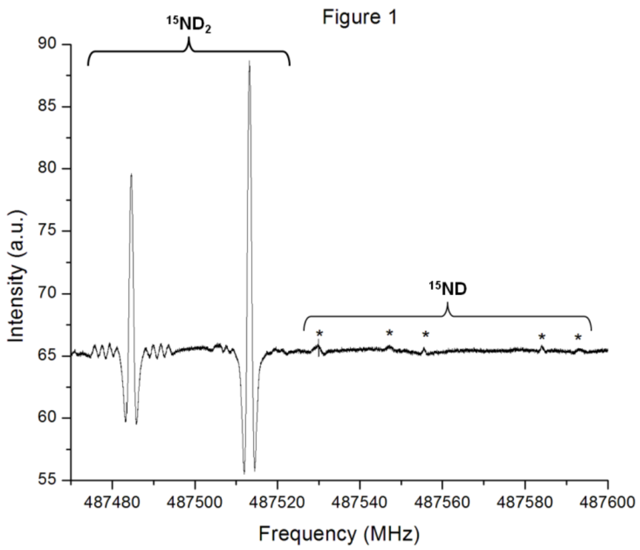
Figure 1

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New liquid crystalline elastomers investigated by ^{2}H NMR and X-ray measurements

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Liquid crystal elastomers (LCEs) are a unique class of soft materials, which combine rubber elasticity with the orientational order typical of liquid crystals. Depending on the chemistry of these materials, LCEs undergo reversible, anisotropic shape change in response to a number of stimuli, such as heat, UV-vis light, type of solvent and electro-magnetic waves. LCEs are indeed very promising materials for nanometer- to centimeter- scale robotic applications. In the recent years, many efforts have been spent in developing new LCE chemistry and processing [1-4], reaching impressing results, such as large and controlled deformations, high motion complexities and multi-step functionality. Most of the investigations are related to LCEs exhibiting a nematic phase, while few studies are known about smectic LCEs. Moreover, the interplay between molecular structure and macroscopic physical properties, such as shape responsiveness, orientational distributions and ordering are poorly understood.

In this work, we report the physical-chemical study of new side-chain liquid crystal elastomers prepared in the form of thin films having uniaxial actuation. A new smectic (semi-flexible) crosslinker (see *Figure 1*) was used to prepare monodomain films [5] showing isotropic-nematic or isotropic-smectic phase transitions, depending on the relative crosslinker/monomers concentration.

Detailed physical-chemical investigations based on ^{2}H NMR spectroscopy [6,7] and small angle and wide angle X-ray diffraction measurements, thermo-mechanic and thermo-elastic properties are discussed in view of molecular properties of these new systems and compared with LCEs prepared with conventional flexible crosslinkers [8].

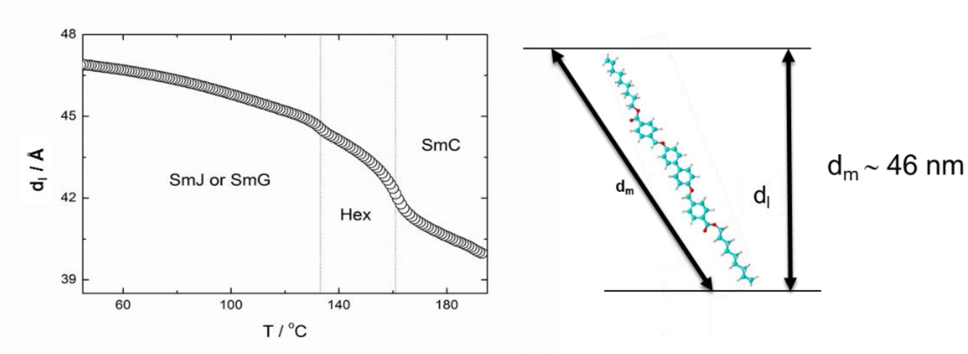

Figure 1. Interlayer distance (d_l) as a function of temperature (T) in smectic phases formed by the semiflexible crosslinker (on the right) used to prepare new nematic and smectic LCEs [5].

Acknowledgements:

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Near UV-Visible Absorption Spectroscopy of Extra-Virgin Olive Oils

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Extra-Virgin Olive Oil (EVOO) is an essential food in Mediterranean cuisine, and is nowadays an appreciated and recognized ingredient in many other cultures. Olive oil is produced from the olive fruits of the *Olea europeae L*. trees, and due to the high content of monounsaturated fatty acids and bioactive compounds, olive oil is considered beneficial for human health [1]. Among the quality factors of EVOOs, the colour is very important and several efforts have been devoted to the identification of quantitative parameters related to the colour of olive oils [1,2]. The chemical-physical origin of the colour of EVOOs is related to the presence of pigments, one of the class of minor components present in olive oils. EVOOs contain a relatively rich variety of pigments, divided in carotenoids (i.e., β-carotene, lutein, violaxanthin, neoxanthin, and other xanthophylls) and chlorophyll derivatives (i.e., chlorophylls A and B, pheophytins A and B, and other minor derivatives) [2]. In this work, we present a mathematical approach to analyse the near UV-visible absorption spectrum of edible oils, in particular olive oils [3], able to determine the concentration of four main pigments: β-carotene, lutein, pheophytin A and pheophytin B (*Figure 1*). This approach has been applied to EVOOs produced in several Mediterranean countries from different cultivars [3-6]. A further step in the mathematical devonvolution of near UV-visible absorption spectra of EVOOs in terms of other minor pigments [7,8] is presented and discussed.

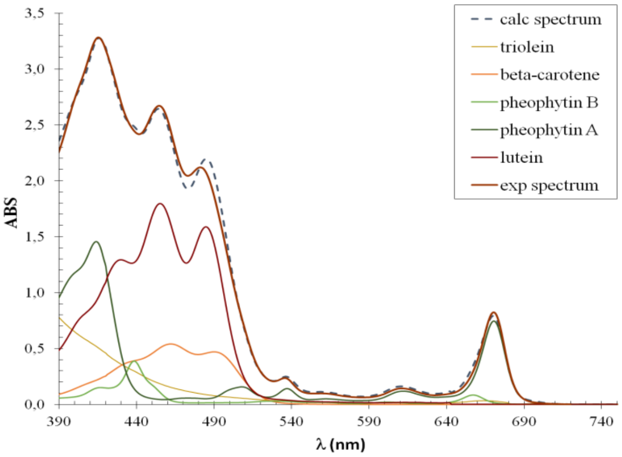

Figure 1. Example of spectral deconvolution of the near UV-visible spectrum of an extra-virgin olive oil in terms of main chemical components.

Acknowledgements:
Authors thank the former students Donatella Ancora, Francesco Buti and Cristina Lazzerini for their contributions. Prof. Maurizio Zandomeneghi and Dr. Andrea Serani are acknowledged for having introduced us to the interesting field of olive oils and for the helpful discussions and suggestions.

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A method to reduce the OFF-axis haze in polymer-dispersed liquid

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Polymer-dispersed liquid crystals (PDLCs) are composite materials formed by micron-sized droplets of liquid crystals (LCs) dispersed in a polymer matrix, which can be turned from an opaque state to a transparent one by application of a suitable electric field. PDLCs have been proposed in applications related to the control of light transmittance on large surfaces (light shutters, displays, rear mirrors). Despite several advantages, PDLCs' main drawback is haze, i.e. the fast decay of transmission at large viewing angles. In this paper, a method for achieving highly transparent PDLC devices over a wide range of viewing angles is proposed. The method is based on the use of PDLCs with tilted elongated LC droplets and driven by opportune electric fields, which are experimentally calculated and able to ensure an almost constant value for OFF-axis transmittance (1).

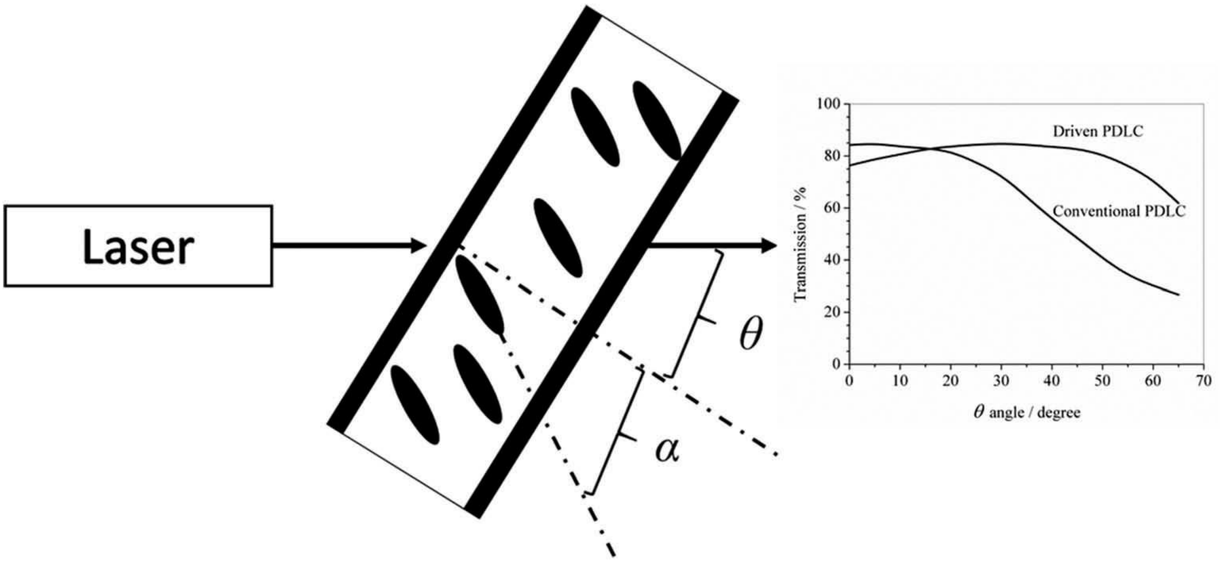

Figure 1. Angular behaviour of the opportunely driven transmittance for a PDLC with 30° tilted directors. The driving field was the sum of 4 V μm^{-1} DC bias and a 50 Hz sinusoidal electric field of 24 V μm^{-1}. The transmittance of similar PDLC with spherical droplets and driven by an electric field of about 20 V μm^{-1} at 1 kHz is reported for comparison.

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Chiral mesoscopic structures obtained by self-assembly of disubstituted steroid-porphyrins

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Aggregation studies carried out on a porphyrin template functionalized with two steroid groups revealed the formation of mesoscopic supramolecular architectures, endowed with peculiar chiral properties.

Aggregation of the steroid-porphyrin building blocks has been induced exploiting hydrophobic effect, by adding increasing volumes of water to micromolar methanol/water solution of the steroid compound investigated. Spectroscopic studies showed that the monomers forming the mesoscopic aggregate attain a J-type conformation, characterized by a slipped-out stacked arrangement of vicinal porphyrin building-blocks. Most interestingly, Circular Dichroism measurements carried out on the mesoscopic aggregates, show a dichroic signal, the shape of which is characteristic of porphyrin units coupled by exciton interaction over long distances.

Atomic Force Microscopy imaging shows that the morphology of the supramolecular architectures strongly depends on the aggregation mechanism, and specifically on the nucleation step seeding aggregation.

The latter is strongly dependent on the concentration of the steroid-porphyrin compound. At low concentration, the hydrophobic effect is predominant, leading to aspecific aggregation and formation of globular species, that, at longer times, self-assemble forming micrometric rod-like structures. At higher concentrations, the globular structures maintain their shape for long times and did not show long-range ordering.

The amphiphilic properties of the steroid-porphyrins allowed for the formation of a porphyrin film by Langmuir-Blodgett deposition. The film, formed at the air-water interface, was transferred on a transparent substrate, allowing optical spectroscopy characterization (UV-Vis absorption, Circular Dichroism, fluorescence). Microscopy techniques with nanometric resolution (AFM, SEM), revealed the formation of micrometric bundles formed by entwined porphyrin nanorods (Figure 1).

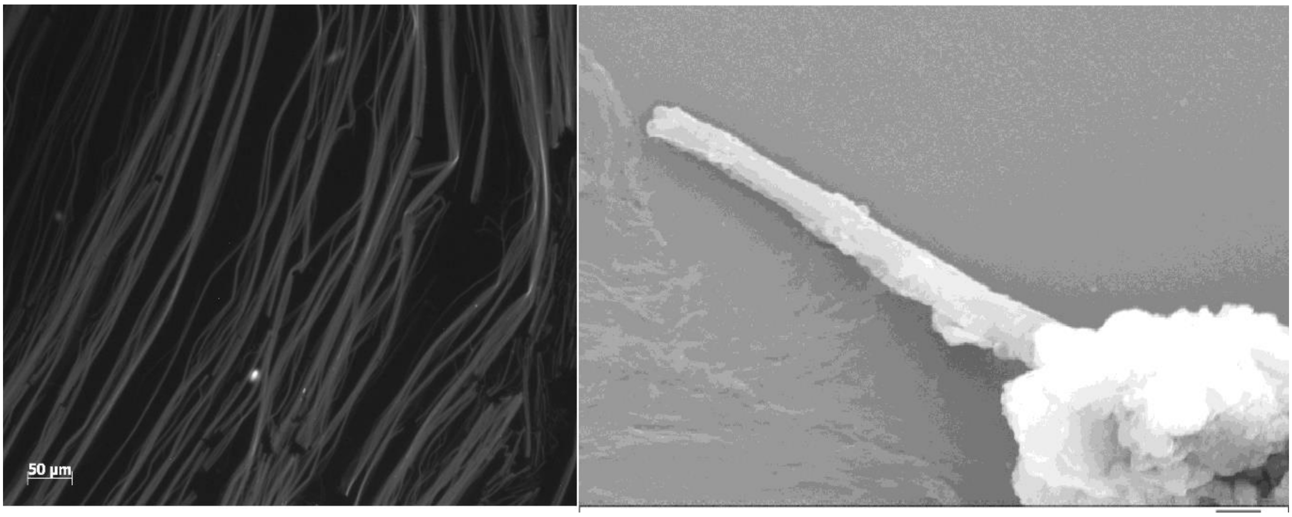

Figure 1. Fluorescence microscopy (left) and Scanning Electronic Microscope image (right) of the micrometric bundles formed by the steroid-porphyrin compound investigated. Note the rod structure originating from a large globular structure in the SEM image reported on the right.

Excited state interactions of porphyrin units mediated by conformationally constrained oligopeptides: the influence of structure and dynamics

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The excited-state interactions between two tetraphenylporphyrin units separated by conformationally constrained oligopeptides of different length (*n* = 2, 4, 6) (Figure 1) were characterized by time-resolved spectroscopy methods from the micro- to the femtosecond time scale.

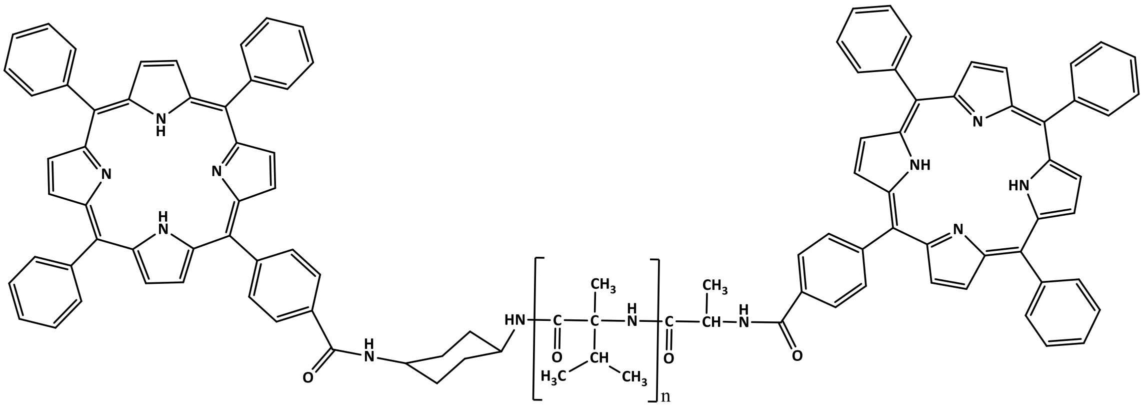

Figure 1. Molecular scheme of the bis-porphyrin-peptide compounds investigated (bPPn, *n*=2,4, 6).

In particular, time-resolved fluorescence and transient absorption techniques were applied to study the electronic coupling between the two porphyrin units mediated by the peptide spacer. The oligopeptides used are predominantly formed by the non-coded, C$^{\alpha}$-tetrasubstituted chiral amino acid C$^{\alpha}$-methylvaline, with the aim at controlling the conformational properties of the compounds investigated, and therefore, the distance and orientation between the two porphyrin moieties.

The application of time-resolved techniques allowed us to distinguish between ground-state and excited-state interactions, and to characterize the dynamical properties of the porphyrin-peptide conjugates. The porphyrin-peptide-porphyrin compounds here investigated have already been shown to be coupled *via* excitonic interaction by circular dichroism measurements (1). Goal of this study is to determine the dependence of the exciton coupling on the time-dependent distance and orientation of the porphyrin moieties, and therefore on 3D-structural properties, *i.e.* on the conformations attained by the peptide main chain, and on dynamic factors, *i.e.* the conversion rate among the populated conformers.

This study is expected to open new perspectives in the design of photosensitizers to be used in photodynamic therapy of tumors.

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Investigation of gelatin-based composites as scaffolds for bone tissue engineering

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The need of new materials for the treatment of bone defects and diseases has dramatically grown in the last few years, due to the aging of the population and the increase in traumas and tumors (1). Together with the advances in the "traditional" medicine, the developing field of tissue engineering aims at regenerating damaged tissues by combining living cells with highly porous scaffolds, which act as templates for tissue regeneration and guide the growth of new tissue (2). Among the biocompatible and biodegradable materials that can be considered to this purpose, gelatin holds an important role, since it has the same composition of the organic component of the natural extra-cellular matrix. The use of gelatin in this field is nevertheless limited by its fast dissolution rates in physiological conditions, making it necessary to increase the stability of gelatin-based materials by means of chemical crosslinking and/or integration with fillers (3). In our research group, a great interest lies in the preparation and characterization of composite gelatin-based materials: we are mainly focused in the understanding of the interactions between gelatin matrix and inorganic fillers, as well as with others biocompatible polymers, that can lead to the design of a scaffold endowed with the right features to become a potential candidate for bone regeneration. In this contribution, we report on two case studies that address this issue. First, we describe the inclusion of imogolite clays within a macroporous gelatin matrix, whose dissolution at physiological temperature is slowed down using a non-toxic chemical cross-linker, namely glycerol diglycidyl ether (GDE). The effect of imogolite and GDE on the formation of gelatin network was evaluated by means of Differential Scanning Calorimetry (DSC) and Small Angle X-rays Scattering (SAXS), while the morphology of the corresponding xerogels was observed using Scanning Electron Microscopy (SEM). Using a cryo-formation process, we were then able to generate macropores in the hydrogel network, matching the proper dimensions for the permeation of cells. Such hybrid material was used as a scaffold for the formation of hydroxyapatite. By means of X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) we demonstrated that imogolite acts as nucleation site for the formation of the mineral phase and promotes the formation of hydroxyapatite enriched in carbonate ions, mimicking the composition of bone mineral phase. The second case study deals with the characterization of gelatin and poly(vinyl alcohol) (PVA) hydrogels, especially in terms of the self-assembly and interaction with water, and with the evaluation of their use as scaffolds for bone mineralization. We constructed a ternary phase diagram at varying concentration and gelatin/PVA ratio and we evaluated the stability at 37 °C. A point of the phase diagram was then selected and characterized at multi-scale levels by means of SEM, DSC, SAXS and rheology. The selected specimen was cross-linked with GDE and BDGE (1,4-butanediol diglycidyl ether). The freeze-dried cross-linked hydrogels were soaked in a simulated body fluid (SBF) at 37 °C and the mineral phase formed was characterized through TGA, SEM and XRD. The results demonstrate that hydrogels cross-linked with BDGE show in SBF very promising stability and mineralization properties.

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[10]Cyclophenacene: one more case of NICS failure

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Nucleus independent chemical shift (NICS) (1) is considered to be a useful measure of the magnetic shielding effect caused by the aromatic ring current. Owing to the easiness of the calculation and the presumed accuracy, NICS has become very popular especially among organic chemists. However, several criticisms have been raised so far concerning its validity (2). Here, we show a very clear example of a wrong application of the NICS, leading to the conclusion that [10]cyclophenacene is an aromatic molecule (3). Actually, the NICS value calculated in the center of gravity at B3LYP/6-31G(d) is -5.3, which indicates a substantial aromatic character; but, quite remarkably, this is the negative of the isotropic component of the shielding tensor formed by three large and opposing diagonal components, whose values are: xx=16.14, yy=16.08, zz=-16.34. The zz component is the result of a large paratropic, i.e., antiaromatic, global ring current induced by a magnetic field parallel to the main symmetry axis of the molecule.

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A new 3D-nanostructured organic/inorganic material for industrial applications

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The crystallization of biological macromolecules is of great interest in the scientific community. Nevertheless the crystallographic data currently available are often deficient and can represent a serious limit to the progress of molecular biology applications. The development of simple, easily reproducible and economical crystallization techniques also fascinates the biopharmaceutical sector: to date, 80% of the final cost of the biofarm lies in the purification phase, which involves the use of expensive chromatographic separation methods.

In this work the preparation and characterization of a new 3D-nanostructured organic/inorganic material for alternative crystallization of biological compounds is presented.

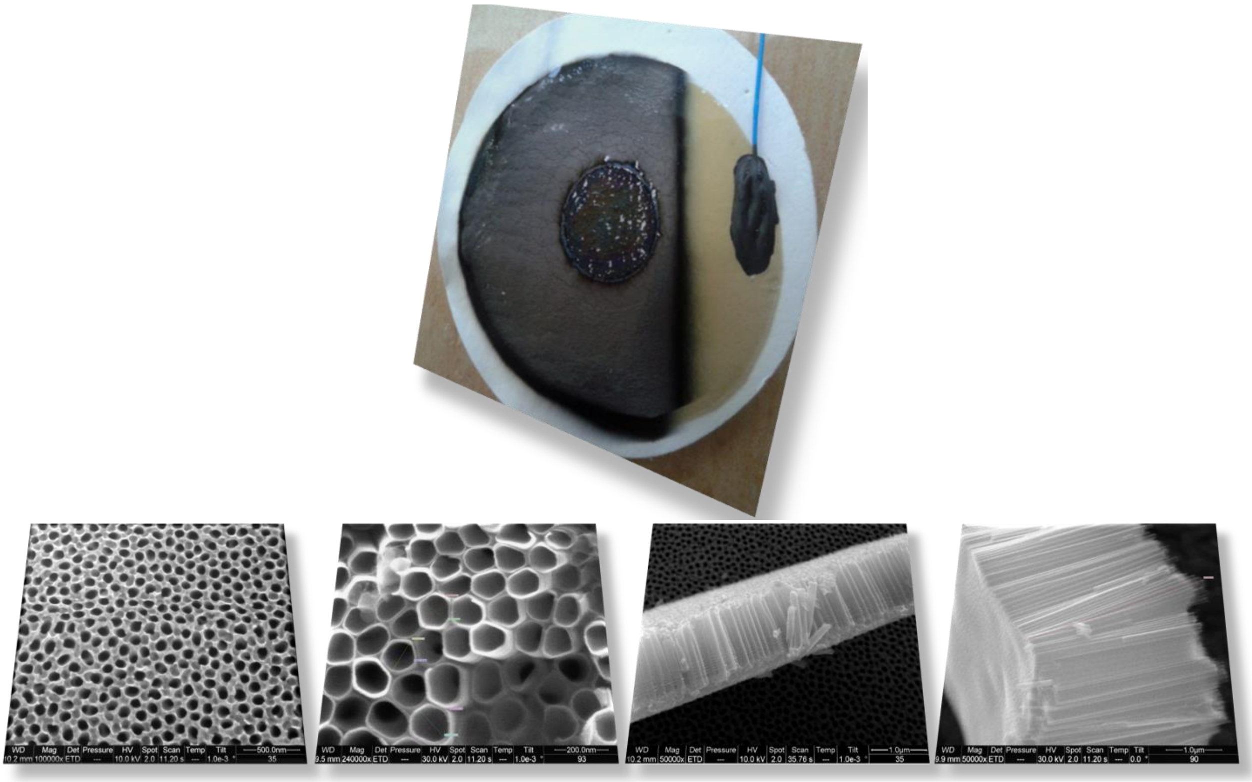

Figure 1. The new 3D-nanostructured organic/inorganic material is formed by titania nanotubes obtained from electrochemical treatment of metal titanium sputtered on porous polymer membranes.

Effect of $VNbO_x$ on the hydrogen storage properties of MgH_2

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Solid state hydrogen storage represents one of the most promising solution for the diffusion of Fuel Cell technology for on- and off-board applications. In the last years several efforts were addressed to find a valid candidate that fits the parameters fixed by the department of energy of US (DOE)(1). In this context, MgH_2 has attracted many attentions thanks to its high gravimetric capacity of 7.6 wt% of H_2, low cost and availability. But the high desorption temperature (450 °C) and high pressure required for the re-hydrogenation, represents a not yet overcome issue limit for practical applications.(2) In last 20 years various strategies were developed to improve the sorption properties of MgH_2. In particular, the addition of V-based and Nb_2O_5 compounds allowed to release hydrogen reversibly at 300-350 °C.(2)

Based on this considerations, we investigated, for the first time by our knowledge, the effect of the addition of $VNbO_x$ compound on the sorption properties of MgH_2. The sorption measurements showed a significant reduction of the desorption temperature from 330 °C to 230 °C for the doped sample. Interesting, 5 wt% of hydrogen was re-absorbed in 5 minutes at 160 °C under 20 bar of hydrogen pressure and at 275 °C for 70 consecutive cycles. The reduction of the activation energy in the desorption process (98 kJ/mol) confirmed the high performing catalytic activity of dopant.

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Halloysite Nanotube/Polymer Composites as Sustainable Consolidation and Protection Protocol for Waterlogged Archaeological Wood

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Within the cultural heritage issue, waterlogged archaeological wood plays a relevant role and its conservation is a challenging task (1). In this work, we proposed an innovative consolidation protocol based on Halloysite nanotube dispersions in different polymers. The nanotubes are used like nanocontainers for loading and triggered release of calcium hydroxide.

The incorporation of $Ca(OH)_2$ into the nanotube lumen retards the carbonatation delaying the reaction with CO_2 gas. The obtained materials were tested for wood protection and consolidation.

A comprehensive characterization of the materials was carried out through morphology, wettability, thermal degradation and tensile properties. The treatment with pristine halloysite nanotubes does not generated an enhancement of the mechanical performance and did not alter the thermal properties of the woods. The co-presence of polymer and $Ca(OH)_2$ loaded nanoparticles generated a more uniform nanotubes distribution in the lignin channel structures and a significant enhancement of the mechanical properties with respect to the pristine halloysite treatment. Afterwards, the co-presence of the polymer and calcium hydroxide trigger the response to acid exposure minimizing the pH drop-down.

This work proposes the use of halloysite/polymer mixture in a new protocol for waterlogged archaeological wood consolidation and represents a starting point to develop, with a biocompatible approach, smart composite material in which the nanotube cavity is filled with active species for wood protection or active response to external stimuli.

These features are promising for a composite nanoadditive in long-term smart protection of waterlogged archeological woods.

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ZnO@Ag Patchy Nanostructures for Photo-degradation of Organic Contaminants

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Nowadays, the possibility to tune and to enhance the charge separation at a metal@semiconductor interface for the fabrication of solar energy conversion devices is deeply investigated [review Bari]. Basically, semiconductors, i.e. zinc oxide (ZnO) and titanium dioxide (TiO_2), widely employed for Dye Sensitized Solar cells and as photo-catalyst for the removal of environmental pollutants, can be interfaced with noble metals, in particular silver (Ag) or gold (Au) nanoparticles, in order to ensure a photo-induced electrical communication across the nano-junction. Different charge transfer pathways can be (photo)induced depending on the size and geometry of the nanostructures [2]. The fabrication of nanostructures with a semiconductor core (ZnO or TiO_2) with a surface decoration obtained by the deposition of Ag or Au nanoparticles was demonstrated to ensure charge transfer from the conduction band of the SC to the Fermi level of the metal, so that reducing the charge recombination and enhancing the photocatalytic performance [3]. In this contribution, a simple synthesis procedure to obtained ZnO@Ag patchy nanostructures ensuring ZnO wurtzite phase was proposed. Morphological and physico-chemical characterizations of such nanojunctions were carried out. Then, the photocatalytic activity of bare ZnO and ZnO@Ag patchy nanostructures was investigated by using methylene blue as standard compound to be degraded. The reaction rate was found to be improved by 212% under 370-800 nm wavelength range illumination in presence of silver. Finally, the degradation of 2,4-Dichlorophenol (as an example of a real contaminant) was followed under sunlight illumination. In this case the reaction rate for ZnO@Ag hybrid nanostructures was improved by 490%.

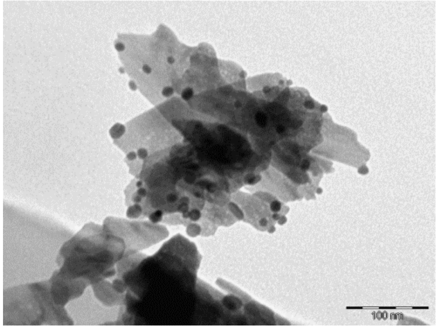

Figure 1: Transmission Electron Microscopy image of the synthetized ZnO@Ag Patchy Nanostructures.

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Nanomaterials for Enzymatic Immobilization

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In recent years research involving nanoparticles and nanoscale materials has generated a great deal of interest from scientists and engineers of nearly all disciplines. This interest has been motivated to a large extent by reports that a number of physical properties including optical and magnetic properties, specific heats, melting points, and surface reactivity are size-dependent. These size-dependent properties are widely believed to be a result of the high ratio of surface to bulk atoms as well as the bridging state they represent between atomic and bulk materials.

The interest in biocatalysts for chemical production continues to grow because they generally have high stereo-, chemo-, and regioselectivity. The fragile nature, high cost, and high loadings required for commercial production limits the use of free enzymes. Enzyme immobilization is utilized to surmount the stability, recovery, and recyclability disadvantages of using enzymes in solution, making them industrially and commercially viable (1).

Nanomaterials are particularly suitable for enzymatic immobilization.

Among nanomaterials, nanofibers represent one of the most attractive nano-device for the production of high added value products. When the diameters of polymer fiber materials are shrunk from micrometers to sub-microns or nanometers there appear several amazing characteristics such as very large surface area to volume ratio flexibility in surface functionalities, and superior mechanical performance (stiffness and tensile strength) compared with any other known form of the material.

Membranes of electrospun Nylon 6 and polyurethane nanofibers were prepared and functionalized to be used for laccase and lipase immobilization (2).

Other materials like ordered mesoporous silicas (1) or magnetic nanoparticles (3) have been synthesized, functionalized and used for enzymatic immobilization.

The different supporting materials are analyzed and the enzymatic immobilization efficiency has been calculated and compared.

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Thermal Analysis and Biological Properties of Silica/PEG hybrids synthesized via Sol-Gel methods

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Sol-gel is the method of making glasses and ceramics at low temperature. The low processing temperature combined with the high sol homogeneity make the sol-gel an ideal technology for the fabrication of organic-inorganic hybrid nanocomposites by entrapping various thermolabile organic polymers in a glassy matrix. Moreover, it is found that sol-gel materials exhibit higher bioactivity and biocompatibility (1) than the same materials prepared using other techniques (e.g. melt-quenching technology), due to the hydroxyl groups on their surface, which stimulate hydroxylapatite nucleation, thus promoting the osseointegration. In this work, inorganic/organic hybrid materials containing SiO_2 and 60 or 70 wt% of polyethylene glycol (PEG) with average molar mass of 400 g/mol were prepared by means of sol-gel process, using tetraethyl orthosilicate as metal alkoxide precursor of the inorganic phase. PEG, previously dissolved in ethanol, was added to the synthesized silica sol. The thermal behavior of the obtained gels was investigated by simultaneous thermogravimetry/differential thermal analysis (TG/DTA) to establish the best temperatures for their heat treatment. The two materials undergo a two-step dehydration followed by three different exothermic effects in the range 200-400 °C, accompanied by mass losses of about 35 and 58% for the hybrids containing 60 and 70% of PEG, respectively. Moreover, the large mass loss observed indicates that the thermal decomposition of PEG occurred simultaneously in the same temperature range: the higher the mass loss percentage the higher the PEG content in the hybrid gel (4). At temperatures higher than 600°C PEG seems to be completely absent from the material. The chemical structure of the obtained SiO_2/PEG 60 and 70wt% was also investigated by FTIR spectroscopy. In the spectra of both samples, all the typical bands of the silica sol-gel materials are present but with a reduced intensity. Moreover, some polymer bands whose intensity increases with the PEG amount are observed. SEM micrographs showed that the materials are homogeneous and no significant differences were present between the two materials. In the SEM images apatite deposition is clearly visible on sample surfaces in recorded after SBF test (3). The EDS confirms that the observed layer is composed of calcium and phosphate. Cytotoxicity assays were performed using a WST-8 assay, a colorimetric test. The NIH-3T3 murine fibroblast cell line (ATCC, USA) were grown in DMEM medium (Gibco, CA, USA) and treated with the extracts of the materials. The results show that in the presence of hybrids, cells are more viable than control cells (2). The best results were obtained for the material with 70wt% of PEG.

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Novel Approaches To Remove And Recover Tetracycline From Wastewater

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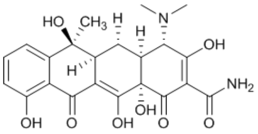

Figure 1. Tetracycline

For years, many articles have been reported in literature and related to the presence of new compounds, called "emerging pollutants", in wastewater and aquatic environments. As reported by Deblonde et al. (1) these pollutants are considered new products or chemicals without regulatory status and whose effects on environment and human health are unknown.(1) The number of these chemicals and compounds are increasing due to the development of resources and technologies. As a result, these undesirable compounds are being released, knowingly or unknowingly, into the aquatic environment affecting the whole living organisms. (2) Consequently many efforts and suitable remediation methods have been developed to remove these pollutants from water. In this work due to our expertise in color removal form wastewater using suitable adsorbent materials (3, 4, 5), alginate micro beads wrapped with chitosan were presented removing tetracycline from water (see Figures 1 and 2). Along with the removal of tetracycline from water, the recovery of the pollutant was obtained modifying the ionic strength of the water suspension of alginate beads loaded with tetracycline. However, under these experimental conditions the degradation of beads occurred and for that reason an alternative strategy was proposed. The use of alginate/chitosan beads modified with TiO_2 enabled, under UV irradiation, the degradation of the blocked tetracycline inside the beads reusing the adsorbent material for several cycles of adsorption. The use of advanced method of oxidation was also proposed using H_2O_2 and Fe^{2+}/H_2O_2. As a result the recycle of both the pollutant and the adsorbent material was presented in this work.

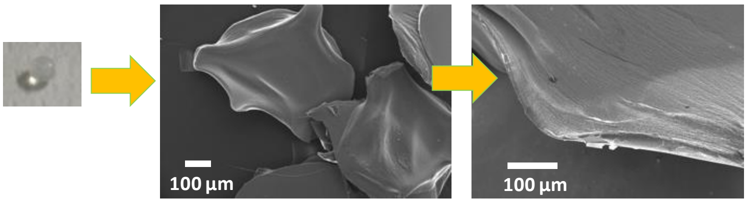

Figure 2. Camera Picture of a single Alginate micro bead and the related SEM images

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An innovative application of polyamidoamine-based hydrogel for removal of blue and red dyes from wastewater

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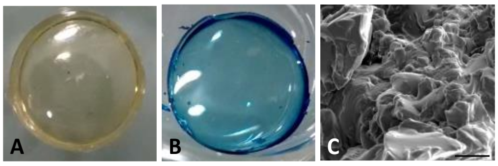
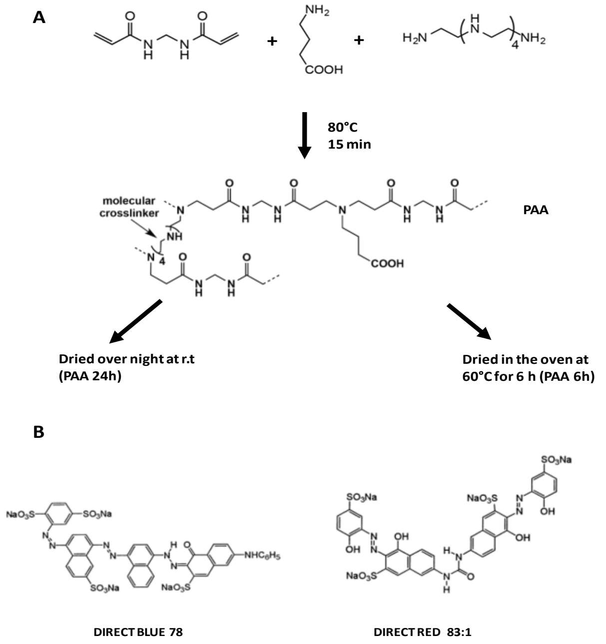


Figure 1. Camera pictures of unloaded hydrogel **(A)** and DB dye loaded hydrogel **(B)**; SEM image of hydrogel, scale bar is 50μm **(C)**.

One of the major problems related to the use of dyes in industrial applications is their elimination from the water or the soil and eventually their recovery and reutilization. We report the use of a polyamidoamine-based hydrogel (PAA), prepared by Michael-type polyaddition in water (1), to efficiently adsorb two anionic textile dyes, Direct Red and Direct Blue, from aqueous solutions (Scheme 1 and Figure 1). We have investigated several parameters, such as the pH of solutions containing dyes, the amount of hydrogel and dye, and the effect of the temperature values. The hydrogel can be dried in different conditions and reswollen using water solution containing the dyes. We have observed that the temperature for the dehydration play a major role in determining the subsequent adsorbing behavior. The results showed that the adsorption process could be attributed to a combination of electrostatic attraction and intermolecular interactions between hydrogel functional groups and the dye molecules. Visible absorption spectroscopy and FTIR-ATR were used to support the findings and to determine the rate of the adsorption, which follow a pseudo-second-order kinetics. The excellent ability of PAA to sequester the dyes suggests that such type of hydrogel could be used as a promising adsorbent material for the removal of anionic molecules from wastewater. As an example, in Figure 1, results related to the adsorption of Direct Blue are reported.



Scheme1. (A) Steps related to the synthesis of hydrogel: N,N'-methylenebisacrylamide was dissolved and mixed with 4-aminobutyric acid; then pentaethylenehexamine was added and the hydrogel PAA was obtained. PAA was dried for 24h (PAA 24h) and in the oven for 6h (PAA 6h). **(B)** Chemical structures of DB and DR dyes. The color index, as a world identification system of recognition, associated to each dye is also reported.

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Olive pomace as a wide-ranging bioremediation strategy to adsorb and recover dangerous disperse industrial dyes from wastewater

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In this work industrial dyes, Disperse Blue, Disperse Red and Orange (DB, DR and DO, respectively), were studied as model pollutants to show the excellent performance of olive pomace (OP) to sequester and recover these dangerous dyes from wastewater (Figure 1). (1) Several complementary techniques were adopted to characterize the nature of interaction and the adsorption processes. In batch systems with respect to contact time, pomace dosage, pH and temperature were investigated. SEM, FTIR-ATR, TG and XPS analyses appeared as powerful tools to characterize olive pomace, before and after the adsorption of dyes, while UV-Visible analyses were used to quantify the amount of loaded dyes on adsorbent material. The pseudo-second order kinetic model well fitted the experimental data and described the kinetic of the adsorption processes. The dyes desorption in glacial acetic acid was also obtained enabling the recovery of dyes. The recycle both of adsorbent material and dyes were presented. Five consecutive cycles of adsorption and desorption were performed and the absence of any degradation processes affecting the dyes after the adsorption/desorption cycles were observed. The recorded absorption spectra, in acetic acid solutions, before and after the desorption, confirmed these results. An environmentally friendly and a low cost material is thus presented, showing the excellent olive pomace potential both in disperse dyes adsorption (with an efficiency of around 100%) and desorption (with a mean value of 80% for each cycle). An alternative environmental friendly use of olive oil solid residues is presented.

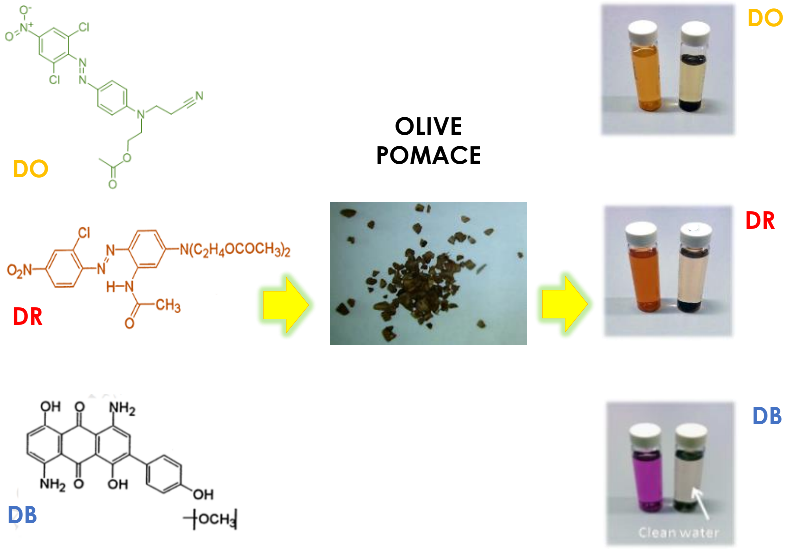

Figure 1. Schematic illustration of the adsorption process. The camera pictures of water containing dyes before and after the adsorption process are reported.

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Electrochemical removal of humic acids from water using aluminum anode

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Humic substances (HS) represent an important fraction of the recalcitrant material to biological treatment of the landfill leachates (1). They are organic macromolecules with high structural complexity, composed of a skeleton of aromatic blocks. They have a significant influence on the efficiency and operation costs of water treatment processes. Several studies have been developed with the aim to remove humic substances from wastewater (2). The most common and economically feasible process is considered to be coagulation/flocculation by using iron, aluminum or calcium ions. In recent years there is an increasing interest on electrochemical processes (EC) as an attractive technique for wastewater treatment (3). Different reactions can occur at the electrodes and in solution. Among the anodic reactions, the oxidation of the metal electrode in its cation and the oxidation of organic pollutants are of particular interest. Using aluminum anodes the following semireaction can occur: $Al \rightarrow Al^{3+}_{(aq)} + 3e^{-}$. Similar reaction is produced using iron anodes. Moreover, using the appropriate electrodes and the electric potential, oxidation of organic compounds can occur directly on the anode, or in solution via oxidant compounds produced at the anode, such as chlorine from chloride ion : $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$. In this communication we report a study on the effect of density current and NaCl concentration on electrochemical removal of humic acids via electrocoaculation and electrooxidation, using aluminum electrodes. The dissolution of these electrodes by oxidation to ions should decrease the electro passivation due to the accumulation of organic compounds at the surface of the **electrodes.** The following figure reports the main result (Figure 1).

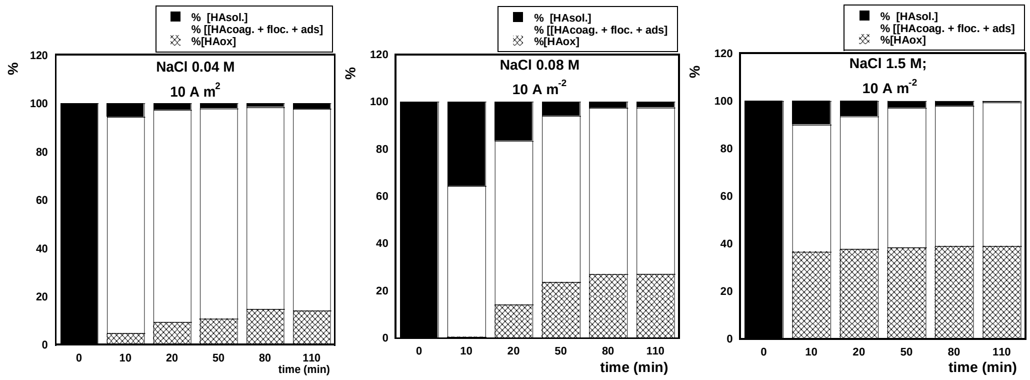

Fig 1. time dependence of the % HA removed by precipitation or by oxidation for different NaCl concentrations.

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Microstructural and physicochemical characterization of $(AlCl_3)_x$: (1-ethyl-3-methyl-imidazolium chloride)$_y$ solutions as electrolytes for Aluminium rechargeable batteries

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Al-ion technology is now getting much attention from research on rechargeable batteries, thanks to the huge natural abundance of aluminum and to the potentially high energy density that can be obtained through a 3-electron redox process. In this work, thanks to a multi-technique approach, the ionic liquid composed by aluminum chloride and 1-ethyl-3-methyl-imidazolium chloride is systematically studied, varying the molar ratio of the two components (from 1.1 to 1.7), to find out which is the best composition to be employed in a rechargeable V_2O_5-based system. The several employed techniques, ranging from NMR to DSC, from EIS to galvanostatic cycling, show that the 1.2 molar ratio composition is the best compromise among high ionic conductivity, use of low quantity of the highly toxic $AlCl_3$, and consistent presence of $Al_2Cl_7^-$ complex.

$TiO_2/BiVO_4$ Heterojunction for Photoelectrochemical Water Splitting

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Photoelectrochemical (PEC) water splitting is a promising strategy to capture and store solar energy into hydrogen as clean fuel. The $TiO_2/BiVO_4$ heterojunction has recently attracted increasing attention, since it allows to exploit the intrinsic properties of the two materials, namely the photoactivity of $BiVO_4$ under visible solar irradiation and the highly negative (respect to RHE) conduction band (CB) position of the TiO_2 component (1). Such combination should allow to obtain a stand-alone composite photoanode able to carry out complete water splitting under visible light and without the application of an external bias. Even though the electron transfer from a low-lying CB of $BiVO_4$ to a more negative CB of TiO_2 is in principle thermo-dynamically unfavourable (2,3), preliminary evidences of this phenomenon are reported in recent literature (3,4). The injection of visible-light excited high-energy electrons from $BiVO_4$ to TiO_2 (Figure 1) can account for the observed hydrogen production through bias-free photocatalytic water splitting (3).

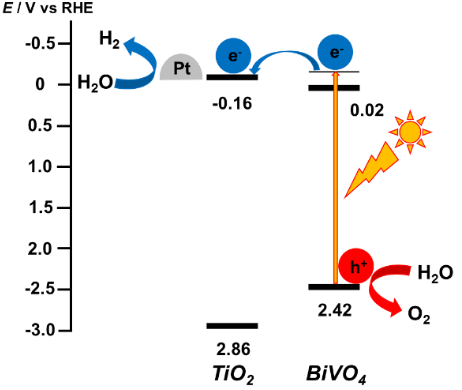

Figure 1. Proposed electronic interaction mechanism for water splitting with the $TiO_2/BiVO_4$ heterojunction.

Inspired by this counterintuitive electron transfer, we prepared transparent $TiO_2/BiVO_4$ heterojunction photoanodes by spin coating onto FTO and characterized the films through PEC measurements. As shown in Figure 2, the coupled system is active at wavelength > 420 (trace a), suggesting that TiO_2 gets sensitized $BiVO_4$, while negligible photocurrent response was attained with the TiO_2 film (trace c). Back-side irradiation (through FTO, Figure 2 trace a) leads to larger photocurrents respect to front side irradiation (trace b), because of the poor electron transport typical undoped $BiVO_4$. Noteworthy, the heterojunction system produces photocurrent under visible light irradiation even without external bias (inset in Figure 2), supporting highly reducing photoexcited electrons in $BiVO_4$ are able to flow into the TiO_2 CB.

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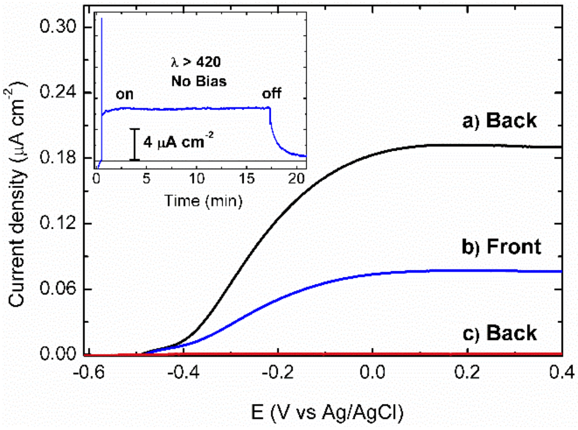

Figure 2. Visible light ($\lambda > 420$ nm) photoelectrochemical analysis in 0.5 M Na_2SO_3, 0.5 M potassium phosphate buffer, pH = 7: linear sweep voltammetry analysis of a), b) $TiO_2/BiVO_4$ and c) TiO_2. Inset: chronoamperometric analysis of $TiO_2/BiVO_4$ without any external bias.

Further evidence of this mechanism is gathered through incident photon to current efficiency measurements, showing that in the coupled system TiO_2 is sensitized by $BiVO_4$ up to 490 nm, while $BiVO_4$ alone is active up to 520 nm. This suggests that electrons in $BiVO_4$ need to be excited with a small extra amount of energy in order to be transferred to the TiO_2 CB.

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Structural and transport properties of $Na_{0.44}MnO_2$, a tunnel oxide cathode material for rechargeable Na-ion batteries

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Nowadays, lithium-ion batteries (LIBs) are considered the best technology for rechargeable energy storage because of their high energy density, high efficiency and long cycle life. However, due to a predicted ever-growing demand of lithium, concerns arise about its future availability and cost, in particular for large-scale energy storage applications. For this reason, research efforts are devoted to find alternative chemistries, based on abundant, cheap and environmentally friendly materials. In this context, sodium-ion rechargeable batteries are acquiring increasing importance.

Among various cathode materials with potential use in Na-ion batteries, one of the most interesting cathode material is $Na_{0.44}MnO_2$. This oxide is characterized by a peculiar crystalline structure, in which Mn (III) ions, in pyramidal coordination, and Mn (IV) ions, in octahedral coordination, are connected to form tunnels running along the *c* crystallographic axis. Within the tunnels, the Na ions are placed on partially occupied crystallographic sites, either within small tunnels (Na1) or larger S-shaped tunnels (Na2 and Na3). This characteristic structure ensures high ion conductivity for the material, especially along the direction of the tunnels, which offers an advantageous path for the intercalation and migration of sodium ions.

In this study we investigate the structural and transport properties of $Na_{0.44}MnO_2$ by means of high temperature neutron diffraction and molecular dynamics simulations, in order to shed light on the intercalation properties of this interesting material.

The evolution of structural parameters along with temperature shows that no phase change is expected in the whole temperature range considered (30-800°C) and that the three sodium ion positions are all partially filled, even at room temperature.

Na-ion migration within the tunnels is clearly visualized through analysis of the Na-ion trajectory plots from molecular dynamics and both intra and inter channel diffusion are investigated. Attention is paid to the potential formation of Na-Mn antisite defects in the structure and their effect on the intercalation mechanism.

Gellan gum hybrid hydrogels for the cleaning of paper artworks contaminated with Aspergillus versicolor

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The degradation of archive materials is related to irreversible phenomena induced by light, temperature, humidity, air pollution, micro-organisms, and use. Among biological factors, fungi can induce harmful effects in paper artworks. Further forms of damage (e.g. artwork swelling, fibre lifting and sheet delamination) can be caused by water immersion, which is one of the most commonly used methods for cleaning paper. To avoid damage it is necessary to control the amount and absorption rate of water by paper. Recently, gellan gum hydrogels have been proposed as effective tools to allow contaminant removal from paper supports, owing to the controlled water release and adhesive properties of gellan gum. In this study hybrid hydrogels were fabricated by doping gellan gum either with calcium compounds (calcium sulphate, hydroxide, chloride, and acetate) or titanium dioxide nanoparticles in order to evaluate their ability in cleaning different types of paper (1).

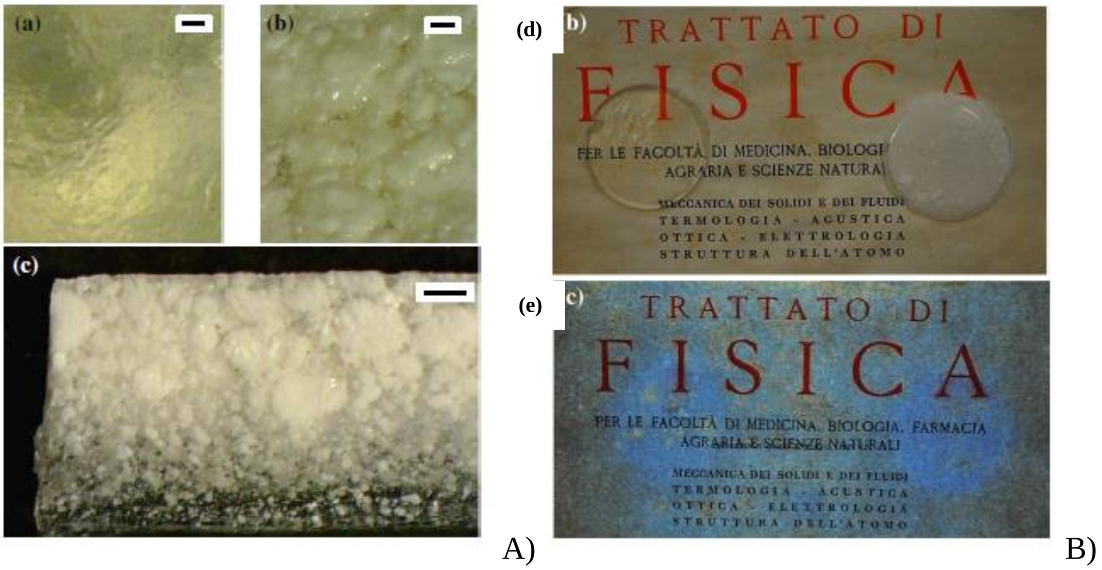

Figure 1. A) on the left: a) Top view of a gellan gum hydrogel; b) top view and c) cross section of a gellan gum hydrogel loaded with titanium dioxide nanoparticles. B) on the right: Cleaning, decolouring action, and biostatic/biocidal activity by gellan gum/calcium acetate/TiO_2 nanoparticle hybrid hydrogels d) during the treatment, and e) after a further 15 days in a climatic chamber under a Wood's lamp.

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Wild-type, Nickel-substituted and mutated (N47S/M121L, HPAz) Azurin DFT models: Structures and Redox Potentials

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Azurin (Az) from *Pseudomonas aeruginosa* is a blue copper protein belonging to the family of cupredoxins (1,2). The T1 copper active site consists of a trigonal bipyramidal coordination geometry where the copper ion is coordinated by a cysteine (Cys112) thiolate group and two histidine (His46 and His117) nitrogen atoms. The thioether group from a Met residue (Met121) and the backbone amide oxygen of a glycine (Gly45) constitute axial ligands. Cupredoxins span a wide range of reduction potentials (E^0) going from stellacyanin having the lowest potential of ca. 184 mV to rusticyanin showing the higher potential of ca. 680 mV. Several works have been devoted to the understanding of the factors influencing E^0 by changing primary coordination sphere ligands or exploring secondary coordination sphere mutations. To this goal, a series of Az mutants have been designed and showed that E^0 could be tuned over a very broad range (between 90 mV and 640 mV) without significantly perturbing the metal binding site. Among these mutants, the HPAz variant (containing the mutations: Met44Phe, Asn47Ser, Phe114Asn, Gly116Phe and Met121Leu) (3) showed the highest E^0 value (970 mV) ever reported for Az while a significant lowering of E° value (-590 mV) has been reached in a Ni-substituted Az (4).

In the present work, DFT models were used to evaluate the E^0 of wild-type Az, Ni-subst Az and two mutants (N47S/M121L and HPAz) of protein Az. The active site models were constructed including the copper or nickel ion and the coordinated residues (Cys112, His46, His117, Met121 and Gly45). The Met44, Asn47, Phe114 and Gly116 residues relevant for this study were also included. The computed structures for the oxidized and reduced forms of wild-type Az, N47S/M121L and HPAz mutants nicely reproduce the geometrical features of T1 copper sites. Moreover, the DFT models revealed the expected hydrogen bonding patterns within secondary coordination spheres. B3LYP energies and Gibbs free energies computed on the optimized structures of the oxidized and reduced species were combined to evaluate E^0. All calculations were performed using the ORCA program package (5). The results show that the implemented strategy is able to reproduce the experimental lowering or increasing of E^0 among the studied Az proteins.

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Elettropolymerization of push-pull copolymer for flexible optoelettronic device

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Push-pull polymer systems containing naphthalenediimide (acceptor) and thiophene (donor) derivatives exhibit high air-stability, good processability, low band gap and large electron mobilities, principally due to their substantial crystalline structure or ordered supramolecular packing (1,2). In addition, recent reports demonstrated the capability of new symmetric naphthalenediimidequaterthiophene (s-NDI2ODT4) systems to electropolymerize alone or with EDOT, yielding polymers with controlled donor/acceptor monomer ratios along with low band gaps, a wide optical absorption range extending to the near IR region, tuned electrical properties, tunable thin-film surface morphology and hydrophilicity as well as high coloration efficiency in electrochromic devices (3). Moreover, fulleropyrrolidine derivatives tailored with thiophene substituents have been succesfully employed as electron acceptors especially for the fabrication of organic heterojunction solar cells (4).

Herein, copolymers of new bithiophene fulleropyrrolidine bisadducts (bis-C60Bi) systems and s-NDI2ODT4 have been successfully obtained by anodic oxidation of the monomers on flexible ITO/PET electrodes. XPS and UV-VIS spectroscopy as well as cyclic voltammetry have been employed for characterizing the thin film chemical features, the band gap and the HOMO and LUMO levels. The electronic transfer data show that both the homopolymers and the copolymer behave as acceptor at the interface with P3HT and also an intramolecular charge transfer in the copolymer, confirmed by DFT data. This class of copolymers showed interesting physico-chemical properties and applications including efficient plastic photovoltaic and sensor devices will be shown.

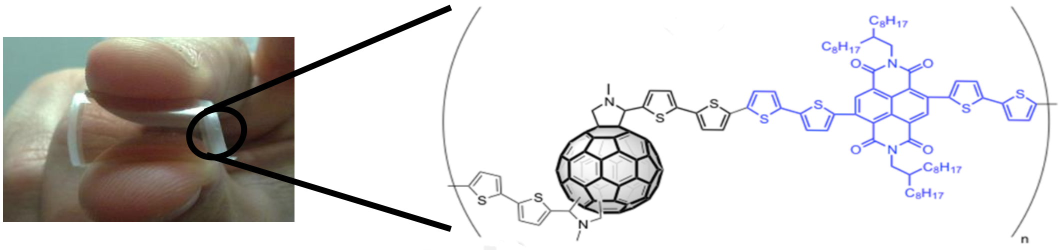

Figure 1: Structure of the new copolymer deposited in thin film for plastic devices.

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Fluorescent discrimination of amine compounds in aqueous matrices

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Detection of amines is very important for monitoring industrial and environmental pollution, checking the quality of food products and medical diagnosis of certain diseases. Moreover, aliphatic amines are found in waste water effluents from pharmaceutical industries, agriculture, and food processing units. Biogenic amines are biomarkers for certain types of diseases such as lung cancer, uremia and hyperammonemia.[1] Several amines affect nervous system, cause abnormalities of blood vessels and cell membranes permeability, induce liver dysfunctions and dystrophy [2]. Therefore, the researchers focused their attention on the development of systems for the detection and removal of these organic compounds from different aqueous matrices [3]. In this work, a highly sensitive «ON–OFF» fluorescent amines trace amounts sensor has been proposed based on a perylene derivative compound.

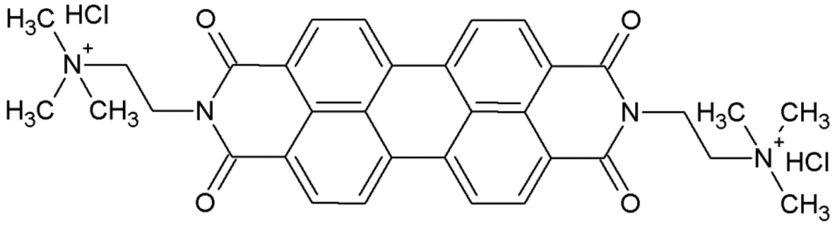

Figure1: Chemical structure of perylene derivative (FR80).

Different class of organic amines, aliphatic, heterocyclic and aromatic ones, were tested and a different electronic communication among amines and the perylene derivative was demonstrated to be the key mechanism for the selective discrimination in aqueous matrices down to 10^{-9} M aromatic amine.

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A multi-analytical non-invasive and micro-invasive approach to oil paintings on canvas or wood. General considerations from some specific cases

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The investigation of artwork to understand story, state of conservation and to know about the composing materials is an issue that is getting growing attention in specialized literature. From a methodological point of view the scientific community is trying to reach a common proposal that could contribute to define a Standard Operating Procedure (SOP) for the application of portable non-invasive and microinvasive techniques for in-situ analyses.

In this work the oil painting on canvas "St. Girolamo nello studio" by Nicolò Buttafoco (1), the oil painting on canvas S. Maria delle Grazie of Cappella Palatina in Palermo, four painted slabs, called "Tavolette fuori posto" (Slabs out of place), of Galleria Interdisciplinare Regionale della Sicilia — Palazzo Abatellis (Palermo, Italy) and two painted slabs belonging to the decoration of the wooden ceiling of the "Hall of Barons" of the Palazzo Chiaramonte, said Steri, in Palermo (Italy) (2,3), were investigated to known the materials and techniques used by the artist as well as to evaluate its preservation status.

The survey has been conducted by applying in situ non-destructive techniques. Depending on specific questions arising during the survey, microsamples were taken and analyzed by micro-destructive techniques. The applied methodology to the specific painting can be considered an application of best practices useful to define the SOP. The obtained information were preparatory to the restoration work and have been used to plan and direct the relative choices.

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This work is part of the project "Development and Application of Innovative Materials and processes for the diagnosis and restoration of Cultural Heritage - DELIAS" - PON03PE_00214_2 (Programma Operativo Nazionale Ricerca e Competitività 2007-2013).

A physical-chemical approach to the investigation of Objects of artistic and archeological interest

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The scientific approach for the Diagnostic of Cultural Heritage allows the knowledge of the constituent materials of an artifact, observing their distribution, studying the phenomena occurring at the interface with the environment, interpreting the changes due to the time and to natural or accidental events, to the understanding the technique used by the artists, and the conservative history of the object.

Sometimes, a specific questions of archeologists and of conservators need a precise answer. The identification of the materials provides a decisive contribution to the correct historical and artistic placement of an artefact or to the history of an archeological object. In addition, the identification of materials allows to trace the cause of any problem, identifying the formed products generated by the transformation of the original materials, the presence of foreign materials to the original work and provide a support for an appropriate project of restoration work.

Generally, a correct protocol of investigation involves a first screening by non-invasive techniques. Only, if necessary and possible, in a second step, the micro-sampling can be done and the samples analyzed in laboratory using micro-destructive techniques.

In this work, some examples of a physical-chemical approach applied to several kind of opera and objects, of archeological and artistic interest, are presented.

This work is part of the project "Development and Application of Innovative Materials and processes for the diagnosis and restoration of Cultural Heritage - DELIAS" - PON03PE_00214_2 (Programma Operativo Nazionale Ricerca e Competitività 2007-2013).

A Ni-Bisdipyrrin Metalloligand as Sensitizer Inserted Into a Zr-based Framework

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As a derivative of the dipyrrins, bisdipyrrin can be regarded as a parent structure of corroles (1). This class of molecules, exhibiting wide visible light absorption, has been described long ago (2), but its use has been limited to the preparation of helicate complexes (3,4), though appearing attractive as sensitizers for solar light capture and optoelectronic applications.

Thus, we synthesized a Ni-based 2,2'-bisdipyrrin complex (Ni-bisdpmCOOH) with absorption extending up to the NIR region (Figure 1). Through electrochemical tests, we found that such molecule has an extremely high LUMO energy, which can potentially allow sensitization of thermodynamically uphill reactions, such as proton and carbon dioxide photoreduction. Therefore, a photo-anode was prepared by absorbing Ni-bisdpmCOOH onto a TiO_2 film, to verify its ability to inject electrons into the TiO_2 conduction band.

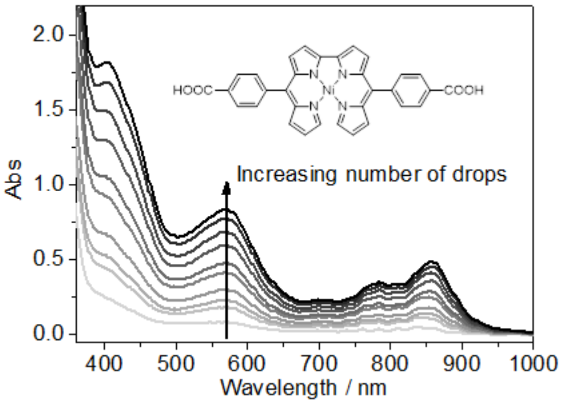

Figure 1. UV-Vis-NIR absorption spectrum of Ni-bisdpmCOOH adsorbed onto a TiO_2 film through drop/drying cycles.

The incident photon to current efficiency (IPCE) measured at 0.61 V vs RHE reported in Figure 2 shows that the sensitized electrode generates photocurrent also under visible light irradiation, which confirms that electronically excited Ni-bisdpmCOOH is effectively able to inject electrons into the conduction band of TiO_2.

Furthermore, aiming at obtaining a material that combines the visible light activity of Ni-bisdpmCOOH with the high chemical stability of metal organic frameworks (MOFs), we succeeded in incorporating this complex into the Zr-containing UiO-66 MOF through the one-pot mixed-ligand approach (5), despite the length of the Ni-bisdpmCOOH molecule largely exceeds that of the primary ligand (terephthalic acid).

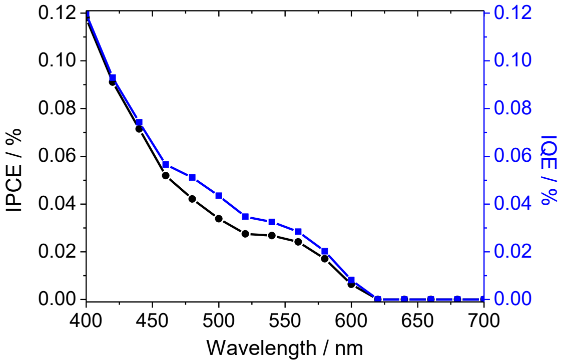

Figure 2. IPCE analysis of Ni-bisdpmCOOH adsorbed onto TiO_2.

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Visible light active self-cleaning materials based on porphyrin-sensitised titanium dioxide

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Starting from second half of last century, nanostructured semiconductors have had a crucial function in the material science because of their wide application field going from renewable energy to organic/hybrid electronics up to photocatalysis.

Among those materials, titanium dioxide is probably the most used because of some important characteristics like the chemical/mechanical stability, environmental sustainability, its low cost and versatility. Indeed, it has been successfully employed as photo- and electro-active component in electronic devices as well as photocatalytic agent[1] in water de-pollution application. Interestingly and importantly together, titanium dioxide may also be applied in the protection of cultural heritages[2] by using its photocatalytic properties to prepare self-cleaning materials able to passivate the manufact surfaces and degrade organic pollution, in this way limiting blackening and reducing maintenance costs.

Unluckily, the photoactivity of TiO_2 under the natural sunlight exposition or artificial illumination is greatly reduced because its low absorption in the Vis range. Hence, in order to improve the material performance under the environmental illumination conditions, the extension of the absorption range in the visible region is crucial.[3]

To this end, we prepared novel TiO_2-based photocatalysts functionalized *in-bulk* with *meso*-tetra(carboxyphenyl)-porphyrin (TCPP) and its metal complex (Me-TCPP) working as visible-light antennas. The peculiar sol-gel synthesis used for the preparation allows porphyrin dye to be bonded inside the TiO_2 structure rather than being easily adsorbed onto the outer surface due to the *in situ* incorporation of the dye during the synthesis of the TiO_2.[3,4] The material structure, composition and electronic properties were investigated by Raman, diffuse reflectance spectroscopy and photoelectron spectroscopy while photocatalytic properties were studied by following the degradation kinetic of carminic acid by UV-Vis spectrophotometry under both UV and visible light.

The sensitised materials showed an enhanced photocatalytic activity in the visible range compared to commercial titanium dioxide under different illumination conditions, indicating that *in-bulk* dye sensitisation is a valuable strategy for effective visible-light TiO_2 photocatalysts.

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2DES reveals ultrafast energy transfer in an organic-biological hybrid made of a synthetic antenna and the reaction center of photosynthetic bacteria

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The photosynthetic Reaction Center (RC) from purple bacterium *Rb Sphaeroides* has unique photoconversion capabilities that can be ideally used to build up bio-hybrid devices for solar energy conversion. Recently, an efficient covalent functionalization of the bacterial RC with an '*ad-hoc*' synthetized organic chromophore has been successfully implemented (1-3). Heptamethyne Cyanine dyes were purposely synthesized to acts as a light harvesting antennas in the visible spectral range, leading to a robust increase in ability of energy photoconversion compared to the pristine native system. We have characterized the dynamics of energy and charge transfer in this bio-conjugated RC employing 2D electronic spectroscopy (2DES). This technique has specific abilities to reveal complex patterns of energy migration and couplings among interconnected chromophores with femtosecond time resolution. Our results reveal the occurrence of ultrafast energy transfer from the artificial light harvesting chromophore towards the monomer bacterio-chlorophyll located in the active branch of the photosynthetic RC.

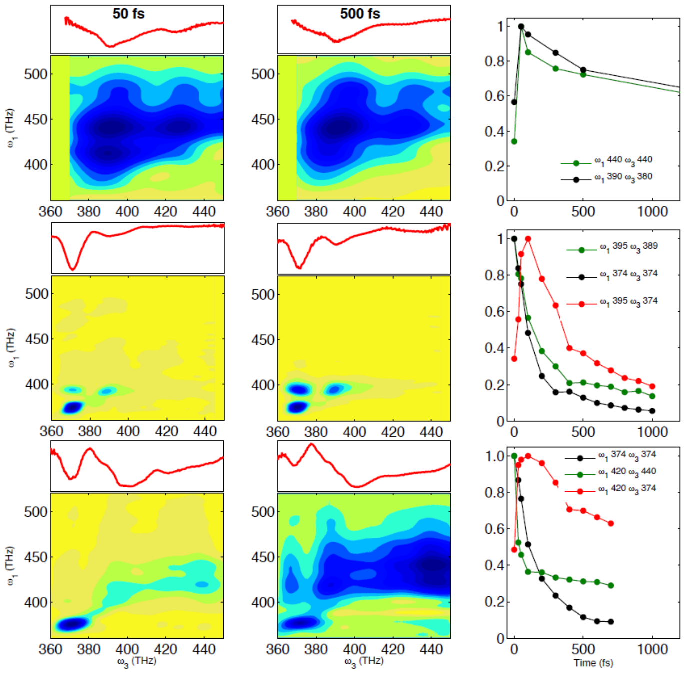

Figure: 2DES Spectra of Heptamethyne Cyanine dye (Top Panel); Bacterial RC (Middle Panel) and Bio-Conjugate RC (Bottom Panel)

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“Active” drop-like particle-based modelfor living cells dynamics

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Liquid droplets and biological cells share some morphological features and mechanical properties. Here, we propose a drop-like, particle-based model to describe the process of cell adhesion onto materials surfaces. The cell is made of “parcel of fluids” or beads and is treated as an active mechanical object that is able to generate adhesion forces. The beads are described by few quantities/parameters related to fundamental chemical forces such as hydrophilicity and lipophilicity that represent an average of the properties of a patch of material or an area of the cells surface. The simulations are able to describe with a single model different cell features and properties, such as adhesion dynamics, motility, shape deformation, and multiple cell organizations onto homogeneous and chemically patterned surfaces.

Langmuir-Schäfer Transfer of Nanocellulose Crystals (NCCs)/Cationic Fullerene dyads onto Solid Substrates

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Nanocellulose crystals (NCCs), bearing sulfate moieties arising from the preparation procedure, are negatively charged and form stable aqueous dispersions; this prevents their assembly at the air-water interface for subsequent transfer onto solid substrates by means of Langmuir-Blodgett methods. An approach that can be employed to allow the assembling of organized NCCs Langmuir films at the air-water interface is the deposition of floating films of suitable amphiphilic substances, able to bind NCCs dissolved in the aqueous sub-phase. The choice of the proper amphiphilic compound has a key role, since chemical or physical interactions among these species and those dissolved in the sub-phase drive the assembly of the hybrid film. A similar approach was employed to realize hybrid films containing both water soluble molecules and amphiphilic compounds (1).

More in detail, in this work, two cationic fullerene derivatives (fulleropyrrolidines), bearing one and two positive charges, were used as amphiphilic compounds to assist the assembly of NCCs at the air-water interface, by exploiting the electrostatic interactions among the positive charges of fullerene derivatives and the negative charges of the sulfate groups present on the NCCs. Subsequently, the transfer of these hybrid layers onto solid substrates was achieved by Langmuir-Schäfer method (2). It was found that NCCs, dispersed in the water sub-phase, could interact with fullerene derivatives floating films, leading to modifications on Langmuir isotherms, yielding to a marked shift towards higher limiting area values. Moreover, the presence of NCCs promoted a decrease of amount and size of fullerene aggregates in floating layers at the air-water interface, as revealed by Brewster angle microscopy. The floating layers were transferred onto ITO/glass substrates and the NCCs presence in the hybrid films was confirmed by multireflection FT-IR spectroscopy with bands at 3340 cm^{-1} (O–H stretching) and at 2850 cm^{-1} (C–H symmetric stretching). Increasing the NCCs concentration in the sub-phase results in a higher NCCs amount in the hybrid film. In addition, the efficiency of Langmuir-Schäfer transfer was confirmed by a linear dependence of infrared absorbance on the number of transferred layers. The typical morphology of NCCs interacting with fullerene films was highlighted by Atomic force microscopy.

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Tracing the geographical origin of lentils by infrared spectroscopy and chemometrics

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Lentil (*Lens culinaris* Medik.) is the fourth most important pulse crop in the world after bean (*Phaseolus vulgaris* L.), pea (*Pisum sativum* L.), and chickpea (*Cicer arietinum* L.). Canada is the world's largest exporter of lentils, while in Italy lentils are a minor legume and can be found in restricted areas. However, Italian lentils present unique and characteristic qualities giving them a higher value, so that many of them have obtained international and national marks linked to their geographical origins, such as "protected geographical indication" (PGI), "traditional food products" (PAT) and Slow Food Presidium. For these reasons, there is a growing demand for analytical methods able to certify the declared lentil geographical origin, in order to protect consumers and producers from fraud and unfair competition.

In this work, the potential of infrared spectroscopic fingerprinting technique for the geographical origin traceability of lentils was investigated. In particular, lentil samples from two different countries, i.e. Italy and Canada, were collected and analysed by Fourier transform near- and mid-infrared spectroscopy (FT-NIR, FT-MIR). Linear Discriminant Analysis (LDA) was used examining the FT-NIR and FT-MIR fingerprints separately and in combination in order to evaluate the spectral range mostly influenced by geographical origin. The LDA classification results were expressed in terms of recognition and prediction abilities (cross validation and external validation). Good classification results were obtained for both FT-NIR and FT-MIR ranges with FT-MIR one giving better prediction abilities, i.e. 95% and 92% for cross and external validation, respectively. The combination of the FT-MIR and F-NIR did not improve the model performances. These findings demonstrated the suitability of the developed methods to discriminate geographical origin of lentils and confirmed the applicability of the infrared spectroscopy, in combination with chemometrics, to solve geographic origin issues of foodstuffs.

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	FIS PO15
Giotta Livia*	FIS PO09
Giovanni Bruno	FIS OR05
Girlando Alberto*	FIS OR25
Gironi Beatrice	FIS OR15
Giunta Carolina	FIS PO47
Gontrani Lorenzo	FIS OR62
Gorecka Ewa	FIS PO20
Gosetti Fabio	ABC/ANA/FISOR07
Gradzielski Michael	FIS OR17
Grigioni Ivan	FIS PO38
	FIS PO46
Grimaldi Antonio	FIS OR69

Groppo Elena*	FIS OR19
Gruttadauria Michelangelo	FIS OR06
	FIS PO42
Guaragnone Teresa	FIS OR34
Guascito Maria Rachele	FIS PO09
	FIS PO10
	FIS PO15
Gubitosa Jennifer	FIS OR30
Guffanti Paolo	FIS OR05
Hamplova Vera	FIS PO20
Harir Mohammed	FIS PO13
Herrebout Wouter	FIS OR18
Holmberg Krister	FIS OR31
Howes Philip D.	FIS OR11
Hreniak Dariusz	FIS OR21
Iacobazzi Rosa Maria	FIS OR11
	FIS OR09
Iagatti Alessandro	FIS PO48
Ilaria Palchetti	FIS OR05
Ingrosso Chiara *	FIS OR05
Innamorato Valentina	FIS PO51
Invernizzi Fabio	FIS OR53
Invernizzi Lucrezia	FIS OR24
Iovino Pasquale	FIS PO36
Isca Clelia	ABC/ANA/FISOR06
Iuliano Veronica*	FIS PO02
Izzo Irene	FIS PO01
	FIS PO02
Izzo Lorella	FIS OR29
	FIS OR60
Janssens Koen	ABC/ANA/FISKN01
Kastro Kepa	ABC/ANA/FISKN02
La Gatta Simona	FIS PO09
	FIS PO48
La Gatta Simona*	FIS OR56
La Mendola Diego	FIS OR47
	FIS PO03
La Nasa Jacopo	ABC/ANA/FISKN02
La Rocca M. Vincenzo*	FIS OR60
Lamberti Francesco*	FIS OR51
Lapedota Angela	FIS OR09
Lapini Andrea	FIS OR15
	FIS PO48
Laquintana Valentino	FIS OR11
Laquintana Valerio	FIS OR09
Latterini Loredana	FIS PO18
Lazzara Giuseppe	FIS OR17
	FIS PO29
Le Donne Alessia	FIS OR52
Le Donne Andrea	TEO OR02
Legrand Stijn	ABC/ANA/FISKN01
Leone Maurizio	FIS OR49
Leone Vincenzo*	FIS PO36
Leonelli Francesca	FIS OR23
Lettieri Raffaella	FIS OR23
Lippolis Vincenzo	FIS PO51
Lisi Luciana	ELE OR20
Litti Lucio	FIS OR51

Paiano Aurora	FIS PO08
Painelli Anna	FIS OR61
Painelli Anna*	FIS OR07
Palermo Anna Maria	FIS PO40
Palleschi Antonio	FIS OR37
	FIS PO23
	FIS PO24
Palumbo Giuseppe	FIS OR44
Pane Katia	FIS OR69
Panero Stefania	FIS OR55
Pannacci Danilo	FIS OR02
Panniello Annamaria	FIS OR20
Panniello Annamaria*	FIS OR03
Paolantoni Marco	FIS OR15
Paolone Annalisa	FIS OR55
Paolucci Francesco	FIS OR50
	ELE OR20
Parisi Filippo	FIS OR17
	FIS PO29
Pati Swapan	FIS OR07
Patrini Maddalena	FIS OR53
Pavel Nicolae Viorel	FIS OR14
	FIS OR70
Pedroni Matteo	FIS OR54
Pelicci Pier Giuseppe	FIS OR50
Pellicer José Antonio	FIS OR43
Perna Filippo	FIS PO15
Perrone Mara	FIS OR30
Perugini Luisa*	FIS PO05
Petraccone Luigi	FIS OR69
Petrella Andrea	FIS OR30
	FIS PO33
	FIS PO35
Petronella Francesca	FIS OR05
	FIS OR01
Petrozza Annamaria	FIS OR51
Piercarlo Mustarelli	FIS PO37
Pieroni Carlotta	FIS OR61
Pierri Giovanni	FIS PO02
Pierri Giovanni*	FIS PO01
Pietralunga Silvia	FIS OR54
Pietropolli Charmet Andrea	TEO OR03
Pifferi Valentina	FIS OR05
Pignataro Bruno	FIS OR06
	FIS OR49
	FIS PO42
	FIS PO47
Pina Joao	FIS PO24
Piovano Alessandro	FIS OR19
Pitonzo Rosa	FIS PO45
Placidi Ernesto	FIS PO23
Placido Tiziana	FIS OR01
Pociecha Damian	FIS PO20
Poggi Giovanna	FIS OR65
Poggi Giovanna*	FIS OR68
Pogni Rebecca	FIS PO13
Pogni Rebecca*	FIS PO31
Polo Annalisa*	FIS PO38

Poma Alessandro*	FIS PO46
Porchetta Alessandro	FIS OR49
Prasetyanto Eko Adi	FIS OR35
	FIS PO34
Prati Silvia	ABC/ANA/FISKN01
Pugliese Diego	ELE OR22
Pulvirenti Alfredo	CSB OR3
Purrello Roberto	CSB OR3
Puzzarini Cristina	FIS OR59
Quarta Alessandra	FIS PO30
Quartieri Simona	FIS OR64
Ragni Roberta	FIS OR56
	FIS PO48
Ramundo Andrea	FIS OR38
Rapino Stefania	FIS PO49
Rapino Stefania*	FIS OR50
Reale Priscilla	FIS OR55
Renda Vincenzo	FIS PO44
	FIS PO45
Resetic Andraz	FIS OR16
	FIS PO20
Ribechini Erika*	ABC/ANA/FISKN02
Ricci Francesco	FIS OR49
Ricci Maria Antonietta	FIS OR35
Rico-Santacruz Marisa	FIS PO47
Ridi Francesca	FIS OR12
	FIS OR27
	FIS OR31
	FIS PO25
Ridi Francesca*	FIS OR22
Ridolfi Stefano	FIS PO44
	FIS PO45
Righetti Pier Giorgio	ABC/ANA/FISOR07
Righini Roberto	FIS PO48
Rimola Albert	FIS KN01
	FIS OR58
Rizzi Gian Andrea	ELE OR21
Rizzi Vito	FIS OR35
	FIS OR43
	FIS PO07
	FIS PO33
Rizzi Vito*	FIS OR30
Rizzi Vito*	FIS PO34
Rizzi Vito*	FIS PO35
Robotti Elisa	ABC/ANA/FISOR07
Rondinini Sandra	ELE OR24
Rosanna Pagano	FIS PO50
Rossi Federico	FIS OR29
Ruffo Riccardo*	ELE KN01
Ruso Krauss Irene	FIS OR10
Russina Olga*	FIS OR63
Saladino Maria Luisa*	FIS OR21
Saladino Maria Luisa*	FIS PO44
Saladino Maria Luisa*	FIS PO45
Salgado Gilmar	FIS PO12
Salustro Simone	TEO OR01
Salvestrini Stefano*	FIS OR40
Sanyal Somananda	FIS OR07

Sartorio Camillo*	FIS OR06
Sassi Paola	FIS PO18
Sassi Paola*	FIS OR15
Satriano Cristina	FIS PO03
Satriano Cristina*	FIS OR47
Saviano Michele	FIS OR11
Scarano Domenica	FIS OR04
Scavo Maria Principia	FIS OR09
Schettini Rosaria	FIS PO02
Schingaro Emamuela	FIS PO01
Scianatico Sonia	FIS PO33
Sciubba Fabio*	FIS OR46
Sciutto Giorgia	ABC/ANA/FISKN01
Scopelliti Michelangelo	FIS PO47
Scudero Martino	FIS OR22
Sebastiani Marco	FIS OR27
Selli Elena	FIS OR54
	FIS PO38
	FIS PO46
Semeraro Paola	FIS OR35
	FIS PO33
	FIS PO34
	FIS PO35
Semeraro Paola*	FIS OR43
Semeraro Paola*	FIS PO07
Serpa Carlos	FIS PO24
Serrano Elena	FIS PO47
Serva Alessandra	FIS OR08
Sessa Francesco*	FIS OR08
Shadi Sawalha*	FIS PO50
Sibillano Teresa	FIS OR01
	FIS OR28
Simona Bettini	FIS PO50
Sinicropi Adalgisa*	FIS PO41
Sissa Cristina	FIS OR07
Smith Vincent J.	FIS PO01
Sodupe Mariona	FIS KN01
Soldà Alice	FIS OR50
Sorrentino Roberto	FIS OR51
Sortino Salvatore	FIS OR35
Spada Lorenzo	FIS OR59
Spicer Christopher	FIS OR11
Spinella Alberto	FIS PO45
Spinelli Daniele	FIS PO31
Stano Pasquale	FIS PO16
Stella Lorenzo	FIS OR23
Stephan Arul M.	ELE OR22
Stevens Molly M.	FIS OR11
Stoppa Paolo	TEO OR03
Stręk Wiesław	FIS OR21
Striccoli Marinella	FIS OR03
	FIS OR05
	FIS OR09
	FIS OR11
	FIS OR20
	FIS OR28
Syrgiannis Zois	FIS PO43
Tabacchi Gloria	FIS OR26

	FIS OR64
Tadini Buoninsegni Francesco*	FIS OR45
Taliani Sabrina	FIS PO12
Tamassia Filippo	FIS PO19
Tartaro Giuseppe	FIS OR28
Tasinato Nicola*	TEO OR03
Taylor Annette F.	FIS OR29
Tealdi Cristina*	FIS PO39
Tedesco Consiglia	FIS PO01
	FIS PO02
Tempesti Paolo	FIS OR67
	FIS PO25
Terenziani Francesca	FIS OR07
Tolmino Riccardo	FIS PO40
Tonelli Monica*	FIS OR27
Toniolo Claudio	FIS PO24
Trabace Maddalena	FIS OR66
Trapani Adriana	FIS OR48
Trapani Giuseppe	FIS PO03
Trifuoggi Marco	FIS PO36
Triggiani Leonardo	FIS OR20
Triggiani Leonardo*	FIS OR28
Trotta Massimo	FIS OR56
	FIS PO09
	FIS PO10
	FIS PO11
	FIS PO16
Trotta Massimo*	FIS PO15
Truppi Alessandra*	FIS OR01
Tursi Antonio*	FIS OR39
Ugliengo Piero	FIS OR58
Ugliengo Piero*	FIS KN01
Vaccaro Lavinia	FIS PO47
Valente Gianpiero*	FIS OR11
Valenti Giovanni	FIS OR50
Valentina Dall'Asta*	FIS PO37
Valentoni Antonio *	FIS PO28
Valle Francesco	FIS OR50
Valli Ludovico	FIS PO09
	FIS PO30
	FIS PO43
Vassallo Espedito	FIS OR54
Vecchio Ciprioti Stefano*	FIS PO32
Venanzi Mariano	FIS OR23
	FIS OR37
Venanzi Mariano*	FIS PO23
Venanzi Mariano*	FIS PO24
Venditti Francesco	FIS OR42
Venditti Francesco*	FIS OR41
Ventruti Gennaro	FIS OR44
	FIS PO01
Verlato Enrico	ELE OR20
Versace Carlo C.	FIS PO27
Vertova Alberto	ELE OR24
Vetri Valeria	FIS OR49
Vezzalini Giovanna	FIS OR64
Vezzù Keti	FIS OR53

Vicini Silvia	FIS PO17
Villa Silvia	FIS OR09
Vischio Fabio*	FIS OR09
Visibile Alberto	ELE OR24
Volpin Stefano	ABC/ANA/FISOR06
Zaccaro Laura	FIS OR11
Zalar Bostjan	FIS OR16
	FIS PO20

Zamirri Lorenzo*	FIS OR58
Zanasi Riccardo	FIS OR18
Zanasi Riccardo*	FIS PO26
Zangarelli Agnese	FIS OR02
Zerbetto Francesco	FIS OR50
	FIS PO49
Zolin Lorenzo	ELE OR22
Zupancic Blaz	FIS OR16