Università di Roma
Tor Vergata

# *Chimica@Tor Vergata*

## *Giornata della Ricerca*
## *del*
## *Dipartimento di Scienze e Tecnologie Chimiche*

**Macroarea di Scienze**
***Aula Magna P. Gismondi***
***Via della Ricerca Scientifica***

**26 Giugno 2017**
**Workshop**

*Benvenuti!*

*Illustri Ospiti, Cari Studenti, Cari Colleghi,*

*è con grande piacere e orgoglio che vi do il benvenuto a questa prima giornata di divulgazione delle attività del Dipartimento di Scienze e Tecnologie Chimiche dell'Università degli Studi di Roma "Tor Vergata".*

*Il nostro "piccolo" Dipartimento ha raggiunto negli anni in cui ho avuto il privilegio di dirigerlo ottimi risultati grazie al contributo di tutti i suoi componenti.*

*Ci siamo fortemente impegnati nelle tre missioni dell'Ateneo: la didattica, cercando di mantenere standard elevati e di migliorarci continuamente, la ricerca, dalla quale abbiamo avuto grandi soddisfazioni sia in termini di pubblicazioni eccellenti che di progetti approvati da agenzie nazionali e internazionali, la terza missione, fornendo servizi di consulenza di elevato livello e curando in particolare la diffusione della cultura della chimica nel territorio e nel Paese.*

*Abbiamo cercato di puntare sui giovani e, nonostante i numerosi vincoli posti dalla legislazione sul reclutamento, abbiamo visto crescere il numero dei nostri ricercatori.*

*Troverete di seguito una breve descrizione delle nostre attività.*

*Oggi ci rivolgiamo ai nostri Colleghi, Studenti e Stakeholders per aggiornarli sul nostro lavoro, confidando che questa giornata possa rappresentare non solo un momento di divulgazione, ma anche, e soprattutto, l'occasione di conoscerci meglio e sviluppare sinergie e collaborazioni.*

*Vi ringrazio di essere qui con noi e vi auguro buon lavoro!*

*Il Direttore del Dipartimento*
*Prof. Silvia Licoccia*

# Dipartimento di Scienze e Tecnologie Chimiche

Il Dipartimento di Scienze e Tecnologie Chimiche dell'Università di Roma "Tor Vergata" offre opportunità di studio e ricerca nelle scienze chimiche. La Chimica è una scienza centrale per uno sviluppo sostenibile: permette di offrire una migliore qualità di vita all'umanità attraverso lo studio di processi di sintesi innovativi, catalizzatori più efficaci, produzione di energia sostenibile, comprensione, attraverso teoria e sperimentazione, dei processi alla base dei complessi sistemi naturali, diagnosi e cura di molte malattie, sviluppo di materiali con nuove proprietà e molto altro ancora.

Il DSTC è identificato dal MIUR come uno dei 350 Dipartimenti di eccellenza nelle Università italiane. L'alto livello della qualità della ricerca è ampiamente documentato sia nei ranking nazionali che in quelli internazionali. La ricerca condotta nel Dipartimento investe la maggior parte delle tematiche connesse alla chimica moderna e alle sue applicazioni. L'ampio spettro delle ricerche, spesso svolte in collaborazioni con istituzioni pubbliche e private nazionali e internazionali, riflette l'interdisciplinarietà presente nel Dipartimento in cui si svolgono attività nelle aree di chimica analitica, chimica fisica, chimica organica, chimica inorganica, chimica applicata, biochimica, fisica e scienza dei materiali. Questa varietà di interessi e attività, assieme a un'ampia attività seminariale, permette di offrire ai nostri studenti una formazione di elevata qualità stimolando lo sviluppo dello spirito critico necessario alle loro attività future.

Altri elementi qualificanti dell'attività di ricerca sono rappresentati dalla partecipazione a numerosi progetti europei e progetti bilaterali così come i numerosi contratti di ricerca con industrie nazionali e internazionali.

Per quanto attiene alle attività di formazione, Il DSTC è il Dipartimento di riferimento per i Corsi di Laurea triennale in Chimica e Chimica Applicata, per la Laurea Magistrale in Chimica e per i Corsi di Dottorato di Ricerca in *Scienze Chimiche* e in *Materials for Health, Environment and Energy*. Al DSTC afferiscono inoltre il CdL triennale in Scienza dei Materiali e Magistrale in Scienza e Tecnologia dei Materiali, di cui il Dipartimento di Fisica è il Dipartimento di riferimento, il corso quinquennale a ciclo unico abilitante (unico in Italia) di "Conservazione e restauro dei beni culturali" nel Percorso Formativo Professionalizzante "Materiale librario ed archivistico", che fa riferimento al Dipartimento di Studi Umanistici. L'offerta didattica non è però limitata a tali corsi, né alla Macroarea di Scienze: i docenti del DSTC sono inseriti nel corpo docente delle Macroaree di Ingegneria e Lettere e nella Facoltà di Medicina.

La qualità delle attività del Dipartimento permette ai giovani laureati e dottori di ricerca che hanno condotto i loro studi presso di noi di trovare in tempi brevi occupazione qualificata presso Università o Centri di ricerca italiani o stranieri e presso realtà industriali.

http://www.stc.uniroma2.it; chimica@uniroma2.it

**9:00** **Apertura lavori:** - **G. Novelli**, Rettore dell'Università di Roma "Tor Vergata"
- **S. Licoccia,** Delegato del Rettore per la Ricerca di Ateneo e Direttore del Dipartimento

**9:15** La ricerca nell'area chimica in Italia: stato dell'arte e prospettive
**R. Purrello (Rappresentante CUN Area 03 – Scienze Chimiche)**

**9:30** Chimica e sostenibilità: materiali per energia ed ambiente
**10:00** Biosensori ottici ed elettrochimici per applicazioni in campo clinico, alimentare e dei beni culturali
**10:30** Cinetica delle trasformazioni di fase: modellizzazione e applicazioni

**10:45** ***Pausa Caffè***

**11:00** L'interazione di H-NS con il suo target DNA
**11:15** Chimica Organica a Tor Vergata: dalla teoria, ai meccanismi, ai prodotti
**11:45** Chimica Inorganica: dalle macromolecole ai materiali
**12:15** Chimica-Fisica applicata alla biomedicina, ai biomateriali e ai beni culturali
**13:00** Collaborazioni internazionali**:** "A Personal History of Porphyrin Syntheses"
**Prof. Kevin M. Smith (Louisiana State University, USA)**

**13:30** ***Pranzo***

**14:30** Collaborazioni internazionali**:** "Templated Materials as Electrocatalysts for Polymer Electrolyte Fuel Cells"**Prof. Plamen Atanassov (University of New Mexico, USA);**
"Understanding Water Transport in Low Temperature Fuel Cells with X-ray Computed Tomography"
**Dr. Iryna V. Zenyuk (Tufts University, USA).**

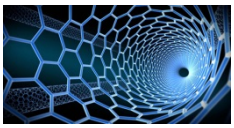
***Sessione presentazioni Dottorandi-Borsisti***

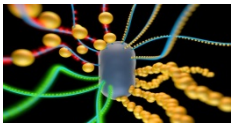
**15:00** **M. Raggio**: Batteri fonti di energia: materiali di carbonio e corroli per catalizzare la riduzione dell'ossigeno
**15:10** **M.R.Tomei**: Sviluppo di sensori elettrochimici in campo ambientale: attività di ricerca all'interno dello Spin-off TECNOSENS
**15:20** **M.Ciocci**: Dalla Biochimica alla Scienza dei Materiali: "*Scaffold*" per la Medicina Rigenerativa
**15:30** **E. Tamburri**: Polimeri e materiali di carbonio nanostrutturati per la progettazione di bioscaffolds e interfacce neurali
**15:40** **C. Marcoaldi**: Sviluppo di campionatori passivi per l'analisi di inquinanti emergenti in acqua marina
**15:50** **R. Carcione**: Il diamante: un gioiello dell'elettronica, ottica e medicina rigenerativa
**16:00** **S. Politi**: Studio dei meccanismi di nucleazione e crescita di metalli e polimeri nei processi di sintesi elettrochimica
**16:10** **F. Sabuzi**: Dal Laboratorio al Mercato: nuovi antibatterici targati Tor Vergata
**16:20** **Tavola rotonda** (PLS ed altre iniziative del Dipartimento)
**17:00** Conclusione lavori

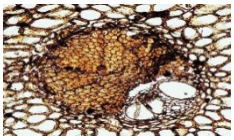
*Durante l'intera giornata saranno esposti poster di approfondimento delle tematiche di ricerca.*

## Chemistry and Sustainability: Materials for Energy and Environment

*S. Antonaroli , A. D'Epifanio, E. Di Bartolomeo, C. D'Ottavi, S. Licoccia, B. Mecheri, F. Mandoj, S. Nardis, R. Paolesse, M. Stefanelli*

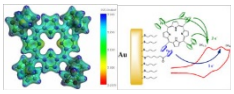




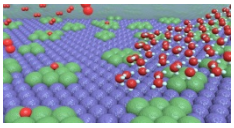


The term sustainability deals with policies and strategies able to agree the current economic, social, and environmental needs of society with the welfare of future generations. The role of chemistry is determining in finding sustainable solutions for various ambitious challenges, as guarantee access to inexpensive, sustainable, and modern energies for all and environmental preservation by reducing the adverse impacts of cities and factories.
Our research activities aim to give a contribution to meet such goals Focus is posed to energy related chemistry and environmental monitoring.
Three main topics can be identified:

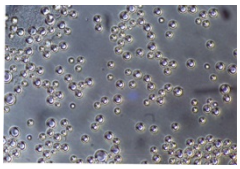
- Materials for Energy Conversion and Storage: research is focussed on the preparation and characterization of nanostructured organic, inorganic and hybrid materials for energy applications. Tailoring the interplay of morphology, microstructure, and surface chemistry on electrochemical properties, we have been developing catalysts, polymer electrolytes, and ceramic oxides for high and low temperature fuel cells, redox flow batteries, and bioelectrochemical systems.

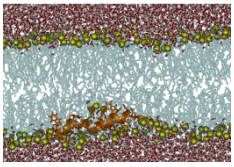


- Biomass for Energy and Fuels: microalgae are promoted as an ideal third generation biofuel feedstock because of their rapid growth rate, $CO_2$ fixation ability, and high production capacity of lipids. We study and select microalgal biomass to obtain high lipids production with good percentage of unsaturated fatty acid extracted.



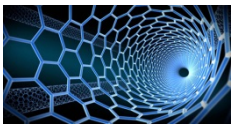
- Environmental monitoring by chemical sensors: research addresses the fine preparation of nanostructured sensitive materials based on porphyrinoids, also in combination with inorganic nanostructures (CNTs or metal oxide NPs). Such hybrid systems possess in fact increased potentialities with respect to single components in sensor applications. The developed chemical sensors and their use in arrays are exploitable for the analysis of gaseous or liquid environmental matrices, giving important contributions for air or water quality control and monitoring.

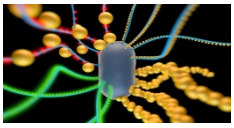


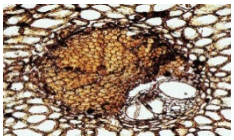


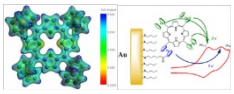
## Optical and electrochemical biosensors for clinical, food and cultural applications: some examples

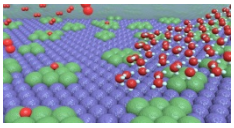
*F. Arduini, D. Moscone, L. Micheli, G. Palleschi, S. Piermarini, A. Porchetta, F. Ricci, G. Volpe*

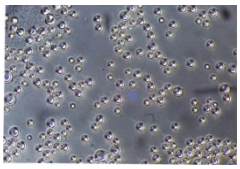


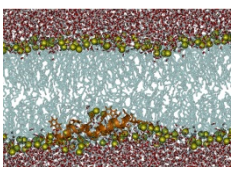












In this talk, some results of optical and electrochemical biosensor applications will be presented:

- for *Diagnostic and Drug Release Applications* using engineering DNA-based Nanodevices. Nature has invented a number of tricks and strategies by which the behavior of proteins and other biomolecular machines can be finely controlled. These highly optimized and evolved mechanisms allow controlling biological pathways with different chemical and environmental stimuli. We have characterized and recreated in-vitro several naturally-occurring mechanisms to control the response of DNA-based nanodevices for diagnostic and drug-delivery applications. Using these mechanisms we can control the activity of DNA-based nanodevices with different chemical and environmental stimuli including pH, antibodies, enzymes, small molecules and electronic inputs;

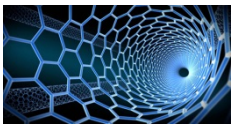
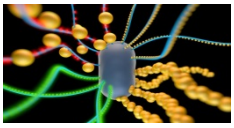
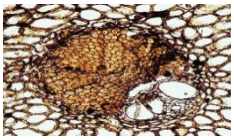
- for *Detection of Bacteria, Virus and Toxin*. We have developed sensitive and selective immune-systems assays with optical/electrochemical detection to measure pathogenic bacteria and virus in and highly dangerous toxins present such as algal toxins in water. These systems are based on the use of magnetic particles coupled with screen printed electrodes (SPEs);

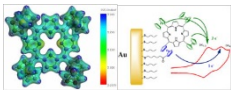
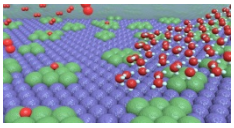
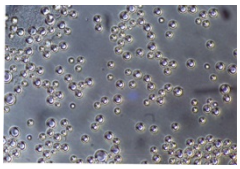
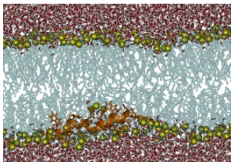
- for *Cultural Heritage applications* (Laura Micheli). Many biosensors, developed for other fields, are also potentially useful as non-invasive diagnostic tools in Cultural Heritage areas, being applicable to several important materials such as paper, paintings, textiles or glass. The electrochemical biosensors, based on SPEs, could be easily combined with rigid hydrogel as wet cleaning material, in order to realize a "real-time" monitoring cleaning system. The hydrogel/biosensor tool is an innovative diagnostic, non- invasive and suitable system to detect the "health condition" of artworks, avoiding lengthy and sometimes unnecessary cleaning material applications.

*Acknowledgements. Special thanks go to the PhD students and postdoc that work on these project:* A. Amodio, A. Idili, S. Cinti, N. Colozza, E. Del Grosso, L. Fabiani, D. Neagu, D. Mariottini. V. Mazzaracchio, K. Petropoulos, M. Tomei, S. Ranallo, M. Rossetti.

## Phase transformation Kinetics : Modeling and Applications

*M. Tomellini*

Phase transformations are among the most important topics in Materials Science. Crystallization of amorphous materials and other solid-state transformations, as well as film formation via vapor condensation at solid substrate, usually involve nucleation and growth. The presentation focuses on two analytical approaches for describing phase transformation kinetics ruled by nucleation and growth, namely the statistical model (and successive extensions) by Kolmogorov, Johnson, Mehl and Avrami (KJMA) and that based on mean field rate equations. The limit of the KJMA model are reviewed and the possibility to go beyond the original formulation of the theory briefly discussed. Owing to its analytical formulation the KJMA theory is widely employed to analyze experimental data, nevertheless some hypotheses of the model are often not met by real systems. For instance, the presence of spatial correlation among nuclei, the anisotropic growth of the nuclei as well as non-isothermal conditions of the growth, all limit the applicability of the theory. Some results on the application of the probabilistic approach to deal with spatial correlation and non-isothermal condition are illustrated [1,2].

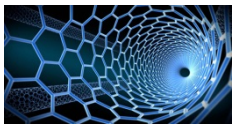
Mean field rate equations are usually employed in the case of atomistic nucleation, when the size of the critical cluster is microscopic and classical nucleation theory does not apply. The formation of a new phase at solid substrate very often takes place under high supersaturation values which imply critical nuclei made up of few monomers only. Rate equations are employed for describing the salient processes occurring at the surface such as, adsorption, desorption, diffusion, nucleation and cluster growth. An application of rate equations for describing the kinetics of polymerization at Cu surface is illustrated. In particular, I report on recent study of surface confined polymerization using Ullmann coupling reaction. The reaction kinetics is measured through fast-X-ray photoelectron spectroscopy and devise a model based on rate equation involving a surface transient. The model accounts for the main features of the kinetics and allows one to determine the activation energies of surface reaction [3].

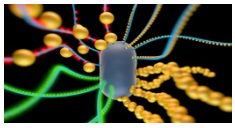
*References*

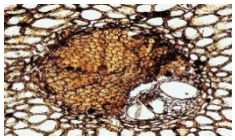
1. M. Tomellini, M. Fanfoni, Phys. Rev. E **90** (2014) 052406
2. M. Tomellini, J. Mater. Sci. **50** (2015) 4516
3. M. Di Giovannantonio et al, J. Am. Chem. Soc. **138** (2016) 16696

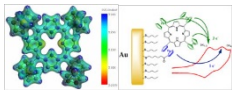
## The interaction of H-NS with its target DNA

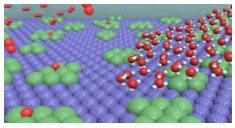
*M. Sette*

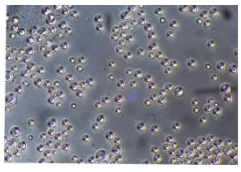


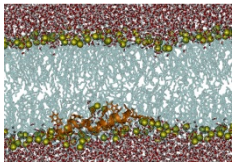








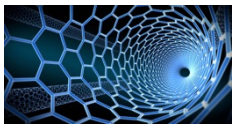


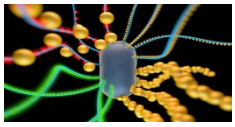


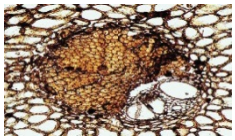
Histone-like Nucleoid Structuring protein (H-NS) is a DNA-binding protein, known to condensate DNA and to act as a transcriptional repressor on bacterial Gram-negative genes. It is referred as a “genome sentinel” because of its ability to bind DNA and to silence the expression of foreign DNA.
H-NS-like proteins contribute to the transcriptional regulation of genes within pathogenicity islands.
Thus, H-NS is assuming the dual role of structuring and regulating a vast set of genes of the genome (Pon et al., 2005, In: Ohyama, T (ed). *DNA Conformation and Transcription*. Landes Bioscience, Georgetown, TX, pp. 52–65).
The structure of H-NS has been inferred by the structure of isolated part of the protein but the structure of the full-length protein is still unknown. This is largely due to the equilibrium in solution between different species (dimers, tetramers, oligomers) and to the formation of heteromeric species with different H-NS-like proteins (like StpA, etc.).
The function of H-NS is also largely unknown, and only some of the DNA binding features have been highlighted by different groups.
Nevertheless the details of the interaction are still unclear. In particular, inside the targeted DNA region, the protein binds to many different DNA positions, all of which are similar to the DNA consensus sequence.
In this presentation I will discuss the recent development about structural and functional studies on this important bacterial protein. In addition, I will present our past and present results, as well as future plans.
Since H-NS is involved in the regulation of several pathogenic bacteria, our studies may be useful for the design of specific molecules that modulates this interaction.

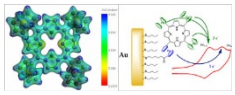
## Organic Chemistry at Tor Vergata: from theory to mechanisms and products

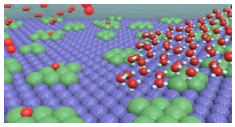
*M. Bietti, V. Conte, G. Ercolani, P. Galloni, M. Salamone*

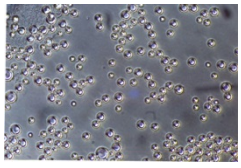


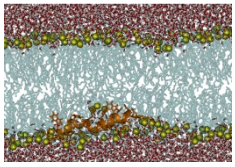












A research topic under investigation in the organic chemistry group concerns the mechanistic study of the reactions of oxygen centered radicals, such as alkoxyls and aminoxyls, important reactive intermediates that are involved in a wide variety of chemical and biological processes. Particular attention has been devoted to the role of these species in hydrogen atom transfer (HAT) and electron transfer (ET) processes. Detailed kinetic studies have provided quantitative information on the role of structural and medium effects on HAT from the aliphatic C–H bonds of a variety of substrates, leading to the definition of a set of rules for selective aliphatic C–H bond functionalization.

The research in O2C group (http://stc.uniroma2.it/O2C/) is focused on the properties of a new class of polyquinoid compounds, called KuQuinones, that show very interesting electrochemical and photophysical properties as well as attractive biomedical activities.

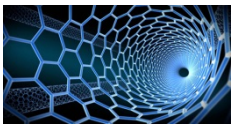
Their studies of a highly sustainable two-phase procedure for oxidation and oxybromination reactions, recently allowed to patent innovative procedures for fuel desulphurization and aromatic substrates bromination. A spin-off of Tor Vergata University is now operative (http://www.bt-innovachem.com/).

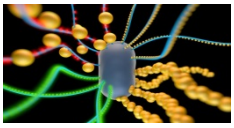
The group is also involved in the characterization of metal free and metallated 5,10,15,20-tetraferrocenylporphyrin, which showed interesting mixed-valence states and reversible electrochemical behaviour in solution and on surface.

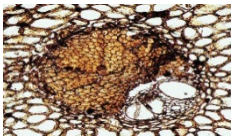
As to the basic research, the focus of the Ercolani's group is on systems chemistry, an area that seeks insight into complex networks of interacting molecules and their emerging system-level properties. Recent contributions regard: (i) theoretical modelling of a complex network of equilibria involving a virtually infinite number of oligomers of different topology (chains, rings, and catenanes); (ii) study of cooperativity in the self-assembly of well-defined, discrete supramolecular architectures from a given set of components under thermodynamic equilibration; and (iii) reaction mechanisms of asymmetric autocatalysis with amplification of chirality, with the aim of understanding the origin of homochirality in biological molecules. As to the applied research, the group is involved in the synthesis and the study of properties of protonic, anionic, and amphoteric polymer electrolytes to be used in electrochemical devices, such as fuel cells and electrolyzers.

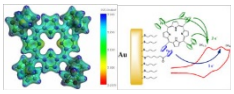
## New carbon-based materials for e-transfer studies and technological applications

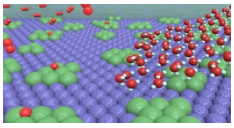
*P. Tagliatesta, F. Limosani, F. Possanza, A. Leoni*

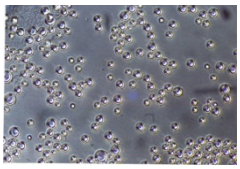


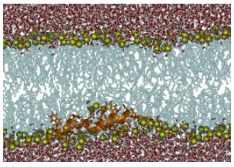












Photosynthesis is based on the electron-transfer phenomena between natural tetrapyrrolic pigments, like chlorophylls and quinones, both embedded in a protein matrix. [1] The process, which involved electron-transfers induced by light, is still under investigation by many groups and more informations were obtained in the past by using synthetic models. [2] In the last years, our group has been involved in investigations concerning the synthesis and photophysical characterization of several porphyrins bearing different chromophores in the beta positions. [3] Ferrocene and/or C60 were linked through single or conjugated triple bonds which act as molecular wires, giving interesting results as fluorescent dyes. Recently, based on our experience with the fullerenes, we shifted our interest on other allotropic forms of carbon such as graphene and carbon nanospheres obtaining new materials able to give interesting new properties in the photoinduced electron transfer.

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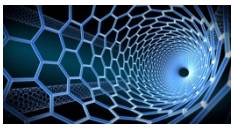
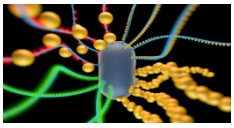
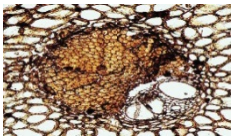
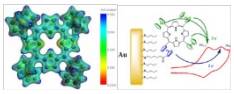
## Chirality at porphyrin nano-scale

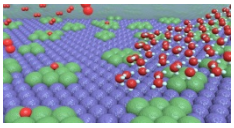
*D. Monti*

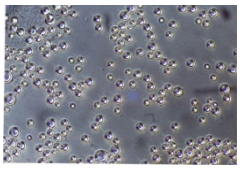


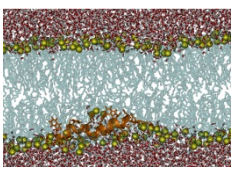






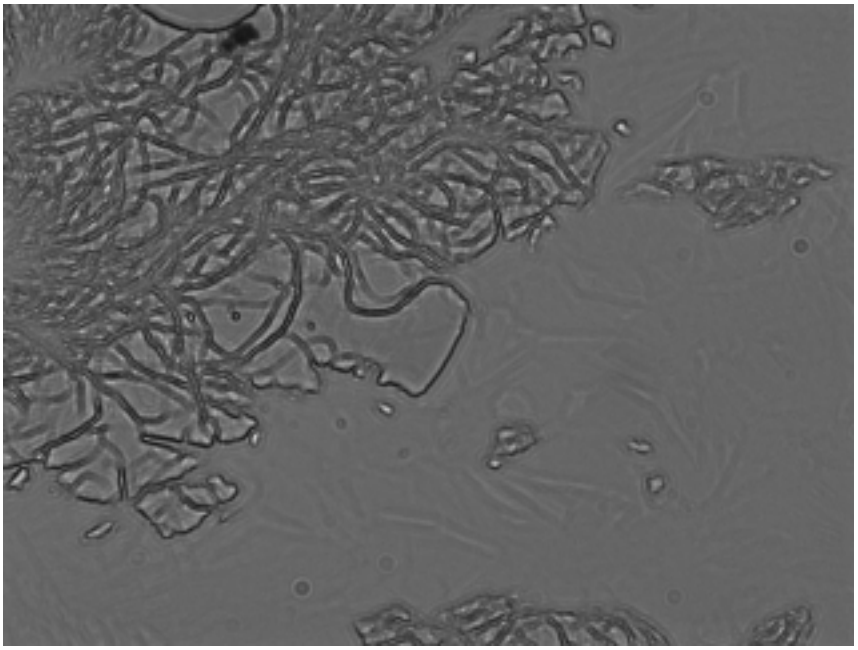






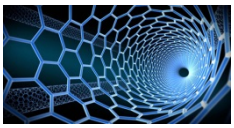
Dissymmetry is one of the still uncleared aspect of the evolution of the Universe. The emergence of chirality, i.e. dissymmetry at molecular level, is a closely related aspect that represents a key issue of life itself.

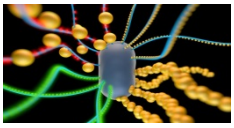
The possibility to achieve synthetic systems, such as porphyrin assemblies featuring supramolecular chirality, is an extremely challenging goal far to be fully exploited, of striking importance in many field of chemistry and technology. The recent results obtained demonstrate the possible construction of chiral porphyrin-based supramolecular materials.

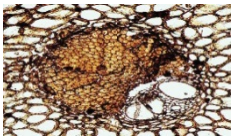


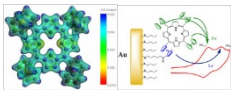
## Sustainable: From polyphenolic waste biomass to smart (nano) materials.

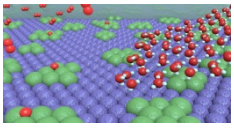
*C. Crestini, Polyphenols & Material Science Laboratory*

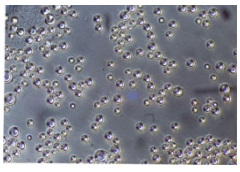


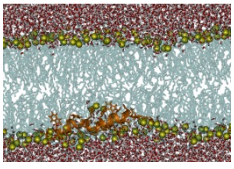












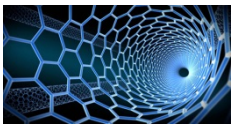
The work of Polyphenols Chemistry & Material Science research group aims at eventually providing major advances in the science, technology and applications of the lignocellulosic and polyphenolic substrates and at the same time to develop sustainable processes in a circular economy perspective.
We always embark from a deep fundamental understanding of the structure and chemical makeup of waste natural polyphenols to develop applications and novel materials from it.
In particular, the activity is focused in the:

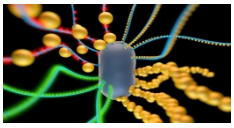
- Development of new stimuli responsive materials and products by structural modification of natural polyphenolic substances:
  - Thermoreversible gels; Light-sensitive systems as molecular switches; surface mofifiers.
- Development of new nanostructured materials for controlled active release:
  - polyphenols nanoparticles, nanocapsules and nanofibers with synergistic biological activities.
- Development of new methods of structural analysis of polyphenolic polymers by means of advanced mono and two-dimensional mono-and two-dimensional nuclear magnetic resonance NMR and phosphorous conjugated chemistry techniques dedicated to the structural elucidation of polyphenolic systems.
- Study of the mechanisms of activation of oxygen and hydrogen peroxide in oxidative enzymatic systems: laccase and laccase-mediator systems, lipoxygenase.
- Development of supported oxidative enzymes. Development of supported multi-enzymatic biocatalysts. Study of their reactivity in the oxidation of lignins, phenols and polyphenols.
- Development of biomimetic systems of peroxidase and cytochrome P-450 as homogeneous and heterogeneous catalysts.

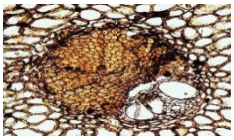
Development of homogeneous and heterogeneous oxidation catalysts. Oxidative catalysis studies in the oxidation of natural substances such as lignans and neolignans, tannins, and melanin.

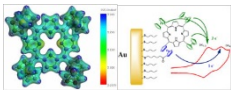
## From tungsten minerals to sintered cemented tungsten carbides: the carbothermic reaction shortcut

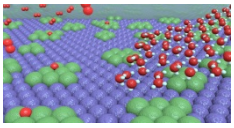
*R. Polini*

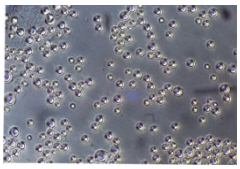


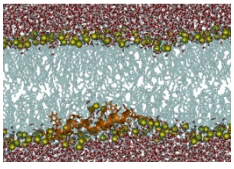












About two thirds of known world tungsten deposits are in the form of scheelite ($CaWO_4$) mineral. China accounts for more than 80% of world tungsten mine production and Chinese domestic demand continues to grow faster than in the rest of the world, thus representing about 50 % of the total world consumption (Europe's share is 13%).

More than 60 % of the world consumption of tungsten is in the form of cemented tungsten carbides (WC-Co, *hardmetals*) that represent the main driving force behind tungsten demand. Cemented carbides (WC-Co) have outstanding properties owing to the combination of high hardness and strength of tungsten carbide (WC) with the toughness and plasticity of the metallic binder. As a result, the application of cemented carbides has become universal in the manufacturing sector due to their high hardness, toughness, and elevated temperature strength properties to resist plastic deformation at high temperatures.

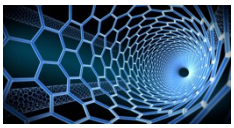
As a consequence of the above mentioned technical, geopolitical and economic reasons, on May 2014 European Union has classified tungsten as the critical raw material with the largest economic importance (http://tinyurl.com/hnz8gun). Additionally, processes which could allow producing WC powders by reducing the use of chemicals and the amount of industrial waste, as well as by decreasing the number of high-temperature processing steps, are particularly appealing from an environmental and sustainability point of view.

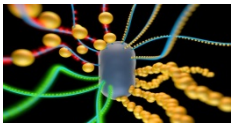
For all these reasons, there is a renewed interest in the direct synthesis of WC powders by carbothermic reduction of tungstates and, in particular, of scheelite. The carbothermic reduction of enriched scheelite minerals with carbon black has been successfully studied in our department since 2014 (European Patent Application EP3098199A1, filed on 26/05/2016, Applicant: FILMS SpA). Following 2-6 h reaction at 1100-1200 °C in flowing Ar, leaching treatments have been developed to remove undesired phases and obtain WC powders usable for manufacturing cemented carbides (WC-Co) goods with the expected properties.

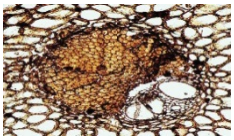
Therefore, the carbothermic reduction of scheelite does represent a viable process for eco-friendly, energy efficient and lower cost synthesis of cemented tungsten carbides.

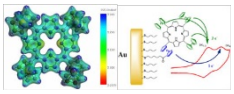
## Femtosecond pump-probe spectroscopy: probing ultrafast dynamics of molecules and complexes

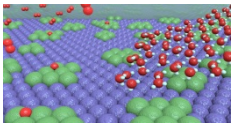
*S. Piccirillo*

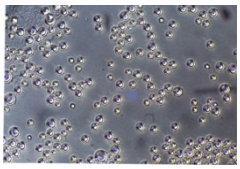


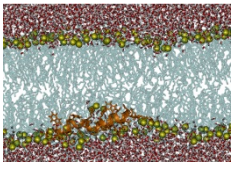












Femtochemistry addresses the very nature of the chemical bond, aiming at unraveling the ultrafast chemical and physical processes in molecular systems. Pump–probe femtosecond spectroscopy uses an ultrashort laser pulse to trigger a chemical process and subsequently another femtosecond pulse probes a specific feature of the evolving system.

Our recent pump-probe experiments include ultrafast time-resolved photoelectron spectroscopy (TRPES) for the investigation of the relaxation dynamics of 2-nitrophenol (2-NP) and femtosecond transient absorption spectroscopy (FTAS) for the study of the recognition of the mono-, di- and tri-phosphorylated forms of adenosine by zinc–salophen complexes in solution.

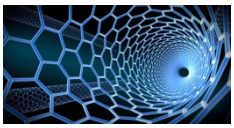
2-NP belongs to a class of nitroaromatic compounds which play a significant role as atmospheric pollutants of environmental concern. TRPES measurements were performed with the CITIUS ultrafast VUV source, a state-of-the-art fs-laser facility based on laser high-order harmonic generation in gas. In particular, we employed an ultrafast uv laser pulse to prepare the 2-NP molecule in an electronically excited state and we followed the dynamics by time delayed photoionization with a high-order harmonic (HHG) pulse at 23.2 eV. The results are interpreted in the light of quantum chemical calculations. Ultrafast relaxation pathways were identified, involving both internal conversions and intersystem crossing. The photochemistry of the process was also recognized by the signal due to reaction products.

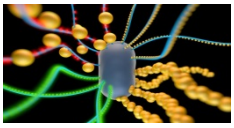
The investigated Zn-salophen receptors display great sensitivity and selectivity for phosphates and for the mono-, di- and tri-phosphorylated forms of adenosine and, furthermore, they act as fluorescent sensors since they display marked changes of the spectroscopic emission properties when complexed with AMP, ADP or ATP. This can be associated with the existence of π···π stacking interactions between the salophen aromatic rings and those of the adenosine nucleobase.

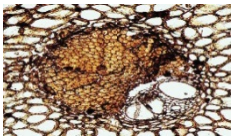
FTAS measurements on Zn salophen complexes in ethanol solutions were conducted at the EuroFEL Support Laboratory (EFSL-CNR –ISM Tor Vergata) Theoretical calculations are in progress in order to identify the excited state dynamics of the Zn-salophen receptors and their complexes with the nucleotides.

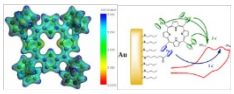
## Nanoparticles: properties and applications

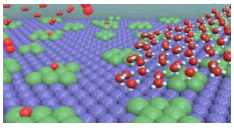
*M. Carbone*

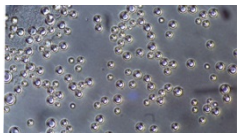


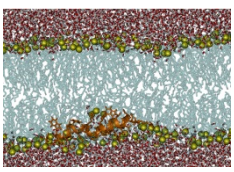








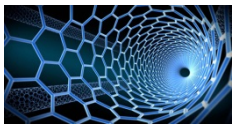


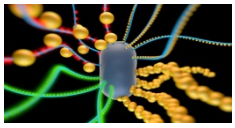


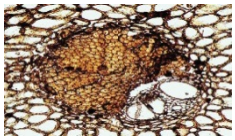
Worldwide, the tattooed population is on the raise, and simultaneously a tendency is observed of many tattooed individuals to undergo a therapy for tattoos removal. Within this framework the “think-before-you-ink” research line aims at determining the chemistry of most frequently used pigments and inks, their stability in time, the risks involved in the tattooing process. Moreover, the chemical processes undergoing the removal procedures are investigated, with particular attention to possibly toxic fragmentation products as well as undesired re-agglomeration collaterals.

## Development of peptide-based drugs to fight multiresistant bacteria and cancer

*S. Bobone, G. Bocchinfuso, A. Bortolotti, P. Calligari, A. Palleschi, F. Savini and L. Stella*



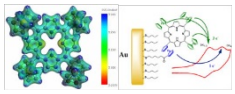


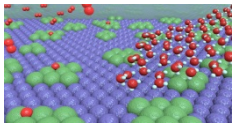


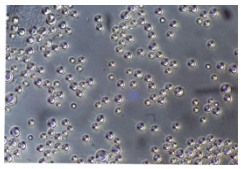
Peptides are short chains of amino acids (i.e. they are small proteins) naturally present in our body, with multiple functions, such as hormones, neurotransmitters and anti-infectives. Their ability to potently modulate several biological processes makes them ideal drug candidates. Several of these molecules already have fundamental therapeutic applications (insulin, oxytocin, vasopressin, etc.). In our group, we combine multiple spectroscopic and computational approaches to understand the mechanism of action of bioactive peptides, with the aim of designing new molecules with improved activities and pharmacological properties. We mostly focus on two areas:

*1) Antimicrobial peptides*

Bacteria are rapidly becoming resistant to available antibiotics. This phenomenon could rapidly bring us back to a pre-antibiotic era, where a simple wound or the most basic surgical operation could become deadly. Antimicrobial peptides (AMPs) are natural peptides that kill microbes very quickly, mainly by damaging their cell membranes and constitute a possible solution to the spreading multidrug resistant bacterial strains. Our studies are aimed at understanding how these molecules kill bacteria, using experimental systems ranging from model phospholipid vesicles to cells, and combining spectroscopic studies with molecular dynamics simulations.

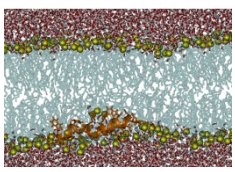






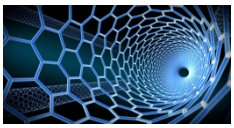
*2) Peptide inhibitors of protein-protein interactions involved in cancer*

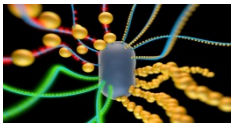
Many biological processes are mediated by the association of two proteins. Therefore, inhibiting protein-protein interactions (PPIs) is a natural way to interfere with pathological processes, such as the uncontrolled cell division that takes place in cancer. However, PPIs are characterized by an extended interaction surface and therefore the small molecules normally used as drugs cannot efficiently perturb them. By contrast, peptides are ideal candidates for this purpose, since in this case their size and structure is comparable to those of the interacting molecules. We are currently developing peptide inhibitors of several PPIs involved in cancer, such as those of the phosphatase SHP2, whose mutations cause several forms of leukemia.

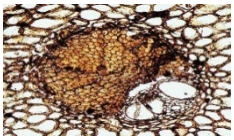


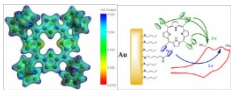
## The super(ficial) physical chemistry: from ancient papers to bio-functionalized surfaces

*C. Mazzuca, B. Di Napoli, G. Ripani, G. Bocchinfuso, A. Palleschi*



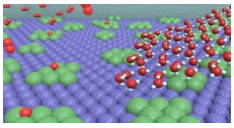


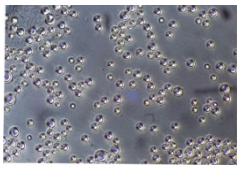




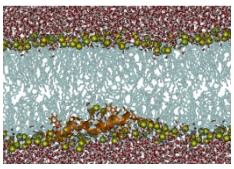
In this talk, the results of two different studies, focused on different kind of surfaces, will be presented:

1. Paper artworks. Paper, due to its complexity and fragile structure, is a very difficult system to restore. Wet cleaning, a required step of paper restoration, is performed usually by means of water bath, that can cause swelling of fibers and dissolution of several components. Recently, to overcome these drawbacks, cleaning methodologies based on application of suitable hydrogels have been proposed. The application of rigid, retentive hydrogels reduces water uptaken, being more respectful for the original integrity of the artwork. In this context, in our group, we have explored the suitability of several hydrogels, based on gellan or poly(vinyl–pyrrolidone) embedded in a poly(2-hydroxyethylmethacrylate) network [1]. To assess the capability of the proposed gels as cleaning materials, a methodological approach based on different surface techniques, has been optimized and applied on paper samples from different centuries. This approach is based on a combined usage of Fourier Transform Infrared Spectroscopy with attenuated total reflectance cell, UV-Vis reflectance spectroscopy, pH measurements, colorimetric analysis and scanning electron microscopy.





2. Peptides or proteins on surfaces. We are using the Fourier Transform Infrared Reflectance Absorption Spectroscopy to characterize orientation with respect to the surface and conformation of peptides or proteins linked to a reflective surface (gold or silica oxide with controlled roughness) [2]. The experimental results have been compared with data obtained from Molecular Dynamics and Monte Carlo Simulations, which give structural and dynamics information on the investigated systems.



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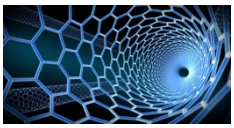
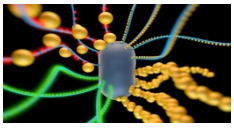
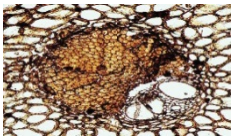
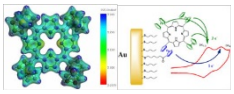
## 2D and 3D bio-inspired nanostructures for health, sensing and solar energy conversion

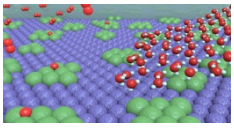
*E. Gatto, G. Bocchinfuso, A. Palleschi, M. De Crescenzi, E. Placidi, M. Scarselli, M. Venanzi*

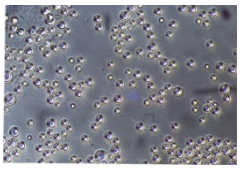


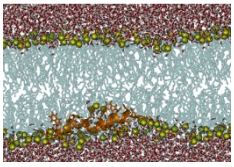












Molecular self-assembly is a fundamental process in the construction of biologic macromolecular assemblies. The growth of supramolecular assemblies can be thermodynamically or kinetically controlled, and the aggregation process can be tuned by slightly perturbing the experimental conditions.
In our group we design and study the aggregation properties of biomolecules (predominantly peptides, porphyrins and phospholipids), with two principal aims:
1. To understand the physico-chemical parameters triggering the growth of supramolecular aggregates in 3D and determining the morphology of the supramolecular structures at nanometric and mesoscopic scale. In this connection, the study of peptide aggregation may give important insights on the evolution of several neurodegenerative diseases and precious information for the design of new molecules with pharmacological properties.
2. To engineer the surface properties at the nanoscale. Molecular layers can be built on surfaces by the self assembly and the Langmuir-Blodgett techniques, making possible to control the film thickness, morphology and molecular composition. In addition, 2D materials can show new properties, unknown at the single component level, because collective properties come into play.
In this talk, I will describe the design, characterization and properties of selected 2D bio-inspired materials and highlight their potential for applications in optoelectronic devices and sensing. Examples include helical peptide-modified surfaces able to control the distance of a probe from the surface and having antibacterial properties, and a new generation of 2D phospholipids-based sensor, able to hook and quantify tumor biomarkers in blood serum, for early cancer detection.
All the systems investigated in our laboratory are characterized by spectroscopic and electrochemical techniques, and visualized by scanning probe microscopies with nanometric resolution, in collaboration with the Department of Physics.

# Chemistry@TorVergata
# Dipartimento di Scienze e Tecnologie Chimiche
# Giornata della Ricerca 2017

## Physical Chemistry in the Design of Micro- and Nano- Devices for Theranostics

*B.Cerroni, E.Chiessi, F.Domenici, L.Oddo, G.Paradossi, Y.Toumia*
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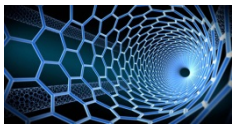
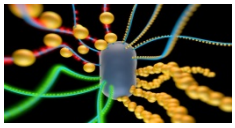
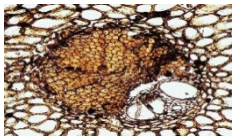
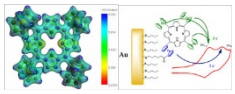
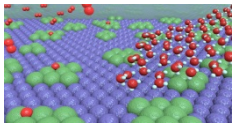
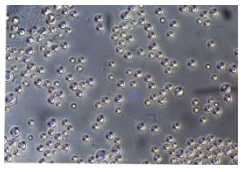
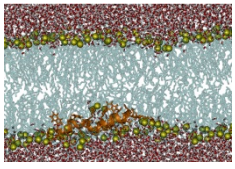




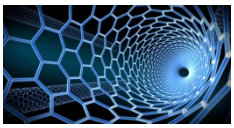
The Group of Physical Chemistry of Macromolecules is engaged in the research of new micro- and nano- devices as support to the multi-modal molecular imaging (diagnostics) and to the controlled release of drugs (therapy). The components of the new formulations are chosen on the basis of the most recent achievements of the Soft Matter and of the Physics and Chemistry of macromolecules. The activity of the group is organized in: i) engineering of the materials, ii) in vitro study of the interaction among the designed systems and several cell lines, iii) 3D micro- nano- structure morphology and dynamical features (deformation and bioadhesion under shear stress) and iv) computer simulation using molecular dynamics approach. Some recent examples of biocompatible microparticles responsive to temperature and ultrasound will be described in the presentation. These systems are designed to match the needs of molecular imaging and of controlled and focal release of drugs.

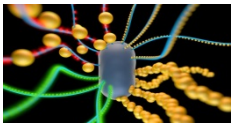
For any kind of theranostics (diagnostic imaging and therapy) application, targeting is crucial since the device, injected in the circulatory system, should reach the specific pathological site (target) of the organism. To this aim, contrasting the strong drag forces caused by the blood flow and the primary immune response is mandatory. With micro- and nano-particles these capabilities have been accomplished by biofunctionalization of the drug-loaded particles surface, allowing for targeting through the membrane receptors overexpressed in pathological cells. These engineered systems, once adhered, are induced to an efficient release and cell uptake of the drug, by triggering external stimuli such as ultrasound irradiation. Recently we formulated a hybrid micro-device for photoacoustic imaging made up of a polymer shelled microbubble coupled with graphene chips, opening the possibility to collect real time images, as in a conventional sonography, but with a very high resolution (30 µm).

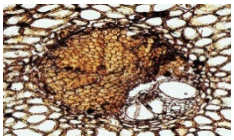
In this framework we are collaborating with INAIL in order to shed new light towards a more safe and informed medical and occupational use of ultrasound, as well as to plan new drug delivery strategies with multiple clinical relevance.

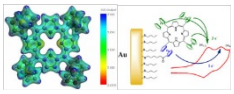
## Bacteria as an energy source: carbon materials and corroles to catalyze the oxygen reduction reaction

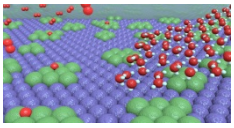
*M. Raggio, B. Mecheri, A. D'Epifanio, S. Nardis, R. Paolesse, S. Licoccia*

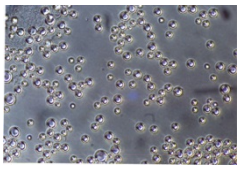


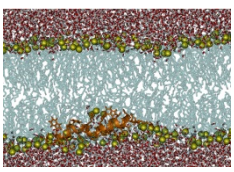












Among the numerous energy sustainable devices, Microbial Fuel Cells (MFCs) have attracted the attention of the scientific community. Such devices allow the conversion of chemical energy in electrical energy through biologic organisms, by using various substrates as fuels. MFCs are mainly utilized for energy recovery systems and wastewater treatment. In MFCs, bacteria perform the oxidation of organic substances at the anode, whilst the Oxygen Reduction Reaction (ORR) takes place at the cathode.

To develop high performance catalysts for the ORR is a key passage in order to achieve commercialization and diffusion of sustainable energy devices. One of the major barriers to this target is represented by platinum as catalyst for the ORR. Platinum is a highly efficient catalyst, but it is very expensive and can be easily poisoned by many of the substances contained in waste [1]. In the last decade the development of non noble metals, coordinated to tetrapyrrolic macrocycles and supported on carbon materials, led to the creation of possible alternatives to platinum [2].

Among these molecules, corroles represent an interesting class of ORR catalysts. Research concerning these macrocycles experimented a great boost in the last 15 years, thanks to the ideation of faster and more efficient preparation methods [3].

In this work two different corroles metal complexes of Co(III) and Fe(III) have been synthesized and supported on carbon materials. Carbon nanotubes and black pearls were selected as supports, because of their good electrical conductivity and high surface area. The catalytic activity of these compounds towards the ORR was investigated through electrochemical techniques (cyclic voltammetry and linear sweep voltammetry with a rotating disk electrode). Results are certainly positive and show substantial room for improvement.

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## Environmental electrochemical sensor: research within the Spin-off TECNOSENS

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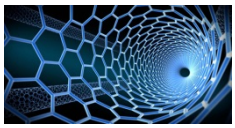
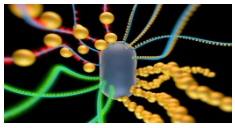
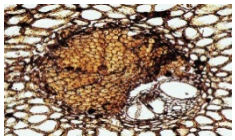
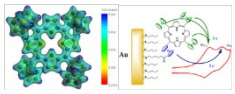
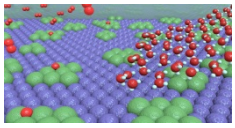
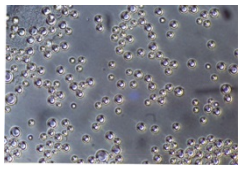
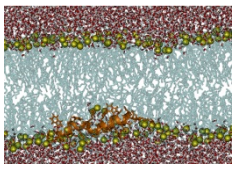
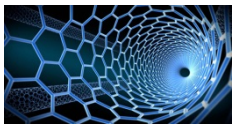
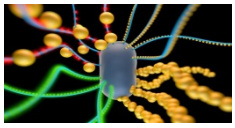
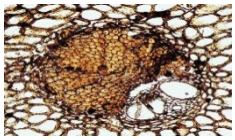




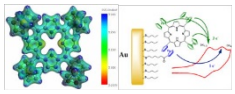
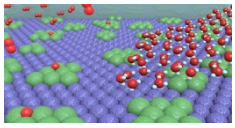
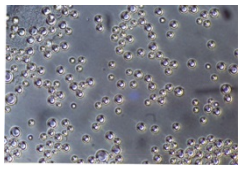
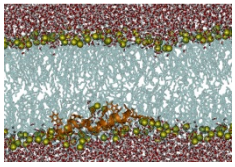





Chlorination is the most common treatment for the disinfection of drinking water and swimming pools using sodium hypochlorite thanks to its high disinfectant power and easiness to use.
In aqueous solution, chlorine produces hypochlorite ion and hypochlorous acid, and the sum of these two species is defined as "free chlorine".
However, the reaction between free chlorine and organic substances present in water can generate harmful by-products and therefore alternative disinfectants, such as chlorine dioxide have been investigated. Chlorine dioxide is often used because of its excellent oxidizing and disinfecting properties, combined with the absence of harmful by-products, such as trihalomethanes.
Regardless of the disinfectant agent used, it is necessary to monitor its concentration to ensure right level of disinfection and satisfying health conditions for the end users of treated water.
Thus, cost-effective and easy to use sensors to control the disinfectant level are highly required. In this overall scenario, the goal of the Tecnosens Spin-off is to develop and fabricate miniaturized and sustainable electrochemical probes for the monitoring of disinfectant compounds.
Herein, we describe the development of two sensors to detect free chlorine and chlorine dioxide.
The probes are realized using screen-printed electrodes modified with carbon black, a raw cost effective nanomaterial selected for its excellent electrocatalytic properties.
The working conditions (amount of carbon black, applied potential, pH, and ionic strength of buffer solution) were optimized in order to obtain the best sensitivity and repeatability, reaching a detection limit of 0.01 ppm for free chlorine sensor and 0.03 ppm for chlorine dioxide. Their analytical performances have been evaluated in the optimized conditions and the accuracy of the sensors estimated through a recovery test. The results were satisfactory and confirmed the possibility to use the developed sensors in real samples.

## Biochemistry and Material Sciences: Scaffolds for Regenerative Medicine

*M. Ciocci, E. Di Giovanni and S. Melino*

The design of biocompatible and biodegradable scaffolds remains one of the most important challenges for Regenerative Medicine. Current idea is that the interaction between cell and scaffold could drive cell fate by regulation of gene expression and protein organization. In this context protein hydrogels, for their physical, chemical, electrical and biological properties, can be ideal scaffolds, mimicking the extracellular matrix. Moreover, the microarchitecture and porosity of the hydrogel scaffold play a key role in the exchange of nutrients, removal of waste products and cell-cell interaction. Therefore, a combination of biochemical and mechanical properties has been optimized in order to produce a novel 3D hydrogel "*Scaffold in Scaffold*" able to favour cell-structure interactions, cell alignment and to promote a functional differentiation of human mesenchymal stem cells (MSCs).[1] Furthermore, scaffolds able to release bioactive molecules is also mandatory in tissue repair and regenerative medicine. Recently, we have demonstrated the beneficial effects of the endogenous *gasotramsmitter* hydrogen sulfide ($H_2S$) on both 2D- and 3D-cell culture systems of MSCs.[2,3] New $H_2S$ slow-releasing agents have been produced by garlic extract[4] and used to functionalize PLA nanofibers (PNFs). The potentiality of PNFs for tissue regeneration and repair has been also evaluated by *in vitro* studies. Therefore, the new stem cell culture systems here presented may represent good models to improve the knowledge on the biochemical mechanisms involved in the cell-material interaction and for future applications in tissue repair and regeneration.

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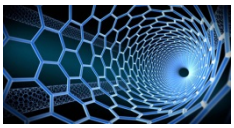
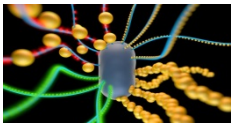
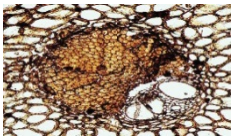
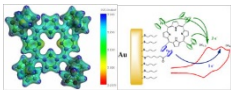
## Nanostructered carbon materials and polymers for the engineering of bioscaffolds and neural interfaces

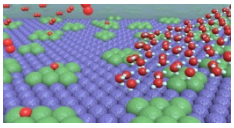
*E. Tamburri, S. Orlanducci, M. L. Terranova*

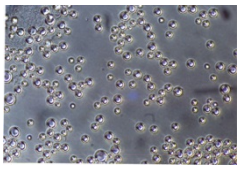


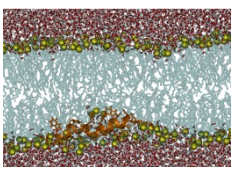












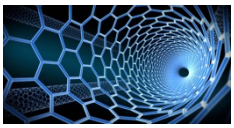
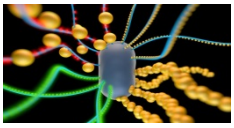
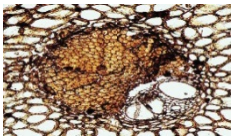
Carbon materials are between the most abundant and technologically important resources. The interest to study carbon nanostructures is rapidly growing with motivation to use them for various application extending from electronics, photonics, photovoltaics, sensors up to bio-medicine. Most of such applications require creation of composite structures of nanocarbons with polymers. Therefore, nanocomposites based on carbon nanomaterials and polymers are currently investigated from theoretical, experimental and technological point of view with the aim to improve inherent limitations and gain new functionalities. In particular, the need to produce new biomaterials for a wide range of applications, including artificial muscles, neural interfaces and biosensors, is driving the attention of the scientific community towards the classes of hybrid systems based on conductive polymers and hydrophilic biopolymers.

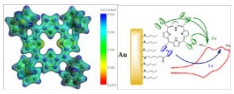
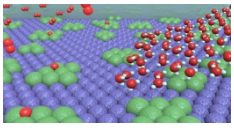
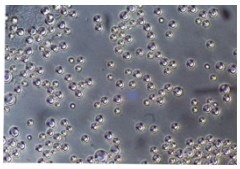
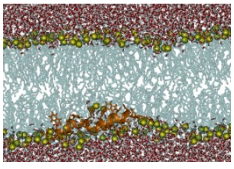
Due to their intrinsic conductivity, the good charge-transfer properties and the low impedance, conducting polymers can be used as coating of implantable electro-stimulation electrodes providing interfaces suitable to improve soft-tissue integration. Moreover the volume changes induced by oxidation/reduction processes, make these polymeric materials promising electro-chemo-mechanical systems to be explored for production of artificial muscles.

On the other hand, nanocomposites based on hydrophilic biopolymers and nanostructured carbons are eco-friendly and biodegradable materials which show enhanced mechanical and thermal properties with respect to the pure polymers. The high processability, the facility of casting and film forming, coupled with the high flexibility and the total reversible stretchability under dry conditions and in the swollen state, make these systems promising bio-mimetic model materials.

## Development of passive samplers for the analysis of emerging pollutants in marine water

*C. Marcoaldi, G. Palleschi, S. Chiavarini (ENEA)*

The evaluation of the current state of the marine environment is of utmost importance if we are to fully understand the global environmental perspective. At present, considerable deficiencies exist in the monitoring of seawaters for residues of the so-called new emerging pollutants like pharmaceuticals, pesticides and toxins. The synergy between active and passive sampling systems will allow the detection of contamination at levels below the ng/L, as required in the quality objectives of the Water Framework Directive.
Monitoring by passive sampling (PS) is based on mass transfer due to the different chemical potentials of analytes between a given environmental compartment and the collection medium inside a dosimeter. The flow of analytes from the sample surrounding the dosimeter into the inside part of the trap placed in the sampler is completely free. The main driving force and separation mechanism is based on the differences in concentration. Therefore, passive sampling techniques are characterized by a simple construction and easy maintenance. Several designs of passive samplers have been proposed: SPMD (Organotin compounds), POCIS-pest and pharm (Diuron and Sulphonamides), SPATT (Okadaic acid toxin). These ones are used for environmental monitoring and it is important to distinguish the kinetic or equilibrium steady state in which it is located. The sampling rate depends on the volume of water with which the sampler has come into contact. Therefore it will be important to have information on the dynamic absorption of toxins and will also be important to evaluate indesiderable matrix effects.

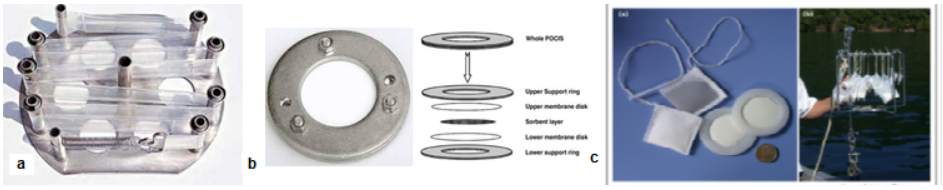


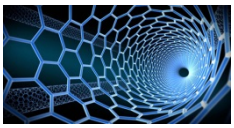

*Fig. a. SPMD sampler; b. POCIS sampler; c.SPATT samplers*

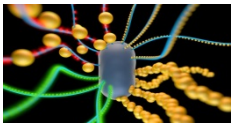
Particular aspects of the research were designed to participate in a research conducted by ENEA as partner of the EU project SMS [1] coordinated by Rome 2 Tor Vergata University. The objects of the work were to perform a preliminary assessment about the possibilities of the use of these devices for the compounds detection described above in seawater.

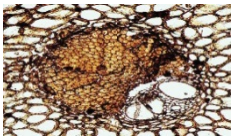
[1] Progetto Europeo del 7° Programma Quadro "SMS—Sensing toxicants in Marine waters makes Sense using biosensors".

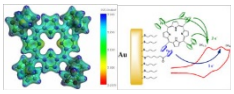
## The diamond: a jewel for electronics, optics and regenerative medicine

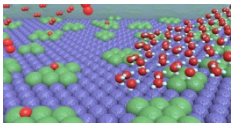
*R. Carcione, M. L. Terranova*

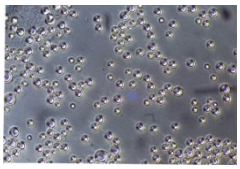


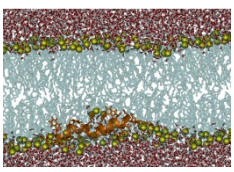












The covalent bonding of $sp^3$-hybridized carbon atoms gives to diamond unique physical, chemical and mechanical properties, unmatchable by any other material, such as high energy gap, high diffusion energies for defects and impurities, very high thermal conductivity, hardness and chemical inertness. Pure diamonds are characterized by high electrical resistivity, but doped diamonds exhibit a tunable electrically semi-conducting behavior.

The doping of diamond with foreign species allows also the introduction of luminescent color centers and so emitting diamond has recently emerged as a stable alternative for the development of robust light sources.

Thus, a proper doping of diamond can lead to the realization of electronic and optoelectronic devices with exceptional controlled properties, that attract the interest of the scientific community.

We have developed a strategy to fabricate doped diamond films using an ad-hoc modified Hot Filament Chemical Vapor Deposition (HFCVD) reactor which allows to insert metal species into the diamond lattice directly during the diamond synthesis from $CH_4/H_2$ mixtures.

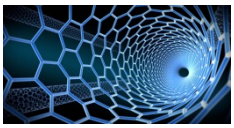
By modulating the doping level, it is possible to produce conductive and/or luminescent diamond films that retain the crystalline quality and the outstanding properties of the diamond phase. Titanium, Neodimium, Gadolinium and Nickel are the metals presently used for diamond doping.

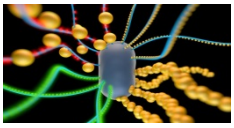
Furthermore, this method allows to produce “Boron-free” electrodes and functional interfaces characterized by biocompatibility, high stability and long-time reliability, suitable in regenerative medicine as scaffolds for tissue growth and culture platforms.

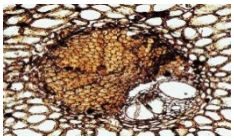
All these peculiarities make the diamond grown by CVD technologies a jewel for electronics, optics and biomedical applications.

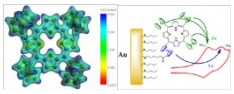
## Nucleation and growth mechanisms of metals and polymers in electrochemical synthesis

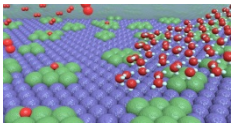
*S. Politi, S. Orlanducci*

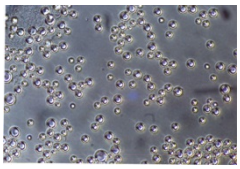


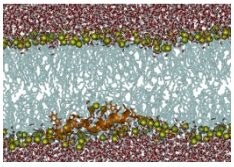












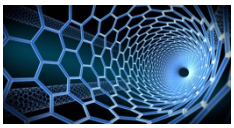
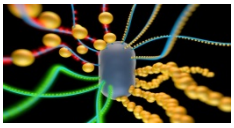
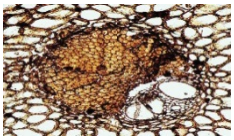
Potentiostatic transients during electrochemical depositions have been the subject of several theoretical and experimental studies. These investigations are motivated by the possibility to gain insights into the fundamental mechanism of new phase formation, ruled by nucleation and diffusion-controlled growth, in dependence of overpotential. Theoretical models have been proposed for describing the current density in terms of either 3D- or 2D-nucleation and growth processes which have been profitably employing to interpret experimental chronoamperometric transients.

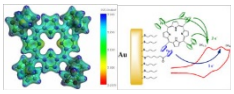
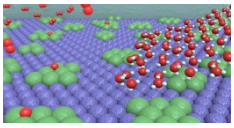
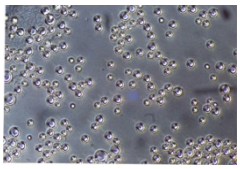
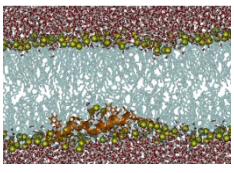
Until now the most of the investigations deal with electrodeposition of metal species onto different substrates. However, the potentiostatic electropolymerization of conducting polymers was found to be characterized by nucleation and growth mechanisms very similar to those of metals. In this view the processes related to the electrodeposition of conducting polymers can be investigated by adopting the models developed for metals. In particular, instantaneous and progressive nucleation along with two-dimensional (2-D) and three-dimensional (3-D) growth are taken into consideration to explain the mechanisms of polymer formation. Nevertheless, temperature, pH value, concentration, dopants, nature of the substrate are experimental variables that affect the electropolymerization process. Therefore, a study that also takes into account the morphology, structure and functionality of the deposit is a challenging task in order to a complete characterizations of the produced material.

For this purpose, in the present research theoretical models will be proposed to explain the processes of polymers growth, and at the same time Raman spectroscopy, SEM, TEM, STM and AFM techniques will be employed for a complete analysis of the synthetized polymers.

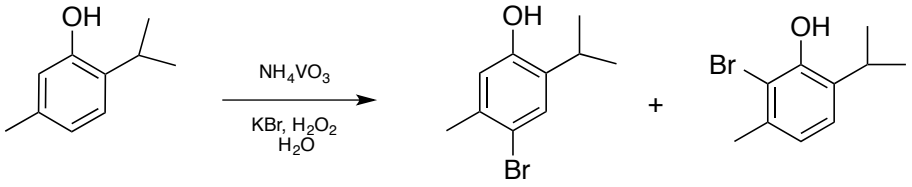
## From Lab to Market: new antibacterial agents branded "Tor Vergata"

*F. Sabuzi, P. Galloni and V. Conte*

Recently, in our laboratories, we have developed a very simple and efficient system for the bromination of thymol, a natural compound extracted from *Thymus vulgaris* essential oils, that is one of the most used active ingredients in many products for personal and home-care. Following the bromination of thymol, 4-bromothymol was obtained as the main product.[1]




The most relevant feature of such reaction is that it is carried out in water, in the absence of organic co-solvents and with economic, non-toxic and readily available reagents. These features make this process easily scalable at an industrial level since generally risks related to the scaling-up of laboratory processes are associated with the use of toxic and harmful reagents as well as flammable solvents.

In addition, biological tests have shown that 4-bromothymol has antibacterial and antifungal activity up to 15 times higher than thymol and lower toxicity.[2]

Based on these results, we founded BT-InnoVaChem srl, a spin-off of the University of Rome Tor Vergata. The aim of this spin-off is to produce new and effective antibacterial, antifungal and pesticide agents, i.e. 4-bromothymol, with an efficient, cheap and sustainable approach, in order to introduce them into the market of antimicrobial compounds.

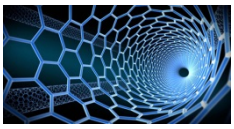
In this communication, the transfer of results obtained in lab into a small business reality will be presented.

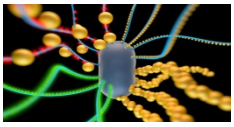
*References*

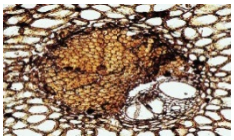
1. Sabuzi F., Churakova E., Galloni P., Wever R., Hollmann F., Floris B., Conte V., *Eur. J. Inorg. Chem*., **2015**, 3519.
2. Galloni P., Conte V., Sabuzi F., Thaller M. C., Migliore L., Matteucci G., Italian Patent N. 102016000090701, *pending*).

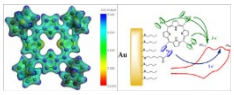
## Recent research activities at the Analytical Chemistry laboratory

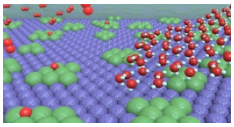
*F. Arduini, D. Moscone, L. Micheli, G. Palleschi, S. Piermarini, A. Porchetta, F. Ricci, G. Volpe*

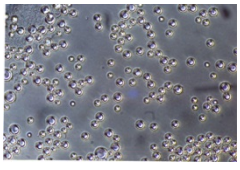


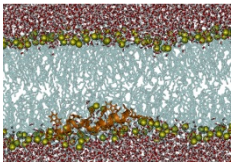










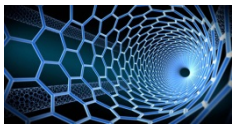


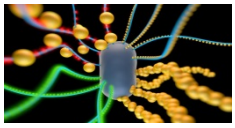
Biosensors have been realised to solve practical problems in the areas of clinical, food, environmental and Cultural Heritage fields.
DNA nanomachines that can signal the presence of specific antibodies in whole blood have been developed. We designed a conformational switching, optically signaling stem-loop DNA nanodevice that supports the introduction of two copies of a wide range of polypeptide, small molecule, or oligonucleotide recognition elements. The binding of the antibody to this DNA nanomachine causes a structural change, producing a fluorescence signal related to the target's concentration.
Enzyme-Linked-Immuno-Magnetic-Electrochemical assays are developed to detect bacteria, virus and algal biotoxins. These systems are based on the use of magnetic beads as solid support for the immunochemical chain and an array of 8 screen printed electrodes as sensing platform coupled with a portable instrumentation.
Printed electrochemical sensors modified with bismuth film in order to detect simultaneously heavy metals were developed and applied in bioremediation of environment. Printed sensors were also modified with a plenty of nanomaterials such as carbon black and gold nanoparticles to quantify As(III) in drinking water and Hg(II) soil. Carbon black with Prussian blue served to detect ppb levels of nerve agents and a lab-on-a-chip approach was adopted to detect Sarin gas in case of terroristic attacks. These sensors were also used for the impedimetric detection of *Bacillus Anthracis* spore simulant. Paper was exploited as novel substrate for the fabrication of electrochemical platforms for Zn(II), phosphate and nerve agent detection.
Electrochemical biosensors were applied in the Cultural Heritage field. Selective electrochemical biosensors were coupled with an hydrogel and a flow sampling plate in order to evaluate simultaneously the degradation status of the artworks and monitoring the cleaning process.

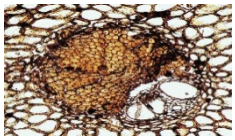
*Acknowledgements. Special thanks go to the PhD students and postdoc that work on these project:* A. Amodio, A. Idili, S. Cinti, N. Colozza, E. Del Grosso, L. Fabiani, D. Neagu, D. Mariottini. V. Mazzaracchio, K. Petropoulos, M. Tomei, S. Ranallo, M. Rossetti.

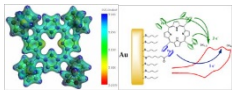
## Sensing toxicants in Marine waters makes Sense using biosensors

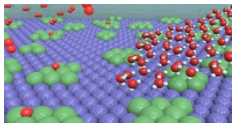
*L. Micheli, G. Palleschi, S. Piermarini, A. Porchetta, F. Ricci, G. Volpe*

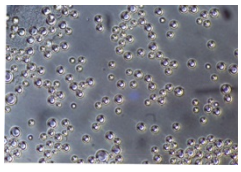


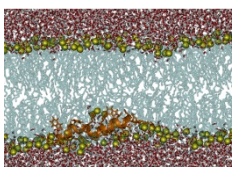












Sensing toxicants in Marine waters makes Sense using biosensors (SMS) will deliver a novel automated networked system that will enable real-time in situ monitoring of marine water chemical and ecological status in coastal areas by the detection of a series of contaminants regulated by the Marine Strategy Framework Directive (MSFD). SMS will design a multi-modular apparatus that will host in a single unit—the Main Box (MB)—a Sampling Module and an Analysis Module. The former will contain sample collection and treatment components, whereas the latter will include four biosensor sub-modules that will enable detection and measurement of algal toxins and their associated algal species. The MB will be equipped with a communication module for real-time data transfer to a control center, where data processing will take place, enabling alarm functionality to Health Warning Systems.

In this framework the Analytical Chemistry laboratory aimed to develop a novel automated networked system for *in situ* monitoring of Okadaic acid (OA), Saxitoxin (STX) and Domoic acid (DA) using a colometric assay based on the use of magnetic beads.

OA is a lipophilic marine toxin produced by *Dinophysis* and *Prorocentrum*, and is responsible for causing diarrheic shellfish poisoning (DSP) to humans after ingestion of contaminated shellfish. DA is a naturally occurring neurotoxin produced by several species of marine diatoms from the genus *Pseudo-nitzschia* and is responsible for causing a human intoxication syndrome known as amnesic shellfish poisoning (ASP), characterized by severe gastrointestinal and neurological disorders. STX is one of the most lethal non-protein toxins, induces a lethal disease known as Paralytic Shellfish Poisoning (PSP) and is the only marine natural product that has been declared chemical weapon. An early detection of these toxins, directly in marine water, is an important aspect for public safety and natural environment.

*Acknowledgements. Special thanks go to the PhD students and postdoc that work on this project: M. Rossetti, K. Petropoulos, L. Fabiani.*

Università di Roma Tor Vergata

**Dipartimento di Scienze e Tecnologie Chimiche**

# Poster

Università di Roma Tor Vergata

# BIOCHEMISTRY

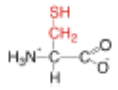
Dipartimento di Scienze e Tecnologie Chimiche

Sonia Melino, Marco Sette, Matteo Ciocci, Emilia Di Giovanni, Alessio Bocedi and Giorgio Ricci

## BIOCHEMISTRY FOR HEALTH AND ENVIRONMET

### *Erythrocyte Glutathione transferase, a new biomarker to check environmental pollution or to evaluate the efficiency of dialytic treatments*

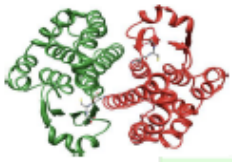
Glutathione transferase is and enzyme able to detoxify our organism from a variety of toxic compounds. In the Lab directed by Prof. G.Ricci it was observed an increased expression of this enzyme in erythrocytes of patients affected by kidney diseases or of health subjects exposed to toxic compounds. Thus, this enzyme can be used as a novel biomarker to evaluate environmental pollution or to assess the efficiency of dialytic treatments. The analysis is simple, rapid, non-expensive and can be performed through a simple finger puncture.




### *Studies on amyloid diseases like Parkinson and Alzheimer*

About 20 human diseases including Parkinson's disease, Alzheimer's and Huntington's diseases and Amyotrophic lateral sclerosis are characterized by incorrect protein aggregations, i.e. amyloid fibers or amorphous aggregates. Many of these proteins show disulphide bonds in their native status, and the reduction of these links or their incorrect formation are the origin of these diseases. In the Lab of Prof. Ricci it was discovered in two proteins (albumin and Lysozyme) an unknown hyper-reactivity of selected cysteines toward natural disulfides finalized to prevent such deleterious aggregations. Studies on amyloid disease are undergoing on selected proteins to verify the importance of this new property for a correct folding.

### The role of glutathione transferase to minimize the toxicity of nitric oxide



Recent studies in the laboratory of Prof Ricci revealed an unknown role of the glutathione transferase superfamily to detoxify the cell from nitric oxide (NO), a toxic free radical present in polluted areas but also produced inside the cell. Experiments are undergoing to verify the importance of this property to protect DNA from NO.

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Alessio Bocedi, Annalisa Noce, Raffaele Fabrini, Nicola Di Daniele, Francesco Galli and Giorgio Ricci *Biomarkers in Kidney Disease* 1-22 (2016)
Raffaele Fabrini, Alessio Bocedi ,Erica Del Grosso, Laura Morlol, Giorgio Federici,Antonio Pellecchi and Giorgio Ricci *Biochemical and Biophysical Research Communications* 426, 71–75 (2012)
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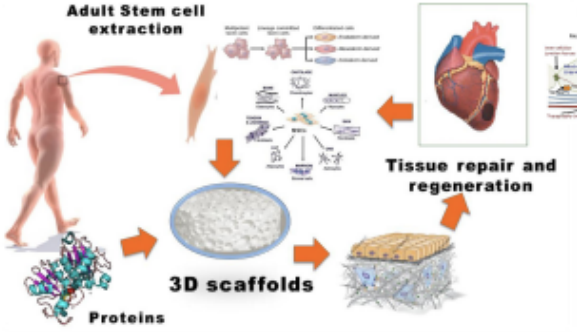
Bocedi, A., Fabrini, R., Lo Bello, M., Caccuri, A.M., Federici, G., Mannervik, B., Cornish-Bowden, A. and Ricci, G. *J. Biol. Chem.* 291, 26739-26749 (2016)
Bocedi, Fabrini, Pedersen, Federici, Iavarone, Martelli, Castagnola, Ricci. *FEBS J.* 283, 4113-4127 (2016)

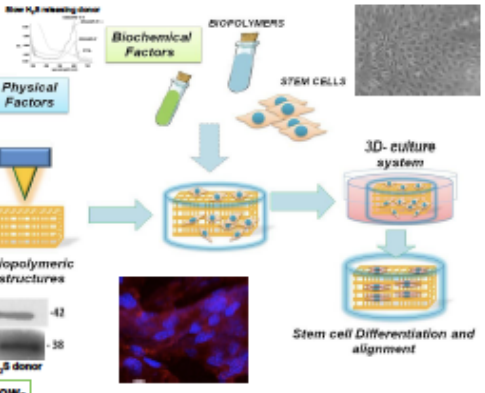
Contact: Professor G. Ricci – riccig@uniroma2.it

## BIOCHEMISTRY FOR TISSUE REPAIR

### *BIOSIGNALING AND REGENERATIVE THERAPY*




A relevant step in the Regenerative Medicine is the development and optimization of biocompatible scaffolds mimicking the ECM. The design of 3D-stem cell culture systems with appropriate microarchitecture, right biochemical and physical factors, able to improve the cell growth, proliferation and migration, is pivotal for providing functional tissue structure.




Physical stimuli and slow-$H_2S$ releasing agents can drive the fate of mesenchymal stem cells (MSCs).

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Bhabyan AI, Papajani VT, Paci M, Melino S *Molecules*, 20, 1721-50 ( 2015)
Mauretti A, Neri A, Kossover O, Seliktar D, Nardo PD, Melino S. *Macromol Biosci.* 18(8):847-58 (2018)
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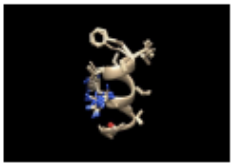
Ciocci M, Micchi F, Carotenuto F, Di Giovanni E, Prospositio P, Francini R, De Matteis F, Rashetov I, Casalboni M, Di Nardo P, Melino S *Stem Cell and Development (in press)* (2017)

Contact: Professor S. Melino – melinos@uniroma2.it

## STRUCTURAL BIOCHEMISTRY & SPECTROSCOPY

***Structural and functional studies of antimicrobial peptides***
M. Aschi (IT), A. Bozzi (IT), E. Breukink (NL), N. Bouchemal (FR), M. Sette (IT)



***Protein-mediated metal transport in bacteria studied by NMR and molecular biology***
M.Sette (IT), M. Piccioli (IT), A. Battistoni (IT)

***Structural studies of H-NS and its interaction with DNA***
A. Bonvin (NL), N. Ulyanov (USA), A. Battistoni (IT), C. Gualerzi (IT), S. Rimsky (FR), T. Madl (A) J. Amato (IT), C. Giancola (IT), M. Sette (IT)

***Probing protein cavities by NMR spectroscopy***
M. Sette (IT), F. Mulder (DK)

Contact: Dr. M. Sette – sette@uniroma2.it

# Recent Research Activities at the Analytical Chemistry Laboratory

Università di Roma Tor Vergata

Dipartimento di Scienze e Tecnologie Chimiche

F. Arduini, D. Moscone, L. Micheli, G. Palleschi, S. Piermarini, A. Porchetta, F. Ricci, G. Volpe

## NATURE-INSPIRED DNA-BASED NANODEVICES

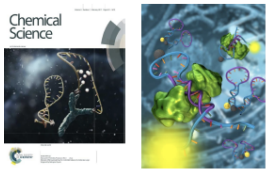
**Mimic Nature to design nucleic acid based nanodevices able to detect cancer markers and monitor treatment efficacy.**

**GOAL:** Mimic Nature to design nucleic acid based nanodevices able to detect cancer and monitor treatment efficacy.

### DNA-based nanoswitches for diagnostic applications


Idili *et al.*, **Nano Lett** 2015, 15, 5539–5544.
Idili *et al.*, **Anal Chem** 2014, 86, 9013–9019.

### DNA-based nanomachines for drug-delivery applications



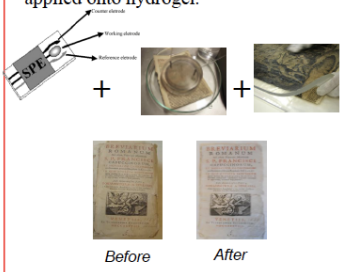

Ranallo *et al.*, **Nat Comm**, 2017,*(in press)*.
Rossetti *et al.*, **Chemical Science**, 2017, 8, 914-920.

### DNA nanodevices using Nature "tricks"


Del Grosso *et al.*, **Nanoscale** 2016, 8, 18057-18061.
Ricci *et al.*, **Acc Chem Res** 2016, 49, 1884–1892.

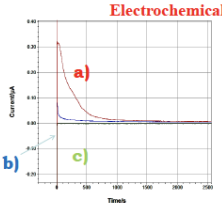
## BIOSENSOR/HYDROGEL for paper and wood artworks

***Non invasive «real-time» diagnostic tool for paper and wodd arworks*** is constituted of an electrochemical biosensor coupled with a flow sampling plate applied onto hydrogel.




*Before* *After*

**Electrochemical monitoring**

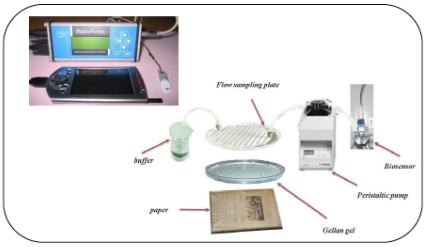



a) Material removed from *Breviarium* page

b) Specific degradation product of cellulose, i.e. glucose, removed from *Breviariium* page

c) Filter paper

Detection: - 50 mV vs Ag using Palm Sens instrumentation
Flow rate: 0.1 mL/min; Gel application and Sample analysis: 1 h

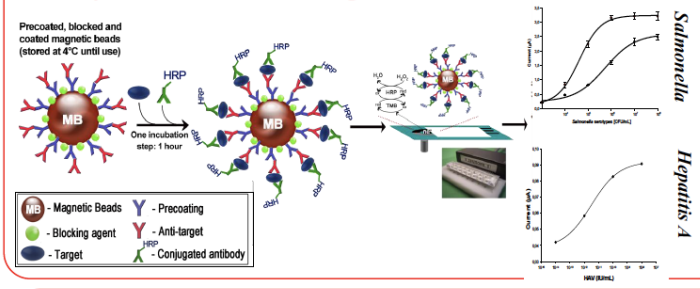


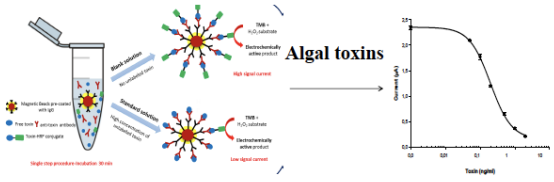

Sampling Flow System
(**paper-gel-system under continuos flow**)
coupled with thin-layer cell with biosensor

Changing the gel hydrophilicity and the selectivity of biosensors, this tool could be applied on different materials such as wood or parchment.

Mazzuca C. et al. (2017) **J Coll Interf Science** (2017) 502, 153-164; Micheli L. et al. (2016) **Microchem J** (2016) 126, 32-41; Micheli L. et al. (2014) **Advances in Chemistry**, 2014, 1-10

## Enzyme-Linked Immuno-Magnetic Electrochemical/Colorimetric assay (ELIME) for bacteria, virus and algal toxins

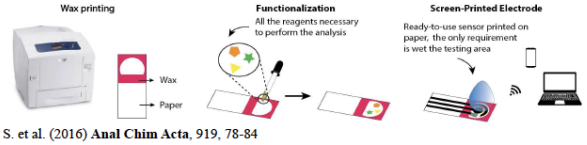



Volpe G. et al. (2016) **Talanta** 149, 202-10; Micheli L. (2017) **Proceedia Technol.** (in press)

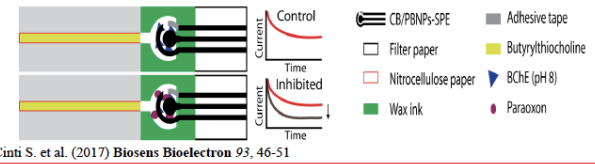
## SUSTAINABLE (BIO)SENSORS FOR ENVIRONMENTAL APPLICATIONS

### Paper-based sensor for phosphate detection in river water

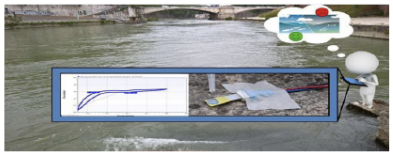



Cinti S. et al. (2016) **Anal Chim Acta**, 919, 78-84

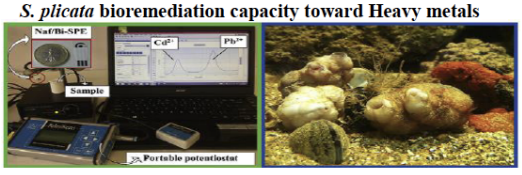
### Paper-based biosensor for nerve agent detection




Cinti S. et al. (2017) **Biosens Bioelectron** *93*, 46-51



### Bismuth-based sensor to evaluate the marine organism *S. plicata* bioremediation capacity toward Heavy metals




Colozza N. et al. (2017) **Sci Tot Environ** 584, 692-700

*Acknowledgements.* *Special thanks go to the PhD students and postdoc that tcollaborate and work on these project:* A. Amodio, A. Idili, S. Cinti, N. Colozza, E. Del Grosso, L. Fabiani, D. Neagu, D. Mariottini. V. Mazzaracchio, K. Petropoulos, M. Tomei, S. Ranallo, M. Rossetti.

Università di Roma Tor Vergata

# Detection of Okadaic and Domoic Acid in Sea Water by Colorimetric Assays

Dipartimento di Scienze e Tecnologie Chimiche

L. Micheli, G. Palleschi, S. Piermarini, A. Porchetta, F. Ricci, G. Volpe

## INTRODUCTION

In the frame of SMS project, aimed to develop a novel automated networked system (Figure 1) for *in situ* monitoring of marine water contaminants in coastal areas, we proposed two colorimetric assays for the detection of Okadaic acid (OA) and Domoic acid (DA).

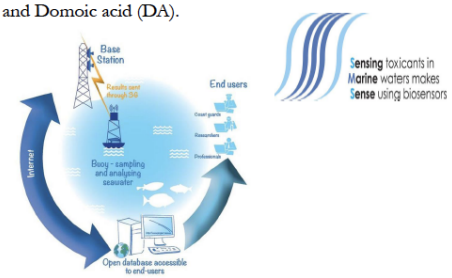



Fig. 1 - Scheme of the wireless transmission system proposed.

In order to achieve this goal the scientific team of SMS has been engaged to design a **multi-modular miniaturized apparatus** that will host both a **Sampling Module** and an **Analysis Module** (Figure 2) in a single unit. This apparatus will be located in buoys already existing in marine areas of Europe for continuous monitoring of OA and DA. With the wireless transmission capability for real-time data, as well as remote access to collected data it will be possible to realize an **automated water quality monitoring** and **alarm system** that will be fairly easy to deploy.

Fig. 2 - SMS modular automated measurement prototype with portable analyzer touch screen.

## OKADAIC ACID DETECTION

In order to detect OA a colorimetric assay, based on the inhibition of protein phosphatase type 2A (**PP2A**), was set up. The enzymatic activity was determined by measuring the rate of colour production of the yellow *p*-nitrophenol using *p*-nitrophenyl phosphate as the substrate (Figure 3).

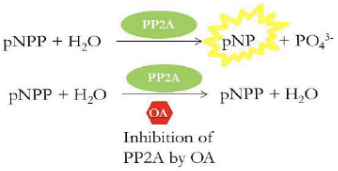



Fig. 3 - Schematic representation of the assay principle.

## RESULTS FOR OKADAIC ACID

Different calibration curves for OA and other toxins such as DTX-1, DTX-2, domoic acid, palytoxin and saxitoxin, were constructed using a non automated colorimetric apparatus. As shown in Figure 4, the system is able to detect OA, DTX-1 and DTX-2 (toxins belonging to the DSP class). On the contrary, the PP2A enzyme was not inhibited by other marine toxins. (Figure 5).

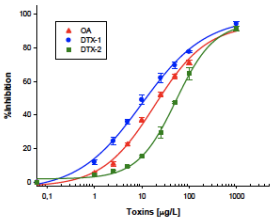



Fig. 4 - Calibration curves of DTX1 and DTX2 compared to OA.

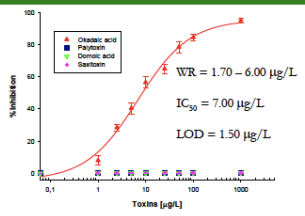



Fig. 5 - Calibration curves of PTX, DA and SAX compared to OA.

Promising results were obtained analyzing two standard solutions of OA with the SMS modular automated prototype and the non automated system. As shown in Fig. 6 both systems gave similar percentages of inhibition.

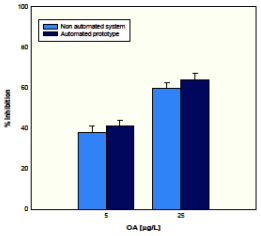



Fig. 6- Comparison of the non automated system with the automated prototype.

## DOMOIC ACID DETECTION

A competitive **ELIMC** (Enzyme-Linked Immuno-Magnetic Colorimetric) assay was developed for the detection of DA. In a single step procedure the main reagents (DA, DA-HRP and rabbit polyclonal antibody) were mixed, in an Eppendorf tube, together with magnetic beads (MBs, pre-coated with anti-rabbit IgG) and incubated for 30 minutes (Figure 7). The MBs, covered with the immunological chain, were then dispersed in a solution containing 3,3,5,5-tetra-methylbenzidine and hydrogen peroxide, as substrates for the HRP enzyme (Figure 7). The amount of enzymatic product is detected at 450nm.

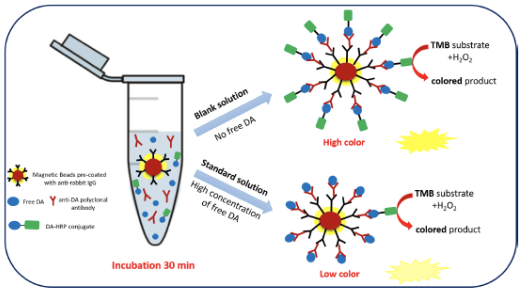



Fig. 7- Schematic representation of the ELIMC assay principle.

## RESULTS FOR DOMOIC ACID

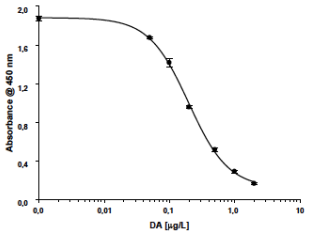



Fig. 8 - Calibration curve of DA.

A typical sigmoidal calibration curve is reported in Figure 8. A working range between 0.15 and 1.50 µg/L, an $IC_{50}$ value of 0.20 µg/L and a LOD of 0.025 µg/L were calculated.

## CONCLUSIONS

The colorimetric assay proposed for OA detection has been integrated on a miniaturized automated apparatus and measurements *in loco* will be organized. The integration of the ELIMC assay in an automated apparatus is still in progress.

*The authors would like to acknowledge the financial support from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 613844.*

***Acknowledgements.*** ***Special thanks go to the PhD students and postdoc that to collaborate and work on these projects: M. Rossetti, K. Petropoulos, L. Fabiani.***

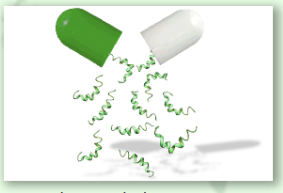
Università di Roma Tor Vergata

# Physical Chemistry @ Tor Vergata
# From Bioactive Molecules to Smart Materials

Dipartimento di Scienze e Tecnologie Chimiche

## Development of peptide-based drugs against multiresistant bacteria and cancer

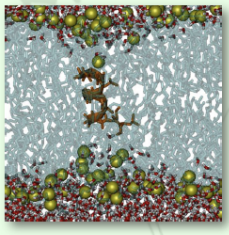
Peptides are short chains of amino acids, naturally present in our body. Their ability to potently modulate several biological processes makes them promising drug candidates.



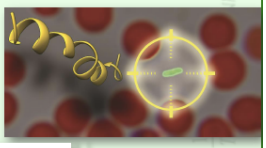
We combine multiple spectroscopic and computational approaches to understand the mechanism of action of bioactive peptides, focusing mostly on two areas:

**1) Antimicrobial peptides**

Bacteria are rapidly becoming resistant to available antibiotics and soon a small wound or the most basic surgical operation could become deadly again. Antimicrobial peptides kill microbes very quickly and are a possible solution to this problem. We want to understand how these molecules kill bacteria, without damaging human cells.

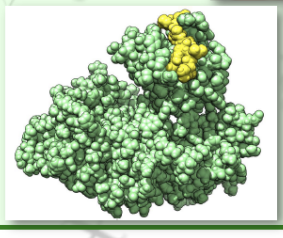


*Experimental data and computer simulations allow us to understand how antimicrobial peptides insert in cellular membranes and form pores that kill bacteria, but not human cells.*



**2) Peptide inhibitors of protein-protein interactions involved in cancer**

Many biological processes are mediated by the association of two proteins. Therefore, inhibiting protein-protein interactions is a natural way to interfere with pathological processes. We are developing peptides to inhibit the interactions of the phosphatase SHP2, which is involved in cancer.

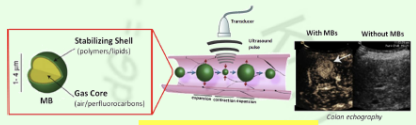


*SHP2 association to other proteins is needed for its activation, that controls cell proliferation and differentiation.*

## "SMART" Devices for Biomedicine

### IMAGING

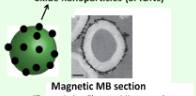
**Microbubbles (MBs) as Ultrasound Contrast Agents (UCA) for Echography**



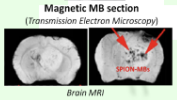

**MBs for multimodal imaging**

**MBs for magnetic resonance imaging (MRI)**

Superparamagnetic iron oxide nanoparticles (SPIONs)



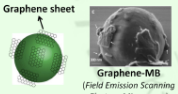
Magnetic MB section
(Transmission Electron Microscopy)



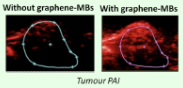

Brain MRI

**MBs for photoacoustic imaging (PAI)**

Graphene sheet



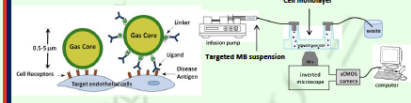
Graphene-MB
(Field Emission Scanning Electron Microscopy)

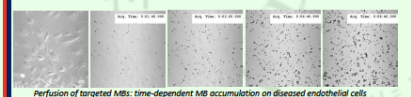



Tumour PAI

### TARGETING

**Targeted MBs**

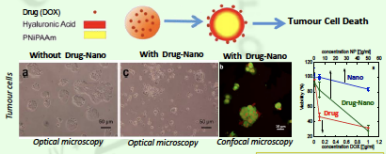


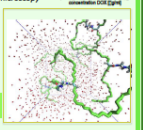
*Perfusion of targeted MBs: time-dependent MB accumulation on diseased endothelial cells*

### DRUG DELIVERY

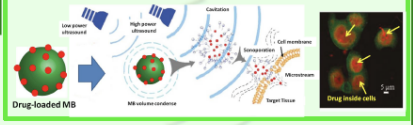
**Thermoresponsive nanogels**




**and computer simulations:**



**Drug-loaded MBs**




### THERANOSTICS

**Therapy & Diagnosis in one delivery formulation**

## A physical chemistry approach in the cultural heritage field

Paper artworks with time tend to become brownish, brittle and to smell. To restore them, a wet cleaning process is necessary.

Recently, the use of hydrogels to clean paper artworks during restoration has been proposed

***The chosen hydrogel:***

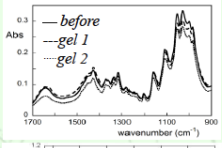
- ✓ must be applied and removed on a paper sheet as one body, without leaving residues on paper. → texture analyzer, rheology
- ✓ must release water in a controlled way, minimizing the swelling. → water uptake, weight loss measurements
- ✓ must be an efficient cleaning system → infrared spectroscopy (FTIR/ATR), scanning electron microscopy, high performance liquid chromatography, pH measurements, optical microscopy
- ✓ must have the mesh size large enough to allow the removal of degradation products from paper and the diffusion of hydrolytic enzymes, needed to remove glue → fluorescence microscopy (FRAP), scanning electron microscopy

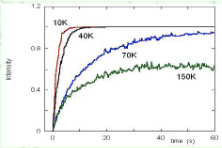
*before*

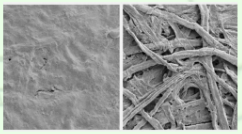
*during*

*after*

*FTIR/ATR spectra*



*Scanning electron microscopy images before and after cleaning with a gel to remove old glue*

*FRAP experiments to study the mobility of molecules into a gel using fluorescent dextrans of different size*

Università di Roma Tor Vergata

# Physical Chemistry @ Tor Vergata
# From Bioactive Molecules to Smart Materials

Dipartimento di Scienze e Tecnologie Chimiche

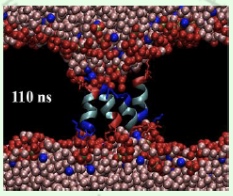
## Molecular dynamics simulations of biological systems

$$\frac{d^2\vec{r}_i(t)}{dt^2} = m_i^{-1}\vec{F}_i \qquad \vec{F}_i = -\frac{\partial}{\partial \vec{r}_i}V(\vec{r}_i,\ldots\vec{r}_N)$$

It is possible to create *simple* models of the investigated molecular systems. Thanks to these models and the power of the modern computer clusters, it is possible to «follow» *in silico* the dynamics of the molecules to predict their behavior.

### A few examples ….

**Antimicrobial peptides (AMPs)**

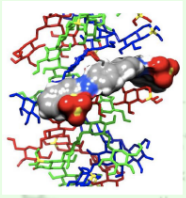



AMPs kill bacteria by perturbing their cellular membrane. Simulations clarify their mechanism of action

**Mutations and pathologies**

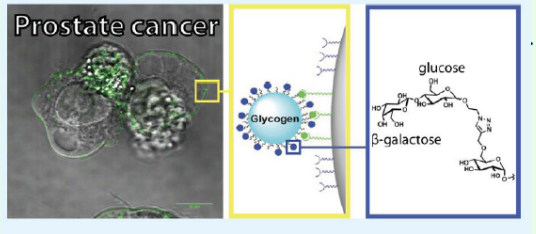
Single amino acid substitutions in proteins perturb their correct activity. *In silico* we can predict the molecular basis of the anomalous behavior

**Polysaccharides designed to regulate the drug release**

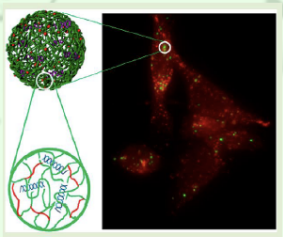


Simulations can be used to design innovative molecular systems for controlled drug release

## The engineering of biofunctional nanoparticles for siRNA delivery and targeting of cancer cells




Glycogen nanoparticles can be used as a biosourced glycoscaffold for engineering multivalent glyconanoparticles. Nano-particles made of glycogen, a naturally occurring highly branched polymer of glucose, were functionalized with lactose through copper(I)-catalyzed alkyne–azide cycloaddition chemistry, for targeted interaction with lectins *ex situ* and on prostate cancer cells.



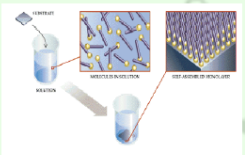
Engineered redox-responsive nanoporous poly(ethylene glycol)–poly(L-lysine) particles (NPEG–PLLs) exhibit no toxicity while maintaining the capability to load and deliver a small interfering RNA sequence (siRNA) targeting the anti-apoptotic factor, survivin, in prostate cancer cells.

## Bio-Inspired Functional Nanomaterials

### Surface modification techniques

**1. Self-assembly**

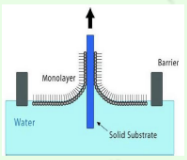
Spontaneous organization of molecular *building-blocks* to generate supramolecular architectures.



*Self assembly is a key nanotechnological approach for the construction of nanometric structures with defined geometries.*

**2. Langmuir-Blodgett (LB)**

LB technology is based on the tendency of amphiphilic molecules to orient themselves at an air/water interface. Thin films can be built up by transferring the monolayer onto a solid support.

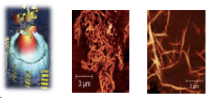



*Advantages:*
- *control of thickness and molecular organization*
- *homogeneous deposition over large areas*
- *possibility to transfer monolayers on almost any kind of solid substrate*

### Applications

**Health**

Study of peptide aggregation, to understand the evolution of several neurodegenerative diseases.

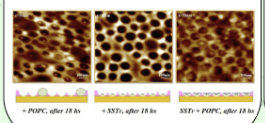


**Energy**

Development of bio-inspired dye sensitized solar cells (DSSC). Next step will be the use of waste products.

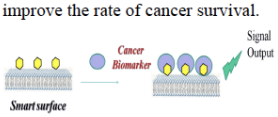
**Coating**

Development of antimicrobial coatings, by using peptide monolayers.



**Sensors**

Development of lipid-based sensors for the detection of tumor biomarkers in blood. This would allow early diagnosis of tumors, and would improve the rate of cancer survival.



# Carbon-Based Compounds: Versatile Materials for Photocurrent Generation in Photovoltaic Devices and as a Fluorescent Platform for Heavy-Metal Ion Sensing

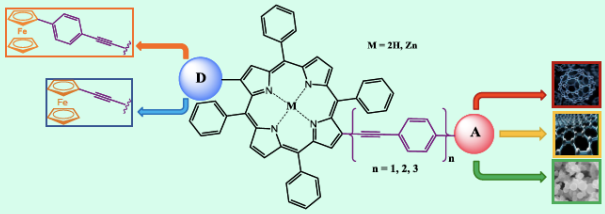
Università di Roma Tor Vergata

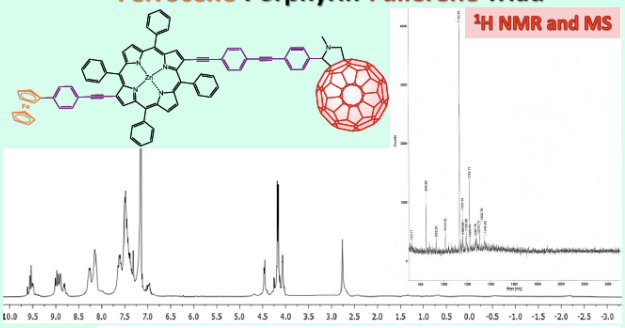
Dipartimento di Scienze e Tecnologie Chimiche

F. Limosani, F. Possanza, C. Lorecchio, A. Leoni, P. Tagliatesta

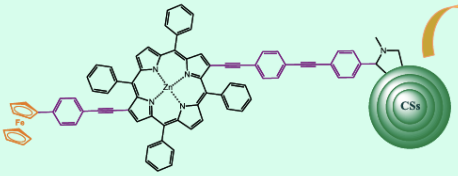
The research objective is the synthesis and characterization of porphyrins linked to different electron **donor** and **acceptor** moieties through '**molecular wires**' of variable lengths. The basic concept relies on the realization of composite material based on Ferrocene-Porphyrin and Carbon nanomaterials (**Fullerene**, **Carbon Spheres** and **Graphene**). The goal of our study is the selection of the more stable and reproducible material that can be applied in future as active dye in solar energy conversion devices.

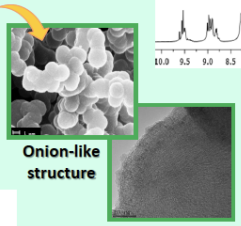
## Ferrocene-Porphyrin-Fullerene Triad

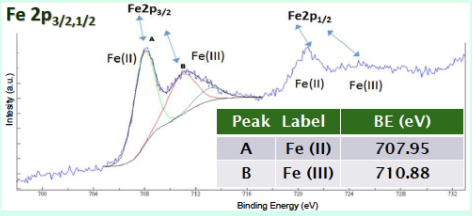


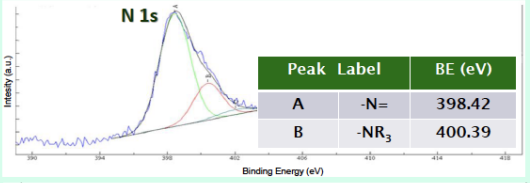

## Ferrocene-Porphyrin-Carbon Spheres (CSs) Triad



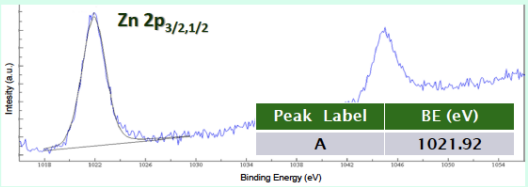




| Peak | Label | BE (eV) |
|---|---|---|
| A | Fe (II) | 707.95 |
| B | Fe (III) | 710.88 |




| Peak | Label | BE (eV) |
|---|---|---|
| A | -N= | 398.42 |
| B | -$NR_3$ | 400.39 |

**XPS Spectroscopy**

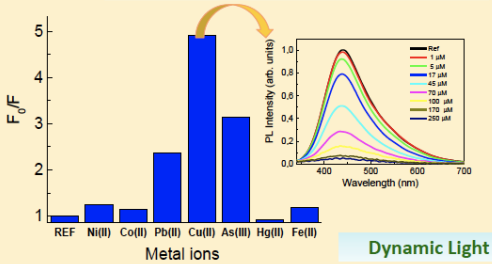



| Peak | Label | BE (eV) |
|---|---|---|
| A | | 1021.92 |

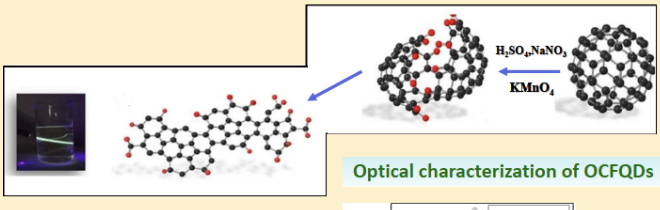
- Atomic ratio Zn: Fe is 1 ⟶ confirm the anchored species
- Co-presence Fe (II) e Fe(III), Fe (III) produced by the electronic charge transfer interaction between Fe(II) and CSs

A novel type of graphene-like quantum dots, synthesized by oxidation and Cage-Opening of $C_{60}$ Fullerene (OCFQDs), has been studied as a fluorescent and absorptive probe for several heavy-metal ions. OCFQDs behave quite differently in the presence of heavy-metal ions, in that a multiple sensitivity to $Cu^{2+}$, $Pb^{2+}$ and $As^{3+}$ was observed through comparable quenching of the fluorescent emission and different variations of the transmittance spectrum. DLS measurements confirm, that this response is due to multiple complexation and subsequent aggregation of OCFQDs.

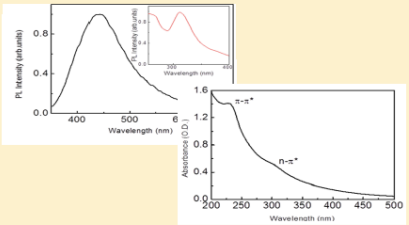
### The Quenching effect of heavy-metal ions on the PL of OCFQDs



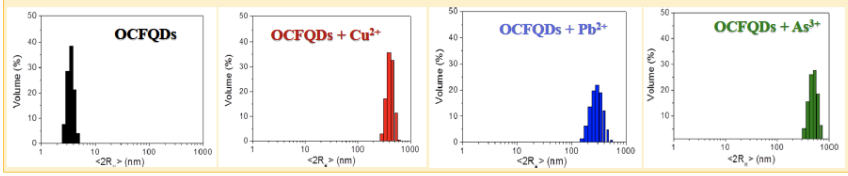

### OCFQDs: Modified *Hummer method*




### Optical characterization of OCFQDs




### Dynamic Light Scattering (DLS)



# Understanding KuQuinones Equilibria for Biomedical Applications

Università di Roma Tor Vergata

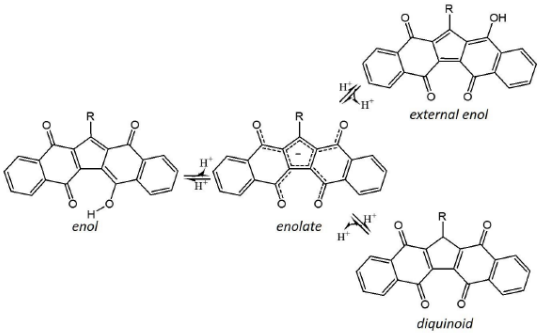
Dipartimento di Scienze e Tecnologie Chimiche

F. Sabuzi, V. Conte, B. Floris, P. Galloni

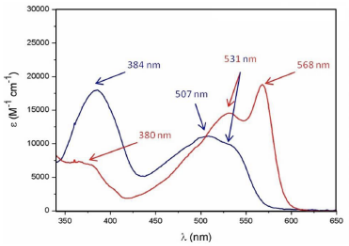
Recently, we described a one-pot reaction for the synthesis of a new class of quinoid compounds, called KuQuinones (KuQs), that are characterized by a pentacyclic skeleton.[1] Since KuQuinones structure is composed by two naphthoquinone units, keto-enol tautomerization is expected, leading to the formation of four different species (Scheme 1).

To better understand KuQuinones equilibria in solution, spectroscopic experiments have been performed in three solvents differing in polarity and ability to participate in hydrogen bond formation.

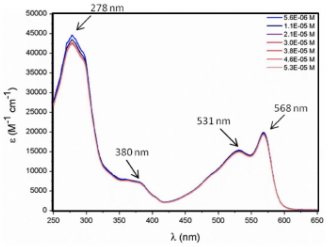
Such study resulted an appropriate tool to understand the nature of the prevalent KuQs species in biological media that are responsible of the antitumor activity of such compounds.



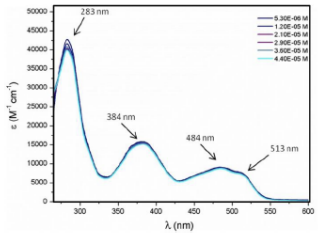

Keto-enol tautomerization in KuQuinones.



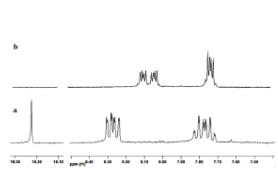

UV-vis absorption spectra of KuQTEG in $CHCl_3$ (red line) and in $CHCl_3$ + NaOH excess (blue line).



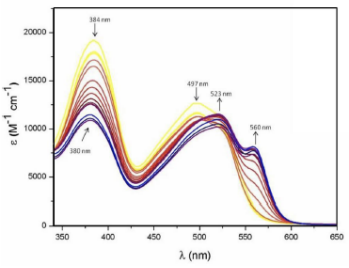

Comparison between $^1$H NMR spectra of KuQTEGMe in a) $CDCl_3$, b) DMSO-$d_6$



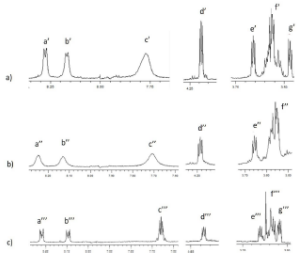

Molar extinction coefficient of KuQTEG in DMSO at different concentrations.



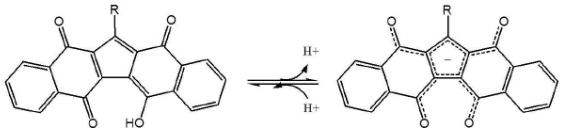
Molar extinction coefficient of KuQTEG in $CHCl_3$ at different concentrations.



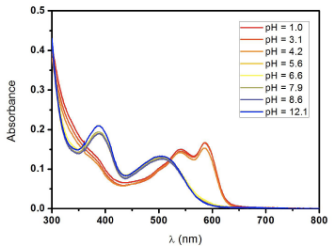

UV-vis absorption spectra of KuQTEGMe in MeOH at different concentrations.



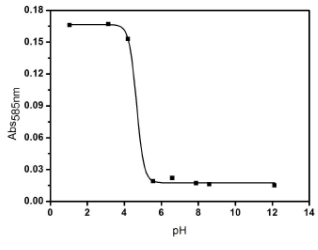
$^1$H NMR spectra in MeOD: a) $1.0 \cdot 10^{-5}$ M; b) $5.0 \cdot 10^{-6}$ M; c) $1.0 \cdot 10^{-6}$ M




Acid-base equilibrium in KuQuinones.




Spectrophotometric titration for KuQTEGMe in aqueous solutions at different pH




Curve of KuQTEGMe for pKa determination

Collected experimental data suggest that in the analysed solvents, KuQuinones exclusively undergo to acid-base reaction at the enol group. In fact, all the observed spectral variations seem to be due to the acid-base reaction in which the enol group is involved; furthermore aggregation phenomena are also plausible in highly concentrated solutions. Moreover, till date no spectroscopic evidence has been achieved to confirm the existence of the *diquinoid* species or *external enol* species in solution. For this reason, considering the exclusive acid-base equilibrium in KuQuinones, the pKa value of KuQTEGMe has been calculated spectroscopically. The dependence of the absorbance at 585 nm on pH describes a sigmoidal curve, which allows the calculation of a pKa=4.7±0.1.

Such low pKa value constitutes an explanation that in MeOH and DMSO water traces in the solvent may be responsible of the deprotonation of the acidic enol proton

**References:**

[1] Coletti, A.; Lentini, S.; Conte, V.; Floris, B.; Bortolini, O.; Sforza, F.; Grepioni, F.; Galloni, P. *J. Org. Chem.* **2012**, *77*, 6873-6879.

[2] Arnò, B.; Coletta, A.; Tesauro, C.; Zuccaro, L.; Fiorani, P.; Lentini, S.; Galloni, P.; Conte, V.; Floris, B.; Desideri, A. *Biosci. Rep.* **2013**, *33*, 269-279.

Università di Roma Tor Vergata

# Materials for Energy Conversion and Storage

Dipartimento di Scienze e Tecnologie Chimiche

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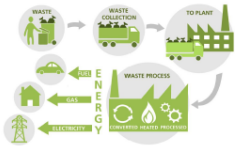
MaDE@UTV http://made.uniroma2.it/

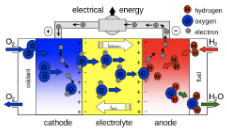
Sustainability calls for policies and strategies that meet society's present economic, social and environmental needs without compromising the ability of future generations to meet their own needs.



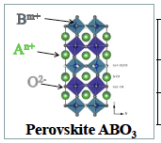


## HIGH TEMPERATURE FC (500-1000°C) SOLID OXIDE FUEL CELL SOFC

Functional ceramics with ionic and mixed ionic/electronic conductivity




### MATERIALS

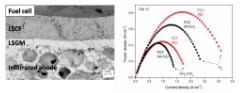



| | |
|---|---|
| *Anode* Cermet (metal + electrolyte) | Me=Cu, Ni, Co + $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ |
| *Electrolyte* $H^+/O^{2-}$ conductors | $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ |
| *Cathode* Perovskite oxides | $La_{1-x}Sr_xFe_{1-y}Me_yO_{3-\delta}$ Me=Co, Cu, Pd, Cr, Mn |

### CELLS FABRICATION

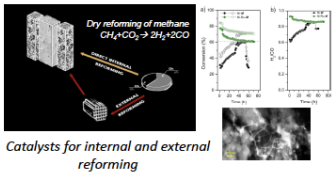
**Electrolyte supported cells** → Symmetric cells

**Anode supported cells** → Infiltrated anode




### FUEL FLEXIBILITY

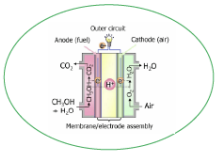
$H_2$, Syngas, Biogas




*Catalysts for internal and external reforming*

## LOW TEMPERATURE FC (60-120°C) POLIMERIC FUEL CELL PEM

### DIRECT METHANOL FUEL CELL



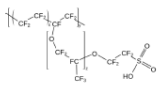

### ELECTRODE

### IONE EXCHANGE MEMBRANE

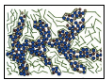
### MEMBRANE REQUIREMENTS:

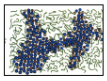
- high ionic conductivity
- as low as possible electrolyte permeability
- good chemical and mechanical resistance
- low manufacturing costs

- fluorocarbon-based polymers



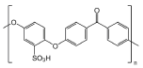
Nafion



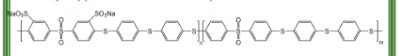


channel network interconnection and size

- hydrocarbon-based polymers



- poly(ether ether ketone)

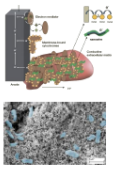


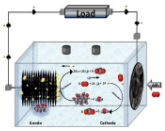
- sulfonated poly(phenylene sulfide sulfone) (sPSS)

- hybrid organic/inorganic electrolytes

## BIOELECTROCHEMICAL SYSTEMS (BES)

A BES converts chemical energy, available in a **bio-convertible substrate**, directly into electricity



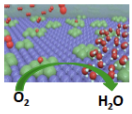



(MFCs) are efficient and flexible platforms for integrated waste (domestic and agricultural )treatment and energy recovery.

Substrate $\rightarrow CO_2 + H^+ + e^-$

### CATALYST AND CATALYST SUPPORT

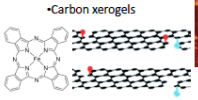
Development of non precious, inexpensive catalysts for **oxygen reduction reaction (ORR)** at cathode side of MFCs

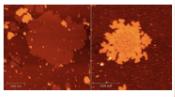



Non-PGM: M-N-C (transition metal, nitrogen, and carbon) catalysts

**Conductive Carbon support** ⟺ **Iron, Nitrogen, and Carbon source**

- Graphene oxide
- Multiwalled cabon nanotubes
- Carbon nanofibers
- Carbon xerogels





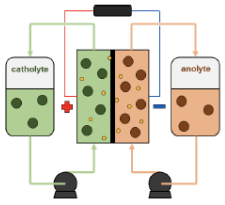
GO_ N doped FePc/GO_N composites

## REDOX FLOW BATTERIES

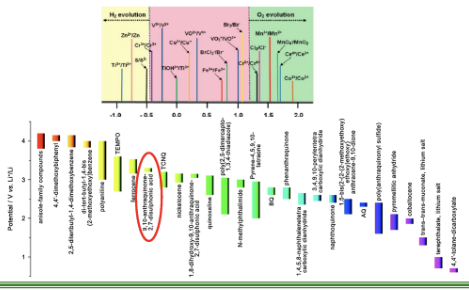
Redox Flow Battery (RFB): one of the most important and suitable technology for large-scale energy storage and renewable power sources.

### Advantages

- ✓ decoupled battery capacity and power density
- ✓ long life cycle
- ✓ flexible design
- ✓ high efficiency
- ✓ quick response time

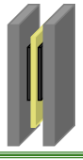



### ELECTROLYTES for INORGANIC and ORGANIC RFB




### RFBS SETUP

- ✓ Polymer membrane separators
- ✓ Advanced electrodes: *Electrode Materials and Structures – Catalysts*



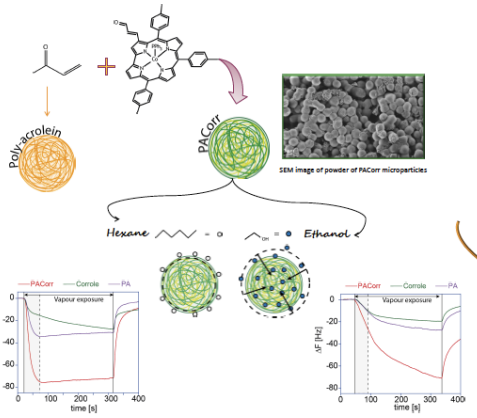
Università di Roma Tor Vergata

# Porphyrinoids @ Tor Vergata

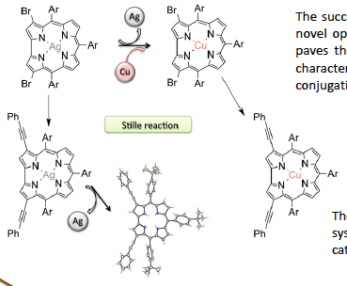
Dipartimento di Scienze e Tecnologie Chimiche

B. Berionni Berna, F. Caroleo, L. Lvova, F. Mandoj, S. Nardis, G. Pomarico,
M. Raggio, A. Savoldelli, M. Stefanelli, R. Paolesse

## SYNTHESIS

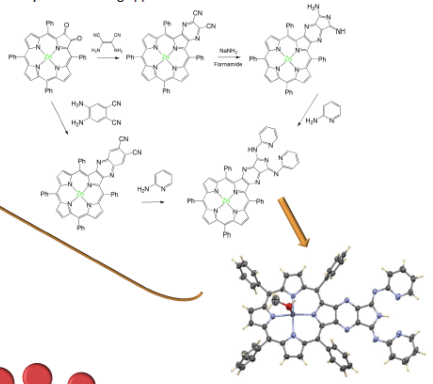



An efficient β-functionalization of [5,10,15-tris-(4- methylphenyl)corrolato]cobalt derivatives, through a Vilsmeier-type reaction, introduces an acrolein substituent, which was subsequently copolymerized with pure acrolein. The obtained hybrid microspheres (average diameter = 800 nm) were exploited as nanogravimetric chemical sensors towards several VOCs, showing enanched sensitivity with respect to pure PA and corrole.



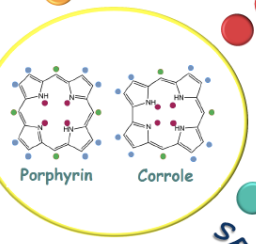

The successful preparation of β-alkynyl-substituted corroles represents a novel opportunity to modulate the properties of corroles, and this also paves the way for the preparation of novel multichromophoric species characterized by extensive full π conjugation and also for subsequent conjugation with biomolecules by using "click" chemistry.

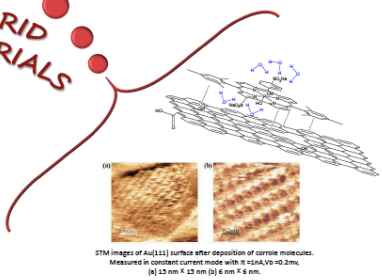
The fused porphyrin-BPI molecule is a novel sophisticated chelating system, bearing two different binding centers, appealing for both catalytic and sensing applications.



## NANOSPHERES

## HYBRID MATERIALS



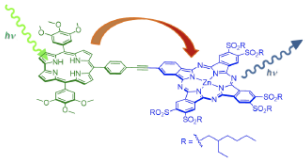



STM images of Au(111) surface after deposition of corrole molecules. Measured in constant current mode with It =1nA,Vb =0.2mv, (a) 15 nm X 15 nm (b) 6 nm X 6 nm.

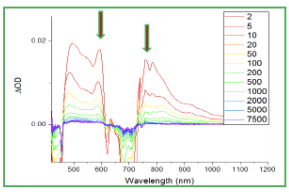
Reduction of graphene oxide in the presence of corrole leads to a water soluble hybrid. STM analysis shows the growth of a homogenous layer of corrole, induced by the underlaying layer of reduced graphene oxide (RGO) .
This hybrid material represents a potential and versatile substrate for sensor devices.

## OPTOELECTRONICS

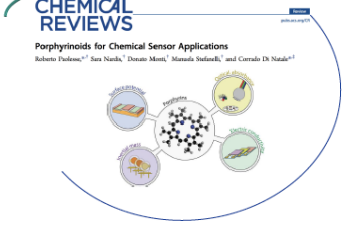
The electronic properties of push-pull molecules make them potentially useful in optoelectronics, nanoscale applications and in solar energy conversion.
The new synthesized dyad consists in a *meso* functionalized conjugated free-base corrole linked to a zinc phthalocyanine through a covalent bond.




As demonstrated from transient absorption studies (figure below), excitation of the corrole (450 nm) results in the formation of a charge-separated species, proving the electron transfer to the zinc phthalocyanine.




## SENSORS




This idea was applied in our several studies and the utility of such an approach for the classification of seed and olive oils, monitoring of natural waters heavy metal pollution and detection of prohibited food additives have been shown.

A recently developed sensing approach, showed in the figure below, is called multitransduction approach: the analyte-sensing layer interactions are transduced by two or more different mechanisms, giving the evident increase of the analysis efficiency. Considering the transparent transducer material covered with a conducting layer, ITO glass for instance, and modified with a sensing film with particular properties, one can manage to register the electrical (potentiometric or voltammetric) and optical signals of such a sensor under analyte exposure.