**PROGETTO BORSA PREMIALE**

**Title**: Development of hybrid quantum/classical approaches for the modeling of the effects of protein matrices on the physico-chemical properties of chromophores
**Supervisor**: Prof. Giorgio Moro
**SSD**: CHIM/02
**Short description**: Light-driven phenomena are among the most fascinating and complex processes in Biology. Photosynthesis or light-induced motion of some algae can be considered as two examples where the solar energy is converted in chemical or mechanical energy, respectively. As it often happens, these natural phenomena inspired the development of human technologies, such as photovoltaics and optogenetics, just to mention two examples. Albeit deeply characterized at experiment level, a clear description of the underpinning chemical mechanism is often missing, due to the intrinsic complexity of the systems and of the reactions involved. In such cases, molecular modeling represents a way to fulfill the gap in knowledge, leading to the identification of the microscopic mechanisms.
The goal of this project will be to develop specific computational models, based on a smart combination of Quantum and/or Molecular Mechanics models (QM/MM or QM/QM') to describe the optical properties and the associated (photo)chemistry of photoactive centers in biological environments. The challenges of the project will be in an accurate reproduction of the physico-chemical properties, obtained with a robust description of the molecular electronic and of their modulation induced by the static and dynamic effects of the surrounding protein. A particular attention will be devoted to the mentioned fields of biological transformations of solar energy.
The research will be carried out in joint supervision with the Institute of Chemistry for Life and Health Sciences (École Nationale Supérieure de Chimie de Paris Chimie – Chimie ParisTech), under the supervision of prof. Carlo Adamo.

**CALL FOR INTEREST - CHEMICAL SCIENCES**

**Title**: Sistemi e tecnologie per l'implementazione di Proficiency test applicati a microinquinanti gassosi
**Supervisor**: Prof. Ezio Bolzacchini
**SSD**: CHIM/12
**Short description**: Proficiency Tests (PTs) are widely used in order to certify capabilities of laboratories, determine and validate uncertainties and validate new sampling and analysis methods for determination of an wide number of chemical compounds. One of the major difficulties in the field of gaseous compounds are due to realisation of a stable and 'metrological correct' gas matrix, and, since now, the most common approach is based on emissions gases taken from real cases but, in this case, the chemical behaviour of the matrix may be different from real cases. Synthetic Reactors Bench Loops give the possibility to fill this gap, but require particular protocols for definition of reference values and their uncertainties. This project has the aim to analyse and develop innovative experimental approaches in the area of proficiency testing, with particular focus on organic pollutants like HCOH and CH3COH, aldehydes that have a great importance in the field of decarbonisation. This project aims to support decarbonisation of industrial productions by the means of increasing of accuracies of emission measurements.. The research will be financed by Ricerca sul Sistema Energetico - RSE S.p.A.

**Title**: Geochemical study of unstable minerals persistence in the sedimentary records
**Supervisor**: Prof. Fabio Gosetti
**SSD**: CHIM/01
**Short description**: Weathering of accessory carbonate and sulfide minerals is a geologically relevant source of CO2 and their impacts for Earth's carbon cycle is demonstrated. This research aims to identify the chemical and geomorphological factors that lead to the finding of unstable minerals, such as carbonate and sulfide in sediments, to better understand the mechanisms that cause or not their alteration and

preservation in the geological record. Real case histories of different geological settings and climate regime from rivers and beaches in Taiwan, from Pearl, Indus and Bermejo river catchments will be investigated. Appropriate analytical techniques will be used to characterize the sediment mineralogical fractions (optical microscope, FTIR, e and Raman spectroscopy) and identify the potential presence of catalytic metals (ICP-OES) or environmental organic marker (TOC, GC-MS and LC-MS) also through laboratory simulations based on experimental design. Moreover, the correlation of river water chemical-physical parameters and the micropollutant determination will be investigated to evaluate the dissolution kinetics of minerals and to assess the impact of climate changes and water pollution on their persistence. All the collected data will be reprocess using machine learning and data fusion approaches. This project will be held in collaboration with Sergio Andò at DISAT and with external partners. Collaboration with Chinese and European Universities and Research Centres, as well as participation in seminars and workshops is expected.

**Title**: Transforming Antigorite into a shallow reservoir for $CO_2$ capture and storage
**Supervisor**: Prof. Luca Ferrero
**SSD**: CHIM/12
**Short description**: In the last decades many studies focussed on carbon capture and storage (CCS) to find a possible remedy to reduce the large increase of anthropogenic carbon dioxide ($CO_2$) that is driving rapid global warming. CCS can potentially sequester billions of tonnes of $CO_2$ per year using the Earth as the widest laboratory available for long-term storage. Among chemical CSS, mineral carbonation is emerging as one of the best long-term solutions, being an almost complete irreversible process. The $CO_2$ transformation into carbonates (and bicarbonates) spontaneously occurring at environmental conditions is still too slow to compensate the emissions rate of $CO_2$ from industrial activities. Therefore the carbonate reaction acceleration represents a strategic asset. The surface structure of antigorite (the high temperature polymorph of serpentine) is characterised by a corrugation where $SiO_2$ layers alternate to $Mg(OH)_2$ (brucite) valleys. The dissolution and precipitation process yielding to the carbonation thus occurs on a composite crystalline substrate. In this project the kinetics of $SiO_2$ dissolution and of magnesite precipitation on the basal layers of brucite will be investigated using model crystals of lizardite, talc and brucite, whose structures reproduce the antigorite's hills and valleys. Experiments will be performed with the new microwave reactor at ANTICARB laboratory of DISAT, using different reactants. The carbonation products will be then investigated by TEM at the Microscopy Platform of DISAT. Particular attention will be paid to the possible formation of highly toxic elements such as Cr(VI) in reactions performed on natural antigorite where the production of magnetite may oxidise Cr(III). This project will be held in collaboration with Nadia Malaspina at DISAT and with external partners.

**Title**: Polysaccharides derived from biomass for the development of innovative materials
**Supervisor**: Prof. Laura Cipolla
**SSD**: CHIM/06
**Short description**: Biomass and some industrial waste are rich in polysaccharides, that can be considered as renewable source alternative to fossil-based raw materials. However, polysaccharides (i.e. starch, chitin, chitosan, cellulose) by themselves possess poor mechanical properties compared to fossil-based synthetic polymers. These drawbacks can be overcome by crosslinking, eventually in blends with suitable additives. The project will be focussed on the design of innovative polymers with suitable mechanical properties as an alternative to fossil-based polymers, through the development of extraction procedure of polysaccharides from waste and sustainable cross-linking chemistry. The use of biocatalysis will be also considered. The project may benefit of international mobility (potential destination Boku, Vienna).

**Title**: Multiscale simulations of stimuli responsive bioinorganic nanosystems for biomedical applications.
**Supervisor**: Cristiana Di Valentin
**SSD**: CHIM/03
**Short description**: The project involves the use of multiscale theoretical approaches, from quantum mechanical methods (QM) to molecular mechanics (MM), aiming at the study of complex bioinorganic nanosystems that are composed of an inorganic core nanomaterial with photophysical or magnetic properties and a bioactive component for their application to drug delivery, targeting or imaging.

**Title**: Theoretical studies of enzymatic and biomimetic catalysts for sustainable applications in prevention and abatement of air pollution
**Supervisor**: Prof. Ugo Cosentino
**SSD**: CHIM/02
**Short description**: The PhD project will regard the study of enzymes and of bio-inspired molecular catalysts able to activate small gaseous molecules that are present in traces in Earth's atmosphere. In particular, focus will be on the elucidation of the catalytic mechanisms of the CO-oxidizing enzyme Cu/Mo CO-dehydrogenase, and of the methane-oxidizing particulate methane monooxygenase (pMMO) enzyme. Investigations will be performed by means of quantum chemical methods, quantum mechanics/molecular mechanics approaches and hybrid dynamic simulations. PhD candidates will have the possibility to spend a research period abroad at the laboratory of Prof. Ulf Ryde (Lund, Sweden)

**Title**: Wet chemistry process for new generation solar cells based on sustainable chacogenide thin film
**Supervisor**: Prof. Simona Binetti
**SSD**: CHIM/02
**Short description**: This research project is focused on the optimization of the precursors ink and of the wet low cost deposition techniques for inorganic chalcogenide thin films (employable as absorbers in new generation solar cells) as well as for their corresponding Cd-free and non-toxic buffer layers. The quaternary alloys involved in this research are structured as Cu2XY(S,Se)4 (with X = Zn, Mn and Y = Sn, Ge), already known and well-documented in the literature thanks to their good performances, high stability, high sustainability and possibility to modulate the energy gap aiming to make them suitable for tandem applications with silicon or perovskites. The corresponding Cd-free n-type buffer layer that will be examined in this project are Zn(O,S), ZnS, ZnSnO e TiO2. In this project will be investigated the most-performing wet chemical deposition techniques among chemical-bath deposition, film applicator deposition, spray pyrolysis, ink-jet printing and Atomic Layer Deposition (ALD). The optimization of the back contact with a proper transparent conductive oxide will make the devices suitable for bifacial or tandem application, allowing to overcome theoretical efficiency limitations. The collaborations with other European research centers such as Tallinn University of Technology, Technische Universiteit Delft and Institut Photovoltaique d'Ile-de-France will allow the candidate to spend a period abroad, expanding its knowledge by learning complementary characterisation skills and techniques for the above-mentioned materials.

**Title**: Study of quantitative relationships between structural determinants and redox properties in flavoproteins through machine learning
**Supervisor**: Prof. Luca De Gioia
**SSD**: CHIM/03
**Short description**: The relationship between the redox properties of cofactors and apoproteins is an important area of study both for basic research and technological applications. Flavoenzymes catalyse a large array of redox reactions in biology, which requires proper orientation and electrochemical tuning of the flavin cofactor for optimal reactivity with the acceptor or donor redox molecule. It is known that different redox behaviours of flavins depend on their specific polypeptide environments, and systematic studies revealed as major determinants specific hydrogen-bonds as well as global electrostatic and hydrophobic interactions, π-π stacking between the isoalloxazine ring and aromatic residues as well as redox-state induced conformational changes of the tricyclic ring and the contacting polypeptide. However, the quantitative relationship between structural determinants and redox properties, which is crucial for the rational design of tailored molecular devices, is far from being understood.
In this project, machine learning approaches will be used to define the quantitative relationship between the structural properties of flavins and their molecular environment with thermodynamic properties such as redox potentials and pKs. The developed computational tools will then be used to predict redox properties and consequently rationally design and synthesize (in the period abroad at the Bioénergétique et Ingénierie des Protéines CNRS Institute of Marseille) artificial flavoproteins with potential application in the field of energy conversion.

**Title**: Starch-based nanocomposites enclosing natural silicate fillers for food packaging applications
**Supervisor**: Prof. Massimiliano D'Arienzo
**SSD**: CHIM/03
**Short description**: The project focuses on the development of innovative starch-based bio-nanocomposites, with improved mechanical, gas-barrier and antimicrobial properties, enclosing natural occurring silicate fillers (e.g. sepiolite, palygorskite, montmorillonite and kaolinite). Both the prepolymer and the clays will be suitably modified with surface functionalities able to provide matrix-filler compatibility and bearing reversibly photocrosslinkable groups, which deliver to the final materials the possibility to be cured to guarantee better performances, and to be dismantled "on demand" just changing the wavelength of the irradiation light. Besides intense efforts in the preparation and functionalization of fillers, a comprehensive structural (XRD, NMR), morphological (SEM, TEM, SAXS), thermomechanical (TGA, DCS and DMA) and functional characterization (mass transfer properties, oxygen transmission rate, far-infrared emissivity and antibacterial tests) will be carried out on both filler and nanocomposites. Finally, the collaboration with other University groups in Italy and abroad (e.g. University of Montpéllier, ICMM-CSIC Madrid) along with the contact with several companies will offer educational and professional tools, which will strongly boost career perspectives.

**Title**: Molecular dynamics methods for the study of properties and interactions of biomolecules
**Supervisor**: Prof. Laura Bonati
**SSD**: CHIM/02
**Short description**: Biology largely runs on the operation of complex biomolecular systems involving protein folding and dimerization, binding of small molecules, and allosteric communication. The study of these processes at atomistic level is of great relevance for the comprehension of mechanisms behind physiological processes, human diseases, pharmacological and toxicological activity of chemical compounds, as well as for the development of new drugs. Such processes, however, involve large systems up to thousands or even millions of atoms and may happen on timescales of seconds, thus their study requires the use of methods based on the Molecular Mechanics approximation. The PhD project will be focused on the use of Molecular Dynamics (MD) simulations to study diverse biological processes. When the timescale of the mechanism under study is beyond current computational limits, enhanced sampling methods (such as steered MD, Metadynamics, or accelerated MD) will be used to speed-up the calculation and obtain a deeper understanding of the underling free-energy landscape. During the PhD period the candidate will be part of a research group and collaborations with international groups will be carried out.

**Title**: Development of biomaterials for artificial 3D-printed tissues/organs
**Supervisor**: Prof. Laura Russo
**SSD**: CHIM/06
**Short description**: Regenerative medicine requires the development of cell microenvironments allowing cell survival and inducing their proliferation and differentiation. The development of artificial tissues mimicking specific organs in pathological states is the new frontier for animal free drug testing, allowing to develop personalized therapeutic approaches.
The proposed project will develop biomaterials suitable for the production of different human tissues, in particular brain, pancreas and gum, exploiting also a 3D-bioprinting approach. Biopolymers such as collagen, elastin, gelatine, hyaluronic acids or chitosan, will be properly functionalized and crosslinked in order to generate "bioinks" suitable to provide, by 3D bioprinting in presence of the specific cells, the required morphology and stiffness of the tissue, and induce cell proliferation and differentiation. For regenerative medicine purposes particular attention will be devoted to the generation of biomaterials with antibacterial activity and coating properties. New or improved chemoselective approaches will be studied to make more efficient the conjugation and crosslinking protocols, requiring fast kinetics and experimental conditions compatible with cell survival. The project includes accurate chemical and morphological characterization of the obtained constructs, and the biomedical applications in collaboration with the clinical partners. Furthermore, microfluidic apparatus containing the synthesized artificial organs (organ

on chip) will be generated to study the "ex vivo" performance. A potential stage abroad at the University of Maastricht (NL) can be considered to optimize the organ on chip providing angiogenetic properties.

**Title**: Development, Synthesis and Characterization of nanodevices to address Alzheimer disease with a multitarget approach
**Supervisor**: Prof. Barbara La Ferla
**SSD**: CHIM/06
**Short description**: Alzheimer's disease (AD) is the most common cause of dementia among neurodegenerative diseases in the elderly population. A central pathological feature of AD is the accumulation of misfolded amyloid-β (Aβ) peptides. In our laboratory we have identified and developed a new class of compounds able to interact with toxic amyloid-β peptides and to contrast their pathological effect in vitro.
Recent developments in biological systems and overall clinical experience have revealed that the single-target drugs may not always induce the desired effect to the entire biological system due to compensatory strategies and other effects. Thus, scientists have recently proposed the multi-target drug design concept. In this regard, and looking at the context of Alzheimer disease, the present PhD project has the aim of addressing the pathology in a multifunction-multitarget approach, combining the aβ peptides ligands with other "active ingredients" in a synergistic fashion exploiting a multifunctional platform. In particular the goal is to combine amyloid-β peptides ligands with beta secretase (BACE1) inhibitors (being BACE1 the enzyme responsible for the overproduction of the aβ peptides), thus "hitting the enemy from two fronts" to use a military term in the war against this pathology. In addition, compounds with antioxidant actions can be combined to reduce oxidative stress always present in a biological environment presenting neurotoxic condition. As platforms both small multifunctional dendrimers and polymeric nanoparticles will be considered. Possible destinations abroad Bilbao, Patras.

**Title**: Nanotechnological strategies to enhance the efficiency of thermoelectric materials
**Supervisor**: Prof. Dario Narducci
**SSD**: CHIM/02
**Short description**: Thermoelectricity has been a cornerstone in irreversible thermodynamics. At the same time, it has been largely used as a tool to either convert heat into electric energy or to pump heat in refrigerating machines - in both cases with no need for moving parts. Still, efficiency of both classes of devices needs to be improved to fully exploit thermoelectricity as a viable strategy for heat harvesting and management. To this aim, the thesis explores different routes to enhance the efficiency of thermoelectric materials (and devices, thereof), all making use of nanotechnology. This includes bottom-up and top-down strategies to energy filter charge carriers, fabrication of dimensionally constrained inorganic nanostructures, and the chemical control of the oligomerization process of thiophenes. The project is carried out in collaboration with several European universities and research centres, including the University of Warwick (UK), Aix-Marseille University (France) and the Institute of Micro and Nanotechnology of the Spanish National Research Council of Madrid (Spain), where the Ph.D. candidate might spend research stages.

**Title**: Lactose as s building block for sustainable bio-based polymers
**Supervisor**: Prof. Laura Cipolla
**SSD**: CHIM/06
**Short description**: Cheese whey (CW) is a polluting waste, however in the last decades, it received attention as a source of value-added products containing, among others, significant amounts of lactose. The project is focussed on the design of new "building blocks" for the synthesis of bio-based polymers from lactose obtained as by-product from cheese production, within a circular economy approach. In particular, carbohydrates derived from CW (i.e. lactose, glucose and galactose) will be suitably functionalised as building blocks for the synthesis of novel aliphatic polymers. The underlying hypothesis is that the reactivity of sugars can be properly modified by chemical methods. The use of biocatalysis will be also considered. The project may benefit of international mobility (potential destination Boku, Vienna).