**Title:** Synthesis and Characterization of New Metal Carbonyl Clusters

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**Object.** The proposed project will focus on the synthesis and characterization of new metal clusters belonging to one of the following three categories: 1) homo- and hetero-metal carbonyl nanoclusters, 2) carbonyl clusters decorated by N-heterocyclic carbenes (NHCs), 3) water-soluble heteroleptic clusters. These compounds will be prepared under inert atmosphere using Schlenck techniques. Project 1 will focus on the synthesis of high nuclearity metal carbonyl clusters with reversible redox properties which may be viewed as models of ultra-small metal nanoparticles [1]. Possibly, bimetallic clusters will be used also as precursors of catalytic-active metal nanoparticles with controlled dimensions and composition [2]. The aim of project 2 will be the synthesis of carbonyl clusters containing NHC ligands. The approach for their synthesis will be the reaction of preformed anionic metal carbonyl clusters with M(NHC)Cl complexes (M = Au, Ag or Cu) on the attempt to isolate unprecedented high nuclearity or otherwise unstable carbonyl compounds [3]. Finally, project 3 will concern the synthesis of heteroleptic platinum clusters using water-soluble phosphines in order to test their potential antitumor activities.

**Characterization.** The compounds will be characterized via X-ray crystallography and by combined FT-IR, ESI-MS and NMR spectroscopy studies. Finally, preliminary electrochemical studies will be carried out in the case of clusters with multivalent behavior.


**Keywords:** cluster, multivalent behavior, carbonyl, N-heterocyclic carbene (NHCs)
Title: Asymmetric organocatalysis in the preparation of biologically relevant compounds

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Topic

This thesis will focus on the development of new catalytic asymmetric methods directed at the preparation of biologically relevant compounds in enantioenriched form. Due to strikingly different biological profiles often shown by the two enantiomers of chiral molecules, there is a stringent need for synthetic methods guaranteeing the controlled obtainment of a desired (single) stereoisomer. Besides, in the broader context of sustainable development, new synthetic methods should comply with green chemistry principles. In this latter respect, catalytic methods employing organic catalysts (organocatalysis) feature considerable advantages and will be used throughout this work.

A representative research project is the development of a new synthetic access to enantioenriched 1,2,3,4-tetrahydroquinolines through a Brønsted acid catalysed aza-Diels-Alder reaction. The 1,2,3,4-tetrahydroquinoline scaffold is a privileged structure in medicinal chemistry, as it is present in several pharmacologically interesting compounds (antibacterials, antivirals, agonists and antagonists of steroid receptors, etc). Importantly, the catalytic products feature a synthetic handle amenable to further synthetic manipulations. This reaction thus constitutes a versatile platform for the preparation of various biologically intriguing 1,2,3,4-tetrahydroquinolines.

A student involved in such a thesis will first optimise the catalytic reaction by varying different reaction parameters (catalyst structure, solvent, temperature, additives). Then, she/he will explore various synthetic transformations on the catalytic products. The student will thus acquire considerable expertise in different fields, ranging from organic synthesis techniques, structural elucidation and characterisation by e.g. NMR spectroscopy, as well as planning and process optimisation skills.

keywords: organic chemistry, asymmetric synthesis, organocatalysis

Title: Structural and electronic studies on high voltage cathode materials for rechargeable batteries

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Topic

Batteries are currently being developed to power an increasingly diverse range of application, from cars to microchip. Among the cathode materials, layered transition metal oxides have been investigated extensively. LiCoO2 is the most important commercial material because of its very good electrochemical performances, despite its major drawbacks such as high cost, toxicity and safety problems. Solid solution of layered cathode materials such as the combination of Li2MnO3 and LiMO2 (M= Mn, Co, Ni...) have been shown as promising candidate for cheaper, higher capacity and safer cathode for lithium batteries. The presence of cobalt reduces the electrode polarization and improves the activation of the Li2MnO3 component, even if present in a small amount of Co, but certainly represents an issue with regard to cost. This thesis is aimed to study the structure of the new high voltage layered Li[Li0.2Mn0.6-0.5xNi0.2-0.5xCox]O2 cathode material, using the XAS technique. As demonstrated by study in the fields of batteries, the XAS technique will be very helpful in this context because can probe the local structure around a selected atom (photoabsorber) and can be applied to disordered, amorphous, and crystalline materials, giving information in a range of 3-5 Å around the photoabsorber. Both XANES and EXAFS experiments at the K-edges of Mn, Ni and Co will be recorded and analysed. In particular, an in-situ cell which has been recently adapted and the XAFS beamline of ELETTRA will be used to test the charge discharge characteristics at very low current rate, which allows monitoring the local structure modification occurring at the metals site.

Please note that this work may include experiments to be performed at synchrotron radiation facilities (ELETTRA, ESRF) depending on the experiment schedule and funding availability.

References

keywords: Batteries, X-ray Absorption spectroscopy, synchrotron radiation
Title:
Materials for architectural and artistic applications: interaction with the environment and decay processes

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Topic
The work aims to study the decay of materials used for architectural and artistic applications in relation to their environmental exposure. Metals, such as bronze and steel, are mainly investigated, but further classes of materials can be also considered.
In order to study and follow the evolution of the decay processes, specimens of the considered material will be artificially aged by laboratory accelerated tests in conditions simulating different aggressive environments, the presence of different pollutants and different outdoor exposure geometries (e.g. unsheltered areas, exposed to rainwater runoff, or sheltered areas, exposed to PM accumulation, rain stagnation or moisture). At the same time, specimens could be also exposed to natural ageing in coupon racks (unsheltered/sheltered conditions) installed in an environmentally monitored site in Rimini (marine urban environment). During the exposure, at increasing time intervals, both the exposed surfaces and the ageing solutions (artificial or natural) will be characterized. The characterisation of the exposed surfaces is performed by microscopy and spectroscopic techniques such as SEM+EDS, micro-Raman, XRD, while the ageing solutions are analysed by wet chemical analysis, e.g. by AAS and IC. During natural ageing, monitoring and analysis of environmental conditions and pollutants could be performed.
The work could include also tests to evaluate the effectiveness of new protective products in order to reduce material decay.

Final Aim: Identification of the decay processes in relation to the environment of exposure for the design of effective conservation strategies.

Keywords: environment, pollutants, decay, corrosion, cultural heritage, conservation
Molecular-based fluorescent organic nanoparticles (NP) recently emerged as a promising alternative toward optical nanomaterials and fluorescent probes for acute bio-imaging applications. This thesis will address the theoretical investigation of structural and optical properties of such fluorescent organic nanoparticles, typically composed of donor-acceptor small molecules.

Molecular dynamics simulations of the NP formation in water/organic solvent mixtures will be associated to quantum chemical calculations, in order to provide insights on the nanoparticles formation process, the molecular orientation at the interface with solvent, surface energy and potential, as well as on the (aggregation-induced) emission and nonlinear optical properties. This theoretical work will be conducted in collaboration with experimental groups in Bordeaux (Dr. Mireille Blanchard-Desce and Prof. Vincent Rodriguez). The computational investigations will provide insights on the impact of collective interactions on the energy and electron density of the ground and relevant excited states of the aggregates. Nonlinear optical responses of the NP will also be computed and compared to second harmonic scattering measurements in order to characterize the local orientation of the molecular dyes at the interface with the solvent.

The student is expected to learn how to: i) model organic solvent and dyes with molecular mechanics force fields ii) carry out molecular dynamics simulations with state-of-the-art software iii) analyze simulation results and calculate physical observables characterizing the structure of the NP iv) calculate UV/VIS absorption and emission spectra, and non linear optical properties with quantum chemistry techniques iv) discuss and present the results in an interdisciplinary context composed by theoretical and experimental chemists.

[1] ACS Photonics, 2015, 2, 1209-1216 http://dx.doi.org/10.1021/acsphotonics.5b00301

keywords: aggregation-induced emission, organic nanoparticles, atomistic molecular dynamics, density functional theory, semiempirical methods
Title: Modeling fluorinated self-assembled monolayer for hydrophobic coatings

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Self-assembled monolayers (SAMs) coated on insulating or conducting substrates, such as SiO₂ or gold or on transparent conductor indium tin oxide (ITO), are of great interest for use in a variety of electronic devices, including sensors, transistors, electroluminescent, LCD and plasma displays. In this context, fluoroalkylsilane self-assembled monolayers (FSAMs) are extremely attractive candidates for the possibility of tailoring the surface physico-chemical properties such as surface potential, wettability, biocompatibility and corrosion resistance at molecular level. In addition, because such fluorinated compounds are both hydrophobic and lipophobic materials, efforts have been devoted to surface modification for the production of self-cleaning, anti-scratch, and anti-fouling systems, mimicking the well-known lotus effect. [1,2]

This thesis is aimed at the computational screening of new possible SAM-forming molecules with the twofold objective of minimizing then number of fluorine atoms in their molecular formula (so as to avoid CFC pollution issues) and at the same time granting optimal hydrophobic properties when coated on oxide surfaces. The most promising compounds will then be synthesized and experimentally characterized in the group of Prof. Cassani. The activity will consist in simulating the self-assembling of the SAMs on oxide surfaces via atomistic molecular dynamics simulations [3,4], in the calculation of the physical properties of the final structure, and in the simulation of the contact angle of a water droplet on the SAM.

The student is expected to learn how to: i) perform the molecular modeling the organic SAM and the inorganic substrate ii) carry out molecular dynamics simulations with state-of-the-art software iii) analyse the simulation results in terms of physical properties iv) discuss and present the results in an interdisciplinary context composed by theoretical and experimental chemists.

[1] Langmuir 2015 31, 6988-6994 http://dx.doi.org/10.1021/acs.langmuir.5b01416

keywords: Molecular Dynamics Simulations, Self-Assembled Monolayers, X-ray photoelectron spectroscopy, contact angle, fluoroalkylsilanes, indium-tin oxide
Title: A coarse-grained molecular dynamics simulations of smectic ionic liquid crystals

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Recently the ion-transport behavior in self-assembled ionic liquid crystals (ILCs) in columnar and smectic phases have been studied since the structures of ILCs have been considered as highly promising media for efficient ionic conductivity along preferential pathways. In the conventional design, the ionic mesogenic molecule consists of a positively charged cationic head and long-chain hydrophobic alkyl substituent. The driving forces leading to the formation and stabilization of the ionic mesophase, in a first approximation, are cation-cation repulsion and the van der Waals hydrophobic interactions between long alkyl tails. Microsegregation of incompatible units, aggregation of compatible units and the minimization of volume in bulk of ionic mesogens lead at suitable temperature conditions to appearance of a smectic thermotropic ionic mesophase.

The aim of this project is to investigate a class of thermotropic ILC compounds through a coarse-grained model and molecular dynamics simulations in order to: 
1) understand the role of the electrostatic interactions in stabilizing ionic smectic phases by means of orientational and translational order parameters and by distribution functions.  
2) shed some insight on the diffusion behaviour of ionic species.

A student enrolled in this project will develop expertise in molecular modeling and will learn how to carry out a computer simulation and analyze the relevant observables, taking into account the comparison with experiment.


keywords: ionic liquid crystals; molecular dynamics simulation; coarse-grained model; ionic diffusion
Title: Batteries and supercapacitors: synthesis, characterization and testing

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Topic
Nowadays, energy storage plays an important role due to its technological applications. Both batteries and capacitors are of great interest, and many researchers are looking for new active materials, synthetic routes and formulations to improve the ability of such devices to undergo several cycles of charge/discharge with high efficiency. Batteries stores energy by electrochemical reaction occurring at several electroactive couples (Faradaic process) and are characterized by a large Energy density. Capacitors differ from batteries, as they possess a higher power density and can undergo a larger number of cycles, due to the absence of faradaic processes [1, 2]. Pseudocapacitors, named also supercapacitors, represent a new class of capacitors, whose capacitance is due not only to static double-layer charge distribution, but also to a faradaic contribution. The resulting capacitance commonly increases by an order of magnitude [3].

The aim of this work would be to investigate the active material for battery and/or supercapacitors, i.e. Prussian Blue like material such and the copper hexacyanoferrate or MnO2, first by synthesizing it through different routes available in literature [3, 4], second by characterizing it to check different morphological and structural properties, and finally by testing it by means of both cyclic voltammetry and galvanostatic charge/discharge curves to establish the electrochemical performances. The electrochemical tests indicate the most suitable use in either batteries or supercapacitors. The structural characterization of the material will be done using both scattering and absorption x-ray methods of analysis.

Please note that this work may include experiments to be performed at synchrotron radiation facilities (ELETTRA, ESRF) depending on the experiment schedule and funding availability.

References

keywords: Batteries, X-ray Absorption spectroscopy, Synchrotron radiation
The main goal of our research is the study of high-resolution infrared spectra of molecules of atmospheric and astrophysical importance. The spectra are recorded in our laboratory with a Fourier Transform Infrared (FTIR) spectrometer at a maximum resolution of 0.004 cm\(^{-1}\).

The investigated species are generally stable but also transient molecules, such as ions or radicals, can be studied. This type of research is carried on in collaboration with the Chemistry Department of Bologna, where a millimetre-wave spectrometer suitable for the production of unstable species is available. In this case, only pure rotational spectra are studied.

The combination of infrared and submillimetre laboratory spectroscopy provides an extremely accurate background for undertaking astronomical searches, which are not confined to the investigation of molecules in our galaxy and in the interstellar medium, but also in the atmospheres of exoplanets and even in distant galaxies.

The species chosen for this investigation are usually less abundant isotopomers of fundamental molecules. Examples are doubly deuterated diacetylene C\(_4\)D\(_2\), \(^{14}\)ND\(_3\) and \(^{15}\)ND\(_3\). The experimental study of the rare \(^{15}\)ND\(_3\) isotopologue, although of less astrophysical relevance, provides very useful spectroscopic parameters that can be used by theoreticians to test their quantum chemical calculations.

The detection of molecules containing less abundant isotopes, for example deuterium, \(^{13}\)C or \(^{15}\)N, is crucial to estimate the values of the D/H, \(^{13}\)C/\(^{12}\)C and \(^{15}\)N/\(^{14}\)N isotopic ratios in various space environments. In the case of deuterium, the interstellar processes that lead to the formation of molecules highly enriched in D are the same that lead to complex organic species. Therefore, deuterium is a special tracer for studying the cosmic evolution of organics. It has also a cosmological significance, as it can be a test for the cosmic microwave background results. In the case of nitrogen, the measurements of its \(^{15}\)N/\(^{14}\)N isotopic ratio shows great variations in different astrophysical environments. Its evaluation can therefore provide very useful information about the evolutionary processes in the regions involved.

Molecules of atmospheric importance, mainly halogen substituted organic species, have also been investigated by FTIR spectroscopy. The laboratory analysis of their spectra is very useful for the identification of such species in the atmosphere.

Some recent publications.
1) Fine and hyperfine structure of the \(N = 1\leftarrow 0\) transition of ND\((X^3\Sigma^-)\) in vibrational excited states. L. Dore, L. Bizzocchi, C. Degli Esposti, F. Tamassia. Mol. Phys., 109, 2191 (2011).


_keywords:_
Title: Study of gas-solid interactions in catalytic reactions for the transformation of renewable raw materials by means of in-situ Diffuse-Reflectance Infrared Spectroscopy and reactivity experiments

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**Topic**

The research will be aimed at studying the interaction between gaseous reactants and the surface of heterogeneous catalysts by means of in-situ Diffuse Reflectance FTIR Spectroscopy, combined with reactivity experiments in continuous flow reactors. The DRIFT apparatus is equipped with a cell for operation at high temperature, a control system for the feed of gaseous reactant (or vaporization of liquids), and with a downstream on-line MS-quadrupole for the determination of the reaction products. The research will deal with the investigation of the interaction between bio-alcohols and catalysts based either on mixed metal oxides with bifunctional properties (ie, combining both acid/base and redox properties), or on supported metal nanoparticles, under either aerobic or anaerobic conditions. In fact, nowadays the valorization of bio-alcohols into bio-fuels of bio-chemicals is a topic of major interest for the chemical industry. In function of catalyst type and reaction conditions used, the reactant can be transformed either into longer-chain compounds (eg, C4 hydrocarbons from ethanol), or into oxidized compounds (acetaldehyde, acetic acid). The aim of the research will be that of investigating the mechanism of the reaction, and finally find out how it is possible, by means of a proper modification of the catalyst features, to improve the catalytic performance.

**keywords:** DRIFT spectroscopy, heterogeneous catalysis, gas-phase reactions, bio-alcohols, renewable raw materials, mixed oxide catalysts, supported nanoparticles, bio-fuels, bio-chemicals, reaction mechanism.
keywords:
Title: IR and NMR mechanistic investigations for homogeneous catalysis

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Topic
The project deals with the synthesis, characterization and study of the reactivity and catalytic activity of ruthenium complexes bearing ligands such as carbonyls, cyclopentadienones and N-substituted N-heterocyclic carbene (an example in Figure 1).

![Figure 1. Ruthenium based catalyst for hydrogen transfer reactions](image)

The main program will regard the use of IR and NMR spectroscopy, assisted by DFT calculations, in order to shed light on the activation and mechanism of, for example, hydrogen transfer reaction catalyzed by the ruthenium complex prepared. In situ ATR-IR and NMR spectroscopy allow to follow the transformation of functional groups of both substrate and catalyst giving back information on active catalyst and intermediates.

![Figure 2. In-situ ATR-IR of hydrogen transfer reactions catalyzed by Ruthenium based complexes](image)

The present project is integrated in a collaboration between the laboratory of inorganic chemistry (Prof. Valerio Zanotti, Dr. Rita Mazzoni) and the laboratory of catalysis (Prof. Francesco Basile). Furthermore within a collaboration with the University of Insubria (Dr. Carlo Lucarelli, Prof. Massimo Mella) DFT calculations will be exploited to predict IR spectra. The DFT feedback will be also useful in order to design novel experiments.

*keywords: IR spectroscopy, NMR spectroscopy, homogeneous catalysis, DFT calculations.*
This Master Thesis deals in synthesis and characterization of metal nanoparticles on different substrates. In recent years considerable attention has been drawn to the possibility of deposition of metal nanoparticles onto substrates (conducting or not conducting) due to its great importance in the fabrication of practical devices such as heterogeneous catalytic systems, electronic sensors, biosensors or biomaterials. Several methods have been reported to accomplish this purpose; among these chemical and electrochemical synthesis have been proved to be very striking because of the simple instrumentation needed and the capability to readily control the size and morphology of the as-deposited nanostructures through adjusting the experimental parameters. The aim is to provide the necessary tools for the preparation of non conductive (i.e. silica, hydroxyapatite, hydrotalcite) or conductive (i.e. Indium Tin Oxide (ITO), Glassy Carbon (GC)) surfaces modified with metal nanoparticles via polyelectrolyte mediated chemical synthesis or one step electrosynthesis, respectively. The effect of some variables as the choice of precursor used, the presence of additives, the kind of substrate, the electrolyte employed or the electrodeposition conditions on the nanoparticles size and distribution have been investigated. Moreover catalytic tests will be performed. These studies could offer a new approach to cost-effective way to prepare supported metal nanoparticles.

From an experimental point of view the student at the end of the training should have gained a valuable experience in the field of the synthesis and characterization of nanomaterials and their use in catalysis. Moreover a good knowledge of the following techniques and instruments will be acquired: FT-IR (Perkin Elmer), Cyclic voltammetry, Scanning Electrode Microscopy, UV-Vis spectroscopy and X-Ray Diffraction. In addition, the project is expected to improve the skills of the student in scientific communication, research work in a multidisciplinary environment and presentation of research results. Such experience will be a valuable contribution to the development of the research abilities of the young researcher and a help for their future jobs in a scientific career.

BIBLIOGRAPHY
keywords: Metal nanoparticles, composite nanomaterials, electrosynthesis, catalysis, biomedical applications.
Title: Computer simulations of reentrant nematics

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Abstract:
The purpose of this research project is to map by molecular dynamics computer simulations the phase diagram of model mesogenic particles expected to form reentrant nematic liquid crystalline phases.

Scientific background:
A puzzling phenomenon (and not yet clarified) is the observation first reported by Cladis in the mid 70s [1, 2] that some thermotropic liquid crystals have unusual reentrant properties upon decreasing temperature. These are very surprising spontaneous phase transitions from a phase with higher ordering to another with lower one, typically from smectic to nematic. This behaviour is just the opposite of what is typically observed by cooling a smectic phase towards a crystal. The phenomenon is particularly surprising because it was observed for both polar and apolar compounds [3], and to date there is still no convincing explanation [4]. Experimental results show that an anomalous reentrant phase transition can be induced by a pressure increase [5], and this is a strong hint that molecular flexibility or ‘’softness’’ may be behind this anomalous effect.

Description of project:
The master student will use for the first time a soft anisotropic potential we have developed [6, 7] to model prolate particles of various length and degree of softness to trace by molecular dynamics computer simulations the phase diagram and check whether it is possible to obtain a sequence of reentrant thermotropic liquid crystalline phases. This is a theoretical research project and the master student will learn how to perform state-of-the-art molecular dynamics computer simulations to study the collective properties of liquid crystalline phases. No prior computer programming skills are required.

References:

Keywords:
Soft Matter, Liquid Crystals, Molecular Dynamics