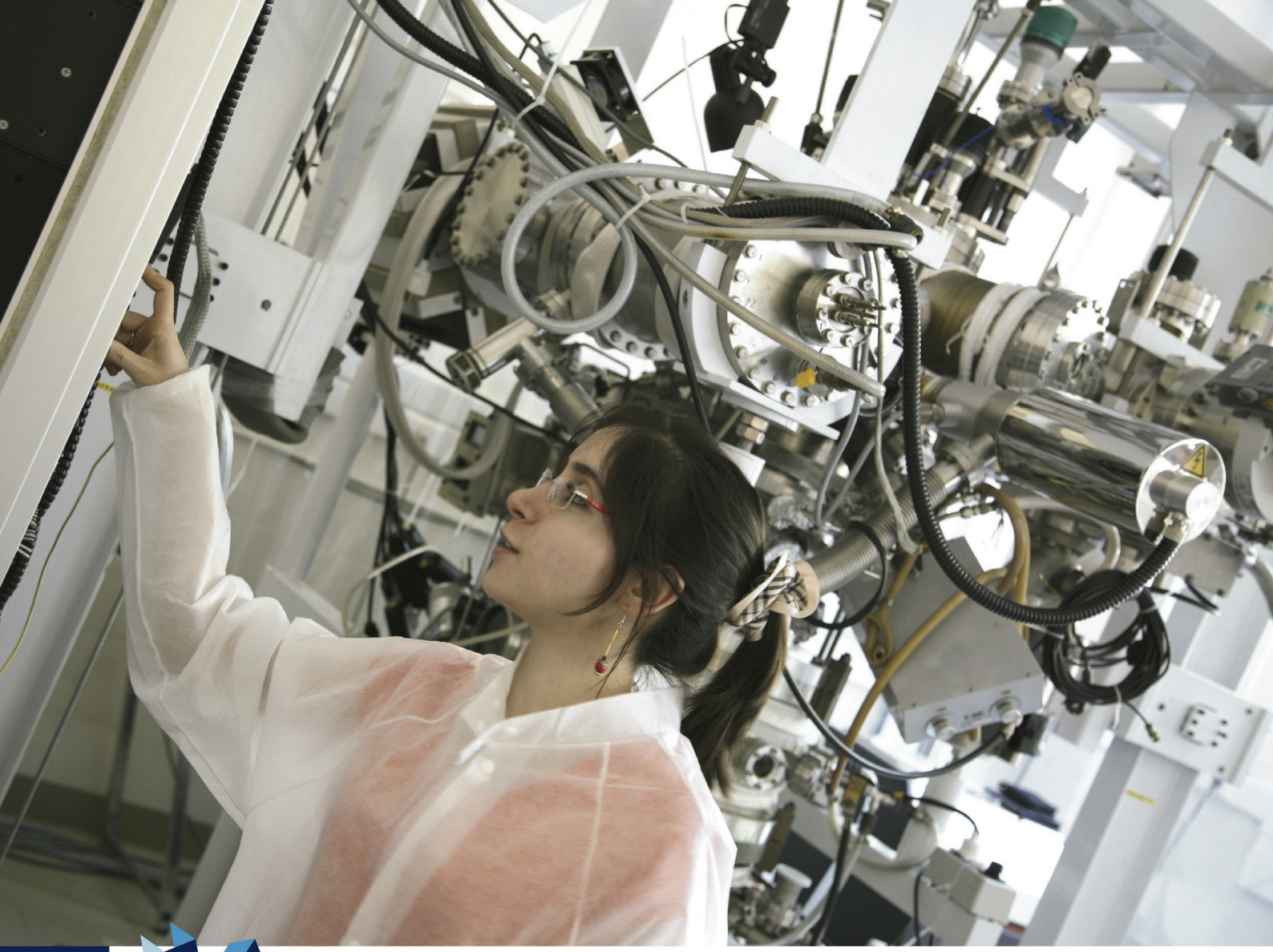


ESPCI ParisTech

ÉCOLE SUPÉRIEURE DE PHYSIQUE ET DE CHIMIE INDUSTRIELLES
DE LA VILLE DE PARIS

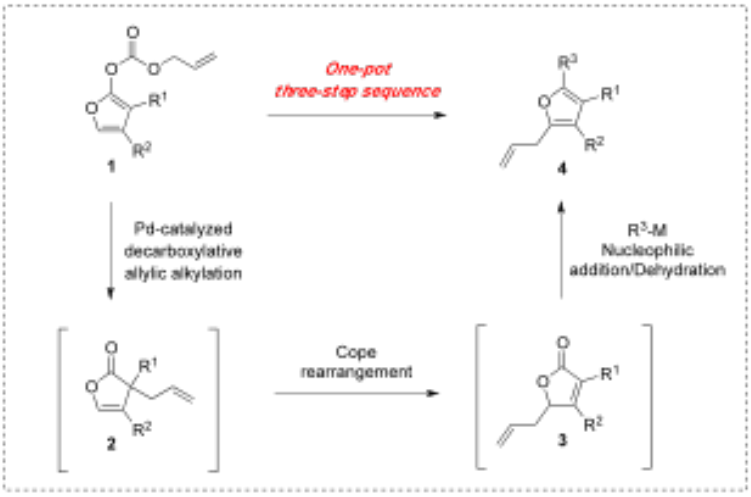
Research projects 2013

Contents

1 Organic chemistry

1.1 Projet CO4 : Straightforward synthesis of polysubstituted furans

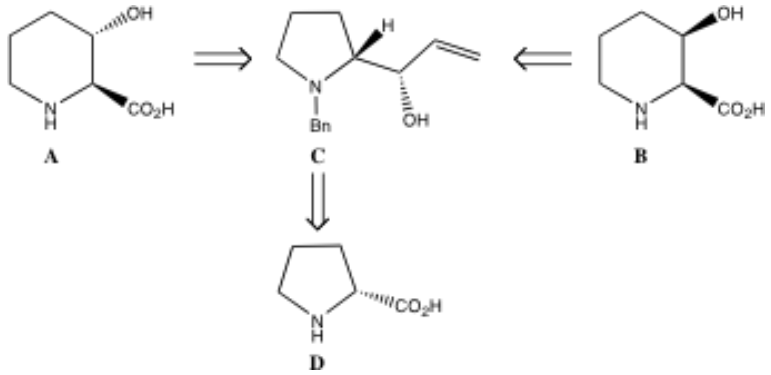
Description du projet: Functionalized furans represent an important class offive-membered heterocycles prevalent in a number of biologically active naturalproducts as well as in various relevant pharmaceuticals and agrochemicals. Theyare also particularly useful building blocks finding use in fields ranging fromsynthetic organic chemistry, to material science, non-linear optics and evensupramolecular chemistry. In this project, we wish to explorea new palladium-catalyzed allylic alkylation-based strategy which would enable toaccess a wide variety of polysubstituted furans (4) in an efficient and straightforward fashion starting from cyclicallyl dienol carbonates of type 1.



Required profile: Highly motivated and pro-active
Supervisor: Stellios Arseniyadis
Contact: stellios.arseniyadis@espci.fr

1.2 Projet CO5 : Synthesis of trans- and cis-3-hydroxypipecolic acids

Description du projet: Functionalized piperidines are important structures found in variousnatural products, pharmaceuticals, and synthetic intermediates. Among thesepiperidines, hydroxylated piperidine alkaloids are frequently found in livingorganism and display a wide spectrum of biological activities, being able tomimic carbohydrate substrates in a variety of enzymatic processes. In addition,3-hydroxypipecolic acids are structural motifs often encountered in a varietyof functional molecules. The goal of this project is todevelop an efficient asymmetric synthesis of trans- and cis-3-hydroxypipecolicacids A and B from d-proline D by ring enlargement of prolinol C.



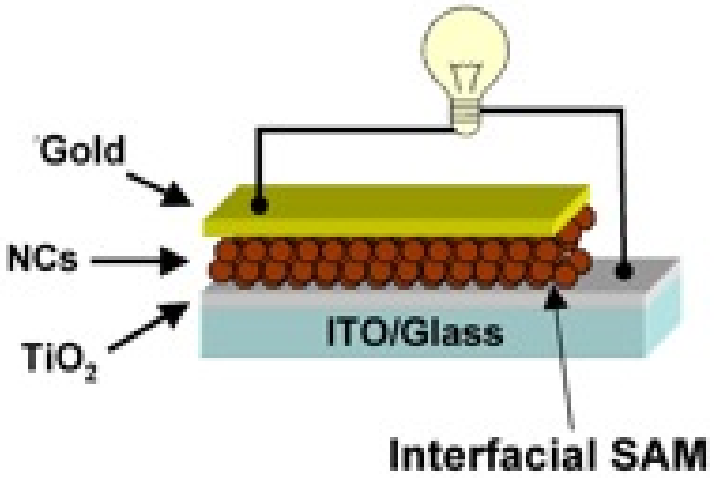
Required profile: Highly motivated students. Interest in experimental work for organic chemistry will be appreciated.
Supervisor: Domingo GOMEZ PARDO (Assistant-professor, LCO)
Contact: Laboratoire de Chimie Organique, bureau G1.01, phone: 01 40 79 46 63 Domingo.gomez-pardo@espci.fr

2 Physics and Materials

2.1 Projet LPEM4: The Application of $CuInS_2$ Nanocrystals in Solar Cells

Description du projet: Colloidal nanocrystals (NCs) have been fascinating since their discovery in the 1980s due to their unique size and morphology-tunable optical and electronic properties in the quantum confinement regime. Highly monodispersed samples of II-VI and IV-VI semiconducting NCs can now be prepared with precise synthetic control.Combining advantages of tunable absorption/emission and the ease of solution-processing, semiconducting NCs are highly attractive for their applications in large-area and low-cost optoelectronics, such as solar cells, light-emitting diodes, and field-effect transistors.
As one of the emerging colloidal systems, nanocrystals based on cadmium-free $CuInSe_2$ and $CuInS_2$ (CIS) compositions have aroused extensive interest recently. Their thin film counterparts are among the most promising candidates for photovoltaic applications due to their environmental benign and earth-abundant compositions, high absorptioncoefficient from the visible to the near-IR, and excellent radiation stability. As the performance of these CIS-based solar cells is often strongly influenced by material stoichiometry and surface compositions, colloidal synthesis offers not only opportunities in low-cost fabrication but also in the precise control on their dimensions, structure, and surfaces. Up to now size and morphology-tunable colloidal synthetic protocols have been discovered and improved continuously over the last few years[(1)]. These results have stimulated intense international competitions to study their use in inorganic and hybridphotovoltaics/photodetectors[(2)]. Strategies such as ligand exchange[(3)] and various deposition methods[(4)], which have led to improved solar cell performance on II-VI NCs, are promising directions to test in CIS NCs-based solar cells.
In this project we aim to study aspects starting from material/surface adaptation, structural/optical characterization, device fabrication to measurements on $CuInS_2$ NCs solar cells. Practically, the student shall accomplish: (1) Adapt as-synthesized $CuInS_2$ NCs for their use in solar cells by testing different ligand exchange and active layer deposition

methods; (2) Explore a few basic device structures (e.g. Schottky or heterojunction solar cells, all-inorganic or hybrid structures) and fabricate functional nanocrystal solar cells (3) Evaluate device characteristics correlate them to the material modification methods and device structure used.



Schematic example of a heterojunction solar cell based on nanocrystals. SAM = self-assembled monolayers

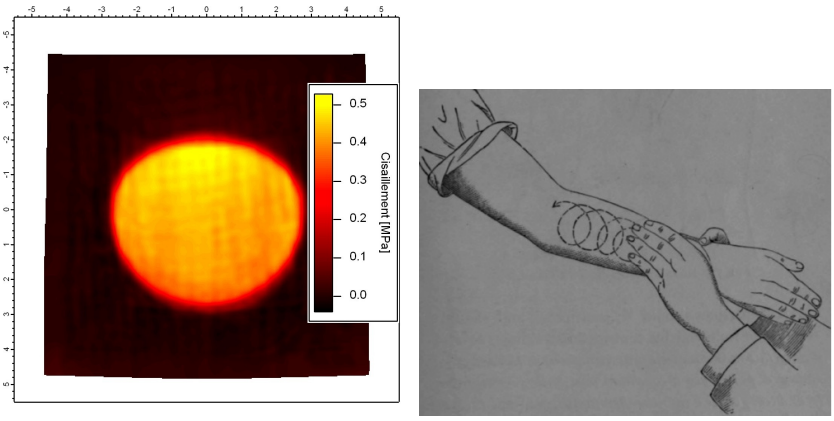
References : [1](a) T. Pons et al. ACS Nano, 4, 2531-2538 (2010); (b) J.-J. Wang et al. JACS, 132, 12218-12221 (2010); [2](a) Q. Guo et al. Nano Letters, 8, 2982-2987(2008); (b) J. W. Cho et al. ACS Appl. Mater. Interfaces, 4, 849-853 (2012); [3](a) J. Tang et al. ACS Nat. Mater., 10, 765-771; (b) K. S. Jeong et al. ACS Nano, 6, 89-99 (2012); (c) C. J. Stolle et al. ACS Appl. Mater. Interfaces, 4, 2757-2761 (2012); [4](a) P. K. Santra et al. JACS, (2013) DOI: 10.1021/ja310737m; (b) J. Tang et al. Adv. Mater., 23, 12-29 (2011).
Techniques in use : colloidal synthesis, TEM, UV-Vis-NIR absorption, photoluminescence, powder XRD, spin-coating and/or electrophoretic deposition, thermal evaporation, and current-voltage diode measurement
Student profile : Physics (applied physics) or physical chemistry
Encadrants: Z. Chen, T. Pons
Contact: zhuoying.chen@espci.fr, 01 40 79 45 96

3 Engineering and Sciences of Soft Matter

3.1 Projet SIMM3: Friction with curved sliding trajectories

Project summary :
Though studied for many years, physics of friction remains poorly understood. For example, we still do not know precisely the role played by surface roughness or the relevance of the friction coefficient which is often defined at the macroscopic scale. We have developed a new technique where the displacements induced at the surface of a silicone rubber by the frictional sliding of a glass lens are continuously monitored. Using this experimental set up, we have recently addressed topics such as the frictional behavior of rough contacts or stick-slip motions. In the present project, another intriguing aspect of friction will be investigated: how varies friction during non straight sliding trajectories or at non constant velocity ? Preliminary analysis revealed unexpected results in these non-conventional

situations (stick-slip events, memory effects...). In this exploratory project, the existing experimental setup will be modified in order to optimize the observations conditions. In parallel, simple mechanical models will be developed to account for friction with curved sliding trajectories.



Left : Frictional stress in a sphere/plane contact. Right : Non-rectilinear friction ■

Supervisors: Antoine Chateauminois, Christian Frétigny
Contact: antoine.chateauminois@espci.fr, christian.fretigny@espci.fr

3.2 Projet SIMM5: Adhesive properties of polymer binders for Si-Li Battery applications

Project summary :
This project is based on a collaboration between the team of Pr. Nitash Balsara in the Chemical Engineering Department of UC Berkeley (California) and the PPMD laboratory at ESPCI. Higher capacity and lighter Li-Batteries are an important research area in the energy field. A current research direction seeks to develop new Si-based electrodes, which have a higher capacity per unit weight but are composite materials undergoing large changes in volume during charging and discharging cycles. Therefore the integrity of the interfaces between components during cycles is a particular challenge.
In the Soft Polymer Networks team (ESPCI), the objective of the internship is to characterize the adhesion between a silicon surface and a thin film of polymer, typically used as a binder in electrodes. This film will be prepared by spin-coating, before being floated on the surface of a lens of PDMS. A JKR contact test will be performed to measure the energy of adhesion between the two surfaces (Fig.1).

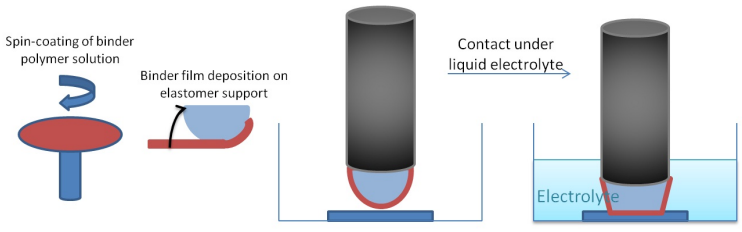
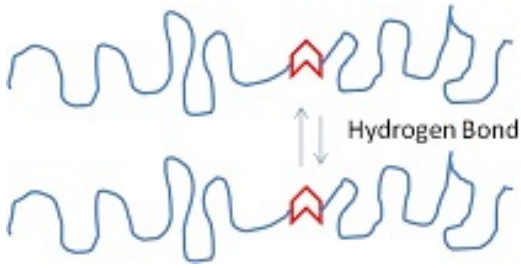


Figure 1

Different kinds of polymers will be tested such as polyvinylidenefluoride (PVDF) and carboxymethylcellulose (NaCMC). The experiment will be first realized in air, then in a liquid medium such as an ionic liquid representing the electrolyte.
We must show here the influence of the nature of the polymer and the testing conditions on the adhesive energy.
This new methodology should be then applicable to measure, in a glove box under Argon atmosphere, the adhesion between a polymer binder material and a variety of electrode active materials supplied by the Berkeley research team.
Supervisors: Costantino Creton, Jennifer Macron
Contact: costantino.creton@espci.fr, jennifer.macron@espci.fr

3.3 Projet SIMM6: Model Polymers for Self-healing Materials

Project summary :
New organic materials showing unusual self-healing properties were recently discovered1. While these materials don't adhere on themselves and are clearly non flowing solids, two freshly broken pieces can self-repair by simple contact with neither chemical reaction, nor heat. This self-healing capacity of solids which is promising for many industrial applications is due to the reversible interactions between molecules in the polymer matrix (1).
This particular system is based on a mix of fatty acids functionalized by different polar groups1. While they get very promising material with non-toxic and renewable building-bloc, their system remains chemically complex. New studies on more simple chemistry need to be done in order to better understand the link between the self-healing capacity of solids and the supramolecular structure. That's why our project aims to characterize and understand the self-healing properties of a simpler supramolecular system displaying solid properties. The main component of this system is a centrally functionalized polymer synthesized by Pr. Bouteiller's team at UPMC, which is composed of two non-polar side chains.

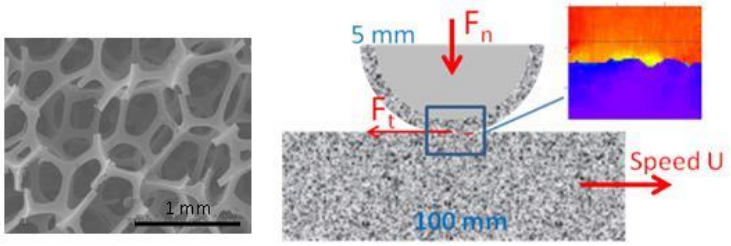


The level of the hydrogen bonds between chains can be tuned by changing the nature of the polar core or by changing the nature or the molecular weight of the side chains. Rheological and self-adhesive experiments will be carried out on selected model systems.
(1) Nature, 2008, 451, 977-980.
Supervisors: Xavier Callies, Costantino Creton, Guylaine Ducouret
Contact: xavier.callies@espci.fr, costantino.creton@espci.fr, guylaine.ducouret@espci.fr

3.4 Projet SIMM7: Experimental study of the friction at a solid foam/foam interface

Project summary :

Solid foams are used in many practical applications (thermal and acoustic insulation, packaging, filtering, structural material...) and exhibit some amazing properties. Amongst them is the very large friction force developed between two blocks of foams even under very weak normal load. Although foam properties are very well documented, the understanding of the mechanisms at stake is only very partial.
In this project, we will focus on the friction between two blocks of open-cell foam and will address the following questions: How does the friction force depend on the area of the interface? How does the geometry of the cells respond to the normal load and adapt to the shearing when the interface slides? Hypotheses are that the friction may have two contributions: one would be a "Velcro" mechanism across the interface (see foam image below where hooks and loops are visible) and the other would be the "classical" friction of the constitutive material. Systematic experiments made by varying the interface area, the normal load, and the thickness of the foam block should provide some insights to this problem.
We will use an experimental setup recently developed in our laboratory. A block of foam is sheared against a cylinder covered with a thick layer of foam at a given speed (see figure below). The normal load is controlled and the friction force is measured with time. A side view allows the observation of the interface and of the structure of the cells. The analysis of these images provides a measure of the field of displacements within the foam away from the interface. We will look at the mapping of the strain and the fluctuations in time and space of the cell movements.



(Left) Scanning electron microscopy image of an open cell foam. (Right) Experimental set-up. (Inset) Velocity analysis of the fluctuations in the displacement field from side views images.

Supervisors: Antoine Chateauminois, Christian Frétigny, Emilie Verneuil
Contact: emilie.verneuil@espci.fr, 01 40 79 47 88, 01 40 79 47 87

4 Signal processing and machine learning

4.1 Projet SIGMA2 : IMPROVING MAGNETIC RESONANCE IMAGING BY GRAPH MACHINE LEARNING

Description
Magnetic Resonance Imaging (MRI) is a very powerful technique for medical diagnostics. In order to improve the quality of the image, paramagnetic contrast agents must be used, among which, gadolinium(III) complexes are very popular. Free gadolinium(III) being toxic, it must be trapped into a complex (called chelate) with a proper organic molecule (called ligand) so as to be safe and inert while retaining its useful paramagnetic properties. Similar

complexes, in particular Ga(III) complexes, are used as diagnostic and therapeutic radiopharmaceuticals to investigate biochemical systems. Since the stability of such complexes is essential, the dynamic stability constant (Ktherm) is a critical figure for a good contrast agent or imaging probe.

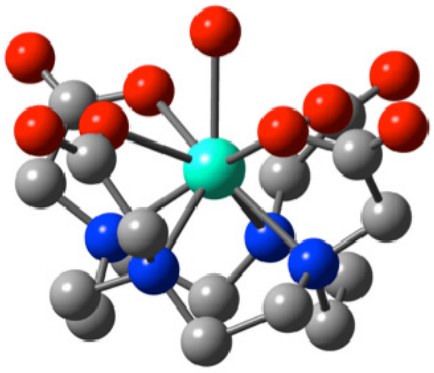
As the Ktherm measurement is often long and tedious, it is highly desirable to develop new prediction methods (structure-property relationship or QSPR) of this key stability constant, in particular to design new contrast agents. With this goal in mind, we have built a new prediction algorithm based on statistical graph learning (graph machines).[1] First results obtained for the prediction of Ktherm of gadolinium(III) complexes are very good and are currently being published.[2] Briefly, our method is able to predict stability constants of fresh chelates (i.e. compounds that have not yet been synthesized but seem to be good candidates for efficient chelation) from the structure of the corresponding new ligands alone, with $\pm$ 10% accuracy.

Our next step consists of updating and improving the machine learning tool, which, at present involves various techniques (Matlab, NeuroOne, Java...), by translating the programs used for graph machine generation and during the training and prediction steps into the *Python* language. The main reason is that, besides using a more modern environment, a more accurate tuning of the machine parameters is needed, and this is only possible though the use of Python. This work started last year with the release of a first Python program for graph machine generation. A fair knowledge of Matlab is necessary; some familiarity with Python will be appreciated. An understanding of the principles of machine learning, and an understanding of the algorithms involved therein, are mandatory.

The present database of polyamino-polycarboxylic ligands will be used for debugging. Once the method updated, an innovative step could consist in predicting relaxivities – a property related to the contrast of the images – of the same complexes. Then, the graph machines could be used to predict properties of other transition metal chelates of interest, like those of Ga(III) complexes which are of increasing importance in PET imaging.

[1]A. Goulon, T. Picot, A. Duprat, G. Dreyfus, Predicting activities without computing descriptors: graph machines for QSAR, SAR and QSAR in Environmental Research 2007, 18, 141-153.

[2]F. Dioury, A. Duprat, G. Dreyfus, C. Ferroud and J. Cossy, Gadolinium(III) complexes with polyamino-polycarboxylic ligands for MRI: a new QSPR method for predicting their stability constants. Submitted to Inorganic Chemistry.



pictorial view of a chelate

Supervisor: Arthur DUPRAT
Contact: Arthur.Duprat@espci.fr

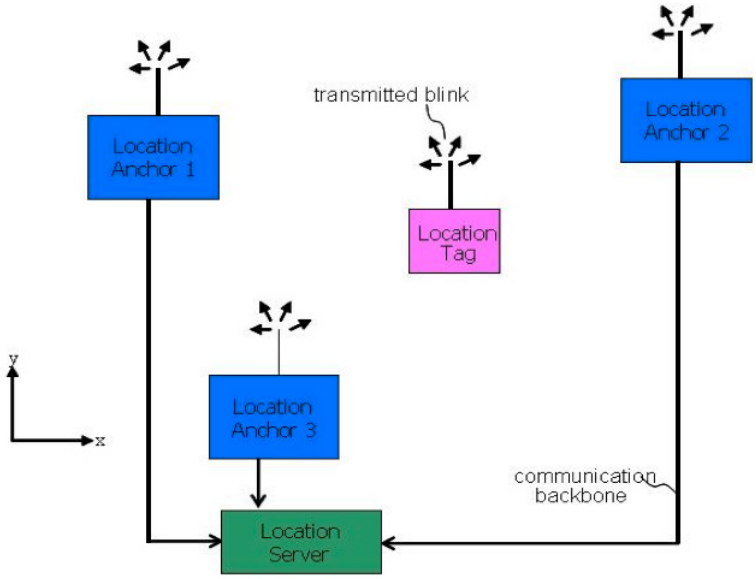
4.2 Projet SIGMA4 : LOCATION-AWARE AUDIO GUIDES

Description

For some indoor applications, such as guided visits in musems, the precise location of the mobile station (visitor) is needed inside a building (museum). For such submeter location systems, IEEE has developed a standard based on the popular ZigBee technology and ultra wideband impulse radio (IEEE 802.15.4 – 2011). This standard allows to deliver precise ranging information between two devices, even in the absence of a line of sight propagation path. Further, when ranging information from three or more base stations is available, the precise location of the mobile station can be computed using trilateration methods (Fig. 1).

However, when there are not enough base stations (less than three in the above example), the provided ranging information is not enough for a real-time location system. Instead of ensuring enough redundancy for the number of available base stations, one might use data provided by motion sensors embedded in a mobile device (acceleremeters, gyrometers, magnetometers) in order to continuously provide location information.

The goal of this project is to use data provided by acceleremeters, gyrometers and magnetometers for real-time indoor location. The internship will allow students to acquire skills in signal processing methods used for data fusion, in motion sensors embedded in mobile devices (e.g. smartphones, tablets) and in indoor location methods. Knowledge in digital signal processing and scientific programming using MATLAB is required.



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