

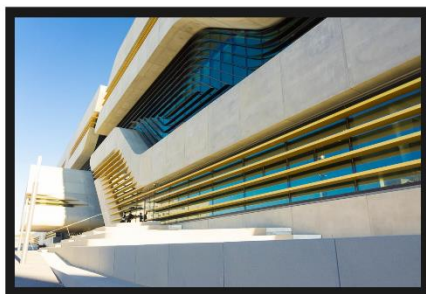
# 3<sup>rd</sup> Mediterranean Young Researchers Days



École Nationale  
Supérieure de Chimie

Montpellier

October 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup>



Languedoc-Roussillon and  
Provence-Alpes-Côte d'Azur sections

3<sup>èmes</sup> Journées Méditerranéennes  
des Jeunes Chercheurs



## Welcome words

Building on the success of last year's Young Researchers Days 2013 and 2014, the French Young Chemists Network, Languedoc-Roussillon and Provence-Alpes-Côte d'Azur sections, cooperate once more in organizing the 3<sup>rd</sup> Mediterranean Young Researchers Days.

In order to have an overview of the different fields of chemistry, industrial and academic renowned lecturers and Ph.D students honor us by presenting their work.



The organizing committee would like to express its sincere gratitude to the different sponsors for their financial support, the speakers for their involvement and the participants for their interest in this scientific congress.

We would like to particularly thank the ENSCM and his dean, Pr. Pascal Dumy, for supporting and welcoming the event.

The Organizing Committee



## Organizing committee

	Languedoc-Roussillon	Provence-Alpes-Côte d'Azur
<b>Team Communication</b>	Sammy Drissi Amraoui Maxime Rossato Eline Bartolami Nicolas Sevrain	Jean-Baptiste Chéron Estelle Sfecci Claire de March Marie-Aude Tribalat Johana Revel Maxime Dousset
<b>Team Partnership &amp; Sponsorship</b>	Emmanuelle Cordeau Julien Bergès Mélicca Rosell Audrey Beillard	Pierrick Ondet Antoine Millet Mélody Maloubier Lama Rezig Vincent Morizur
<b>Team Logistics</b>	Julien Bergès Rémi Blicck Yujia Liu Benoît Guénot	Hélène Bouges

## Partnerships

The organizing committee of the Mediterranean Young Researchers Days is very grateful to their partners for supporting the event.

L'Ecole Nationale Supérieure de Chimie de Montpellier  
La Région Languedoc-Roussillon  
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La Ville de Montpellier  
Les Réseaux des Jeunes de la Société Chimique de France  
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L'Actualité Chimique  
New Journal of Chemistry



## Program of Monday, October 12<sup>th</sup>

8h00	Registration
8h30	Welcome words
9h00	<b>Plenary lecture 1: William Moerner</b> Light and single molecules open a new window into super-resolution imaging in cells
10h00	#1: Guillaume Compain Influence of fluorination on the hydrogen bond properties of an adjacent hydroxyl group
10h20	#2: Mohamed Belkacem Chemical diversity of microbial volatiles from Burkholderia sp.
10h40	Coffee break
11h00	#3: Abhijeet Lale Polymer-derived ceramics and nanocomposites for H <sub>2</sub> production from chemical hydrides
11h20	#4: Yohan Dudognon Organocatalytic multicomponent synthesis of enantioenriched polycyclic 1,2,3,4-tetrahydropyridines: Key substrate selection to enable productivity, regio- and stereoselectivities
11h40	#5: Ana M. Antolin Water denitration by heterogeneous (photo)catalytic reduction
12h00	#6: Meriam Belaïba Study of chemical composition, anti-inflammatory, antioxidant activities of <i>Pituranthos tortuosus</i> aerial part essential oil
12h20	Lunch break
14h00	<b>Industrial lecture 1 : BioPreserv</b>
14h40	#7: Anthony Angeli Synthesis of glycoclusters and study of their affinity on glycoarray against lectins 1 or 2 of <i>Pseudomonas aeruginosa</i> (LecA or LecB)
15h00	#8: Coralie Charrat Formulation of highly functionalizable non viral DNA vectors based on 1,2-dithiolane derivatives



15h20	#9: Sébastien Alazet Electrophilic trifluoromethylthiolation using trifluoromethanesulfenamide
15h40	Coffee break
16h00	#10: Fabien Perez Organocatalytic deuterium shuttling properties of NHCs
16h20	#11: Anna Dikova Nosylates – novel and efficient electrophilic partners in palladium-catalyzed cross-coupling reactions
16h40	#12: Cécile Echalié From silylated peptides to bioactive hydrogels
17h00	Poster session Cheese and wine tasting



## Program of Tuesday, October 13<sup>th</sup>

8h00	Registration
8h40	#13: Jean-Patrick Francoia KISS (Keep It Simple, Sensor)
9h00	#14: Thibaut Boibessot Synthesis of triazole amino acids as potential antibacterial agents
9h20	#15: Duy Linh Nguyen Nanofiltration rejection of pesticides used in the Mekong Delta Area
9h40	#16: Hella Amdouni Expedient preparation of fully decorated 1,2,3-triazoles towards the discovery of potent anti-leukemic compounds
10h00	<b>Industrial lecture 2: Anton Paar</b>
10h40	Coffee break
11h00	<b>Meet the start-up</b>
12h20	Lunch break
14h00	<b>Plenary lecture 2: Marcel Hibert</b> Fluorescent molecular probes for receptor studies
15h00	#17: Denis Frath Diarylethene self-assembled monolayers: Cocrystallization and mixing-induced cooperativity highlighted by scanning tunneling microscopy at the liquid/solid interface
15h20	#18: Thibault Tintillier Synthesis of highly selective and reversible inhibitors of Nitric Oxide Synthases: Solid-phase synthesis and biological evaluation
15h40	Coffee break
16h00	<b>Industrial lecture 3: Galderma</b>
16h40	#19: Mylène Roudier Claisen fragmentation: A key step for enantioenriched building blocks synthesis





17h00	#20: Doria Voisin Covalent organosilica networks where is incorporating Phenylene-Vinylene motifs
17h20	#21: Flavien Sciortino A new strategy to form assemblies of nanoparticle: Application to the elaboration of magnetic clusters for Magnetic Resonance Imaging
17h40	#22: Abdelaaziz Ouahrouch Design, synthesis of novel ribonucleosides of 1,2,3-triazolyl benzyl-aminophosphonates and evaluation for antiviral activity
⋮	⋮
21h00	Share the moment ! Let's meet at "the Black Cat" bar

## Program of Wednesday, October 14<sup>th</sup>

8h00	Registration
8h40	#23: Gerard Massons Biological fouling resistance optimization of reverse osmosis membranes
9h00	#24: Nathalie Saraiva Rosa Synthesis of small $\alpha/\beta$ peptides containing a chiral trifluoromethylated $\beta^{3,3}$ -amino acid
9h20	#25: Natalia Esteves-López UV photochemistry of pyridine-water complex: evidence of water dissociation
9h40	<b>Plenary lecture 3: Grégoire Danger</b> From astrochemistry to prebiotic chemistry: The evolution of organic matter toward life?
10h40	Coffee break
11h00	#26: Mathéo Berthet Amazing MgI <sub>2</sub> : An alternative to conventional deprotection methodologies
11h20	Doctoral School Balard Ph.D thesis award : Jonas Croissant Two-photon-actuated theranostic organosilica nanomedicine
12h00	Conclusion words

# Plenary lectures





# Light and single molecules open a new window into super-resolution imaging in cells

## William E. MOERNER

Professor of Chemistry and Professor, by courtesy, of Applied Physics  
Stanford University

More than 25 years ago, low temperature experiments aimed at establishing the ultimate limits to optical storage in solids led to the first optical detection and spectroscopy of a single molecule in the condensed phase. At this unexplored ultimate limit, many surprises occurred where single molecules showed both spontaneous changes (blinking) and light-driven control of emission, properties that were also observed in 1997 at room temperature with single green fluorescent protein variants. These observations form foundations for super-resolution microscopy beyond the diffraction limit with single molecules, and tracking of single molecules in cells continues to yield surprises. A new world of optical visualization in cells is now available, with detail far beyond the optical diffraction limit.

**Biography:** W. E. Moerner, the Harry S. Mosher Professor of Chemistry and Professor, by courtesy, of Applied Physics at Stanford Univ., conducts research in physical chemistry and chemical physics of single molecules, single-molecule biophysics, super-resolution imaging and tracking in cells, and trapping of single molecules in solution. His interests span methods of precise quantitation of single-molecule properties, to strategies for three-dimensional imaging and tracking of single molecules, to applications of single-molecule measurements to understand biological processes in cells, to observations of the photodynamics of single photosynthetic proteins and enzymes. He has been elected Fellow/Member of the NAS, American Academy of Arts and Sciences, AAAS, ACS, APS, and The Optical Society. Major awards include the Earle K. Plyler Prize for Molecular Spectroscopy, the Irving Langmuir Prize in Chemical Physics, the Pittsburgh Spectroscopy Award, the Peter Debye Award in Physical Chemistry, the Wolf Prize in Chemistry, and the 2014 Nobel Prize in Chemistry.

# Fluorescent molecular probes for receptor studies

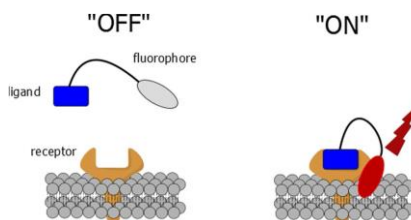
Marcel HIBERT and Dominique BONNET

Laboratoire d'Innovation Thérapeutique, UMR7200 CNRS/Université de Strasbourg, Labex Medalis

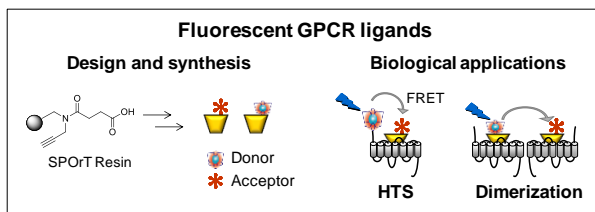
G-protein-coupled receptors (GPCR) represent the largest family of cell surface membrane proteins encoded by the human genome and more than 40% of all marketed therapeutics act on them. However, these drugs target only few members of the family: there is an enormous potential to exploit the remaining family members, including the orphan receptors for which no existing ligands have so far been identified. Besides, in the last decade, homo- and hetero-oligomerization of GPCRs have been described as a new way to modulate receptor pharmacology and functional activity. Thus, heteromer-based drug discovery opens new perspectives in both Academic pursuits and for the Pharmaceutical industry.

In this context, we have set up innovative fluorescent-based assays in order to gain a better understanding of GPCR functional architecture but also to set up new receptor-selective high-throughput screening (HTS) assays for classical, orphan and heterodimeric GPCRs. Owing to their high sensitivity and to their reduced environmental safety risk, fluorescent technologies represent a powerful molecular tool to study ligand-GPCR interactions<sup>1</sup>. However, the prerequisite to develop such methods is to design and to synthesize high affinity and selective fluorescent probes.

As we will illustrate, synthetic methods have been set up to facilitate the access to original fluorescent GPCR probes with potential applications in drug discovery. For instance, the first environment sensitive ("Turn-on") probe was developed to detect and to monitor oxytocin GPCR at the surface of living cells<sup>2,3</sup>.



We have also designed and synthesized fluorescent compound-based libraries allowing the discovery by FRET of the first ligand of the apelin receptor<sup>4</sup>. Finally, selective fluorescent non-peptidic ligands were developed to detect vasopressine V1a-V2 heterodimers at the cell surface and to set up a novel TR-FRET assay to screen for heterodimers<sup>5</sup>.



- (1) (a) Durroux, T. et al. *Nat. Chem. Biol.* **2010**, *6*, 587-594. (b) Ilie, B. et al. *J. Med. Chem.* **2012**, *55*, 2125–2143.
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- (3) Hibert and coll., *J Med Chem.* **2015**, *58*, 2547-2552.
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- (5) Bonnet, D. et al. Patent FR 2012/12306; PCT/EP2013/070837; *J. Med. Chem.* **2012**, *55*, 8588–8602.

# From Astrochemistry to prebiotic Chemistry: The evolution of organic matter toward life?

Grégoire DANGER

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Understanding the chemical evolution of organic matter in astrophysical environments gives clues on the chemical composition of the organic matter that may have seeded primitive planets. The organic matter present in dense molecular clouds in the form of ice mantles at the surface of interstellar grains can evolve toward a complete planetary system. All along this evolution, new and more complex molecules are formed thanks to various energetic processes including UV irradiation and thermal effects. Therefore, there is probably a link between the molecules contained in cometary or asteroids, and molecules present in interstellar grains of the dense molecular cloud. Small bodies of planetary systems (asteroids and comets) eventually serve as a reservoir of this organic matter and as vectors for its delivery at the surface of telluric planets such as the primitive Earth. Furthermore, in specific environment such as the primitive Earth environment, this organic matter could have taken a part in the development of a prebiotic chemistry, a chemistry that precedes the emergence of biochemical systems.

During this presentation, based on experimental approaches developed in our laboratory, we will try to understand this chemical evolution and determine which chemical processes can take place in these astrophysical environments [1-5]. This will allow us to obtain a better understanding of the origin and the evolution of the matter that makes up objects of our solar system. Finally, we will present an experimental approach for studying prebiotic chemical processes in terrestrial planets such as on the Earth [6-9]. These processes could then represent the first stage for the development of the chemistry of living organisms.



- (1) G. Danger, F-R. Orthous-Daunay, P. de Marcellus, P. Modica, V. Vuitton, F. Duvernay, L. Le Sergeant d'Hendecourt, R. Thissen, and T. Chiavassa, *Geochimica & Cosmochimica Acta*, 2013, 118, 184-201.
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- (3) G. Danger, F. Duvernay, P. Theulé, F. Borget, and T. Chiavassa, *The Astrophysical Journal*, 2012, 756,11.
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# Industrial lectures

## Industrial lectures

#1



#2



#3



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## Meet the start-ups !

#1



#2



#3



# Oral communications



## #1: Influence of fluorination on the hydrogen bond properties of an adjacent hydroxyl group

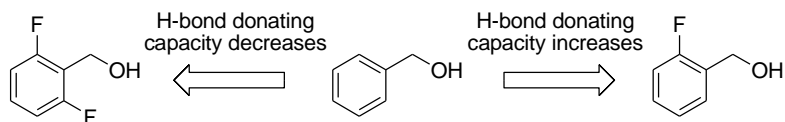
Guillaume COMPAIN<sup>a</sup>, Elena BOGDAN<sup>b</sup>, Florent PERON<sup>a</sup>,  
Neil WELLS<sup>a</sup>, Zhong WANG<sup>a</sup>, Clément FONTENELLE<sup>a</sup>,  
Nicolas GALLAND<sup>b</sup>, Lewis A. MTASHOBYA<sup>a</sup>,  
Jean-Yves LE QUESTEL<sup>b</sup>, Jérôme GRATON<sup>b</sup>, Bruno LINCLAU<sup>a</sup>

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The hydrogen bond (H-bond) is an important specific interaction between a molecule and its local environment.<sup>1</sup> Given the strong electrostatic contribution to the overall energy of a H-bond, the introduction of a small and highly electronegative fluorine atom is expected to significantly increase the H-bond donating capacity of an adjacent H-bond donor.<sup>2</sup>

We have shown on conformationally constrained fluorohydrins that a OH-F interaction can occur and in that case, can strongly decrease the H-bond donating capacity of the alcohol.<sup>3</sup> This study led us to focus our attention on the fluorinated benzyl alcohol derivatives which are common building blocks of drugs (e.g. antimuscarinic drugs, neuroprotective agents, anticonvulsant agents). Surprisingly, while one fluorine promotes an increase of the H-bond donating capacity of alcohol, adding a second fluorine led to the unexpected opposite effect (see figure below).<sup>4</sup> Encouraged by these results, we investigated acyclic fluorohydrins by NMR spectroscopy and DFT calculations and we recently observed for the first time <sup>h1</sup>J<sub>OH...F</sub> coupling constants.<sup>5</sup>



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(5) Linclau, B.; Peron, F.; Bogdan, E.; Wells, N.; Wang, Z.; Compain, G.; Fontenelle, C.; Galland, N.; Le Questel, J.-Y.; Graton, J. *Submitted article*.

## #2: Chemical diversity of microbial volatiles from *Burkholderia sp.*

Mohamed Amine BELKACEM<sup>a, b</sup>, Hicham FERHOUT<sup>c</sup>, Laila MZALI<sup>c</sup>,  
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Research to date has shown that a wide array of microorganisms ranging from fungi to bacteria are an unlimited source of microbial Volatile Organic Compounds (mVOCs), many of which have been used in agriculture and pharmaceutical practice<sup>1</sup>. The *Burkholderia* genera show the ability to produce a large variety of mVOCs and to name only a few products with high importance, *B. pyrrocinia* produced pyrrolnitrin which is a phenylpyrrol antibiotic, dimethyl trisulfide and 4-octanone emitted by *B. ambifaria* with a significant growth inhibition of fungi<sup>2</sup>. In this study, we found that a bacterium which lives in the soil remarkably promotes plant growth and was identified as *Burkholderia sp.* This bacteria were able to grow up by using different carbon sources and in order to expand our knowledge about this strain, the bacteria was cultivated in two different carbon sources (dextrose and glycerol). The chemical composition of the volatile compounds from the two culture mediums was carried out by gas chromatography-mass spectroscopy and derivatization reactions and results showed the ability of *B. sp.* to produce a variety of compounds using different carbon sources.

Furthermore, the anti-inflammatory and anti acetylcholinesterase assays were performed and results showed that the activities were linked to the produced mVOCs

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- (2) Kanchiswamy C. N., Malnoy M., Maffei M. E. *Front. Plant Sci.* **2015**, *6*, 151.

### #3: Polymer-derived ceramics and nanocomposites for H<sub>2</sub> production from chemical hydrides

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Institut Européen des membranes, IEM UMR-5635, Université de Montpellier, ENSCM, CNRS  
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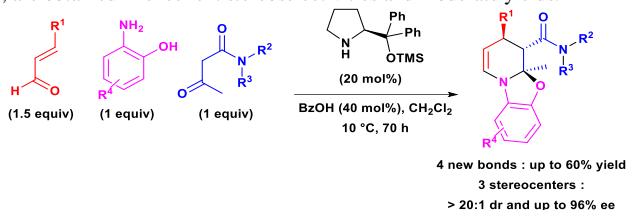
Proton exchange membrane fuel cell-based systems are attractive alternatives to current energy conversion technologies due to their potential to directly convert hydrogen into electrical energy. They consist of three subsystems - fuel cell stack, hydrogen generator, and hybrid power management system. Despite recent advances, there are still several issues which limit the widespread use of the fuel cell technologies. One of the most critical issues is the hydrogen source to meet the overall energy requirements for civil vehicle applications. 95% of hydrogen is produced from natural gas which means evolution of CO<sub>2</sub>. Liquid-phase hydrogen carriers such as alkaline solutions of sodium borohydride NaBH<sub>4</sub> are attractive alternatives because of zero emission (excepted water) and high efficiency. However, the hydrolysis of NaBH<sub>4</sub> is exothermic, very alkaline and requires catalysts. For that purpose, we develop porous ceramic supports for the growth of metallic nanoparticles and the use of the resulting nanocatalysts for the catalytic hydrolysis of NaBH<sub>4</sub>. Mesoporous Silicon Nitrides and Carbides monoliths as well as mesoporous monolithic Titanium Nitride/Silicon Nitride Nanocomposites have been synthesized by a solvent nanocasting route using mesoporous activated carbon as hard template and preceramic polymers like polysilazanes, co-polycarbosilazanes and polycarbosilanes. The preceramic polymers were infiltrated in the activated carbon template under vacuum and then converted to ceramic at 1000 °C under various gases depending on the ceramic desired. For some ceramics the conversion step includes the template removal while for others the template removal is done under air after conversion to ceramic. The procedure resulted in formation of mesoporous framework with high specific surface areas in all cases along with high pore size and pore volume in a few cases. The mesoporosity was analyzed using BET and SEM-EDX was performed to investigate the chemical composition and microstructure of the monoliths. The as-obtained monoliths were impregnated with Pt (nano)particles to form a supported catalyst system. The as-obtained catalyst support systems are used for hydrolysis of alkaline solution of NaBH<sub>4</sub> at 80 °C. We present the performance of the catalyst support system for the catalysis of the above mentioned reaction as our main result and also discuss the effect of using different preceramic polymer to obtain the same ceramic on the properties of the ceramic. Results show that the metal-supported ceramics are interesting nanocatalysts in pursuit of practical implantation of NaBH<sub>4</sub> as a hydrogen source for fuel cell.

## #4: Organocatalytic multicomponent synthesis of enantioenriched polycyclic 1,2,3,4-tetrahydropyridines: Key substrate selection to enable productivity, regio- and stereoselectivities

Yohan DUDOGNON, Haiying DU, Jean RODRIGUEZ,  
Xavier BUGAUT and Thierry CONSTANTIEUX

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Multicomponent reactions are an important tool for the efficient synthesis of structurally complex molecules that would otherwise require multiple steps.<sup>1</sup> 1,3-Dicarbonyl compounds, with their numerous electrophilic and nucleophilic positions are interesting substrates for such transformations.<sup>2</sup> Since 2008, organocatalysis has established itself as a powerful method to prepare enantioenriched polyhydropyridines by the condensation of  $\alpha,\beta$ -unsaturated carbonyl compounds either with preformed enamines,<sup>3</sup> or with a combination of a  $\beta$ -dicarbonyl and an amine.<sup>4</sup> We have developed the first multicomponent synthesis of enantioenriched polycyclic 1,2,3,4-tetrahydropyridine derivatives under iminium activation. The key to the success of this reaction was the use of polyfunctional substrates including 2-aminophenols and scarcely used  $\beta$ -ketoamides to control the regio- and diastereoselectivities. The title products, in which four new bonds are created and three stereogenic centers are forged, are obtained in excellent stereoselectivities and moderate yields.<sup>5</sup>



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## #5: Water denitration by heterogeneous (photo)catalytic reduction

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Francesc MEDINA<sup>a</sup>

<sup>a</sup>Universitat Rovira i Virgili, Tarragona, Spain.

<sup>b</sup>École Nationale Supérieure de Chimie de Montpellier, France.

High levels of nitrates ( $> 50$  ppm  $\text{NO}_3^-$ ) in drinking water are potentially risky to human health<sup>1,4</sup>. In the recent years, the trend of nitrate concentration in groundwater, an important source of potable water, is rising in the EU and other countries. Its presence is due to farmer, agricultural and industries sources<sup>2</sup>. The possibility of nitrate removal using solar irradiation by heterogeneous photocatalysis is a very promising and friendly technique<sup>5</sup>. The nitrate reduction into nitrogen gas ( $\text{N}_2$ ) leads frequently to some toxic intermediates and by-products, such as nitrite ( $\text{NO}_2^-$ ), ammonia ( $\text{NH}_4^+$ ), and  $\text{NO}_x$  gases<sup>6</sup>. There is few literature on nitrate reduction by photocatalysis.

In this research, different mono- and bimetallic nanocatalysts containing 2% wt. Ag and 2% wt. Ag- 4% wt. Pt supported on Aeroxide Titania P25 (P25) have been tested under ultraviolet irradiations ( $\lambda = 254$  nm (UV-C);  $\lambda = 365$  nm (UV-A)), and presence/absence of hydrogen as a reducing agent. The 2% Ag/P25 catalyst showed the best catalytic behavior for nitrate conversion and nitrogen selectivity under UV-A radiation.

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## #6: Study of chemical composition, anti-inflammatory, antioxidant activities of *Pituranthos tortuosus* aerial part essential oil

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In this study, we investigated the chemical composition and the biological activity of essential oil of *Pituranthos tortuosus* aerial part. This plant has been used for many years in traditional medicine. *Pituranthos* species belong to the family of Umbellifereae that provide a high number of bioactives compounds with numerous biological activities. *P. tortuosus* essential oil was obtained by hydrodistillation. Qualitative and quantitative determination of its chemical composition was performed by GC-MS. The Anti-inflammatory activity was evaluated by inhibition of 5-Lipoxygenase assays. *In vitro*, the antioxidant properties of this essential oil were evaluated via its ability to scavenge DPPH radical.



## #8: Formulation of highly functionalizable non viral DNA vectors based on 1,2-dithiolane derivatives

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During the last decade, a new generation of non viral DNA vectors called "synthetic" or "artificial" viruses has emerged.<sup>1</sup> These vectors are supramolecular, multicomponent and multifunctional devices. To be effective, they need to combine different features: nanosized homogeneous population, ability to evade the immune system, cell tropism, cytoplasmic delivery, nuclear targeting, and efficient gene expression. Among the huge amount of molecules and concepts envisaged so far for non viral gene therapy, compounds combining ionic interactions with polymerizable/reducible properties, appear particularly appealing, especially the ones based on thiol-disulfide redox system.<sup>2</sup> Indeed, the reduction of disulfide into thiol in intracellular reducing medium should facilitate the gene release from DNA NPs into the cell after their internalization.

In that context, we developed a two-step strategy to produce small monodisperse and highly functionalized DNA vectors, based on ionic compounds bearing the 1,2-dithiolane polymerizable moiety (Figure 1). First, cationic amphiphiles containing the polymeric inducer were prepared and utilized to efficiently condense a DNA plasmid into a highly monodisperse population of quasi monomolecular (in pDNA content) cationic DNA nanoparticles (NPs) ( $D_h \sim 100$  nm). In a second step, a surface functionalization was achieved by the decoration of the positive surface with anionic pegylated conjugates that would diminish interactions with serum proteins, and aggregation with blood components.

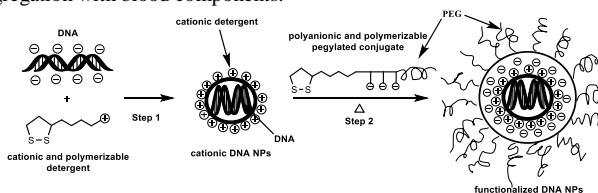


Figure 1: Formulation of DNA NPs in a two-step process involving polymerizable 1,2-dithiolane derivatives

Here, we will present the synthesis of cationic detergents and polyanionic PEG conjugates both bearing the 1,2-dithiolane polymerizable moiety, as well as the formulation and physicochemical characterization of these novel DNA NPs.

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## #9: Electrophilic trifluoromethylthiolation using trifluoromethane-sulfenamide

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In recent years, there has been growing interest in the association of the trifluoromethyl group with heteroatoms such as  $\text{CF}_3\text{O}$  or  $\text{CF}_3\text{S}$ . The  $\text{CF}_3\text{S}$  moiety is of particular interest, because of its high hydrophobicity parameter ( $\pi=1.44$ ). Consequently compounds bearing this group are potentially important targets for applications in pharmaceuticals and agrochemicals. However, among the numerous methods described in the literature to introduce this group into organic substrates, most of them are indirect strategies. An elegant way is the direct trifluoromethylthiolation of substrates by the formation of the  $\text{C}-\text{SCF}_3$  bond. Such a strategy is more convenient from a retrosynthetic point of view, as the direct disconnection of the  $\text{SCF}_3$  group could be envisaged anywhere onto the target and at any time of the synthesis. Trifluoromethanesulfenamides (1<sup>st</sup> and 2<sup>nd</sup> generation) have demonstrated their potential in the electrophilic trifluoromethylthiolations (Figure 1). These two reagents of direct trifluoromethylthiolation can react with strong nucleophiles as lithium species (lithium amide,<sup>1</sup> alkyl lithium,<sup>2</sup> lithium enolate<sup>3</sup>), Grignard reagent (made by Magnesium exchange<sup>2</sup> or selective deprotonation<sup>4</sup>). Under acidic condition (Bronsted or Lewis acid), alkynes,<sup>5</sup> arenes,<sup>6</sup> alkenes,<sup>5</sup> ketones<sup>7</sup> can be trifluoromethylthiolated in good yields.

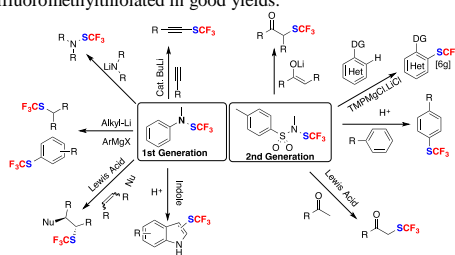


Figure 1: Trifluoromethanethiolation reaction on various substrates.

In conclusion, we developed the scalable synthesis of two trifluoromethanesulfenamides ( $\text{PhNMeSCF}_3$  and  $\text{TsNMeSCF}_3$ ) which are now established as a new valuable alternative to  $\text{CF}_3\text{SCl}$ . Some research groups in the world have proved these reagents are easy to handle by applications in various syntheses. Because of their interesting reactivity, these 2 generations of trifluoromethanesulfenamides are now in the toolbox of organic chemist for the electrophilic trifluoromethylthiolation.

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## #10: Organocatalytic deuterium shuttling properties of NHCs

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N-heterocyclic carbenes (NHCs) have explosively moved from the status of under-studied laboratory curiosities to routine molecular objects in organometallic chemistry and catalysis over the past two decades.<sup>1</sup> On the one side, NHCs are excellent  $\sigma$ -donating ancillary ligands in transition metals complexes with a multitude of applications. And on the other side, free NHCs have also found a number of applications as organocatalysts.<sup>2</sup> Organocatalysis with NHCs can either involve their ambiphilic properties to trigger catalytic “umpolung” reactivity of aldehydes and enals,<sup>3</sup> their Lewis base properties for nucleophilic activation, or also their Brønsted base properties for applications requiring a proton shuttle.<sup>4</sup> Of course, the reactivity profiles of the various classes of NHCs are very dependent on their intimate electronics and sterics.

In the course of our studies on NHC-catalyzed (hetero-)Michael additions using NHCs as catalytic proton shuttles,<sup>5,6,7</sup> we have come to observe that the stable and commercially available NHC 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) catalyzed efficiently the hydrogen / deuterium exchange reaction between pseudoacids ( $pK_{aDMSO} = 12-25$ ) and deuterated chloroform (Figure 1). This intriguing NHC-catalyzed H/D exchange reaction was further examined both experimentally and computationally, which allowed rationalizing previous experimental observations and our own ones, together with gaining further insight into the Brønsted base properties of NHCs and their insertion reactions into the C–H bonds of pseudo-acids.<sup>8</sup>

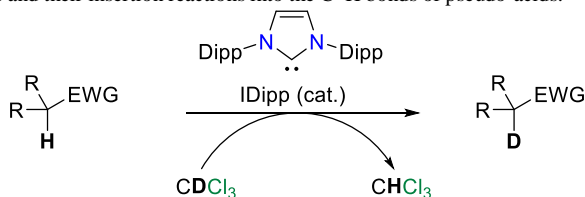


Figure 1 : IDipp-Catalyzed H/D exchange reaction

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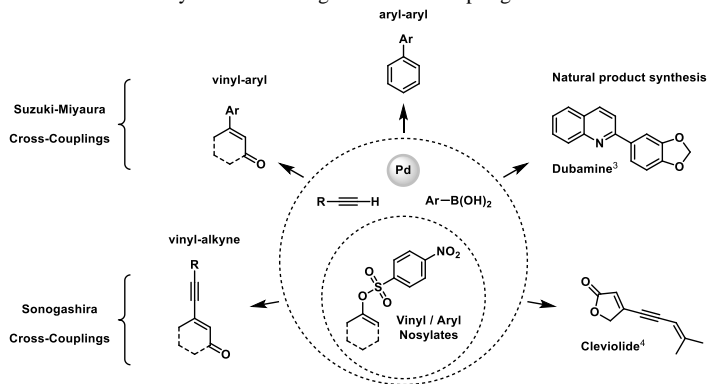
## #11: Nosylates – Novel and Efficient Electrophilic Partners in Palladium-Catalyzed Cross-Coupling Reactions

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Palladium-catalyzed cross-coupling reactions are one of the most popular and powerful transformations able to build carbon-carbon bonds or carbon-heteroatom bonds. They have been extensively used since their discovery, even in industry. To reach this popularity, the cross-coupling processes were constantly modified and improved. In our Laboratory, we focused our efforts on the development of a novel leaving group – nitrobenzenesulfonates (nosylates) – and we demonstrated that they exhibit all the required properties to be engaged in various palladium-catalyzed cross-coupling reactions.<sup>1</sup> This preliminary study showed that nosylates are a stable and an inexpensive leaving group that allows for rapid and very efficient transformations in mild conditions with excellent yields. Furthermore, this electrophilic partner is a useful alternative to other sulfonate derivatives most commonly used.

In this communication and in the continuity of our work, we describe in more detail the scope and the limitations of the preparation of nosylate derivatives and their use in Suzuki-Miyaura<sup>2</sup> and Sonogashira cross-couplings.



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## #12: From silylated peptides to bioactive hydrogels

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Estelle JUMAS BILAK<sup>c</sup>, Jean MARTINEZ<sup>a</sup>, Ahmad MEHDI<sup>b</sup>,  
Gilles SUBRA<sup>a</sup>

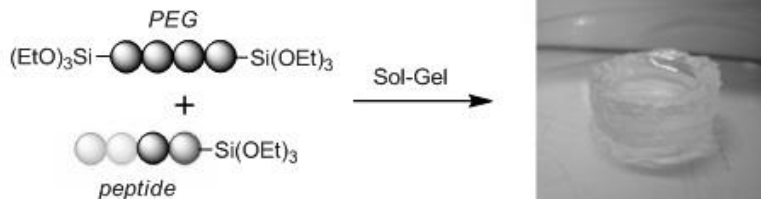
<sup>a</sup>Institut des Biomolécules Max Mousseron, UMR 5247, Faculté de pharmacie, Montpellier, France;

<sup>b</sup>Institut des Matériaux Charles Gerhardt, UMR 5253, Faculté des Sciences, Montpellier, France;

<sup>c</sup>Ecologie des systèmes marins côtiers, UMR 5119, Faculté de pharmacie, Montpellier, France.

The design of biocompatible materials is important in tissue engineering, reconstructive surgery and drug release.<sup>1,2</sup> One of the main challenge is to introduce covalently attached bioactive molecules, in particular peptide ligands, in these biomaterials. In this context, we developed a sol-gel process for preparing hybrid hydrogels by a bottom-up approach.<sup>3</sup>

We first functionalized polyethylene glycol-based units by trialkoxysilane groups. These building blocks were used to form hydrogels in biocompatible conditions. The influence of temperature, building block concentration and additives on gelification and gel properties was studied. Finally, different biological properties were given to hydrogels by incorporation of active hybrid peptides.



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## #13: KISS (Keep It Simple, Sensor)

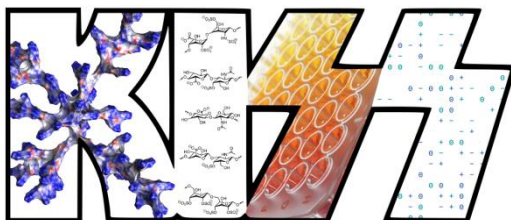
Jean-Patrick FRANCOIA, Laurent VIAL

Institut des biomolécules Max Mousseron, CNRS, université de Montpellier

The last few decades have seen supramolecular chemistry flourish. Many beautiful structures have been produced – such as knots, helicates or borromean rings – and fundamental insights into molecular recognition have been obtained.<sup>1</sup>

Despite such impressive progresses, considerable challenges still lie ahead and one of the most significant of them is the elaboration of synthetic receptors that can communicate efficiently with biologically relevant molecules.<sup>2</sup> Developing such molecular receptors is not only a stimulating academic exercise but also a brilliant research field for the supply of innovative therapeutics or bio-sensing devices to the community.<sup>3</sup>

Here, we present the use of “tree-like” polymers of lysine (Dendri-Graft Poly-L-Lysines or DGLs)<sup>4</sup> as protein mimics for the fluorescent sensing of glycosaminoglycans such as heparin – a highly sulfated biopolymer widely used as an injectable anticoagulant – in competitive media and biological fluids.<sup>5,6</sup>



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## #14: Synthesis of triazole amino acids as potential antibacterial agents

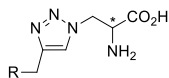
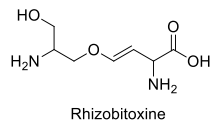
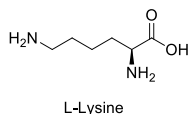
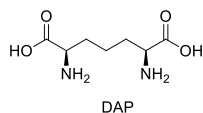
Thibaut BOIBESSOT, Zohra BENFODDA, David BENIMELIS,  
Patrick MEFFRE

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The golden age of antibiotics extend from the beginning of 40's to the end of 20th century is finished. Since the 90's, the excessive use of antibiotics has results in emergence of bacterial multidrug resistant pathogens and this is considered as one of the greatest public health threats in the 21st century<sup>1</sup>.

The biosynthesis of the principal constituent of bacteria cell membrane (peptidoglycan) is one of the most studied for antibacterial action<sup>2</sup>. For example, the two antimicrobial agents penicillin and vancomycin act by inhibiting cell wall synthesis in gram-positive bacteria. The two cytoplasmic enzymes MurE and DapF in peptidoglycan biosynthesis have been considered recently as attractive targets for the development of new antimicrobial compounds<sup>3</sup>.

Moreover, unusual  $\alpha$ -amino acids such as Rhizobitoxine have been reported to present antimicrobial properties<sup>4</sup>. In the present work, we will report the synthesis of 1,2,3-triazole  $\alpha$ -amino acids analogues of lysine, diaminopimelic acid (DAP) or Rhizobitoxine. The new compounds are prepared in a multistep synthesis starting from L and D-serine. In the near future, we will study the biological properties of compounds.



1,2,3-triazole  $\alpha$ -amino acids

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## #15: Nanofiltration rejection of pesticides used in the Mekong Delta Area

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The pollution of recently used pesticides in surface water, a main drinking water source, in Mekong Delta is increasing on both the concentration residues and the polluted area. The performance of nanofiltration membrane to eliminate the three most frequent detected pesticides (fenobucarb, isoprothiolane and pretilachlor) in aqueous solution is carried out in this study. The adsorption of pesticides on the NF membranes and their adsorption kinetic are performed in batch experiment in order to evaluate the adsorption on surface of membrane and the effect on rejection of pesticides. The membrane separation experiments are carried out with a crossflow filtration pilot. The influence of pressure applied, coexisting pesticide and the presence of salts like real river water is investigated. It is found that the adsorption gets equivalent after 48h, the amount of pesticide adsorbed increases in a corresponding with increasing of hydrophobicity of pesticides in a single pesticide system and also in a mixture of three pesticides system. The comparison between adsorption isotherms is shown that Freundlich isotherm is more fixed than Langmuir isotherm and they are physico adsorption with multi adsorption layers. The results of rejection are shown that NF90 membrane is a crucial choice for removing pesticide with very high rejection. With NF270 membrane, the rejection of each pesticide can be explained by the combined influence of their molecular weight and dipole moment, whereas the performance in the mixture of three pesticide solution seems to be influenced by a competitive adsorption of pesticides on the membrane surface. The increasing of the transmembrane pressure posed no effect on the pesticide rejection. In the presence of salts, the rejection tends to reduce for all pesticides and membranes used, while the rejection of salts seems to be independent on the presence of pesticides. Especially, there is an increasing of pure water flux after each experiment with the presence of salts in both cases of the two membranes.

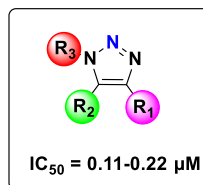
## #16: Expedient preparation of fully decorated 1,2,3-triazoles towards the discovery of potent anti-leukemic compounds

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Anthony R. MARTIN,<sup>a</sup> Patrick AUBERGER,<sup>b</sup> Rachid BENHIDA<sup>a</sup>

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<sup>b</sup>Centre Méditerranéen de Médecine, Université de Nice-Sophia Antipolis, C3M–France.

Chronic myeloid leukemia (CML) is a cancer of the white blood cells, the granulocytes, at all stages of differentiation. To date, the main treatment available is a BCR-ABL inhibitor, imatinib, marketed as Glivec®. However, the emergence of resistance phenomena in some patients makes scientists look for other molecules able to circumvent them.<sup>1,2</sup> In this research work, we are interested in the design, synthesis and evaluation of new derivatives as antitumor agent for the treatment of CML and other hematological malignancies and solid cancers. For this purpose, a series of 1,4,5-trisubstituted-1,2,3-triazole<sup>3-6</sup> derivatives was synthesized using a straightforward click/electrophilic addition or click/oxidative coupling tandem procedures. As part of collaboration with the group of the Mediterranean Centre for Molecular Medicine in Nice, we evaluated the potential anti-CML activities in vitro of these compounds using cell culture assays and an SAR analysis was achieved. This work led to the discovery of two lead compounds belonging to a 5-alkynyl-1,2,3-triazole series and exhibiting potent anti-leukemic effects on several hematologic malignancies including chronic myeloid leukemia (CML), acute myeloid leukemia (AML) and myelodysplastic syndromes (MDS) both sensitive (SKM1-S) and resistant (SKM1-R) to 5-azacytidine (Vidaza®). These two compounds represent a new generation of highly promising drug candidates for use in hematologic cancer therapy and particularly in AML and high-risk MDS resistant to 5-azacytidine



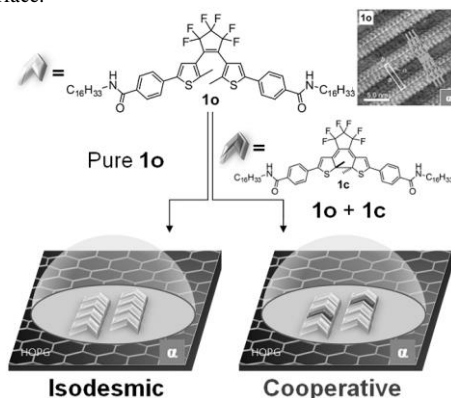
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## #17: Diarylethene self-assembled monolayers: cocrystallization and mixing-induced cooperativity highlighted by scanning tunneling microscopy at the liquid/solid interface

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Yokoyama SOICHI, Takashi HIROSE, Kenji MATSUDA

Graduate School of Engineering, Kyoto University

The control over 2-D multi-component molecular orderings on surfaces is a key technology to realize advanced materials with stimuli-responsive properties. The fractional coverage ( $\theta$ ) at a given concentration can be determined from two parameters: the equilibrium constant ( $K_e$ ) and the degree of cooperativity ( $\sigma$ ). The parameters for the formation of self-assembled monolayer of pure diarylethene isomers were obtained by STM measurements on HOPG. These mono-component parameters were used as references to highlight a cocrystallization process between the open- and closed-ring isomers. Moreover it was observed that the presence of the closed-ring isomer induces cooperativity in the formation of the molecular ordering of the open-ring isomer. The quantitative analysis of the ordering formation process by using a model simulation presented in this work provides a better understanding of mixing of components in a molecular ordering and photoinduced interchanges at the liquid/solid interface.



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## #18: Synthesis of highly selective and reversible inhibitors of Nitric Oxide Synthases: solid-phase synthesis and biological evaluation

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Nitric-oxide synthases (NOSs) are enzymes which catalyze the conversion of L-arginine into nitric oxide (NO) and citrulline. In humans, NOSs exist as three different isoforms namely the neuronal (nNOS), the endothelial (eNOS) and the inducible (iNOS) enzymes. Calcium-dependant nNOS and eNOS are involved in neural transmission and regulation of vascular functions, respectively, whereas iNOS is involved in the immune system. Because the over-production of NO by these enzymes is involved in many diseases including neurodegeneration, arthritis, diabetes ... their inhibition is of great pharmacological interest.

However, the quasi-total conservation of the active site among the three isoforms makes the synthesis of selective inhibitors difficult.

So our goal is to synthesize such inhibitors composed of i) a substrate analog which interacts with the active site, to which is added on the carboxylic side ii) an extension expected to interact within the substrate access channel where differences exist between the three isoforms. These two parts are connected by an amide or a heterocyclic type link. A solid-phase strategy has been developed in our laboratory to synthesize such inhibitors and has permit to obtain more than 200 compounds till today. Two interesting inhibitors have been obtained for iNOS and nNOS and are currently modified to increase the affinity and the selectivity.

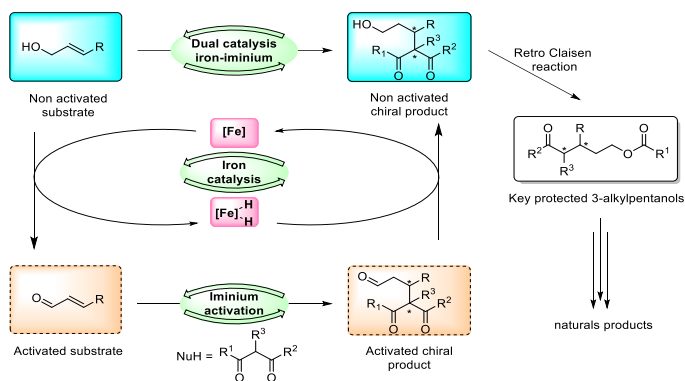
The activity of the molecules is measured on the three recombinants enzymes then the IC<sub>50</sub> is calculated for the more interesting compounds. Furthermore, cellular tests have been set up on RAW264.7 (macrophage) and INS-1 (β-pancreatic cell) to assess the cellular permeability of the compounds.

## #19: Claisen fragmentation: A key step for enantioenriched building blocks synthesis

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Rapid access to functionalized building blocks from simple and available substrates remains a challenge for both academics and industrials. Despite the emergency of new concepts such as step and/or atom economy, some units are still difficult to obtain. In this context, a new enantioselective approach involving an iron-iminium dual catalysis has been developed in order to functionalize allylic alcohols.<sup>1</sup> This methodology merges three successive key catalytic steps; oxidation, Michael addition and reduction. In this reaction, a reversible oxidation of a non-activated allylic alcohol occurs, combined with a 1,4-enantioselective organocatalyzed addition. The rapid access to key fragment of odorant molecule or biologically active natural products highlights the efficiency of this method.<sup>2,3</sup>



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## #20: Covalent organosilica networks where is incorporating Phenylene-Vinylene motifs

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Works of our group about synthesis of hybrid polysilsesquioxane, resulting from the hydrolysis-polycondensation of organotrialkoxysilanes, allowed the emergence of a large variety of organosilica with very interesting properties such catalytic properties, optoelectronic...<sup>1</sup>

These materials, showing an organosilica network, are prepared according to the sol-gel chemistry, under a kinetically controlled process. Consequently, most of these hybrid silicas are amorphous materials. It is possible to obtain partially organized materials using organosilica precursors with self-assembling properties (hydrogen bonding,  $\pi$ -stacking, hydrophobic properties...). The supramolecular organisation of the molecules has been transcribed within the solid, to obtain nanostructured materials.<sup>2</sup> Recently, we used this approach to synthesis nanostructured hybrid films with organic groups containing large  $\pi$ -conjugated fragments. Thanks to the control of the  $\pi$ -stacking of this type of groupements, optic and optoelectronic properties were modulated.<sup>3</sup> However, the organisation of these hybrids is limited to the organic sub-structures, there is no long-range organisation of the silica motifs.

In this context, we explored a new approach to build a network from an elementary brick of silica: a cubic structure usually called POSS (Polyhedral Oligomeric SiSesquioxane). This cube is formed of eight silicon atoms located at the corners and twelve oxygen atoms at the middle of the edges. This structure, fully condensed, potentially offers eight functionalization sites and could allow the synthesis of porous and organized hybrid networks

To reach this goal, we synthesized a new POSS derivative decorated with eight aldehyde functions. This molecule was obtained from the Metathesis between the Poss(octavinyl) and the paravinylbenzaldehyde. Engaging the octa-aldehyde in Wittig reaction with bis or tris-phosphoniums, gave us the opportunity to develop a new class of three-dimensional organosilylated covalent network. The subsequent materials are porous and exhibit fluorescence properties. They could be useful as sensitive materials for the detection of analytes by fluorescence quenching, or for the detection of solvents by fluorescence enhancement.

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## #21: A new strategy to form assemblies of nanoparticle: application to the elaboration of magnetic clusters for Magnetic Resonance Imaging

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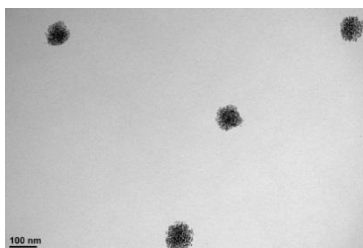
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We will present clusters of nanoparticles obtained by a new strategy. Clusters of well-defined size can be coated with different biocompatible polymer to provide stabilization and dispersability in aqueous media. Structure of clusters was investigated by combining TEM, cryo transmission electron microscopy (cryo-TEM), static (SLS) and dynamic light scattering (DLS) and atomic force microscopy (AFM). Different coatings enable the chemical functionalization of these clusters which can potentially be used in various biomedical applications including hyperthermia, drug targeting and medical imaging. This strategy was applied to assemble superparamagnetic nanoparticles to enhance contrast in magnetic resonance imaging (MRI)<sup>1</sup>. First in vivo results on small animal MRI 4.7T are promising.



Iron Oxide clusters

We extended this strategy to other materials (plasmonic particles, fluorescent probes, quantum dots) for developing new multimodal imaging agents.

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## #22: Design, synthesis of novel ribonucleosides of 1,2,3-triazolyl benzyl-aminophosphonates and evaluation for antiviral activity

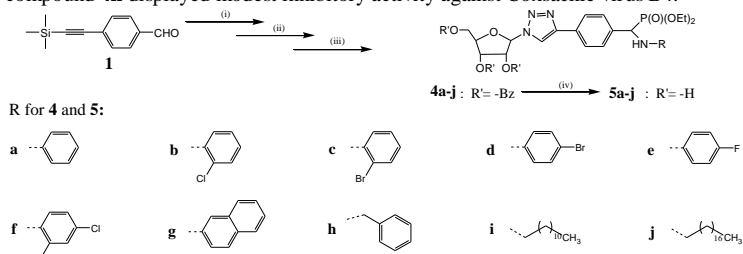
Abdelaziz OUAHROUCH<sup>a,b,c</sup>, Moha TAOURIRTEA,  
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A novel series of ribonucleosides of 1,2,3-triazolylbenzyl-aminophosphonates was synthesized through the Kabachnik-Fields reaction using **1** as catalyst [1-3] followed by copper-catalyzed cycloaddition of the azide and alkyne reaction (CuAAC) [4]. All structures of the newly prepared compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS spectra. The structures of **2e**, **2f**, **3d** and **3g** were further confirmed by X-ray diffraction analysis. These compounds were tested against various strains of DNA and RNA viruses; compounds **4b** and **4c** showed a modest inhibitory activity against respiratory syncytial virus (RSV) and compound **4h** displayed modest inhibitory activity against Coxsackie virus B4.



Scheme 1. Reagents and conditions: (i) R-NH<sub>2</sub> (1.2 equiv), H(O)P(OEt)<sub>2</sub> (1.2 equiv), I<sub>2</sub> (0.2 equiv.), MeCN, r. t., 1h; (ii) TBFA (1 equiv.), THF, r. t., 30 min; (iii) azido-ribose (2.5 equiv.), CuI (0.1 equiv.), Et<sub>3</sub>N (1.1 equiv.), MWI, 5 min; (iv) MeONa (1 equiv.), MeOH, r. t., 30 min.

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(3) Wu, J.; Sun, W.; Xia, H. G.; Sun, X. *Org. Biomol. Chem.* **2006**, *4*, 1663.

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## #23: Biological fouling resistance optimization of reverse osmosis membranes

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Biofouling in reverse osmosis (RO) elements is the phenomenon by which bacteria settles in the feed channel of an element and starts building a biofilm. This causes an exponential increase of the feed-concentrate pressure drop ( $\Delta P$ ) in the RO system<sup>1</sup>. It additionally generates an additional resistance layer, which lowers the permeability. This decline in productivity, results in higher energy consumption and the need to clean the system more frequently<sup>2</sup>. If the  $\Delta P$  becomes too high, the elements are at risk of irreversible mechanical damage. This presentation describes how novel RO elements can be designed to specifically mitigate biological fouling and improve long performance.

In order to demonstrate the importance of feed spacer design and membrane chemistry effect in preventing fouling, several small experimental plants are used. Membrane Fouling Simulators (MFS) units has been successfully tested as a method to simulate biofouling trends on industrial elements. The use of MFS simulators enables quicker screening of improved feed spacer designs and provides an efficient tool for studying biofouling fundamentals in RO.

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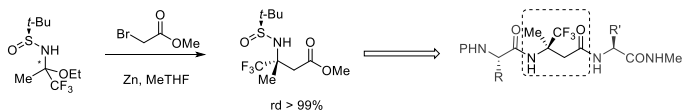
## #24: Synthesis of small $\alpha/\beta$ peptides containing a chiral trifluoro-methylated $\beta^{3,3}$ -amino acid

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$\alpha/\beta$ -peptides have received a great deal of attention due to their unique folding properties and their specific biological activities.<sup>1</sup> In spite of the extensive studies on the effect of substituents on the conformation of these peptides, the influence of enantiopure geminally disubstituted  $\beta$ -amino acids and of the trifluoromethyl group was never examined.

We recently developed the first short and gram-scale synthesis of enantiopure  $\beta$ -alkyl(aryl) $\beta$ -trifluoromethyl  $\beta$ -amino esters.<sup>2</sup> In this communication, we will present that despite the low nucleophilicity and steric hindrance of the amine function adjacent to the electron withdrawing and bulky trifluoromethyl group,  $\beta$ -methyl  $\beta$ -trifluoromethylamino acid derivatives can be successfully used as residue for the elaboration of various heterogeneous peptides. The conformational studies of these original peptides will be further evaluated.



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## #25: UV photochemistry of pyridine-water complex: evidence of water dissociation

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The study of intramolecular hydrogen bond complexes is of a crucial interest in many physical chemistry domains, like astrochemistry, molecular dynamics and biochemistry. These complexes are a stand model of the proton transfer in molecular wires. This study is part of the research of chromophores that can be used as catalyzers for the homolytic photochemical splitting of water. One the simplest model is the Pyridine-Water complex. A recent theoretical study<sup>1</sup> proposes that under UV irradiation, a proton transfer reaction occurs in Pyridine-Water complexes leading to the  $\text{PyH}\cdot\text{OH}\cdot$  bi-radical structure that exists with a lower energy than that of locally excited states. The photochemistry of this complex is an example of the proton-transfer reactions driven by electron-transfer processes. There are not any experimental studies able to demonstrate the existence of such complex. One experimental method that one can use to observe this weakly bonded species are the cryogenic matrices<sup>2</sup>. We have obtained the first results in argon, neon and nitrogen matrices that show that upon broad band UV irradiation, one of the products obtained is the non-radical protonated Pyridine. We have obtained the same products using ammonia as Pyridine partner, what is comforting the former results. One of the most salient result of this series of experiments is that indeed hemolytic water dissociation can occur using Pyridine as a UV photobase partner.

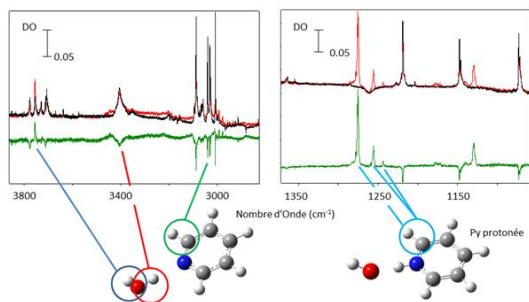


Figure 1. Effects observed upon broad band UV irradiation (non-focalized, 300 W, 180 minutes) of Pyridine-Water complexes in Argon (2/10/1000), in the  $\nu\text{OH/CH}$  (left side) and  $\delta\text{CH}$  (right side) regions. Spectrum before irradiation (black), after irradiation (red) and the difference between the two (green).

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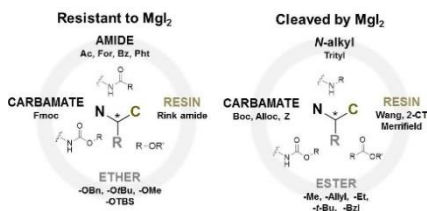
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## #26: Amazing $MgI_2$ : an Alternative to Conventional Deprotection Methodologies

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<sup>a</sup> IBMM, UMR 5247, CNRS-Université de Montpellier

It is obvious that protecting groups have tremendous positive impact to successfully achieve the liquid or solid phase construction of various biomolecules. In a context in which the use of attractive protecting groups is often limited by harsh deprotection conditions and restrictions in chemoflexibility,  $MgI_2$  <sup>[1,2]</sup> offers, by the execution of a remarkably simple, mild and quantitative protocol, a fresh vision with unprecedented chemoselective cleavages of usual protecting groups or solid-phase support. For example, by applying our method on various amino acids or peptides, we accomplished a selective cleavage of a methyl or ethyl ester preserving a Fmoc residue,<sup>[3]</sup> we succeeded to keep a benzyl ether moiety during the deprotection of a benzyl ester and we realized an efficient and mild releasing of peptides from Merrifield resin.



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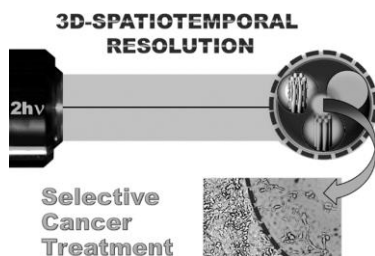
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# PhD thesis award: Two-Photon-Actuated Theranostic Organosilica Nanomedicine

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Two-photon-actuated nanomedicine has become one of the main proponents for the achievement of the spatiotemporal selectivity needed for nanomedicine. Indeed, the purpose of the medical application of nanotechnology for cancer treatment is to lower and suppress the side effects caused by chemotherapy and radiotherapy, due to their lack of selectivity. Among various nanoparticles, organosilicas have attracted increasing attention for their low cytotoxicity and the ability to carry multiple cancer *therapy* and *diagnosis* features in a single nanovehicle: the so-called *theranostic* nanomedicine. In this presentation, two-photon-actuated fluorescence imaging, drug-delivery, and photodynamic therapy via mesoporous silica,<sup>1,2</sup> bridged silsesquioxanes,<sup>3,4</sup> and periodic mesoporous organosilica nanomaterials will be described.<sup>5</sup>



- (1) J. Croissant, M. Maynadier, A. Gallud, H. P. N'Dongo, J. L. Nyalosaso, G. Derrien, C. Charnay, J-O. Durand,\* L. Raehm, F. Serein-Spirau, N. Cheminet, T. Jarrosson, O. Mongin, M. Blanchard-Desce, M. Gary-Bobo,\* M. Garcia, J. Lu, F. Tamanoi, D. Tarn, T. M. Guardado-Alvarez, J. I. Zink,\* *Angew. Chem. Int. Ed.*, **2013**, *125*, 14058.
- (2) J. Croissant, A. Chaix, O. Mongin, M. Wang, S. Clément, L. Raehm, J-O. Durand,\* V. Hugues, M. Blanchard-Desce, M. Maynadier, A. Gallud, M. Gary-Bobo,\* M. Garcia, J. Lu, F. Tamanoi, D. P. Ferris, D. Tarn, J. I. Zink,\* *Small*, **2014**, *10*, 1752.
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# Posters

## Poster session

#1	Simultaneous detection of glucose and ethanol on glassy carbon electrode modified with nickel oxides in alkaline medium
#2	Valorisation of plant extracts from the Reunion Island biodiversity
#3	Stereoselective synthesis of (hetero)aromatic amino acids and applications for the development of modified neurotensin
#4	Performance of the LAAP-ToF-MS
#5	Five-step synthesis of original imidazo[1,2- <i>a</i> ]pyridine derivatives and their biological evaluation <i>via</i> a flow cytometry method
#6	Pharmacological Evaluation of <i>Frankenia Laevis</i> L. from Tunisia
#7	Chemical composition (Indices, 2, 2-Diphenyl-1-picrylhydrazyl and Sterols) of food oils in Mauritania
#8	A new concept of dual targeting drugs: DTP-348 A carbonic anhydrase ix inhibitor specific for hypoxic tumors
#9	Synthesis of organic complexing molecules (amino arylidene aryl); Application fixing Cu <sup>2+</sup>
#10	Synthesis and bioevaluation of peptides as potential inhibitors of <i>Leishmania</i> and <i>Trypanosoma</i> HslVU, a proteasome-like complex.
#11	<i>In vitro</i> evaluation of the antioxidant, anticancer, acetylcholinesterase activities of <i>Thymelaea hirsuta</i> extracts
#12	Anti-xanthine oxydase, anti alpha amylase activities and chemical composition of <i>Croton lobatus</i> leaves
#13	Synthesis and reactivity of quaternary trifluoromethylated aminals derived from (L)-tartaric acid
#14	Density Functional Theory study of gold, copper and gold-copper alloy surfaces under reactive gas: CO and NO
#15	Characterization of oligomeric distributions in aluminum chlorhydrates by capillary electrophoresis
#16	Valorization of olive by-products through vermicomposting
#17	Multivalent inhibitors of carbonic anhydrases

#18	Pharmacological evaluation of <i>Frankenia Laevis</i> L. from Tunisia
#19	Lewis base and L-proline co-catalyzed Baylis–Hillman reaction of arylaldehydes with 1-phenylprop-2-en-1-one
#20	Synthesis and characterization of new materials/composites based on hydrazine borane and lithium amide
#21	Comparison of dynamic light scattering and nanoparticle tracking analysis for measurements of size distribution of colloids in wastes leachates
#22	Thermodynamic modelisation of binary systems using PC-SAFT equation of state
#23	In vitro evaluation of some Mediterranean medicinal plants aqueous extracts on the growth of some pathogenic fungus
#24	A projection method to obtain VB coefficients from Multi - Configurational MO wave functions
#25	Molecular modelling, design, and synthesis of new NTS2-selective neurotensin analogues
#26	Study of the quality control of oxytetracycline and ivermectin injectables for Mauritania veterinary
#27	Composition and antifungal activity of the essential oil of <i>Nashia inaguensis</i> Millsp. (Verbenaceae) cultivated in French Guiana
#28	GARANT' AIR : a targeted odors treatment From Chemistry to Processing of Boron-Modified
#29	Polycarbosilazanes: Toward the Preparation of SilicoBoron CarboNitride Ceramics
#30	Effect of the amount of silver on the physicochemical properties of Ag-ZrO <sub>2</sub> aerogel catalysts for the total oxidation of CH <sub>4</sub>
#31	From Chemistry to Processing of Boron-Modified Silicon Carbide Precursors
#32	Natural formulation: attractive of dog to achieve their needs

# #1: Simultaneous detection of glucose and ethanol on glassy carbon electrode modified with nickel oxides in alkaline medium

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In this work, we have modified the surface of a glassy carbon electrode with an oxide layer of nickel<sup>1</sup>; the deposit formed on the surface of the working electrode was characterized using several electrochemical and physical techniques such as cyclic voltammetry, polarization resistance, electrochemical impedance spectroscopy and scanning electronic microscopy. This modified electrode was used in alkaline solution for the simultaneous determination of glucose and ethanol<sup>2,3</sup>. The voltammograms recorded during this electrooxidation show a series of anodic and cathodic peaks which increase directly with increasing of glucose and ethanol concentration in the alkaline solution<sup>4</sup>. This modified electrode shows a good reproducibility, a very short response time and a high sensitivity.

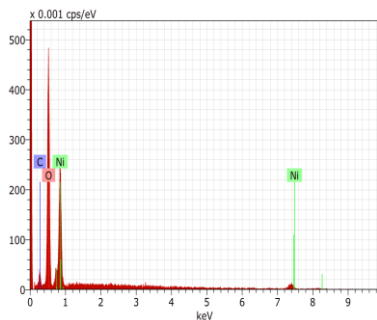


Figure 2: Voltammograms recorded before and after glucose and ethanol oxidation

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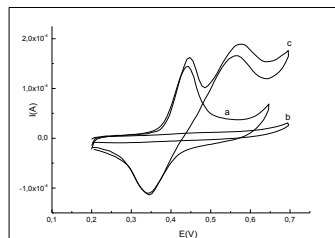


Figure 1: SEM microscopy of GCE modified with nickel oxides

## #2: Valorisation of plant extracts from the Reunion Island biodiversity

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Nature has been a source of medicinal agents throughout the ages and continues to be an abundant source of novel leads for the development of innovative products. Its ongoing exploration has prompted an increasing demand of more efficient extraction techniques and notably the partial replacement of conventional extraction processes with “green” procedures based on microwave irradiation. In the last two decades, advances in microwave extraction have resulted in a number of innovative techniques such as Solvent-Free Microwave Extraction (SFME) and Microwave Hydro-Diffusion and Gravity.<sup>1</sup>

Collaborating with the Institute of Chemistry (Nice), the start-up Extraits de Bourbon (Saint-Denis) aims at valuing various eco-extracts (essential oils, hydrosols, and macerates) obtained via SFME of plants from the Reunion Island. If the chemistry of some essential oils obtained by microwave-assisted procedures has been investigated over the last decade,<sup>2</sup> it is not the case for both hydrosols and macerates. Fifteen plants have been selected based on their indigenous/endemic character, their traditional uses or because their cultivation is emblematic from the island: geranium, ravintsara, etc.<sup>3</sup> The project consists in the extensive phytochemical characterisation of these eco-extracts by mean of analytical technologies including GC/MS, GC-FID and HPLC-UV-ELSD. Their olfactory and gustatory properties, as well as their biological and toxicological properties are also evaluated. The identification of the molecules responsible for specific activities/properties will further be undertaken by bio-guided fractionation of the corresponding extract and by their isolation/characterization (MS, NMR). Eco-extracts presenting a high potential will then be used to develop ingredients dedicated to a multitude of applications: cosmetics, perfumery, pharmaceutical industry, etc.

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### #3: Stereoselective synthesis of (hetero)aromatic amino acids and applications for the development of modified neurotensin

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ZAHARIA,<sup>b</sup> Florine CAVELIER.<sup>a\*</sup>

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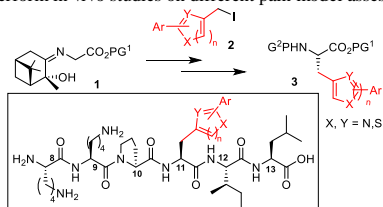
<sup>b</sup>Iuliu Hațieganu University of Medicine and Pharmacy, Department of Organic  
Chemistry, Victor Babes 41, Ro-400012, Cluj-Napoca, Romania.

<sup>c</sup>Département de physiologie et biophysique, Faculté de  
médecine et des sciences de la santé, Université de Sherbrooke.

Pain treatment represents a huge market and the development of drugs tolerance with limited secondary effects is an urgent demand. In this field, neurotensin (NT) exerts various biological functions including hypothermic, antipsychotic properties and analgesic responses that are mediated by its NTS1 and NTS2 receptors. However its poor bioavailability is the major obstacle for its biological activity and therapeutic effects.

Previous work focused on neurotensin structure-activity relationships either by introduction of unnatural amino acids or by structural modifications.<sup>1</sup> In particular, it has been established that the residue at position 11 must have an aromatic side chain and the substitution of tyrosine by an aliphatic chain (leucine or alanine) suppressed its central or peripheral activity.<sup>2</sup> Among the (hetero)aromatic amino acids, thiazoles derivatives are of considerable interest for the development of bioactive peptides.<sup>3</sup>

Herein, we describe the diastereoselective synthesis of novel thiazoles  $\alpha$ -amino acids **3** starting from the hydroxy-pinane derived Schiff base **1**. These amino acids were obtained in good yields and enantioselectivities (e.e. > 99%) and were then introduced at the position 11 of NT [8-13] (Scheme 1). Structure-activity relationships studies pointed out several selective NTS2 receptor analogues to perform in vivo studies on different pain model assessment.



Scheme 1 : Asymmetric synthesis of thiazoles derived  $\alpha$ -amino acids **3** and NT [8-13] analogues.

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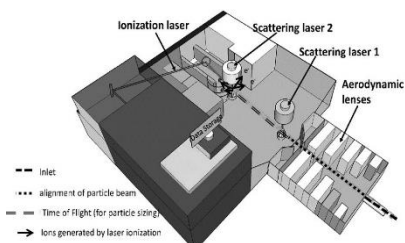
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## #4: Performance of the LAAP-ToF-MS

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Johannes T. VAN ELTEREN<sup>b</sup>, Nathalie HAYECK<sup>a</sup>,  
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Nanoparticles are increasingly used within industry sector which consequently implies their increased presence in the ambient atmosphere. Recent studies demonstrated that the nanoparticles exhibit potential health and environmental risks.<sup>1</sup> It is therefore of crucial importance to characterize the chemical composition of nanoparticles. Mass spectrometry shows promising capacity to characterize the chemical composition of nanoparticles in real time. Here we present the performance of a new very compact Laser Ablation Aerosol Particles - Time of Flight - Mass Spectrometer (LAAP - ToF - MS). The principle of LAAP-ToF-MS is based on the following: the nanoparticle is first detected by two diode lasers at  $\lambda=405$  nm then it is ionized by an excimer laser operating at  $\lambda=193$  nm. For each detected particle two important information are gathered, that is its aerodynamic size and its chemical composition. To evaluate the performance of the LAAP-ToF-MS, we generated standard spherical particles (polystyrene latex) and then in the second time we validated the results with real atmospheric particles.

The obtained results demonstrated that the detection efficiency and the hit rate are influenced by many parameters like the particles size, the chemical composition and the shape of the particles. The emerged results exhibited that the temporal evolution of the atmospheric particles is feasible under certain conditions. These results are based on a comparison with a particle counter CPC. The developed analytical methodology associated with this instrument will be tested during an experimental campaign which will be held in September. The validation of the instrument will be performed by intercomparison with several off-line techniques such as ICP-MS, electronic microscopy.

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## #5: Five-step synthesis of original imidazo[1,2-*a*]pyridine derivatives and their biological evaluation *via* a flow cytometry method

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Sébastien HUTTER<sup>b</sup>, Michèle LAGET<sup>b</sup>, Pierre VERHAEGHE<sup>c</sup>,  
Pascal RATHELOT<sup>a</sup>, Patrice VANELLE<sup>a</sup>, Nadine AZAS<sup>b</sup>.

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<sup>b</sup>Aix-Marseille Université, UMR MD3, Infections Parasitaires, Transmission et Thérapeutique, Faculté de Pharmacie, 27 Boulevard Jean Moulin, 13385 Marseille, France.

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Looking for original heterocyclic molecules presenting anti-infective activity, our research team develops a new program focusing on azaheterocyclic compounds with antiprotozoal activity, especially against *Leishmania* parasites<sup>1,2,3</sup>. Thus, in 2013, we reported the identification of a promising antileishmanial pharmacophore centered on the 3-nitroimidazo[1,2-*a*]pyridine scaffold<sup>4</sup>. We present herein, as a part of a pharmacomodulation work, the synthetic pathway of imidazo[1,2-*a*]pyridine molecules, diversely substituted at positions 6 and 8. Starting from a 2-aminopyridine derivative, the chemical reactions involved are successively halogenation, cyclocondensation, nitration, sulfonation, and nucleophilic aromatic substitution. A series of twenty five original derivatives bearing a phenylsulfane substituent at position 8 and a chlorine atom at position 6 was especially synthesized. The preliminary biological evaluation phase highlighted a lead compound, displaying very good *in vitro* activity on the promastigote stage of *Leishmania donovani* (IC<sub>50</sub> = 1 μM) in comparison with the most active antileishmanial drug on the market (Amphotericin B) and the only orally available antileishmanial drug on the market (Miltefosine). Determination of the *in vitro* activity on the amastigote stage of *L. donovani* was carried out using a simple and efficient flow cytometry method, and also displayed very low concentrations (IC<sub>50</sub> = 1,3 μM). Moreover, the lead compound did not show any cytotoxicity on the human HepG2 cell line (CC<sub>50</sub> > 62.5 μM). The research for the mechanism of action of the lead molecule, also carried out by a flow cytometry method, showed negative results for most of the usual pharmacological actions known for the other antiprotozoal drugs, suggesting an original mode of action for this lead compound. The evaluation of its activity toward other protozoan (to assess its selectivity) and the determination of its physicochemical properties and *in vitro* pharmacokinetic parameters are under progress.

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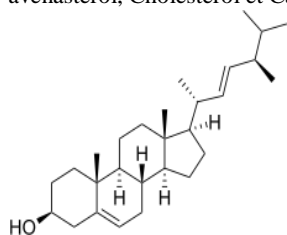
## #7: Chemical composition (Indices, 2, 2-Diphenyl-1-picrylhydrazyl and Sterols) of food oils in Mauritania

Bocar Kalidou M'BAYE<sup>a, b</sup>, Sylvie CAZAUX<sup>a</sup>,  
Mohamed Brahim EL KORY<sup>b</sup>, Jalloul BOUJILA<sup>a</sup>

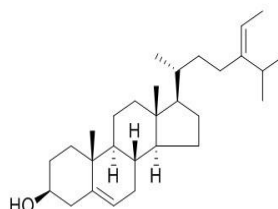
<sup>a</sup>University of Toulouse, Pharmacy Faculty of Toulouse, Laboratory IMRCP UMR CNRS 5623,  
University Paul Sabatier, 118 road of Narbonne, F-31062 Toulouse, France.

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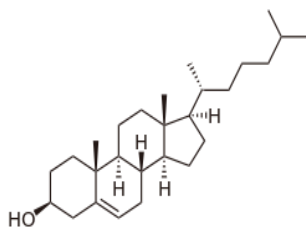
This present study focuses on analyzes of oil collected on Mauritanian markets. Vegetable oils are chemically unstable due to the sensitivity to oxidation of their unsaturated fatty acids. The determination of the various indices is made by the ISO methods. Sterols contents are evaluated by GC-MS. the 2,2-diphenyl-1-picrylhydrazyl (DPPH) is determined by a reader Scanit, The method used to measure antioxidant activity is of scavenging free radicals using the DPPH\*. The acidity indices range from  $0.027 \pm 0.02$  to  $0.5 \pm 0.34$  (mg KOH / g of oil), the results of free fatty acids and the degree of acidity are dependent on acidity of the indices. The Peroxides indices vary from  $5.93 \pm 0.12$  to  $55.33 \pm 1.53$  meq O<sub>2</sub> / kg oil). The indices of iodine vary from  $112.24 \pm 1.76$  to  $123.38 \pm 2.48$  (g iodine / 100 g of oil). The results of DPPH vary from  $15.26 \pm 0.74$  to  $30.42 \pm 2.65\%$ . For sterols the results consist of Brassicastérol, Delta-5-avenastérol, Cholestérol et Campestérol.



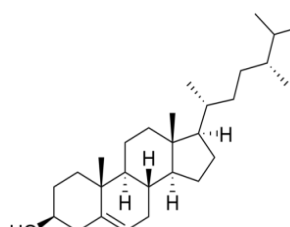
Brassicastérol



Delta-5-avenastérol



Cholestérol



Campestérol

## #8: A new concept of dual targeting drugs: DTP-348 A carbonic anhydrase ix inhibitor specific for hypoxic tumors

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<sup>c</sup>Department of Chemistry, Laboratory of Bioinorganic Chemistry, Università degli Studi di Firenze, Italy

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Hypoxia is one of the most devastating phenomenon while treating remote and solid tumors by radio/chemotherapies. pH regulating transmembrane carbonic anhydrase IX is associated with poor prognosis and therapy resistance. This made carbonic anhydrase IX as potential anticancer therapeutic target.

We developed series of nitroimidazoles incorporating sulfamide/sulfonamide/sulfamate moieties were having radio/chemo sensitization property to target tumor-associated carbonic anhydrase isoforms IX and XII. Most of the new compounds were nanomolar inhibitors of these isoforms. Inhibition efficacy of these molecules strongly suggested by crystallographic studies on adduct of DTP-348 with hCAII. By reducing hypoxia-induced extra cellular acidosis in HT-29 and HeLa cell lines these molecules showed significant activity of CAIX inhibition, this was shown by crystal structure. (in vitro)

Lead molecule in sulfamide series (DTP-348) showed chemosensitization co-treated with Doxorubicin and radiosensitization (in vivo) of carbonic anhydrase IX containing hypoxic tumors.

We were motivated to proceed with pre-clinical trials on DTP-348 with encouraging ADME (in vitro) screening results, pharmacokinetic and cytotoxicity data.

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## #9: Synthesis of organic complexing molecules (amino arylidene aryl); Application fixing $\text{Cu}^{2+}$

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Some Schiff bases with aryl groups have a biological activity, which attracted the attention of many researchers in recent years<sup>1</sup>. The condensation of primary amines with aldehydes was investigated by Schiff. That is why the resulting products are known as Schiff bases. The synthesis and characterization of benzylideneanilines were made in the organic chemistry laboratory applied. The resulting molecule which is an aromatic molecule p- (benzylideneamino) phenol) was characterized by UV spectroscopy and IR confirmed the presence of characteristic bands of azomethine group C = N-1 to 1615nm.

Our work focuses on the preparation of purified clay and intercalated with aryl amino arylidene. Synthesized clays play a role in the field of pollution by trapping toxic heavy metals (Cd, Pb, Hg, Cu, Ni). We therefore studied the behavior of copper fixed on hybrid materials (intercalated clay). The results show that the adsorption of  $\text{Cu}^{2+}$  by intercalated clay with N- (4- nitrobenzylidene) aniline is higher than that of montmorillonite clay.

The reaction was followed by TLC, infrared spectroscopy and X-ray diffraction.

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## #10: Synthesis and bioevaluation of peptides as potential inhibitors of *Leishmania* and *Trypanosoma* HslVU, a proteasome-like complex.

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<sup>c</sup>Laboratoire de Parasitologie-Mycologie, Faculté de Médecine, Université de Nice-Sofia Antipolis.

<sup>d</sup>MIVEGEC, UMR2724 CNRS, IRD, Université de Montpellier.

It is urgent to develop more efficient treatments for Leishmaniases and Trypanosomiases. We propose to target a proteasome-like complex, the HslVU peptidase, which is present in the parasite mitochondrion, essential for parasite growth and has no analogue in the human. This complex is constituted by two central HslV peptidase rings, which are sandwiched between two HslU ATP-ase rings. As HslV shares a similar enzymatic mechanism with the host proteasome, we propose to inhibit the assembly of the complex in order to be selective. According to studies on bacterial HslVU,<sup>1,2</sup> the C-terminal segment of HslU represented a privileged target.

Recombinant HslV is inactive alone, but a synthetic C-terminal HslU dodecapeptide (C12-U2) was able to induce the digestion of a fluorogenic substrate. To get more insight of the interaction of C12-U2 with HslV, series of analogues, including constrained analogues, were synthesized and tested. The identified structural requirements could lead to high affinity and stable ligands able to inhibit the interaction between the HslU and HslV rings, obligatory for the degradation of proteins by HslVU. Finally, we considered the mitochondrial addressing of C-ter HslU-derived peptides. Fluorescently-labeled mitochondria-penetrating peptides were synthesized and incubated with parasites. Some were found to enter the parasites but without specific accumulation in the mitochondrion.

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## #11: *In vitro* evaluation of the antioxidant, anticancer, acetylcholinesterase activities of *Thymelaea hirsuta* extracts

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Nowadays, studies on the medicinal plants and their secondary metabolites are more increasing. The secondary metabolites having less side effects and also more than one effect of herbal drugs than the synthetic components for the treatment of many disease. *Thymelaea hirsuta* is a shrub of the family Thymeleaceae. This plant has a medical importance since the past for its powerful antiseptic, anti-inflammatory properties, for the treatment of diabetes and other biological activities.

In the present work, extracts from the aerial parts of *T. hirsuta*, cultivated in Tunisia, were prepared by sequential method with solvents of increasing polarity namely hexane, ethyl acetate, ethanol and methanol. Then, the crude extracts obtained were used for the determination of the chemical composition (polyphenols, flavonoids, tannins, anthocyanins) and some biological activities. Anti-acetylcholinesterase and antioxidant (DPPH and ABTS assays) activities have been evaluated. Cytotoxicity activity of all extracts was assessed *in vitro* against two different human cell lines (MCF-7 (human breast cancer cell) and OVCAR (human ovarian cancer cell)). The extracts were rich of polyphenols 39.45 to 279.58 mg gallic acid equivalent/g dry mass. The methanol extract showed, for the DPPH· and ABTS·<sup>+</sup> assay, the best result with an IC<sub>50</sub> of 15.9±0.36 mg/L and 6.4±0.43 mg/L, respectively. For the cytotoxicity activity against MCF-7 and OVCAR, the ethyl acetate extract exhibited the best percentage of inhibition 70% at 50 mg/L.

## #12: Anti-xanthine oxydase, anti alpha amylase activities and chemical composition of *Croton lobatus* leaves

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Around the world, plants are used to cure or prevent disease. Over 4000 medicinal plants are used in Africa<sup>6</sup>. Among these plants there is *Croton lobatus*. It belongs to the family Euphorbiaceae. It is widely used in traditional medicine in Benin and intervenes in the treatment of spasms, threats, abortion, high blood pressure<sup>1</sup>. It has been little studied, only its antimicrobial properties<sup>3,4,5</sup> were evaluated and isolated alkaloids<sup>2</sup>. His biological profile is poorly developed in the literature. It is important to deepen his knowledge. This will be done through the study of its phytochemistry and evaluation of some biological activities. Thus, successive extractions with solvents of increasing polarity (cyclohexane, dichloromethane, ethyl acetate, methanol) were performed. The extracts obtained were tested for their antidiabetic, antixanthine oxidase and for their content of polyphenols, flavonoids, tannins, anthocyanins. The result of evaluation showed that at 50 mg/L of extracts, the percentage inhibitions were 52.8-64.3% for anti-alpha-amylase, 22.2-62.60% for anti-xanthine oxidase activity. Moreover, *C. lobatus* had low polyphenol content (gallic acid equivalent 2.3-20.2 mg/g dry mass) and flavonoids (quercetin equivalent 6.3-8.1 mg/g dry mass), does not contain anthocyanins or tannins.

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## #13: Synthesis and reactivity of quaternary trifluoromethylated amins derived from (L)-tartaric acid

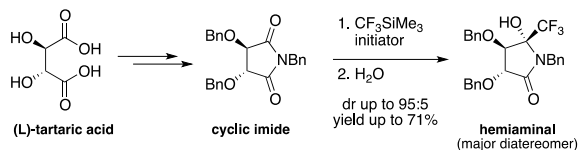
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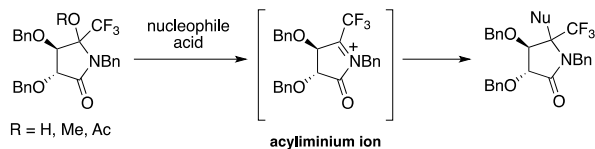
Organofluorine compounds have found a wide range of applications as pharmaceuticals, agrochemicals or materials due to the beneficial properties brought by fluorine atom. One of the most important fluorine containing substituent is the trifluoromethyl group. The latter is relatively large, its Van der Waals radius lies between those of *i*Pr and *t*Bu, its electronegativity is similar to that of oxygen and its hydrophobic parameter is large. Moreover, the trifluoromethyl group often improves the biological activity and the metabolic stability.<sup>1</sup>

Our research group is interested in the preparation of enantiopure *N*-heterocycles containing a quaternary trifluoromethylated group starting from the easily available (L)-tartaric acid.<sup>2</sup>

Herein we wish to report the synthesis of trifluoromethylated hemiaminals derived from (L)-tartaric acid by nucleophilic trifluoromethylation with the Ruppert-Prakash reagent (CF<sub>3</sub>SiMe<sub>3</sub>) of a cyclic imide and the preparation of their ether and acyl derivatives.



Our first attempts to generate the corresponding trifluoromethylated acyliminium ion from these synthons will although be discussed.



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## #14: Density Functional Theory study of gold, copper and gold-copper alloy surfaces under reactive gas: CO and NO

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In the last decade, the improvement of the activity and/or the selectivity of metallic catalysts by adding a second metal have attracted much attention. Gold-copper alloys have been found to be effective for various catalytic hydrogenation or oxidation reactions.<sup>1</sup>

Another rising interest regarding bimetallic catalysts is the evolution of surface composition during exposure to reaction atmosphere, i.e., the changes of the surface alloy in the presence of adsorbed atoms, which leads to change in catalytic activity. For Cu-Au bimetallic alloy, although the gold surface enrichment is predicted to be thermodynamically favourable under vacuum conditions,<sup>2</sup> a reversed segregation of Cu as a more active component to the surface is reported to occur in the presence of adsorbates.<sup>3</sup>

In this work, a Density Functional Theory (DFT) study of gold, copper and gold-copper alloy low index surfaces is investigated. The analysis includes surface energy, segregation and reactive gas adsorption. The segregation of copper and gold in alloy diluted limits under vacuum and reaction conditions are presented. The DFT calculations predict a more affinity of CO and NO to copper than gold and confirm the observed segregation of copper in Au-Cu alloys under reaction conditions.

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## #15: Characterization of oligomeric distributions in aluminum chlorhydrates by capillary electrophoresis

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Aluminum salts have been used for several years as flocculant for water treatment, as leather tanning agents or as catalytic agents in organic synthesis. In cosmetic industry, aluminum chlorhydrates (ACH) have been also used as antiperspirant agents. A recent study linked the antiperspirant activity of aluminum chlorhydrates to the presence of specific structures of aluminum polycations.<sup>1</sup> The characterization of these polycations and more particularly their size distribution as a function of the physico-chemical parameters of the medium (pH, ionic strength) is a key topic to better understand the antiperspirant properties of ACH.

Currently, structural information on ACH are obtained using <sup>27</sup>Al NMR or by potentiometric titration, giving access to average chemical composition such as the hydrolysis ratio  $h$  ( $h = [\text{OH}^-]/[\text{Al}]_{\text{tot}}$ ).<sup>2</sup> In this work, capillary electrophoresis (CE) was investigated to determine the distribution of polycations in ACH raw materials. As a separation technique based on differences in charge to size ratio, CE appears as a complementary approach to get the oligomeric distribution of aluminum species. Though a few pioneering works have studied the analysis of aluminum salts under monomeric form ( $\text{Al}^{3+}$ ) by CE using indirect UV detection, there is still no work describing the distribution of aluminium polycations in ACH.

In this presentation, different background electrolytes have been compared showing the importance in the choice of the chromophore as well as the counter-ion on the separation of Al species. Kinetics of exchange between Al species have been studied by changing the effective capillary length. Stability study on the sample preparation has also demonstrated that samples should be prepared 3 days before analysis to reach equilibrium. Finally, several antiperspirant raw materials and some polycations standards have been analyzed to study the influence of pH on the distribution of the oligomeric species

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## #16: Valorization of olive by-products through vermicomposting

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In Morocco, large quantities of olive by-products (olive mill wastes and pomace) are produced annually. These by-products create serious problems for the environment, particularly groundwater and surface. Although several biotechnological processes (composting, anaerobic digestion, evaporation...) have been proposed to dispose of or recover the waste, but cost and technicality limited their application. The aims of this study to propose vermicomposting as a process adapted to the technical and economic requirements of the Souss region. Vermicomposting mastery of several mixtures of olive waste is conducted in order to both enhance and improve the quality of fertilizing waste processing into vermicompost. Two mixtures M1 and M2 are prepared from the pomace, manure and sugar cane bagasse. The mixture M2 was soaked by the olive mill wastes diluted to ¼, the mixtures were inoculated earthworms of the species *Eisenia foetida* and *Eisenia andrei*. The results showed that the mixture M1 recorded biomass gain of 126 mg / worm against 12.5 mg / worm to the mixture M2. Similarly the reproduction rate of earthworms in the mixture M1 was 12.72 cocoon / week against a rate of 8.22 cocoons / worm for the M2 mixture. At the end of vermicomposting decreased C / N ratio was recorded for both mixtures (from 29 to 19.25 M1 and M2 from 38 to 27). This decrease demonstrates the stabilization and mineralization of organic matter in the vermicomposting process. The total phenols concentration contained in the mixture M2 is reduced by 76%. The phytotoxicity test of vermicompost obtained revealed no toxicity against the germination of tomato seeds (overall germination index >80%).

## #17: Multivalent inhibitors of carbonic anhydrases

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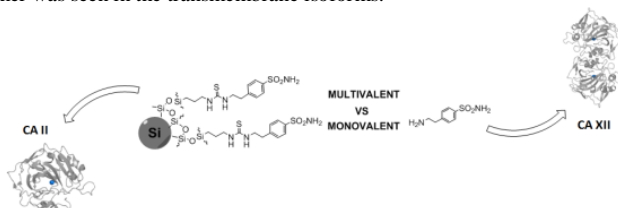
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Carbonic anhydrases (CAs, EC. 4.2.1.1) are ubiquitous zinc metalloenzymes which catalyze the reversible hydration of CO<sub>2</sub> with formation of bicarbonate and release of a proton. On the 13 active isoforms present in human, some of them are involved in pathological processes. CAs are known for more than 50 years as a therapeutic targets, and inhibitors are currently in clinic or in (pre)clinical studies for the treatment of glaucoma, epilepsy, obesity and cancer. Nevertheless the lack of selectivity against the different isoforms responsible of side-effects requires the development of new strategies.<sup>1</sup>

The aim of this work is to develop a new strategy for CA inhibition taking advantage of multivalent clusters to selectively and efficiently inhibit CA isoforms. Indeed, multivalent clusters represent an emerging class of compounds for enzymes inhibition.<sup>2</sup> This strategy has been recently shown for CA inhibition and activation, some studies reporting improvement of inhibitory potency and selectivity.<sup>3</sup>

We prepared multifunctional silica nanoparticles coated with sulfonamides as CA inhibitors. The inhibition effect and specificity of the multivalency were investigated between cytosolic isoforms (hCA I, hCA II) and transmembrane tumor associated isoforms (hCA IX, hCA XII). Excellent inhibitory effects were observed with these nanoparticles (K<sub>i</sub> = 6.7-0.67 nM). We observed a significant selectivity between nanoparticles and the monovalent CA inhibitor alone. Multivalency effect was seen for the inhibition of the cytosolic isoforms and the selectivity of the monomer was seen in the transmembrane isoforms.<sup>4</sup>



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## #18: Pharmacological evaluation of *Frankenia Laevis* L. from Tunisia

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The saltcedar *Frankenia laevis* belongs to Frankeniaceae, a small family of one genus and six species of small halophytic shrubs or herbs of mostly temperate distribution. The genus *Frankenia* has not been the subject of many biological and chemical investigations. The only phytochemical studies concerning *F. laevis* L.<sup>1</sup> led to the identification of diverse aromatic compounds, flavonoid and phenolic sodium sulfates.<sup>1</sup> Moreover, Harborne<sup>2</sup> reported that the majority of Frankeniaceae species contained bisulphates, ellagic acid, kaempferol, quercetin, flavonol, methyl ethers and proanthocyanidins.

As a part of our phytochemical and biological investigations of unexploited Tunisian flora for the search of new potential bioactive compounds, we describe herein the total phenolic and flavonoid contents and the antioxidant (DPPH), anti-inflammatory, anti-acetylcholinesterase, anti-xanthine oxidase and cytotoxicity potentialities (MCF-7, HTC116, OVCAR) of organic extracts obtained from the aerial part of *F. laevis*. The results showed that the EtOAc and n-BuOH extracts were the richest ones in total flavonoids and phenols. The n-BuOH extract was found to be good acetylcholinesterase and xanthine oxidase inhibitor and exhibited an interesting antioxidant activity (IC<sub>50</sub> = 8.58 µg/mL) and also a significant anti-inflammatory effect (IC<sub>50</sub> = 25.84 µg/mL). The best anticancer activity against the HTC116 cell line was obtained also with the n-BuOH extract.

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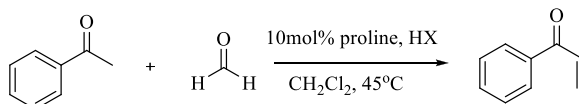
## #19: Lewis base and L-proline co-catalyzed Baylis–Hillman reaction of arylaldehydes with 1-phenylprop-2-en-1-one

Hichem Sadrik KETTOUCHE

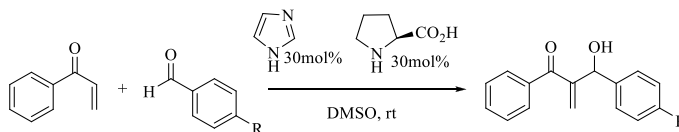
Laboratoire des produits naturels d'origine végétale et de synthèse organique, Département de Chimie, Université Mentouri de Constantine. Route Aine El Bey, 25000 Constantine, Algérie

The present work describes the organocatalytic enone-aldehyde condensation reaction by L-Proline in the presence of imidazole as co-catalyst (Morita-Baylis-Hillman Reactions)<sup>1</sup>.

In the first time the enone (1-phenylprop-2-en-1-one) has been prepared according, the condensation reactions between an aldehyde (formaldehyde) and ketone (acetophenone) organocatalyzed by L-proline in the presence of acid co-catalyst ( $\alpha$ -methylenation reaction)<sup>2</sup>, or the L-Proline-catalysed aldol reaction of acetophenone with formaldehyde (*Hajos-Parrish-Eder-Sauer-Wiechert* reaction)<sup>3</sup>, followed by crotonisation reaction.



Subsequently, we used this enone substrate in an attempt to synthesized new version of aldols by varying the aldehyde to condense with.



The desired Morita-Baylis-Hillman product was obtained in good yields for a wide range of aldehydes aromatic.

These reactions carry the advantage of being very atom-economic, since almost no waste is formed at the end of the reaction and obeying the green chemistry principle.

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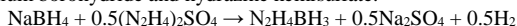
## #20: Synthesis and characterization of new materials/composites based on hydrazine borane and lithium amide

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In the beginning of the 2000s, a big interest has been given to ammonia borane ( $\text{NH}_3\text{BH}_3$ ), which is an attractive material for solid-state hydrogen storage. Ammonia borane contains three hydridic hydrogens ( $3\text{H}^\delta^-$ ) and three protic hydrogens ( $3\text{H}^\delta^+$ ). Then, it has a high gravimetric capacity of hydrogen, being of 19.6 wt%, and this has attracted a flurry of recent investigations focusing on hydrogen release from this borane.<sup>1</sup>

In this context, other nitrogen-containing boranes have been also considered and synthesized. One of these materials is hydrazine borane ( $\text{N}_2\text{H}_4\text{BH}_3$ ), prepared from sodium borohydride and hydrazine hemisulfate:



Like ammonia borane, it has a high gravimetric capacity of hydrogen, with 15.4 wt%, owing to four protic hydrogens ( $4\text{H}^\delta^+$ ) and three hydric hydrogens ( $3\text{H}^\delta^-$ ).<sup>2</sup> Under heating, the decomposition of hydrazine borane starts at low temperature ( $60^\circ\text{C}$ ), but besides the expected hydrogen high amounts of the unwanted and toxic hydrazine  $\text{N}_2\text{H}_4$  are released. Therefore, alternatives have been searched for with the objective to propose a material that produces only hydrogen<sup>3</sup>.

When reacted with an alkali hydride MH ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ), hydrazine borane transforms to a hydrazinidoborane derivative.<sup>3</sup> Another strategy is to make hydrazine borane react with an alkali amide. Both approaches have been considered in our laboratory, the latter being the newer. Recently, we used the hydrogen-richest lithium amide  $\text{LiNH}_2$  in the aim to have a new material (a derivative or a composite) that shows improved dehydrogenation properties in comparison to the parent hydrazine borane. The synthesis was done by ball milling at different ratios of the borane, and the as-obtained samples were fully characterized.

This meeting is an opportunity to present, for the first time, our results about the aforementioned novel material.

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## #21: Comparison of dynamic light scattering and nanoparticle tracking analysis for measurements of size distribution of colloids in wastes leachates

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A large proportion of contaminants in aqueous natural media are believed to be transported as colloids of different sizes which could influence the speciation, mobility and the toxicity of these pollutants<sup>1</sup>. In this context, it is necessary to bring understandings on colloids emission and transport when they are generated by industrial waste.

Analytical methods are not yet satisfactory to be used for developing standard methods that should be able to evaluate rapidly the presence and composition of colloids in waste leachates. The DLS technique is a powerful technique and very useful to determinate size distribution of homogeneous and monodisperse colloidal suspension<sup>2</sup> but this application is more complex in the study of environmental samples which are heterogeneous and polydisperse which is demonstrated by our first results of our study. The NTA technique is considering as an emerging technique for submicrometer particle sizing<sup>3</sup> and there are many applications in biology and medicine (protein aggregations studies and virus and vaccine development, analysis of exosomes and microvesicles)<sup>4</sup> on the one side and in study of nanoparticles (Nanoparticles toxicity and environmental impact, analysis of nanoparticles applied in industry...) <sup>5</sup> on the other side.

It seems to be interesting to compare both techniques for environmental samples to find a fast, easy, accurate technique for complex colloids characterization. In this context, 5 different wastes were studied: Bauxite residue, coastal marine sediments, sludge of wastewater treatment plant, crushed wastes and ashes from household incineration. After leaching, filtrations and measurements of size and zeta potential will be occur by DLS and NTA to compare results obtained by both of them.

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## #22: Thermodynamic modelisation of binary systems using PC-SAFT equation of state

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The equations of state play a significant role in the prediction of equilibrium between phases of systems with two or several components. This work:

- Enters within the framework of a research program on the prediction of fluid phase equilibria using the equations of state for the pure substances and the mixtures of two or several components.
- Is devoted to the correlation and the prevision of phase diagrams of the binary systems containing component non associated.  
Scope:
- Study of VLE of binary systems containing non associating components, by applying PC-SAFT model with Van der Waals one fluid mixing rules.
- To carry out calculations by considering a certain number of binary mixtures containing esters.
- To examine the capacity of PC-SAFT to predict the vapor-liquid equilibria diagrams without corrections

Among the many equations modelling the fluid phase equilibria of solutions, our choice went to PC-SAFT equation of state:

- This equation adopts a hard-sphere chain fluid as a reference fluid, it can be applied as well for gases, liquids and polymers, and allows the determination of fluid phase equilibria and thermophysical properties.
- PC-SAFT accounts for the essential characteristics for real molecules :
  1. Repulsive interactions.
  2. Non spherical shape of molecules (chain formation).
  3. Attractive interactions (dispersion).
  4. The integration of long molecules in the procedure of adjustment of all suitable constants of the model.

The PC-SAFT equation of state used for modeling phase equilibria of esters systems. The prediction of VLE diagrams allowed us:

- To show that PC-SAFT equation was able to represent correctly the boiling and dew curves on the whole range of composition.
- For some systems, calculations were carried out by considering  $k_{ij} \neq 0$  we noted that these values are relatively low, which highlights (to underline) the great predictive capacity of equation PC-SAFT



## #23: In vitro evaluation of some Mediterranean medicinal plants aqueous extracts on the growth of some pathogenic fungus

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This study investigated in-vitro the control of fungal species associated with crops using some Mediterranean plant extracts the Arian party of *Artemisia herba alba*, *Cotula cinerea* and *Asphodelus tenuifolius*, on two pathogenic fungus (*Fusarium graminearum* and *Fusarium sporotrichioide*). The results of the investigation revealed that, *Artemisia herba alba*, *Cotula cinerea* and *Asphodelus tenuifolius* were effective in the inhibition of *Fusarium graminearum* and *Fusarium sporotrichioide* effectively inhibited the mycelial growth. *Asphodelus tenuifolius* extract was equally effective in the reduction of mycelial growth it achieve a antifungal index of 60% with a concentration of 20 % This last has an antifungal activity important.. In the overall, a significant reduction in mycelia growth of the pathogens was found associated with treatment with most of the plant extract tested.

Phytochemical test the aqueous extracts of the three plants has revealed the presence of a few chemical compound (tannins, flavonoids, saponins, steroids and alkaloids) likely to express the antifungal activities sought.

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(2) Moury, R. et al. *Phys. Chem. Chem. Phys.* **2012**.

## #24: A projection method to obtain VB coefficients from Multi - Configurational MO wave functions

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We present here a method<sup>1</sup> based on CI (Configuration Interaction)  $|\Psi^{MO}\rangle$  wave function to evaluate the coefficients ( $C_k^{VB}$ ) of a Valence Bond wave functions  $|\Psi^{VB}\rangle$  (1).

$$|\Psi^{MO}\rangle = \sum_{i=1}^m C_i^{MO} |\Phi_i^{MO}\rangle \quad |\Psi^{VB}\rangle = \sum_{k=1}^n C_k^{VB} |\Phi_k^{VB}\rangle \quad (1)$$

This method can be used for any state. If  $|\Psi^{MO}\rangle$  and  $|\Psi^{VB}\rangle$  describe the same state,  $\mathcal{E}$  is small in Equation (2). Moreover, we considered that  $|\Phi_{rest}\rangle$  does not span the same space already spanned by the  $|\Phi_k^{VB}\rangle$  (3). The  $|\Phi_k^{VB}\rangle$  can be optimized independently and the coefficients  $C_k^{VB}$  of the VB wave function are obtained.

$$|\Psi^{MO}\rangle = N \{ |\Psi^{VB}\rangle + \mathcal{E} |\Phi_{rest}\rangle \} \quad (2)$$

$$\langle \Phi_{rest} | \Phi_k^{VB} \rangle = 0 \quad (3)$$

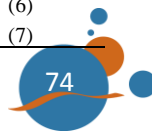
The overlap between MO and VB wave functions is used as a trust factor (4).

$$\tau = \langle \Psi^{MO} | \Psi^{VB} \rangle \quad (4)$$

The emblematic example of ethylene (Table 1) is chosen to test the method. The vertical excitation energy between N-state and V-state will be discuss. All calculations were carried out with XMVB<sup>2</sup> and GAMESS US<sup>3</sup> programs.

Table 1: Energy difference between N-state and V-state for ethylene on experimental geometry (D<sub>2h</sub>).

method	$\Delta E_{N-V}$	nber CSF	reference
This work	8.07	7	(1)
VB-QMC	7.93	7	(4)
MR-CISD	7.70	80	(5)
NEVPT2	7.70	8	(6)
EXP	7.66	/	(7)



Being based on local orbitals, VB approaches<sup>1,4</sup> can bring a different understanding of excited states than methods based on delocalized (MO) orbitals.<sup>5,6</sup> Moreover, in this case an accuracy similar to the VB-QMC approach is obtained although the  $|\Phi_k^{VB}\rangle$  are optimized independently and no special treatment of the correlation is considered.

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## #25: Molecular modelling, design, and synthesis of new NTS2-selective neurotensin analogues

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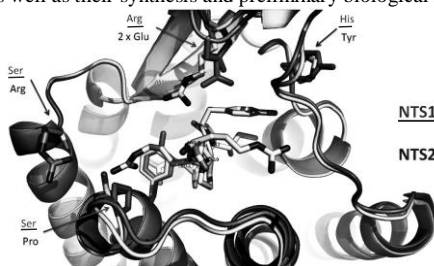
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Neurotensin (NT) is a tridecapeptide which was first isolated from bovine hypothalamus.<sup>1</sup> Over the last decade, neurotensin receptors NTS1 and NTS2 were shown to participate in the antinociceptive action of NT when injected directly into the brain. NT also induces other physiological effects, such as hypothermia and hypotension. Structure-activity relationship studies showed that the C-terminal fragment of NT, so called NT[8-13], is the minimal bioactive sequence. In order to improve activity and stability, we recently developed several NT[8-13] analogues using different approaches including unnatural amino acid incorporation,<sup>2</sup> peptide bond modification, and cyclisation.<sup>3</sup> Among the NT receptor subtypes, Sarret et al.<sup>4</sup> showed that selectivity toward NTS2 is fundamental to exert analgesic effect without unwanted effects such as hypothermia and hypotension.

The interaction between neurotensin and its receptor NTS1 has been clarified by the crystallization of the receptor with its ligand NT[8-13].<sup>5</sup> Based on the differences between NT receptors NTS1 and NTS2 with molecular modeling studies, we observed that Tyr11 residue is located in a pocket bearing a basic residue (Arg) in NTS1 and an acid residue (Glu) in NTS2. Therefore, we designed new NT analogues replacing Tyr11 with an amino acid bearing a basic function on the side chain to increase selectivity toward NTS2.

Here, we present molecular modeling studies for the rational design of these new analogues as well as their synthesis and preliminary biological results.



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## #26: Study of the quality control of oxytetracycline and ivermectin injectables for Mauritania veterinary

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In developing countries the prevalence of residues of veterinary drugs in food of animal origin is less than 1% in Europe, while it reached 94% in some African countries.<sup>1</sup> A study on the quality of drugs found that 48% of drugs in circulation in Benin and Togo are fake drugs.<sup>2</sup> These findings are supported by surveys in Mauritania, Benin, Togo, Mali, Cameroon and Chad, where nearly 61% of controlled veterinary drugs are not in accordance.<sup>3</sup> These studies have contributed to the current setting up a system of harmonization of laws and regulations at the Economic and Monetary Union of West Africa. To our knowledge, regarding the quality of veterinary drugs in Mauritania, few studies have been conducted. Given this lack of precise information, it is important to survey the conformity and the non-conformity of the veterinary drug in Mauritania market by technical analytic some samples taken in local market of Nouakchott city. In this study, we determined the non-conformity and the conformity of these substances (oxytetracycline and ivermectin) using a high performance liquid chromatography in reverse phase with UV-Vis detector (HPLC-UV). Two causes of non-conformity were recorded in our study: (i) samples showed low active and (ii) without active substance.

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## #27: Composition and antifungal activity of the essential oil of *Nashia inaguensis* Millsp. (Verbenaceae) cultivated in French Guiana

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French Guyana is a part of Amazonia rainforest identified as a biodiversity hotspot due to the number of species threatened with extinction it counts.<sup>1</sup> With the generalized awareness of this endangered richness a number of conservation and promotion actions have been undertaken over the last years. As part of these valorization activities, the society *Guyarômes* produces mainly essential oils from local plants aimed to be sold on the French market.

*Nashia inaguensis* Millsp. (Verbenaceae family), an evergreen shrub native to the east Caribbean Islands,<sup>2</sup> is one of the selected plant for such a valorization action. The species is commonly cultivated in the Antilles and in French Guiana to be sold on local markets as a spice, a food condiment and for the preparation of herbal teas used to cure intestinal gas and digestive problems.<sup>3</sup>

The present poster reports for the first time the analysis of the chemical composition by GC/FID and GC-MS of the essential oil of *N. inaguensis* organically cultivated in French Guiana, and the evaluation of its antimicrobial and antiparasitic activities against strains of several *Candida* spp. and *Leishmania guyanensis* respectively.

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## #28: GARANT' AIR : a targeted odors treatment

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Restaurants are principally concentrated in cities and the relationship with neighbors could be difficult due to cooking odors they release as offensive odors are felt as a source of stress. Considered as an environmental pollution, these odors constitute the second reason of complaint after noise pollution.<sup>1</sup> Industrials and restaurants are more and more frequently confronted with this issue and are actively seeking for a solution to counteract this problem generalized by the continuous emergence of snacks, fast-food restaurants, etc.

For this purpose the GARANT' AIR project aims at the characterization of ill-smelling compounds composing cooking odors and then at the development of neutralizing solutions dedicated to the destruction of the compounds responsible for offensive odors (targeted odors treatment). The analytical approach initiated is the characterization of cooking odors by GC/MS coupled with olfactometry to target compounds displaying an olfactory impact. The sampling method used is dynamic head space (DHS) extraction with a Tenax trap and desorption is promoted thermally by an autosampler thermodesorber (ATD). This poster presents the analytical strategy adopted for this purpose and the first results obtained after sampling cooking odors from some restaurants.

This project was financially supported by the region PACA (APRF 2013).



DHS extraction system

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## #29: From Chemistry to Processing of Boron-Modified Polycarbosilazanes: Toward the Preparation of SilicoBoron CarboNitride Ceramics

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Silicon-based non-oxide ceramics ( $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ) have attracted much attention, primarily due to their good mechanical and chemical properties, and also their reliability at room and elevated temperatures. They have great potential for many industrial uses as engineering components. The addition of a second ceramic (nano)phase to  $\text{SiC}$  or  $\text{Si}_3\text{N}_4$  leads to materials which promise applications in many fields and offer solutions for most of the market demands. However, the preparation of these materials is still a challenging task according to the fact that the conventional processes unavoidably lead to size and structure inhomogeneities of the different phases and presence of impurities (because of the use of sintering additives to consolidate the materials) which affect the properties. Here, we propose an alternative strategy using a “ceramic through chemistry” concept. The Polymer-Derived Ceramics (PDCs) route is an attractive means for the design of advanced ceramics; in particular in non-oxide systems. Pre-ceramic polymers are of great interest as they allowed obtaining multi-element ceramics with controlled chemical composition and depending on the composition, they can provide high temperature resistant materials.

The principle consists to incorporate one or more elements in the precursor (molecular or polymeric) at molecular scale to ensure compositional homogeneity. For example, boron can be added by specific reactions to polycarbosilazanes to be found after pyrolysis in the final ceramic, i.e., silicoboron carbonitride ( $\text{Si/B/C/N}$ ), in the desired proportion. The type of backbone and functional side chains of precursor molecules influences the ceramic yield, the chemical composition, and the microstructure of  $\text{Si/B/C/N}$  materials. This is the objective we have fixed in our study. In particular, we demonstrate through FTIR, NMR that we can control the addition of boron in a particular way to deliver after pyrolysis  $\text{Si/B/C/N}$  materials with tailored structural properties. Furthermore, the boron content plays a key role in the processing of boron-modified polycarbosilazanes. This is demonstrated in the present paper.



### #30: Effect of the amount of silver on the physicochemical properties of Ag-ZrO<sub>2</sub> aerogel catalysts for the total oxidation of CH<sub>4</sub>

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The catalytic combustion of methane has been extensively studied as an alternative to conventional thermal combustion.<sup>1,2</sup> From an environmental point of view, the main advantage of this technology is the ability to operate at lower temperatures than for conventional flame combustion, this leads to the reduction of the emission of many pollutants, especially nitrogen oxides.<sup>3</sup> The most active catalysts for CH<sub>4</sub> oxidation are Pd-based catalysts.<sup>4</sup> These have been extensively studied.<sup>5</sup> In the present work, a series of silver supported zirconia aerogel catalysts (xAg-ZrO<sub>2</sub>) containing various amounts of silver (x= 2, 4, 6, 8 and 10 wt.%) were prepared by sol gel method then dried under the super-critical conditions of the solvent and calcined at 550 °C. The physicochemical properties of the obtained catalysts were examined by N<sub>2</sub> physisorption at 77 K, XRD, H<sub>2</sub>-TPR and infrared spectroscopy. Their catalytic performances were evaluated in the total oxidation of CH<sub>4</sub> between 400 and 500 °C, under atmospheric pressure, in a dynamic microreactor over the oxidized sample (100 mg) using a mixture containing 1% CH<sub>4</sub>, 4 % O<sub>2</sub> and He as balance gaz. The results showed that all the xAg-ZrO<sub>2</sub> are well structured materials and develop both the diffraction peaks of tetragonal and monoclinic phase of ZrO<sub>2</sub>. On the other hand, these catalysts are classified as mesoporous materials and exhibit high surface area and pore volume which decrease with the increase of the amount of silver. It was also shown that the CH<sub>4</sub> conversion to CO<sub>2</sub> is strongly affected by the amount of silver. High conversion of methane to carbon dioxide was obtained in the case of 6Ag-ZrO<sub>2</sub> catalyst.

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## #31: From Chemistry to Processing of Boron-Modified Silicon Carbide Precursors

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In a recent past, silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>) and silicon carbonitride (Si/C/N) systems attracted increasing interest for environmental (diesel filters, water treatment) and energy (fission nuclear reactors) applications according to their properties (high thermal robustness, oxidation and corrosion resistance, low bulk density, high thermal conductivity, high mechanical strength).

The manufacturing process of SiC was initiated by Acheson in 1892<sup>1</sup> and is still today applied to produce the commercially available **SiC** ( $\alpha$ -**SiC**). However, most of the actual and future industrial challenges related to SiC require the development of materials in which compositions, shapes and textures are tuned on demand. Traditional techniques are energy-ineffective and severely limit the shape and texture complexities of the part which can be manufactured. Furthermore, the ability to control the purity and crystalline form of the product is restricted. These inherent difficulties can be overcome by the development of synthetic paths where molecular chemistry and chemistry of materials are combined rationally. The *Polymer-Derived Ceramics* (PDCs) route represents one of these synthetic path solutions. The chemistry (elemental composition, compositional homogeneity and atomic structure), the processing properties and the reactivity (thermal and chemical) of related polymers can efficiently be controlled and tailored to supply, after shaping and pyrolysis processes, ceramics with the desired compositional phase distribution and homogeneity as well as shape. This concept is applied here to the preparation of silicon carbide. In particular, we demonstrate that we can provide various shapes of SiC going from powders to monoliths, some of them can be prepared with controlled porosity by controlling the chemistry of SiC precursors at very small length scales in an early stage of the fabrication of SiC. This study gives us information about the chemical and physical properties of SiC precursors based on infrared and NMR spectroscopies coupled with thermogravimetric analysis. In particular, we demonstrate that the boron content has a strong effect on the chemistry and processability of SiC precursors. The high temperature of SiC is also investigated.

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## #32: Natural formulation: attractive of dog to achieve their needs

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This work falls within the “Eco Innov” framework of the Midi Pyrénées region. The project called "Caniclean" whose partners are AGRONUTRITION a Midi-Pyrénées company and the laboratory of IMRCP UMR CNRS 5623, pharmacy antenna, has benefited of financial help from FAEDER EU funds and Midi-Pyrénées region.

The first objective is to attract dogs to the dedicated caniparc sites in urban areas and keep them there long enough to make their needs. The solutions to be developed must be olfactory since olfaction is the most developed sense in dogs.

The second objective is to induce micturition reflex in dogs drawn to caniparcs, in order to shorten the time required for the dog to make its needs. Indeed, this time may be more or less short and must fit into the context of daily walk, whose main objective is often to allow the dog to do its needs. It is therefore imperative to attract dogs in designated areas as quickly as possible, while causing the voiding reflex.

The objective of this project therefore is to develop a product that attracts dogs in the planned sites, with a length and a radius of satisfactory efficacy in dogs and cause the voiding reflex. It will also be environmentally friendly, with total safety and biodegradability. Finally, it must be accepted by dog masters and by the neighbors.

We have developed rapid analytical methods and less expensive than those in the literature to evaluate the chemical composition of complex mixtures and the stability in time of these formulations.

We assessed the analysis of samples by GC-MS because the desired compounds are quite volatile. Follow-up work of the stability of selected formulations was carried out (i) as a function of time and (ii) depending on the storage conditions. All these studies are used to verify the effectiveness of the formulations and their chemical transformations. For the three formulations, the stability of the compounds is of the order of 95% for the majority compounds for a period of 3 months.

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