

CULTURCHEM : SEPTEMBER 2023

Monday Sept 4th Auditorium Astier 11h



Emmanuel LACÔTE (Laboratoire des Hydrazines et Composés énergétiques polyazotés-Université C. Bernard Lyon 1/CNRS/CNES/ ArianeGroup)

<u>emmanuel.lacote@univ-lyon1.fr</u> New opportunities for low energy-photons: dispersed media and energetic materials

<u>Abstract.</u> The recent developments in synthetic chemistry have focused on the use of renewable or low-energy photons to induce new reactions, or greener versions thereof. In the present talk we will explore how the longer wavelengths can be exploited in two new domains, where more energetic photons are not suited.

We will first present how NHC-Boryl radicals initiate photopolymerizations in dispersed media (emulsion and dispersion – below) using visible light, resulting in the formation of monodisperse latexes with particles sizes up to the micrometer-scale. Then we will show how IR photons interact with energetic materials, here TNT.



September 11th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Sébastien PAPOT (University of Poitiers, UMR 7285 (IC2MP) sebastien.papot@univ-poitiers.fr Understand and manipulate biological processes with programmed

<u>Abstract.</u> The rise of chemical biology has led to the development of sophisticated

molecular devices designed to perform specific tasks within living systems. Most of these molecules have built into their structure a "chemical program" that determines their behaviour during their interaction with biological environments. Thus, such molecular systems can be programmed to explore or manipulate processes of the living through the controlled formation and/or breaking of chemical bonds. Within this framework, we developed various molecular devices programmed for cancer diagnosis and therapy. Such compounds include programming components like self-immolative linkers, chemical amplifiers, self-opening macrocycles, enzymeresponsive biorthogonal triggers, artificial cell membrane markers etc ... allowing them

to interact with living systems in a stringently controlled fashion. Our most recent advances in this field will be presented during the conference



CYCLE OF SEMINARS ON SUSTAINABLE DEVELOPMENT

FRIDAY September 15 th , 11h Corridor 14/24, room 207	Giovanni POLI (IPCM, SU) giovanni.poli@sorbonne-universite.fr
Campus P et M Curie	Chemistry and energy transition
Sorbonne Université	
	Abstract. At a time when microplastics are found from the highest mountaintops to the deepest ocean trenches, most glaciers are melting, and weather events are becoming more and more extreme, our community needs to understand the challenges associated with overcoming the warming of our planet. Understanding how climate change came about and how scientists are acting to save our planet requires the coordinated contributions of scientists from many disciplines: physics, meteorology, chemistry, climatology, environmental science, geography, geology, oceanography, ecology, social science, and others. This lecture will try to explain in a simple way the origin of Earth's global warming and how chemistry can contribute toward the solution of this problem, which is closely linked to the energy resources needed for human activity.

September 18th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Muralee MURUGESUE (University of Ottawa, Canada) <u>m.murugesu@uottawa.ca</u> A new generation of lanthanide-based molecular magnets

Abstract. Rare-earth systems and especially Dy^{III} , Er^{III} , Yb^{III} -based materials have sparked much interest in the area of molecular magnetism due to the large intrinsic magnetic anisotropy of the lanthanide ions. When such a unique property is combined with a high-spin ground state (*S*) in a molecular complex, it causes slow relaxation of the magnetization as seen for Single-Molecule Magnets (SMMs). To enhance the magnetic anisotropy of the metal centers, our research has focused on engineering at the molecular level of the crystal field. In addition, to improve the magnetic communication between metal ions, radical bridged complexes provide an alternative approach for inducing strong magnetic coupling between the spin carriers. Such an approach could ultimately allow efficient coupling of 4*f* ions and yield SMMs with record-breaking blocking temperatures.













September 25th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Stéphane BELLEMIN-LAPONNAZ (Université de Strasbourg) bellemin@unistra.fr Nonlinear Behaviour and the Limits of

Mechanistic Understanding in Asymmetric Catalysis

Abstract. Asymmetric amplification is a phenomenon that plays a key role in the emergence of homochirality in life. In asymmetric catalysis, theoretical and experimental models have been investigated for understanding how chiral amplification is possible, in particular through non-linear effect.(1) Recently we have proposed models that have led to an understanding of more complex non-linear effects, such as hyperpositive and enantiodivergent non-linear effects, which include a coexistence of active monomeric and active dimeric species.(2,3) A higher degree of complexity seems attainable if one considers that higher levels of aggregation could be envisaged.(4)

We show here how different ligands, issued from the same privileged chiral structure, exhibit completely different systems-level behaviours and thus also different reaction outcomes – although they differ only by small chemical modifications. Mechanistic studies showed that the metal complexes aggregate and generate additional catalytic species in distinct ways. These results were obtained through a combination of nonlinear effect studies and other related studies and simulations have confirmed the possibility of such systems-level behaviour.

Overall, these results highlight the need to be cautious with certain paradigms of asymmetric catalysis, as structures alone do not necessarily predict systems-level behaviour that could bias the outcome of the catalytic reaction.

(1) Guillaneux, D.; Zhao, S.-H. ; Samuel, O. ; Rainford, D.; Kagan, H. B. J. Am. Chem. Soc. 1994, 116, 9430–9439.

(2) Geiger, Y.; Achard, T.; Maisse-François, A.; Bellemin-Laponnaz, S. Nat. Catal. 2020, 3, 422-426.

(3) Geiger, Y.; Achard, T.; Maisse-François, A.; Bellemin-Laponnaz, S. Chem. Sci. 2020, 11, 12453-12463.

(4) Thierry, T.; Geiger, Y.; Bellemin-Laponnaz, S. ChemRxiv 2023, doi.org/10.26434/chemrxiv-2023-qgm7t.











September 26th, 11h Amphitheater 56B Campus P et M Curie Sorbonne Université



Paul KNOCHEL (University of Munich, Chemistry Department, Butenandtstr. 5-13 D-81377 Munich, Germany) Paul.Knochel@cup.uni-muenchen.de Li, Na, Mg and Zn organometallics for organic synthesis

• Preparation of enantioenriched secondary alkyllithiums in batch and continuous flow. A practical in situ quench (ISQ) procedure involving the generation of chiral secondary alkyllithiums (1) from secondary alkyl iodides (2) (including functionalized iodides bearing an ester or a nitrile) in the presence of various electrophiles (3) such as aldehydes, ketones, Weinreb amides, isocyanates, sulfides, or boronates will be demonstrated. This ISQ-reaction allowed the preparation of a broad range of optically enriched ketones, alcohols, amides, sulfides and boronic acid esters (4) in typically 90–98% ee. Remarkably, these reactions were performed at - 78°C or - 40°C in batch. A continuous flow set-up permitted reaction temperatures between - 20°C and 0°C and allowed a scale-up up to a 40-fold without further optimization.



•Preparation of organosodium reagents in continuous flow. Furthermore, a lateral sodiation of alkyl-(hetero)arenes (3) using on-demand generated hexane soluble (2-ethylhexyl)sodium (1) from 3-(chloromethyl)heptane (2) in the presence of TMEDA was developed. (2-Ethylhexyl)sodium is prepared *via* a sodium packed-bed reactor and used for metalations at ambient temperature in batch as well as in continuous flow. The resulting benzylic sodium species are subsequently trapped with various electrophiles including carbonyl compounds, epoxides, oxetane, allyl/benzyl chlorides, alkyl halides and alkyl tosylates. Furthermore, the utility of this lateral sodiation is demonstrated in the synthesis of pharmaceutical relevant compounds. Thus, *fingolimod* is prepared from *p*-xylene applying the lateral sodiation twice.

E-X: aldehydes, ketones, Weinreb amides, isocyanates, sulfides or boronates



For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











CULTURCHEM : OCTOBER 2023

October 2nd, 11h Amphitheater Moissan Chimie ParisTech – PSL 11 rue P et M Curie



Antoine SIMONNEAU (Laboratoire de Chimie de Coordination) antoine.simonneau@lcc-toulouse.fr Activation of Small Molecules and Strong Bonds with a Vintage Flavour

Abstract. Activation of small molecules and strong bonds have attracted the attention of chemists because of the inherent fundamental challenges it poses. Over the last decades, reactive organometallic species fit for that purpose have burgeoned in the literature, sometimes achieving catalysis, with the underlying motivation of solving current societal issues, such as global warming, energy efficiency or depollution. Without proposing any disruptive solution to those problems, this lecture will show how we exploited "vintage" organometallic and inorganic species to re-explore their reactivity in the context of small molecules activations, with an emphasis on our work targeting N₂ functionalization. Pinches of CO_2 , H₂ and C–F bond activations will spread thinly over the talk.

October 9th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Amandine BELLEC (Université Paris Cité / CNRS) amandine.bellec@u-paris.fr Thermal, optical and electric control of spin-crossover/metallic interface

<u>Abstract.</u> Spin-crossover molecules present two spin states that can be controlled by external stimuli such as light or temperature. This makes them promising candidates for incorporation in molecular spintronic devices. In this purpose, it is mandatory to understand how the properties of spin-crossover molecules are modified when in direct contact with metallic substrates. Here, we will discuss the influence of metallic substrates on the spin-crossover conversion of Fe[HB(3,5-(CH3)2Pz)3]2 (Pz=pyrazolyl) ultra-thin films (from sub-monolayer to a few layers) induced by temperature, light or electric field.

October 16th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie



Mathieu PUCHEAULT (Université de Bordeaux / CNRS) mathieu.pucheault@u-bordeaux.fr Small molecules with a boron-nitrogen bond: Preparation and applications

<u>Abstract.</u> Organoaminoboranes are essential compounds in modern chemistry, serving as versatile building blocks with remarkable reactivity. Their significance lies in their capacity to facilitate innovative synthetic routes, promote diverse reactions, and contribute to the development of novel materials, thus fueling advancements in chemical research and applications. This conference will underline the crucial role of organoaminoboranes in the toolbox of chemists, from accessing organoborane to driving progress in various domains of the field.













October 20th, 11h FRIDAY C 32-42. R 101 Campus P et M Curie Sorbonne Université



Morgan DONNARD (Université de Strasbourg, UMR 7042 - LIMA) <u>donnard@unistra.fr</u> Captodative Aminoalkenes : Great Precursors to Access Original Heterocycles

<u>Abstract.</u> Captodative enamides are particularly functionalized building blocks, opening up a wide range of applications in synthetic chemistry, particularly in heterocyclic synthesis. However, access to these compounds remains particularly limited, especially in the case of tetrasubstituted C=C double bonds, due to regio- and stereoselectivity problems. In this lecture, we present the selective and efficient synthetic routes to captodative enamides that we have developed. These syntheses are based on ynamide difunctionalizations, and we will then present our first applications of these building blocks to obtain totally original heterocycles, including unprecedented silacyclic fluorophores.

October 23rd, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Heinz GORNITZKA (Laboratoire de Chimie de Coordination du CNRS) heinz.gornitzka@lcc-toulouse.fr NHC-gold and iridium complexes for biomedical applications

Abstract. *N*-heterocyclic carbenes (NHCs) play an important role in the development of biologically active metal complexes. These versatile neutral ligands can stabilize the metal centers and fine-tune the electronic and steric effects as well as the lipophilicity of the corresponding complexes by introducing different groups into the ligand. In addition, bioactive building blocks can be integrated to optimize biomedical activities. In this talk, I will present some gold and iridium complexes developed for biomedical applications in our team "Medicinal Chemistry and Biology for Oncology".

No seminar on October 30th, 11h

For any information, please contact:











CULTURCHEM : NOVEMBER 2023

November 6th, 11h Amphitheater Herpin Esclangon Building Campus P et M Curie Sorbonne Université



Amandine GUERINOT (ESPCI Paris, C3M) amandine.guerinot@espci.fr Earth-abundant metal (photo)catalysis: radical games

Abstract. Over the last decades, earth-abundant metal complexes (Fe, Co, Cu, Ni) emerged as an attractive alternative to precious metal catalysts, especially for C-C bond formation through cross-coupling reactions. Beside their natural abundance, iron, cobalt, nickel or copper catalysts exhibit a complementary reactivity compared to other transition metal catalysts. In particular, when 2e⁻ processes are favored in Pd-catalyzed cross-coupling reactions, single-electron transfers are prevalent when first row transition metals are used. The transient formation of radical intermediates thus marked a divergence of reactivity opening new synthetic opportunities.

Visible-light photocatalysis offers another mild entry to radical chemistry. Particularly, light excitation can highly modulate Ru(II)- and Ir(III)- photocatalysts redox properties allowing outer-sphere electron transfers to occur. The scarcity of Ir and Ru stimulated the evaluation of earth-abundant metal-based photocatalysts. To tackle the ultra-short excited lifetimes of the latter, alternative approaches based on an inner-sphere ligand-to-metal charge transfer have been designed.

A first section of this presentation will be devoted to cobalt-catalyzed cross-coupling reactions and aryl migrations, both affording α -aryl amides. In a second part, an iron catalyzed, visible-light driven decarboxylative oxygenation will be disclosed.



For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











approach for organic electronic materials

November 13th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



© Hiroko Yamada

Les Ambassadeurs de CNRS Chimie



Hiroko YAMADA, Professor at the Organoelement Chemistry, Institute for Chemical Research (Kyoto University- Japan) <u>Hiroko Yamada hyamada@scl.kyoto-u.ac.jp</u> Synthesis of pi-extended aromatic compounds using precursor

Abstract. Pristine p-extended aromatic compounds are attractive as organic functional materials, including organic semiconductors, but are difficult to synthesize in pure form due to their low solubility in common organic solvents. We have developed a precursor approach as a method to synthesize pure low-soluble p-extended aromatic compounds. In this approach, soluble precursors are first prepared and purified, then are converted quantitatively to the target molecules via retro-Diels–Alder reactions or Strating–Zwanenburg photodecarbonylation reactions. This approach is also effective for the on-surface synthesis of the large acenes like heptacene and nonacene under ultra-high vacuum. Tetrabenzorpohyrins are one of the promising organic semiconductors. The charge carrier mobilities of tetrabenzorporphyrins as organic field effect transistors have been improved using the precursor approach in combination with substituent effects. In this talk, I would like to focus on our recent results on the synthesis and morphological control of p-extended aromatic compounds

On November 13th 2023, Hiroko Yamada will start a series of lectures in several French CNRS laboratories as the <u>Ambassador in Chemical Sciences in France</u>.

for organic electronic materials using the precursor approach.

In 2019, CNRS Institute of Chemistry has initiated a program called "Ambassadors of Chemical Sciences in France". Its ambition is to give prestigious foreign researchers an opportunity to visit a series of French laboratories active in their field. These visits not only include top-notch conferences by the ambassador, but are also a good opportunity to establish preliminary contacts and foster international collaborations for the visited French laboratories.

https://ipcm.fr/index.php/en/2023/10/10/ipcm-welcomes-hiroko-yamada-cnrsambassador-for-chemical-sciences/

November 20th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



Aurélien DE LA TORRE (Institut de Chimie Moléculaire et des Matériaux d'Orsay)

aurelien.de-la-torre@universite-paris-saclay.fr Asymmetric catalysis, dual catalysis and total synthesis

Abstract. Asymmetric catalysis is a key topic in organic synthesis, as it allows the formation of new bonds while controlling stereogenic centers, which are inherent to natural products and biologically active substances. On the other hand, dual catalysis is an efficient approach to operate multiple chemical operations through a one-pot process. In this presentation, we will discuss our recent developments in asymmetric catalysis and dual catalysis, as well as their application to a concrete total synthesis problem.

For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











November 27th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



Tibor SOOS (HUN-REN, Research Centre for Natural Sciences, Budapest, Hungary) <u>soos.tibor@ttk.hu</u>

Metal-Free Protocols for Elusive Transformations

Abstract. The topic of this lecture will be on the research and development of metalfree transformations in my laboratory. As part of this overview, I will discuss the discovery and use of various organocatalysts, including bifunctional thioureas and frustrated Lewis pair (FLP) catalysts. In addition to applications of bifunctional organocatalysts in total synthesis, special emphasis will be placed on a novel ester-toaldehyde reduction protocol which has been utilized in ton-scale. Then, widely applicable metal-free protocols will be presented. First, relying on alkenyl thianthrenium salts, various traceless umpolung transformations of non-activated olefins will be discussed. Then, a metal-free retro-Friedel-Crafts reaction will be highlighted. This unique C-C fragmentative transformation opens new vistas for accessing challenging carbonyl compounds.

In summary, the primary aim is to demonstrate through a number of examples that the metal-free option is not only a step towards more sustainable chemistry, but perhaps more importantly, that metal-free limitation is the ultimate source of discovery and innovation.

Selected papers:

[1] Vakulya, B.; Varga, Sz.; Csámpai, A.; Soós, T. *Org. Lett.* **2005**, *7*, 1967.
 [2] Varga, Sz.; Angyal, P.; Martin, G.; Egyed, O.; Holczbauer, T.; Soós, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 13547.
 [3] Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem. Int. Ed.* **2008**, *47*, 2435.
 [4] Erős, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. Angew. Chem. Int. Ed. **2010**, *49*, 6559.
 [5] Dorkó, É.; Szabó, M.; Kótai, B.; Domján, A.; Soós, T. *Angew. Chem. Int. Ed.* **2017**, 56, 9512.
 [6] Soós, T.; Gyömöre, Á.; Dudás, Á.; Fegyverneki, D.; Gyöngyösi, M.; Sőregi, P.; Kolozsvári, N. WO2022/129966.
 [7] Angyal, P.; Kotschy, A. M.; Dudás, Á.; Varga, Sz.; Soós, T. *Angew. Chem. Int. Ed.* **2023**, e202214096

For any information, please contact:



CULTURCHEM : DECEMBER 2023

December 4th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



Henri-Pierre JACQUOT DE ROUVILLE (Université de Strasbourg) hpjacquot@unistra.fr

Acridinium Recognition Units in Complex Supramolecular Systems

Abstract. Equilibria involving multiple interacting life components gave rise to complex assemblies (double helix of DNA, G-quadruplex secondary structures). In addition, living organisms are endowed with numerous remarkable and complex functions (transmission of information, chemical transformations, transport, regulation) mediated by physical and chemical stimuli. In consequence, understanding and mimicking these functions using switchable artificial supramolecular systems is of paramount importance and still remains a current challenge.

We recently reported bis-acridinium supramolecular receptors able to bind guest molecules (Figure 1).¹ Surprisingly, acridinium-based receptors are scarcely exploited in supramolecular chemistry despite their multi-responsive properties. Indeed, they respond to chemical and redox signals by reversibly modifying their shape, their chemical and optical properties.² This class of receptors exhibits i) self-complementary behaviors leading to the formation of entwined dimers, ^{1a} ii) narcissistic self-sorting, ^{1b} iii) π -donor/ π -acceptor host-guest behaviors and were also studied as selective phase transfer agents in perfluorocarbons.³ In addition, the multi-switching properties of these receptors were investigated to alter their recognition events with guests. An increasing complexity has been achieved by the introduction of acridinium units in mechanically interlocked molecules.⁴ The dual-readout of the mechanical response of a [2]rotaxane structure was thus probed. Finally, the combination of the acridinium unit to another multi-responsive unit, namely porphyrin core, led to complex supramolecular systems exhibiting more than eight different states.⁵



Figure 1. Increasing Complexity in Multi-Responsive Acridinium Supramolecular Systems.

[1] a) H.-P. Jacquot de Rouville, N. Zorn, E. Leize-Wagner, V. Heitz, *Chem. Commun.*, **2018**, *54*, 10966–10969 ; b) H.-P. Jacquot de Rouville, C. Gourlaouen, V. Heitz, *Dalton Trans.*, **2019**, *48*, 8725–8730.

[2] H.-P. Jacquot de Rouville, J. Hu, V. Heitz, ChemPlusChem, 2021, 86, 110–129.

[3] J. Hu, J. S. Ward, A. Chaumont, K. Rissanen, J.-M. Vincent, V. Heitz, H.-P. Jacquot de Rouville, *Angew. Chem. Int. Ed.*, **2020**, *59*, 23206–23212.

[4] J. Hu, S. Adrouche, E. S. Gauthier, N. Le Breton, M. Cecchini, C. Gourlaouen, S. Choua, V. Heitz, H.-P. Jacquot de Rouville, *Chem. Eur. J.*, **2022**, *28*, e202202840.

[5] A. Edo-Osagie, D. Serillon, F. Ruani, X. Barril, C. Gourlaouen, N. Armaroli, B. Ventura, H.-P. Jacquot de Rouville, V. Heitz, *J. Am. Chem. Soc.*, **2023**, *145*, 10691–10699.

The CNRS, the université de Strasbourg, the agence nationale pour la recherche (ANR) and the fondation Jean-Marie Lehn are thanked for financial support.

For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











December 11th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



Damien BOURGEOIS (Institut de Chimie Séparative de Marcoule, ICSM, Bagnols sur Cèze) damien.bourgeois@umontpellier.fr Palladium separation and molecular chemistry: from nuclear fuel cycle to precious metals recovery from waste

Abstract. Hydrometallurgy is an important technology for the production of various metals. After dissolving metals in aqueous solutions, these are recovered either as salts by precipitation or by liquid-liquid extraction, or as metals by electrowinning. Liquidliquid extraction (or solvent extraction) is particularly used for refining base metals (copper, nickel, zinc, etc...), extracting rare and precious metals from ores, separating and purifying platinum group metals, and reprocessing spent nuclear fuel. It is based on the transfer of targeted metal cations from an aqueous phase to an organic phase, a complex fluid where various interactions, both strong (coordination) and weak (supramolecular organization), allow the stabilization of these cations. In this presentation, we will see how studies dedicated to the behaviour of palladium in separation processes of fission products present in spent nuclear fuel led us to propose effective techniques for the recovery of palladium from electronic waste. All process steps will be discussed, with peculiar emphasis on the behaviour of palladium(II) in organic media, and the design of the structure of the extractant molecules used, including a new approach based on dynamic covalent chemistry.

December 11th, 14h30 Corridor 24/25 Room 101, 1st floor Campus P et M Curie Sorbonne Université



Ilan MAREK (Schulich Faculty of Chemistry and Resnick Sustainability Center for Catalysis) chilanm@technion.ac.il

Stereoselective S_N1 at Non-Classical Carbocation

Abstract. Nucleophilic substitution at sp³ carbon center is one of the most fundamental and common transformations in organic synthesis. While the stereochemical outcome for a S_N2 reaction proceeds with inversion of configuration, the unimolecular nucleophilic substitution S_N1 provides, in most cases, a racemic product in addition to potential elimination of a proton, as well as undesired hydride and alkyl rearrangements. Therefore, the control of the stereochemical outcome for a S_N1-type reactions remains very complex. Here, we intend to discuss a predictable and reliable approach that would control the stereochemistry for a S_N1 -type transformation, opening new avenues in stereoselective synthesis in acyclic systems through the use of non-classical carbocations.

FRIDAY December 15 th , 11h Corridor 32/42, room 101	Giovanni POLI (IPCM, SU) giovanni.poli@sorbonne-universite.fr
Campus P et M Curie Sorbonne Université	Chemistry and energy transition - Part II
	Abstract. At a time when microplastics are found from the highest mountaintops to the deepest ocean trenches, most glaciers are melting, and weather events are becoming more and more extreme, our community needs to understand the challenges associated with overcoming the warming of our planet. Understanding how climate change came about and how scientists are acting to save our planet requires the coordinated contributions of scientists from many disciplines: physics, meteorology, chemistry, climatology, environmental science, geography, geology, oceanography, ecology, social science, and others. This lecture will try to explain in a simple way the origin of Earth's global warming and how chemistry can contribute toward the solution of this problem, which is closely linked to the energy resources needed for human activity.

For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. 20144 27 38 50. Courriel : cyril.ollivier@sorbonne-universite.fr











Ton Avenir au Canada



Lieu : Sorbonne Université – Campus Pierre et Marie Curie Date & Heure : Le mardi 12 décembre 2023, de 14 h à 16 h Saile : Tour 32, couloir 32-42, salle 101

Pourquoi cette visite?

Désormais unis, Sygnature Discovery et NuChem Sciences s'affichent comme leader mondial en tant qu'organisation de recherche sous contrat spécialisée dans les services intégrés pour la découverte de nouveaux médicaments. Nous sommes à la recherche de jeunes talents passionnés et motivés par l'idée d'avoir un impact significatif et positif sur la découverte des médicaments de demain. Nous recrutons aux niveaux M2, Ph.D. et Post-doc.!

Pourquoi y participer?

Ne manquez pas cette opportunité unique de découvrir notre univers et de donner un élan à votre carrière dans la recherche pharmaceutique. Venez découvrir comment NuChem Sciences pourrait être le tremplin de votre réussite professionnelle.

Agenda

- Présentation de NuChem Sciences et des activités d'une organisation de recherche sous contrat
- Présentation scientifique
- Séance de Q&A Posez-nous toutes vos questions !
- Entrevues personnalisées pour les étudiant(e)s intéressé(e)s; recevez des conseils pour postuler efficacement et découvrez toutes les opportunités chez NuChem.

Réserve ta rencontre individualisée !

Nos Ambassadeurs



Guillaume Revol, Ph.D. Chercheur principal en chimie Diplômé de l'École Polytechnique (Pr. Samir Zard)



Romain Laporte, Ph.D. Responsable marketing scientifique Diplômé de Normandie Université (Pr. Thierry Lequeux)

Pour toute demande d'information : romain.laporte@nuchemsciences.com nuchemsciences.com in | sygnaturediscovery.com in

For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











December 18th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne Université



Colin BONDUELLE (Université de Bordeaux, CNRS, LCPO) LCPO (Laboratoire de Chimie des Polymères Organiques), ENSCBP, 16 avenue Pey Berland, F-33600, Pessac, France. <u>colin.bonduelle@enscb.fr</u>

From natural proteins to polymer synthesis

Abstract. Proteins are natural building blocks that have many features still unrivaled by their synthetic counterparts, including chemical diversity, hierarchical structure, specific chemical modification, programmed system dynamics, etc. Combined with their possible metabolism in living systems (biodegradation, etc.), these properties make proteins very interesting for designing the polymers of tomorrow. While significant advances in genetic engineering have been achieved, a major remaining challenge is to optimize proteins production (extraction, recombinant protein, etc.) and large-scale protein preparation from living systems is often difficult.

Interestingly, the most economical and efficient route to polypeptides is a chemical methodology: the ring-opening polymerization (ROP) of amino acid Ncarboxyanhydride (NCA) monomers (figure 1).[1] Compared to proteins, peptidic polymers are much simpler macromolecules in which amino acids are statistically repeated. However, those polypeptides combine advantageous features of synthetic polymers (solubility, process, rubber elasticity, etc.) with those of natural proteins (secondary structure, functionality, biocompatibility, etc.).[2] NCA polymerization still suffers from significant limitations including tedious monomer purification steps, significant sensitivity to moisture, and processing in toxic solvents. Recent progresses have been impressive: efforts have focused on promoting the polymerization without the use of a catalyst, exploring more reactive initiators, and using heterogeneous processes including emulsion polymerization.[3] In this context, this talk will illustrate 1) how the combination of coordination chemistry or DNA binding to polypeptide polymers can be used to prepare smart polymeric systems, [4] 2) how aqueous ROP of NCA monomers can be extended to a PISA process, [5] and 3) how polymerization of NCA can afford simplified analogues of antimicrobial peptides or thermoresponsive tandem repeat proteins.[6]



For any information, please contact:

Dr Cyril OLLIVIER, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











<u>CULTURCHEM</u>

JANUARY 2024

January 8th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Luc NEUVILLE (Institut de Chimie des Substances Naturelles ICSN-CNRS) 1, avenue de la Terrasse, 91190 Gif-sur-Yvette France <u>luc.neuville@cnrs.fr</u> Enantioselective Synthesis of Nitrogen containing cyclic units from (poly)enecarbamates

Abstract. Chiral nitrogen derivatives, in particular (hetero) cyclic once, are key units of numerous prescribed drugs, but also core of natural products and play an important role in material sciences, not to mention their value as synthetic intermediate. Search for effective synthetic methodology to access them is there for a continuously stimulating area especially when considering enantioselective strategies. Enecarbamates are interesting building blocks that have been used as partner in selected transformations. Our lab has long been involved in their study in the context of chiral phosphoric acid (CPA) organocatalysis. In our lecture will highlight some of our recent achievements allowing building various heterocycles based on the reactivity of (poly) enecarbamates and show how subtle change can influence reactivity.

January 15th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Daniele PASSARELLA (Università degli Studi di Milano, Italy) daniele.passarella@unimi.it https://sites.unimi.it/passalab/

Natural Products as Targets, Leads and Building Blocks in Chemical Synthesis

<u>Abstract.</u> Natural products and in particular the ones with relevant pharmacological activities, have a long history. Their importance as irreplaceable source in drug discovery and their singular behavior, makes them challenging items in chemical synthesis. In our lab, we take care of natural products as key players of different research projects with 3 different rules. We consider them as important target for the study of new total synthesis, as lead compounds for the rational design and synthesis of new analogs with new biological activities and as building blocks for the construction of conjugate compounds with new properties. The discussion will regard the representative cases of three class of compounds: cannabinoids, epothilones and maytansinoids.

For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











January 22nd, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Anna HIRSCH (Helmholtz Institute for Pharmaceutical Research Saarland (HIPS)) anna.hirsch@helmholtz-hips.de

Addressing underexplored anti- infective drug targets

Abstract. The challenges associated with anti-infective drug-discovery are tackled by combining various hit-identification strategies with phenotypic antibacterial screening.¹ I will illustrate this approach with a selection of un(der)explored targets. The first is a vitamin transporter from the energy-coupling factor (ECF) class unique to Gram-positive bacteria.² We report on a structure-based virtual screening campaign to afford the first selective inhibitors of the ECF transporters with good in vitro and wholecell activity and a good in vitro ADMET and in vivo PK profiles.³ A newly established cell-based uptake assay accelerated our screening and hit-to-lead optimisation campaign.⁴ Secondly, we succeeded in fragment merging and linking, affording highly selective and potent inhibitors of the extracellular metalloprotease and virulence factor of *Pseudomonas aeruginosa*, the elastase LasB.⁵ Multiparameter optimisation based on extensive biological profiling, including the establishment of complex biological assays led to chemically diverse lead compounds with good lung exposure and in vivo efficacy. Our approach promises to deliver the urgently needed antiinfective agents featuring both new chemical scaffolds and unprecedented modes of action. Finally, we succeeded in the identification of synthetic small-molecule inhibitors of the b-sliding clamp DnaN,⁶ showing good affinity, functional inhibition, broad-spectrum antibacterial activity and a balanced in vitro ADMET profile.

January 29th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Petr Štěpnička (Charles University, Prague, Czech Republic) stepnic@natur.cuni.cz Functional ferrocene phosphines

Abstract. Ferrocene-based ligands are indispensable in coordination chemistry and catalysis. This particularly applies to their archetypal representative, 1,1'bis(diphenylphosphino)ferrocene (dppf). The wide practical applications of this iconic ligand naturally initiated the search for analogous compounds with varied phosphine substituents, chiral derivatives, and also functional analogues in which one phosphine moiety is replaced for a functional group that can be used to alter both physicochemical properties and coordination behaviour. This lecture will provide an overview of the recent research in my team focused on the design and applications of such compounds. Particular attention will be paid to compounds bearing nitrile, isonitrile, and guanidine substituents as well as to the newly disclosed compounds combining phosphine and stibine donor groups.



For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. 201 44 27 38 50. Courriel : cyril.ollivier@sorbonne-universite.fr













FEBRUARY 2024

February 5th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Véronique RATAJ (Centrale Lille Institut) veronique.rataj-nardello@univ-lille.fr Development of nano- and microdispersed reaction media for oxidation catalysis

Abstract. Many catalytic reactions involve hydrophilic reagents and hydrophobic substrates. In order to facilitate mass transfer, phase transfer catalysts (PTCs) have been widely used. However, such systems do not fully respect the principles of green chemistry and are not always well suited. An elegant and effective solution is to use nano- and microdispersed systems such as microemulsions and emulsions respectively. In this context, we have developed the concepts of "balanced catalytic surfactants", "Pickering interfacial catalysis" and "Colloidal tectonics" applied to catalysis. Catalytic amphiphilic compounds were designed to form three-liquid-phase microemulsions and Pickering emulsions, respectively. Balanced catalytic surfactants spontaneously form three-phase microemulsion systems called Winsor III in the presence of water and an appropriate oil, without the addition of a cosurfactant or an electrolyte. They are based on a cationic amphiphilic moiety electrostatically linked to an anionic catalyst such as molybdate ion, capable of disproportionate hydrogen peroxide into singlet oxygen, a very powerful and selective oxidant. When the cationic amphiphilic moiety is combined with a polyoxometalate, it self-assembles into solid nanoparticles that stabilize water-in-oil emulsions to form Pickering emulsions. These two concepts will be illustrated by various oxidation reactions involving H₂O₂. Finally, we will show that the combination of two surfactants or two nanoparticles makes it possible to obtain very interesting synergistic effects both on the properties of the emulsions and on the catalytic performances. Références:

[1] V. Nardello-Rataj et al. J. Am. Chem. Soc. 2008, 130, 14914.

[2] B. Hong. et al. *Catalysts* **2016**, *6*(12), 184.

- [3] L. Leclercq et al. Chem. Eur. J. 2012, 18, 14352.
- [4] L. Leclercq et al. ChemSusChem. 2013, 6, 1533.
- [5] M. Pera-Titus et al. Angew. Chem. Int. Ed. 2015, 28(5), 316.
- [6] L. Leclercq et al. *Langmuir*, **2017**, 33, 3395.
- [7] B. Yang et al. Green Chem. **2017**, 19, 4552.
- [8] D. Dedovets at al. Angewandte Chemie, 2022, 61(4), e202107537
- [9] Y. Feng, Green Chem. 2023, 25, 1417-1423

For any information, please contact:











February 12th, 17h Amphitheater Friedel Chimie ParisTech - PSL 11 rue P et M Curie



Jason HOLLAND (University of Zurich) Jason.Holland@chem.uzh.ch New tactics in radiopharmaceutical design

Abstract. Radiopharmaceuticals play an increasingly important role in the clinic as both diagnostic tools and state-of-the-art molecularly targeted radiotherapies. Optimising the therapeutic effects whilst minimising patient exposure to high-energy sources of ionising radiation require new chemistry to control drug and radiotracer pharmacokinetics at the tissue and cellular levels. This presentation will begin with an overview of current applications of radiotracers in basic science and Nuclear Medicine at the University of Zurich. Then we will delve into the new chemical methods that my group is developing to create radiolabelled antibodies (mAbs) and control their distribution, metabolism, and therapeutic efficacy *in vivo* (Figure 1). Topics will include photochemistry and non-covalent supramolecular strategies for labelling mAbs, automation tools, and applications of radiotracer in cancer imaging and therapy.



Jason Holland is an Associate Professor and chair of Medicinal radiochemistry at the University of Zurich. He is originally from Yorkshire in the United Kingdom and received a master's degree in Chemistry from the University of York (MChem, 2004) followed by a doctorate from the University of Oxford (D.Phil, 2008).

February 19th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



David CANEVET (Université d'Angers) david.canevet@univ-angers.fr Stimuli-Responsive Single & Double-Stranded Foldamers

Abstract. Foldamers constitute a class of oligomers that can fold into conformationally ordered architectures. Such compact conformations show structural and functional similarities with biopolymers, mimicking their highly ordered structures and functions. This notably explains the intensively growing interest regarding their supramolecular chemistry.

A wide variety of building blocks (*e.g.* peptides, ureas,...) have been reported to fold through weak intramolecular interactions and have displayed remarkable properties in the context of chiral materials, molecular recognition or catalysis, for instance. While important efforts have been devoted to the study of these dynamic structures and their conformational changes, π -functional helical foldamers have focused less attention to date.

In this context, we have recently developed various light or redox responsive foldamers, which hybridize to form double helical structures. These systems were designed to afford dynamic architectures with appealing optical and electronic properties, and have allowed for controlling their single or double state in a reversible manner or their handedness.

For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











February 26th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Jérôme HANNEDOUCHE (Université Paris-Saclay / CNRS) jerome.hannedouche@universite-paris-saclay.fr Well-defined low-coordinate iron(II) complexes: novel opportunities for applications in catalysis

<u>Abstract.</u> The stabilization of low-coordinate transition metal complexes that show relevance as intermediates/reactive species in biological and molecular catalysis remains a challenging and dynamic research area. This conference will highlight our investigations into the design of discrete low-coordinate b-diiminate Fe(II) complexes for the development of novel reactivities in catalysis as well as the understanding of mechanistic pathways.



4 place Jussieu, 75005 Paris. 🕿 01 44 27 38 50. Courriel : cyril.ollivier@sorbonne-universite.fr





MARCH 2024

March 4th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Guillermo MINGUEZ ESPALLARGAS (Instituto de Ciencia Molecular, University of Valencia) <u>guillermo.minguez@uv.es</u> Solvent-free synthesis of Metal-Organic Frameworks: a route towards elusive materials

<u>Abstract.</u> Metal-organic frameworks (MOFs) have emerged in the last 30 years as revolutionary molecular materials with applications in societal and industrially relevant domains such as storage of fuels, capture of gases, separation, drug delivery and catalysis, among others. The common property for all these open crystalline frameworks is their permanent porosity constructed from the assembly of inorganic sub-units and organic linkers, providing an assortment of topologies and different architectures that can be intended by chemical design.

Herein we will present an uncommon synthetic approach, very versatile, for the preparation of elusive porous materials, based on the absence of solvents.



For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











March 11th 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Patricia MELNYK (Univ. Lille, Inserm, CHU Lille, UMRS1172 - LilNCog -Lille Neuroscience & Cognition) patricia.melnyk@univ-lille.fr A ligand-based approach for the design of multi-action anti-Alzheimer compounds

Abstract. Alzheimer's disease (AD) is a multifactorial slow and progressive dementing disease that combines two pathophysiological mechanisms: the amyloid pathology and the Tau pathology. In parallel with these hallmarks, several dysfunctions are observed such as neuroinflammation, cellular death, altered proteostasis, lysosome dysfunctions, damaged mitochondria and altered synaptic transmission. Disease-modifying small molecules currently in clinical trials only act on either one of these processes or even on symptoms.

In the past years, thanks to a phenotypic screening and the identification of the two first active families, we developed a ligand-based approach and built a pharmacophoric model. From this model, we succeeded in identifying several families of compounds able to modulate the APP metabolism, reduce the Tau pathology development in vivo and improve the cognitive deficits in transgenic mouse models of hippocampal Tau pathology and amyloid pathology. We also highlighted the effect of some compounds on neuroinflammation and protein homeostasis.

The presentation will focus on the design, synthesis and activities of one of these compounds.



For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : <u>cyril.ollivier@sorbonne-universite.fr</u>











March 18th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Frederic KANOUFI (Université Paris Cité) <u>frederic.kanoufi@u-paris.fr</u> High throughput nanoelectrochemistry: hype or reality?

Abstract. Electrochemical processes are pivotal for fostering green and sustainable approaches to a broad range of chemical and environmental challenges. Their adaptability, efficiency, and cost-effectiveness, combined with the employment of clean, inexpensive electrons, eliminate the dependence on harmful chemical agents, underscoring the eco-friendly essence of electrochemistry. Furthermore, the field's capacity to produce valuable products via electrocatalysis and its vital contribution to energy storage technologies, such as batteries, underscore its significance in promoting sustainable energy conversion and storage practices.

To progress in this endeavor, a synergistic collaboration between electrochemists, computational and synthetic chemists, both material and molecular, is essential [1]. With the annual introduction of hundreds of 'novel electrocatalysts,' the aim transcends the synthesis of a new, highly efficient organic or inorganic molecule or nanomaterial and the characterization of its electrocatalytic properties for a specific reaction. This era has also marked the development of innovative electroanalytical methodologies that enable high-throughput catalysts benchmarking [2].

This presentation will explore recent advancements in what is termed nanoelectrochemical techniques, which facilitate the imaging and quantification of electrochemical processes with unparalleled spatial and temporal resolution. It all started in the mid-1980s – a time when most of your supervisors were, at best, PhD students – with the advent of microelectrodes used as local electrochemical probes. Since then and over the past 15 years, the toolbox of electrochemists has grown considerably. This includes confining reactions within a nanoscale domain using a nanopipette [3], capturing individual active nanomaterials on the fly [4], or integrating electrochemistry with super-resolution optical microscopy [5] or electron microscopy [6] to provide operando insights into electrochemical reaction mechanisms.

This presentation will not only illustrate these techniques and their applications, but also highlight the challenge they pose: the generation of vast amounts of data, making data analysis the bottleneck of experiments. Additionally, it will demonstrate how the field is increasingly intersecting with artificial intelligence, marking a fascinating turn of events. This evolution necessitates that the next generation of PhD students—PhD 2.0—acquire new competencies in robotics, computing, and data analysis to stay at the forefront of this transformative journey.

[1] Zhi Wei Seh *et al.*, Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* 2023, **355**, eaad4998 (2017). DOI:<u>10.1126/science.aad4998</u>

[2] Xiangdong Xu et al., The new era of high throughput nanoelectrochemistry. *Anal. Chem.* 2023, **95**, 319–356. DOI: <u>10.1021/acs.analchem.2c05105</u>

[3] Neil Ebejer et al, Scanning Electrochemical Cell Microscopy: A Versatile Technique for Nanoscale Electrochemistry and Functional Imaging, *Annu. Rev. Anal. Chem.* 2013, **6**, 329-351. DOI: <u>10.1146/annurev-anchem-062012-092650</u>

[4] Fato Tano et al., Single Nanoparticle Electrochemistry, *Annu. Rev. Anal. Chem.* 2019, **12**, 347-370. DOI:<u>10.1146/annurev-anchem-061318-114902</u>

[5] Frédéric Kanoufi, Electrochemistry and Optical Microscopy. In Encyclopedia of Electrochemistry, A.J. Bard (Ed.), 2021, pp1-80. DOI: <u>10.1002/9783527610426.bard030108</u>
[6] Yao Yang et al., Operando methods: A new era of electrochemistry, *Curr. Op. Electrochem.* 2023, **42**, 101403, DOI: <u>10.1016/j.coelec.2023.101403</u>

For any information, please contact:

Dr Cyril Ollivier, Sorbonne Université, Campus Pierre et Marie Curie, Tour 32-42, 5^{ème} étage, case 229, 4 place Jussieu, 75005 Paris. ☎ 01 44 27 38 50. Courriel : cyril.ollivier@sorbonne-universite.fr











March 25th, 11h Amphitheater Herpin Esclangon building Campus P et M Curie Sorbonne University



Christophe BUCHER (Laboratoire de Chimie UMR 5182 CNRS - ENS de Lyon)

<u>Christophe.bucher@ens-lyon.fr</u> Radical approaches towards electrochemically powered (supra)molecular self-assemblies

Abstract. Electron-responsive molecular materials have recently been the subject of intense research activities. This growing interest stems largely from the myriad of exciting applications envisioned for such electronically-addressable compounds capable of responding to electrical stimulation with changes in structure and function. These particular properties can lead to applications in various domains as in molecular electronics, in analytic science, with switchable hosts allowing the controlled binding/release of pollutants or drugs or in materials science with the development of adaptive supramolecular polymers.

Our group has been focusing over the past few years on the development of tailormade redox-controllable molecular or supramolecular systems involving electrogenerated organic π -radicals as key responsive and/or assembling elements. In this lecture, we will focus on the physico-chemical properties of a series of responsive molecules whose assembly or function can be controlled with an electrical stimulus. Particular attention will be given to transformable supramolecular polymers and gels and to molecular systems exhibiting electron-switchable magnetic properties. The properties of these redox-responsive molecular architectures and molecular materials will mainly be discussed on the basis of electrohemical, spectroelectrochemical and ESR experiments supported by quantum chemical calculations

For any information, please contact: