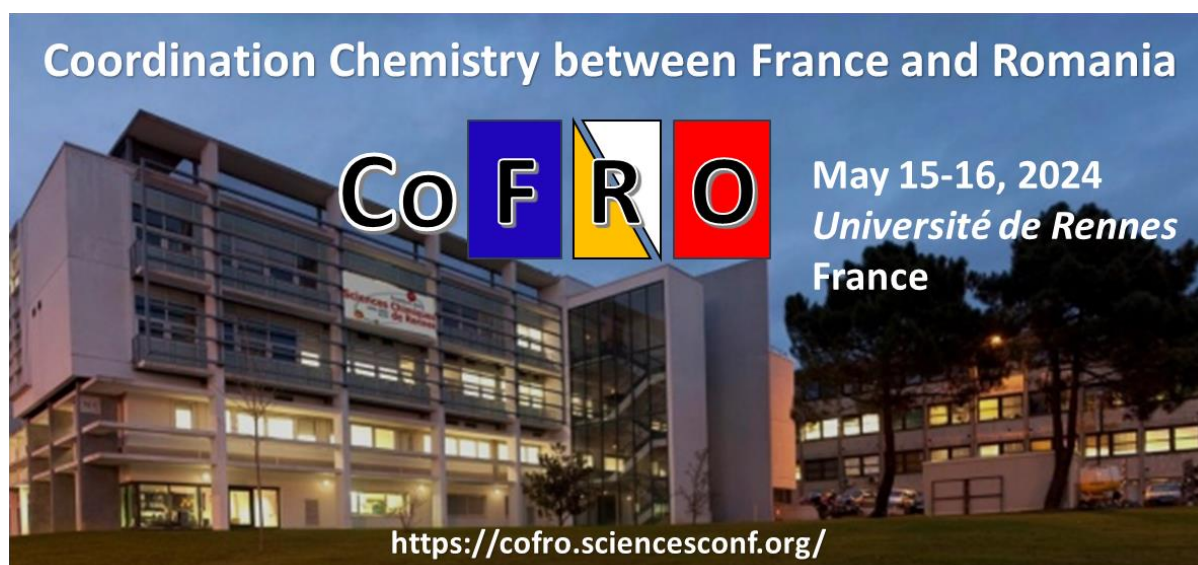


CoFRO 2024

Coordination Chemistry between France and ROmania



Book of Abstracts

French and Romanian chemistry in the spotlight !

Dear colleagues and friends, welcome to Rennes and to CoFRO !

CoFRO is a two-day workshop dedicated to French and Romanian chemists from the fields of organometallic, inorganic and coordination chemistry:

cofro@sciencesconf.org.

The workshop is an open venue where chemists from both countries are invited to present their research in a binational event, and are actively encouraged to seek and propose collaborations for joined projects. The ambition is to offer a platform where all topics of our disciplines are discussed, in order to encourage joined research proposals between the two countries or, simply, to trigger new and exciting informal collaborations. A total of 28 oral communications of over 30 posters will be presented by you, the attendees!

Beyond these presentations, the workshop is hosting four invited speakers, all of whom share close links with both Romania and France:

Dr. Narcis AVARVARI, CNRS Research director at UMR 6200 MOLTECH, University of Angers, France

Dr. Gábor BALÁZS, Associate Professor at the University of Regensburg, Germany

Dr. Ala Bunescu, Assistant Professor at the University of Bonn, Germany

Dr. Dragoş ROŞCA, Assistant Professor at the University of Rennes, France

So, enjoy CoFRO, and get talking with your colleagues!

Chimia franceză și română în centrul atenției !

Dragi colegi și prieteni, bine ați venit la Rennes și la CoFRO !

CoFRO este un workshop de două zile dedicat chimiștilor francezi și români din domeniul chimiei organometalice, anorganice și de coordonative:

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Workshop-ul este un spațiu destinat chimiștilor din ambele țări, unde sunt invitați să își prezinte cercetările în cadrul unui eveniment bilateral. Participanții sunt încurajați în mod activ să caute și să propună colaborări pentru viitoare proiecte comune. Scopul organizatorilor este de a oferi o platformă în cadrul căreia să se discute subiectele noastre de cercetare, pentru a încuraja propuneri de cercetare comună între cele două țări sau, măcar, pentru a porni noi și interesante colaborări. În total, vor fi prezentate de către participanți 28 de comunicări orale și peste 30 de postere!

Pe lângă aceste prezentări, atelierul va găzdui patru invitați, toți având legături strânse atât cu România, cât și cu Franța:

Dr. Narcis AVARVARI, CNRS Cercetător științific la UMR 6200 MOLTECH, Universitatea din Angers, Franța

Dr. Gábor BALÁZS, Lector la Universitatea din Regensburg, Germania

Dr. Ala Bunescu, Lector la Universitatea din Bonn, Germania

Dr. Dragoș ROȘCA, Lector la Universitatea din Rennes, Franța

Așadar, bucurați-vă de CoFRO și discutați împreună cu colegii dumneavoastră!

La chimie française et roumaine à l'honneur !

Chères et chers collègues, bienvenue à Rennes pour le CoFRO !

Le symposium CoFRO s'étale sur deux jours. Il est dédié aux chimistes français et roumains des domaines de la chimie organométallique, inorganique et de coordination :
cofro@sciencesconf.org.

Le workshop est un forum pour les chimistes des deux pays, qui sont invités à présenter leurs travaux de recherche lors d'un événement binational et, à terme, encouragés à proposer des collaborations et des thématiques pour des projets communs. L'objectif est d'offrir une plateforme où tous les sujets de nos disciplines seront abordés, afin d'encourager des collaborations entre les deux pays. Un total de 28 communications orales et plus de 30 posters seront présentés par les participants au symposium.

Au-delà de ces présentations, quatre conférenciers invités sont également accueillis. Ils partagent tous des liens étroits avec la Roumanie et la France :

Dr. Narcis AVARVARI, Directeur de recherche CNRS à l'UMR 6200 MOLTECH, Université d'Angers, France

Dr. Gábor BALÁZS, Professeur associé à l'Université de Regensburg, Allemagne

Dr. Ala BUNESCU, Maître de Conférence à l'Université de Bonn, Allemagne

Dr. Dragoș ROȘCA, Maître de Conférence à l'Université de Rennes, France

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Adrien Schlachter (Postdoctoral research assistant, INSA Rennes)

Do not hesitate to ask any of us if you have questions or if you require assistance, we will be happy to help!

Day 1 – Wednesday, May 15th, 2024

08:00 – 08:45 **Registration**

08:45 – 09:00 **Opening**

1st Session chaired by Dr. Dragos Roşca

09:00 – 09:20

OC 1

Marc Fourmigué – *ISCR University of Rennes*

Chemistry at ISCR & a few words about chalcogen bonding (ChB)

09:20 – 09:40

OC 2

Marius Andruh – *Institute of Chemistry Costin D. Nenitzescu*

The chemistry of heterometallic complexes in Bucharest

09:40 – 10:20

Plenary lecture 1

Narcis Avarvari

Dithiolene, tetrathiafulvalene and anilate ligands for functional metal complexes and coordination networks

10:20 – 10:40

OC 3

Ingrid Popovici – *Laboratoire de Chimie Moléculaire, Palaiseau*

Iminophosphorane ONP supported nickel(II) complex : from ligand synthesis to hydrosilylation catalysis

10:40 – 11:10

Coffee break

2nd Session chaired by Dr. Ala Bunescu

11:10 – 11:30

OC 4

Daniel Müller – *ISCR University of Rennes*

Al(III)-promoted formation of all-carbon quaternary centers from aliphatic tertiary chlorides and alkynyl silanes

11:30 – 11:50

OC 5

Noemi Deák – *University Babeş-Bolyai, Cluj-Napoca*

Sulfonyl and sulfinyl containing pincer ligands in *p*-block chemistry

11:50 – 12:10

OC 6

Simona Nica – *Institute of Chemistry Costin D. Nenitzescu, Bucharest*

Self-assembly of azulene-based imine cages: synthesis and supramolecular organization

12:10 – 12:30	OC 7 Daniel Pla – <i>LHFA University of Toulouse 3</i> Molecular and surface-mediated catalytic strategies towards multicomponent reactions for the valorization of C1 feedstocks
12:30 – 12:50	OC 8 Raluca Malacea-Kabbara – <i>ICMUB University of Bourgogne, Dijon</i> Coordination chemistry of phenoxy-amidine ligands and application in catalysis
12:50 – 12:55	Aurélien Billot – ABCR
12:55 – 14:10	Lunch + posters
3rd Session chaired by Pr. Marius Andruh	
14:10 – 14:50	Plenary lecture 2 Gabor Balázs The manifold reactivity of polyphosphorus complexes
14:50 – 15:10	OC 9 Cristian Silvestru – <i>University Babeş-Bolyai, Cluj-Napoca</i> Coordination and organometallic chemistry at the Faculty of Chemistry and Chemical Engineering Babeş-Bolyai University of Cluj-Napoca
15:10 – 15:30	OC 10 Karoly Kozma – <i>Institut Lavoisier de Versailles</i> Super-reduced Dawson-type POM $[P_2W_{15}Mo^{IV}_3O_{59}(H_2O)_3]^{6-}$
15:30 – 15:50	OC 11 Augustin Mădălan – <i>Faculty of Chemistry, University of Bucharest</i> Luminescent complexes with imino/amino podands containing extended π systems
15:50 – 16:20	Coffee break
4th Session chaired by Dr. Pierre de Frémont	
16:20 – 16:40	OC 12 Pim Puylaert – <i>University of Bremen</i> Versatile coordination of tridentate SPO ligands
16:40 – 17:00	OC 13 Catalin Maxim – <i>Faculty of Chemistry, University of Bucharest</i> Modulation of chiroptical properties in Zn(II)-based amino acids helices
17:00 – 17:20	OC 14 Julien Legros – <i>COBRA University of Rouen</i> Organometallic chemistry (Li, Mg) in flow microreactors

- 17:20 – 17:40 OC 15
Madalin Damoc – *Petru Poni Instit. of Macromolecular Chemistry, Iași*
Merging silicones/hydrocarbons within metal complexes. From crystals to soft matter and their applications
- 17:40 – 18:00 OC 16
Sylvie Ferlay – *Institut Le Bel, University of Strasbourg*
New electrode materials based on alloxazine derivatives
- 18:00 – 19:30 ***Drinks + socialising***

Day 2 – Thursday, May 16th, 2024

5th Session chaired by Dr. Gabor Balazs	
09:00 – 09:40	Plenary lecture 3 Ala Bunescu Valorization of carboxylic acids via photoinduced carboxylate to iron charge transfer
09:40 – 10:00	OC 17 Aurelia Visa – <i>Coriolan Dragulescu Institute of Chemistry, Timisoara</i> Green synthesis and applications of metal(II) coordination polymers based on bisphosphonates and imidazole ligands
10:00 – 10:20	OC 18 Marie Fustier-Boutignon – <i>LHFA University of Toulouse 3</i> Geminal dianions : versatile ligands for polymetallic organoiron complexes
10:20 – 10:40	OC 19 Claudiu Sergentu - <i>Alexandru Ioan Cuza University of Iasi</i> Tetravalent cerium coordination: Understanding the L3-edge X-ray absorption structure in organocerium complexes
10:40 – 11:10	Coffee break
6th Session chaired by Dr. Narcis Avarvari	
11:10 – 11:30	OC 20 Mihai Răducă - <i>Institute of Chemistry Costin D. Nenitzescu, Bucharest</i> The design of homo- and hetero-di-radicals as ligands for the synthesis of 3d and 4f complexes
11:30 – 11:50	OC 21 Anca Silvestru – <i>University Babeş-Bolyai, Cluj-Napoca</i> Organochalcogen compounds and their metal complexes. Synthesis, structure and potential applications
11:50 – 12:10	OC 22 Diana Ciuculescu-Pradines – <i>SOFTMAT University Toulouse 3</i> A double hydrophilic copolymer as versatile scaffold for the incorporation of inorganic matter

12:10 – 12:30	OC 23 Elisabeta Szerb – <i>Coriolan Dragulescu Instit. of Chemistry, Timisoara</i> Metallomesogens as modifiers of carbon-based electrodes in electrochemical sensing
12:30 – 12:50	OC 24 Thangavel Thirunavukkarasu – <i>CEMCA Univ. Bretagne Occidentale</i> Cooperative spin crossover dinuclear Fe(II) complex
12:50 – 14:10	Lunch + posters
7th Session chaired by Pr. Cristian Silvestru	
14:10 – 14:50	Plenary lecture 4 Dragos Roşca Adventures in cycloaddition chemistry with iron complexes: the enabling role of redox-active ligands
14:50 – 15:10	OC 25 Chloé Blais – <i>ISCR University of Rennes</i> Lanthanide-based coordination polymers: recent advances on their shaping
15:10 – 15:30	OC 26 Nicolas Bogliotti – <i>PPSM University Paris-Saclay</i> Light-responsive arene-Ru(II) complexes derived from azobenzene for the control of chemical reactivity
15:30 – 15:50	OC 27 Matthieu Hédouin – <i>COBRA University of Rouen</i> A novel approach for accessing alkyl and arylcalciums
15:50 – 16:10	OC 28 Sergiu Calancea – <i>Institut Lavoisier de Versailles</i> Mo₂O₂S₂-thiosemicarbazone complexes: Electrocatalysis, Mo-polyurethanes and Supramolecular chemistry
16:10 – 16:20	Closing

Plenary Lectures

PL1

Dithiolene, tetrathiafulvalene and anilate ligands for functional metal complexes and coordination networks

N. Avarvari

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Tetrathiafulvalene (TTF), metal bis(dithiolene) and anilates (An) are outstanding redox-active units which, upon suitable functionalization, can provide electroactive coordination polymers (CP) or metal-organic frameworks (MOF). Accordingly, we have used TTF based ligands, such as bis(vinylene-dithio)-TTF (BVDT-TTF) tetrapyridine (Fig. 1)¹ or TTF-tetracarboxylates,^{2,3} metal bis(dithiolene) tetrabenzo-carboxylate and diverse ditopic anilate ligands,^{4,5} including chiral ones, to construct redox-active coordination networks provided with additional properties.

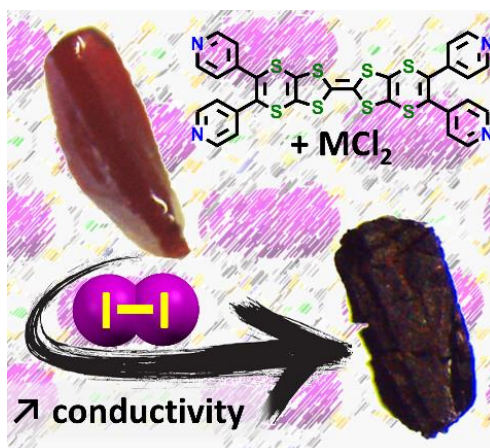


Figure 1 Electroactive transition metal MOFs based on BVDT-TTF with tunable conductivity.

1 F. Solano, P. Auban-Senzier, I. Olejniczak, B. Barszcz, T. Runka, P. Alemany, E. Canadell, N. Avarvari, N. Zigon, *Chem. Eur. J.*, **2023**, 29, e2022031.

2 F. Manna, M. Oggianu, P. Auban-Senzier, G. Novitchi, E. Canadell, M. L. Mercuri, N. Avarvari, *submitted*

3 N. Zigon, F. Solano, P. Auban-Senzier, S. Grolleau, T. Devic, P. N. Zolotarev, D. M. Proserpio, B. Barszcz, I. Olejniczak, N. Avarvari, *Dalton Trans.*, **2024**, 53, 4805.

4 S. Ashoka Sahadevan, F. Manna, A. Abhervé, M. Oggianu, N. Monni, V. Mameli, D. Marongiu, F. Quochi, F. Gendron, B. Le Guennic, N. Avarvari, M. L. Mercuri, *Inorg. Chem.*, **2021**, 60, 17765.

5 F. Manna, M. Oggianu, J. R. Galán-Mascarós, F. Pop, B. Le Guennic, M. L. Mercuri, N. Avarvari, *Dalton Trans.* **2024**, 53, DOI : 10.1039/d4dt00175c

PL2

The Manifold Reactivity of Polyphosphorus Complexes

G. Balázs, R. Wolf, M. Scheer

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The environmentally friendly synthesis of organophosphorus compounds is one of the most important research topics in current chemical research. Classically, most organophosphorus compounds are synthesised by converting white phosphorus (P_4) to PCl_3 or $P(O)Cl_3$ followed by reactions with organolithium or Grignard reagents. This produces stoichiometric amounts of by-products. To reduce the amount of by-products, a catalytic or a cyclic process to convert P_4 to organophosphorus compounds would be desirable. In addition to the recently reported radical-based processes for the synthesis of aryl phosphines or phosphonium salts,¹ we have developed a cyclic process in which $[Cp^*Fe(P_5)]$ ($Cp^* = C_5Me_5$) acts as a platform for the synthesis of phosphines (Figure 1).² This method can be used to synthesise cyclic phosphines³ and phosphines containing functional groups.⁴

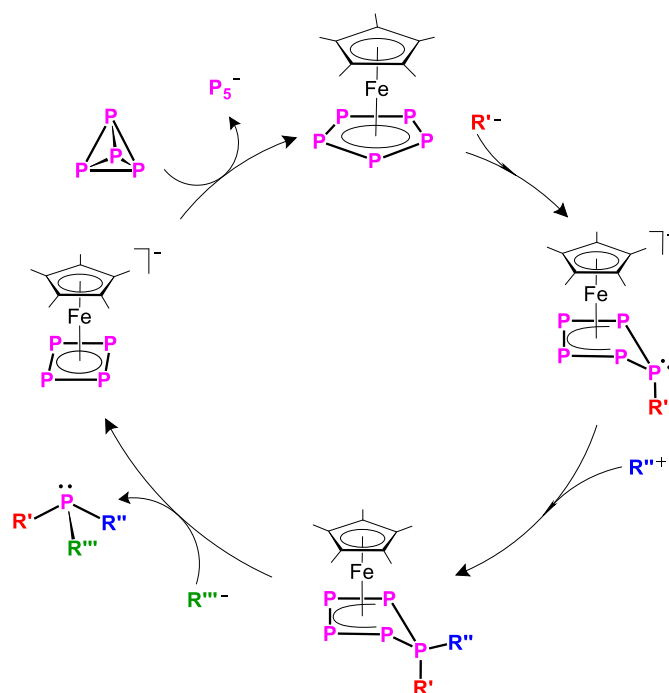


Figure 1 “One pot” cyclic process for the synthesis of phosphines mediated by $[Cp^*Fe(P_5)]$.

1 D. J. Scott, *Angew. Chem. Int. Ed.* **2022**, 61, e202205019.

2 S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, *Nat. Commun.* **2021**, 12, 5774.

3 S. Reichl, G. Balázs, M. Scheer, *Chem. Sci.* **2023**, 14, 3834. Corrections: *Chem. Sci.* **2023**, 14, 5527.

4 S. Reichl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, *Chem. Sci.* **2023**, 14, 7285.

PL3

Valorization of carboxylic acids via photoinduced carboxylate to iron charge transfer

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Carboxylic acids represent a structurally diverse and easily accessible class of building blocks in organic chemistry. Photocatalyzed decarboxylative functionalizations have gained considerable traction in organic synthesis to generate new carbon-carbon and carbon-heteroatom under mild reaction conditions. We developed an iron-catalyzed decarboxylative C(sp³)-O bond-forming reaction under mild, base-free conditions with visible light irradiation. The transformation uses readily available and structurally diverse carboxylic acids, iron-based photocatalysts, and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) derivatives as oxygenation reagents. The process exhibits a broad scope in acids possessing a wide range of stereoelectronic properties and functional groups. The developed reaction was applied to late-stage oxygenation of a series of bio-active molecules. The reaction leverages the ability of iron complexes to generate carbon-centered radicals directly from carboxylic acids by photoinduced carboxylate-to-iron charge transfer. Kinetic, electrochemical, EPR, UV-Vis, and DFT studies revealed that TEMPO has a triple role in the reaction: as an oxygenation reagent, an oxidant to turn over the Fe-catalyst, and an internal base for the carboxylic acid deprotonation. The obtained TEMPO adducts represent versatile synthetic intermediates that were further engaged in C-C and C-heteroatom bond-forming reactions using commercial organo-photocatalysts and nucleophilic reagents.

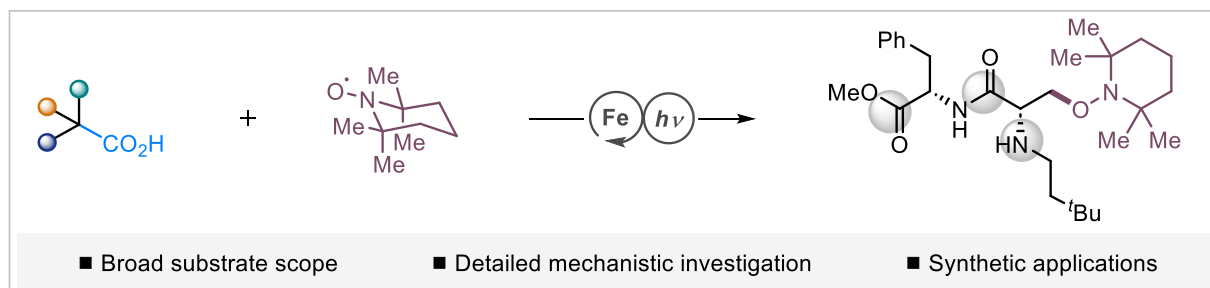


Figure 1 Iron-Catalyzed Decarboxylative Oxygenation of Aliphatic Carboxylic Acids

PL4

Adventures in cycloaddition chemistry with iron complexes: the enabling role of redox-active ligands

D.-A. Roşca^{a,b}

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^b Institut des Sciences Chimiques de Rennes (ISCR), CNRS, Univ Rennes, 35042 Rennes, France

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Despite their high abundance and low price, first row transition metals with partially occupied d-shells are prone to rapid spin- and oxidation-state changes, making their reactivity difficult to control. Redox-active ligands can reversibly store electrons on their backbone, often enforcing net 2-electron transfers through redox metal-ligand cooperativity and therefore suppressing the otherwise selectivity-eroding radical reaction pathways.

Our research programme focuses on using redox-active ligands as tools for the development of efficient catalytic applications based on iron and cobalt complexes. Pyrimidine-imine motifs play a central role as they can provide greater catalyst stability by hindering deleterious kinetically accessible pathways, compared to the established pyridine analogues. This enhanced stability was demonstrated in various catalytic transformations, with a focus on cycloaddition and hydroelementation reactions. In an effort to better understand the reaction mechanisms, our work also focused on elucidating the identity of the active species and their magnetic properties. The present contribution will detail on ligand structure-catalytic activity relationships in the context of iron- and cobalt-based transformations.

Oral Communications

OC1

**Chemistry at ISCR
& a few words about Chalcogen Bonding (ChB)**

M. Fourmigué*

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France

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In this communication, we will first introduce the different aspects of the research conducted at ISCR, with more than 200 academics involved in eight research departments, with a specific focus on organometallic, inorganic and coordination chemistry approaches, highlighting also the close relationships already existing with Romanian chemistry.

In a second part, our own contributions to main-group element chemistry will be illustrated by recent results obtained by activation of sigma-holes on chalcogenated molecules (Se, Te), in their co-crystals with Lewis bases and their topochemical reactions.

OC2

The chemistry of heterometallic complexes in Bucharest

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^b University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory
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Coordination chemistry has a long tradition at the University of Bucharest, that started with the school created by Professor Gheorghe Spacu (1883 – 1955). G. Spacu did his PhD (1916) at the University of Iasi with Professor Neculai Costachescu (1876 – 1939), who spent two years in Alfred Werner’s laboratory in Zürich (1906 – 1908). Modern Romanian coordination chemistry was built on this foundation. The chemistry of the heterometallic complexes in Bucharest flourished under the influence of the late Professor Olivier Kahn (1942 - 1999). The main interest in such complexes arises from the unique magnetic and optical properties they exhibit. The last twenty years or so, we focused mainly on complexes containing three different paramagnetic metal ions.¹ From the synthetic point of view this is a challenging problem. Then, the presence of three different paramagnetic centers can lead to interesting properties, especially when the metal ions, through their electronic peculiarities (spin, magnetic anisotropy), act in a synergistic way. We have extended this strategy towards other molecular systems constructed from three different spin carriers, one of them being a paramagnetic organic radical.² This lecture will give an overview of the chemistry of hetero-tri-spin systems developed in our laboratories at the University of Bucharest and the Romanian Academy.

¹ M. Andruh, *Chem. Commun.*, **2018**, 54, 3559.

² M. G. F. Vaz, M. Andruh, *Coord. Chem. Rev.*, **2021**, 427, 213661.

OC3

Iminophosphorane ONP supported Nickel(II) complex : from ligand synthesis to hydrosilylation catalysis

I. Popovici,* N. Casaretto, A. Auffrant

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Coordination chemistry offers an almost unlimited set of options to tune the steric and electronic properties of a metal via the choice of the appropriate ligand. Ligand design is therefore essential to ensure good catalytic performances, in particular when using first row earth abundant metals in place of rare and noble metals.

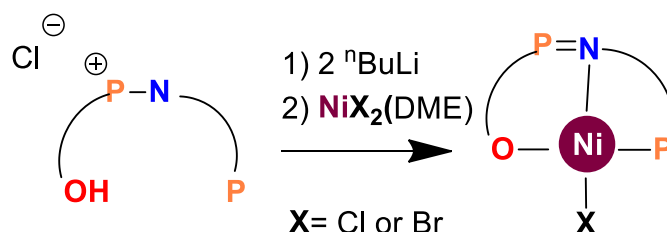


Figure 1 Synthesis of the [LNiX] complexes

Our group has synthesized a tridentate proligand containing a phenoxy, a central aminophosphonium and a terminal phosphine moiety. The ONP ligand featuring a lateral phenoxide and a central iminophosphorane moieties was generated in situ before the addition of the metal precursor. Iminophosphoranes are very good electron donors¹ and have an affinity for depleted earth abundant metals, therefore the ONP ligand was coordinated to Ni^{II} to form the [LNiX] complexes. (Fig. 1) Moreover, while iminophosphorane supported Ni^{II} complexes were employed successfully to catalyze C-C coupling reactions, or ethylene dimerization,² we are not aware of previous catalytic hydrosilylation reports. This reactivity as hydrosilylation catalysts was thus tested with the [LNiX] complexes trying to use mild conditions and low catalysts loadings.

In this communication we will present the synthesis of this original complex and its abilities as hydrosilylation catalyst as well as some mechanistic insights concerning the catalytic transformation.

¹ I. Popovici, C. Barthes, T. Tannoux, C. Duhayon, N. Casaretto, A. Monari, A. Auffrant, Y. Canac, *Inorg. Chem.* **2023**, 62 (5), 2376.

² T. Tannoux, A. Auffrant, *Coord. Chem. Rev.* **2023**, 474, 214845.

OC4

Al(III)-Promoted Formation of All-Carbon Quaternary Centers from Aliphatic Tertiary Chlorides and Alkynyl Silanes

D. Müller,* P. Charki

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Despite the accessibility of numerous alkynes through coupling or substitution reactions, the synthesis of trialkyl-substituted alkynes is still a major challenge. Within this context, we reexplored the electrophilic alkynyl substitution between tertiary aliphatic chlorides and silylated alkynes.¹ We were able to demonstrate that this approach is significantly more general than originally demonstrated by Capozzi¹ and even tolerates several functional groups. Furthermore, we report diastereoselective reactions which in some instances gave excellent diastereoselectivity (dr > 95:5). For the particular case of methyl cyclooctyl chloride we found C-H activation instead of substitution reaction.

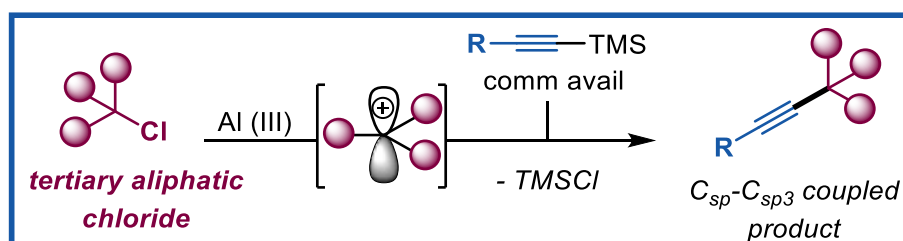


Figure 1 Cationic sp³-sp fragment coupling

¹ P. Charki, D.S. Müller *J. Org. Chem.* **2024**, accepted.

² C Capozzi, G.; Romeo, G.; Marcuzzi, F. *J. Chem. Soc., Chem. Commun.* **1982**, 959; Capozzi, G.; Ottana, R.; Romeo, G., Marcuzzi, *Gaz. Chim. Ital.* **1985**, 115, 311–314.

OC5

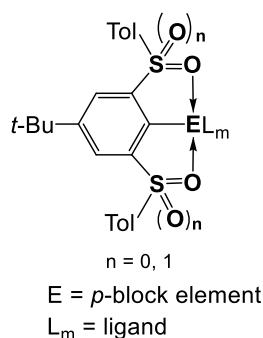
Sulfonyl and sulfinyl containing pincer ligands in *p*-block chemistry

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^a Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University
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Pincer ligands are widely used in organometallic chemistry due to their particular electronic and structural characteristics. They have as a main feature the ease to modify their properties by adjusting the structure (the ligand backbone and its substituents, the donor groups).¹ For this reason, lately the role of these ligands in the stabilization of heavy *p*-block elements also came in focus.² In the last few years our research group designed a new family of pincer type ligands,^{2,3} containing sulfonyl or sulfinyl moieties as donor groups.



Scheme 1 General structure of the pincer-type ligand stabilized compounds presented here

In this work we present the results obtained on the synthesis, characterization and reactivity of different *p*-block element containing derivatives supported by sulphur-based O,C,O-chelating pincer-type ligands (Scheme 1), containing sulfonyl or sulfinyl moieties as *ortho* substituents.³

The presented work is the result of the successful collaboration between the research teams from FCIC-UBB and LHFA-UPS.

1 R. Jambor, L. Dostál, *Top. Organomet. Chem.*, **2013**, *40*, 175.

2 N. Deak, D. Madec, G. Nemes, *Eur. J. Inorg. Chem.*, **2020**, 2769.

3 a) N. Deak, P.M. Petrar, S. Mallet-Ladeira, L. Silaghi-Dumitrescu, G. Nemes, D. Madec, *Chem. - Eur. J.* **2016**, *22* (4), 1349. b) N. Deak, O. Thillaye du Boullay, I.-T. Moraru, S. Mallet-Ladeira, D. Madec, G. Nemes, *Dalton Transactions*, **2019**, *48*, 2399. c) N. Deak, O. Thillaye du Boullay, S. Mallet-Ladeira, I.-T. Moraru, D. Madec, G. Nemes, *Eur. J. Inorg. Chem.*, **2020**, 3729.

OC6

Self-assembly of azulene-based imine cages: synthesis and supramolecular organization

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Self-assembly of small organic building blocks into complex molecular architectures under thermodynamic control is of high research interest, due to the structural beauty and the potential applications of the resulting assemblies in material science.¹ The involved interactions vary from strong covalent bonds, metal-ligand bonds or weak supramolecular forces, such as hydrogen and halogen bonds or π - π interactions.² Dynamic covalent chemistry (DCC) proved to be an advantageous strategy to develop complex molecular structures, providing thermodynamically stable products *via* one-pot reaction. Depending on the number and the spatial arrangement of the reactive functional groups in the precursors, either discrete cage structures or covalent organic frameworks (COFs) can be obtained.³ Compared to COFs, organic cages are generally soluble in organic solvents, enabling ease purification and post-synthetic functional transformations, which make them more attractive for specific applications.⁴

We describe herein the self-assembly process of tris(2-aminoethyl)amine with azulene-1,3-dicarboxaldehyde, through [1+1] and [2+3] imine condensation reactions. We were interested in understanding the role of the azulene-1,3-dialdehyde in the molecular organic cage assembling, and in the crystal packing of the resulting solids. The organic cages were characterized both in solution and solid state, to confirm their stability. These new cage-like molecules showed ability to support secondary interactions, such as coordination bonds and halogen interactions with appropriate halogen bond donors. The conformational flexibility was confirmed by variable temperature ¹H NMR spectroscopy.

Acknowledgement: The financial support from European Union through NextGenerationEU, programme-PNRR-III-C9-2022-18 (contract no.760110) is gratefully acknowledged.

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OC7

Molecular and surface-mediated catalytic strategies towards multicomponent reactions for the valorization of C1 feedstocks

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To illustrate how catalysis enables solutions to provide disruptive strategies in the synthesis of fine chemicals from C1 feedstocks, this talk overviews both molecular strategies as well as surface-catalyzed transformations using tailored nanoparticle systems (below 5 nm) with high specific surface areas. Herein, we present a sequential multi-catalytic process encompassing a Ni-catalyzed tri-reforming of methane (involving both CH₄ and CO₂ transformation) operating at 800-850 °C and 1.4 bar for the formation of syngas (stable CH₄ conversion and high H₂/CO selectivity).^[1] Most notably, the organometallic methodology employed enabled the preparation of Ni-based hydroxyapatite composites precluding the replacement of Ca(II) by Ni(II) on the support which is otherwise unavoidable using a conventional incipient wetness impregnation approach and ultimately diminishes the stability of the catalysts. Downstream transformation of the syngas via a Rh/Co-catalyzed four-component hydroaminomethylation (HAM) strategy was applied to the diverted synthesis of homologated terpenic amines in high selectivity via a molecular pathway, combining the synergy between 3d and 4d transition metals with glycerol, acting as a boosting solvent via hydrogen transfer.^[2] Thus, moderate to excellent yields of linear amines were obtained using a low catalyst loading (1 mol% [Rh], 5 mol% [Co], 2 mol% phosphine) and relative low pressure of H₂ and CO (total pressure 10 bar).^[2-3] This sequential multi-catalytic approach involving innovative heterogeneous and homogenous catalysts represents an efficient way to upgrade greenhouse gases into high-added value chemicals, from both environmental and economic viewpoints.

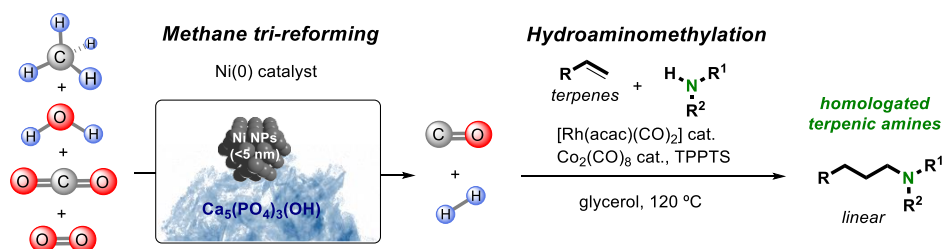


Figure 1 Streamlining TRM and HAM processes for the synthesis of terpenic amines

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OC8

Coordination chemistry of phenoxy-amidine ligands and application in catalysis

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Since few years our team is interested in the coordination chemistry and catalytic activity of a new class of ligands called phenoxy-amidines (FA). These ligands could be considered as a variant of the well-known phenoxy-imine (FI) ligands whose general structure corresponds to a phenol fragment, bearing an imine moiety in *ortho* position (*figure 1*). Replacing the imine moiety with a N,N,N'-trisubstituted amidine allowed us to obtain new phenoxy-amidine ligands with different structures in function of the amidine position. We further described the synthesis of ethylene and a phenylene-bridged bis(salicylamidine) that we called FAlen ligands. The strong σ and π -donor character of the amidine functions was expected to provide additional stability to metal ions, resulting in robust complexes. The coordination chemistry of these ligands was investigated. Alkane elimination from AlMe_3 and ZnEt_2 was employed to yield new heteroleptic or homoleptic Al and Zn complexes adopting monomeric or dimeric structures. Bidentate, tridentate or tetradentate ways of coordination of these ligands were also confirmed in the solid state by X-ray diffraction studies. DFT calculations were used to understand the fluxional properties and polyvalent denticity of FAlen ligands. Finally, these Al and Zn complexes revealed to be active catalysts for the ROP of *rac*-lactide. We were thus able to compare the influence of various substituents in terms of stability, coordination chemistry and catalytic activity.

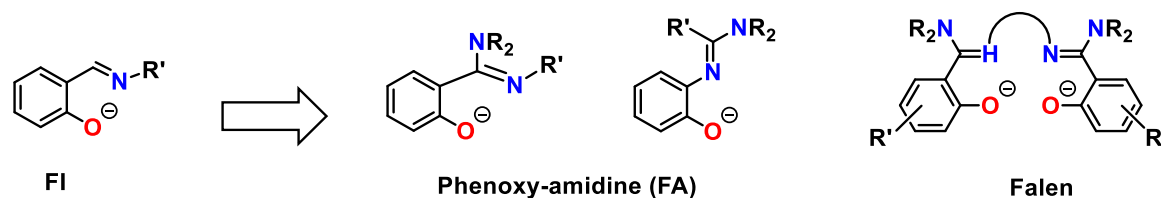


Figure 1 – from phenoxy-imine to phénoxyamidines and FAlen ligands

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OC9

Coordination and Organometallic Chemistry at the Faculty of Chemistry and Chemical Engineering Babeş-Bolyai University of Cluj-Napoca

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After a very short history of the beginning of inorganic and coordination chemistry at the Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University of Cluj-Napoca, Romania, the early development of a new field, *i.e. organometallic chemistry*, will be presented. Then, the emphasis will turn to the last 25 years of development of research topics, mainly in fundamental Main Group organometallic chemistry, with some contributions related to potential applications (biological activity, catalysis, C-H activation), but also in coordination and bioinorganic chemistry. The main research groups will be shortly presented, including the members and their research interests. The importance of collaborations with foreign research groups, including French ones, will be also pointed out.

OC10

Super-Reduced Dawson-Type Polyoxometalate [P₂W₁₅Mo^{IV}₃O₅₉(H₂O)₃]⁶⁻

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Polyoxometalates (POMs) are of interest for developing innovative electrochemical-energy storage systems, however their super-reduction processes and the corresponding structures are less explored.^{1,2}

In this communication, I will first present the super-reduction of [P₂W₁₅Mo₃O₆₂]⁶⁻ Dawson structure (notated as {P₂W₁₅Mo₃}-0) and its six-electron reduced version {P₂W₁₅Mo₃}-VI'. Both species exhibit stability under ambient conditions, making them ideal candidates to investigate chemical property changes associated with the reduction process. The {P₂W₁₅Mo₃}-VI' species features three Mo-Mo bonds in the {Mo₃} triad and terminal water molecules on the Mo sites, verified by single-crystal X-ray diffraction (SC-XRD) and extended X-ray absorption fine structure (EXAFS) measurements. This structural insight may significantly impact the chemical properties of the POM, influencing its solution behavior.³ To test this hypothesis, we investigated the ion-pair interactions of our POMs with rare earth elements (REE) using multinuclear nuclear magnetic resonance techniques (³¹P, ⁹⁵Mo, and ¹⁸³W-NMR) for solution studies and SC-XRD for deciphering the interactions in the solid-state. In this study, we will also present this set of data revealing that super-reduced POM {P₂W₁₅Mo₃}-VI' exhibits significantly stronger interactions compared to {P₂W₁₅Mo₃}-0 while both compounds exhibit the same anionic charge.

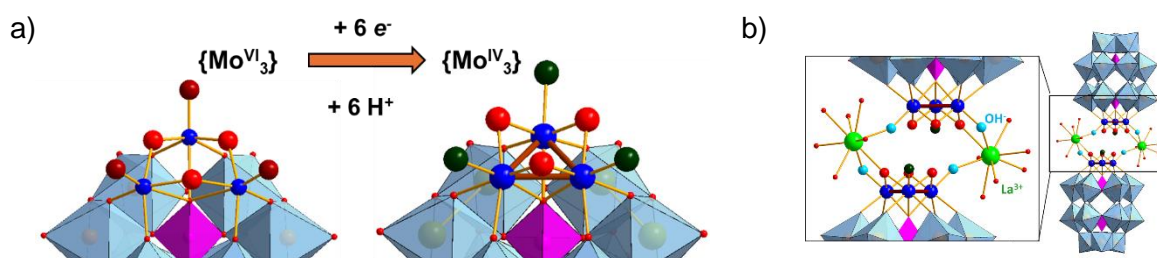


Figure 1 Visual representation of reduction process (a) and the interaction with La³⁺ observed in solid state by SC-XRD (b). Color code: light blue polyhedra, W; pink polyhedral, P; blue sphere, Mo; red spheres, O; dark green sphere, H₂O, lime spheres, La.

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OC11

Luminescent complexes with imino/amino podands containing extended π systems

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Polydentate imino and amino ligands play a significant role in the design of homo- and heteropolynuclear complexes containing 3d and 4f metal ions. Within the category of podands, the tripodal ligands are molecules projected to encapsulate more fully their guest. The presence of extended π systems as pendant arms of the ligands can contribute to the luminescent properties of the complexes [1] and, also, to non-covalent interactions with different chemical species.

In Zn(II) mononuclear complexes with the tripodal ligand resulted from the condensation of tris(2-aminoethyl)amine with 9-anthracenecarboxaldehyde, these non-covalent interactions of the anthracene moieties with solvent molecules or halide anions coordinated to the metal ion induce conformational changes of the ligand (Figure 1).

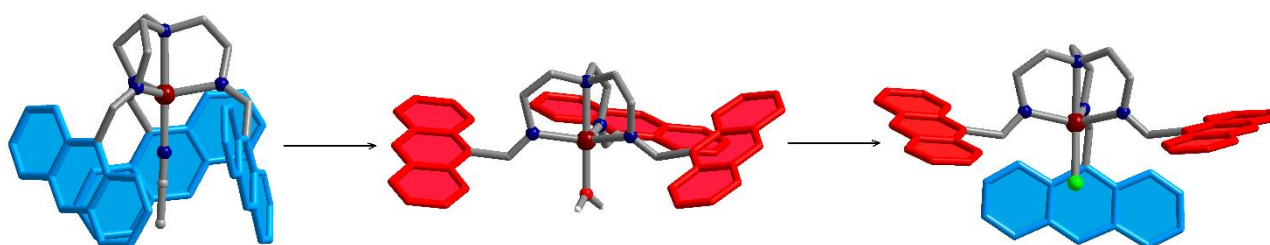


Figure 1 Conformational changes of a tripodal ligand in Zn(II) mononuclear complexes induced by the solvent coordinated to the metal ion or by halogen- π interactions

Polydentate imino ligands possessing pendant arms with extended π systems can be used for the sequential synthesis of heteroleptic complexes taking the advantage of π - π interactions established by the pendant arms with the secondary ligand.

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OC12

Versatile Coordination of Tridentate SPO Ligands

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Secondary phosphine oxides (SPOs) are a versatile class of ligands with a rich coordination chemistry and various applications in homogeneous catalysis.^{1,2} The literature, however, contains surprisingly few examples of multidentate SPO ligands.³⁻⁵

We have recently reported the tridentate, proximity-enforcing SPO ligand **1** (Figure 1). **1** was established as crystallographic benchmark for P–H bond lengths, as the results from X-ray data treated with Hirshfeld Atom Refinement were in good agreement with neutron diffraction.⁶ The small bite-angle ligand system proved suitable for the study of coordination modes and reactivities with various metals. Over a dozen closely related rhodium complexes, including intermediates, zwitterionic resting states, and side products were identified and studied by ³¹P-NMR spectroscopy and single crystal X-ray diffraction. For several complexes, we were able to obtain ¹⁰³Rh-NMR shifts.

Recent results include the Ru-SPO-catalysed bifunctional transfer hydrogenation and the coordination chemistry of various tridentate SPO ligands with group 6 metals Cr, Mo and W. For these metals, their coordination chemistry is dominated by their Lewis acidity, which in some cases led to dramatic results such as ligand decomposition and intramolecular rearrangement.

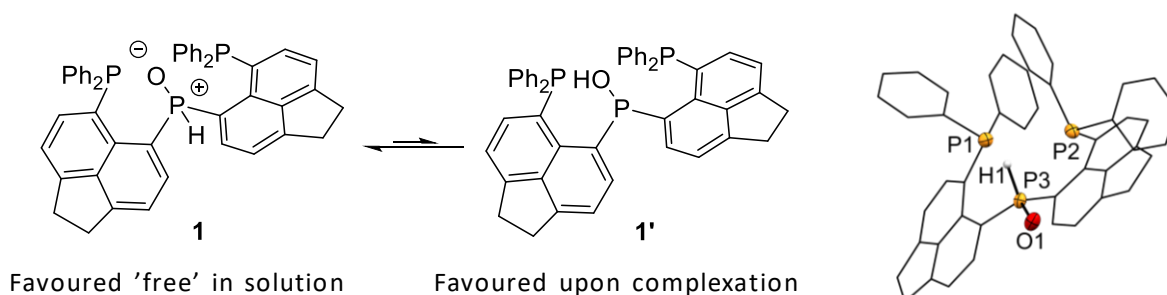


Figure 1 Equilibrium behaviour and crystal structure of the tridentate SPO **1**

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OC13

Modulation of chiroptical properties in Zn(II)-based amino acids helices

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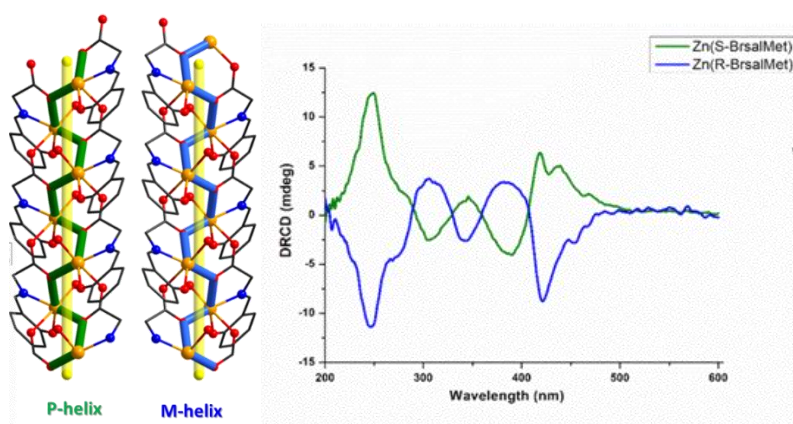
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Chirality plays a decisive, albeit low-profile role in various scientific disciplines, including chemistry, biology, and materials science. The modulation of the chiroptical properties is achieved by altering the optical activity of the involved chiral molecules through external stimuli such as light, temperature, electric/magnetic fields, and chemical environment.¹ This manipulation can lead to changes in the magnitude and/or direction of chiroptical responses and consequently offers new opportunities for controlling molecular chirality and designing functional materials with tunable optical properties. The most reliable strategy for introducing the chiral information into a metal ion-based network consists in employing an enantiomerically pure ligand. In this respect, the usage of natural amino acids is a straightforward and effective alternative.² The study to be presented focuses on a set of tridentate salicylaldimine-type ligands containing different halogen substituents of the aromatic ring. As highlights, we mention: (i) the supramolecular architectures of simple organic chiral Schiff base, (ii) the Zn(II) helices assembled by exploiting these organic compounds as ligands, (iii) their optical properties (UV-Vis, PL, CD, and CPL spectra).



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OC14

Organometallic chemistry (Li, Mg) in flow microreactors

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Miniaturized flow reactors involve the reaction of chemicals in motion inside tubes (or channels) of micrometer/millimeter diameter, without ever interrupting the reaction. The intrinsic characteristics of this technology make it possible to solve many problems encountered in chemical synthesis. Rapid mixing and efficient heat transfer are now well-established features of continuous flow reactors and they are often used for reactions sensitive to local stoichiometry, two-phase systems, highly exothermic and high-temperature processes with sensitive compounds.¹ These miniaturized reactors have the potential to solve both fundamental chemistry issues and safety problems, including in organometallic chemistry.² Thus, this presentation will describe the input of flow systems for the control of highly reactive organo-lithium and -magnesium species (flash chemistry)^{3,4} with applications in “halogen dance” control,⁵ synthesis of active pharmaceutical ingredient (anti-cancer drug Bortezomib)⁶ and neutralization of chemical warfare agents (sulfur mustard).⁷

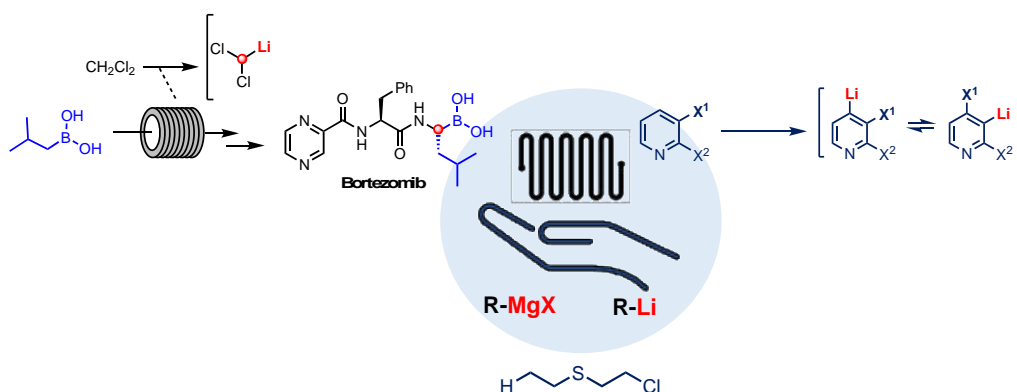


Figure 1 Applications of organo-lithium and -magnesium chemistry in miniaturised flow reactors

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Merging silicones/hydrocarbons within metal complexes. From crystals to soft matter and their applications

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Benefiting from their high flexibility, degrees of freedom, and conformational entropy, either silicones or hydrocarbons when merging with rigid structures affords various physical states of soft matter.¹ Among them can be listed liquid crystals, rubbery, and glassy states. The chemical coupling of silicones/hydrocarbons with metal complexes provides a unique combination of the aforementioned physical states with the properties of metal ions: magnetic, luminescence, and electric peculiarities.^{1,2} Herein, we present three classes of metal complexes from the perspective of soft matter and their particularities: siloxane-spaced metal complexes as liquid crystals, alkyl/trimethylsilyl-tailed dinuclear Au(II) complexes, and ionic liquids having AuCl₄⁻ counterion (**Figure 1**). A Co(II) complex belonging to the first class, which combines the anisotropic and flow features of nematic liquid crystals and the metal ion' magnetic susceptibility is explored as a magnetic actuator and a new type of ferronematic (**Figures 1b–1c**).²

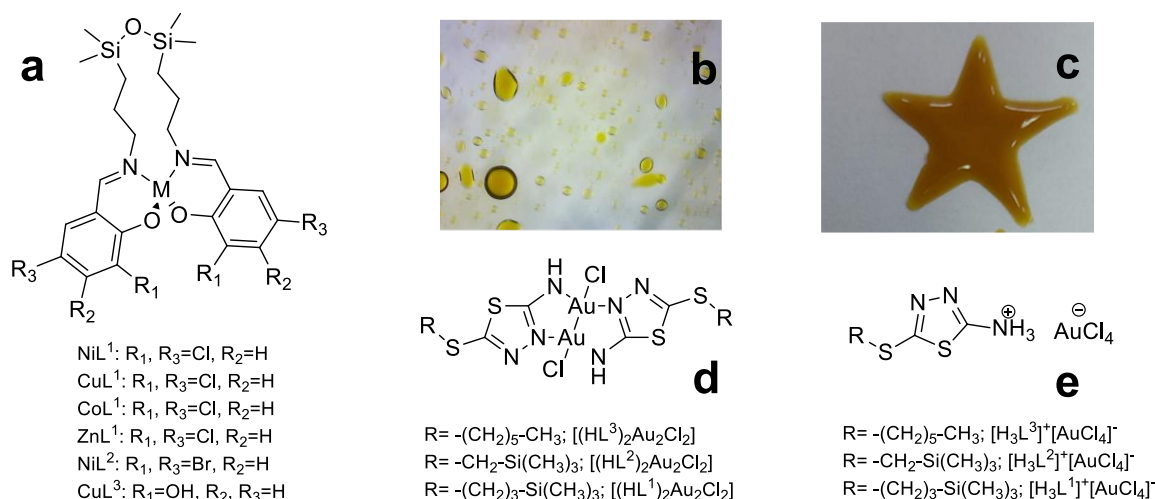


Figure 1 Siloxane-spaced metal complexes (a); nematic droplets (b) and a 3D printed magnetic actuator (c) of a Co(II) complex; dinuclear Au(II) complexes (d); ionic AuCl₄⁻ compounds (e)

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OC16

New electrode materials based on alloxazine derivatives

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Metal-Organic Frameworks (MOFs) are well known for their porosity and their properties for adsorbing gas, delivering drugs, or storing energy^[1]. We aim to propose new redox active core centered on their organic part of the MOFs, which will contribute to their electronic or ionic conductivities for energy storage devices. We focused on the use of Alloxazines, bio-inspired compounds, that are allowing the presence of three stable redox states^[2], the alloxazine motif promoted as ligand can be a promising candidate for synthesizing new redox active MOFs.

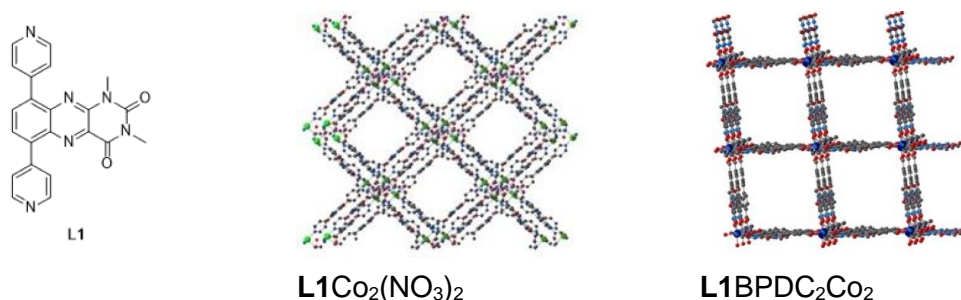


Figure 1 a) Redox active organic ligand containing an alloxazine core, b) Coordination polymers based on alloxazine core obtaining by the two component strategy c) MOFs based on alloxazine core obtaining by the three-components strategy (BPDC : 4,4'-BiPhenylDiCarboxylic acid)

We have successfully synthesized a large library of organic ligand favorizing the MOFs formation (**Figure 1a**), based on the alloxazine core. By combining them with a metal salt, coordination polymers containing the alloxazine core have been formed (**Figure 1b**). Then by using a three components strategy^[3] (by combining two different organic ligands and one metal salt) we obtained series of robust bi and tridimensional Metal Organic Frameworks (**Figure 1c**).

The physico-chemical and electrochemical properties of these new MOFs have been studied in the solid state. They present a certain porosity allowing them to adsorb and release gas. Some of them have been also used as electrode materials in ionic batteries.

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OC17

Green synthesis and applications of metal(II) coordination polymers based on bisphosphonates and imidazole ligands

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When organic pollutants (OPs) are present in higher quantities than allowed, both the environment and human health may be affected, making it essential to clean out contaminants from wastewater before releasing them. This work reports on the green synthesis of metal (II) coordination polymers (CP) from phosphonates or mixed imidazole ligands and phosphonates, which are obtained by reacting 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), imidazole and divalent metal salts (Zn^{2+} , Co^{2+} , or Ni^{2+}) under differed hydrothermal conditions, followed by green application as adsorbent materials¹ or electrocatalyst².

Imidazolium base ionic liquids, namely 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium nitrate, 1-butyl-3-methylimidazolium chloride, and 1-hexyl-3-methyl-imidazolium chloride, were used to modify CPs and to form (ILs@CPs) composite materials, which retain the structural characteristics of CPs, and add the advantages of ILs as adjustable physical and chemical properties. The ILs@CP composites are used as adsorbent materials for phenol derivatives, i.e., 2,6-dimethylphenol and 4,4'-dihydroxybiphenyl. The adsorption employs batch-type experiments to investigate the impact of various factors, including pH of the solution, solid:liquid ratio, initial concentration of organic pollutants, and contact time, on the efficiency of adsorption. Several empirical isotherms, including Langmuir, Freundlich, and Dubinin–Radushkevich³ isotherms, were used to determine the maximum adsorption capacity of the studied materials. The characteristic parameters for each isotherm and the correlation coefficient (R^2) have been identified. The examined ILs@CPs adsorption capabilities were enhanced by the ILs modification of CPs⁴.

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OC18

Geminal dianions : versatile ligands for polymetallic organoiron complexes

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The interest for carbon-based ligand for polymetallic iron assemblies has been renewed by the elucidation of the nature of the central atom in nitrogenase cofactors, namely FeMo-co clusters. Since the establishment of its carbide nature,¹ numerous mimics have been proposed in recent times.² In this variety of structures, scarce are the examples in which both carbon-iron and sulfur-iron interactions are present, requiring sophisticated ligand design. We propose to use the readily accessible bis(dimethylthiophosphinoyl)methanediide as a convenient and versatile ligand for the building of polyiron assemblies, in which iron-carbon and iron-sulfur interactions are maintained regardless of number of metallic centers or their redox state.³ Recent exploration of their reactivity toward small molecules will also be evocated.

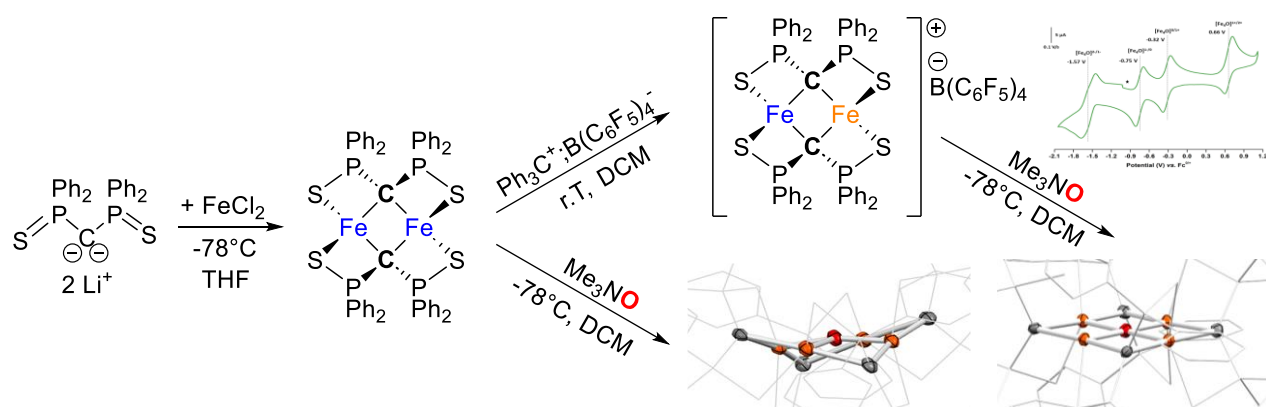


Figure 1 Evolutionary family of polymetallic organoiron complexes, where S-Fe and C-Fe are maintained upon redox and structural changes

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OC19

Tetravalent cerium coordination: Understanding the L₃-edge X-ray absorption structure in organocerium complexes

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The electronic structure of organocerium^{IV} complexes has been plagued by misinterpretations ever since the race to stabilize such compounds began in the '70s.¹ This is because charge transfer into the metal 4f⁰5d⁰ configuration results in a significant 4f population (n_f) resembling that of genuine trivalent cerium. In laboratory studies, fitting of the two-peak Ce L₃ X-ray absorption structure (XAS) provides n_f between 0.5–0.9 electrons for a variety of formally tetravalent cases. Analogies with the ambiguous cases of Ce(C₈H₈)₂ and CeO₂, enabled their classification as complexes with a mixed-valence or intermediate-valence (multiconfigurational) ground state (GS).²

Recently, we have established the use of multiconfiguration wavefunction approaches as the most adequate route to calculate and rationalize XAS structures in relation to GS bonding in complexes of the f-elements.^{3,4} Initial efforts resolved the two-peak Ce L₃ XAS puzzle of Ce(C₈H₈)₂ and CeO₂ after decades of trials.⁵ If the Ce L₃-edge structure indeed reproduces the intermediate valence character of the GS for Ce(C₈H₈)₂, this is not true for the CeO₂ case with a covalently-bonded single-configuration GS. This time, the L₃-edge structure represents the multiconfigurational character of the probed core ESs. We have now designed an even simpler computational protocol, based on accurate coupled-cluster and time-dependent density functional theory runs, to calculate the Ce L₃-edge structure and rationalize the GS metal-ligand bonding even in large and unsymmetric complexes of tetravalent cerium. This contribution showcases the protocol, demonstrating that the tetrakis(tropolonate) and tetrakis(acetylacetonate) complexes of cerium, Ce(trop)₄ and Ce(acac)₄, were mischaracterized² as cases where the cerium-ligand bonding results in intermediate valence or multiconfigurational GSs.

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The design of homo- and hetero-di-radicals as ligands for the synthesis of 3d and 4f complexes

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Paramagnetic ligands containing two identical or different radical moieties ($S = 1$) play an important role in molecular magnetism.^{1,2} The nitronyl nitroxide, 2-(2-hydroxy-3-formyl-5-methylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (HL), due to its available carbonyl unit, was used to generate homo- and hetero-di-radicals via Schiff condensation. For example, HL was condensed with 1,3-diaminopropane and 4-amino-TEMPO to generate the paramagnetic ligands H₂L¹ and HL². Both ligands have been reacted with hexafluoroacetylacetonato complexes of 3d and 4f metal ions generating mono- (Figure 1), and dinuclear complexes with different spin topologies. Their similarities and differences have been investigated. The (pseudo-)polymorphism is present in the case of [M(HL²)(hfac)₂], where M = Mn, Co, Ni, Zn, and [Yb₂(H₂L¹)(hfac)₆]. The crystal structure of [Ni(HL²)(hfac)₂] presents channels with 1 nm diameter.

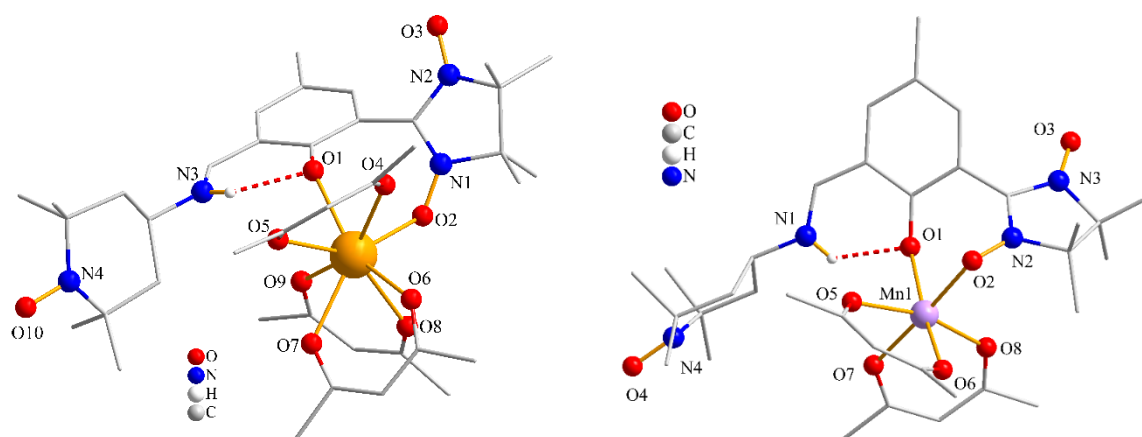


Figure 1 Perspective views of the crystal structures of [Gd(HL²)(hfac)₃] (left) and [Mn(HL²)(hfac)₂] (right). A part of the hydrogen atoms and all fluorine atoms were removed for clarity.

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OC21

Organochalcogen compounds and their metal complexes. Synthesis, structure and potential applications

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Organoselenium compounds continue to attract a significant interest as valuable candidates in medicinal chemistry,¹ catalysis and organic synthesis,² or as key species for optoelectronic devices.³ A special attention was paid during last years to derivatives bearing organic groups with nitrogen or oxygen donor atoms, showing an increased thermal and hydrolytic stability and enhanced specific properties.

Our recent studies were focused on new classes of diorganodichalcogenides or homo- and heteroleptic diorganochalcogen(II) compounds bearing organic groups with N or O donor atoms, as well as on their main group or late *d* metal complexes.

We report here about compounds of type R_2Se_2 and R^1R^2E ($E = S, Se$), where $R^1, R^2 = 2-XC_6H_4CH_2$ ($X = Br, Me$), $2-(R_2NCH_2)C_6H_4$ [$R = Me, Et; R_2 = (CH_2CH_2)_2O$], CH_2CH_2pz ($pz =$ pyrazole), CH_2Phtz ($Phtz =$ phenylthiazole), as well as upon several pyridine based derivatives bearing pendant arms with donor atoms.

Their coordination behavior towards main group (Sn, Sb) and late *d* metals (Cu, Ag, Au, Zn, Cd) is discussed. Selected compounds were investigated for their biological properties, *e.g.* antiproliferative or antioxidant activity, as appropriate. Optical properties of selected metal complexes and of the corresponding free ligands are also presented.

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OC22

A double hydrophilic copolymer as versatile scaffold for the incorporation of inorganic matter

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In various processes such as crystallization, catalysis, or biomedical applications, structures where inorganic matter is assembled within confined spaces hold particular interest. Block copolymers, consisting of two or more chemically different polymer segments, covalently connected, are a very popular platform for designing this kind of hybrid (organic/inorganic) materials. Among, double hydrophilic block copolymers (DHBCs) have unique advantages for the design, for example, of vectors incorporating either metallic ions or inorganic nanoparticles. Typically, one of the blocks which is ionizable can interact with polyvalent metal ions, spontaneously inducing self-assembly of the copolymer into micelle structures and encapsulation of metal ions into the core, through multiple electrostatic interactions, while the second non-ionizable block forms the shell of micelles in contact with the exterior medium. Inversely, if the nonionizable block is the interacting block, with for example inorganic nanoparticles their assembly could be triggered by an external stimulus like the pH.

I will report on the interaction of the poly(acrylic acid)-*block*-poly(*N*-vinyl-2-pyrrolidone) (PAA-*b*-PVP) DHBCs with lanthanide ions (Gd^{3+} , Eu^{3+} , Y^{3+}) and with gold nanoparticles (AuNPs). Their characterization, mechanism of formation and some applications as contrast agent will be described.

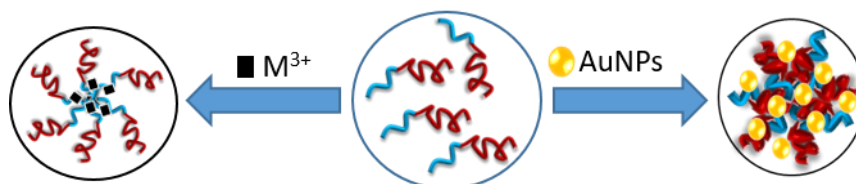


Figure 1 Schematic representation of the formulation of hybrid assemblies

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OC23

Metallomesogens as modifiers of carbon-based electrodes in electrochemical sensing

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Metallomesogens (MMs) are functional materials that were proposed mainly in electrooptics for obtaining polarized emission.[1-2] However, their main drawbacks, respectively high viscosities in the mesophase and poor thermal stabilities reduced lately the interests in this fields.

The combination of MMs properties derived from liquid crystals (order and mobility, anisotropy of properties, self-healing, etc.) and the presence of metal centers (optical, magnetic, redox, etc.) may be exploited also in non-enzymatic electrochemical sensing. Herein, we will present new paste-electrodes based on nanostructured carbon modified with MMs for detection of bioanalytes in human serum. The order and mutual disposition of the metal centers is controlled by the symmetry of the mesophase. The molecular structure-supramolecular structure-electrochemical performance of electrodes modified with Cu(I), Cu(II) or Zn(II) MMs is presented.[3]

Finally, we exploited the miscibility property of iso-structural MMs whose chemical structures are presented in Figure 1 to obtain by mechanical mixing bimetallic homogeneous materials with liquid crystalline supramolecular order. The new bimetallic materials were used as modifiers for carbon-based paste electrodes for performant detection of glucose from human serum, avoiding interference from uric acid.

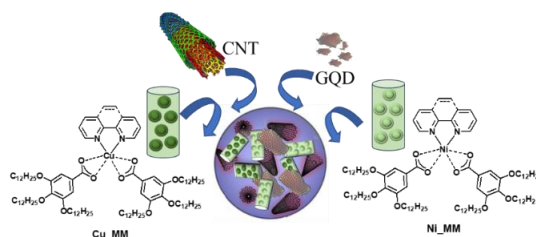


Figure 1 Hybrid paste electrode for non-enzymatic electrochemical sensing of glucose.

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OC24

Cooperative spin crossover dinuclear Fe(II) complex

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The Spin-crossover (SCO) materials, based on the first-row transition metal complexes with $3d^4$ - $3d^7$ electronic configurations that can switch reversibly between high-spin (HS) and low-spin (LS) states, represent one of the most attractive systems of switchable molecular solids.¹⁻³ More specifically, in Fe(II) metal complexes involving pseudo-octahedral FeN_6 coordination spheres, the spin transition that can be induced by different external stimuli such as temperature, pressure, and light irradiation, occurs between the HS ($S=2$, $^5T_{2g}$) and LS (LS ; $S=0$, $^1A_{1g}$) states,¹⁻⁵ for which the associated magnetic and optical changes can be considered for various potential applications such as memory, sensors, Organic Light-Emitting Diode (OLED), or displays⁶⁻⁸

Here we present, a new iron(II) binuclear complex of formula $[Fe_2(C_5H_9-trz)_5(tcm)_4]$ (C_5H_9-trz = 4-cyclopentyl-1,2,4-triazole, tcm^- = tricyanomethanide), characterized by single crystal X-ray diffraction, *differential scanning calorimetry* (DSC) and magnetic measurements. The crystal structure of binuclear complex revealed, three bidentate ligands bridged by through N1 and N2 of the 1,2,4-triazole. The octahedral coordination sphere around each iron atom is completed by two tricyanomethanide anions and one monodentate 1,2,4-triazole ligand. The magnetic and DSC studies reveal an abrupt High Spin (HS) \leftrightarrow Low Spin (LS) transition with a hysteresis loop of 10 K ($T_{1/2} \approx 201 \downarrow$ K; $T_{1/2} \approx 210 \uparrow$ K).

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Lanthanide-based coordination polymers : recent advances on their shaping

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Over the past 20 years, our group is interested in research on lanthanide-based coordination polymers, for their interesting optical properties, making them relevant for many applications such as anti-counterfeiting markers.^[1] These compounds are made of metallic ions connected by organic ligands such as 1,4-benzene-dicarboxylate. The obtained polymers can be mono-, bi- or three-dimensional networks. For several years, we used to synthesize molecular alloys based on the similarities between the chemical properties of the lanthanides.^[2] On one hand, those compounds have the particularity to have the same crystal structure but different color of emission. On the other hand, there are significant intermetallic transfers between rare-earth ions due to their random distribution and their proximity, resulting in reduced luminescence intensity. To avoid this phenomenon, we synthesized some core-shell particles, allowing us to reduce the intermetallic transfer at the interface between the core and the shell.^[3] Based on recent thermodynamic studies,^[4] it is now possible to predict with more precisions, what it the best shaping for the core-shell compounds that we are studying in the group (Figure 1). Here, we propose to describe our recent advances on lanthanide-based coordination polymers shaping.

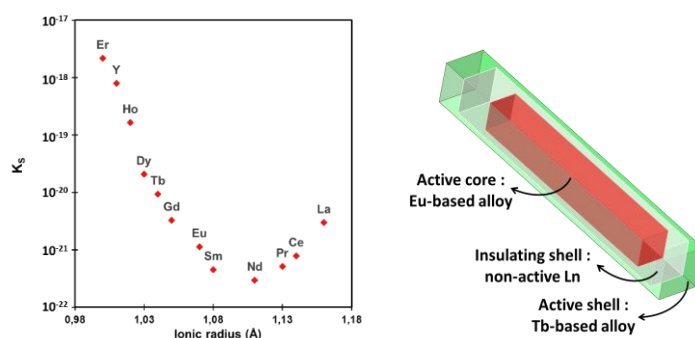


Figure 1 Left: Solubility product of homonuclear lanthanide-based coordination polymer $[\text{Ln}_2(\text{bdc})_3(\text{H}_2\text{O})_4]_\infty$ with Ln = La-Er plus Y and bdc = 1,4-benzene-dicarboxylate ligand, Right: optimized shaping of an emissive core-shell particle with terbium and europium.

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OC26

Light-responsive arene-Ru(II) complexes derived from azobenzene for the control of chemical reactivity

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With the aim to prepare novel light-responsive systems able to control chemical transformations,^{1,2} we have investigated the coordination behavior of azobispyridine and sulfonamide azobenzene (pro)ligands towards arene-Ru(II) centers. Depending on structural features in proximity to the N=N bond and metal atom, complexes showing a variety of coordination patterns were obtained, exhibiting distinct photochemical behavior.^{3,4,5,6} The synthesis, properties and utilization of these complexes in the context of the control of chemical reactivity with light will be presented.

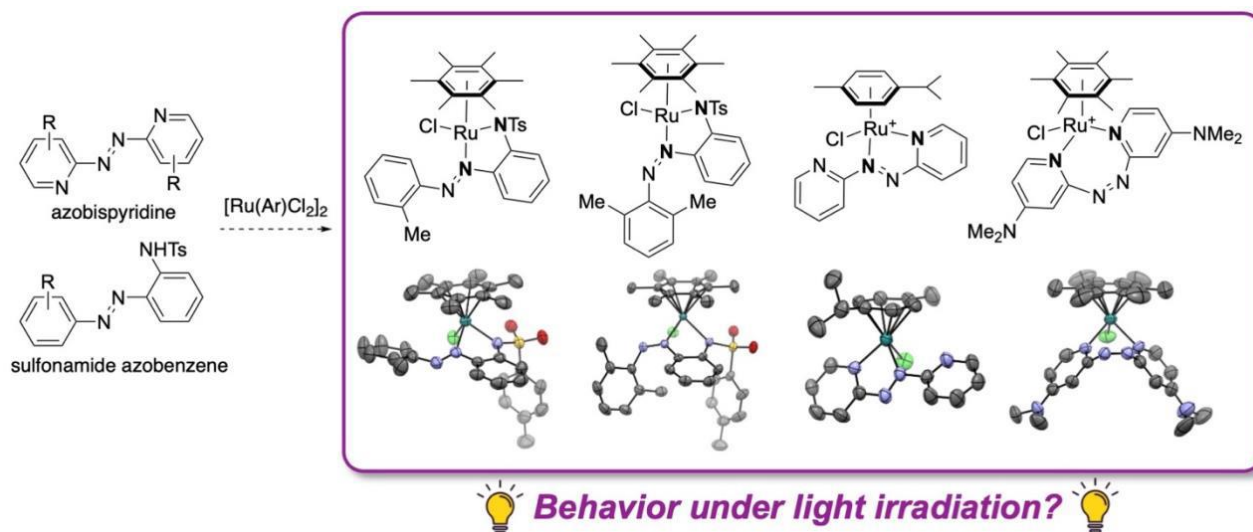


Figure 1 Overview of the light-responsive azobenzene-derived arene-Ru(II) complexes synthesized and studied

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OC27

A novel approach for accessing alkyl and arylcalciums

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Alkali and alkaline earth metal compounds are two of the most widely used classes of polar organometallic reagents, due to their high nucleophilicity and Brønsted basicity. While organomagnesium and organolithium compounds are the most popular species of these classes, organic derivatives of calcium have advanced rapidly during the past decades¹. However, the development of calcium catalysts has lagged behind due to the lack of alkyl and hydrido complexes, which are the best candidates for catalysis. The high reactivity and ensuing problems, as well as deficiency of synthesis protocols, precursors, and the solubility issues, have largely hampered the development of the organocalcium chemistry.

Despite these challenges, the synthesis of alkylcalcium was recently achieved, albeit being a real challenge due to their high reactivity towards common solvents such as THF. Building on Harder's work, Anwander's group made a significant contribution to this issue by synthesizing and elucidating dimethylcalcium.² The preparation was achieved by metal exchange between Methyllithium and $\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$ in diethylether. The resulting crystal was found to have a high stability in polar ethereal solvent, such as THF, under low temperature conditions.

In this communication, we will present a new innovative pathway for accessing alkylcalciums in polar solvents and its broader applicability for the preparation of arylcalciums.

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Mo₂O₂S₂-thiosemicarbazone complexes: Electrocatalysis, Mo-polyurethanes and Supramolecular chemistry

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The molybdenum (Mo) is an important element found in many enzymes catalyzing different transfer reactions. In Versailles we are interested in developing chemistry based on the cluster [Mo₂O₂S₂]²⁺ combined either with polyoxometalates¹ or with organic ligands², to give original supramolecular assemblies, complexes actives for HER or complexes with various biological activities. In particular, we are exploring coordination chemistry of [Mo₂O₂S₂]²⁺-TS (TS = thiosemicarbazones) complexes showing interesting biological and electrocatalytic properties coming from both intrinsic components and also shaping of these complexes into polymer matrix for potential applications (**Figure 1**).³ In this presentation we are going to speak about (i) [Mo₂O₂S₂]²⁺-TS complexes as efficient and stables electrocatalysts for the HER, (ii) control of supramolecular chemistry of [Mo₂O₂S₂]²⁺-TS assembles and (iii) shaping of the complexes into polyurethane matrix leading to the different ordered polymer composites.

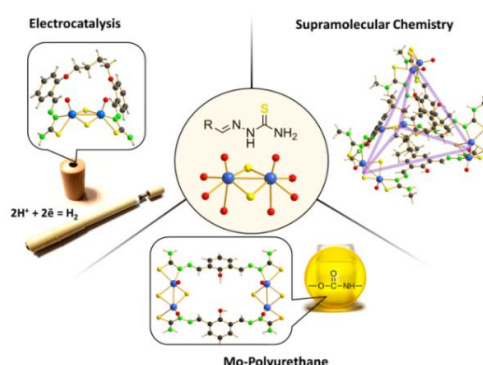


Figure 1 Electrocatalysis, supramolecular chemistry and embedding into polymer matrix of Mo₂O₂S₂-thiosemicarbazones based complexes.

1. E. Cadot, M. N. Sokolov, V. P. Fedin, C. Simonnet-Jégat, S. Floquet, F. Sécheresse, *Chem. Soc. Rev.* **2012**, *41*, 7335.

2. A. Fuior, *J. Inorg. Biochem.*, **2022**, 111627.

3 (a) D. Cebotari et al. *Dalton Trans.*, **2023**, 52, 3059; (b) A. Fuior et al. *ACS Omega*, **2022**, *7*, 16547; (c) D. Cebotari et al. *J. Inorg. Biochem.*, **2023**, *245*, 112258.

Posters

PO1

Catalytic utilization of converter gas – an industrial waste for the synthesis of pharmaceuticals

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Converter gas is one of the largest waste products of the steel industry¹. Millions of tons of converter gas formed are being burned producing significant amounts of carbon dioxide waste². Therefore, it is highly desirable not to burn converter gas but rather to apply it in the chemical industry for the synthesis of valuable products. In this work we address this challenge and demonstrate that converter gas can be used as a reducing agent for the production of a variety of pharmaceuticals in such two major chemical processes as amination and amidation using simple and easily available air-stable coordination compounds $\text{Rh}_2(\text{OAc})_4$, $[(\text{cymene})\text{RuCl}_2]_2$ or $[(\eta^4\text{-cyclooctadiene})\text{Rh}(\eta^6\text{-2,3,6,7-tetramethoxy-9,10-dimethylanthracene})]\text{BF}_4$ ³.

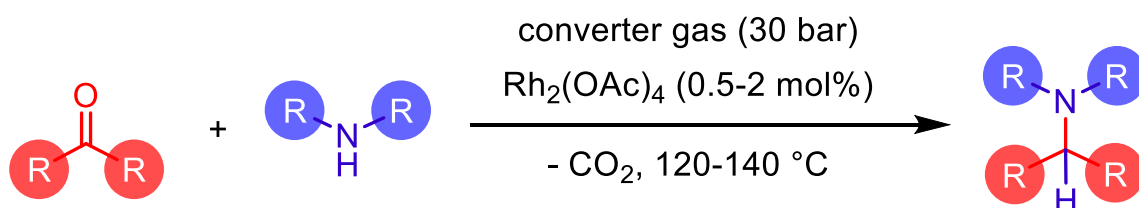


Figure 1 Catalytic reductive aminations using converter gas

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³ S.A. Runikhina, O.I. Afanasyev, E.A. Kuchuk, D.S. Perekalin, R.V. Jagadeesh, M. Beller and D. Chusov, *Chem. Sci.*, **2023**, *14*, 4346.

Heterodispin 2p-3d and heterotrispin 2p-3d-4f complexes derived from nitronyl nitroxide ligands obtained from nitro-*o*-vanillin and bisphenol A

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Heterospin complexes may be synthesized using stable and persistent organic radicals as ligands and metal ions.¹ The nitronyl nitroxide organic radical derived from nitro-*o*-vanillin and 3d (Mn, Co, Ni, Zn) and 4f (Gd, Tb, Dy) metals ions led to 2p-3d and 2p-3d-4f heterospin complexes while the radical derived from bisphenol A with 3d (Co, Ni) metal ions led to 2p-3d heterospin complexes.^{2,3} The structures of the new compounds have been solved by single-crystal x-ray diffraction and investigated by X-ray powder diffraction, elemental analysis, and spectroscopic techniques (IR, UV-Vis). The cryomagnetic studies have revealed a strong magnetic interaction within the molecules, results which are sustained by theoretical DFT calculations.

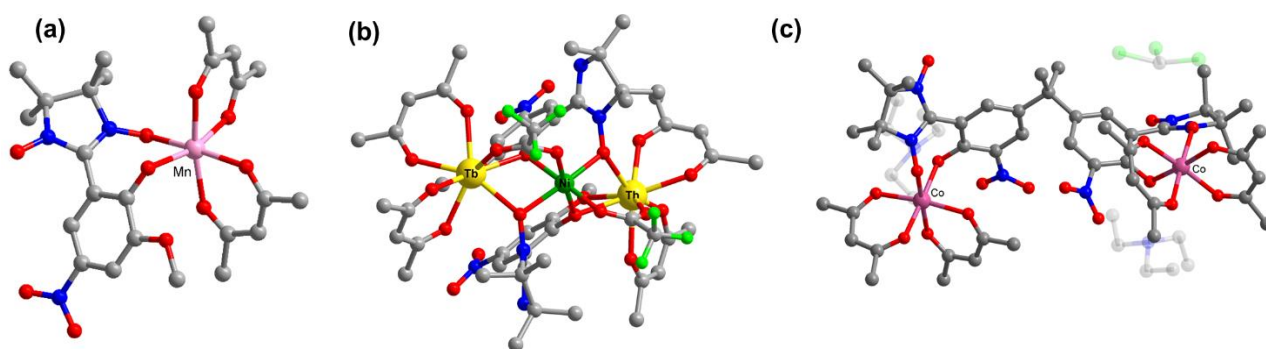


Figure 1 Molecular structure of (a), (b) 2p-3d heterodispin and (c) 2p-3d-4f heterotrispin complex

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2 M. Zhu, L. Li, J.-P. Sutter, *Inorg. Chem. Front.*, **2016**, 3, 994.

3 C. A. Spinu, C. Pichon, G. Ionita, T. Mocanu, S. Calancea, M. Raduca, J.-P. Sutter, M. Hillebrand, M. Andruh, *J. Coord. Chem.*, **2021**, 74, 1-3, 279.

PO3

Diketopyrrolopyrrole decorated with hetero-[7]helicene

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Dithia-[7]helicene have been formed on the thiophene-diketopyrrolopyrrole fused with a thiophene unit by C-H activation cross coupling with 2-bromo-3,3'-bisnaphthothiophene. Dithia[7]helicene is known to give stable stereoisomers.⁽¹⁾ This chromophores have been designed to ensure high molar absorptivity (due to DPP) and high expression of chirality (due to dithia-[7]helicene) in order to induce strong optoelectronic and chiroptical properties. The racemic mixture of dithia[7]helicene-diketopyrrolopyrrole is reported in here together with its characterization by spectroscopy.

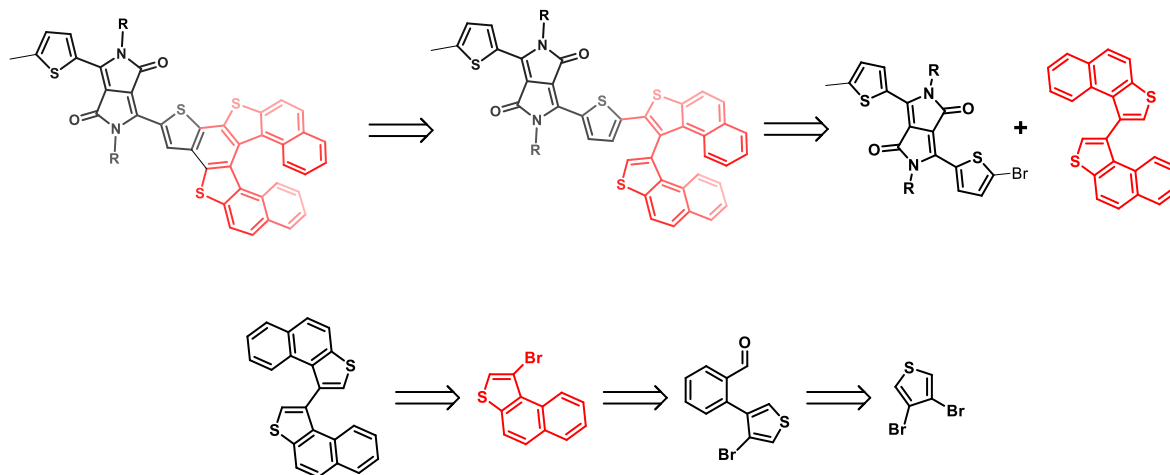


Figure 1 Retrosynthetic scheme to the main target compound

Electrochemical aptasensor for the detection of *Staphylococcus aureus*

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A major issue around the globe concerns the spread of highly resistant bacteria to the available antibiotherapy, such as *Staphylococcus aureus* (*S. aureus*), and its methicillin-resistant variant (MRSA). A useful strategy for the healthcare systems in the fight against the increasing antimicrobial resistance is the rapid and sensitive detection of the pathogens, using faster analytical techniques compared to conventional ones^[1]. Targeting the virulence factors produced by *S.aureus* (the surface component – protein A), this study aimed to develop an electrochemical biosensor to detect the presence of the bacteria in both spiked and real culture and serum samples. The biosensor was developed on a gold screen-printed electrode (AuSPE), on which the specific aptamer for protein A was immobilized via multipulse amperometry (MPA)^[2], the remaining unbound sites were blocked via MPA, using an agent containing a SH-group and the target, protein A, was incubated in time. After each step, the electrode surface was analyzed using differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). The MPA immobilization of the aptamer to the AuSPE was optimized. Various blocking agents were tested and also different methods of blocking the SPE surface. The incubation of protein A was also optimized, choosing the most convenient time. The aptasensor proved a good sensitivity across a wide linear range from 25 nM to 1000 nM, with a limit of detection (LOD) of 8.33 nM in standard solutions of the target and showcased high selectivity towards PrA against other tested proteins. Moreover, *S. aureus* was detected in commercial human serum and culture samples displaying a good correlation of the signal and the number of bacteria colonies.

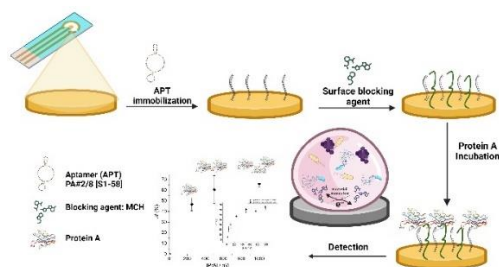


Figure 1. Steps in the development and testing of the aptasensor

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PO5

On The Way to Dibutylcalcium

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Alkyl derivatives of the heavier alkaline earth metals have gained increasing attention over the past decade.¹ Of particular interest in recent years was the study of Ca–C bond and finding new methods of accessing highly reactive species for the wider implantation in organosynthesis and for catalytic applications, yet stable enough to be isolated and manipulated. Whereas in the case of Mg the lighter congener, examples of simple alkyl derivatives are well established, *i.e.* *n*-butylmagnesium halides and di(*n*-butyl)magnesium,² similar species are still elusive for the heavier metals Ca, Sr and Ba. In 1991, Lappert and co-workers reported the first dialkylcalcium, [Ca{CH(SiMe₃)₂}₂·(1,4-dioxane)₂].³ Later, the bulkier, non-solvated [Ca{C(SiMe₃)₃}₂] was described in 1997.⁴ Hill reported the structure of [Ca{CH(SiMe₃)₂}₂·(thf)₂], and that of its strontium and barium analogues, in 2008.⁵ Just recently, Anwander and co-workers disclosed the complete authentication of [CaMe₂]_∞, obtained by treatment of the dimeric [Ca{N(SiMe₃)₂}₂]₂ with halide-free methyllithium.⁶ One very notable absence from this list of calcium alkyls is di(*n*-butyl)calcium.

We describe herein the outcome of our attempts at preparing calcium di(*n*-butyl) by reaction of [Ca{N(SiMe₃)₂}₂]₂ or [Ca{N(SiMe₃)₂}₂·(thf)₂] with various amounts of *n*-BuLi. In the course of this work, we have also been led to investigate the formation, structural features and reactivity of several heterobimetallic calcium-alkali amides.

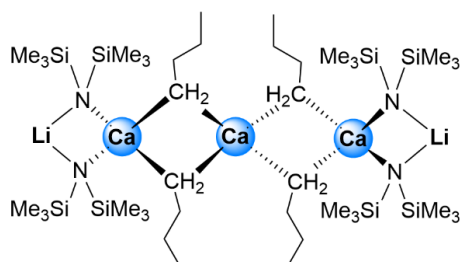


Figure 1. New Ca–alkyl species

1 M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.*, **2016**, *45*, 972.

2 D. Seyferth, *Organometallics*, **2009**, *28*, 1598.

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4 C. Eaborn and P. B. Hitchcock, *Chem. Commun.*, **1997**, 1961.

5 M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon, P. A. Procopiou, *Chem. – Eur. J.*, **2008**, *14*, 11292.

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PO6

An original synthetic approach leading to heterometallic 4f-4f complexes

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Homonuclear lanthanide complexes are known for their interesting magnetic and luminescent properties^{1,2}, which result from the electronic configuration of 4f metal ions. Additionally, using two different lanthanides in a single complex, these properties can be enhanced³. However, the synthesis of genuine pure heterometallic 4f-4f complexes represents a real challenge because of the similarity of the lanthanide ions, which can lead to statistical mixtures of compounds. An efficient strategy for obtaining 4f-4f complexes relies on the employment of the lanthanides with different ionic radii and on asymmetric ligands (with small and large compartments).

In this work, we report a novel family of octanuclear complexes [Ln₄Ln'₄], which are assembled using a Schiff base ligand (H₄L¹) obtained from the condensation of 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde with 1,8-diamino-3,6-dioxaoctane: [Ln₄Yb₄(L¹)₂(HL¹)₂(NO₃)₈(X)(Y)(μ₄-O)], where Ln = La(1), Nd(2), Sm(3), Eu(4), and X=Y=MeOH and/or H₂O. If the Schiff-base ligand (H₄L²) is derived from 2,3-dihydroxybenzaldehyde and 1,8-diamino-3,6-dioxaoctane, the following complexes have been synthesized: [Ln_(4-x)Yb₄L_(4-x)(H₂L²)_x(NO₃)₄(CH₃COO)_(4-x)(μ-H₂O)], where Ln = Pr(5), Nd(6) and x = 0.72 (5), 0.56 (6). All complexes have been characterized by single crystal X-ray diffraction, mass spectrometry, UV-VIS and IR spectroscopy.

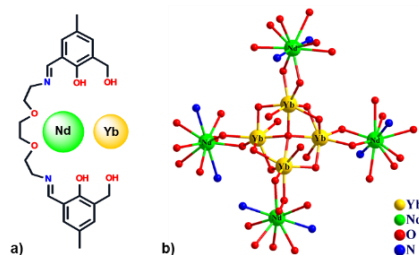


Figure 1 a) Schematic representation of the H₄L¹; b) View of the central cluster core of **2**

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3 D. Aguilà, G. Aromí et al., *J. Am. Chem. Soc.*, **2014**, 136, 14215.

Phosphorescent Soft Salts Based on cyclometalated Platinum(II) Complexes: Synthesis, Characterization, Photophysical Properties and Response to External Stimuli

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Luminescent materials exhibiting reversible change of their optical properties under different external stimuli have huge application potentials in various optoelectronic fields. Thus, small molecules, metal complexes, and polymers have been developed as materials with photochromic, mechanochromic, vapochromic, electrochromic, and thermochromic properties. Due to their high photoluminescence quantum yields (PLQY), remarkable stimuli, platinum (II) complexes are potential candidates for constructing luminescent materials.¹ Among them, soft salts based on ion-paired cyclometalated platinum (II) complexes are attracting increasing interest as potential candidates for the construction of stimulus-responsive luminescent materials. These complex salts (S1) showed original properties due to Pt(II)···Pt(II) and π - π stacking interactions between anionic (A1) and cationic (C1) complexes enabling selective responses to various external stimuli by accurately regulating various intermolecular interactions.² In this communication, we will present the synthesis of a series of soft salts based on two oppositely charged cyclometalated platinum complexes **S1-9** ($[\text{Pt}(\text{C}^{\wedge}\text{N})\text{ed}]^+[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{CN})_2]^-$). Appropriate combination of cationic and anionic components allows tuning the photoluminescence properties of the formed salts. Our approach was to investigate the structure-property relationships within a class of Pt(II) soft salts bearing modified C[∧]N ligands. The structure-property relationships were highlighted by a comparative study of the photophysical properties of this class of salt (PLQY, AIEE, etc.). To demonstrate the potential materials for anti-counterfeiting applications of these soft salt complexes, vapochromism studies have been successfully explored.

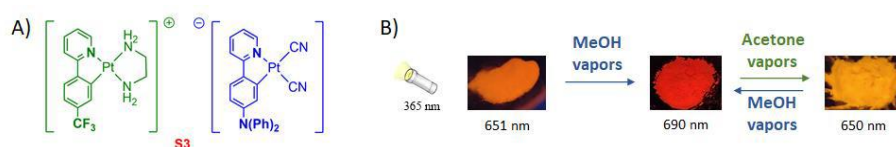
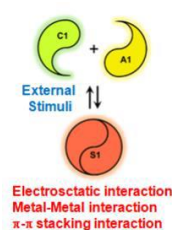


Figure 1 A) Structure of **S3**; B) Vapochromic behavior of **S3** in the solid state (KBr powder with 1% wt of soft salt). Pictures were taken in the dark upon irradiation with a handheld UV lamp ($\lambda_{em} = 365 \text{ nm}$)

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Heterotriscin $2p$ - $3d$ - $4f$ complexes with nitronyl-nitroxide radicals

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Heterospin complexes containing three different paramagnetic centers are of high interest in molecular magnetism.¹ Such complexes are still rare due to the synthetic difficulties that must be overcome by chemists. In this work we present heterotriscin complexes containing two different paramagnetic metal ions and nitronyl-nitroxide paramagnetic organic radicals.

The nitronyl-nitroxide radicals played a very important role in the history of molecular magnetism.² We recently described a novel family of end-off bicompartamental ligands bearing a nitronyl-nitroxide arm, which are very useful in designing various heterospin molecular systems. These ligands can selectively interact with $3d$ and $4f$ metal ions, leading to $2p$ - $4f$, $2p$ - $3d$, and $2p$ - $3d$ - $4f$ complexes.³ By employing new chiral nitronyl-nitroxide radicals, we obtained a $2p$ - $3d$ - $4f$ heterotriscin structural prototype, having the radical as a bridge between $3d$ and $4f$ metal ions through only one O atom, creating a direct connectivity through the three different spin carriers. The CoDy-R(+)_{rad} complex exhibits a high blocking temperature of 28 K (Figure 1).⁴

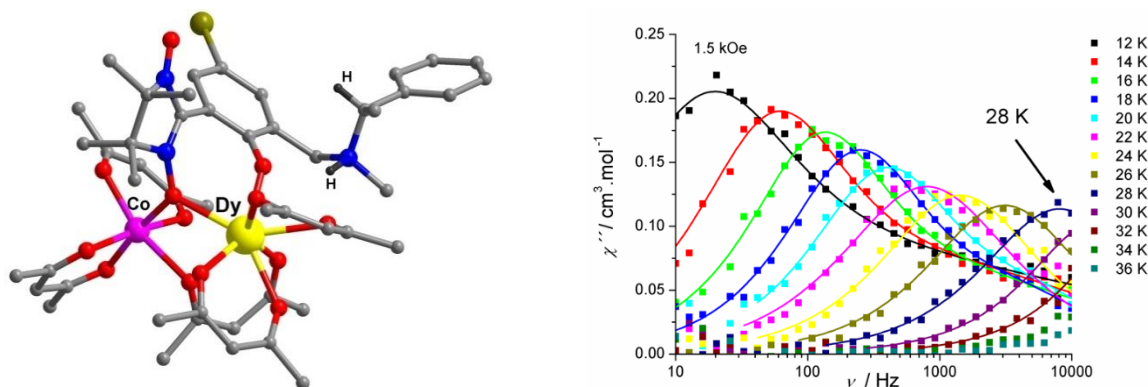


Figure 1. Perspective view of CoDy-R(+)_{rad} compound and the frequency dependence of the out-of-phase ac magnetic susceptibility χ''

1 M. Andruh, *Chem. Commun.*, **2018**, 54, 3559.

2 A. S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.*, **2015**, 289-290, 149.

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4 A. A. Patrascu, M. Briganti, S. Soriano, S. Calancea, R. A. Allão Cassaro, F. Totti, M. G. F. Vaz, M. Andruh., *Inorg. Chem.*, **2019**, 58, 13090.

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Iron-catalyzed Hydrosilylation of Secondary Carboxamides for a Chemoselective Preparation to Aldimines

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This contribution described the first iron-catalyzed chemoselective reduction of secondary carboxamides to aldimines under hydrosilylation conditions as (figure 1).^[1]

Indeed, imines are key intermediates in molecular chemistry and can exhibit potent anti-microbial, anti-malarial or anti-bacterial activities. Among their numerous preparations,^[2] the chemoselective reduction of carboxamides is one of the direct valuable one. In this area, the selectivity could be seen as one of the most challenging issues, owing to (i) the high stability of carboxamides making them less reactive with hydride species, the most common metallic hydride reagents used being aluminium and boron hydride reagents,^[3] (ii) the chemoselective issues (C-O vs C-N bond cleavages), and (iii) the possibility of performing over reductions, thus leading to amines.

Based on our recent contributions involving iron-catalyzed reduction of carboxylic derivatives,^[4] the selective reductions of secondary carboxamides was performed *via* a catalyzed hydrosilylation using $\text{Fe}(\text{CO})_4(\text{IMes})$, diphenylsilane as the reductant under UV irradiation (350 nm) at room temperature for 16 h. Aldimines were then obtained, after a basic quench, in 32–95 % isolated yields.

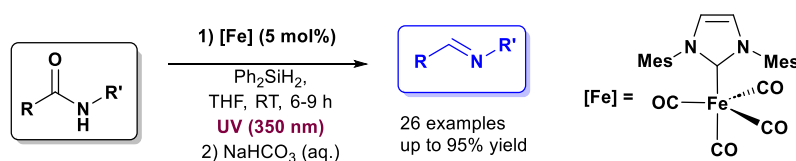


Figure 1 Selective reduction of secondary carboxamides to aldimines

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PO10

Formation of Sn-O bonds: novel organotin(IV) alkoxides and siloxides

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Organotin(IV) species containing Sn-OR bonds (alkoxides) or Sn-OSiR₃ bonds (siloxides) have mostly been studied in the last decades, and they are known for their biological activity¹ as well as precursors for hybrid organic-inorganic materials.² Examples of such compounds are scarce, and their reactivity was less investigated compared to that of their Sn(II) analogs.

Organotin(IV) alkoxides and/or siloxides are generally obtained reacting a tin halide with a metal alkoxide of Na/K³ or with the Li alkoxide obtained from an alcohol and *n*-butyllithium.⁴ Other methods describe *trans*-alcoholysis reactions⁵ or the reaction of tin(IV) amides with lactides, following a ring opening mechanism.⁶

We present here a series of triaryltin(IV) alkoxides and siloxides bearing one phenyl group and two ortho substituted phenyl-1,3-dioxolane fragments as ligands. The reactivity, solution behavior, as well as their structural features will also be discussed.

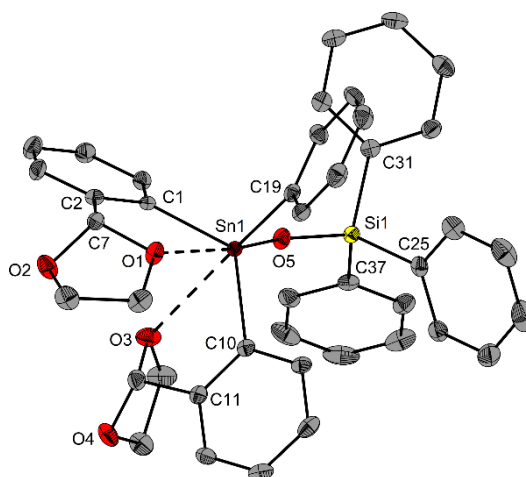


Figure 1. Molecular structure of [2-((CH₂O)₂CH)C₆H₄]₂PhSnOSiPh₃

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Novel organoantimony(III) halides and cations

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Organoantimony(III) halides are useful starting blocks for a wide array of compounds in the antimony chemistry. With the increase of the halogen atom radius a better leaving group is obtained.

We report the synthesis of a new organoantimony(III) halide and two organoantimony(III)cationic species bearing a CNC ligand. The halide $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{SbCl}$ (1) obtained through an improved synthetic method, was used as the starting material in all syntheses. The organoantimony(III) iodide $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{SbI}$ (2), amidodiborate $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{Sb}^+\{\text{H}_2\text{N}[\text{B}(\text{C}_6\text{H}_5)_3]_2\}^-$ (3) and hexafluorophosphate $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{Sb}^+\text{PF}_6^-$ (4) were obtained in good yields. Compounds (2-4) were characterized by multinuclear (^1H , ^{11}B , ^{13}C , ^{19}F , ^{31}P) NMR spectroscopy. Compound (2) was also characterised by VT NMR spectroscopy. The attempt to synthesize the organoantimony(III) fluoride starting from compound (3) gave mixed results. All organoantimony(III) compounds with the CNC ligand presented are air- and moisture-stable.

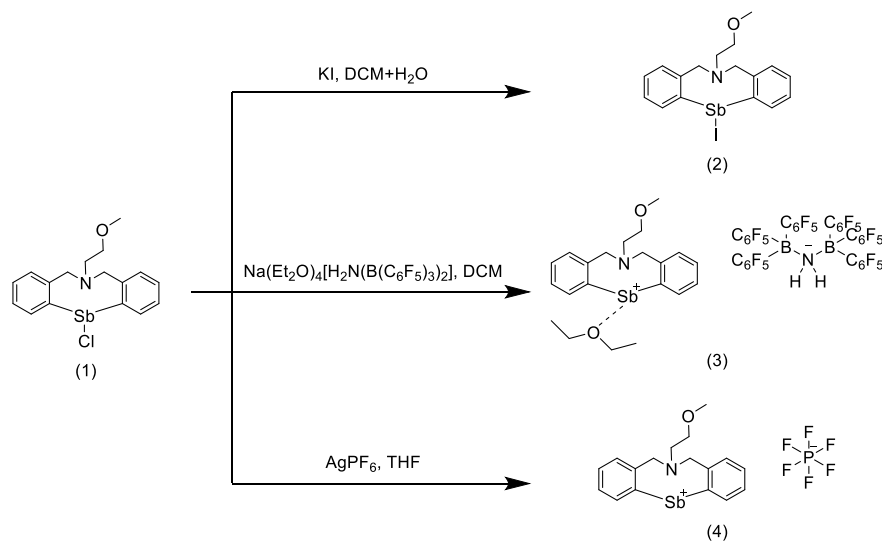


Figure 1 Synthetic pathway for novel organoantimony(III) compounds

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PO12

The dehydrocoupling of hydrosilanes and terminal alkynes with alkaline earth catalysts

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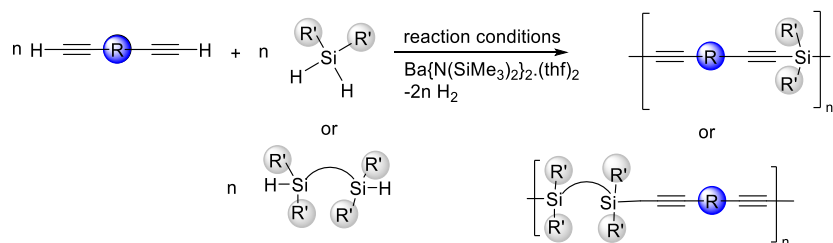
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Based on this approach, the synthesis of dehydrocoupling reactions began with two benchmark substrates which are phenyl acetylene and dimethylphenylsilane. While the optimization of reaction parameters, dehydrocoupling between those substrates in the presence of $\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2 \cdot (\text{thf})_2$ catalyst was successfully achieved but with few challenges as well in the beginning it observed the reactions was sluggish even with 10% mol catalyst concentration and it came up that this type of dehydrocoupling is solvent dependent. Among all the solvents were used to make the dehydrocoupling faster, pyridine was the best all of them.

However, S. Harder reported, about the reactivity of pyridine with hydrosilanes^[1], to overcome this challenge we use all the possible spectroscopic methods to identify the reactivity of pyridine in our reaction for instance ^1H NMR, ^{29}Si NMR and Mass spectroscopy to make sure about the desirable product and not formation of side products.

Moreover, to get the best reactivity in pyridine, we test via changing the various external parameters of the reaction for instance concentration of catalyst, temperature and reaction time. Eventually, the main objective of this project to synthesis of polymers, very few examples are already in literature^[2] and study the applications of those polymers.



The general scheme of synthesis of polymers with hydrosilanes and alkynes.

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PO13

One-step synthesis of axially chiral bismacrocycles from linear achiral precursors

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The Nobel-prize-winning CuAAC click reaction has become widely used due to its high yields, mild conditions, good selectivity, and broad applicability. These features make it suitable for the synthesis of macrocyclic molecules, which are often challenging to obtain. However, this reaction is not always clean: side reactions can occur in the presence of oxygen, leading to the formation of axially chiral bistriazole units.^{1,2}

In this study, we showed that the combination of a Cu(I) N-heterocyclic carbene catalyst³ with conditions specific to macrocyclization reactions leads to the formation of chiral bistriazole bismacrocyclic compounds starting from achiral linear precursors (Figure 1). This significant increase in molecular complexity is achieved in good yields, and the chirality of the obtained molecules is discussed.

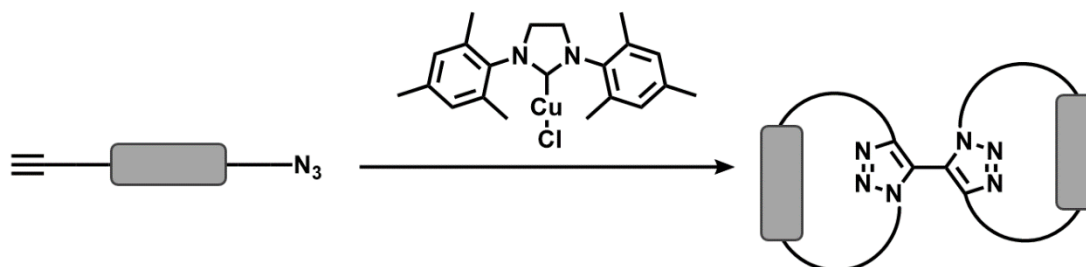


Figure 1 Schematic representation of the synthesis of bistriazole-based bismacrocycles.

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PO14

Synthesis of structurally constrained cyclobutane-fused methylphenidate analogs via iron-catalyzed [2+2]-cycloaddition

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The synthesis of cyclobutane rings by [2+2]-cycloaddition is thermodynamically favorable, but in principle violates orbital symmetry rules. While a common strategy to circumvent this limitation is photocatalysis, our research pursues an alternative route using low-valent iron catalysts with pyridinediimine and pyrimidinediimine (PDI, P^{Py}mDI) pincer ligands. These redox-active PDI ligands have a flexible electronic structure, which can accommodate ligand-based as well as metal-based redox activity, enabling net two-electron processes for 3d transition metals.¹

Our work demonstrated this in the context of iron catalysis, where a functional-group tolerant methodology for intramolecular [2+2] cycloadditions of unactivated dienes was developed. The method makes use of mild thermal conditions and allows the synthesis of a series of strained cyclobutane-containing bicyclic building blocks.² The resulting motifs, azabicyclo[3.2.0]heptane and its higher homologous bicycles, are attractive building blocks for pharmaceutical chemistry as they can function as bioisosteres of various saturated N-heterocycles (e.g. pyrrolidine, piperidine).³

In the course of developing this methodology, we have synthesised new rigid cyclobutene-fused analogs of methylphenidate, commonly commercialised as Ritalin®, which is a widely prescribed stimulant for the treatment of attention deficit hyperactivity disorder (ADHD), narcolepsy and depression. Its multistep organic synthesis, mechanistic aspects and the electronic structure of reactive metal intermediates will be discussed.

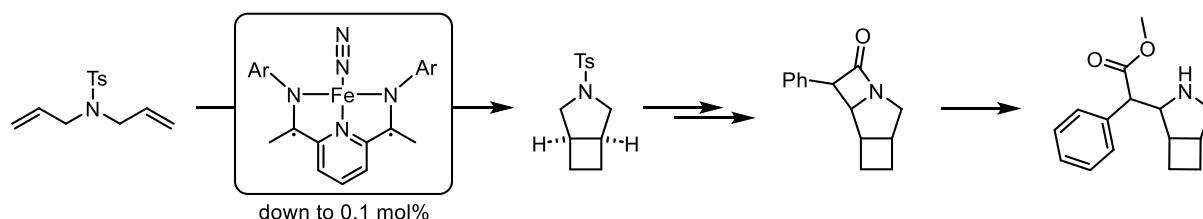


Figure 1 Synthesis scheme for the preparation of cyclobutane-fused methylphenidate analogs via iron-catalyzed [2+2] cycloaddition.

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DETECTION OF IONS BY LMOFs: FIRST TRIALS USING Tb AND Eu OH-BENZENEDICARBOXYLATES

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Metal Organic Frameworks (MOFs) are porous coordination polymers that have been studied for the past twenty years due to the multiplicity of their crystal structures and their various possible applications (molecules storage/separation, catalysis...). Such diversity comes from the MOFs' porosity and their building units, organic ligands associated with metallic polyhedra. Due to their high coordination degree and their numerous very thin emission bands, lanthanide ions can help forming stable MOFs with a signature in luminescence measurements (Eu³⁺/red, Tb³⁺/green). Combining one lanthanide ion with a chosen ligand, one may be able to trap analytes inside the MOF framework and to obtain a quick luminescent response, hence forming a chemical sensor. [1,2,3]

In this work, the focus has been directed on MOFs using Tb³⁺ or Eu³⁺ ions with 2-hydroxy-1,4-benzenedicarboxylic acid (OH-H₂BDC) previously studied in our group [4] and particularly in one structure, obtained for homo nuclear lanthanides (La-Nd). The MOFs crystalize in the cubic system with large square section channels (11x11 Å, Fig. inset) that contain crystallization water molecules. The driven idea was to synthesize Eu³⁺ or Tb³⁺ based MOFs possessing this crystal structure, to use the channels and/or the hydroxy functions to trap analytes in solutions and then to investigate the luminescence response (excitation and emission spectra, lifetime decay) of these materials. MOFs have been successfully synthesized for Eu/La and Tb/La mixtures and their chemical stability has been studied (pH, temperature, solvents). Reactions in solutions containing various analytes (transition metals cations and anions) were done to finally assess the luminescence evolution due to the analyte presence (Fig.). In most cases a quenching of the initial luminescence of the lanthanide cation is observed within the MOF framework due to interactions with the analytes which need to be further understood.

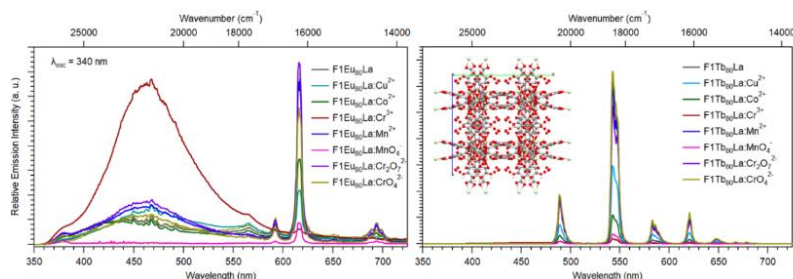


Figure 1 Solid-state visible emission spectra at room temperature of (left) Eu₈₀La MOF vs Eu₈₀La + analytes, (right) Tb₈₀La MOF vs Tb₈₀La + analytes) and projection along the a-axis of the crystal structure of [Tb_{0.8}La_{0.2}(OH-HBDC)(OH-BDC)·9H₂O]_∞

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PO16

Carbide formation issue in the context of CO hydrogenation catalyzed by ultra-small organometallic RuNPs

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The current research focuses on the Fischer-Tropsch synthesis (FTS),¹ a technological process of high interest for its potential application in liquid fuel production with low environmental impact. FTS involves the catalytic transformation of syngas (mixture of CO and H₂) into long-chain alkanes, yet liquid alkenes, gaseous hydrocarbons, alcohols, or ketones are obtained in smaller yields. Metal nanoparticles (MNPs) have shown an increased catalytic activity for CO hydrogenation, with Ru being, among several metals (e.g., Fe, Co, Ni), the most efficient and selective toward liquid alkane production. From a mechanistic viewpoint, FTS reveals a complex reaction scheme involving myriads of intermediates and several competing pathways. Although known for over a century, the fundamental understanding of the CO hydrogenation mechanism remains an open point.

The key step in FTS is the CO bond-breaking, given the increased stability of the C≡O triple bond. A better understanding of the cleavage mechanism should enable higher efficiencies of targeted nanocatalysts. The combined theoretical/experimental study reported herein brings fundamental insights into the early steps of the CO hydrogenation catalyzed by RuNPs.² Based on in-depth DFT studies and complementary ¹³C-NMR solid-state or hydrogen temperature-programmed reduction experiments, we emphasize for the first time that long-lifetime carbides are systematically formed, during CO dissociation, in standard surface sites of ultra-small organometallic RuNPs (Figure 1).

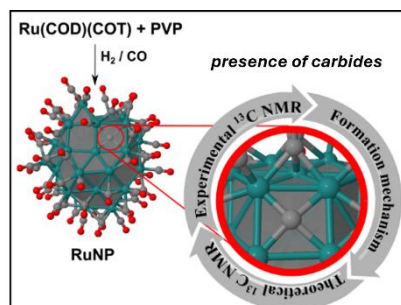


Figure 1 Surface carbide formed via hydrogen-assisted CO bond dissociation pathway on RuNPs.

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The Redox Behaviour of the Heavier Bis(ferrocenyl)pnictogenium Ions

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The isolation of highly reactive main group cations is of high interest due to their potential applications in catalysis and material science.¹ Although challenging, there are two universal strategies to “tame” such species: kinetic stabilisation using bulky substituents or electronic stabilisation using donor ligands. The increased stability provided by the ferrocenyl unit in carbenium or silylium ions ($[\text{FcERR}]^+$; E = C, Si) was attributed to electronic stabilisation.² The isoelectronic $\text{FcB}(\text{C}_6\text{F}_5)_2$ show similar structural properties to group 14 cations, namely intramolecular Fe–E interactions. Interestingly, the Lewis acidity of such boranes increased dramatically upon oxidation of the iron atom, as the intramolecular stabilisation was lost.³

The previously reported and revisited phosphonium ion $[\text{Fc}^2\text{P}]^+$, isoelectronic to neutral carbenes, is also a Lewis super acid.⁴ Herein, the series of $[\text{Fc}_2\text{E}]^+$ (E = As (**2**), Sb (**3**) and Bi (**4**)) was extended and structurally characterised. Their Lewis acidity and (electro-)chemical behaviour was explored, showing that the P and As analogues are the most stable in the series. The one-electron oxidation of $[\text{Fc}_2\text{E}]^+$ (E = P (**1**), As (**2**)) led to the formation of the mixed valent dication for **2**, and the highly reactive dication for **1**, while the one-electron reduction resulted in the formation of the corresponding diphosphine and diarsine (Figure 1).

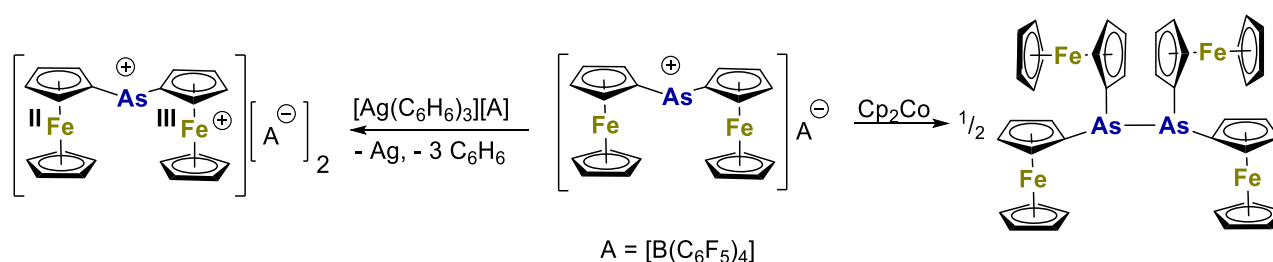


Figure 1 One-electron oxidation (left) and reduction (right) of $[\text{Fc}_2\text{As}][\text{B}(\text{C}_6\text{F}_5)_4]$

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Luminescence and Magnetic Investigation of Yb(III) amides

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Single-molecule magnets (SMMs) based on Ln(III) ions are enticing candidates for magnetic data storage due to their strong single-ion anisotropy and large unquenched angular momentum.^[1] Among Ln(III) ions, Kramers ion-Dy^{III}, Yb^{III}, and non-Kramers ion-Tb^{III} are often exploited to design SMMs. Among these, Yb^{III} SMMs are far less studied systems. Here, we set out to explore the luminescent and magnetic properties of Yb^{III} amides, Yb{N(SiMe₃)₂}₃ (**1**) and Yb{N(SiMe₂H)₂}₃·(thf)₂ (**2**). These systems are the synthetic analogues of the theoretical models proposed by Ruiz and coworkers.^[2] A pyramidal geometry (C_{3v}) with Yb^{III} ion above the plane of 3 nitrogen atoms was depicted by **1**, whereas **2** adopts a trigonal bipyramidal geometry (D_{3h}). **1** displayed the largest splitting of c.a. 1312 cm⁻¹ between Kramers doublet (KD)1 and KD2, as seen in the near-infrared luminescence spectra, corroborating the theoretical values. Further, the introduction of 2 THF moieties on the trigonal plane in **2** reduced the splitting to half (690 cm⁻¹). The giant splitting in **1** does not reciprocate in its magnetic behaviour, similarly in **2**. These complexes showed no magnetic hysteresis at low temperatures. However, **1** and **2** depicted striking differences in the magnetic behaviour. **2** showed magnetic relaxation within a limited temperature range up to 4 K, vs till 9 K in the case of **1**. Briefly, a Raman-like pathway with a small contribution of QTM dominating the relaxation dynamics, results in weak SMM behaviour in these complexes.

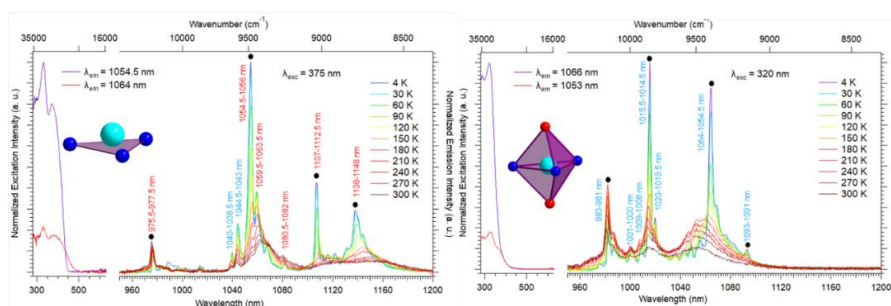


Figure 1 Solid-state emission spectra measured between 4 and 300 K on **1** (left), and **2** (right).

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PO19

Tetrathiafulvalene and dithiolene diamine ligands for d¹⁰ metal complexes

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Nowadays, coordination polymers (CPs) have become a platform for a variety of applications, such as gas sorption, sensing, magnetism, electronic states, or conductivity.¹⁻³ The predictable coordination geometries around the metal center or clusters allows the precise design of 1-D, 2-D or 3-D structures through chosen coordination interactions. The possibility of designing coordination polymers is attractive for researchers thanks to the large variety of metals, structure of ligands, coordination geometry and supramolecular structures available. The reasoned design of coordination polymers allows the control of the structures and dimensionality as a means to modify the properties of compounds.

Based on our previous works in the field of molecular conductors⁴ and in electroactive porous CPs⁵, we are particularly interested in introducing tetrathiafulvalene (TTF) electroactive units into ligands containing primary amines as coordinating chelating groups. The large majority of TTF derivatives are known as excellent precursors for organic conductors.⁶ Through the design of organic linkers and the incorporation of electroactive moieties within porous structures, we aim to control the structure and obtain crystalline conducting materials.

Herein, we present the synthesis and characterization of new ligands containing electroactive TTF or dithiolene units and -NH₂ coordinating chelating groups, which were used in coordination with d¹⁰ metals.

Acknowledgments: MSCA4Ukraine, University of Angers, MOLTECH-Anjou laboratory

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PO20

Viscoelastic switchable materials

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Spin crossover (SCO) complexes, based on first-row transition metals with electronic configurations ranging from $3d^4$ to $3d^7$, are particularly attractive for their properties that can be drastically modified under several stimuli such as temperature, pressure or light, resulting magnetic, structural and optical changes (Cf. Figure 1), which are potentially interesting for many applications in the field of molecular electronic devices such as displays,¹ actuators,² memory and chemical sensing. In the present work, we focus on complexes featuring ferrous ions that can be reversibly switched between HS ($S = 2$, $^5T_{2g}$) and LS ($S = 0$, $^1A_{1g}$) states.

In the last decades, various SCO materials have been reported in the literature as single crystals or polycrystalline powders.³ However, the processing and integration of these materials into devices is a major challenge. To achieve this objective, a common strategy consists in dispersing such systems in the form of nano- or microparticles into appropriate polymer matrices, leading to composite materials.⁴ The choice of the polymer matrix is crucial since a functional polymer can induce additional mechanical and/or physical properties which may affect the SCO behavior, and vice-versa.

In this work, we present the synthesis, magnetic and rheological properties of a new multifunctional composite based on the $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ ($\text{NH}_2\text{trz} = 4\text{-amino-1,2,4-triazole}$) coordination chain and on the polystyrene sulfonate (PSS), which is a viscoelastic and fluorescent polymer.

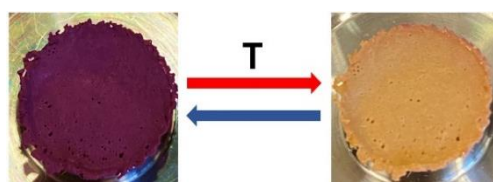


Figure 1. Thermochromism in the multifunctional viscoelastic cooperative nanocomposite $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2/\text{PSS}$

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PO21

Amine-catalyzed substitution in CpFe(CO)₂I with phosphines

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We discovered that amines play a significant role in accelerating iodide substitution in CpFe(CO)₂I (Cp = η⁵-cyclopentadienyl) with phosphines, enabling the synthesis of novel complexes inaccessible through reactions conducted without an amine. Equimolar amounts of CpFe(CO)₂I and triphenylphosphine in toluene containing DIPA yielded [CpFe(CO)₂PPh₃]⁺I⁻ within 5 minutes at room temperature (72% yield, 90% after 24 hours). We also conducted a similar reaction using model bisphosphines 1,3-bis(diphenylphosphino)ethane (dppe) and 1,1'-bis(diphenylphosphino)-ferrocene (dppf). The products varied depending on the reagent ratio, respectively. Additionally, the DIPA-catalyzed reaction of CpFe(CO)₂I with triethyl phosphite produced the product of a Michaelis-Arbuzov-like rearrangement, CpFe(CO)₂[P(O)(OCH₂CH₃)₂].¹

Theoretical calculations of intermolecular interactions between CpFe(CO)₂I and amine molecules were conducted to elucidate the reaction mechanism, proposing two possible pathways to explain product formation.

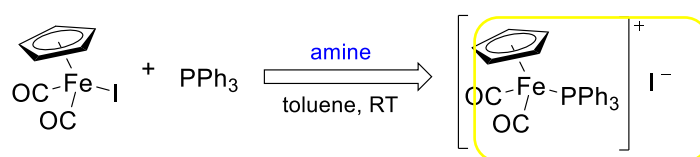


Figure 1 Amine-catalyzed reaction of CpFe(CO)₂I with PPh₃

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PO22

Blue-Light Enhanced Iron Catalysed Hydrosilylation of Carboxamides and Carboxylic Esters at Ambient Conditions

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This contribution described a blue-light-promoted iron-catalyzed reduction of carboxamides and carboxylic esters. During the last two decades, the use of iron as an alternative transition metal in homogeneous catalysis has seen an impressive improvement,^[1] more particularly in reduction areas.^[2] We also published several contributions demonstrating that iron catalysis under hydrosilylation conditions was able to reduce tertiary and secondary carboxamides to amines^[3] and carboxylic esters to alcohols.^[4] Nevertheless, these transformations required quite harsh conditions (~100 °C) with or without white visible light activation. On the other hand, the use of visible light to promote chemical transformations can be viewed as a sustainable and promising alternative to thermic transformations,^[5] mainly when operated at temperatures higher than 100 °C.

In this contribution, conducting the reaction under hydrosilylation conditions and blue light (2×24 W) in the presence of an iron(0) based pre-catalyst, Fe(CO)₄(IMes), amines and alcohols were obtained, respectively, notably at ambient conditions, whereas using white light, higher reaction temperatures up to 100 °C were required.

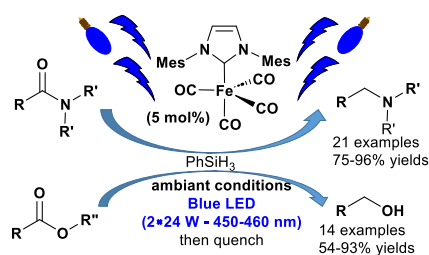


Figure 1 Reduction of carboxamides and carboxylic esters

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PO23

Metal organic framework impregnated with ionic liquid, for recovery of phenol. Regeneration step

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Over the past few decades, there has been a tremendous improvement in the effectiveness and cost-effectiveness of using adsorbents to remove hazardous organic chemicals from water. However, little focus was placed on recycling used adsorbents and recovering hazardous organic compounds from the desorbing agents. A lot of study has been done on the regeneration and reuse of adsorbents. Metal-organic frameworks (MOFs), are an appropriate adsorbent for hazardous organic chemicals from water.

Many different approaches (solvent extraction, enzymatic or thermal treatment in an oxidizing atmosphere) have been proposed for the recovery or elimination of phenols^{1,2}. The in-situ production of hydroxyl radicals ($\bullet\text{OH}$, or active chlorine) is the foundation of the electrochemical method². Many studies have been conducted on the electrooxidation of phenols, however more investigation is required into this process. During the electrooxidation process, phenoxy radicals are produced. These radicals can react with more phenol molecules to form dimeric radicals or mix with other species already present in the solution to form products. This radical can be oxidized in one of two ways, depending on the circumstances: either by quinones or polymers. For basic media and moderate phenol concentrations, quinones formation is preferred; however, polymerization is preferred for high phenol concentrations and basic media³. The oxidation process of quinone results in carboxylic acids. It is also possible to regenerate MOF-type adsorbents impregnated with ionic liquids, which are used to extract phenols from waste water, by electrochemical oxidation. In an acidic, basic, or 3% NaCl solution, the electrochemical performance of Pt, glassy carbon electrodes were examined. With the further increase of the regeneration cycle, the adsorption sites of adsorbent decrease. The adsorption efficiency decreases with 33.5% for Cu-PA-IL after 4 cycles of reuse. The number of cycles in which the adsorbent can be used without losing its absorbance ability is 3.

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PO24

Synthesis and coordination chemistry of a uranium nitrate complex with 8-hydroxyquinoline

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The synthesis of $[U^{VI}O_2(8-HQ)_2(NO_3)_2]$ has been achieved through the reaction of a uranyl nitrate precursor, $UO_2(NO_3)_2 \cdot 6H_2O$, with 8-hydroxyquinoline (8-HQ) in ethanol. The practical interest for such a reaction is supported by the need of novel uranium extraction techniques from ores, low-concentration solutions and purification of residual waters. X-ray crystallography, UV-Vis, IR, and quantum chemistry calculations have been applied to characterize the coordination chemistry of the reaction complex. The single-crystal X-ray diffraction experiments demonstrated the presence of a center of inversion in $[U^{VI}O_2(8-HQ)_2(NO_3)_2]$, with a local metal coordination resembling that of a slightly distorted hexagonal bipyramid. As shown in Figure 1, there is a hexa-oxygen coordination at U^{VI} , completed by two non-deprotonated 8-HQ ligands that bind equatorially to the uranyl backbone. The quantum chemistry calculations confirmed these features of the X-ray structure and further revealed that the metal coordination is stabilized in particular by a network of intramolecular $[^{8-HQ}]N-H \cdots O_3N$ hydrogen bonds. Bonding analyses an essentially ionic metal-ligand bonding with 8-HQ and NO_3 ligand, driven by the weak overlap between the $5f_\phi$ orbitals (pseudoaxial symmetry) and the O atoms, that is quite typical for coordinated uranyls.^{1,2,3}

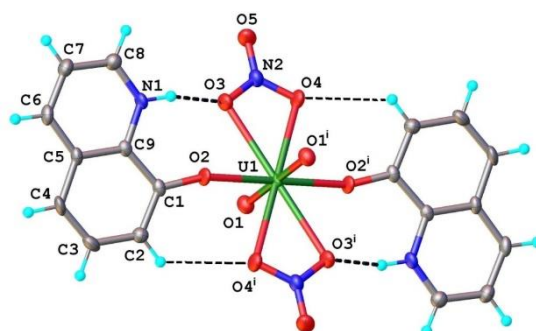


Figure 1 X-ray molecular structure of $[U^{VI}O_2(8-HQ)_2(NO_3)_2]$ with thermal ellipsoids drawn at 50% probability level

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Click-chemistry Generated Electrochemical Aptasensors for Pharmaceutical Pollutants Detection

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Pharmaceuticals are considered part of emerging contaminants that pose a threat to the environment (1). One of the challenges to a better understanding of their hazardous nature is the monitoring of their global occurrence, which is difficult to acquire due to their concentration range of $\mu\text{g/L}$ to ng/L . In this study, electrochemical sensors integrating aptamers that can specifically recognize analytes from complex matrices like the environmental waters were developed.

Firstly, ethynyl diazonium salts with alkylsilyl protective groups are electrodeposited on the surface of the carbon electrode. The use of protective groups hinders the attachment of the phenyl radicals and allows the formation of a thin robust monolayer. They also induce a controlled spacing between each phenyl nucleus that depends on the size of the protective group (2). A deprotection step is then realized to remove the silyl groups and generate a reactive ethynylaryl layer that has the role of an anchor for the aptamer. Through click chemistry, the azide-functionalized aptamers are immobilized on the surface using copper-catalyzed azide-alkyne cycloaddition. A major element that determines satisfactory detection is the difference in the spatial conformation of the free aptamer and the aptamer bound to the analyte. The final aptasensor is incubated with the targeted molecules, representants from the class of antibiotics and anti-inflammatories (Figure 1).

The obtained electrochemical sensors combine the robustness of the ethynylaryl monolayer and the specificity of the aptamers to give an efficient alternative to standard analytical methods when it comes to evaluating the quality of the environment.

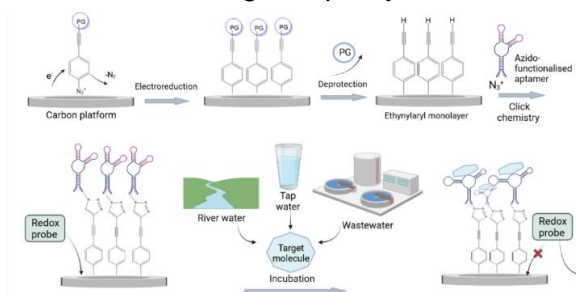


Figure 1. General scheme for the development of the aptasensor by click chemistry

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PO26

Palladium mediated functionalization of closo-decahydrodecaborate

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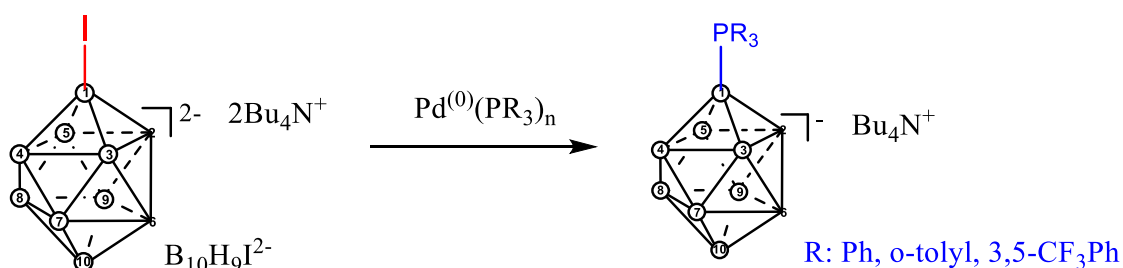
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The closo-decaborate $[B_{10}H_{10}]^{2-}$ represents an interesting compound in polyhedral architecture area, due to their electrochemical properties, three-dimensional aromaticity, modulated biological properties with various applications in metallic coordination chemistry, catalysis, material science, solid state batteries, hydrogen storage or even medicine.^[1–5] Thus, the functionalization or derivatization of polyhedral boron clusters is still a topical area of research.

Following our contribution in closo-decaborate chemistry,^[6–8] in this work, the activation of B-H bond of closo-decahydrodecaborate was targeted and thanks to the use of an equimolar amount of $LnPd(0)$ precursors, the functionalization of $[B_{10}H_9][N(n-C_4H_9)_4]_2$ was realized in basic free conditions in THF. Using various $Pd(0)$ precursors bearing for example triphenylphosphine, tris(*o*-tolyl)phosphine or tris[3,5-bis(trifluoromethyl)phenyl]phosphine, the corresponding monoanionic derivatives closo- $[B_{10}H_9(PR_3)][N(n-C_4H_9)_4]$ were selectively obtained with yields up to 80%. The obtained products were purified and fully characterized, notably by 1H -, ^{13}C -, ^{11}B -NMR, IR and XRD.



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Coordination polymers based on lanthanides and halogenated-benzene-carboxylate ligands : structural and optical characterization for comparison

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In recent decades, coordination polymers have attracted a great deal of interest for their remarkable optical properties, especially used in lighting or anti-counterfeiting marking.^[1] Coordination polymers are made of one or more metal centers, coordinated with one or more organic ligands, to form extended structures, which can be mono-, bi- or three-dimensional. The organization of these crystalline structures depends on the different interactions involved: hydrogen bonds, halogen bonds, π -stacking... The use of halogenated-benzene-carboxylate ligands allows to create coordination bonds with metal centers thanks to their carboxylate clamps and potential halogen bonds. From literature, studies of structures obtained from this type of ligands seem to be promising for the design of new luminescent compounds, and there's still a lot to discover, since no structure exists for all the halogenated-benzene-carboxylate derivatives, associated with rare earths.^{[2],[3]} Here, we propose to describe the first comparison made between three different ligands: the phthalic acid (pta), the 4,5-dichloro-phthalic acid (dcpa) and finally the 4,5-difluoro-phthalic acid (dfpa), for their structural and optical properties (Figure 1).

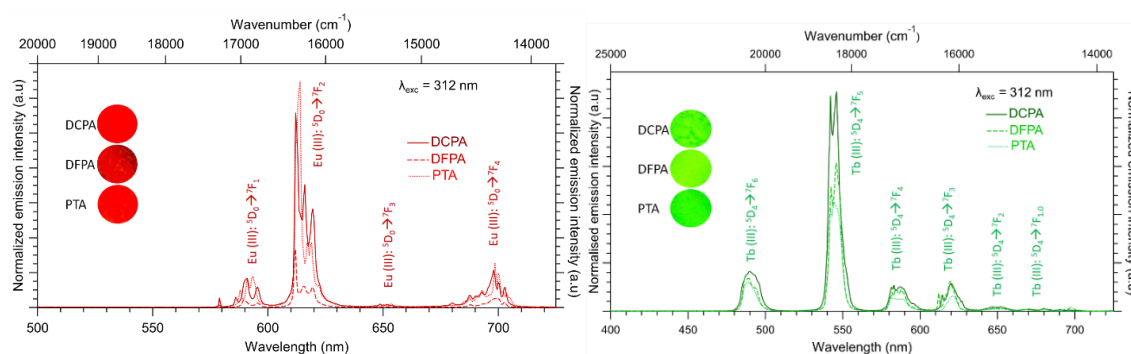


Figure 1 Room temperature solid-state emission spectra and pictures under UV excitation ($\lambda_{exc} = 312$ nm) of Eu-derivatives : $[Eu(pta)]_{\infty}$, $[Eu(dcpa)]_{\infty}$ and $[Eu(dfpa)]_{\infty}$ (left) and Tb-derivatives : $[Tb(pta)]_{\infty}$, $[Tb(dcpa)]_{\infty}$ and $[Tb(dfpa)]_{\infty}$ (right).

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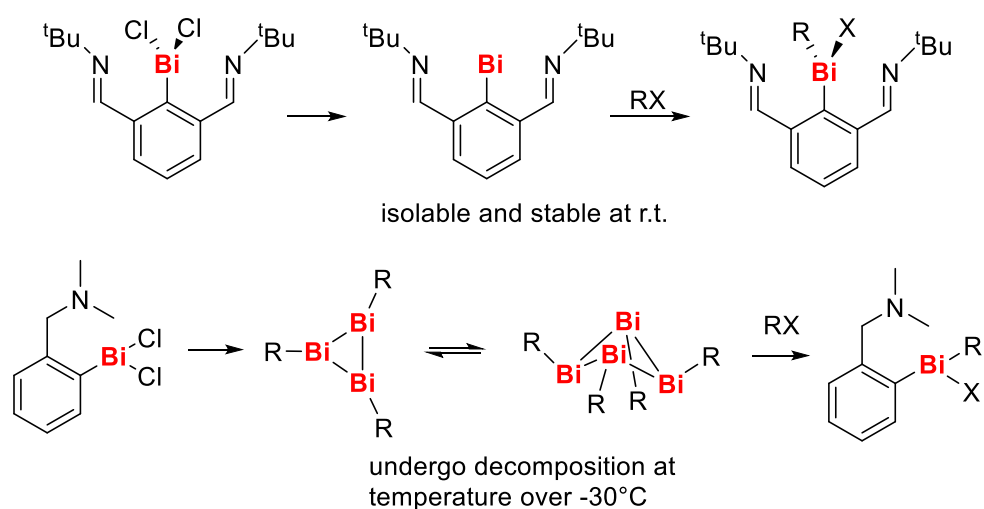
PO28

Study on the reactivity of an *N,C*-chelated cyclobismuthane in comparison with monomeric bismuthinidenes

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Bismuthinidenes are a class of organobismuth compounds analogue to carbenes and, due to their unusual oxidation state of bismuth, they are reactive and unstable. Polydentate chelating Lewis-base ligands are required to stabilize the monomeric species, that will otherwise undergo dimerization or cyclization.¹ Monomeric bismuthinidenes have been recently reported to exhibit interesting application in catalysis or in the activation of small molecules.^{2,3} This reactivity is ascribable to the lone pair of electrons located in a $6p^2$ orbital of bismuth(I) atom. Therefore the metal center in bismuthinidenes has been proven to be nucleophilic and readily oxidized in comparison with the bismuth(III) compounds for which the lone pair is low in energy and rather inert. The main objective of this work is to evaluate the difference and the similarities in the reactivity of an *N,C*-chelated bismuth(I) homocycle towards different species in comparison with the reactivity of monomeric bismuthinidenes.⁴



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Coordination chemistry of a novel CuCl_2L_2 complex with antitumoral activity: A theoretical study

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The hydrated $\text{Cu}^{\text{II}}\text{Cl}_2$ salt was reacted with a 1,2,3-triazole derivative in a methyl alcohol medium, resulting in the formation of a coordination compound CuCl_2L_2 , where $\text{L} = 1\text{-(2-phenyl-2-oxoethyl)-1H-1,2,3-triazole-4-carboxylate}$. This synthesis was inspired by the remarkable antimicrobial and anticancer activity observed in metallodrugs formed from transition metal chelates with triazole-derived Schiff base ligands.¹⁻³ In the initial phase of the study, in the absence of a conclusive X-ray structure, we directed our efforts toward computational investigations to characterize the geometry, chemical bonding, and low-lying electronic states through exploratory density functional theory (DFT) calculations and multireference wavefunction approaches. The equilibrium structure, shown in Figure 1, turned out to be very similar in both the gas phase and methanol solvent, with and without a treatment for explicit water or methanol molecules. This poster contribution highlights key molecular properties that stabilize the coordination sphere around Cu^{II} as well as characteristics of the low-energy spectrum in different solvents.

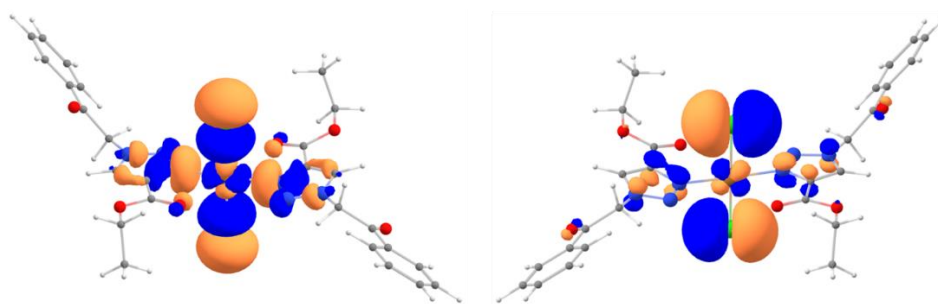


Figure 1 Structure and isosurface plots of the α -spin (left) and β -spin (right) HOMOs of CuCl_2L_2 .

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Dysprosium(III) clusters constructed with salicylaldehyde

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Recently, a family of mixed-ligand mononuclear lanthanide complexes of formula $[\text{Ln}^{\text{III}}(\text{phen})(\text{sal})_3]$ has been synthesized (Hsal = salicylaldehyde, phen = 1,10-phenanthroline, Ln = Nd, Eu, Tb, Dy, Er, Yb, Sm) [1]. Further systematic studies for the use of salicylaldehyde anion in high-nuclearity dysprosium(III) clusters synthesis were undertaken. Thus, in the lack of any ancillary ligands, by using different starting anions (acac^- , hfac^- , Cl^- , NO_3^-) in the reaction system, and from basic methanolic solutions, tetra-, hexa-, nona- and tetradecanuclear dysprosium(III) clusters were synthesized. The following clusters have been crystallographically characterized: a) a centrosymmetric $[\text{Dy}_4(\mu_3\text{-OH})_2]^{10+}$ butterfly core (**1**); b) a Dy_6 skeleton sitting on an inversion center with a central Dy_4 unit connected with two peripheral Dy ions (**2**); c) a diabolo-shaped Dy_9 cluster (**3**), where two square pyramidal pentanuclear units are joint *via* the apical Dy center, and d) a Dy_{14} assembly (**4**), which contains a $[\text{Dy}_6(\mu_3\text{-OH})_8]^{10+}$ octahedron unit that shares two opposing Dy_5 apexes with two $[\text{Dy}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4]^{10+}$ square pyramids. Their structures are displayed in Figure 1.

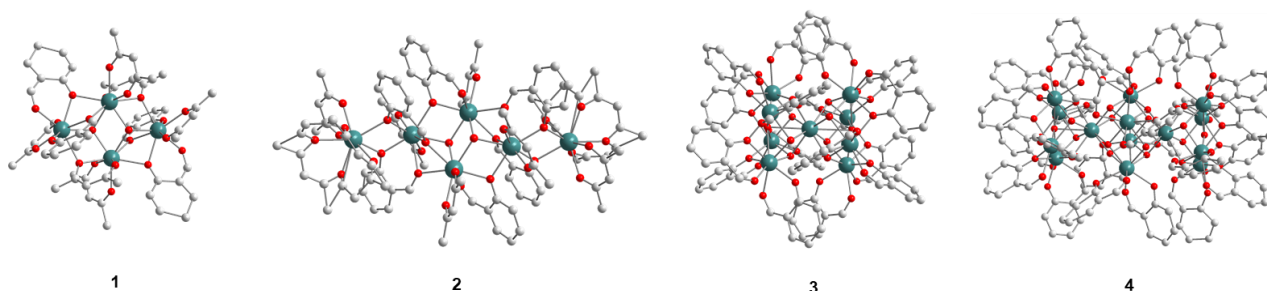


Figure 1 Dysprosium(III) salicylaldehyde-based tetra-, hexa-, nona- and tetradecanuclear clusters discussed in the abstract

Acknowledgements: The financial support from UB project "Heterospin 2p-3d-4f magnetic molecular systems" and from European Union through NextGenerationEU, programme-PNRR-III-C9-2023-I8 (contract no.760230) is gratefully acknowledged.

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PO31

Towards Chiral Single Component Conductors (CSCC) based on selenium containing metal bis(dithiolene) and metal bis(diselenolene) complexes

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Chirality has been well recognized in living systems and biological phenomenon since a while, while more recently it has begun to take on importance in the field of materials science [1]. Building on this base, properties of materials such as conductivity, magnetism, absorption or luminescence, are linked to their molecular and supramolecular arrangements. By creating a multifunctional material that links chirality to a physical property we are able to observe intrinsic behaviour of chirality.

In our group, we are interested in molecular conductors, in particular in the tetrathiafulvalene (TTF) family. Chirality was first introduced into this family by Dunitz and Wallis [2] in the 1980s with the preparation of tetramethyl-bis-ethylenedithio-TTF (TM-BEDT-TTF). This work paved the way for the development of chiral molecular conductors. Especially, introduction of chiral information in TTF derivatives allowed for the first time to observe the electrical magneto-chiral anisotropy effect (eMChA) in the case of bulk enantiopure crystalline conductors [3].

Based on these results, obtained on chiral derivatives of TTF, we will discuss the preparation of new compounds derived from TTF and tetraselenafulvalene (TSF).

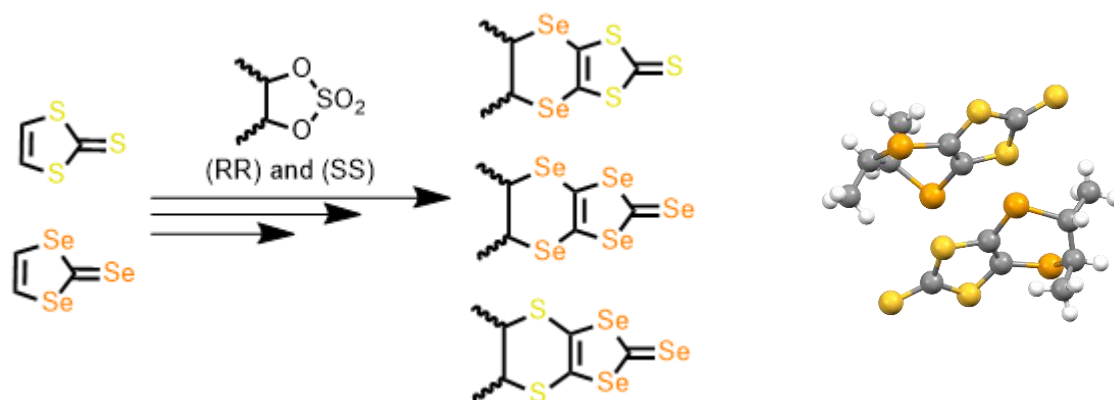


Figure 1 Left: Synthesis of Precursors. Right: X-Ray structures of one of precursors (SS)-DSDT (Carbon: Grey, Sulphur: Yellow, Selenium: Orange, Hydrogen: White)

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Fluorescent pyrimidine-based four coordinate boron complexes

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Organic Light-Emitting Diodes (OLEDs) are being investigated actively as next-generation displays because of their advantages, such as flexibility, brightness, and light weight.^[1] Numerous studies have been conducted on organic fluorescence and phosphorescence emitters in the visible region in recent years to improve the internal quantum efficiency. Recently, Thermally Activated Delayed fluorescence (TADF) materials have been developed as alternatives to fluorescence and phosphorescence materials in OLEDs. It is a process in which an excited molecule in the triplet state can undergo Reverse InterSystem Crossing (RISC) inducing a return in the singlet, increasing the theoretical External Quantum Efficiency up to 100%.^[2] Experimentally, TADF is characterized by a longer emission lifetime, comparable to phosphorescent emitters.

In this communication, we will describe the synthesis and photophysical properties of a series of pyrimidine-based boron complexes bearing various substituents (from moderate electron-withdrawing to strong electron-donating ones) including three different TADF donor groups. When substituted by electron-donating groups, boron complexes are characterized by a strong intramolecular charge transfer as indicated by a significant emission solvatochromism. Some complexes exhibit good photoluminescence quantum yield, one of them also emitting a delayed signal of fluorescence, implying TADF property, as expected in the literature.^[3]

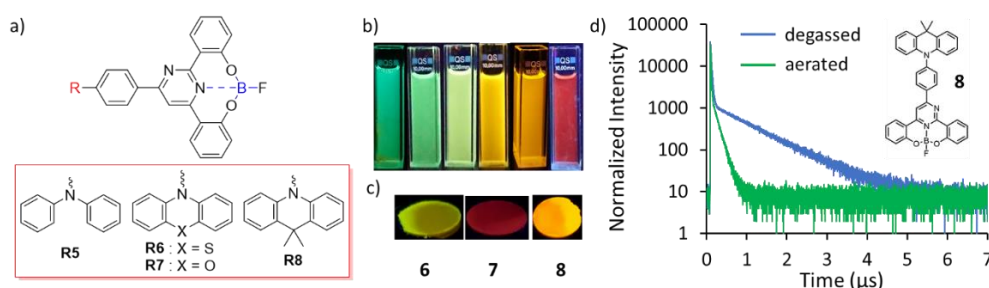


Figure 1 a) Structure of four-coordinate boron complexes. b) Solvatochromism of complex **5** c) Solid state samples of complexes **6**, **7** and **8** (1% in KBr matrix) under UV-light irradiation. d) Luminescence lifetime of complex **8**

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COORDINATION POLYMERS OF VARIABLE DIMENSIONALITIES WITH SILOXANE ENTITIES

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A series of coordination polymers (CP) with tetramethyldisiloxane spaced ligands have been prepared and characterized. The various topology of CP have been achieved through the variation of the nature of the counterion or using different coligands. Thus, starting from metal (M: Mn^{2+} , Zn^{2+} or Cd^{2+}) perchlorates in reaction with 1,3-bis(3-cyanopropyl)tetramethyldisiloxane (Cy) the isostructural 1D coordination polymers with general formula: $\{[MCy(H_2O)_4](ClO_4)_2\}$ (Figure 1) were obtained.

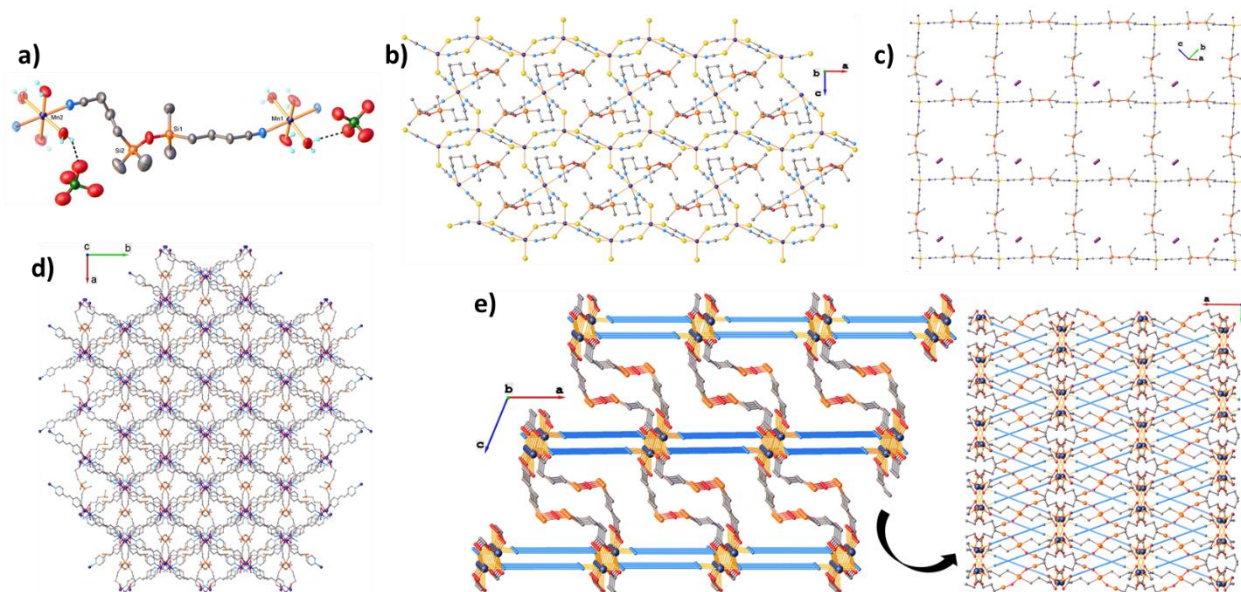


Figure 1 Coordination polymers with different dimensionalities (a-1D, b, c-2D, d, e-3D)

By changing the metal salts with $Co(SCN)_2$ and CuI_3 , 2D coordination polymers were formed. The use of 1,3-bis(carboxypropyl)tetramethyldisiloxane in co-ligation with dipyriddy derivatives for the complexation with $Mn(II)$ and $Cd(II)$ perchlorates afforded 3D coordination polymers. The structures were analyzed using appropriate techniques such as X-ray diffraction, elemental, and spectral analyses, while the properties were evaluated with regard to the peculiarities induced by the dimensionality of the structures.

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