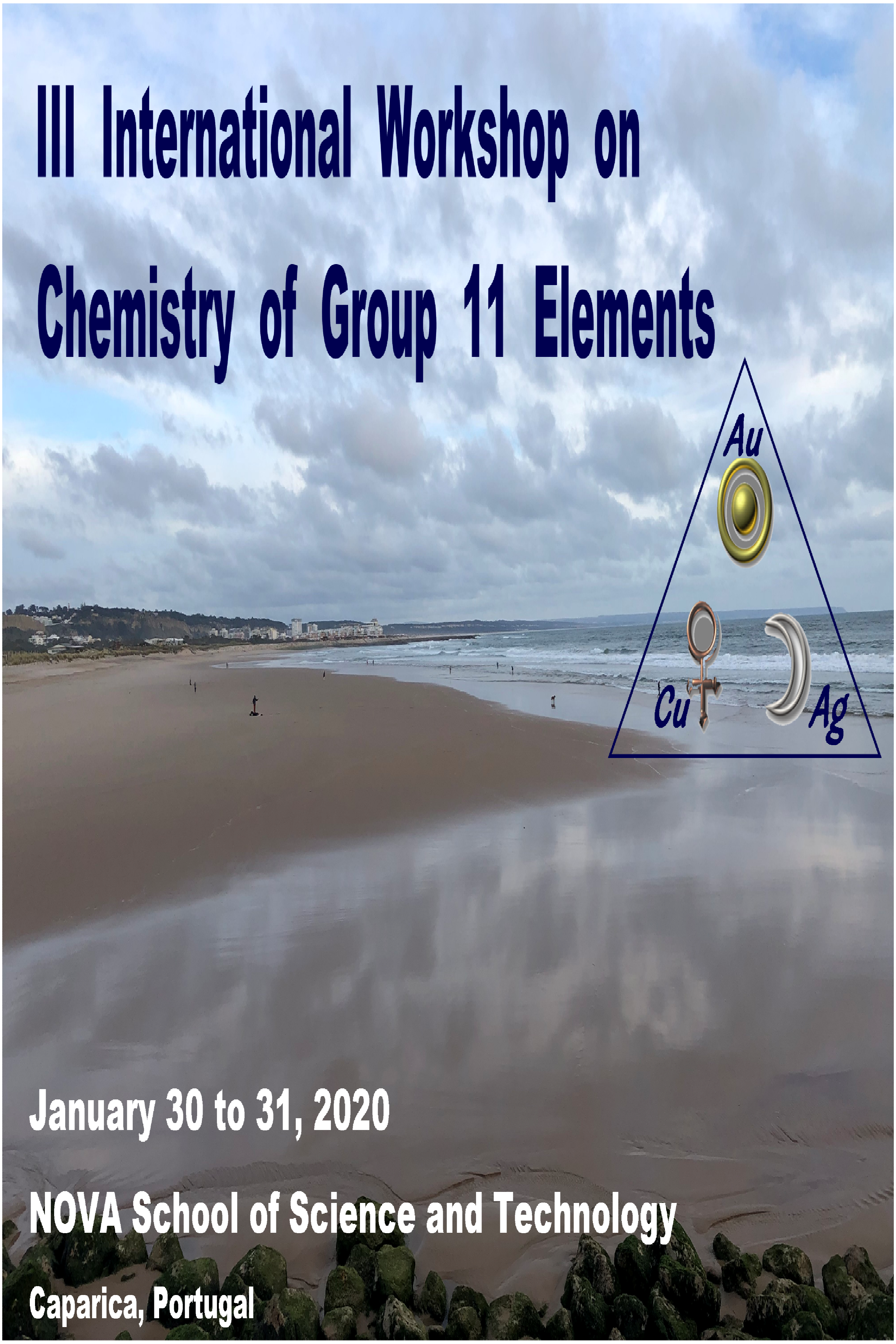
III International Workshop on Chemistry of Group 11 Elements



January 30 to 31, 2020

NOVA School of Science and Technology

Caparica, Portugal

Contents

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Welcome Message

On behalf of the Organising Committee, I welcome you to the **III International Workshop on Chemistry of Group 11 Elements** *and to NOVA School of Science and Technology, Caparica Campus.*

Since the first Workshops, held in Logroño (2011, chaired by José López de Luzuriaga) and Barcelona (2017, organised by Laura Rodríguez), it became clear that the "Group 11 Community" was enthusiastic enough to sustain a regular meeting of its own. It is now our pleasure and honour to host this event in Portugal. This is a great opportunity for researchers working with Group 11 Elements to meet again, exchange ideas and results, to have thrilling discussions and to enhance scientific collaborations. As in the previous Workshops, the relevant roles displayed by copper, silver and gold in Catalysis, Nanotechnology, Functional Materials and Bio-Sciences are covered in the scientific program, which comprises 15 Keynote Lectures, 16 Oral Communications, several Flash Communications and a Poster Session.

The Workshop is also a fantastic opportunity to enjoy the south bank of Rio Tejo, where Almada and its beautiful coastline and surroundings will amaze you, as well to visit Lisboa, with its superb historical and cultural heritage, and to experience the portuguese gastronomy and hospitality.

Bem vindos | Welcome | Bienvenidos | Bienvenue | Benvenuto | Witam
João Carlos Lima
Workshop Chair
January 30-31, 2020

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General Information

<u>Venue</u>

The workshop will take place at the ***Library of the NOVA School of Science and Technology***.

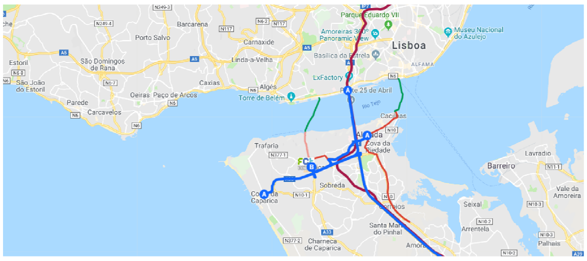
The School *Campus* is located in Caparica/Almada, on the south bank of Rio Tejo (Tagus River), near the beaches and only a few minutes from Lisboa City.

<u>How to get to the Workshop venue</u>?

Detailed directions to reach the NOVA School of Science and Technology *Campus* can be found at <u>https://www.fct.unl.pt/en/about-fct/how-get-fct</u>

The registration fee includes a free Metro / MTS ("Subway"; <u>http://www.mts.pt/rede/</u>) card with six travels.

Those travelling by car are allowed to park inside the *Campus*.



Campus map

(https://www.fct.unl.pt/sites/default/files/documentos/noticias/mapa_campus_2019_en.pdf)

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Bar "Espaço Mais"

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UT Austin / Portugal
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🟨 **CENIMAT** (Institute of Nanostructures, Nanomodelling and Nanofabrication)

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Hangar I
Students' Association
Bar "Teresa Gato"
Hangar II
Inventory Section
Hangar III
VICARTE- Glass and Ceramic for the Arts

🟩 **CANTEEN BUILDING**
Canteen
Bar "Tia"
NOVA Social Action Services
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Bar "My Spot"

⬛ **Main Entrance**

🟩 **UNINOVA**

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Registration

Registration will be open on the January 30, from 08h00, at the Library Auditorium of the NOVA School of Science and Technology.

WiFi

Free wifi is available in all the *Campus* through the Eduroam network.

Presentations guidelines

- The Workshop language is English.
  A strict respect of the time assigned is mandatory and will be enforced by the session chair.
  The presentation MUST BE delivered during the previous coffee/lunch break.
- Keynote Presentations
  Each speaker will give a 25 minutes presentation followed by 5 minutes discussion.
- Oral Presentations
  Each speaker will give a 12 minutes presentation followed by 3 minutes discussion.
- Posters
  The poster size should not exceed 119 cm height and 84 cm width (A0 paper size).
  All posters should be placed on the respective poster board in the "Posters Area", at the Ágora Room in the morning of January 30.
- Flash Presentations
  Authors of selected posters will give a 3 min presentation during the Poster Session.

Group Photo

On Thursday, January 30, after the last morning Communication (12h45), we will meet for a group photo.

Meals and Social Program

- Lunches and coffee breaks will be served in at the Ágora Room.
- The Workshop dinner will take place Thursday, January 30, in the heart of Almada, at ***Teatro Municipal de Almada, Teatro Joaquim Benite*** (at Av. Prof. Egas Moniz), starting with a welcome drink at 20h00 and including a guided visit to the Theatre.

To get to the Theatre Restaurant you should take the Metro / MTS ("Subway"; http://www.mts.pt/rede/) and exit in the "S. João Baptista" station, taking the exit to "Praça São João Baptista". Turn right, to "Rua D. Francisco Xavier de Noronha", and then left to "Rua Padre António Vieira". Finally, turn right to "Av. Prof. Egas Moniz" and, after 230m, the Restaurant will be at your left.

Program

Thursday, January 30

08h00 - 09h00	**Registration**
09h00 - 09h15	**Get together** **Introductory remarks** *Workshop Chair: João Carlos Lima (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)*
09h15 - 10h45	**Bio-Sciences I** Chair: José J. G. Moura (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)
09h15 - 09h45	KN 01: Isabel Moura (LAQV, REQUIMTE NOVA School of Science and Technology, Portugal) "The tetranuclear copper-sulfide catalytic center from the terminal enzyme of denitrification "
09h45 - 10h15	KN 02: Stephane Torelli (Grenoble Alpes University, France) "Copper/sulfur centers as versatile architectures for nitrous oxide and dioxygen reduction"
10h15 - 10h30	OC 01: Sabina Weronika Jaros (University of Wrocław, Poland) "Antimicrobial and sensing properties of new silver(I) and copper(I) coordination polymers driven by adamantane-like aminophosphine building blocks"
10h30 - 10h45	OC 02: Luis G. Alves (CQE, IST, University of Lisboa, Portugal) "Chemical and biological applications of cyclam-based copper(II) complexes"
10h45 - 11h15	Coffee Break
11h15 - 12h45	**Catalysis I** Chair: Teresa Avilés (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)
11h15 - 11h45	KN 03: Alexander Kirillov (University of Lisboa, Portugal) "Custom-made Aggregates: Authentic metal-organic architectures for catalysis & (bio)materials"
11h45 - 12h15	KN 04: Pierre de Fremont (University of Strasbourg, France) "NHC gold(I) POM hybrids: efficient and versatil catalysts"
12h15 - 12h30	OC 03: Anup Paul (CQE, IST, University of Lisboa, Portugal) "Versatility of benzimidazole derived copper (II) complexes"
12h30 - 12h45	OC 04: Christophe Fliedel (CNRS - LCC, France) "Beyond atom transfer radical polymerization the fascinating copper–radical couple"
12h45	Group Photo
12h45- 14h00	Lunch

Thursday, January 30	
14h00 - 16h00	**Smart Functional Materials I** Chair: Artur Moro (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)
14h00 - 14h30	KN 05: Laura Rodríguez (University of Barcelona, Spain) "Luminescent phosphine gold(I) alkynyl complexes. assemblies and applications"
14h30 - 15h00	KN 06: M. Concepción Gimeno (University of Zaragoza, Spain) "Luminescent metal complexes: synthesis and applications"
15h00 - 15h15	OC 05: Luís M. P. Lima (ITQB, NOVA University of Lisboa, Portugal) "Ultrasensitive colorimetric copper(II) chemosensors for environmental applications"
15h15 - 15h30	OC 06: Mani Outis (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal) "Photophysical characterization of two phosphorescent dinuclear copper iodide complexes: impact of crystalline network"
15h30 - 16h00	KN 07: Paulo Martinho (University of Lisboa, Portugal) "Molecular sensors and magnetic switches using group 11 metals"
16h00 - 19h00	**Flash Communications** Chair: Luisa Maia (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal) Ágora Room Coffee Break **Poster Session**
19h00 - 19h30	*Business Meeting*
20h00	**Workshop Dinner**

Friday, January 31

09h15 - 10h45	**Bio-Sciences II** Chair: Sofia Pauleta (UCIBIO, NOVA School of Science and Technology, Portugal)
09h15 - 09h45	KN 08: Simone dell' Acqua (University of Pavia, Italy) "Copper and oxidative stress in neurodegenerative diseases"
09h45 - 10h15	KN 09: Isabel Correia (CQE, IST, University of Lisboa, Portugal) "Therapeutic potential of copper phenantroline complexes"
10h15 - 10h45	KN 10: Enrique Garcia-España (University of Valencia, Spain) "Synthesis and study of SOD mimetics: from azamacrocyclic complexes to nano-structured systems"
10h45 - 11h15	Coffee Break
11h15 - 12h45	**Catalysis II** Chair: Vitor Rosa (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)
11h15 - 11h45	KN 11: Ana Carmen Albeniz (University of Valladolid, Spain) "Transmetalation of hydrocarbyl groups between group 11 and other transition metals: how similar are Cu, Ag and Au? "
11h45 - 12h15	KN 12: Kamran T. Mahmudov (University of Lisboa, Portugal) "Copper(II) arylhydrazonates: synthesis and catalysis "
12h15 - 12h30	OC 07: Manas Sutradhar (CQE, IST, University of Lisboa, Portugal) "Copper(II)-aroylhydrazone catalysts for the oxidation of volatile organic compounds"
12h30 - 12h45	OC 08: Clara Gomes (LAQV & UCIBIO, REQUIMTE, NOVA School of Science and Technology, Portugal) "Cu(I) and Ag(I) complexes bearing aryl-bian ligands: synthesis, structural analysis and applications as catalysts or as cytotoxic agents"
12h45- 14h00	Lunch

Friday, January 31	
14h00 - 15h45	**Smart Functional Materials II** Chair: João Carlos Lima (LAQV, REQUIMTE, NOVA School of Science and Technology, Portugal)
14h00 - 14h30	KN 13: Julio Fernandez Cestau (IMDEA Materials, Spain) "The rise of coinage metal TADF emitters for solid-state lightning"
14h30 - 14h45	OC 09: Szymon Chorazy (Jagiellonian University, Krakow, Poland) "Photoluminescent lathanide(III) single-molecule magnets in polycyanidocuprate(I)-based frameworks"
14h45 - 15h00	OC 10: Guillermo Moreno Alcántar (University of Strasbourg, France) "Tuning the luminiscence of silver(I) compounds"
15h00 - 15h15	OC 11: Francisco Caparrós (University of Barcelona, Spain) "Study of the effect of the environment on the photophysical properties of tetranuclear gold(I) dibenzo[G,P]chrysene derivatives"
15h15 - 15h30	OC 12: Andrea Pinto (University of Barcelona, Spain) "Photophysical effects of the coordination of gold(I) to coumarin chromophores"
15h30 - 15h45	OC 13: Mengxi Lin (University of Barcelona, Spaim) "Sythesis and characteriazation of nanostructured Pt-Ag-based chalcogenide semiconductors"
15h45 - 16h30	Coffee Break
16h30 - 18h00	**Catalysis III** Chair: Clara Gomes (LAQV & UCIBIO, REQUIMTE, NOVA School of Science and Technology, Portugal)
16h30 - 17h00	KN 14: José Maria Muñoz-Molina (University of Huelva, Spain) "Exploring the copper-catalyzed *n-f* bond activation toward intramolecular C-H amination to pyrrolidines and piperidines"
17h00 - 17h30	KN 15: M. Carmen Nicasio (University of Sevilla, Spain) "Copper(I) complexes with terphenyl phosphines for CUAAC reactions on water"
17h30 - 17h45	OC 14: Juan A. Casares (University of Valladolid, Spain) "Study of the oxidation of $[Cu(C_6F_5)(bipy)]$ by aryl iodides"
17h45 - 18h00	OC 15: Tiago Cruz (CQE, IST, University of Lisboa, Portugal) "Catalytic applications of new copper(I) complexes of 2-iminopyrrolyl ligands"
18h00 - 18h15	OC 16: Gabriel Aullón (University of Barcelona, Spain) "Degradation of silver(I) compounds with N-heterocyclic carbenes into saline water"
18h15 - 18h30	**Closing Session**

Program at a glance

Time	**Thursday** **January 30**	**Friday** **January 31**	Time
08h00 - 09h00	*Registration*		08h00 - 09h00
09h00 - 09h15	Get together Introductory remarks		09h00 - 09h15
09h15 - 09h30	KN 01: Isabel Moura	KN 08: Simone dell' Acqua	09h15 - 09h30
09h30 - 09h45			09h30 - 09h45
09h45 - 10h00	KN 02: Stephane Torelli	KN 09: Isabel Correia	09h45 - 10h00
10h00 - 10h15			10h00 - 10h15
10h15 - 10h30	OC 01: Sabina Jaros	KN 10: Enrique Garcia-España	10h15 - 10h30
10h30 - 10h45	OC 02: Luis Alves		10h30 - 10h45
10h45 - 11h15	Coffee Break	Coffee Break	10h45 - 11h15
11h15 - 11h30	KN 03: Alexander Kirillov	KN 11: Carmen Albeniz	11h15 - 11h30
11h30 - 11h45			11h30 - 11h45
11h45 - 12h00	KN 04: Pierre de Fremont	KN 12: Kamran T. Mahmudov	11h45 - 12h00
12h00 - 12h15			12h00 - 12h15
12h15 - 12h30	OC 03: Anup Paul	OC 07: Manas Sutradhar	12h15 - 12h30
12h30 - 12h45	OC 04: Christophe Fliedel	OC 08: Clara Gomes	12h30 - 12h45
12h45 - 14h00	Lunch	Lunch	12h45 - 14h00
14h00 - 14h15	KN 05: Laura Rodríguez	KN 13: Julio Fernandez-Cestau	14h00 - 14h15
14h15 - 14h30			14h15 - 14h30
14h30 - 14h45	KN 06: Concepción Gimeno	OC 09: Szymon Chorazy	14h30 - 14h45
14h45 - 15h00		OC 10: Guillermo Moreno Alcántar	14h45 - 15h00
15h00 - 15h15	OC 05: Luís Lima	OC 11: Francisco Caparrós	15h00 - 15h15
15h15 - 15h30	OC 06: Mani Outis	OC 12: Andrea Pinto	15h15 - 15h30
15h30 - 15h45	KN 07: Paulo Martinho	OC 13: Mengxi Lin	15h30 - 15h45
15h45 - 16h00		Coffee Break	15h45 - 16h00
16h00 - 16h30			16h00 - 16h30
16h30 - 16h45	Coffee Break	KN 14: José Muñoz-Molina	16h30 - 16h45
16h45 - 17h00			16h45 - 17h00
17h00 - 17h15		KN 15: Carmen Nicasio	17h00 - 17h15
17h15 - 17h30			17h15 - 17h30
17h30 - 17h45	Flash Presentations	OC 14: Juan A. Casares	17h30 - 17h45
17h45 - 18h00		OC 15: Tiago Cruz	17h45 - 18h00
18h00 - 18h15	Poster Session	OC 16: Gabriel Aullón	18h00 - 18h15
18h15 - 18h30		Closing Session	18h15 - 18h30
18h30 - 19h00			18h30 - 19h00
20h00	*Workshop Dinner*		20h00

Keynote Lectures

KN 01

THE TETRANUCLEAR COPPER-SULFIDE CATALYTIC CENTER FROM THE TERMINAL ENZYME OF DENITRIFICATION

Isabel Moura

LAQV, REQUIMTE, FCT NOVA, *Campus* de Caparica, Portugal
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Nitrous oxide reductase the last enzyme of this pathway catalyzes the reduction of nitrous oxide at a new tetranuclear copper center (CuZ) the catalytic center overcoming the high activation energy of this reaction. In this center, each Cu atom is coordinated by two imidazole rings of histidine side-chains, with the exception of $Cu_{IV,}$ with only one histidine. This enzyme has been isolated with “CuZ” in two forms CuZ(4Cu1S) and CuZ(4Cu2S), which differ in the Cu_I-Cu_{IV} bridging ligand, leading to considerable differences in their spectroscopic and catalytic properties. The copper atoms in CuZ(4Cu1S) can be reduced to the [$4Cu^{1+}$] oxidation state, and its catalytic properties are compatible with the nitrous oxide reduction rates of whole cells, while in CuZ(4Cu2S) they can only be reduced to the [$1Cu^{2+}$ - $3Cu^{1+}$] oxidation state, that has a very low turnover number. The catalytic cycle of this enzyme has been explored and one of the intermediates, CuZº, has recently been identified and shown to be in the [$1Cu^{2+}$-$3Cu^{1+}$] oxidation state. Contrary to CuZ(4Cu2S), CuZº is rapidly reduced intramolecularly by the electron transferring center of the enzyme, CuA, to [$4Cu^{1+}$] by a physiologically relevant redox partner. The three-dimensional structure of nitrous oxide reductase with “CuZ” center as CuZ(4Cu1S) or CuZ(4Cu2S) shows that it is a unique functional dimer, with “CuZ” center of one subunit receiving electrons from CuA of the other subunit. The complex nature of this center has posed some questions relative to its assembly, which are only partially answered, as well as which is the active form of “CuZ” in vivo.

The structural, spectroscopic and catalytic features of the two forms of “CuZ” center will be addressed here. The understanding of its catalytic features and activation is essential to develop strategies to decrease the release of nitrous oxide to the atmosphere and to reduce its concentration in the stratosphere, as well as to serve of inspiration to synthetic inorganic chemists to develop new models of this peculiar and challenging copper sulfide center.

References

S.R.Pauleta, C.Carreira and I.Moura, “Metal Enzymes in Denitrification: Applications and Environmental Impact”, RCS Metallobiology Series no. 9, Vol. 39, Chapter 7, 141-169 (2017).
S.R.Pauleta, M.S.Carepo and I.Moura, Coord.Chem.Rev. (2019) 387, 436-449.

Acknowledgments: We thank E. Pierce, E. Solomon, S. R. Pauleta, S. Dell’Acqua, S. Ramos, C. Carreira and J. J. G. Moura for many contributions. The work was supported by FCT Projects (PTDC/QUI-BIQ/116481/2010 and PTDC/BBB-BIQ/0129/2014).

KN 02

COPPER/SULFUR CENTERS AS VERSATILE ARCHITECTURES FOR NITROUS OXIDE AND DIOXYGEN REDUCTION

S.Torelli

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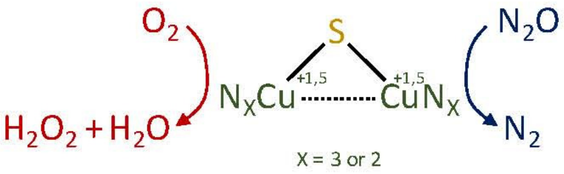
Copper-containing enzymes play a crucial role in living organisms where they are involved in complicated and sophisticated chemical transformations and electron transfer processes.[1] For instance, nitrous oxide (N_2O) reduction into dinitrogen at the unique tetranuclear copper/sulfur site of nitrous oxide reductase (N_2Or) is a key step during the denitrification pathway in bacteria.[2] On the other hand, dioxygen (O_2) activation mainly leads to oxidation reactions.[3] Exploring the multiple facets of the mechanisms involved in these reactions is an amazing playground for chemists. Indeed, studying the reactivity using bio-inspired complexes and comparison with data obtained with biological systems ultimately allow the extraction of important thermodynamic and kinetic parameters to help understanding the overall process.

In line with this, we recently evidenced that mixed-valent dicopper (II,I) complexes with N/S environments are suitable for N_2O and/or O_2 reduction.[4] The reactivity strongly depends on the metal coordination spheres when exogenous positions are present. Both aspects will be discussed in detail and illustrated with a few examples.



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[2] Pauleta, S. R.; Carepo, M. S. P.; Moura, I., *Coord. Chem. Rev.* **2019,** *387*, 436-449.
[3] Elwell, C. E.; Gagnon, N. L.; Neisen, B. D.; Dhar, D.; Spaeth, A. D.; Yee, G. M.; Tolman, W. B., *Chem. Rev.* **2017,** *117* (3), 2059-2107.
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KN 03

CUSTOM-MADE AGGREGATES: AUTHENTIC METAL-ORGANIC ARCHITECTURES FOR CATALYSIS & (BIO)MATERIALS

Alexander M. Kirillov*

University of Lisbon, Instituto Superior Técnico, Centro de Química Estrutural, Lisbon, Portugal
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This presentation will highlight our recent research on the application of versatile self-assembly synthetic methods for the design of a wide variety of Cu and Ag-based metal-organic architectures, including multinuclear metal complexes, metal-organic frameworks (MOFs) and coordination polymers (CPs) [1,2]. The following main topics will be discussed.

(A) Aqueous medium self-assembly synthesis, structural and topological features of Cu-based coordination polymers and multinuclear cores driven by aminoalcohol or aminophosphine building blocks and carboxylate linkers.

(B) Application of the obtained Cu-based coordination compounds as bioinspired catalysts in mild oxidative C−H functionalization of hydrocarbons and other substrates. Mild oxidation and carboxylation of alkanes.

(C) Design of bioactive Ag-based metal-organic architectures toward applications as topical antimicrobial agents and antibiofilm materials. New class of Ag bioMOFs.

(D) Cu and Ag-based aggregates as functional materials for selective sensing, photochemistry, and heterogeneous catalysis.

This work was supported by the Foundation for Science and Technology (FCT) and Portugal 2020 (projects LISBOA-01-0145-FEDER-029697 & UID/QUI/00100/2019).

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KN 04

NHC GOLD(I) POM HYBRIDS: EFFICIENT AND VERSATIL CATALYSTS

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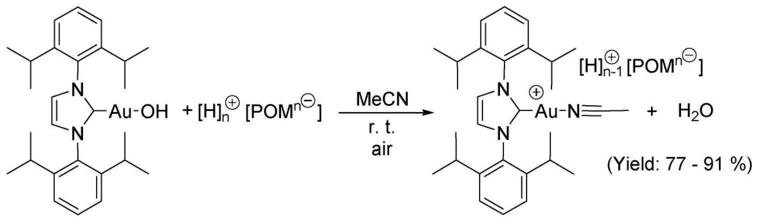
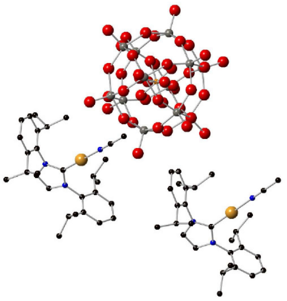
A series of hybrid NHC gold(I) acetonitrile polyoxometalate complexes including $\{[Au(IPr)(MeCN)^+][H^+]_3[SiW_{12}O_{40}^{4-}]$, $[Au(IPr)(MeCN)^+][H^+]_2[PMo_{12}O_{40}^{3-}]$, $[Au(IPr)(MeCN)^+][H^+]_5[P_2W_{18}O_{62}^{6-}]$, $[Au(IPr)(MeCN)^+][H^+]_2[PW_{12}O_{40}^{3-}]$, $[Au(IPr)(MeCN)^+]_3[PMo_{12}O_{40}^{3-}]$ and $[Au(I^tBu)(MeCN)^+][H^+]_2[PMo_{12}O_{40}^{3-}]\}$ were readily synthesized in high yield and characterized by NMR and MS-ESI spectroscopy.





In a preliminary catalytic study, their stability and activity was assessed under heterogeneous conditions for the ene-yne rearrangement reaction and a cycloisomerization reaction. Additionally, their recyclability were tested in the hydration of alkynes under homogeneous conditions.

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KN 05

LUMINESCENT PHOSPHINE GOLD(I) ALKYNYL COMPLEXES. ASSEMBLIES AND APPLICATIONS

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The photophysical properties of coinage-metal complexes, and in particular, gold(I) compounds have been intensely studied in the last two decades due to their fascinating versatility as well as the promising potential for technological applications in very different research fields such as optoelectronics, biological activity, chemosensors, mechanochromism, materials etc. All these properties are based on the study of the luminescence characteristics of these type of compounds, which often depend dramatically on the presence of meta-metal interactions (aurophilicity).

In our group we have studied in the last ten years a large number of gold(I) complexes containing different types of chromophores linked to the metal atom with an alkynyl moiety.[1] The second coordination position is in general occupied by a phosphine since these ligands are ideal to modulate the solubility in media of different polarity and to favor or difficult intra- or intermolecular interactions.

We have observed that aggregation can be induced by changing the polarity of the solvent with direct effects on the resulting luminescence, shapes of the supramolecular assemblies (type of intermolecular contacts and morphologies) and colors.

An overview of some of the important conclusions obtained in our group is presented in this communication together with some selected applications.

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KN 06

LUMINESCENT METAL COMPLEXES: SYNTHESIS AND APPLICATIONS

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Research in light emitting materials have experienced a substantial growth during the last few years and it has become one of the most important topics in transition metal chemistry. Potential applications of luminescent compounds in sensors, OLEDs, photocatalysis and medicine (among other areas) explain the growing research in such species. Metal atom allows efficient harvesting emissive long-lived triplet excited states upon light and/or electrical excitation, which is advantageous for bimolecular photo-catalysis and luminescent sensing.

In one hand, the synthesis and potential applications of gold complexes as dopants in OLEDS will be commented. The variety of ligands with different donor centers that can coordinate to gold in their different oxidation states will permit the tuning of the emission energy almost over the whole of the visible spectrum.

In the other hand, finding luminescent drugs for their use with optical visualization techniques such as fluorescence microscopy is not common. Therefore, an elegant approach to overcome such problem would be the combination of a visualization agent with a selected therapeutic. Such bifunctional bioprobe, known as an optical theranostic or a trackable agent, would be able to provide relevant information regarding its biological interplay. The new knowledge could provide a major impact in medicine allowing the delivery of more efficient drug through a rationalized design. The design of bimetallic Re(I)/Au(I) or Ir(III)-Au(I) optical trackable probes, where the Re(I) or Ir(III) fragment are providing the optical properties whereas the Au(I) provides will be commented.

KN 07

MOLECULAR SENSORS AND MAGNETIC SWITCHES USING GROUP 11 METALS

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The versatility of ethylenediamine-inspired Schiff-base transition metal complexes has been shown in their extensive applications in molecular sensors (e.g. electrochromic, recognition) and molecular switches (e.g. redox, magnetic). Taking this into account, one can design an ethylenediamine-inspired versatile molecule with sensing or switching properties that will be used to fabricate materials with one or both properties combined. For example, while metal salen-type electropolymers of transition metal ions such as Cu(II) have produced exciting results in the activation of small molecules, particularly electrocatalytic reduction of oxygen,[1,2] Fe(III)-salen derived complexes have shown to be able to switch between spin states, thus displaying the spin crossover phenomenon.[3] Additionally, group 11 metals can show luminescent properties which can possibly be used to probe the spin switching ability of Fe(III)-salen derived complexes. Engineering of multifunctional materials with one function or more in the same molecule offers the opportunity to construct complex systems and to fabricate materials towards application to real life objects. Here I show our contribution to the fields of molecular sensors and molecular switches where sensors with molecular recognition using homo- and hetero-binuclear Cu(II) complexes and Fe(III) magnetic switches with luminescent probes using Cu, Ag and Au will be discussed.

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KN 08

COPPER AND OXIDATIVE STRESS IN NEURODEGENERATIVE DISEASES

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Growing evidence supports the view that disruption of metal homeostasis in the brain is linked to neurodegenerative diseases such as Alzheimer and Parkinson's diseases [1]. Toxic effects of metal ions such as iron and copper may be directly associated with the possibility to promote and stabilize oligomers of neuronal peptides, but in most cases these effects depend on the redox properties of metal ions and the production of reactive oxygen species (ROS). In particular, the interaction of these ions with neuronal peptides has an influence on: (i) the metal redox potential and hence their reactivity towards dioxygen or hydrogen peroxide, which leads to ROS production, (ii) the ability to promote metal-mediated oxidation of external substrates present in the environment, and (iii) the post-translational modifications in the endogenous peptides. It is therefore of extreme importance to clarify to which extent the interaction of metal ions with neuronal peptides has pro-oxidant effects.

We are involved in a systematic investigation of the binding and reactivity of copper(II) and copper(I) with peptide fragments of β-amyloid (Aβ), α-synuclein (αS), tau protein ($R_n\tau$), and prion protein (PrP), containing the residues which act as binding sites for the metal ions.

In order to identify and characterize the metal binding environment for copper(I) with αS, NMR spectroscopy in the presence of the isolelectronic ion silver(I) has been performed [2].

For the reactivity studies, the first important exogenous target of the oxidative reactivity of metal-peptide complexes are the catecholamine neurotransmitters, such as dopamine, because of their reactivity and diffusion in the brain. In the case of copper(II), these studies showed that the reactivity markedly depends on the peptide, as Aβ, PrP and $R_3\tau$ strongly promote, $R_1\tau$ slightly enhances, and αS depresses the oxidative capacity of the ion [see e.g. 3,4]. However, also the environment affects the reactivity, as the interaction of copper-peptides with membranes changes the redox properties of the ion.

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KN 09

THERAPEUTIC POTENTIAL OF COPPER PHENANTROLINE COMPLEXES

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Copper complexes are attractive potential alternatives to anticancer platinum drugs, assumed to have efficacy and less toxic effects. 1,10-phenanthroline (phen) is a bioactive molecule and a versatile building block. Phen and its derivatives have been quite extensively used in Medicinal Chemistry, and metal complexes with phen ligands have shown interesting biological properties, such as its potential utility as fluorescent probes and characteristic features for DNA binding. For instance, $[Cu(phen)_2]^+$ inhibits DNA or RNA polymerisation and induces DNA strand scission in the presence of H_2O_2 or thiol [1], by catalyzing the formation of reactive oxygen species. Several ternary complexes of Cu(II) and phen or its derivatives with many other ligands, such as Schiff bases have been prepared and they exhibit properties such as DNA cleavage ability and antitumor action [2]. The Cu-complex containing 4,7-dimethyl-1,10-phenanthroline (Me_2phen) and glycine, $[Cu(Gly)(Me_2phen)]NO_3$, from the group of compounds known as Casiopeinas®, is currently in clinical trials [3]. Our group has been exploring Cu-complexes containing phen derivatives for anticancer therapy. We will present examples of Cu-ternary complexes containing Schiff bases derived from amino-acids, B_6 vitamers and chromones. Their cytotoxic activity in several cancer cell lines, as well as studies on their mechanisms of cell death will be presented. These properties will be compared with data obtained for $[Cu(phen)_2]^{2+}$.

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KN 10

SYNTHESIS AND STUDY OF SOD MIMETICS: FROM AZA-MACROCYCLIC COMPLEXES TO NANO-STRUCTURED SYSTEMS

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Copper, the first element of group 11, has a prominent biological role participating in numerous biological processes, most of them related to dioxygen management and electron transfer. Among these functions, copper is involved as the electroactive metal in the active site of protective SOD1 and SOD3 enzymes, which along with the Mn enzyme SOD2, are in charge of regulating superoxide radical concentration in mammals, getting rid of excess amounts of superoxide anions through their dismutation into hydrogen peroxide and dioxygen. Superoxide is the first product coming out from the reduction of dioxygen to give water. Imbalances between generation and clearance of superoxide anions give rise to the formation of all other reactive oxygen species (ROS) causing oxidative stress. Oxidative stress is related to a variety of health issues that include neurodegenerative disorders such as Parkinson's and Alzheimer's disease (AD).[1] Administration of SODs is however not useful for therapeutic treatment due to the drawbacks that they present -such as the absence of oral activity. In this respect, it has been reported that several copper complexes of aza-macrocyclic ligands have SOD activities in vitro which rank among the highest ones so far reported for synthetic systems.[2,3] A step forward to improve the activity, the likely-cell uptake and bio-distribution of these low molecular weight mimetics might be their incorporation in non-toxic nanoparticles (NPs). The grafting of the molecules to the surface of the nanoparticles may yield pre-concentration and amplification of the signal.

Here we discuss the chemistry of new Cu^{2+} aza-macrocyclic complexes appropriately functionalized to permit their covalent anchorage to boehmite oxidic nanoparticles,[4] and we examine the parameters regulating the general SOD activity enhancement observed.

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KN 11

TRANSMETALATION OF HYDROCARBYL GROUPS BETWEEN GROUP 11 AND OTHER TRANSITION METALS: HOW SIMILAR ARE Cu, Ag AND Au?

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The transmetalation of alkynyl groups between Cu, Ag or Au derivatives and palladium complexes has been studied in detail. This reaction is involved in the classical Sonogashira reaction (Cu),[1] in other group 11 metal versions of the process,[2] and in bimetallic catalytic reactions that get advantage of the cooperation of Pd and Au.[3] Interesting differences are observed for Cu, Ag and Au inferred from mechanistic experiments and the isolation of relevant bimetallic complexes. The relative stability of the metal σ-alkynyl or π-alkynyl bond is important to determine the nature of the complexes formed and the extent of the group exchange.[4,5]

The transmetalation of monoamino- or monoalkoxo-carbene complexes from tungsten to group 11 metals will also be discussed. The exchange of this type of fragment reveals interesting differences between the three metals, silver being the most reluctant metal to form a carbene complex. The analysis of the decomposition products in these reactions shows the nature of the group 11 carbenes and the occurrence of an unexpected demetalation process.

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KN 12

COPPER(II) ARYLHYDRAZONATES: SYNTHESIS AND CATALYSIS

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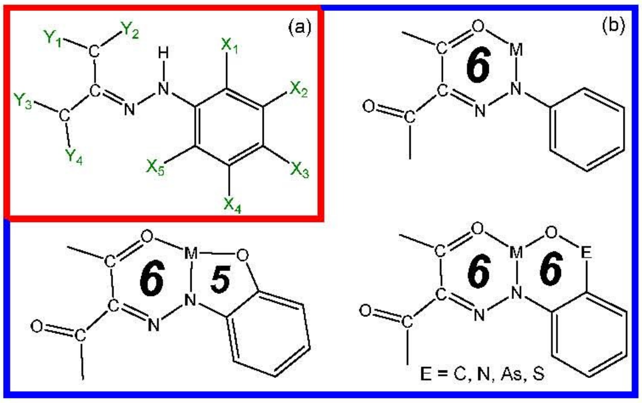
C–N coupling of aromatic diazonium salts with active methylene compounds (Japp-Klingemann reaction) in basic medium lead to arylhydrazones of active methylene compounds (AHAMCs) (Scheme 1a) [1]. AHAMCs are versatile starting materials for a number of organic synthesis leading to compounds which are biologically active, possess liquid crystal properties, can be applied as analytical reagents, indicators, ionophores, molecular switches, hydrazone dyes, etc. [1].



Scheme 1. a) Arylhydrazones of active methylene compounds (AHAMCs); b) Possible chelating modes of coordination within the AHAMC complexes.

With respect to coordination chemistry, AHMACs are valuable ligands for many metal ions allowing one to create different confined and overall geometries and structures [1]. Thus, depending on the position of a substituent and its nature and on the metal ion, different types of coordination (Scheme 1b) can be achieved. Many AHAMC ligands form trivial mononuclear diligand complexes, but the introduction of *e.g.*, a –OH at the *ortho* position of the aromatic part allows one to yield mononuclear complexes with one ligated AHAMC or binuclear diligand complexes. On the other hand, the non-chelating carbonyl of the active methylene fragment can further coordinate to a metal-ion and a coordination polymer can be formed. The position of the substituent in the aromatic part can drastically influence the geometry of the complexes. In addition, variation of the metal ions used for the synthesis allows one to prepare complexes of different topologies and coordination modes using the same ligand.

In this lecture, the synthesis of multinuclear Cu(II)-arylhydrazonates will be discussed. We will also highlight the application of these complexes as catalysts in C–C coupling, oxidation, etc. reactions.

Acknowledgements

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KN 13

THE RISE OF COINAGE METAL TADF EMITTERS FOR SOLID-STATE LIGHTNING

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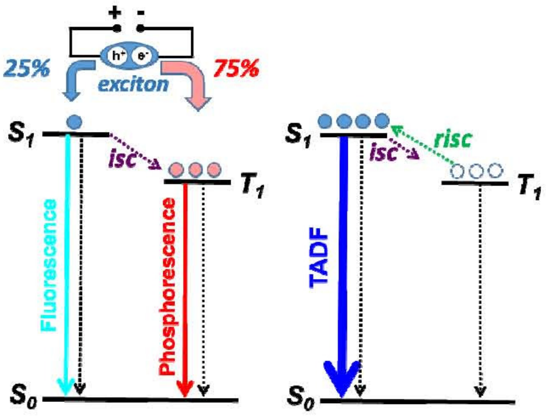
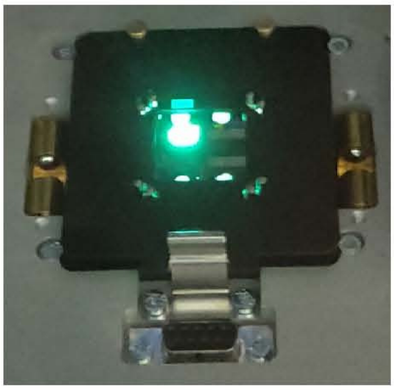
The design of more efficient OLEDs (organic light emitting diods) and LECs (light emitting electrochemical cells) is an important focus of interest in materials science. These systems are key technologies for modern screens in TVs and mobile phones and are also implemented in prototypes of organic solar cells, flexible panels and next-gen devices.

Optical devices require active materials capable of generate electroluminescence. In electroluminescence, the light is generated by the exciton, but according to spin orientation statistics the excitons are formed in a 1:3 ratio singlet:triplet. The relevance of the TADF (thermally activated delayed fluorescence) process lay in the risc (reverse intersystem crossing) mechanism, capable of re-populate the singlet state with the triplet excitons. This means that the theoretical limit in efficiency for the conversion of electrons in photons is 100% (compared to 75% and 25% for phosphorescence and fluorescence, respectively).

The most studied TADF emitters for devices are organic molecules. However, the use of transition metal complexes is becoming an emerging area due to their superior stabilities. Group 11 complexes are a prominent family in the search of efficient TADF emissive materials. In particular, we have explored TADF in Cu(I), Au(I), Au(III), and Ag(I) and we have successfully manufactured efficient TADF group 11 based SSL devices.





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KN 14

EXPLORING THE COPPER-CATALYZED N-F BOND ACTIVATION TOWARD INTRAMOLECULAR C-H AMINATION TO PYRROLIDINES AND PIPERIDINES

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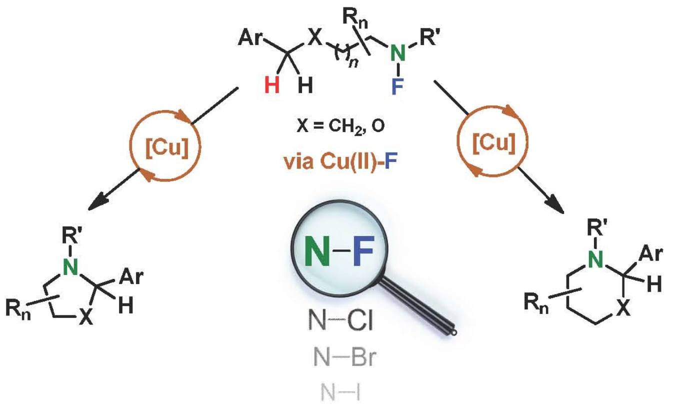
Because nitrogen-containing heterocycles are frequently embedded in the structure of bioactive molecules,[1] developing effective methods for their synthesis remains an important objective. The direct amination of C_{sp3}−H bonds is one of the most attractive strategy to prepare C−N bonds,[2] and such reactions can be accomplished with good efficiency with the aid of catalysts based on transition metals. Among them, copper catalysts can be advantageous from the standpoints of cost and toxicity. In this context, N-halogenated amines represent an attractive entry to C_{sp3}−H amination by means of intramolecular processes. However, the cyclization reactions of fluorine-containing substrates have remained unexplored until now,[3] in contrast to its heavier halogen counterparts,[4-6] due to the lower tendency toward homolytic bond cleavage of N−F bonds.

The contribution will essentially concentrate on: i) our recent efforts to develop the efficient copper-catalyzed synthesis of heterocycles through pathways involving N−F and subsequent C−H bond activation and ii) studies of possible catalytic mechanisms.



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KN 15

COPPER(I) COMPLEXES WITH TERPHENYL PHOSPHINES FOR CUAAC REACTIONS ON WATER

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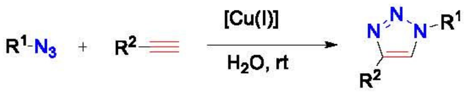
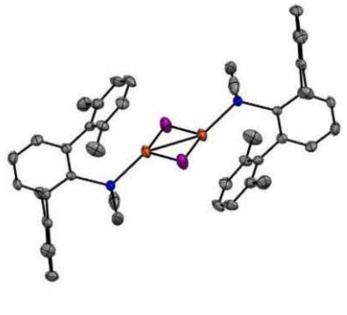
Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) is a highly efficient tool for the regiselective synthesis of 1,4-disubstituted triazoles,[1] heterocycles that find applications in diverse fields including organic synthesis, biochemistry, medicinal chemistry and material science.[2] Competent well-defined Cu(I) catalysts reported to date are mainly supported by polydentate nitrogen-base ligands or N-heterocyclic carbenes. However, the use of phosphines ligands in this transformation is still very limited.[3] This presentation will focus on the use of terphenyl phosphines as ancillary ligands to stabilize a variety of air-stable Cu(I)-halides complexes. The applications of these complexes as catalysts for CuAAC reactions on water, at ambient temperatures, will be discussed.



[Cu(I)] =



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Acknowledgements

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Oral Communications

OC 01

ANTIMICROBIAL AND SENSING PROPERTIES OF NEW SILVER(I) AND COPPER(I) COORDINATION POLYMERS DRIVEN BY ADAMANTANE-LIKE AMINOPHOSPHINE BUILDING BLOCKS

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In recent years, considerable attention has been devoted to the design and synthesis of new functional silver(I) and copper(I) coordination polymers (CPs) and their application as potent antimicrobial, luminescent and sensing materials. Among many parameters that influence the generation, stability, water solubility, and functional properties of Ag(I) and Cu(I) coordination networks, the rational selection of the multidentate *O*-, *N*-, or *P*-ligands is the most crucial one.[1,2]

In this regard, the mixed-ligand approach for the controlled preparation of "tailor-made" antimicrobial and luminescent coordination compounds using an aqua-soluble *N,P*-aminophosphine, 1,3,5-triaza-7-phosphaadamantane (PTA) and 1,3,5-triaza-7-phosphaadamantane-7-oxide (PTA=O), along with different halogen and *O*-type ancillary ligands constitutes a particularly promising research direction. Hence, we report herein the synthesis and full characterization of several rare examples of aqua-soluble bioactive or luminescent silver- and copper-organic networks, namely 1D $[Ag(\mu_3\text{-PTA})(chc)]_n{\cdot}n(Hchc)$ $2nH_2O$ (**1**), 3D $[Ag_2(\mu_3\text{-PTA})_2(\mu_2\text{-chdc})]_n{\cdot}5nH_2O$ (**2**), 2D $[Ag_2(\mu_2\text{-PTA})_2(\mu_4\text{-}H_2chtc)]_n{\cdot}6nH_2O$ (**3**), 1D $[Ag_2(\mu_2\text{-PTA})(\mu_3\text{-PTA})(\mu_2\text{-pga})(H_2O)]_n{\cdot}6H_2O$ (**4**), 2D $[Ag_2(\mu_2\text{-PTA})(\mu_3\text{-PTA})(Hpmal)_2]_n{\cdot}2H_2O$ (**5**), 2D $[Ag(\mu_3\text{-PTA})(Hdmga)]_n$ (**6**), 1D $[Ag(\mu\text{-PTAH})(NO_3)_2]_n$ (**7**), 1D $[Ag(\mu\text{-PTA})(NO_2)]_n$ (**8**) and 2D $[Cu_6(\mu_3\text{-I})_6(\mu_3\text{-PTA=O})]_n$ (**9**) coordination polymers derived from cyclohexanecarboxylic (Hchc), 1,4-cyclohexanedicarboxylic (H_2chdc), 1,2,4,5-cyclohexanetetracarboxylic (H_4chtc), 3-phenylglutaric (H_2pga), phenylmalonic (H_2pmal), or 3,3-dimethylglutaric (H_2dmga) acids and iodide, nitrate, and nitrite anion. These products exhibit significant antimicrobial activity and stimuli-responsive photoluminescence, thus opening up their potential exploration as novel bioactive and sensing materials.[1,2,3,4]

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OC 02

CHEMICAL AND BIOLOGICAL APPLICATIONS OF CYCLAM-BASED COPPER(II) COMPLEXES

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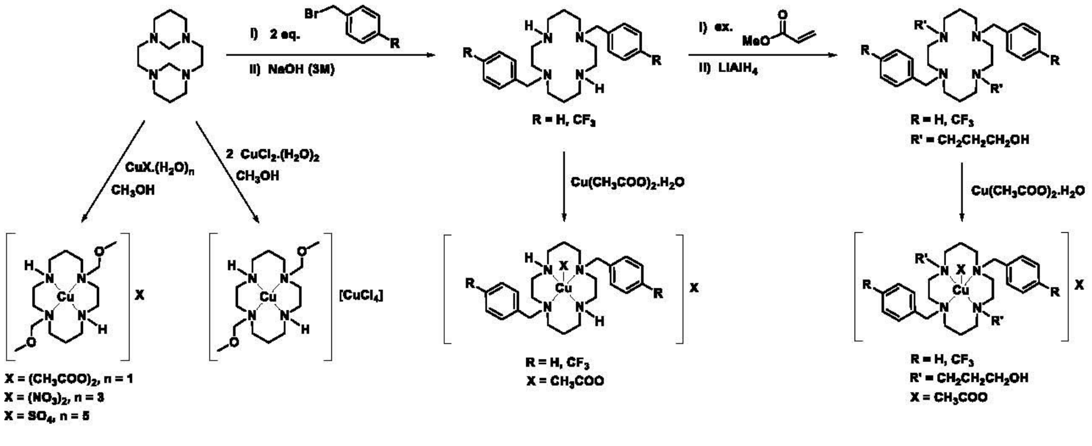
The field of macrocyclic complexes is extremely wide due to their use in catalysis [1], selective metal recovery and recycling [2], sensors [3] and radiopharmaceuticals [4]. Among other macrocyclic ligands, cyclams have been extensively studied because they can accommodate and stabilize a large variety of metal cations in several oxidation states. Taking advantage of the biocompatibility, the high metal chelation stability constants and the possibility of *N*-functionalization of the cyclam backbone, a variety of cyclam derivatives have been studied by us over the last years (see Scheme 1) [5,6]. The most recent results on chemical and biological applications of cyclam-based Cu(II) complexes will be presented and discussed.



Scheme 1

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OC 03

VERSATILITY OF BENZIMIDAZOLE DERIVED COPPER (II) COMPLEXES

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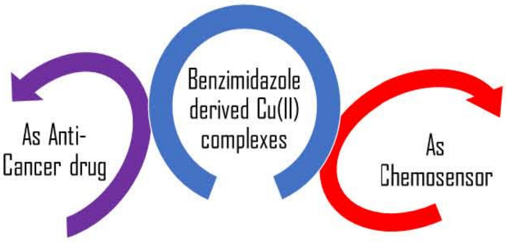
Copper is the third most abundant transition element present in the human body and plays a vital role in fundamental physiological processes. At higher concentration, it can affect blood composition, damage the central nervous system, kidneys, liver and lungs etc. As a result, finding a selective fluorescence chemosensor which can instantaneously detect Cu^{2+} ions have become an interesting and challenging area of research [1]. Further, copper (II) complexes are also in the front line of anticancer drug research owing to their capability of interacting directly with DNA/nuclear proteins [2,3]. On the other hand, the benzimidazole-based ligands are promising systems for the development of biologically active metal complexes, due to the structural similarity of the benzimidazole nucleus with natural compounds such as vitamin-B12 derivatives and purine bases and also as chemosensor [1-3]. Thus, through this presentation, the versatility of such benzimidazole-based copper (II) complexes will be highlighted.



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Acknowledgement: The authors gratefully acknowledge the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its projects PTDC/QEQ-ERQ/1648/2014, PTDC/QEQ-QIN/3967/2014, and UID/QUI/00100/2020. A.P. acknowledges the FCT and IST for a working contract "DL/197/2019"

OC 04

BEYOND ATOM TRANSFER RADICAL POLYMERIZATION THE FASCINATING COPPER–RADICAL COUPLE

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Copper(I) complexes [Cu^I/L] are the most successful mediators of atom transfer radical polymerization (ATRP).[1] ATRP is based on the reversible propagating radical chain ($P_n^\bullet$) deactivation by a copper(II) halide complex [$Y\text{-}Cu^{II}/L$], leading to a dormant polymer chain ($P_n\text{-}Y$) and the copper(I) [Cu^I/L] (re)activator (Figure). However, ATRP faces two limitations that are (1) the extension to less reactive monomers and (2) the contamination by metal-mediated radical termination reactions. Two different phenomena were recently identified as interfering with chain propagation: 1) catalyzed radical termination (CRT) and 2) reductive radical termination (RRT). Both result from an intermediate organometallic dormant species [$P_n\text{-}Cu^{II}/L$], which reacts with either a second radical in CRT or with a proton source in RRT.

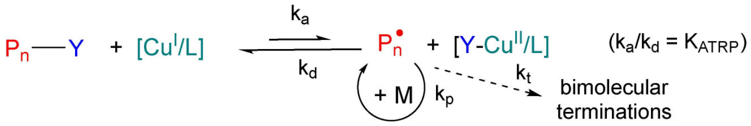

Figure. ATRP equilibrium (P_n-Y: dormant chain; Y: halogen; $P_n^\bullet$: propagating radical.

The present contribution will highlight our efforts to understand how CRT and RRT side reactions may affect ATRP processes. Especially, we are performing extensive studies on the copper-catalyzed termination of model acrylate, methacrylate and other radicals.[2] Our efforts are also dedicated to the generation, characterization and decomposition studies of related organo-copper(II) complexes, to further understand how they are involved in these side-reactions.[3]

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OC 05

ULTRASENSITIVE COLORIMETRIC COPPER(II) CHEMOSENSORS FOR ENVIRONMENTAL APPLICATIONS

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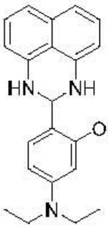
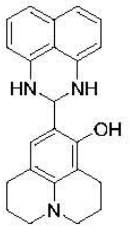
The design of chemosensors for metal cations with facile, selective and ultrasensitive detection ability is still a big challenge, and copper(II) is especially relevant while being a common environmental pollutant with several adverse effects in human health.

Two new and highly efficient colorimetric Cu^{2+} chemosensors, L^1 [1] and L^2 [2], were developed (see scheme) and studied in aqueous methanol media. Both sensors yield intense visible absorptions when in presence of Cu^{2+} in pH=7 buffered medium, considerably redshifted from their own absorptions and not seen for any other tested cation. Their ratiometric response displays remarkably low limits of detection (LoD) at 3.7 or 2.3 nM, respectively for L^1 and L^2. Furthermore, some impressive 1.5 or 0.5 µM LoD are possible by simple naked-eye observations, well below the 31.5 µM (2 mg/L) guidelines for drinking water established by the World Health Organization.

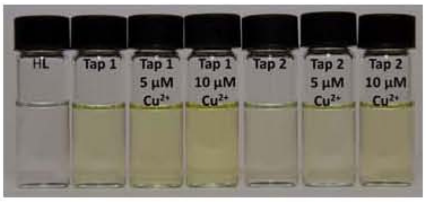


L^1



L^2

The sensors were characterized in their Cu^{2+} binding speciation, equilibrium, and structure by UV-vis spectrophotometry, while the robustness of the sensing phenomena with regard to reversibility and to competition from other cationic species was demonstrated. Application of both sensors to the quantification of Cu^{2+} levels in tap water samples was successfully achieved, both directly and after spiking samples with additional Cu^{2+} (see Figure).



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OC 06

PHOTOPHYSICAL CHARACTERIZATION OF TWO PHOSPHORESCENT DINUCLEAR COPPER IODIDE COMPLEXES: IMAPCT OF CRYSTALLINE NETWORK

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Luminescent Cu(I) complexes have recently gathered much attention due to their potential application in light-emitting diodes. By exhibiting room-temperature phosphorescence or thermally-activated delayed fluorescence, Cu(I) complexes can harness the energy from otherwise dark triplet states without requiring lanthanide or heavy transition metal complexes. Herein, we present two phosphorescent centrosymmetric $\{Cu_2(\mu\text{-}I)_2\}$ based complexes (**1**:$[CuI(PMe_2ArXyl)]_2$ and **2**:$[CuI(PEt_2ArMes)]_2$). Despite their similar structures, these complexes show distinct optical properties. To understand this phenomenon, the photophysical properties of these compounds were studied in solution, dispersion in solid matrix and in powder. The results were complemented with TD-DFT calculations, which shed light on the structure-dependent non-radiative decay mechanism. The results demonstrate the close relation between molecular structure undergoing Jahn-Teller Effect [1], crystal-packing and optical properties, which will influence the design of novel luminescent Cu(I) complexes in the future.

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry LAQV which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265) and also the PhD Grant SFRH/BD/120985/2016 financed by FCT (the Portuguese national funding agency for science, research and technology). The authors would like to thank Prof. Maria José Calhorda from University of Lisbon for the generous supporting and access to Gaussian09 software.

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OC 07

COPPER(II)-AROYLHYDRAZONE CATALYSTS FOR THE OXIDATION OF VOLATILE ORGANIC COMPOUNDS

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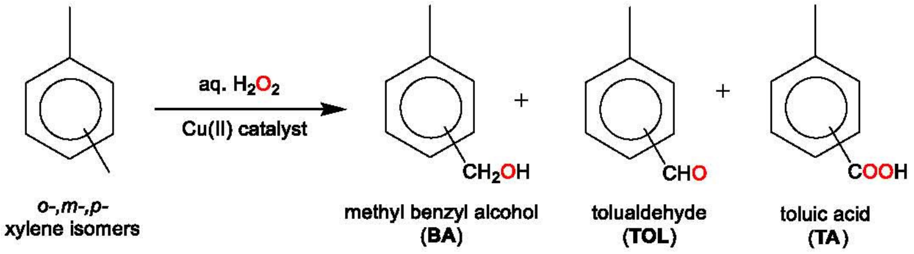
Catalytic oxidation is considered as one of the most interesting and promising pathways for the removal of volatile organic compounds (VOCs). Aromatic hydrocarbons, such as, benzene, toluene and xylene are some of the major VOCs with a high toxic potential to human health. Cu(II)-aroylhydrazones acts as good catalysts for the oxidation of VOCs to useful organic compounds via selective functionalization of aromatic hydrocarbons [1]. However, the cleavage of C-H bond in large scale is still challenging to the researcher in the field of catalysis. In this communication, the oxidation of VOCs (toluene and *o*-, *m*- and *p*-xylene) by Cu(II)-aroylhydrazones catalysts (Scheme 1) to the valuable functionalized product will be discussed.



Scheme 1. Catalytic peroxidative oxidation of xylene.

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OC 08

Cu(I) AND Ag(I) COMPLEXES BEARING ARYL-BIAL LIGANDS: SYNTHESIS, STRUCTURAL ANALYSIS AND APPLICATIONS AS CATALYSTS OR AS CYTOTOXIC AGENTS

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α-Diimines are versatile bidentate nitrogen chelating ligands, which are widely employed as ancillary ligands in the field of coordination/organometallic chemistry. Designing bidentate neutral *N*,*N*-chelating ligands containing sterically demanding groups has been crucial for their use as efficient catalysts in several homogeneous catalytic reactions [1].

We have been interested in the synthesis of Ni(II), Cu(I) and Cu(II) complexes and in their application as effective catalysts in the polymerization of ethylene [2a], cycloaddition reactions of alkynes and azides [2b] and reverse ATRP of styrene [2c].

Herein, we report the synthesis of new aryl-BIAN–Cu(I) and Ag(I) complexes (Figure 1), and their structural characterization by single-crystal X-ray diffraction.

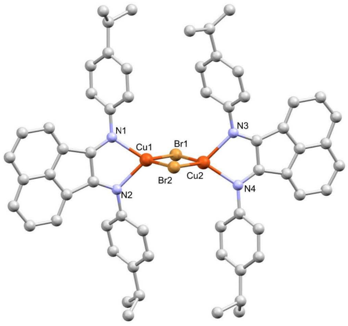

Figure 1: $[Cu((p\text{-}i\text{Pr-BIAN})Br]_2$ (p-iPr-BIAN = 4-iPr(C_6H_4)-BIAN; BIAN = bis-imino acenaphtene) molecular structure. Hydrogen atoms were omitted for clarity.

These complexes were tested and acted as efficient catalysts of the aerobic oxidation of benzylic alcohols (Cu(I)) or as antimicrobial agents (Ag(I)).

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry – LAQV and the Applied Molecular Biosciences Unit – UCIBIO, which are financed by national funds from FCT/MCTES (UID/QUI/50006/2019 and UID/Multi/04378/2019, respectively).

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OC 09

PHOTOLUMINESCENT LATHANIDE(III) SINGLE-MOLECULE MAGNETS IN POLYCYANIDOCUPRATE(I)-BASED FRAMEWORKS

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Cyanide metal complexes arouse a considerable scientific interest as molecular precursors for functional materials exhibiting diverse magnetic, optical and electrical properties. [1,2] These materials are usually composed of heterometallic cyanido-bridged frameworks where polycyanidometallates of d-block metal ions are combined with other complexes of d- or f-block metals. Cyanide metal complexes have been prepared for the most of transition metal ions, including Cu(I), Ag(I) and Au(I). The linear dicyanidometallates, $[\mathrm{M^I(CN)_2}]^-$ (M = Ag, Au) are good sensitizers for lanthanide(III) luminescence as shown in bimetal d-f assemblies. [3] On the contrary, cyanide Cu(I) complexes offer a great structural flexibility, thus, highly dimensional cyanido-bridged frameworks can be achieved. [4] We report the successful application of polycyanidocuprate(I) anions, $[\mathrm{Cu^I_2(CN)_5}]^{3-}$ in the synthesis of 3-D hetero-metallic d–f coordination frameworks, $[\mathrm{Ln^{III}}$(2,2'-bipyridine N,N'-dioxide)$_2(\mathrm{H_2O})][\mathrm{Cu^I_2(CN)_5}]\cdot 5\mathrm{H_2O}$ and $[\mathrm{Ln^{III}}$(4(3H)-pyrimidinone)$_2(\mathrm{H_2O})][\mathrm{Cu^I_2(CN)_5}]\cdot n\mathrm{H_2O}$. The cyanide Cu(I) complexes were, here, used as advanced linkers for lanthanide(III) complexes constraining their coordination geometry towards a single-molecule magnet behaviour co-existing with vis-to-NIR photoluminescence originating from characteristic f-f electronic transitions. [5]

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OC 10

TUNING THE LUMINISCENCE OF SILVER(I) COMPOUNDS

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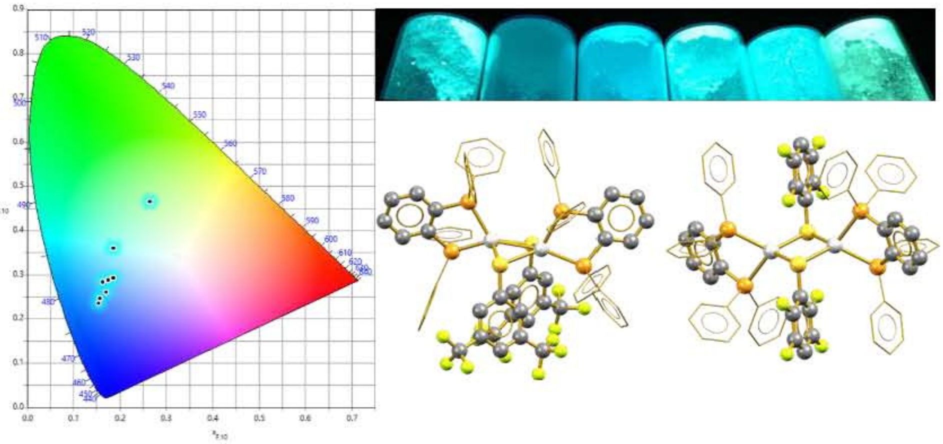
Silver has been one of the most important metals in the development of human civilization. Recently, its importance has scaled up to the next level and the research about further application of silver derivatives is experiencing a considerable increase on interest, particularly, the luminescence of silver(I) compounds had attracted attention due to the high emission efficiency observed in some compounds [1,2].

A series of new silver(I) compounds with 1,2-bis(diphenylphosphane)benzene (dppBz) and fluorophenylthiolates as ligands has been synthesised and characterized. The obtained compounds show a bright luminescence evident to the nude eye. The photophysical behaviour of this compounds has been analysed observing that the emissive behaviour of these compounds is strongly dependent of the aggregation state [3]. Furthermore, the use of different fluorination patterns in the fluorophenylthiolate ligands allows a rational control of the emission wavelength.



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OC 11

STUDY OF THE EFFECT OF THE ENVIRONMENT ON THE PHOTOPHYSICAL PROPERTIES OF TETRANUCLEAR GOLD(I) DIBENZO[G,P]CHRYSENE DERIVATIVES

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Disk shaped organic molecules have gained much attention in the recent years due to their structural and electronic properties with extensive π-electron delocalization. In this group, dibenzo[g,p]chrysene (DBC) derivatives stand out because of their high absorption coefficient, fluorescence quantum yield and photostability.[1,2]

In this work, we synthesized a new tetraalkynyl DCB ligand followed by the formation of two gold(I) derivatives with a phosphine coordinated to the second position (fig 1). After that, we studied the photophysical properties in solution and in organic matrixes.

Analysing the photophysical properties of the new compounds we observe the presence of only fluorescent emission. However, we could observe the presence of a populated triplet state throw laser flash photolysis experiments.

Studying their properties in organic matrixes, we could observe a shift in the emission colour from blue to green when the concentration increases, as well as a quantum yield reduction due to the formation of aggregates.

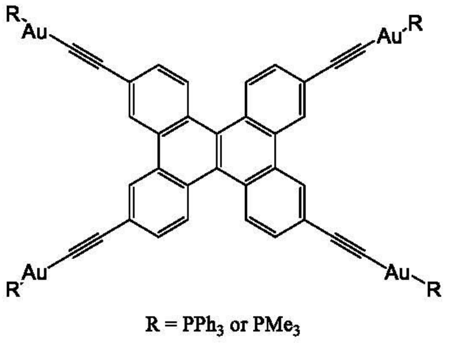

Fig 1. New DBC derivatives studied in this work.

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OC 12

PHOTOPHYSICAL EFFECTS OF THE COORDINATION OF GOLD(I) TO COUMARIN CHROMOPHORES

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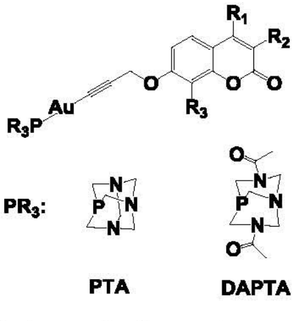
Coumarin derivatives are well-known for their photochemical and photophysical properties. The introduction of substituents into different positions of skeleton of coumarin allows to create compounds that strongly differ in their spectral and emissive abilities [1]. The incorporation of a heavy atom, like gold(I), in the chemical structure can promote the intersystem crossing in order to have phosphorescence emission [2].

In this way, we synthesized a variety of gold(I) derivatives that differ in the substituents in the coumarin skeleton and the phosphine coordinated into the gold atom (Scheme 1). Also, a photophysical study has been done in order to determine which is the effect of the gold(I) in the resultant luminescence of the compounds.



1- R_1=R_2=R_3= H
2- R_1= CH_3, R_2=R_3= H
3- R_1= CH_3, R_2= Cl, R_3= H
4- R_1= CH_3, R_2= H, R_3= NO_2

Scheme 1. General structure of the gold(I) complexes.

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OC 13

SYTHESIS AND CHARACTERIAZATION OF NANOSTRUCTURED Pt--Ag-BASED CHALCOGENIDE SEMICONDUCTORS

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Platinum-based chalcogenides have been gaining a lot of attention due to the special electrical and catalytic properties stemming from both the platinum presence and the semiconductor nature of the material. [1] Colloidal chemistry approaches are found to be a perfect candidate to form homogenous and compositionally complex nanostructured systems.[2] In this work, the silver selenide nanoparticles (NPs) are used as starting materials due to their high conductivity and super-ionic characteristic [3] to explore the possibility of partial cation exchange reaction between Pt and Ag cations from the host lattice of Ag_2Se NPs. Thus, a set of synthesis were designed by changing reaction parameters such as temperature, amount of reactants and also varieties of capping agents in order to form such nanostructured systems. The characterization results suggested that the silver chalcogenide nanocrystals have successfully transformed into compositionally more complex systems by using oleylamine or octylamine as capping agent at certain temperatures by means of cation exchange reaction. Structural and chemical characterization of these novel system suggests the formation of a ternary material with a Ag_3PtSe_2 stoichiometry.

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Acknowledgments:
We acknowledge financial support from the Spanish MINECO through CTQ2012-32247, CTQ2015-68370-P, and ENE2015-63969-R and from the Generalitat de Catalunya through 2014 SGR 129.

OC 14

STUDY OF THE OXIDATION OF [Cu(C_6F_5)(bipy)] BY ARYL IODIDES

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Fluoroaryls have been profusely used to study the mechanism of reactions catalyzed by palladium and nickel.[1] These groups form relatively strong C-M bonds, and very often allow the detection of reaction intermediates that would be too unstable with other aryl groups. In addition, these groups are easily monitored by ^{19}F NMR, allowing very detailed kinetic and mechanistic studies. This strategy for the study of organometallic systems has been scarcely used in the chemistry of copper. In this communication some studies carried out with fluorinated aryl groups, such as R = C_6F_5 and R = $C_6Cl_2F_3$, are presented as well as the study of some transmetalation reactions to palladium complexes.

Financial support is gratefully acknowledged from the Spanish MINECO (Proyect CTQ2016-80913-P) and the Junta de Castilla y León (projects JCyL VA 051P17 and VA062G18).

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OC 015

CATALYTIC APPLICATIONS OF NEW COPPER(I) COMPLEXES OF 2-IMINOPYRROLYL LIGANDS

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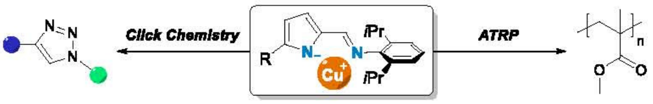
The presence of copper centers in oxygenase enzymes is crucial, owing to their oxygen activation capability [1]. As such, copper complexes are often effective catalysts for oxidation reactions [2]. However, copper-catalyzed regioselective 1,3-dipolar cycloaddition of azides and alkynes, also known as "click-chemistry" [3], or copper-mediated Atom Transfer Radical Polymerization (ATRP) [4] have become ubiquitous applications of copper complexes. The molecular systems thus derived have given rise to new breeds of architectures, with important implications in biological and materials sciences.

In order to have active, well-defined copper(I) catalyst systems, the catalytic intermediates must be properly stabilized, a feature made possible via efficient ligand design. In the present work, we report the synthesis and characterization of copper(I) complexes containing 2-iminopyrrolyl scaffolds with stereochemically and electronically differentiated substituents, in which the Cu(I) atom is stabilized in variable coordination environments (Scheme 1). We found that by varying the nuclearity of the new Cu(I) complexes, one can efficiently catalyze both click-chemistry and/or ATRP reactions.



Acknowledgements: We thank Fundação para a Ciência e a Tecnologia for the financial support (UID/QUI/00100/2019 and PTDC/QUI-QIN/31585/2017) and the fellowship to T.F.C.C. (PD/BD/52372/2013 – CATSUS PhD Program).

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OC 16

DEGRADATION OF SILVER(I) COMPOUNDS WITH *N*-HETEROCYCLIC CARBENES INTO SALINE WATER

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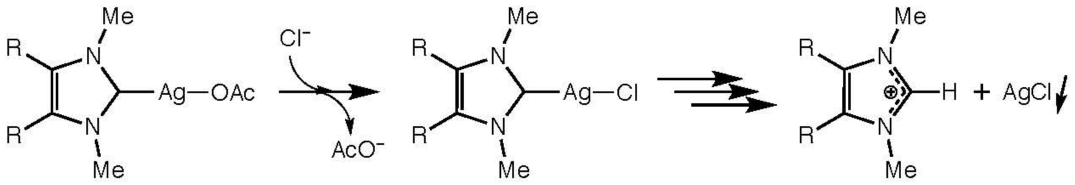
The effectiveness of silver compounds as an antimicrobial agent is known from centuries.[1] Recently, new silver(I) complexes with *N*-heterocyclic carbenes have been synthesized having more powerful antimicrobial activity than conventional drugs.[2]

Nevertheless, silver(I) presents a large affinity for the chloride anion. Consequently, it is the driving force that favors the decomposition of *NHC*-Ag compounds into saline water, and subsequent precipitation of AgCl. The control of this reaction is completely needed to prepare an active drug before its degradation in the human body. Therefore, in view of its applicability, a control of the stability of *NHC*-Ag species would be desirable. For example, the degradation of NHC-Ag-OAc compounds in the saline media can vary widely, from hours (R = H) to months (R = Cl).[3]



This work explores the role of the R substituents in the stability of *NHC*-Ag-OAc complexes in aqueous chloride media. A computational study based in DFT calculations is carried out to provide a mechanism for the sustitution reaction. Moreover, the influence of the R on the reaction is analyzed to understant those factors that stabilize NHC-Ag compounds.

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FCP 01

GOLD(I)-COMPLEX–TITANIA HYBRID PHOTOCATALYST FOR HYDROGEN PRODUCTION THROUGH VISIBLE LIGHT ABSORPTION

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Recent studies in our group show that the integration of TiO_2 with an Au^I complex containing a thiol coumarin moiety resulted in a very efficient photocatalyst for the generation of H_2, and that the role of the gold complex was determinant in the photogeneration of H_2 by accepting the photoinduced electrons originated in TiO_2 upon light exposure [1].

In this communication we present a new family of coumarin ligands to tune the absorption characteristics of the system for efficient production of H_2 through light absorption in the visible.

Au^I-phosphine complexes with these thiol-coumarin ligands (Figure 1) have been successfully synthesized using [AuCl(DAPTA)] as precursor.

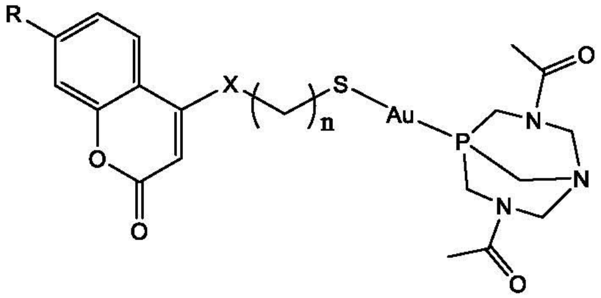

Figure 1. [Au(DAPTA)(S-Coumarin)] complexes.
(R = H, NEt_2; X = O, C; n = 0-10)

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FCP 02

EFFECT OF THE PROXIMITY OF THE HEAVY ATOM ON THE EMISSION OF AROMATIC FLUOROPHOES

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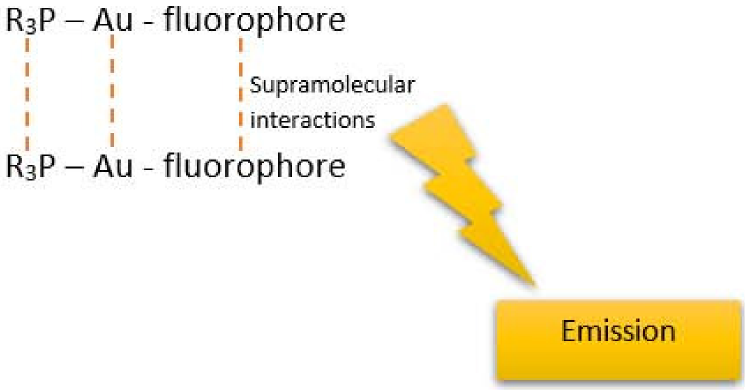
Gold (I) complexes are an expanding area of investigation thanks to the possibility of giving rise to supramolecular aggregates with particular morphologies that can be modulated together with their luminescent properties [1,2]. These properties have found interest in the use of the systems in a wide range of different applications. The *heavy atom effect* is observed to play a direct role favouring triplet harvesting being able to observe phosphorescence emission under mild conditions [3].

In our work, we are synthesising molecules with the structure: fluorophore-Au-PR_3, in order to study their luminescent properties based on the *heavy atom effect* of the gold (I). In addition, we are interested in the study of the supramolecular intra- and intermolecular interactions where our compounds are involved and how the aggregation affects on the resulting luminescence.



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FCP 03

COPPER COMPLEXES AS CATALYSTS IN ALKENE AMINOOXYGENATION REACTIONS

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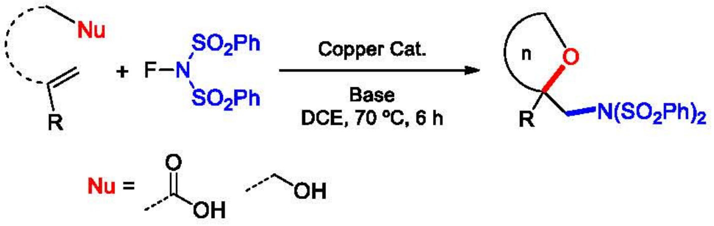
The design of new synthetic methods for the synthesis of oxygen heterocycles has become a field of great interest in organic chemistry,[1] since such structures are present in bioactive molecules, pharmaceuticals and natural products.[2,3] One of these methods consists of the aminooxygenation reaction of alkenes. This type of transformations leads to the formation of the oxygen heterocycle and a carbon-nitrogen bond (Scheme 1). Importantly, the introduction of the amino group alters the chemical and physical properties of the heterocyclic compound.[4] Zhang and Qi reported the copper catalyzed aminolactonization reaction of olefinic carboxylic acids with NFSI (*N*-fluorodibenzenesulfonimide).[4] These processes seem to involve radical reactions and the reversible oxidation of Cu(I) to Cu(II).



Scheme 1. Amino-oxygenation of alkenes[4]

On the other hand, in our group we have reported the use of well-defined Tp^{x}Cu complexes (Tp^x = hydrotrispyrazolylborate ligand) as efficient catalysts for the atom transfer radical addition (ATRA) of polyhalogenated compounds to olefins.[5] Furthermore, we have recently described the pyrrolidines and piperidines synthesis by intramolecular C-H amination using *N*-fluorinated precursors catalyzed by Tp^{x}Cu.[6] Based on these precedents, we decided to study the catalytic capabilities of Tp^{x}Cu complexes aminooxygenation of olefinic carboxylic acids NFSI. In this contribution, we demonstrate that these catalysts display good to excellent catalytic activities in these reactions.

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FCP 04

NEW TETRACOPPER(II) CORES FOR MILD CATALYTIC OXIDATION AND CARBOXYLATION OF ALKANES

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Three new tetracopper(II) coordination compounds were easily generated by aqueous medium self-assembly from Cu(NO$_3$)$_2$, a trifunctional aminoalcohol-sulfonic acid (H$_3$bes, N,N-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid) as a principal building block, and a benzenecarboxylic acid as a supporting ligand (i.e., benzoic (Hba), 4-hydroxybenzoic (Hfba), or 3-hydroxybenzoic (Hthba) acid).[1] The obtained products, $[Cu_4(\mu\text{-}Hbes)_3(\mu\text{-}H_2bes)(\mu\text{-}L)]\cdot 2H_2O$ (L = ba$^-$ (**1**), fhba$^-$ (**2**), and thba$^-$ (**3**)), were isolated as stable crystalline solids and characterized by FTIR, EA, ESI-MS, and single-crystal X-ray diffraction methods.

Compounds **1–3** act as efficient and versatile homogeneous catalysts in the oxidative C−H functionalization of alkanes (propane and cycloalkanes). Two different model reactions were explored: (1) mild oxidation of alkanes with hydrogen peroxide to give alcohols and ketones, and (2) mild carboxylation of alkanes in the presence of carbon monoxide, water, and potassium peroxodisulfate to give carboxylic acids (Scheme 1). For these reactions, effects of different parameters (acid promoter, loading of substrate, oxidant and catalyst, substrate scope, and effect of water), as well as mechanistic and selectivity characteristics, were studied and will be discussed.

Scheme 1. Model reactions for Cu-catalyzed oxidative functionalization of alkanes.

Acknowledgments: This work was supported by the FCT & Portugal 2020 (LISBOA-01-0145-FEDER-029697, UID/QUI/00100/2019). I.F.M.C. acknowledges the FCT for BD grant PD/BD/150418/2019.

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FCP 05

NEW SILVER (THIO)SEMICARBAZONE DERIVATIVES: SYNTHESIS, STRUCTURAL FEATURES & ANTIMICROBIAL ACTIVITY

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The current presentation will describe the synthesis and antimicrobial activity of two new silver(I) compounds that feature the {AgNO} or {AgSO} environments and were derived from semicarbazone and thiosemicarbazone type ligands. Organic ligands HL^1 [**1**, 1-((4-nitrophenyl)(phenyl)methylene)-semicarbazone] and HL^2 [**2**, 1-((4-nitrophenyl)(phenyl)methylene)-thiosemicarbazone] were prepared from 4-nitrobenzophenone via a one-step procedure from semicarbazide or thiosemicarbazide. Discrete silver(I) complexes $[Ag(HL^1)(NO_3)]$ (**3**) and $[\{Ag(HL^2)(NO_3)\}_6]$ (**4**) were obtained in the reaction of $AgNO_3$ with **1** or **2** in acetonitrile-acetone mixture and were fully characterized by standard methods (FTIR, NMR, ESI-MS, EA) as well as single-crystal X-ray diffraction. Antimicrobial activity of all compounds was investigated in terms of the Minimum Inhibitory Concentration (MIC) and Minimum Lethal Concentration (MLC), against Gram positive *S. epidermids* and *S. aure*us, and Gram negative *P. aeruginosa* and *E. coli*. The ability to inhibit biofilm formation was also determined. Of the four tested compounds, only **4** presented antimicrobial activity, including the ability to impair biofilm formation. However, the antimicrobial activity was only observed for the gram-positive bacteria. Further research on the design of other silver(I) coordination compounds and exploration of their antimicrobial potential is currently in progress in our laboratories.

References & acknowledgments

This study was supported by FCT and Portugal 2020 (projects PTDC/QUI-QIN/29697/2017, LISBOA-01-0145-FEDER-029697, UID/QUI/00100/2019, and REM2013), and the RUDN University Program 5-100. TAF acknowledges the FCT for BPD grant SFRH/BPD/119980/2016.

FCP 06

SUPRAMOLECULAR INTERACTIONS OF AU(I) TRIPODAL COMPOUNDS WITH PYRENE IN WATER

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New gold(I) tripodal complexes containing tripropargylamine moiety and the polar phosphines PTA (1,3,5-triaza-7-phosphaadamantane, **1**), DAPTA (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane, **2**) and TPPTS (triphenylphosfine-3,3',3''-trisulfonic acid trisodium salt, **3**) were synthesized [1]. The presence of the hydrophilic phosphine gives the compounds water solubility. Moreover, the tripodal structure of the complexes together with the presence of gold(I) atoms originates hydrophobic pockets that make the compounds ideal to interact with non-polar molecules in water. Thus, the interaction with the highly hydrophobic pyrene fluorescent dye [2] was evaluated with successful results for all the three compounds. Additional studies within cholate hydrogel matrices [3] point out to the stability of the host:guest adducts in different media.

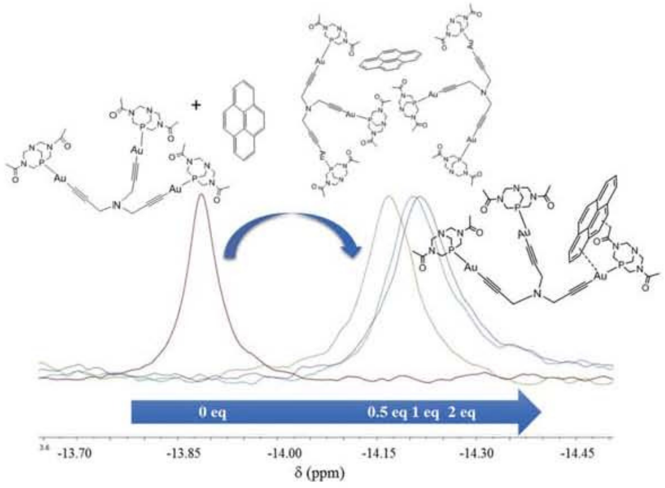

Figure 1. $^{31}P\{^1H\}$ NMR spectra of **2** in D_2O in the absence and in the presence of increasing amounts of pyrene.

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FCP 07

PALLADIUM (II) MEDIATED ACTIVATION OF HALONITRILES

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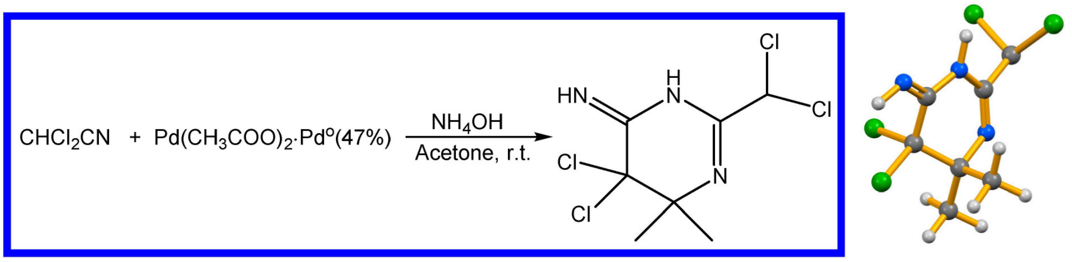
Organonitriles are well known versatile reagents, and their chemistry has been well explored [1]. In fact, activation of C≡N synthon lead to the C–C, C–N, C–O and C–S bonds, which allows to synthesis different class of organic compounds, as well as metal complexes depending on the nucleophiles and conditions used. A C≡N moiety in organonitriles are known to be quite reactive, particularly in the presence of transition metals. Herein, we investigated Pd(II) mediated transformation of C≡N in 2,2-dichloroacetonitrile (Schem).



Scheme. Pd(II) mediated activation of C≡N at $CHCl_2CN$.

Treatment of $Pd(CH_3COO)_2{\cdot}Pd^o(47\%)$ with $CHCl_2CN$ and ammonium hydroxide in acetone (Scheme) leads to 5,5-dichloro-2-(dichloromethyl)-6,6-dimethyl-5,6-dihydropyrimidin-4(3H)-imine, which precipitate in course of reaction. It was characterized by IR spectroscopy, electrospray mass spectrometry (ESI-MS), elemental analysis and single-crystal X-ray diffraction. Hence, this study opens up the possibility to synthesis of pyrimidine derivatives from cheaper starting materials. The study is being extended in our laboratory to other halonitriles and transition metal ions.

Acknowledgements

This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal (UID/QUI/00100/2013 project). KTM and AVG acknowledges the FCT and Instituto Superior Técnico (DL 57/2016 and L 57/2017 Program, Contracts no: IST-ID/85/2018 and IST-ID/110/2018, respectively). The authors also acknowledge the financial support by the Baku State University, Azerbaijan.

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FCP 08

THIOLATE BRIDGED GOLD(I) NHC CATALYSTS: NEW APPROACH FOR CATALYST DESIGN AND ITS APPLICATION TRAPPING CATALYTIC INTERMEDIATES

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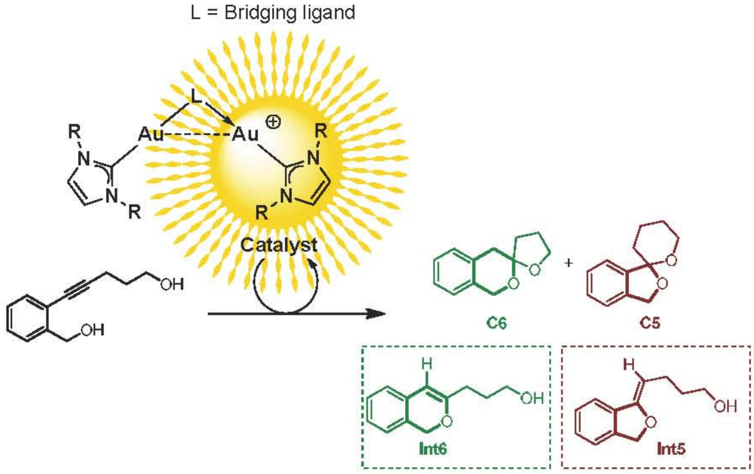
We have developed a series of novel dinuclear *N*-heterocyclic gold complexes with bridging thiolate ligands.[1] These novel complexes can slowly release the active catalytic species $[Au(NHC)]^+$ and the precursor $[Au(SC_6F_5)(NHC)]$ in the reaction medium, in the absence of any silver additive, and both species maintain stable during the whole catalytic cycle. We have taken advantage of these excellent properties to shed light into the gold catalyzed hydroalkoxylation of alkynes, with the aim of clarifying all the steps of the catalytic cycle, together with the characterization of intermediates and final products. Interestingly, we have isolated and characterized the pure final spiroketals and the thermodynamic intermediate of this process for the first time. Moreover, the kinetic intermediate has been also detected for the first time.



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FCP 09

NEW SALPHEN METAL COMPLEXES FOR G-QUADRUPLEX DNA TARGETTING

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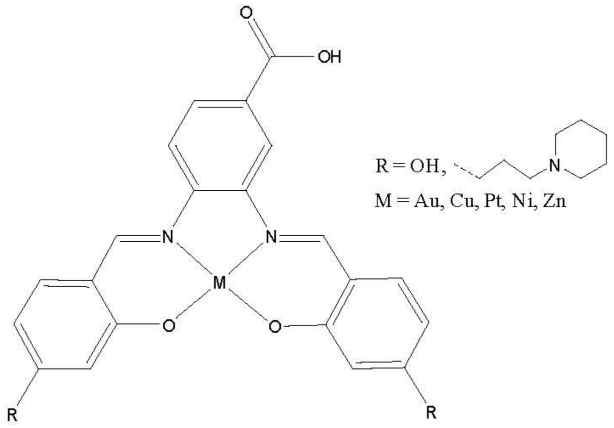
Salphen metal complexes are easily synthesized starting from tetradentate Schiff base ligands with the corresponding metal acetate [1]. These compounds have multiple applications as receptors in supramolecular chemistry.

Another interesting feature of these complexes is their affinity towards the human telomeric G-quadruplex DNA [2], with promising inhibition of telomerase activity. The geometry of the complexes can be tuned by using different metal centers, which is a key factor in the interaction with the G Quadruplex region of DNA.

In this work we report the synthesis and characterization of some metal complexes with different metal centres and different substituents on the ligand, in order to evaluate their differences in structure, properties and behaviour.



Scheme 1. General structure of the salphen complexes.

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FCP 10

OPTIMIZATION OF GOLD NANOPROBES FOR DETECTION OF A SINGLE NUCLEOTIDE POLYMORPHISM RELATED TO LACTOSE INTOLERANCE

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Gold nanoparticles (AuNPs) have unique nanoscale properties, such as high surface area, chemically inert surface, facile functionalization with thiolated ligands, and strong, non-bleaching, optical absorptions [1]. These properties are especially interesting for the development of colorimetric molecular assays for recognizing different biological molecules such as proteins and nucleic acids [2]. Here we report a facile, effective and rapid colorimetric assay based on spherical AuNPs functionalized with a specific thiol-modified oligonucleotide – Au-nanoprobes – for detection of the most prevalent single nucleotide polymorphism (SNP) related to lactose intolerance in humans. Optimized Au-nanoprobes partially aggregate after salt addition in presence of the SNP, causing a color change of the colloid from red to purple. The functionalization was assessed by several techniques including UV–vis spectroscopy, dynamic light scattering, zeta potential and gel electrophoresis analyses. Our results demonstrate that detection sensitivity can be improved by a precise combination of AuNPs sizes (15 or 30 nm), functionalizing methods (salt-aging or pH) and aggregation salts ($MgCl_2$ or NaCl). Specifically, our data confirmed that SNP discrimination is maximized with 30 nm AuNPs functionalized by the pH method and using NaCl as salt for aggregation. These results impact in the preparation and use of robust Au-nanoprobes, finding application in an increasing number of DNA detection assays.

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FCP 11

EXPLORING METALLOPHILIC INTERACTIONS IN CYCLOMETALLATED PLATINUM(II) AND GOLD(III) COMPOUNDS

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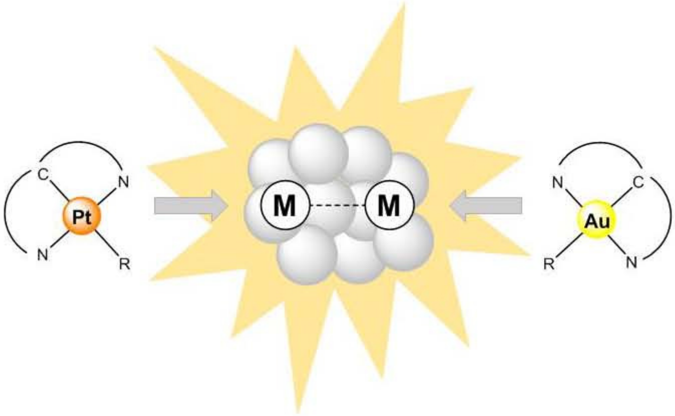
Luminescent platinum(II) cyclometallated compounds have been widely studied in the past years, which are known to display ^{3}MLCT phosphorescence emission.[1] Analogous gold compounds are also known to display similar photophysical properties.[2] Both platinum(II) and gold(III) complexes are able to form aggregates through non-covalent interactions such as π-π stacking or metallophilic interactions. The latter are responsible of the formation of ^{3}MMLCT emission bands that appear at lower energies, which is of interest for the fabrication of optoelectronic devices such as OLEDs or solar cells, among others.[3]

In this work, several analogous platinum(II) and gold(III) cyclometallated compounds were synthesised in order to evaluate their photophysical properties and their ability to form aggregates through metallophilic interactions.



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FCP 12

STUDY OF THE OXIDATION OF [Cu(C_6F_5)(bipy)] BY ARYL IODIDES

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Nowadays, one of the hot topics in homogeneous catalysis is the development of new processes using earth abundant and non-toxic catalysts as those containing complexes of metals from the first transition row. Copper complexes are well known catalysts for cross coupling reactions, however, the elucidation of these reaction´s mechanisms is a goal that has not been fully achieved yet. C-C coupling reactions using aryl iodides constitute a useful synthetic methodology that has been already reported for several substrates.[1] The mechanism has been proven to occur through the oxidative addition of the aryl iodide to organometallic Cu(I) species but the information about this reaction step is scarce.

In this communication we report the study the reaction of complex [Cu(C_6F_5)(bipy)] with several aryl iodides. The reaction leads to quantitative formation of biaryls, product of the heterocoupling reaction. An unexpected behavior is observed when the aryl iodide is $C_6Cl_2F_3I$. In his case large quantities of the homocoupling products are formed. The kinetic study of these reactions by NMR ^{19}F spectroscopy, and a mechanistic proposal will be included.

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Financial support is gratefully acknowledged from the Spanish MINECO (Proyect CTQ2016-80913-P) and the Junta de Castilla y León (projects JCyL VA 051P17 and VA062G18).

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FCP 13

PROBING COPPER/PROTEIN INTERACTIONS IN AN ATCUN-BINDING MOTIF

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The Orange Protein (ORP) is a small bacterial protein of unknown function that contains a unique copper/molybdenum heterometallic cluster, $[S_2MoS_2CuS_2MoS_2]^{3-}$, non-covalently bound. The native cluster can be reconstituted within the apo-protein by the addition of Cu^{2+} plus tetrathiomolybdate to apo-ORP under controlled conditions. To get a deeper insight into the copper/ORP interactions, we inserted an artificial ATCUN motif ("Amino Terminus Cu and Nickel motif"; $Ala_1Ser_2His_3$; Figure below) in the *Desulfovibrio gigas* ORP and studied the copper binding to apo-ATCUN-ORP by EPR spectroscopy.

The apo-ATCUN-ORP binds Cu^{2+} in a 1:1 ratio to yield a Cu^{2+}-ATCUN-ORP complex, as unequivocally demonstrated by the single EPR S = 1/2 signal, characteristic of a Cu^{2+} complex in a square-planar geometry (or square-planar with weak axial ligand(s)), with $g_{||,\perp}$ = 2.183, 2.042 and $A^{Cu}_{||,\perp}$ = 207x10^{-4}cm^{-1}, 19x10^{-4} cm^{-1}. These $g_{||}$ and $A^{Cu}_{||}$ values are characteristic of 4N or 2N2O coordination site (as suggested by the "Truth Diagram" derived originally by Peisach and Blumberg), but preliminary UV–visible data [1] clearly supported the 4N coordination site.

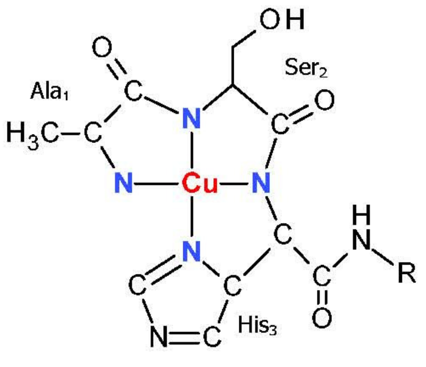

Figure: ATCUN motif

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FCP 14

SYHTESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES FUNCIONALIZED WITH COUMARIN LIGANDS

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The design and the study of nanomaterials with new photophysical properties have received a lot of interest the last years. Among metal nanoparticles (NPs), gold NPs are one of the most studied due to their interesting properties and their high stability. Moreover, they can be easily synthesized and functionalized with organic ligands containing thiol groups.

In this work we describe the synthesis and the characterization of two different coumarin ligands. Then, these coumarin ligands have been used to functionalize gold nanoparticles (Figure 1). Different parameters have been modified in order to evaluate their influence in the luminescent properties of the resulting AuNPs, such as the distance between the coumarin and the thiol group that anchors the gold surface, and the number of coumarin ligands functionalizing the surface of AuNPs.

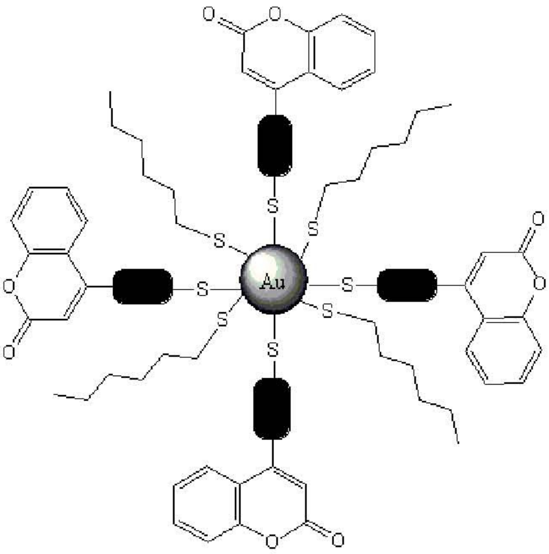

Figure 1. AuNPs functionalized with coumarin and 1-hexanethiol ligands

FCP 15

TRIANGULAR AND SQUARE HETEROMETALLIC CLUSTERS: INFLUENCE OF THE CLOSED-SHELL d^{10} ELECTRONIC CONFIGURATION

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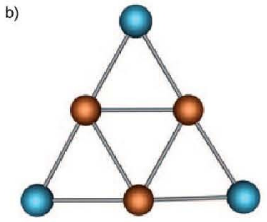
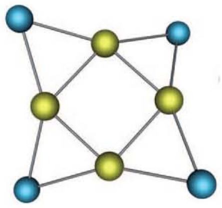
The study of metal–metal bonding in molecules is at the crossroads of the development of the interface between chemical bonding, cooperative reactivity, modeling of the interactions between organic ligands and metal surfaces (particularly in the case of 2D metal cores), multicenter catalysis, and metal-rich nanomaterials. It is now well recognized that small gold particles and surfaces display unique electronic properties and catalytic reactivity that were not anticipated for such a noble metal. The development of synthetic approaches towards organized, heterometallic 2D structures is particularly attractive because of the increased challenges compared to homometallic structures and their possible relevance to modeling of interactions between substrates and alloy surfaces. The synthesis of the first heterometallic complexes containing a metal–metal bond between a Group 11 d10 ion M and another transition metal triggered considerable interest in the synthesis and study of complexes and clusters with M_M' bonds. In some cases, there is structural evidence for additional d10···d10 M_M inter or intramolecular interactions, which cannot be considered as conventional covalent or dative bonds and are of major current interest from experimental and theoretical points of view.

We report here a series of heterometallic clusters of general formula $[MMoCp(CO)_3]_n$ ($Cp=\eta^5$-C_5H_5; M=Cu, n=3;M=Ag or Au, n=4), the nuclearity and structure of which critically depend on the nature of the d^{10} ions. Experimental and theoretical data suggest that $d^{10}\cdots d^{10}$ interactions are responsible for the observed differences.





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FCP 16

THE TETRANUCLEAR COPPER-SULFIDE CATALYTIC CENTER FROM THE TERMINAL ENZYME OF DENITRIFICATION

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Nitrous oxide reductase the last enzyme of this pathway catalyzes the reduction of nitrous oxide at a new tetranuclear copper center (CuZ) the catalytic center overcoming the high activation energy of this reaction. In this center, each Cu atom is coordinated by two imidazole rings of histidine side-chains, with the exception of Cu_{IV}, with only one histidine. This enzyme has been isolated with “CuZ” in two forms CuZ(4Cu1S) and CuZ(4Cu2S), which differ in the Cu_I-Cu_{IV} bridging ligand, leading to considerable differences in their spectroscopic and catalytic properties. The copper atoms in CuZ(4Cu1S) can be reduced to the [$4Cu^{1+}$] oxidation state, and its catalytic properties are compatible with the nitrous oxide reduction rates of whole cells, while in CuZ(4Cu2S) they can only be reduced to the [$1Cu^{2+}$ - $3Cu^{1+}$] oxidation state, that has a very low turnover number. The catalytic cycle of this enzyme has been explored and one of the intermediates, CuZº, has recently been identified and shown to be in the [$1Cu^{2+}$-$3Cu^{1+}$] oxidation state. Contrary to CuZ(4Cu2S), CuZº is rapidly reduced intramolecularly by the electron transferring center of the enzyme, CuA, to [$4Cu^{1+}$] by a physiologically relevant redox partner. The three-dimensional structure of nitrous oxide reductase with “CuZ” center as CuZ(4Cu1S) or CuZ(4Cu2S) shows that it is a unique functional dimer, with “CuZ” center of one subunit receiving electrons from CuA of the other subunit. The complex nature of this center has posed some questions relative to its assembly, which are only partially answered, as well as which is the active form of “CuZ” in vivo.

The structural, spectroscopic and catalytic features of the two forms of “CuZ” center will be addressed here. The understanding of its catalytic features and activation is essential to develop strategies to decrease the release of nitrous oxide to the atmosphere and to reduce its concentration in the stratosphere, as well as to serve of inspiration to synthetic inorganic chemists to develop new models of this peculiar and challenging copper sulfide center.

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FCP 17

$[Au(CH_3CN)_2]^+$: AN ALMOST UNIVERSAL "SENSOR" FOR LIGHT, INERT AND NOBLE GASES

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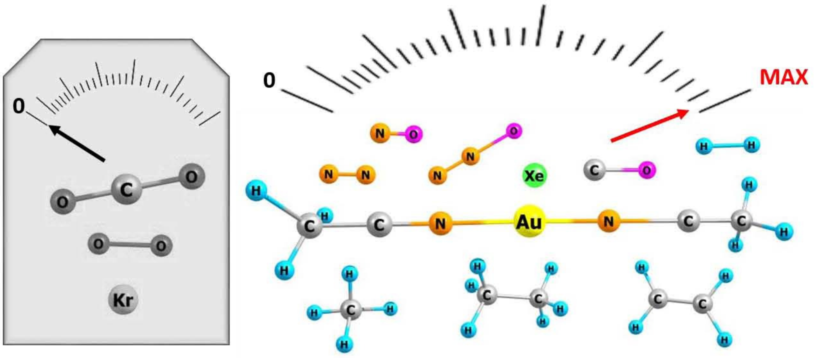
In this work, we have prepared a gold(I) cationic complex, $[Au(CH_3CN)_2]^+$, in the gas-phase, that is very reactive with different light, inert and noble gases, forming $[Au(CH_3CN)_2(L)]^+$ complexes. The examined gases comprised greenhouse gases that cause climate change directly and indirectly (L = N_2, O_2, N_2O, NO, CO, CO_2, CH_4, C_2H_6, C_2H_4, H_2) as well as noble gases (L = Kr, Xe). The study of these interactions between neutral molecules and Au(I) species is of fundamental interest in the coordination chemistry of gold [1].

We used electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT-MS) to produce the $[Au(CH_3CN)_2]^+$ complex from an $Au(CH_3COO)_3$ solution in CH_3CN, directly injected into the ESI source. CID (collision-induced dissociation) of $[Au(CH_3COO)_2(CH_3CN)_4]^+$ showed the formation of $[Au(CH_3CN)_2]^+$ that reacted promptly with water and N_2 present in the ion trap background, instigating the formation of $[Au(CH_3CN)_2(L)]^+$ (L = H_2O, N_2). The formation of the corresponding adducts $[Au(CH_3CN)_2(L)]^+$ was observed with most of the examined gases (L = N_2, N_2O, NO, CO, CH_4, C_2H_6, C_2H_4, Xe) and not observed with O_2, CO_2, H_2 and Kr. Although not forming the adduct, H_2 reacted with the Au(I) complex to yield AuH and $(CH_3CN)_2H^+$. These experimental studies are being complemented with computational calculations to assist the interpretation of the reactivity of the $[Au(CH_3CN)_2]^+$ complex.



Acknowledgements: Work supported by FCT projects PTDC/QUI-QFI/31896/2017 and UID/Multi/04349/2019, and contracts IST-ID/077/2018 and IST-ID/091/2018, and by RNEM – Portuguese Mass Spectrometry Network, LISBOA-01-0145-FEDER-022125, supported by FCT and Lisboa Regional Operational Programme (Lisboa2020), under the PT2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

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FCP 18

COPPER PROTEINS FROM PATHOGENIC BACTERIA – METAL HOMEOSTASIS AND DENITRIFICATION

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Copper ions are present in all cells, as it is an important cofactor for several enzymes and is also part of the immune system response to surpass infection. In addition, copper has been used in animal food as an additive and is becoming a promising antimicrobial agent due to the continue emergence of multi-resistance strains. However, free copper ions are highly toxic due to their ability to generate reactive oxygen species, via Fenton-type reactions, which damage lipids, DNA and proteins [1]. For this reason, it is crucial for any organism to control tightly the intracellular concentrations of free copper ions, a role played by dedicated homeostasis systems, described extensively in gram negative bacteria (*cop* and *cus* operons). In *Staphylococcus aureus*, the homeostasis system is composed by ATPases copper transporters, copper chaperones, copper transcription regulators and more recently a multicopper oxidase and a surface-exposed lipoprotein were described to also play a role in this resistance [2].

Pathogenic microorganisms usually have a truncated denitrification pathway to obtain energy through the reduction of nitrogen oxides in alternative to oxygen, enabling their proliferation in tissues or organs with low oxygen tension.

In the presented work, the multicopper oxidase from *Staphylococcus aureus* was proven to be involved in the copper homeostasis in this gram positive pathogen. The multicopper oxidase gene was cloned for heterologous production in *Escherichia coli*, purified to homogeneity, and biochemically characterized. In addition, the *in vitro* phenoloxidase and peroxidase activity was studied for the purified protein, as well as in cell extracts. The minimal inhibitory concentration (MIC) to copper was estimated for different *S. aureus* strains in aerobic, microaerobic and anaerobic growth conditions, with its copper resistance being oxygen-dependent and strain-dependent. The biofilm formation in the presence of copper has also been performed and preliminary results show that for some strains the biofilm formation increased in the presence of copper ions.

Neisseria gonorrhoeae the denitrification pathway is composed by a Cu-nitrite reductase, AniA, and by nitric oxide reductase (NorB). In the present work we have isolated and spectroscopically characterized AniA. The hypothesis that cytochrome c_2 or the lipid modified azurin [3,4] can function as electron donor in *in vitro* kinetic assays will be tested.

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FCP 19

LUMINISCENT CAGES BASED ON ORGANOMETALLIC GOLD(I) COMPLEXES

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Recently, the design of supramolecular structures that adopt cage conformations has motivated several studies.[1,2] These arrangements can be to encapsulate guess molecules. The inclusion of metallic atoms in their structures, as gold, provides to them a variety of interesting properties, for example, luminescence, catalytic and molecular host-guest properties, among others.[3-5]

Herein, we analyse the effects on luminescent properties of changing the diphosphine spacer length in a series of cage-like diphosphane alkinylgod(I) derivatives containing anthracene moieties. The presence of aurophillic interactions has a central role in the emissive properties.

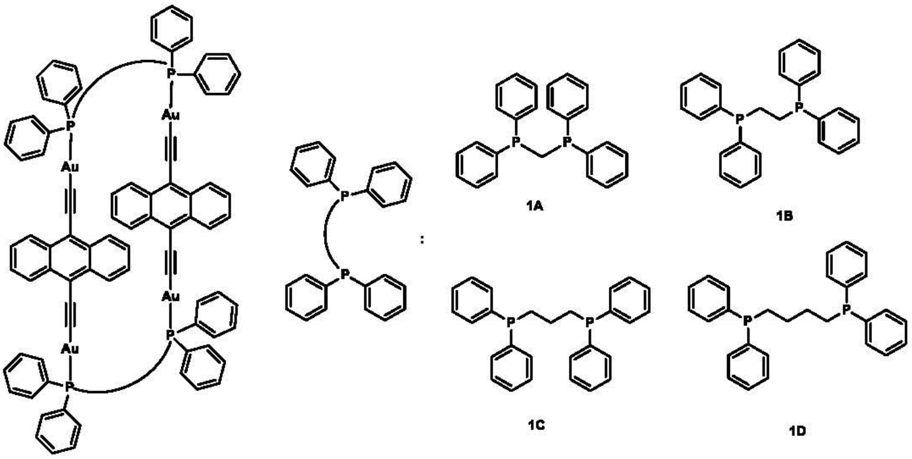

Fig. 1. – Structure of the compounds in this work.

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FCP 20

CRYPTATES FOR CO_2 CAPTURE AND ACTIVATION

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The increasing atmospheric concentration of CO_2 has been predicted by models which suggest dramatic and irreversible changes if actions are not taken urgently. It is now well established that CO_2 may be sequestered and stored as liquid CO_2 or solid carbonate but both solutions are energetically demanding and financially costly.[1] Recently reports of reaction of pressurised CO_2 with epoxides to form polycarbonates[2] or cyclic carbonates[3] have attracted both academic and industrial interest, but generally, the recycling of CO_2 to produce high value products via low-cost catalysts is still in its infant years. Nelson's cryptands[4] are a classical example of a dynamic structure, which demonstrated the ability to capture and convert CO_2 to hydrogen carbonate and methyl carbonate following its coordination to encapsulated metal ions in the cryptate cavity. Here we explore the fixation chemistry of CO_2 by derivatised dinuclear Cu(II), Ni(II), Zn(II) and Co(II) cryptands (Fig. 1) where the phenyl ring was modified towards engineering these metal-organic structures into supramolecular assemblies. The derivatisation of these cryptands allow to study the influence of the substituents on both the capture and activation of CO_2. The new functionalised cryptands were further engineered towards fabrication of new heterogeneous materials that can convert CO_2.

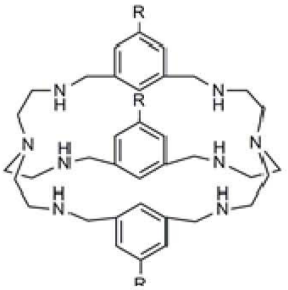

Figure 1. Derivatised Cryptands

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FCP 21

GREEN SYNTHETIC METHODOLOGIES FOR COPPER II COMPLEXES

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The importance of copper compounds on a wide range of fields in chemistry is well-known with its applications varying from drugs to photochemistry, homogenous and heterogeneous catalysis, for a wide array of reactions, and many other uses. Due to its importance, creating new methodologies to synthetize, in a more sustainable approach, those compounds, is paramount. Our group has a vast experience working with both copper I [1] and copper II [2] complexes and has been focusing recently on new synthetic approaches to obtain such compounds with new methodologies. Using bis-aryl-diimino-acenaphthenes (BIAN) as ligand of choice, due to its steric and electronic versatility, and a variety of Cu(II) salts, we synthetized a family of compounds by the mean of traditional techniques, to use as a standard, and also by the means of green synthetic methodologies such as mechanochemistry, sonication and template procedures. Studies of the potential applications of these complexes either as catalysts or antimicrobial agents will be undertaken.

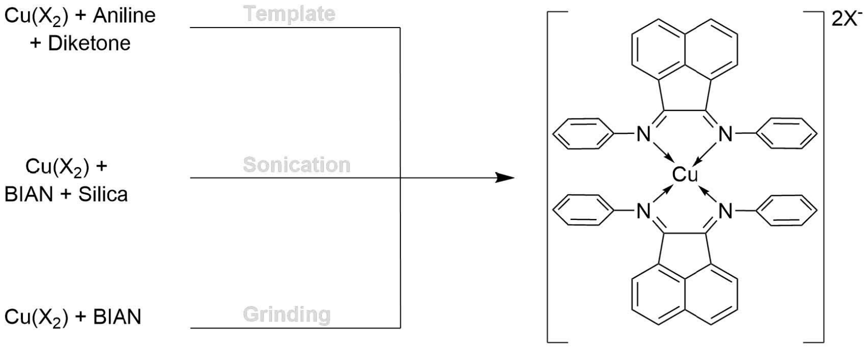

Figure 1: Different green procedures to synthetize Cu(II) complexes.

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FCP 22

DICYANIDOMETALLATES OF SILVER AND GOLD FOR SENSITIZATION OF EUROPIUM(III) PHOTOLUMINESCENCE IN TRIMETALLIC CYANIDO-BRIDGED FRAMEWORKS

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Cyanide complexes of selected transition metal ions exhibiting d^6 (e.g. Co^{III}), d^8 (e.g. Pt^{II}) or d^{10} (e.g. Au^{I}) valence electronic configurations are photoluminescent in the visible-to-NIR ranges. [1,2] Among others, this group include linear dicyanidometallates of Ag^{I} and Au^{I} which are emissive thanks to their metal-to-ligand charge transfer (MLCT) electronic transitions, and tetracyanidometallates of Pt^{II} and Pd^{II} showing emission related to the MMLCT excited states appearing due to the presence of metallophilic d^8–d^8 supramolecular stacks. [2,3] Moreover, polycyanidometallates are able to sensitize lanthanide(III) photoluminescence through an energy transfer process occurring from their d-d or CT electronic excited states. [4] Our goal was to prepare heterometallic d-f coordination systems containing both dicyanidometallates and tetracyanidometallates to employ mixed d^8–d^{10} metallophilic interactions in the sensitization of lanthanide photoluminescence. We report a unique family of heterotrimetallic layered coordination frameworks, $\{[\mathrm{Eu^{III}(4,4'\text{-}bpdo)(H_2O)_2}][\mathrm{M^{II}(CN)_4}]\}\cdot[\mathrm{M^{I}(CN)_2}]\cdot\mathrm{H_2O}$ (M^{II}/M^{I} = Pt/Au; Pt/Ag; Pd/Au; Pd/Ag) bearing both inorganic cyanide bridges, 4,4'-bpdo organic linkers as well as {M^{II}-M^{I}} heterometallophilic dimeric units. The sensitization of red Eu^{III} emission through charge transfer states originating from {M^{II}-M^{I}} interactions is dependent on the applied pair of d^8 and d^{10} transition metal centers which was discussed in terms of crystallographic data, IR and UV-Vis absorption spectra as well as detailed studies of emission properties.

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Contributions List

Only the presenting authors and the respective contributions are indicated.

(KN, Keynote Lecture; OC, Oral Communication; FCP, Flash Communication/Poster)

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Ana Carmen Albeniz	KN 11
Luis G. Alves	OC 02
Inmaculada Angurell	FCP 01
Araceli de Aquino	FCP 02
Gabriel Aullón	OC 16
Tomás R. Belderrain	FCP 03
Francisco J. Caparrós	OC 11
Juan A. Casares	OC 14
Szymon Chorazy	OC 09
Isabel Correia	KN 09
Inês F. Costa	FCP 04
Tiago Cruz	OC 15
Tiago A. Fernandes	FCP 05
Julio Fernandez-Cestau	KN 13
Christophe Fliedel	OC 04
Pierre de Fremont	KN 04
Enrique Garcia-España	KN 10
Raquel Gavara	FCP 06
M. Concepción Gimeno	KN 06
Clara Gomes	OC 08
Atash Gurbanov	FCP 07
Raquel P. Herrera	FCP 08
Valentina Iannace	FCP 09
Alexander Kirillov	KN 03
Sabina W. Jaros	OC 01
Rocío Jurado	FCP 10
Ariadna Lázaro	FCP 11
Luís M. P. Lima	OC 05
Mengxi Lin	OC 13

Olmo Lozano-Lavilla	FCP 12
Kamran T. Mahmudov	KN 12
Luisa Maia	FCP 13
Elizabeth Martínez	FCP 14
Paulo Martinho	KN 07
Abdelatif Messaoudi	FCP 15
Guillermo Moreno-Alcántar	OC 10
Isabel Moura	KN 01, FCP 16
José Maria Muñoz-Molina	KN 14
M. Carmen Nicasio	KN 15
Sandrina Oliveira	FCP 17
Mani Outis	OC 06
Anup Paul	OC 03
Sofia Pauleta	FCP 18
Andrea Pinto	OC 12
Laura Rodríguez	KN 05
Guillermo Romo-Islas	FCP 19
Sara Realista	FCP 20
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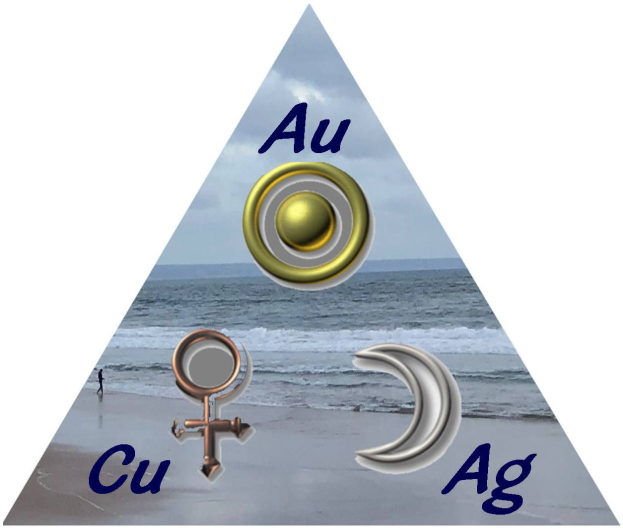
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