



# **JORNADES DOCTORALS**

## **DEPARTMENT OF CHEMISTRY**

**May 22 - 24, 2019**

**Sala d'Actes**

**Faculty of Sciences**

**UAB**

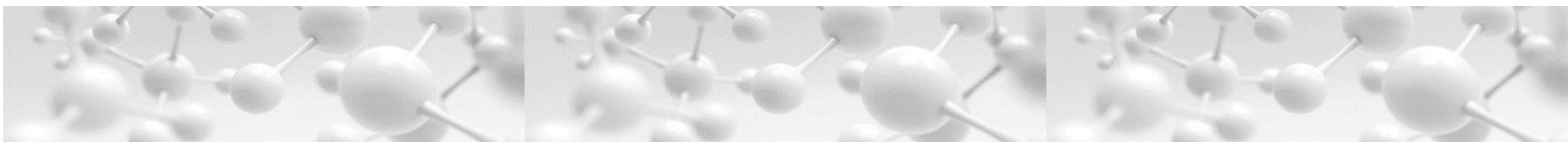
Universitat Autònoma  
de Barcelona

**Sponsored by:**



**RSEQ**  
Secció Territorial Catalana  
[www.rseq.cat](http://www.rseq.cat)







## WELCOME TO JORNADES DOCTORALS 2019

May 22 - 24, 2019

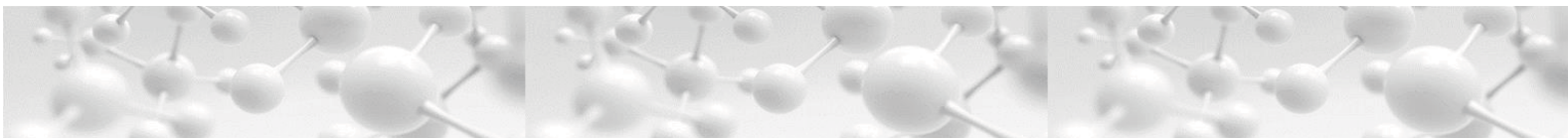
It is our great pleasure to welcome you to the "Novena Edició de les Jornades Doctorals" that are organized by the PhD Chemistry Program and the Chemistry Department. This event aims to strengthen the links between the research groups of our Department, with the ultimate goal of promoting interdisciplinary and more ambitious research projects. In addition, it aims to relate the chemical research performed by the PhD students of the UAB Chemistry PhD program, and related programs, with Industrial and Entrepreneurial Opportunities. In this ninth edition, the "Jornades Doctorals 2019" includes an exciting series of conferences by 3rd-4th year UAB-Chemistry PhD students and three lectures by academic experts.

**Prof. Dr. Javier Vela**, Professor, Chemistry Department, Iowa State University.

He obtained M.S. and Ph.D. degrees working with Prof. Patrick L. Holland (now at Yale) at the University of Rochester in 2003 and 2005, respectively. He was a postdoctoral associate working on polyolefin synthesis and characterization with Prof. Richard F. Jordan at the University of Chicago from 2005 to 2006, and a Director's Postdoctoral Fellow working on semiconductor nanocrystal quantum dots with Jennifer A. Hollingsworth and Victor I. Klimov at Los Alamos National Laboratory's Center for Integrated Nanotechnologies from 2007 to 2009. Trained as a synthetic inorganic and materials chemist, Prof. Vela's current research focuses on new low dimensional (nanoscale) and optical (photoactive) materials, heterostructures, and devices for applications to energy conversion, chemical catalysis, and biological imaging. In 2009, he became a faculty member at Iowa State University, where he has pioneered molecular reactivity approaches to the reproducible synthesis of complex nanostructures. He has also worked to advance diversity and inclusion in the chemical sciences. Dr. Vela is a member of the editorial boards of ACS Energy Letters and Wiley's ChemNanoMat. He has been named Fellow of the AAAS (2018), IUPAC Young Observer (2017), and received the National Science Foundation CAREER Award (2013).



+ information: [https://www.chem.iastate.edu/faculty/Javier\\_Vela](https://www.chem.iastate.edu/faculty/Javier_Vela)



**Prof. Dr. Edwin Charles Constable**, Professor of Chemistry, University of Basel.

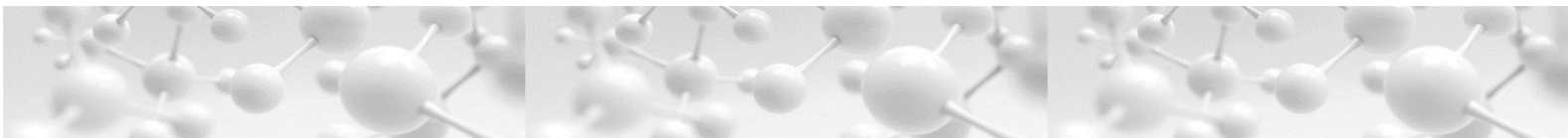
Edwin (Ed Constable) completed his D.Phil at Linacre College, University of Oxford, followed by a number of research fellowships at the University of Cambridge, where he remained until 1993 when he was appointed Professor of Inorganic Chemistry at the University of Basel (Switzerland). In 2000 he left Basel to take up a position as Professor of Chemistry at the University of Birmingham (England). He returned to the University of Basel as Professor of Chemistry in 2002. He publishes widely in all areas of chemistry with over 600 peer-reviewed publications and is highly cited (20,800 citations, h-index 72). His interest cover all aspects of chemistry, chemical history and the communication of science. He is a member of the steering



committee of the European Universities Association Council for Doctoral Education, the executive committee of the Swiss National Science Foundation and is a titular member of Division VIII of IUPAC. He has recently been appointed Chairman of the Swiss Academies Expert Group on Research Integrity and the European Universities Association Task Group on Research Ethics and Integrity. He is a Fellow of the Royal Society of Chemistry. He is or has been on the Editorial Boards of numerous journals, including Chemical Communications, Chemical Reviews, Chemical Society Reviews, Coordination Chemistry Reviews, New Journal of Chemistry, Polyhedron and Supramolecular Chemistry. He is currently one of the editors in chief for "Comprehensive Coordination Chemistry III" to be published by Elsevier and is on the Management Board of the Open Access Publisher MDPI. He has recently been appointed Editor-in-Chief for a new open access journal "Chemistry – an International Journal".

+ information: <https://www.chemie1.unibas.ch/~constable/index.html>





**Prof. Dr. Prashant V. Kamat**, Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory at the University of Notre Dame.

He obtained his doctoral degree (1979) in Physical Chemistry from the Bombay University, and postdoctoral research at Boston University (1979-1981) and University of Texas at Austin (1981-1983). He joined Notre Dame in 1983. Professor Kamat has for more than three decades worked to build bridges between physical chemistry and material science to develop advanced nanomaterials that promise cleaner and more efficient light energy conversion.



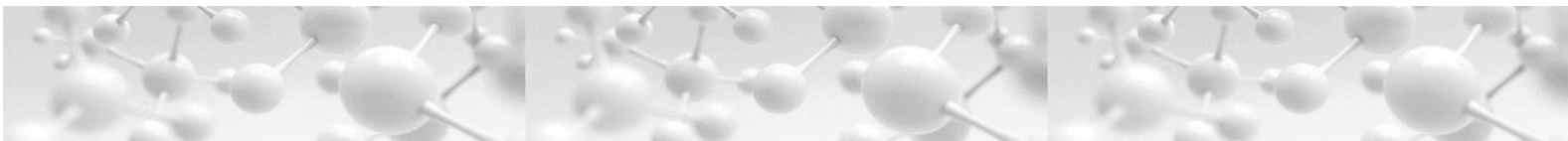
He has directed DOE funded solar photochemistry research for the past 35 years. In addition to large multidisciplinary interdepartmental and research center programs, he has actively worked with industry-sponsored research. He has served on many national panels on nanotechnology and energy conversion processes. He has published more than 450 scientific papers that have been well recognized by the scientific community (64000 citations, h-index 129 –Source Web of Science). Thomson-Reuters has featured him as one of the most cited researchers each year during 2014-2018.

He is currently serving as the Editor-in-Chief of ACS Energy Letters. He has also served as the deputy editor of the Journal of Physical Chemistry Letters. He is a member of the advisory board of several scientific journals (Chemical Reviews, Journal of Colloid & Interface Science, ACS Applied Nanomaterials, Research on Chemical Intermediates, and Applied Electrochemistry). He was awarded Honda-Fujishima Lectureship award by the Japanese Photochemical Society in 2006, CRSI medal by the Chemical Research Society of India in 2011 and Langmuir lectureship award in 2013. He is a Fellow of the Electrochemical Society (ECS), American Chemical Society (ACS) American Association for the Advancement of Science (AAAS) and Pravasi Fellow of the Indian National Science Academy.

+ information: <https://www3.nd.edu/~pkamat/>

We look forward to your participation in this event.

The Organizing Committee



#### Organizing, Scientific and Prizes Committee:

- Prof. Gregori Ujaque, PhD Coordinator of the studies in Chemistry and President of the Chemistry PhD Committee (UAB)
- Prof. Félix Busqué, Master Coordinator of the studies in Chemistry and President of the Chemistry Master Committee (UAB)
- Prof. Xavier Sala, Secretary of PhD and Master Studies Committee (UAB)
- Prof. Rosa M<sup>a</sup> Sebastian, Vocal of PhD and Master Studies Committee (UAB)
- Prof. Clara Viñas, Vocal of PhD and Master Studies Committee (ICMAB)
- Prof. Daniel MasPOCH, Vocal of PhD and Master Studies Committee (ICN2)
- Anna Cebrian, PhD Student, Department of Chemistry, (UAB)
- Arpita Saha, PhD student Department of Chemistry, (UAB)

#### Chemistry Department Administrative Support:

Elena Jiménez, Administrative Assistant PhD Studies in Chemistry.

#### Event sponsored by:

Real Sociedad Española de Química (RSEQ) – Secció Catalana de la RSEQ  
Societat Catalana de Química (SCQ)



RSEQ  
Secció Territorial Catalana  
[www.rseq.cat](http://www.rseq.cat)





## SCIENTIFIC PROGRAM

### May 22

09:30 - 10:00 Opening Ceremony

10:00 - 11:00 Jornades Doctorals Lecture

*Chairman: Prof. Gonzalo Guirado*

#### **“Chemistry of Materials for Sustainability: From Halide Perovskites to Binary Metal Phosphides”**

**Prof. Dr. Javier Vela**

11:00 - 12:00 Coffee Break and Poster Session

12:00 - 13:00 Flash Presentations I

*Chairman: Prof. Javier Vela*

12:00 - 12:15 Nanoparticle Reactivity Beyond the Slab Approach: The BCN\_model platform and application to IrO<sub>2</sub> nanoparticles for Oxygen Evolution Reaction. **Danilo González Forero** (FP1.1)

12:15 - 12:30 Development of New Nanocarriers Based on Catechol Compounds for Biomedical Applications. **Carolina Casagualda Clapés** (FP1.2)

12:30 - 12:45 Influence of a Biostimulant on Se enriching Wheat Plants. **Tingting Xiao** (FP1.3)

12:45 - 13:00 Photoactive Platinum(II) Complexes as Oxygen-Regulated Light-Triggered Photocages. **Kevin Morales Fernandez** (FP1.4)

13:00 - 15:30 Break

15:30 - 17:00 Flash Presentations II

*Chairwoman: Prof. Clara Viñas*

15:30 - 15:45 Synthesis and Catalytic Applications of Soluble Metal Nanoparticles. **Guillem Fernandez Freixes** (FP2.1)

15:45 - 16:00 Syntheses, Structures, and Properties of Carborane-based Cooper Metal Organic Frameworks. **Lei Gan** (FP2.2)

16:00 - 16:15 Water Determination in Parenteral Drug Products. **Laia Garcia Uceda** (FP2.3)

16:15 - 16:30 Synthesis of conformationally restricted cyclohexanyl nucleoside analogues as Antiviral Agents. **Sergio Jurado Moreno** (FP2.4)

16:30 - 16:45 Integrated Instrumental/Computational approach to study metal species binding to proteins. **Giuseppe Sciortino** (FP2.5)

16:45 - 17:00 Study of the Calcium Oxalate Hydrates Transformation and the role of the organic matter on their development by Synchrotron-based  $\mu$ -FTIR spectroscopy. **Iris Henríquez Valido** (FP2.6)



## May 23

10:00 – 11:00 Jornades Doctorals Lecture

*Chairman: Prof. Xavier Sala*

### **“Sustainable Materials Chemistry –Light-emitting electrochemical cells”**

**Prof. Edwin Constable**

11:00 – 12:00 Coffee Break and Poster Session

12:00 - 13:00 Flash Presentations III

*Chairman: Prof. Xavier Sala*

- 12:00 - 12:15 In vitro dental remineralization assisted by amelogenin. **Sandra Diez Garcia** (FP3.1)
- 12:15 - 12:30 Ru-Based Nanomaterials as Co-Catalyst with Carbon Nitride for Light-Driven Proton Reduction. **Luis Ignacio Álvarez Prada** (FP3.2)
- 12:30 - 12:45 Simultaneous Voltammetric determination of Ascorbic Acid, Uric Acid and Acetaminophen by Use of modified screen-printed Electrodes and Chemometrics tools. **Dionisia Ortiz Aguayo** (FP3.3)
- 12:45 - 13:00 Implementing one-shot multiple-FID acquisition into homonuclear and heteronuclear NMR experiments. **Kumar Motiram Corral** (FP3.4)

13:00 - 15:30 Break

15:30 - 17:00 Flash Presentations IV

*Chairman: Prof. Felix Busqué*

- 15:30 - 15:45 Fluorinated Polyurethanes. **Miriam Laiz Treceño** (FP4.1)
- 15:45 - 16:00 New chiral schiff bases for asymmetric catalysis. **Jose Antonio Perez Mejias** (FP4.2)
- 16:00 - 16:15 Computational study of the transglycosylation reaction catalyzed by Glycoside Hydrolases and Glycosyltransferase. **Sonia Romero Tellez** (FP4.3)
- 16:15 - 16:30 Obtention of value-added products from olive oil and wine production wastes through thermochemical treatments. **Cristina del Pozo Carvajal** (FP4.4)
- 16:30 - 16:45 Towards novel electroinduced healing of polybenzoxazines. **Carolina Gascó Catalán** (FP4.5)
- 16:45 - 17:00 Functionalized mesoporous silica nanoparticles for catalytic and biomedical applications. **Hao Li** (FP4.6)





**May 24**

09:30 – 10:30 Jornades Doctorals Lecture

*Chairman: Prof. Gregori Ujaque*

**“Perovskite Photovoltaics. Research Opportunities and Challenges”**

**Prof. Prashant V. Kamat**

10:30 - 11:15 Flash Presentations V

*Chairman: Prof. Gregori Ujaque*

- |               |  |
|---------------|--|
| 10:30 - 10:45 | Process development for the synthesis at industrial scale of a New Chemical Entity (NCE) drug for clinical trials. <b>Javier Santos Ramos</b> (FP5.1)  |
| 10:45 - 11:00 | DFT mechanistic analysis of Alkene Cyclohydroamination of Primary amines catalysed by a Co(II) Complex. <b>Pablo Gómez-Orellana Seguí</b> n (FP5.2)  |
| 11:00 - 11:15 | Multistimuli-Responsive Fluorescent Switches Based on Spirocyclic Meisenheimer Compounds: Smart Molecules for Optical Probes and Electrochromic Materials. <b>Marc Villabona Pedemonte</b> (FP5.3) |

11:15 - 12:00 Coffee Break

12:00 - 13:00 Jornades Doctorals Lecture

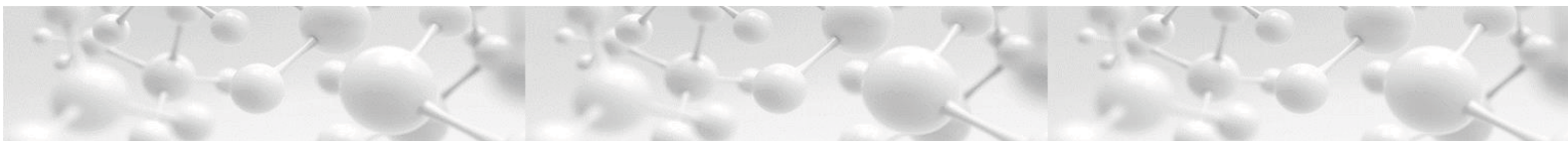
*Chairman: Prof. Gregori Ujaque*

**“The Art of Scientific Publication**

**(How to Make Your Next Paper Scientifically Effective?)”**

**Prof. Prashant V. Kamat**

13:00 - 13:15 Award and closing ceremony. Jornades Doctorals 2019 distinguished Diploma, along with a gift, will be given to the three best Poster-Flash Presentations (Gifts: E-book).



JORNADES DOCTORALS 2019

LECTURES



# Chemistry of Materials for Sustainability: From Halide Perovskites to Binary Metal Phosphides

Javier Vela, Department of Chemistry, Iowa State University

Our group is interested in the soft synthesis and chemical spectroscopy of optical nanomaterials. This talk will highlight some of our recent work in two areas:

*Halide Perovskites: New Semiconductors for Energy Conversion.* Halide perovskites are one the most interesting semiconductors for photovoltaics, with solar cells made of these materials approaching power conversion efficiencies of 25%. We were among the first to synthesize colloidal  $\text{APbX}_3$  (A = methylammonium; X = I, Br) nanocrystals, and showed that, at the single particle level, they display shape-correlated PL emission across whole particles, with little photobleaching and very few off periods [1-3]. In addition, we introduced solid state NMR to probe the extent of alloying and phase segregation in mixed ion halide perovskites [4-5], which show superior performance and stability. Because  $^{207}\text{Pb}$  chemical shifts are highly sensitive to local coordination, electronic structure, and vary linearly with halogen electronegativity and band gap,  $^{207}\text{Pb}$  ssNMR gives the true chemical speciation of samples made by different methods. Nonstoichiometric dopants and amorphous phases are prevalent in samples made from solution, while a novel solid phase synthesis, starting from the parent, single-halide perovskites suppresses phase segregation [6-7]. Our observations are consistent with the presence of miscibility gaps and spontaneous spinodal decomposition in these materials at room temperature, underscoring how different synthetic procedures impact their composition, nanostructuring, and properties.

*Binary Metal Phosphides: From Hydrogen Evolution to Nitrate Removal from Water.* A better understanding of the chemistry of molecular precursors is useful in achieving more predictable and reproducible nanocrystal preparations [7-8]. Using commercially available organophosphite precursors, we have used a chemical reactivity approach to synthesize nickel and nickel phosphide nanocrystals with high selectivity (Ni,  $\text{Ni}_{12}\text{P}_5$  and  $\text{Ni}_2\text{P}$  phases) [9]. Some organophosphites, such as  $\text{P}(\text{OMe})_3$  or  $\text{P}(\text{OiPr})_3$  transiently form zerovalent, metallic nickel; the latter is persistent with the bulky organophosphite  $\text{P}(\text{O}-2,4\text{-tBu}_2\text{C}_6\text{H}_4)_3$ . Along with other first row, transition metal phosphides,  $\text{Ni}_2\text{P}$  is a very active catalyst for the hydrogen evolution reaction, as well as for hydrosulfurization, and other reforming reactions. Based on this information, we hypothesized that  $\text{Ni}_2\text{P}$  should be active in the reduction of oxyanions. Indeed, we have recently succeeded in using this material as a catalyst for the near ambient removal of nitrate from water [10].

1. Zhu *et al.* "Shape Evolution and Single Particle Luminescence of Organometal Halide Perovskite Nanocrystals." [\*ACS Nano\* \*\*2015\*\*, \*9\*, 2948.](#)
2. Rosales *et al.* "Lead Halide Perovskites: Challenges and Opportunities in Advanced Synthesis and Spectroscopy." [\*ACS Energy Lett.\* \*\*2017\*\*, \*2\*, 906.](#)
3. Freppon *et al.* "Photophysical Properties of Wavelength-Tunable Methylammonium Lead Halide Perovskite Nanocrystals." [\*J. Mater. Chem. C\* \*\*2017\*\*, \*5\*, 118.](#)
4. Rosales *et al.* "Persistent Dopants and Phase Segregation in Organolead Mixed-Halide Perovskites." [\*Chem. Mater.\* \*\*2016\*\*, \*28\*, 6848.](#)
5. Hanrahan *et al.* "Enhancing the Sensitivity of  $^{207}\text{Pb}$  Solid-State NMR Spectroscopy for the Rapid, Non-Destructive Characterization of Organolead Halide Perovskites." [\*Chem. Mater.\* \*\*2018\*\*, \*30\*, 7005.](#)
6. Vela & Rosales, "Solvent-Free, Solid Phase Synthesis of Hybrid Lead Halide Perovskites with Superior Purity." U.S. Patent Application No. 15/854,596, December 26, 2017.
7. Guo *et al.* "Shape-Programmed Nanofabrication: Understanding the Reactivity of Dichalcogenide Precursors." [\*ACS Nano\* \*\*2013\*\*, \*7\*, 3616.](#)
8. Ruberu *et al.* "Molecular Control of the Nanoscale: Effect of Phosphine Chalcogenide Reactivity on CdS-CdSe Nanocrystal Composition and Morphology." [\*ACS Nano\* \*\*2012\*\*, \*6\*, 5348.](#)
9. Andaraarachchi *et al.* "Phase-Programmed Nanofabrication: Effect of Organophosphite Precursor Reactivity on the Evolution of Nickel and Nickel Phosphide Nanocrystals." [\*Chem. Mater.\* \*\*2015\*\*, \*27\*, 8021.](#)
10. Lin & Vela, To be communicated.

# Sustainable Materials Chemistry –Light-emitting electrochemical cells

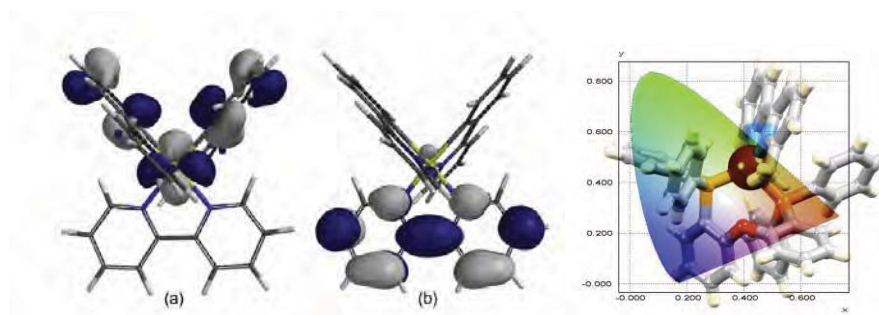
Ed Constable, University of Basel

Mankind needs light. After the sun goes down, life continues as normal. In the evenings, our cities are lit up brighter than daytime. In Australia, lighting accounts for 10% of household electricity usage and 20–40% of commercial usage.

Lighting technology is changing. This talk concentrates upon the light-emitting electrochemical cell (LEC) which is a sustainable alternative to OLEDs. The devices are not dependent on the work function of the electrodes, allowing low-tech solution processing methods to be used for fabrication.

We have shown that iridium complexes of the type  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$  ( $\text{C}^{\wedge}\text{N}$  = cyclometallated ligand,  $\text{N}^{\wedge}\text{N}$  = diamine) can be used to prepare LECs with long lifetimes (years) and high brightness. The lifetimes and turn-on times may be optimized by variations in the ligands, for example by introducing additional intramolecular  $\pi$ -stacking interactions which restrict excited state distortion. The HOMO and LUMO in the complexes are localized on the  $\text{C}^{\wedge}\text{N}$  and  $\text{N}^{\wedge}\text{N}$  ligands respectively, allowing ligand substitution to be used to tune the colour of the emission.

Although the fabrication processes are sustainable, the use of one of the rarest metals on Earth, iridium, is to be avoided. The second part of the talk concentrates upon the development of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes ( $\text{P}^{\wedge}\text{P}$  = chelating diphosphine,  $\text{N}^{\wedge}\text{N}$  = diimine) to replace iridium species in LECs. Devices with improved lifetimes have been prepared, but the challenge of colour tuning remains.



Over the LEC rainbow: colour and stability tuning of cyclometallated iridium(III) complexes in light-emitting electrochemical cells, C.E. Housecroft, E.C. Constable, *Coord. Chem. Rev.*, 2017, 350, 155-177: [doi.org/10.1016/j.ccr.2017.06.016](https://doi.org/10.1016/j.ccr.2017.06.016).



# **Perovskite Photovoltaics. Research Opportunities and Challenges**

Prashant V. Kamat

Radiation laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

Email: [pkamat@nd.edu](mailto:pkamat@nd.edu) Twitter [@kamatlabND](https://twitter.com/kamatlabND)

Metal halide perovskites have drawn significant attention because of its ability to deliver high efficiency solar cells. Since the appearance of the first metal halide perovskite solar cell paper in the April 2009 significant efforts have been made to develop solar cells with efficiencies surpassing 24%. As the field is becoming mature in terms of the solar cell design, it is important to gain insight into the factors governing the operation of the solar cell. Of particular interest are the research opportunities to investigate the excited state dynamics, new hybrid perovskites, bandgap tuning through halide ion composition, thermal and photo induced halide ion mobility, remediation of surface defects and long term stability. The lecture will discuss these aspects and map out opportunities to engage in future research. A better understanding of the photo and thermally controlled processes within the perovskite film would pave the way for the design of next generation solar cells with greater stability.





# **The Art of Scientific Publication**

*(How to Make Your Next Paper Scientifically Effective?)*

Prashant V. Kamat

Department of Chemistry and Biochemistry, Radiation Laboratory

Notre Dame, IN 46556, USA (<http://www.kamatlab.com>)

Sharing scientific knowledge through publications is an integral part of research career. Since more and more organizations evaluate scientific productivity by scholarly publication rates, the impact of published work becomes an important issue.<sup>1-3</sup> New researchers face the challenge of mastering the art of scientific publication to draw attention to their new scientific findings. Whether or not we want to describe science in such terms, scientific publishing is competitive in nature, and thus younger scientists must vie with their more experienced peers for recognition. While the electronic age has made the publication process easier and quicker, optimizing the structure of a scientific paper requires a certain degree of skill and proficiency. It is important to realize that a well-composed manuscript with a compelling scientific story that can appeal to the journal's readership sees a higher rate of success

The lecture will address following questions.

What are common practices in publishing scientific work?

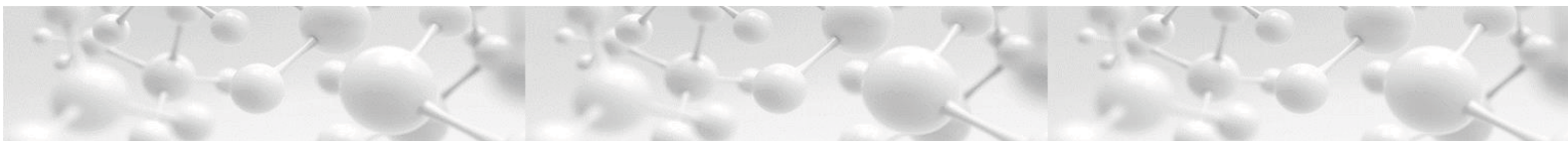
What are common misconceptions?

What are the key steps that are necessary to compose an effective paper?

How to respond to reviewers' comments?

## **Additional Reading:**

1. How to Make Your Next Paper Scientifically Effective. Kamat, P.; Schatz, G. C., J. Phys. Chem. Lett. 2013, 4, 1578-1581. Link: <http://dx.doi.org/10.1021/jz4006916> (OA Article)
2. Kamat, P. V.; Buriak, J. M.; Schatz, G. C.; Weiss, P. S. Mastering the Art of Scientific Publication. J. Phys. Chem. Lett. 2014, 5, 3519-3521. <http://dx.doi.org/10.1021/jz502010v> (OA Article)
3. "On Being a Scientist" –U.S. National Academy Press.  
<http://www.nap.edu/catalog/12192.html> (Free Download)



**JORNADES DOCTORALS 2019**

**ABSTRACTS**



# **Nanoparticle Reactivity Beyond the Slab Approach: The BCN\_model platform and application to IrO<sub>2</sub> nanoparticles for Oxygen Evolution Reaction.**

D. González, L. Rodríguez-Santiago and M. Sodupe.

*Departament de Química,  
Universitat Autònoma de Barcelona*

The most recent advances on several scientific fields like electronics, medicine, and catalysis are closely related to the development of novel materials, especially nanomaterials like nanoparticles (NP). The physical-chemical properties of NPs are controlled and tailored by changing their size and shape extending their applicability.

Combination of experimental and computational techniques have demonstrated to be a successful strategy for understanding the relation between structural and chemical properties of NPs. Nevertheless, computational modeling of NPs is not trivial because of their variety of sizes and shapes and the difficult to construct rational models. By virtue of the intrinsic complexity of NP model construction, the most widely used approach to study NPs reactivity is to represent it as slab cuts of the most relevant faces discarding edges, corners, and tips that are recognized as highly reactive sites.

Present thesis has addressed this point and developed an open-access computational tool, i.e., the Bulk Cut Nanoparticles Models (BCN Models) platform, to generate and characterize stoichiometric Wulff-like nanoparticles in a systematic way for a large variety of ionic binary compounds. Obtained NPs for IrO<sub>2</sub> have been used to study at the DFT level the water adsorption and the oxygen evolution reaction OER mechanisms. This has allowed us to compare it with the usual slab approach and determine the source of the reactivity differences between surfaces and nanoparticles.

# Development of New Nanocarriers Based on Catechol Compounds for Biomedical Applications

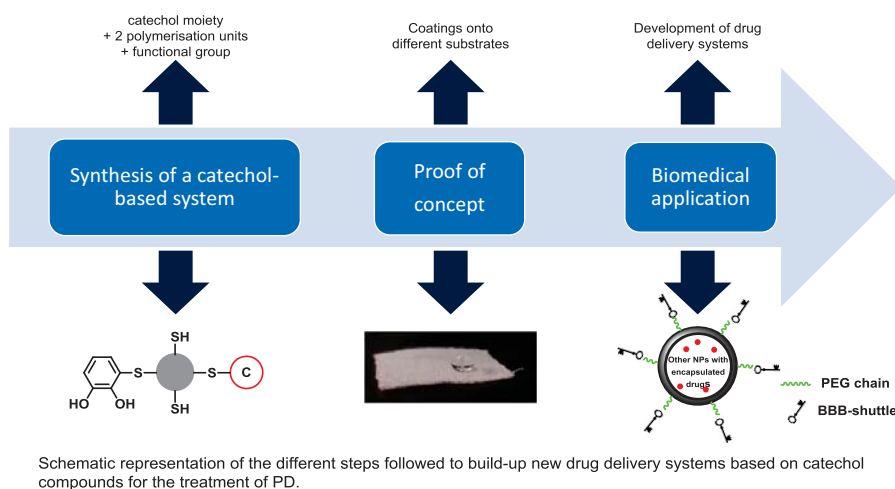
Carolina Casagualda,<sup>a,b</sup> Ramon Alibés,<sup>a</sup> Josep Sedó,<sup>b</sup> Daniel Ruiz-Molina,<sup>\*,b</sup> and Félix Busqué<sup>\*,a</sup>

<sup>a</sup> *Chemistry Department, Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Spain.*

<sup>b</sup> *Catalan Institute of Nanoscience and Nanotechnology (CIN2), 08193 Bellaterra, Spain.*

One of the research line in our groups is focused on the development of different bioinspired functional materials based on catechol compounds.<sup>1</sup> The main objective of this project is to develop novel nanocarriers for therapeutic agents against Parkinson's disease (PD) able to cross the blood-brain barrier (BBB). In order to have a better control on the polymerisation process of this kind of compounds, we have developed an alternative approach based on the use of a building block made of a catechol, two polymerisation units and the functional group with the property to be conferred.<sup>2</sup> As a proof of concept, so far different families of functional catechol coatings have been obtained.

Based on the knowledge acquired from these preliminary studies of coatings with catechol derivatives onto different substrates, the next step is to use this methodology in biomedical applications. Hence, one of the first objectives set is to use as functional unit a polyethylene glycol (PEG) chain bearing a terminal BBB-shuttle. For this reason, we need to achieve the synthesis of heterobifunctional PEG chains by desymmetrisation approach<sup>3</sup> that will act as linkers between a catechol unit (anchor) and the BBB-shuttle (sugar or peptide).



## References:

- [1] Sedó, J.; Saiz-Poseu, J.; Busqué, F.; Ruiz-Molina, D. *Adv. Mater.* **2013**, *25*, 653-701.
- [2] EP17382539.
- [3] Mahou, R.; Wandrey, C. *Polymers*, **2012**, *4*, 561-589.



# Influence of a Biostimulant on Se-enriching Wheat Plants

TINGTING XIAO<sup>1</sup>, ROBERTO BOADA<sup>1</sup>, MERCÈ LLUGANY<sup>2</sup>, MANUEL VALIENTE<sup>1\*</sup>

<sup>1</sup>GTS-UAB Research Group, Department of Chemistry, Faculty of Science, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain (Email contact: [manuel.valiente@uab.cat](mailto:manuel.valiente@uab.cat), [tingting.xiao@uab.cat](mailto:tingting.xiao@uab.cat), [roberto.boada@uab.cat](mailto:roberto.boada@uab.cat))

<sup>2</sup>Plant Physiology Laboratory, Facultat de Biociències, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain (Email contact: [merce.llugany@uab.cat](mailto:merce.llugany@uab.cat))

Appropriate selenium intake is essential for a good human health due to its antioxidant, anti-viral and anti-carcinogenic properties<sup>1,2</sup>. Although the application of selenium-containing fertilizers is becoming an increasingly common practice in many countries to overcome the Se-deficient food produced in Se-deficient soils, there are still issues to be addressed regarding the observed toxicity of Se to the plant itself.

In order to overcome these issues, a plant biostimulant based on hybrid heteropolyoxometalates of Keggin structure mixed with humic acids, named Phyto-Fitness® (BIO Fitos, S.R.O., Czech Republic) has been applied either by foliar or by root application to wheat plants grown hydroponically. The aim of this study is not only to assess the effectiveness of this biostimulant counteracting the Se toxicity on the normal development of plants, but also to evaluate a possible modification on the Se speciation in different plant tissues. For that purpose, plants were exposed 4 weeks to control conditions with no selenium, and with either selenite, selenate or a mixture of both Se species in the presence or absence of the biostimulant. In all the cases, the Se concentration was 10µM. After harvest, plant biomass, mineral elements and selenium speciation were analyzed.

Plant dry weight showed that the biostimulant root application significantly increased the plant biomass under Se exposure making it comparable to the control values. This result indicates the potential of this biostimulant against Se-induced stress in plant growth. Root application of the biostimulant could positively affect plants on their biomass, selenium content and, selenium translocation factor ( $C_{\text{shoot}}/C_{\text{root}}$ ; C=total Se content). Moreover, root applied biostimulant may enhance the elimination of reactive oxygen species (ROS) by consuming a large amount of Zn, Cu and Mn, which are co-factors of the Superoxide Dismutase (SOD) antioxidant enzyme. X-ray absorption spectroscopy characterization allowed us to identify organic selenium as the main Se species in both roots and shoots, especially in those exposed to selenite. Although, the foliar and root application of plant biostimulant both significantly affects the Se speciation in roots, Se speciation in shoots was only affected by the different Se treatments, being the influence of the biostimulant almost negligible.

## References:

- 1 M. P. Rayman, *Lancet*, 2000.
- 2 T. C. Stadtman, *Science* (80-. ), 1974, 183, 915–922.



# Photoactive Platinum(II) Complexes as Oxygen-Regulated Light-Triggered Photocages

Kevin Morales,<sup>a</sup> Jordi Hernando,<sup>a</sup> Julia Lorenzo,<sup>b</sup> Mercè Capdevila,<sup>a</sup> Marta Figueredo,<sup>a</sup> Òscar Palacios\*,<sup>a</sup> Pau Bayón\*<sup>a</sup>

<sup>a</sup> Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès

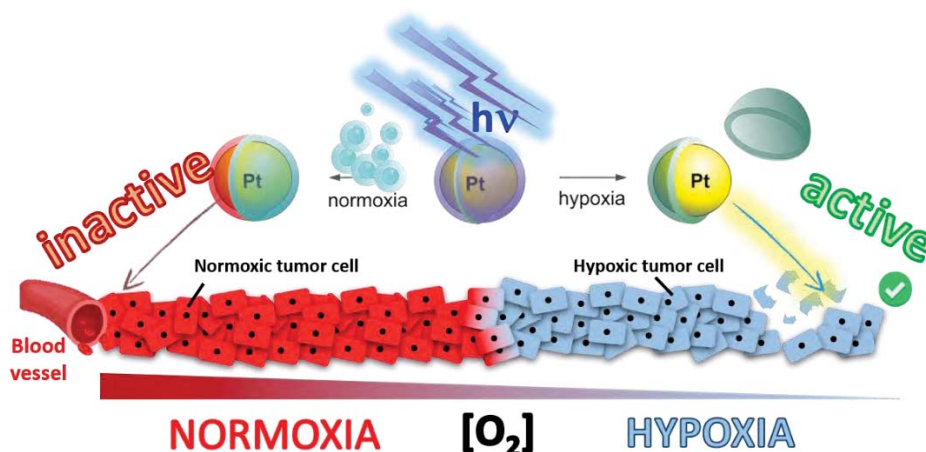
<sup>b</sup> Departament de Bioquímica i Biologia Molecular, Institut de Biotecnologia i Biomedicina (IBB), Campus UAB, 08193 Cerdanyola del Vallès

kevin.morales@uab.cat

Since the serendipitous discovery of cisplatin, platinum-based antitumor agents have constituted a cornerstone of modern cancer chemotherapy. Nevertheless, the effectiveness of these agents has been restricted by its toxicity, low selectivity or acquired resistance of some tumors.

To overcome these limitations, photoactivated chemotherapy (PACT) has become one of the most attractive alternatives that have emerged in the last years.<sup>1</sup> This type of therapy is based on the use of an external radiation, focused on a tumor region, in order to initiate a photochemical process. Thus, an initial harmless species can be modified by an external photo-stimulus to generate an active one, which could perform its action targeting tumor cells. Hence, this process allows to control *when* and *where* drug is activated, increasing its specificity and avoiding an aggressive treatment.

Herein, we deal with a new approach to oxygen controlled PACT based on the preparation of different platinum(II) complexes containing a functionalized cyclobutenedione unit as a photocage. When these complexes are irradiated, the ligands are degraded and the antiproliferative activity is controlled by the O<sub>2</sub> tension.<sup>2</sup>



## References:

[1] Bonnet, S. *Dalton Trans.* **2018**, 47, 10330-10343.

[2] Morales, K.; Samper, K. G.; Peña, Q.; Hernando, J.; Lorenzo, J.; Rodríguez-Diéguez, A.; Capdevila, M.; Figueredo, M.; Palacios, Ò.; Bayón, P. *Inorg. Chem.* **2018**, 57, 15517-15525.

# Synthesis and Catalytic Applications of Soluble Metal Nanoparticles

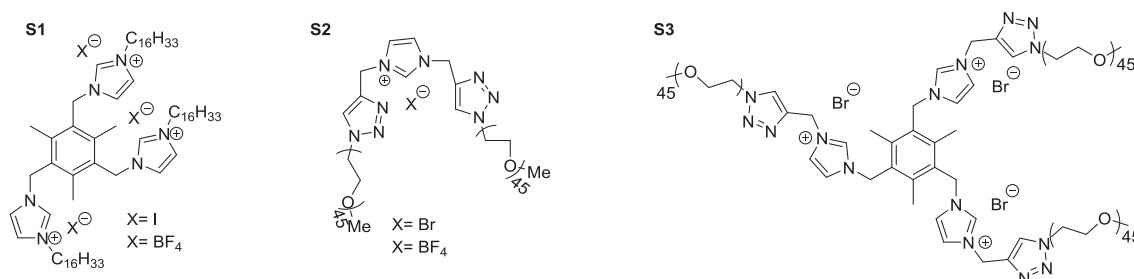
Guillem Fernández, Roser Pleixats\*

*Department of Chemistry and Centro de Innovación en Química Avanzada (ORFEO-CINQA),  
Universitat Autònoma de Barcelona, 08193-Cerdanyola del Vallès (Barcelona), Spain.*

guillem.fernandez@uab.cat

In the last years the research on metal nanoparticles (NPs) for catalytic purposes has grown exponentially. In this subject, our group has recently developed Pd<sup>1</sup>, Rh<sup>2</sup> and Au NPs,<sup>3</sup> which have been used as catalysts in cross-coupling reactions (Pd NPs),<sup>1a,b</sup> in the hydrosilylation of internal alkynes (Pd, Rh NPs)<sup>1c,2</sup> and in the reduction of nitroarenes (Au NPs).<sup>3</sup>

We present herein the synthesis and characterization of Pt<sup>4</sup>, Ni<sup>5</sup> and Au NPs stabilized by three types of ligands based on imidazolium salts, bearing either long hexadecyl chains (Figure 1, S1, soluble in some organic solvents) or polyoxyethylenated chains (Figure 1, S2 and S3, soluble in water and insoluble in diethyl ether). We also describe the catalytic activity and recyclability of the synthesized NPs for the hydrosilylation of internal alkynes (Pt NPs stabilized with S1),<sup>4</sup> the reduction of nitroarenes (Ni NPs stabilized with S1),<sup>5</sup> the three component A3 coupling of aldehydes, alkynes and amines (Au NPs stabilized with S2 or S3) and the cycloisomerization of  $\gamma$ -alkynoic acids into enol lactones (Au NPs stabilized with S2 or S3).



**Figure 1.** Synthesized imidazolium salts for the stabilization of metal nanoparticles.

## References:

1. a) Planellas, M.; Pleixats, R.; Shafir, A.; *Adv. Synth. Catal.* **2012**, *354*, 651-662. b) Planellas, M.; Moglie, Y.; Alonso, F.; Yus, M.; Pleixats, R.; Shafir, A.; *Eur. J. Org. Chem.* **2014**, 3001-3008. c) Planellas, M.; Guo, W.; Alonso, F.; Yus, M.; Shafir, A.; Pleixats, R.; Parella, T.; *Adv. Synth. Catal.* **2014**, *356*, 179-188.
2. Guo, W.; Pleixats, R.; Shafir, A.; Parella, T.; *Adv. Synth. Catal.* **2015**, *357*, 89-99.
3. Guo, W.; Pleixats, R.; Shafir, A.; *Chem. Asian. J.* **2015**, *10*, 2437-2443
4. Fernández, G.; Pleixats, R.; *ChemistrySelect*, **2018**, *3*, 11486-11493
5. Fernández, G.; Sort, J.; Pleixats, R.; *ChemistrySelect*, **2018**, *3*, 8597-8603



# Syntheses, Structures, and Properties of Carborane-based Cooper Metal Organic Frameworks

Gan, Lei,<sup>a</sup> Fonquernie, Pol G.,<sup>a</sup> Light, Mark E.,<sup>b</sup> Norjmaa, Gantulga,<sup>c</sup> Ujaque, Gregori,<sup>c</sup> Choquesillo-Lazarte, Duane,<sup>d</sup> Fraile, Julio,<sup>a</sup> Teixidor, Francesc,<sup>a</sup> Viñas, Clara,<sup>a</sup> Planas, José G.<sup>a</sup>

<sup>a</sup> *Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Carrer dels Tillers, Campus UAB, Bellaterra, Spain.*

<sup>b</sup> *Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK.*

<sup>c</sup> *Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Valles, Catalonia, Spain.*

<sup>d</sup> *Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Av. de las Palmeras 4, E-18100 Armilla, Granada, Spain.*

Porous Coordination Polymers (CPs) or Metal-Organic Frameworks (MOFs) are a class of porous crystalline materials formed by the assembly of metal ions or metal clusters with different types of bridging organic linkers or ligands [1]. Icosahedral boranes and carboranes ( $[\text{B}_{12}\text{H}_{12}]^{2-}$  and  $1, n\text{-C}_2\text{B}_{10}\text{H}_{12}$  ( $n = 2, 7$  or  $12$ )), respectively, are an interesting class of commercially available and exceptionally stable 3D-aromatic boron-rich clusters that possess material-favorable properties such as thermal and chemical stability and hydrophobicity [2]. In this study, we report a series of 2D and 3D  $\text{Cu}_2$ -paddlewheel porous coordination polymers by solvothermal reactions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with a V-shape carborane based carboxylic ligand. We will disclose how the 2D compound  $[\text{Cu}_2(\text{Lcb}(\text{COO})_2)_2(\text{DMF})_2] \cdot 2\text{DMF}$  shows a reversible phase transition by  $\text{B-H} \cdots \text{Cu}(\text{II})$  interactions between layers when solvent is removed from the apical sites of  $\text{Cu}(\text{II})$  paddlewheel units. In the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) it was obtained a 3D MOF  $[\text{Cu}_4(\text{Lcb})_4(\text{DABCO})(\text{H}_2\text{O})_2] \cdot \text{Solvent}$ . The latter exhibits good oil-water separation due to its high hydrophobicity and oleophilicity. Quite interestingly, this  $\text{Cu}_2$ -paddlewheel MOF shows unprecedented water stability in boiling water and is porous to  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ . We will show how the presence of carborane based ligands have a strong impact in the stabilities of the corresponding MOFs and therefore open up new properties or applications for MOFs area.

## References:

[1] a) J. R. Long, O. M. Yaghi, Chem. Soc. Rev., 38, 1213-1214 (2009); b) S. Kitagawa, R. Kitaura, S.-i. Noro, Angew. Chem. Int. Ed., 43, 2334-2375 (2004); c) S. L. James, Chem. Soc. Rev., 32, 276-288 (2003); d) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, Nature, 402, 276-279 (1999).

[2] a) S. Rodriguez-Hermida, M. Y. Tsang, C. Vignatti, K. C. Stylianou, V. Guillerme, J. Perez-Carvajal, F. Teixidor, C. Vinas, D. Choquesillo-Lazarte, C. Verdugo-Escamilla, I. Peral, J. Juanhuix, A. Verdaguer, I. Imaz, D. Maspoch, J. G. Planas, Angew Chem Int Ed Engl, 55, 16049-16053 (2016); b) F. Tan, A. López-Periago, M. E. Light, J. Cirera, E. Ruiz, A. Borrás, F. Teixidor, C. Viñas, C. Domingo, J. G. Planas, Advanced Materials, 30, 1800726 (2018). c) A. Saha, E. Oleshkevich, C. Viñas, F. Teixidor, Advanced Materials, 29, 1704238 (2017).

# Water Determination in Parenteral Drug Products

Laia Garcia<sup>(a),(b)</sup>, Jordi Coello<sup>(b)</sup> and Sasha Nikolic<sup>(a)</sup>

<sup>(a)</sup>Center of Excellence in Lyophilization, Reig Jofre Group

<sup>(b)</sup>Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona

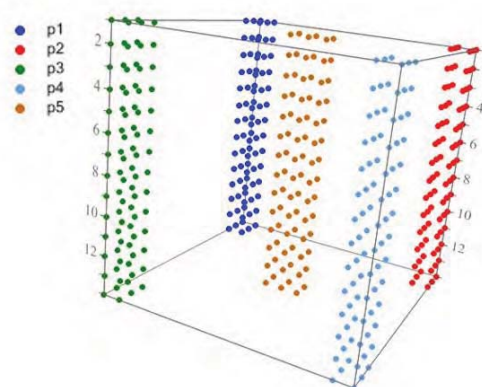
Freeze-drying process is a usual procedure in pharmaceutical industry for manufacturing solid parenteral products. This process is performed to prolong the product shelf life, and it consists of removing the solvent of a solution (commonly water) at low pressure and temperature. One of the evidences used to evaluate freeze-drying process efficiency is the residual moisture content (RMC) in the product. For this reason, RMC is considered a critical quality attribute (CQA).

Karl Fischer titration (KF) is the conventional technique used to determine RMC in freeze-dried products and in primary materials. Nevertheless, it's a destructive, environmentally unfriendly and time-consuming technique. Near Infrared spectroscopy (NIRS) has emerged as an alternative method, solving the drawbacks of KF and allowing more extensive and representative sampling of the freeze-drying process.

In this work, the development of NIRS methods has been carried out for two freeze-dried products (FDP-A and FDP-B) following the specific guideline for pharmaceutical products<sup>1</sup>. At first, a feasibility study and a risk analysis has been performed. Based on the conclusions of these studies, it has been decided that a quantitative NIRS model can be developed to predict RMC for FDP-A, while for FDP-B a semi-quantitative NIRS model approximation can be developed.

Regarding FDP-A, a quantitative multivariate calibration model has been developed and validated according to the methodology recommended for the sector<sup>1</sup>. The first step for validation is to unequivocally identify the product. A spectral library containing the main drug-products manufactured by the company has been developed, and supervised pattern recognition techniques have been used for the identification. Finally, key statistical functions (linearity, range, accuracy and precision...) <sup>2</sup> have been demonstrated. The validated model includes the spectral range 1350 - 2350 nm and the application of SNV pre-treatment. It covers the RMC range from 0.36% to 3.93%. The validated method has been used, in batches of process performance qualification (PPQ), to predict the RMC, and to obtain a freeze-dryer mapping of this CQA. Then the homogeneity in the industrial freeze-dryers, inter and intra batch, has been evaluated.

However, the RMC may not be stable during the freeze-dried product shelf life. One explanation is the water redistribution between rubber stoppers and the vial headspace. In this work, the impact on the product stability of this water redistribution has been studied for a hygroscopic freeze-dried product (FDP-C), which increases its degradation over time in the presence of moisture



**Figure 1. 3D representation of the studied positions in the freeze-dryer chamber.**

<sup>1</sup> EMA. Guideline on the Use of Near Infrared Spectroscopy (NIRS) by the Pharmaceutical Industry and the Data Requirements for New Submissions and Variations. European Medicines Agency; London, UK, 2014.

<sup>2</sup> ICH. Harmonised Tripartite Guideline Q2(R1) Validation of Analytical Procedures: Text and Methodology. 2009.

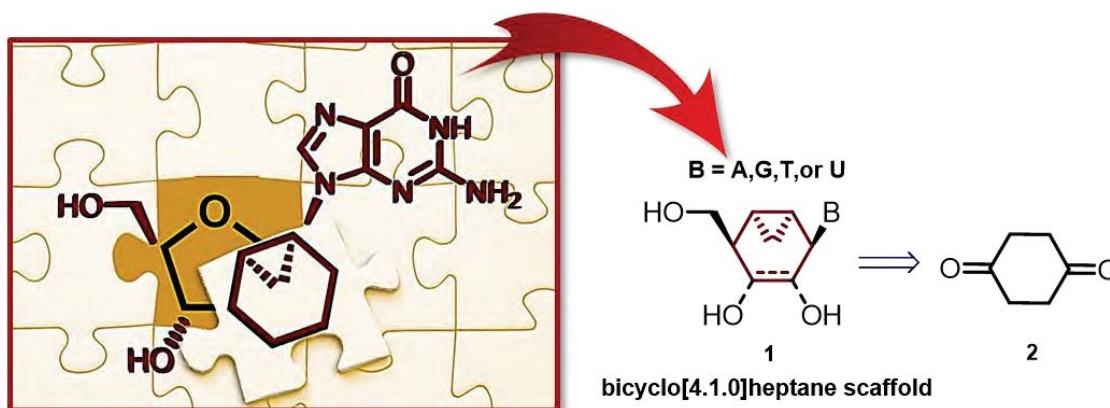


# Synthesis of Conformationally Restricted Cyclohexanyl Nucleoside Analogues as Antiviral Agents

Sergio Jurado<sup>1</sup>, Ramon Alibés<sup>1</sup>, Félix Busqué<sup>1</sup>

<sup>1</sup>Dept. de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, [sergio.jurado@uab.cat](mailto:sergio.jurado@uab.cat)

The application of nucleoside analogues in antiviral and anticancer therapy has been an important option over the last decades.<sup>1</sup> The conformation and puckering of the sugar moiety of nucleosides play a critical role in modulating their biological activity.<sup>2</sup> In this context, new conformationally restricted carbanucleosides analogues have been designed and synthesized in order to mimic the conformational behaviour of the natural furanose ring. In this new nucleosides, the furanose ring have been replaced by a bicyclo[4.1.0]heptane scaffold which is expected to display new biological properties due to their unusual ring puckering.



The asymmetric synthesis of series of these bicyclo[4.1.0]heptane compounds, **1** incorporating different nucleobases has been efficiently completed starting from achiral commercially available 1,4-cyclohexanedione, **2**.<sup>3</sup>

## References:

- [1] a) De Clercq, E.; Li, G. *Clin. Microbiol. Rev.* **2016**, 29, 695–747; b) Shelton, J.; Lu, X.; Hollenbaugh, J. A.; Cho, J. H.; Amblard, F.; Schinazi, R. F. *Chem. Rev.* **2016**, 116, 14379–14455.
- [2] Neidle, S. *Principles of nucleic acid structure*, Academic Press: Amsterdam, 2008.
- [3] a) Domínguez-Pérez, B.; Ferrer, É.; Figueredo, M.; Maréchal, J. D.; Balzarini, J.; Alibés, R.; Busqué, F. *J. Org. Chem.* **2015**, 80, 9495–9505; b) Ferrer, É.; Alibés, R.; Busqué, F.; Figueredo, M.; Font, J.; De March, P. *J. Org. Chem.* **2009**, 74, 2425–2432.



# Integrated Instrumental/Computational approach to study metal species binding to proteins

Giuseppe Sciortino<sup>a,b</sup> Eugenio Garribba,<sup>b</sup> Jean-Didier Maréchal,<sup>a</sup>

<sup>a</sup> Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain

<sup>b</sup> Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy  
Giuseppe.Sciortino@uab.cat

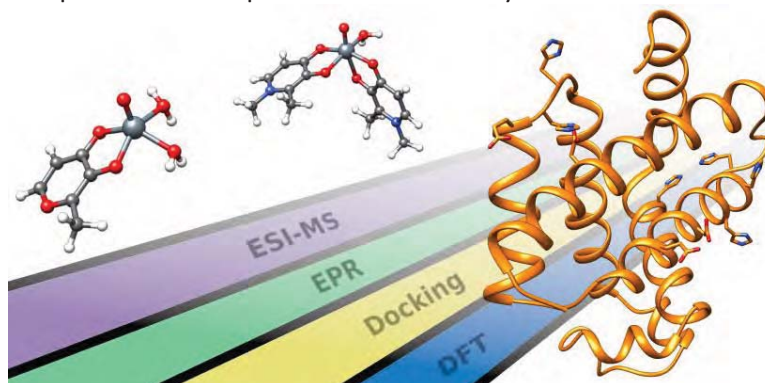
**Keywords:** Molecular Modeling • Bioinorganic Chemistry • Computational Chemistry

Decoding the interaction of coordination compounds with proteins is of fundamental importance in biology, pharmacy, medicine and artificial metalloenzyme design. X-ray and NMR can provide an accurate description of the system, but often couldn't be applied (i.e. lability of the drug-protein interaction and electron beaming, open shell systems *etc.*). Spectroscopy, such as EPR, CD and UV-Vis can give insight on the protein region where the metal species is bound or on the amino acid type involved. ESI-MS based techniques can determine the metal specie-protein stoichiometry, and often tandem MS/MS and fragmentation approaches, can suggest the coordinated amino acids. However, the latter instrumental approaches are not able to provide with a complete 3D description of

the system. Either to predict possible metal mediated binding, or enrich the partial experimental data, computational methods can represent a valuable approach.<sup>1</sup>

A hybrid instrumental/computational strategy to study the binding modes of metal species to proteins was developed during this PhD work. In particular: ESI-MS allows to determine the number of fragments bound to protein; EPR to distinguish the type of donors involved in the coordination; docking<sup>2</sup> and DFT models to predict the specific residues as well as the 3D structure of the adducts.

During the talk, on one hand the theoretical and methodological aspects will be introduced, and on the other, a series of selected examples of the PhD work will be briefly discussed.



## References:

- [1] (a) Neese, F., *JBIC J. Biol. Inorg. Chem.* **2006**, 11 (6), 702-711; (b) Solomon, E. I.; Scott, R. A.; King, R. B., *Computational inorganic and bioinorganic chemistry*. John Wiley & Sons: 2013.
- [2] (a) Sciortino, G.; Garribba, E.; Maréchal, J.-D., *Inorg. Chem.* **2018**; (b) Sciortino, G.; Sanna, D.; Ugone, V.; Lledós, A.; Maréchal, J.-D.; Garribba, E., *Inorg. Chem.* **2018**, 57 (8), 4456-4469.

# Study of the Calcium Oxalate Hydrates Transformation and the role of the organic matter on their development by Synchrotron-based $\mu$ -FTIR spectroscopy

I. H. Valido<sup>a</sup>, M. Resina-Gallego<sup>a</sup>, M. Valiente<sup>a</sup>, M. López-Mesas<sup>a</sup>

<sup>a</sup> Centre Grup de Tècniques de Separació en Química (GTS), Departament de Química, Universitat Autònoma de Barcelona, Facultat de Ciències. Edifici CN. 08193, Bellaterra, Barcelona, Spain

Renal Nephrolithiasis is a clinical condition that implies the formation of microcrystals aggregates on the kidney, commonly known as kidney stones. This disease affects approximately 12% of men and 6% of women, and has a recurrence rate around 40%<sup>1</sup>. There are 11 types of renal calculi, each one with its different subtypes, categorized following the morphoconstitutional analysis guidelines<sup>2</sup> by the chemical composition and formation place. Within this wide range of nephroliths, calcium oxalate stones, considering both the mono (COM) and the dihydrate (COD) forms represent de 66% of the incidence<sup>1</sup>. The studies on the formation of this kind of stones and the interaction between different phases are important in order to understand the pathophysiology, plan a therapy and prevent the recurrence.

One of the most controversial issues in the chemistry of oxalates is the process which accounts for the transformation of weddellite (COD) into whewellite (COM)<sup>3,4</sup>; which has been studied in mineral systems and in vitro<sup>5-7</sup>. As a result of this process, the formed stone (called TRA) that had a total transformation is, chemically, COM, since it only has one water molecule in its crystalline structure. Regarding the morphoconstitutional characterization, it is difficult to differentiate between the monohydrated phases (COM and TRA) due to the high appearance<sup>8</sup>. This distinction is of great importance since both species can be caused by different pathologies; for example, COM calculi are related to hyperoxaluria, while those of COD are related to hypercalciuria<sup>8</sup>, among other pathologies<sup>9</sup>. Therefore, the study of the transformation of these types of kidney stones, as well as the stabilization of the dihydrated specie, are important to understand the physiopathology, to propose an adequate treatment and, above all, to prevent recurrence<sup>10</sup>.

The study carried out in the present research has focused on the analysis of the organic matter (OM) present on three types of kidney stones samples crystallites (COD, TRA and COM) by  $\mu$ -IR spectroscopy, performed at MIRAS beamline at ALBA Synchrotron facility. The objectives of this experiment were to determine if OM, such as proteins, can stabilize the COD crystallites (example of this transformation is shown in Figure 1); to study the type of OM that helps the nucleation and finally to study the type of OM that could inhibits the growth/aggregation of the COM stones. .

As a conclusion, it is possible to distinguish COM and TRA on different kidney stones by  $\mu$ -IR spectroscopy, but further studies are needed in order to understand the differences between the two phases. Furthermore, it is possible to find OM, such as proteins, inside the COD crystallites, which has not been reported previously; and these components participate on the stabilization of the specie during the kidney stone development. Finally due to the observed differences on the C-H stretching region (shown in Figure 2), it is possible to distinguish the OM of the surface and the inner section of the stone, being mostly lipids and proteins respectively.

Further studies will help to understand the pathologies related to the formation of the oxalocalcic stones, which is an important step to avoid the recurrence.

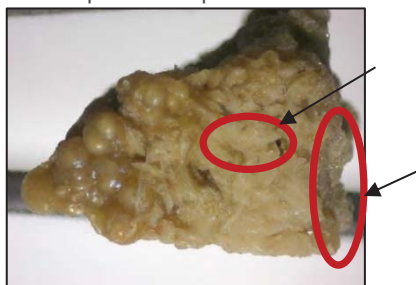


Figure 1: Example of a kidney Stone with different degrees of COD transformation to TRA

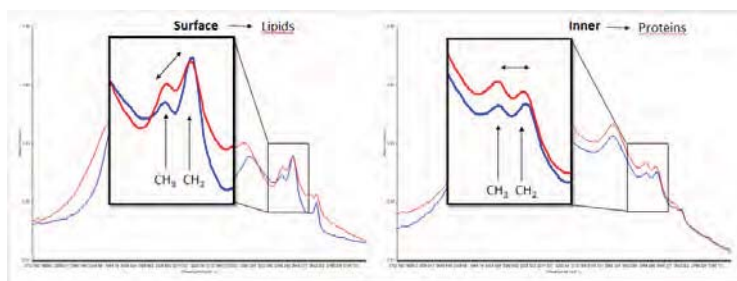


Figure 2:  $\mu$ -FTIR spectra of the Surface (left) and inner (right) section of a COM kidney stone showing the C-H stretching region differences.

<sup>1</sup> Blanco-Lucena, F., Universitat Autònoma de Barcelona, 2014, Doctoral Thesis.

<sup>2</sup> Daudon, M., et. al., *C. R. Chimie*, 2016, 1-22.

<sup>3</sup> Conti, C., et. al., *Phys. Chem. Chem. Phys.* 2010, 12 (43), 14560-14566.

<sup>4</sup> Conti, C., et. al., *Spectrochim. Acta – Part A Mol. Biomol. Spectrosc.*, 2014, 128, 413-419.

<sup>5</sup> Chysty, A. A., et. al., *Appl. Spectrosc.*, 1994, 48 (5), 561-568.

<sup>6</sup> Klopogge, J. T., et. al., *Am. Mineral.*, 2004, 89 (1), 245-248.

<sup>7</sup> Frost, R. L., et. al., *Thermochim. Acta* 2004, 409 (1), 79-85.

<sup>8</sup> Bazin, D., et. al., *C. R. Chimie*, 2016, 19, 1492-1503.

<sup>9</sup> Grases, F., et. al., *Nutr. J.*, 2006, 5, 23.



## ***In vitro* dental remineralization assisted by amelogenin**

Sandra Díez García, María-Jesús Sánchez-Martín, Manuel Valiente Malmagro

*GTS Research Group, Department of Chemistry, Faculty of Science, Universitat Autònoma de Barcelona,  
08193 Bellaterra, Spain*

Enamel, the outer layer of the teeth, is the hardest and most mineralized tissue in vertebrates. It is an acellular mineralized tissue comprised of highly oriented crystallites of calcium hydroxyapatite and fluorapatite. The crystal morphology and alignment of enamel are due to a protein-guided uniaxial growth process. In developing enamel, the hierarchical organization of apatite crystals is mainly leaded by amelogenin that constitutes the 90% of the protein matrix <sup>1</sup>.

Dental caries is a complex disease process that afflicts a large proportion of the world's population, regardless of gender, age and ethnicity <sup>2</sup>. This disease progresses when acid produced by bacterial action on dietary fermentable carbohydrates diffuses into the tooth and dissolves the mineral. Nevertheless, there are protective factors that can prevent or reverse dental caries, such as salivary calcium, phosphate, proteins, salivary flow and fluoride in saliva. Nowadays, fluoride is widely used in dental products because it works primarily via topical mechanisms producing the inhibition of demineralization at the crystal surfaces, the enhancement of remineralization, and the inhibition of bacterial enzymes <sup>3</sup>. The prevalence of dental caries has descended after the water fluoridation and the introduction of fluoridated toothpastes. However, there has been an increase in exposure to fluoride ingestion in children and the risk of toxicity and dental fluorosis has also increased due to the high levels of fluoride released into biological fluids <sup>4</sup>.

Despite the caries reduction of the last decades, the disease is still a major problem for adults and children, and an improved solution for prevention and therapy is currently needed. A new approach for fluoride utilization could be focus on optimizing the slow release of fluoride in the oral environment, together with the delivery of calcium and phosphate ions. For this purpose, NMTD product is proposed. It is a combination of ion-exchange resins loaded with fluoride, calcium, phosphate and zinc, which supplies all these ions simultaneously avoiding the precipitation before the application. The molar ratio of the ions should be close to that of the tooth, the organomineral tissue to be remineralized. The zinc has two effects, it helps to combat the microorganisms which cause caries due to its bactericidal properties, and it is an initiator of the ionic release of the other structural ions.

Our main objective is to study the remineralization process that take place at the interface enamel/saliva. Bovine teeth were treated with NMTD in presence and absence of amelogenin in order to understand the influence of this protein on the remineralization process induced by the presence of the released ions.

### **References:**

1. Carneiro, K. M. M. *et al.* Amyloid-like ribbons of amelogenins in enamel mineralization. *Sci. Rep.* **6**, 1–11 (2016).
2. Hicks, J., Garcia-Godoy, F. & Flaitz, C. Biological factors in dental caries: enamel structure and the caries process in the dynamic process of demineralization and remineralization (part 2). *J. Clin. Pediatr. Dent.* **28**, 119–124 (2004).
3. Featherstone, J. D. Prevention and reversal of dental caries: role of low level fluoride. *Community Dent. Oral Epidemiol.* **27**, 31–40 (1999).
4. Pendrys, D. G. Risk of fluorosis in a fluoridated population. Implications for the dentist and hygienist. *J. Am. Dent. Assoc.* **126**, 1617–1624 (1995).

# Ru-Based Nanomaterials as Co-Catalyst with Carbon Nitride for Light-Driven Proton Reduction

Ignacio Álvarez-Prada, Lluís Escriche, Nuria Romero, Xavier Sala, Jordi García-Antón

*Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain*

The water splitting reaction, which generates oxygen and hydrogen, offers an attractive method to store renewable energy in the form of chemical bonds. Thus, hydrogen is a clean alternative to non-renewable and polluting fossil fuels. To carry out the water splitting, it is necessary to prepare electro or photo-catalysts capable of speed up both concerned half-reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). [1] Metallic nanoparticles are promising for this aim, especially ruthenium nanoparticles are among the most studied catalytic systems to achieve this goal. [2]

In the present work, we report a family of new materials based on Ru nanoparticles, synthesized following the organometallic approach [3] and stabilized onto the surface of carbon-based supports. These materials have been extensively characterized and used as highly active proton reduction photocatalysts when mixed with carbon nitride and using light as energy source.

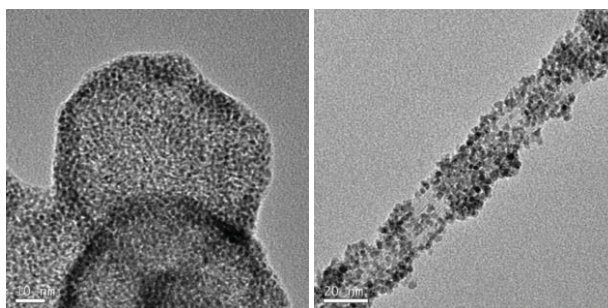


Figure 1. Transmission Electronic Microscopy (TEM) images of Ru NPs synthesized onto carbon nanohorns (left) and single-wall carbon nanotubes (right)

## References:

- [1] Sala, X.; Maji, S.; Bofill, R.; García-Antón, J.; Escriche, L.; Llobet, A., *Acc. Chem. Res.* **2014**, 47, 504-516.
- [2] Creus, J.; De Tovar, J.; Romero, N.; García-Antón, Jordi.; Philippot, K.; Bofill, R.; Sala, X.; *Chem. Sus. Chem.* **2019**, DOI: [10.1002/cssc.201900393](https://doi.org/10.1002/cssc.201900393).
- [3] Amiens, C.; Ciuculescu-Pradines, D.; Philippot, K.; *Coord. Chem. Rev.* **2016**, 308, 409-432.



# Simultaneous Voltammetric determination of Ascorbic Acid, Uric Acid and Acetaminophen by Use of modified screen-printed Electrodes and Chemometrics tools.

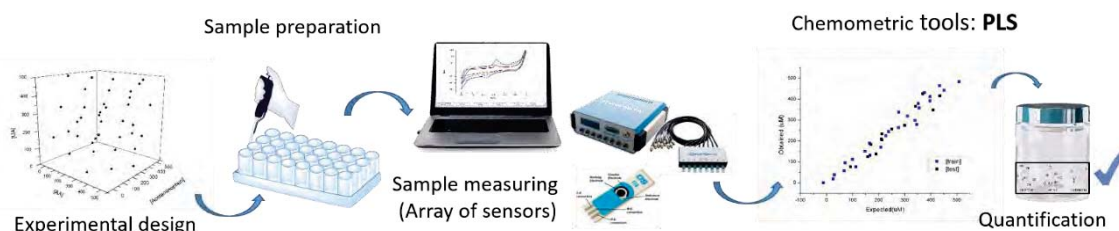
Dionisia Ortiz-Aguayo<sup>1</sup>, M. del Valle<sup>1</sup>, \*

<sup>1</sup>Sensors and Biosensors group, Department of Chemistry,  
Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain  
\*e-mail: manel.delvalle@uab.cat

Ascorbic acid (AA) is a vitamin commonly present in many biological systems and in multivitamin formulations. Its excessive dose may cause headache, trouble sleeping, gastrointestinal discomfort and flushing of the skin. Paracetamol (PA) or acetaminophen (N-acetyl-p-aminophenol) is an antipyretic and analgesic drug commonly used against arthritis, headache, muscle aches, menstrual cramps and fevers. A high amount of PA can cause the accumulation of toxic metabolites, leading to severe and sometimes serious hepatotoxicity and nephrotoxicity [1]. Uric acid (UA) is the primary product of purine metabolism [2]. Continuous monitoring of UA in the body fluid is essential since its abnormal concentration levels lead to many diseases, such as hyperuricemia and gout [3].

Several analytical methods for individual or simultaneous determination of AA, PA, and UA have been reported in the literature [1]. The problem is these methods are expensive and carry out complex procedures. For this reason, there is a need to develop rapid, cheap and effective devices for their detection. To overcome this problem electrochemical sensors are a good alternative. In the present work, the ternary mixtures of AA, PA and UA were detected simultaneously using the Electronic tongue (ET) principle [4][5] and Cyclic Voltammetry (CV) technique. Different electrode modifiers such as graphite, prussian blue, cobalt (II) phthalocyanine and copper oxide (II) were casted on the screen printed electrode surface to construct the sensor array in order to have differentiated response for the three oxidizable compounds. The use of the ET principle allows the possibility to determine and quantify simultaneously substance in the presence of other ones with overlapping redox potential.

## References:



**Figure 2. Scheme of the strategy followed in the resolution of ascorbic acid, uric acid and acetaminophen.**

- [1] N. H. Phong, T. T. T. Toan, M. X. Tinh, T. N. Tuyen, T. X. Mau, and D. Q. Khieu, "Simultaneous Voltammetric Determination of Ascorbic Acid, Paracetamol, and Caffeine Using Electrochemically Reduced Graphene-Oxide-Modified Electrode," *J. Nanomater.*, 2018.
- [2] H. Kaur and B. Halliwell, "Action of biologically-relevant oxidizing species upon uric acid. Identification of uric acid oxidation products," *Chem. Biol. Interact.*, 1990.
- [3] E. Miland, A. J. Miranda Ordieres, P. Tuñón Blanco, M. R. Smyth, and C. Ó. Fágáin, "Poly(o-aminophenol)-modified bienzyme carbon paste electrode for the detection of uric acid," *Talanta*, 1996.
- [4] F. Winqvist, "Voltammetric electronic tongues - Basic principles and applications," *Microchimica Acta*. 2008.
- [5] M. del Valle, "Electronic tongues employing electrochemical sensors," *Electroanalysis*. 2010.





# Implementing one-shot multiple-FID acquisition into homonuclear and heteronuclear NMR experiments

Kumar Motiram-Corral, Míriam Pérez-Trujillo, Pau Nolis and Teodor Parella

*Servei de RMN, Universitat Autònoma de Barcelona. Barcelona, Spain.*

**Abstract:** To date, time-efficient NMR approaches are a challenging task for spectroscopists. The goal is to obtain chemical information reducing experimental time and without considerably losing sensitivity. Different time-efficient methods have been described over the years. For instance, time sharing techniques acquire  $^{15}\text{N}$  and  $^{13}\text{C}$  data in the same spectrum in spectrometers having a triple channel hardware configuration [1]. Non-Uniform Sampling (NUS) algorithms afford a substantial reduction of experimental times by reducing the number of  $t_1$  increments in multidimensional experiments. [2] Recently, the interleaved acquisition of multiple experiments by the NOAH (NMR by ordered Acquisition using  $^1\text{H}$  detection) strategy allow the reduction of long recycle delays in consecutive experiments. [3]

On the other hand, the MFA (Multiple FID Acquisition) strategy was initially proposed many years ago with the COCONOSY experiment [4-6], which collected 2D COSY and NOESY data with a single pulse scheme. We show here how MFA can be implemented in several applications, offering a new novel proof of concept to obtain COSY, TOCSY and HMBC datasets in small molecules. For instance, it is shown how the simultaneous recording of four different NMR experiments in a single-shot acquisition, decreasing close to 60% of experiment time. [7] This approach is based on the recovery of the remaining transverse magnetization after an acquisition period. This magnetization components that usually is lost by relaxation to its original z-position can be manipulated by an appropriate additional mixing process and recorded again to obtain a second or third NMR data provided that  $T_2$  relaxation times are long enough. It is shown how MFA is a powerful strategy for the sequential structural assignment of a whole spin system without ambiguities using a multiple-step RELAY experiment.

## References:

1. Nolis, P., Pérez, M., & Parella, T. (2006). Time-sharing evolution and sensitivity enhancements in 2D HSQC-TOCSY and HSQMBC experiments. *Magnetic Resonance in Chemistry*, 44, 11, 1031-1036, 2006.
2. K. Kazimierczuk and V. Y. Orekhov, *Angew. Chem., Int. Ed.*, 2011, **50**, 5556 -5559
3. Kupče, E., & Claridge, T. D. W. (2018). Molecular structure from a single NMR supersequence. *Chemical Communications*, **54**, 7139-7142, 2018.
4. A. Z. Gurevich, I. L. Barsukov, A. S. Arseniev and V. F. Bystrov, *J. Magn. Reson.*, 1984, **56**, 471 -478
5. C. A. G. Haasnoot, F. J. M. van de Ven and C. W. Hilbers, *J. Magn. Reson.*, 1984, **56**, 343 -349
6. J. Cavanagh and M. Rance, *J. Magn. Reson.*, 1990, **14**, 408 -414
7. Motiram-Corral, K., Pérez-Trujillo, M., Nolis, P., & Parella, T. (2018). Implementing one-shot multiple-FID acquisition into homonuclear and heteronuclear NMR experiments. *Chemical Communications*, 54(96), 13507–13510, 2018.

# Fluorinated Polyurethanes

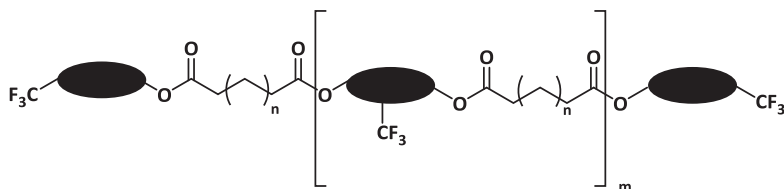
M. Laiz<sup>1</sup>, J.Real<sup>1</sup>, J.C. Bayón<sup>1</sup>

<sup>1</sup>Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Barcelona, Spain,  
miriam.laiz@uab.cat

**Key words:** *Fluorinated monomers, Fluorinated polyols, Polyurethanes*

Thermoplastic polyurethanes (TPUs) are materials with great opportunities to enhance their durability and their thermal and chemical resistance. The infinite ratios and reagents that could be employed in their synthesis provide a wide scope for improvement. Different approaches have been sought, but the incorporation of fluorine on them has been one of the most successful, as it increases the hydrophobicity and decreases the coefficient of friction of the material.<sup>[1][2][3]</sup>

We have synthesized a set of fluorinated polyols to polymerize them as soft segment on a standard formulation of TPUs. In addition, we have studied the effect of introducing trifluoromethyl moieties in a side branch of polyesters.



Several TPUs have been synthesized by “One-shot” method from hexamethylene diisocyanate (HDI), 1,4-butanediol (BDO) as the main chain extender and different combinations of the previously synthesized polyesters. Common mechanical, thermal, optical and surface properties have been studied, having promising results in some of them.

## References

- [1] Wang, X.; Hu, J.; Li, Y.; Zhang, J.; Ding, Y.; *J.Fluor.Chem.*, **2015**, 176, 14-19
- [2] Wu, W.; Zhu, Q.; Qing, F.; Han, C.C.; *Langmuir*, **2009**, 25, 17-20
- [3] Kim, Y.S.; Lee, J.S.; Ji, Q.; McGrath, J.E.; *Polymer*, **2002**, 43, 7161-7170

# New Chiral Schiff Bases For Asymmetric Catalysis

J.A. Pérez, J. Real

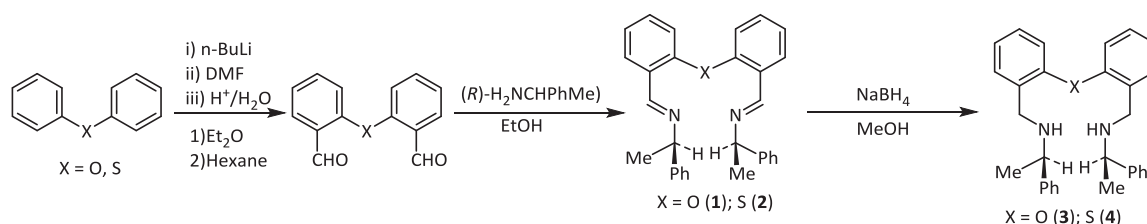
Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Barcelona, Spain,  
joseantonio.perez.mejias@uab.cat

**Keywords:** Schiff bases, chiral ligands, asymmetric catalysis, H-transfer, alkene amination

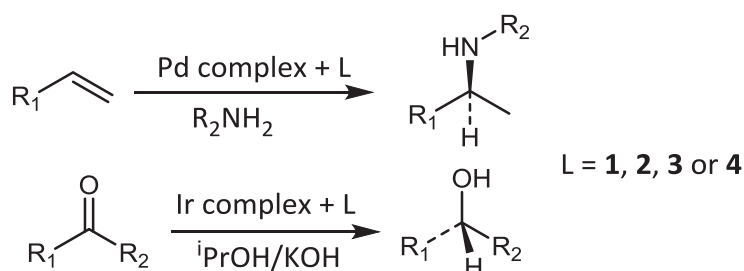
In the manufacture of chemicals, more than 80% of synthesis include a catalytic step. The demand for new specific catalysts has been growing up every year. However, chemists have to be aware of the importance of green chemistry and the huge advantages of catalysis in this field.

The huge demand of enantiopure products have develop the attractive goal, in synthetic chemistry, to produce these valuable products through the chiral multiplication that asymmetric catalysis provides. Along this line, the design of new molecular structures that could increase the limited number of privileged ligands still remains a challenge.[1] Schiff bases are readily accessible molecules, but their use in asymmetric catalysis is less spread out than other ligands, particularly those containing P-donor atoms.[2]

Two new enantiopure bidentate ligands, **1**, **2**, **3** and **4**, have been synthesized in three steps from readily available moieties:



The new ligands have been investigated as chiral auxiliaries for palladium catalyzed asymmetric alkene amination and for the iridium catalyzed asymmetric H-transfer from isopropanol to ketones:



Results on these reactions, as well as on the coordination mode of the ligands will be reported.

## References

- [1] T.P. Yoon, E.N. Jacobsen, *Science* **2003**, 299, 1691-1693.
- [2] C.A. C aputo, N.D. Jones, *Dalton Trans.* **2007**, 4627–4640.



# Computational study of the transglycosylation reaction catalyzed by Glycoside Hydrolases and Glycosyltransferases.

Sonia Romero-Téllez<sup>1,2</sup>, José María Lluch<sup>1,2</sup>, Àngels González Lafont<sup>1,2</sup>, Laura Masgrau<sup>1,2</sup>

<sup>1</sup>Departament de Química, <sup>2</sup>Institut de Biotecnologia i de Biomedicina, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Barcelona, Spain

The synthesis of oligosaccharides and other carbohydrate derivatives is of relevance for the advancement of glycosciences. In Nature, **glycosyltransferases** (GTs) are the main enzymes **catalyzing the synthesis of a new glycosidic bond**, but **some glycoside hydrolases** (GHs) **can also catalyze a transglycosylation (T) reaction that competes with hydrolysis (H)**. Both types of enzymes are explored for enzymatic synthesis of glycans with biomedical<sup>1,2</sup> or industrial interest. This PhD thesis focuses on glycosylation catalyzed by both types of enzymes, using different computational resources.

In the case of GHs, the goal is to increase the T/H ratio, which has been achieved with moderate success in several cases even though the molecular basis for T/H modulation are unclear. Here we have used QM(DFT)/MM calculations to compare the hydrolysis and transglycosylation steps catalyzed by wild type *Thermus thermophilus*  $\beta$ -glycosidase (family GH1), for which a transglycosylation yield of 36 % has been determined experimentally. We found important differences involving the nucleophilicity of the acceptor substrates (a water for hydrolysis and Glucose (Glc) for transglycosylation), and bond distances of the acceptor atoms to the catalytic residues in the transition state, which favour hydrolysis as it is expected for the WT. An interaction analysis between substrates and neighbouring protein residues suggests that perturbing the Glu392-Fuc interaction could increase the T/H ratio, either by direct mutation of this residue or indirectly as reported experimentally in the Asn390I and Phe401S cases.<sup>3</sup>

OleD is a promiscuous GT with a high potential applicability. The glycosylation of the acceptor substrate (e.g. Oleandomycine) is expected to occur when the enzyme adopts a “closed” conformation, for which no crystallized structure has been reported. Based on the crystal structure of an “open” conformation and using molecular modelling and normal modes analysis, we have modelled the active structure (closed-conformation). This opens the door to future computational analyses of the substrate specificity that has been previously reported, as well as that of mutated forms of OleD.

Finally, we are carrying out a methodological study evaluating and comparing different ways to include the system’s structural variability in QM/MM reactivity studies.

1. Teze, D. *et al.* Semi-rational approach for converting a GH1  $\beta$ -glycosidase into a  $\beta$ -transglycosidase. *Protein Eng. Des. Sel.* **27**, 13–19 (2014).
2. Williams, G. J., Zhang, C. & Thorson, J. S. Expanding the promiscuity of a natural-product glycosyltransferase by directed evolution. *Nat. Chem. Biol.* **3**, 657 (2007).
3. Romero-Téllez, S., Lluch, J. M., González-Lafont, À. & Masgrau, L. Comparing Hydrolysis and Transglycosylation Reactions Catalyzed by *Thermus thermophilus*  $\beta$ -Glycosidase. A Combined MD and QM/MM Study. *Front. Chem.* **7**, 200 (2019).



# Obtention Of Value-Added Products From Olive Oil And Wine Production Wastes Through Thermochemical Treatments

Cristina del Pozo<sup>a</sup>, Jordi Bartrolí<sup>a</sup>, Neus Puy<sup>a,b</sup>, Esteve Fàbregas<sup>a</sup>

<sup>a</sup> Department of Chemistry. Universitat Autònoma de Barcelona. Edifici Cn – Campus de la UAB. 08193-Cerdanyola del Vallès. Barcelona, Spain.

<sup>b</sup> Energies Tèrmiques Bàsiques S.L. C/ Maó 22, 2-1, 08022 Barcelona, Spain.

Olive oil and wine production industries are important economic sectors of Mediterranean countries; however, they also generate huge amounts of waste, being Olive Mill Wastes (OMW) and Grape Pomace (GP) main residues. These wastes are composed of different interesting products, including phenolics whose antioxidant properties make them added-value compounds in cosmetic and nutraceutical industries (1,2). Therefore, the rich composition of both OMW and GP could lead them to be used as a source of chemicals and thus transforming the wastes into a resource. This work pursued to determine the use of thermochemical treatments as a suitable process to obtain these value-added compounds. To this end, intermediate pyrolysis and torrefaction products of the residues were studied. Pyrolysis results in a bio-oil made up of two phases, an aqueous phase (AP) and a non-aqueous phase (NAP), and biochar (BP); torrefaction products consisted of a torrefaction liquid (TL) and biochar (BT). First, a study to identify and separate interesting compounds from OMW bio-oil (400 °C) was performed (3); then, a second study was carried out to identify and quantify phenolic compounds from GP intermediate pyrolysis (400 °C) and torrefaction (225 °C) products. GCMS results showed similar composition between OMW and GP bio-oil: AP was composed of acetic acid, monosaccharides and phenolic derivatives while NAP contained phenolic derivatives and fatty acids and their methyl esters. In the first study, acid-base extraction, performed with hexane at pH 12 followed by an ethyl acetate extraction at pH 6, is shown as a successful method to separate value-added chemical groups from bio-oil: acetic acid and monosaccharides were in AP aqueous phase, phenolic derivatives in both AP hexane and NAP ethyl acetate phases; and methyl esters of fatty acids in NAP hexane phase. From all these compounds, phenolics are the most interesting ones, so quantifying them is an important step to valorise the waste. Thus, in the second study, phenolic content of GP pyrolysis and torrefaction products were quantified through FC method and DPPH assay. The results showed intermediate pyrolysis as a successful method not just to obtain value-added compounds from GP, but to form new ones in the thermochemical process; in particular, phenolics which were mostly found in NAP. Torrefaction, on the other hand, seemed not to be as useful as pyrolysis to obtain the antioxidant compounds. Therefore, intermediate pyrolysis treatment would allow valorising olive oil and wine production waste turning it into a potential source of mainly antioxidants and so, coming closer towards circular economy and bioeconomy.

## References

- (1) Beres, C., Costa, G.N.S., Cabezudo, I., Silva-james, N.K., Teles, A.S.C., Cruz, A.P.G., Mellinger-silva, C., Tonon, R. V, Cabral, L.M.C., Freitas, S.P., 2017. Towards integral utilization of grape pomace from winemaking process : A review. Waste Manag. 68, 581–594. <https://doi.org/10.1016/j.wasman.2017.07.017>
- (2) Alburquerque, J.A., González, J., García, D., Cegarra, J., 2004. Agrochemical characterisation of “alperujo”, a solid by-product of the two-phase centrifugation method for olive oil extraction. Bioresour. Technol. 91, 195–200. [https://doi.org/10.1016/S0960-8524\(03\)00177-9](https://doi.org/10.1016/S0960-8524(03)00177-9)
- (3) del Pozo, C., Bartrolí, J., Puy, N., Fàbregas, E., 2018. Industrial Crops & Products Separation of value-added chemical groups from bio-oil of olive mill waste. Ind. Crop. Prod. 125, 160–167. <https://doi.org/10.1016/j.indcrop.2018.08.062>





# Towards Novel Electroinduced Healing Of Polybenzoxazines

C. Gascó, G. Guirado, R.M. Sebastián

*Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Spain. [carolina.gasco@uab.cat](mailto:carolina.gasco@uab.cat)*

Benzoxazines are classically obtained by a Mannich reaction from phenols, formaldehyde and amines. By selecting the appropriated groups linked to phenols and amines, the resulting benzoxazines and polybenzoxazines thermosets can show interesting properties.

Polybenzoxazines are usually made from high-temperature (typically >180°C) bulk ring-opening polymerization of benzoxazine monomers. Nevertheless, the high required temperatures might lead in some cases to destruction and degradation of the corresponding polymer being an important industrial drawback. In our group, catalysts have been employed to promote the ring-opening polymerization at lower temperature which is a significant advantage from the processing point of view.<sup>[1]</sup> The importance of these phenolic resins lies in their useful and attractive properties: low water absorption and flammability, excellent static and dynamic mechanical properties, near-zero shrinkage or volumetric expansion upon curing, considerable molecule-design flexibility and high UV and chemical resistance.<sup>[2]</sup>

Some smart materials based on benzoxazines has been produced the last years, such as recyclable polybenzoxazines coating for metals, shape memory polybenzoxazines, fire-retardant nanofoams, superhydrophobic and self-cleaning surfaces, and electrochromic devices. Other interesting field, but still undeveloped, is the use of benzoxazines as healing agents by combining them with other types of polymers.<sup>[3]</sup> However, there is not much literature related to the self-healing of thermoplastic or thermoset based purely in polybenzoxazines.

The challenge of this work is to find a strategy to extend the life-time of polybenzoxazines after cracking. For that, we proposed repair these non-crosslinked phenolic resins using an external electric stimulus. Taking advantage of studies based on electroinduced dimerization of triphenylamine derivatives, we design polybenzoxazines whose structure contains diphenylamino moieties that can electrodimmerize in solution at low electric potential. Electrochemical studies of model molecules, open-form derived benzoxazines and thermal polymers will be shown, being possible identify the intermediates of the redox process and thus, the capability of self-healing polybenzoxazines under optimized conditions.

## References

- [1] **a)** C. Liu, D. Shen, R. M. Sebastián, J. Marquet, R. Schönfeld, *Macromolecules*, **2011**, 44, 4616–4622. **b)** C. Liu, D. Shen, R. M. Sebastián, J. Marquet, R. Schönfeld, *Polymer*, **2013**, 54, 2873–2878.
- [2] H. Ishida, T. Agag, *Handbook of benzoxazine resins*, 1<sup>st</sup> edition, Elsevier, Amsterdam; Boston, **2011**, 3 - 5. H. Ishida, P. Froimowicz, *Advanced and Emerging Polybenzoxazine Science and Technology*, Elsevier, **2017**.
- [3] M. Arslan, B. Kiskan, Y. Yagci, *Sci. Rep.*, **2017**, 7, 5207

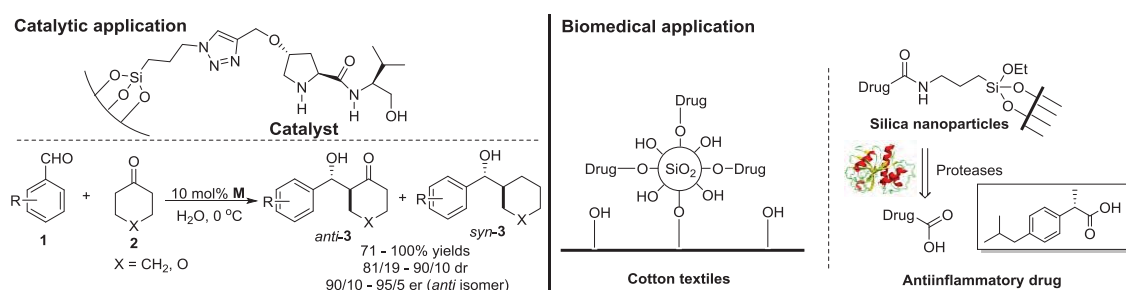
# Functionalized mesoporous silica nanoparticles for catalytic and biomedical applications

Hao Li, Roser Pleixats\*

Department of Chemistry and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universitat Autònoma de Barcelona, Cerdanyola del Vallès-08193 (Barcelona), Spain.

Hao.Li@uab.cat

Mesoporous silica nanoparticles (MSNs) have aroused great attention in recent years thanks to the ability to control and adjust their exclusive physicochemical properties. They have high surface area, firm framework, tunable pore size and pore volume, very good thermal, mechanical and chemical stability, tunable hydrophilicity, enriched surface silanol groups and the possibility of easy surface modifications.<sup>1</sup> These singular properties make them widely used as functional materials for a wide range of applications.<sup>2</sup> We mainly focus on the preparation of functionalized mesoporous silica nanoparticles and their applications in catalysis and biomedicine. In the first part, we present our recent results concerning functionalized MSNs derived from chiral proline-valinol amides as reusable organocatalysts in direct asymmetric aldol reactions in water with high yields, good diastereo- and enantiomeric ratios. In the second part, we describe the preparation of MSNs functionalized with anti-inflammatory drugs through amide bonds which can be cleaved by proteases to release the drugs. Moreover, these functionalized MSNs were loaded onto cotton fabric by dip-coating. Topical applications in cutaneous chronic wounds are envisaged (i.e. bandages and gauzes).



## References:

1. R. K. Sharma, S. Sharma, S. Dutta, R. Zboril, M. B. Gawande, *Green Chem.* **2015**, *17*, 3207-3230.
2. a) 1. Z. X. Li, J. C. Barnes, A. Bosoy, J. F. Stoddart, J. I. Zink, *Chem. Soc. Rev.* **2012**, *41*, 2590-2605. b) C.-Y. Lai, *J. Thermodyn. Catal.* **2013**, *5*, e124.

## Process development for the synthesis at industrial scale of a New Chemical Entity (NCE) drug for clinical trials

Javier Santos Ramos<sup>1</sup>, Xavier Pujol<sup>1</sup> and Ramon Alibés<sup>2</sup>

<sup>1</sup> Famhispania S.A. Passeig del riu Besòs. 08160 Montmeló.

<sup>2</sup> Departament de Química. Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès.

This project was started in 2017 as a result of collaboration between Farmhispania S.A and the Universitat Autònoma de Barcelona. The research project involves the scaling-up [from gram scale (100mL round bottom flask) to 50 kilogram scale (1600L reactor)] of a synthetic process of a New Chemical Entity (NCE) named FH0317. This NCE is under clinical trials (at phase III) and it is intended to be used to treat MyeloDysplastic Syndromes (MDS) and Acute Myeloid Leukemia (AML). In order to conduct the clinical trials, the NCE innovator requested Farmhispania to manufacture FH0317 at kilograms scale following Good Manufacturing Practices (GMP), system for ensuring that products are consistently produced and controlled according to quality standards. For this reason, we have designed a project to develop an industrial process for the manufacturing of FH0317 and to generate all the process knowledge required to support the NDA (New Drug Application) filling necessary for the drug approval.

The preliminary process description received from the NCE innovator consist of five-step synthetic route, based in a lab procedure used to obtain small amounts of FH0317.<sup>1-4</sup> In this project, the overall process has been extensively optimized to reduce costs, solve robustness problems, increase the quality of the obtained product, circumvent safety problems and to make it suitable for the industrial scale operation and process validation. During the optimization of the process, a wide variety of analytical techniques, *in-silico* tools (Chetah, QSAR Toolbox) and experimental approaches (DoE, QRA) has been applied. The suitability of the developed process for its application at industrial scale has been evaluated gradually scaling it up through the use of 250mL, 500mL and 10L reactors in order to detect and solve problems related with the heat transfer, mixing, mass transfer variations associated to the use of industrial scale equipment.

### References

1. Bruice TC, Mayahi MF. The Influence of the Leaving Tendency of the Phenoxy Group on the Ammonolysis and Hydrolysis of Substituted Phenyl Acetates. *J Am Chem Soc.* 1960;82(12):3067-3071. doi:10.1021/ja01497a023
2. Ranu BC, Sarkar A, Guchhait SK, Ghosh K. Catalytic Hydrogen Transfer Reductions Using Ammonium Formate. A Review. *J Indian Chem Soc.* 1998;75:690-694.
3. Gemal AL, Luche JL. Lanthanoids in organic synthesis. 6. Reduction of .alpha.-enones by sodium borohydride in the presence of lanthanoid chlorides: synthetic and mechanistic aspects. *J Am Chem Soc.* 1981;103(18):5454-5459. doi:10.1021/ja00408a029
4. Karel M. J. Brands, Davies AJ. Crystallization-Induced Diastereomer Transformations. *Chem Rev.* 2006;106(7):2711-2733. doi:10.1021/CR0406864

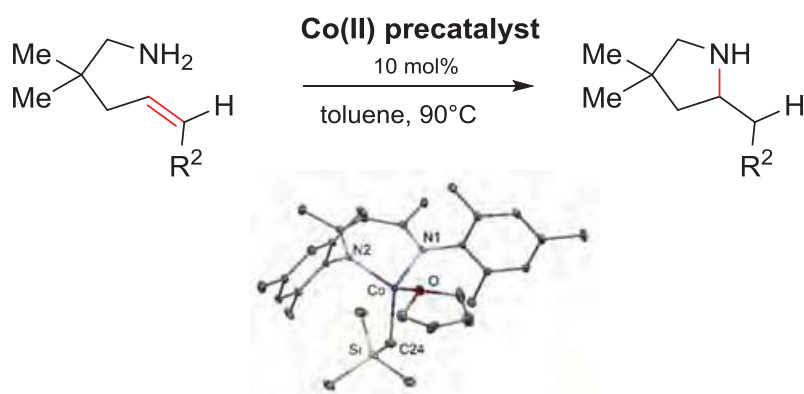
# DFT mechanistic analysis of alkene cyclohydroamination of primary amines catalysed by a Co(II) complex

Pablo Gómez-Orellana, Clément Lepori, Allisa Ouharzoune, Jerome Hannedouche\*, Agustí Lledós\*, Gregori Ujaque\*

*Departament de Química, Unitat de Química Física, Facultat de Ciències de i Biociències,*  
[pablo.gomezorellana@uab.cat](mailto:pablo.gomezorellana@uab.cat)

Transition metal catalysis is turning the attention towards the development of new catalysts based on first row transition metals. Hydroamination is one of the most useful reactions to form C-N bonds,<sup>1</sup> present in the skeleton of a variety of compounds as amino acids, nucleotides, active principles, etc., and many efforts are being devoted to preparing first-row based catalysts for such reactions.<sup>2</sup>

Following the research line in our group on C-N bond forming reactions,<sup>3,4</sup> we have collaborated with the Hannedouche's experimental group in the setting up of an efficient Co(II)  $\beta$ -diketiminatocobalt(II) for the cyclohydroamination of unprotected and electronically unbiased primary aliphatic alkenylamines.<sup>5</sup> The mechanistic aspects of this reaction will be presented in the talk.



## References

1. Huang, M., Gooßen K., Heydt H., Gooßen L. *Chem. Rev.* **2015**, 115, 2596-2697.
2. Lepori, C., Hannedouche J. *Synthesis* **2017**, 49, 1158–1167.
3. Couce-Ríos A., Lledós A., Ujaque G. *Chem. Eur. J.* **2016**, 22, 9311-9320.
4. Kovacs, G., Lledós A., Ujaque G. *Angew. Chem. Int. Ed.* **2011**, 50, 11147-11151.
5. Lepori, C., Gomez-Orellana P., Ouharzoune A., Lledós A., Ujaque G., Hannedouche J. *ACS Cat.* **2018**, 8, 4446-4451.

**Financial support acknowledgment:** Projects nº CTQ2014-54071-P, CTQ2016-81797-REDC

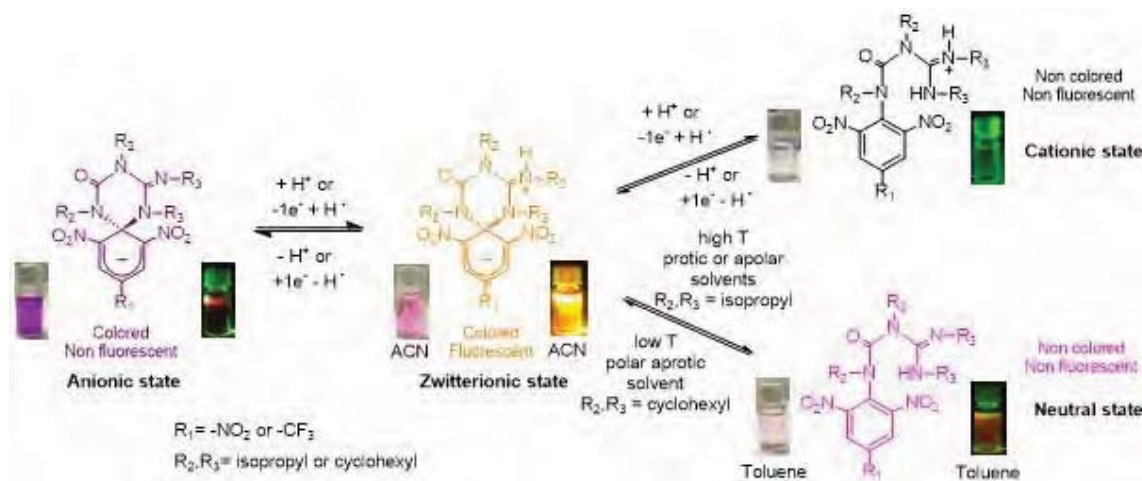
# Multistimuli-Responsive Fluorescent Switches Based on Spirocyclic Meisenheimer Compounds: Smart Molecules for Optical Probes and Electrochromic Materials

Marc Villabona,<sup>a</sup> Marina Benet,<sup>a</sup> Silvia Mena,<sup>a</sup> Rabih O. Al-Kaysi,<sup>b</sup> Jordi Hernando,<sup>a</sup> Gonzalo Guirado<sup>a</sup>

<sup>a</sup> *Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Spain;* <sup>b</sup> *King Saud bin Abdulaziz University for Health Sciences-National Guard Health Affairs, Riyadh, Saudi Arabia*

In the last decades fluorescent switches have emerged as smart functional systems with application in a variety of fields.<sup>1</sup> As such, the development of new molecules enabling stimulus-induced modulation of their emission properties has become an active area of research. A promising class of these compounds are spirocyclic zwitterionic Meisenheimer complexes (SZMC), a family of multi-addressable fluorescent molecular switches that present simple synthetic access, large emission modulation amplitudes, and very versatile switching behavior.<sup>2</sup> SZMCs are composed of a highly fluorescent cyclohexadienyl anion chromophore with strong electron withdrawing substituents, and a triazene group capable to respond to acid-base, electrochemical and thermal stimuli (Scheme 1).<sup>2</sup> This leads to protonation-deprotonation and ring-opening reactions that result in on-off fluorescence switching (Scheme 1).<sup>2</sup>

To further broaden the versatility of SMZCs, in this communication we report new switching mechanisms for these compounds. In particular, we demonstrate: (a) solvent-induced control of the interconversion between their zwitterionic and neutral aromatic isomers; (b) reversible acid-base and electrochemical protonation of the zwitterionic state to yield a non-colored and non-fluorescent cationic aromatic species; (c) variation of the thermal response of the system by introducing new substituents into the triazene ring (Scheme 1).<sup>3</sup> All these novel features have been exploited in the preparation of smart organic materials: wide-range pH optical probes, electrochromic and electrofluorochromic films, and polymer-based fluorescent detectors of organic liquids.<sup>3</sup>

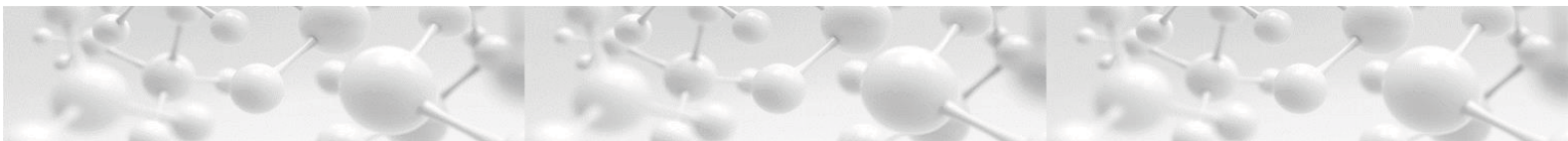


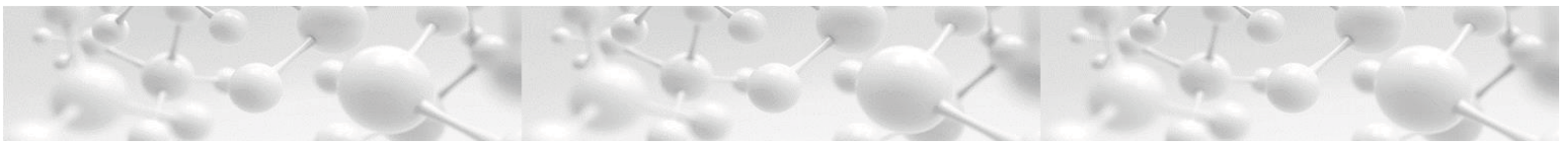
[1] Molecular Switches, Ed. Feringa B.L., Browne, W.R. Wiley-VCH, 2011.

[2] Al-Kaysi R.O., Bourdelande J.L., Gallardo I., Guirado G., Hernando J. Chem. Eur. J. 2007, 13, 7066; Gallardo I., Guirado G., Hernando J., Morais S., Prats G. Chem. Sci. 2016, 7, 1819.

[3] Villabona M., Benet M., Mena S., Al-Kaysi R.O., Hernando J., Guirado G. J. Org. Chem. 2018, 16, 9166.







**Departament de Química**  
**Universitat Autònoma de Barcelona**  
**2019**