GE3C
XXXI Simposio
ICIQ Tarragona
16-19 de enero 2024

Avanzando hacia el Futuro a través de la Cristalografía

Book of abstracts

GE3C

ICIQ Institut Català d'Investigació Química

RSEQ Real Sociedad Española de Química

Real Sociedad Española de Física

Índice

Presentación

La Cristalografía y el Crecimiento Cristalino desempeñan un papel crucial en una sociedad en constante evolución. Estas disciplinas no solo permiten desentrañar los secretos de la organización molecular de los materiales, sino que también impulsan avances fundamentales en áreas como la nanotecnología, la biotecnología y la medicina y el diseño de nuevos materiales con propiedades excepcionales. Su impacto perdura en la vanguardia de la innovación, guiando a la sociedad hacia un futuro donde la comprensión profunda de la estructura cristalina influye en innumerables aspectos de nuestra vida cotidiana.

Al ser una disciplina transversal, su campo de aplicación se encuentra en todas las facetas de la ciencia. En la geología se puede estudiar el desarrollo de un volcán que empezó a formarse hace milenios, proporciona información sobre la evolución del paisaje, la composición de la corteza terrestre y las fuerzas naturales que dan forma a nuestro entorno.

La comprensión de la estructura de las biomoléculas ha llevado a avances esenciales en el desarrollo de medicamentos y terapias dirigidas. La ingeniería de proteínas y la modificación de estructuras moleculares pueden revolucionar el tratamiento de enfermedades y afecciones médicas.

Los estudios estructurales son esenciales para diseñar nuevos materiales con propiedades específicas. Esto tiene implicaciones en la fabricación de productos más eficientes, sostenibles y resistentes, desde superconductores hasta materiales de construcción.

Comprender la estructura de los sistemas naturales y artificiales es fundamental para abordar los desafíos medioambientales. Esto incluye la optimización de procesos industriales, la gestión de recursos naturales y el diseño de tecnologías limpias.

En una sociedad cambiante, la Cristalografía y el Crecimiento Cristalino desempeñan un papel esencial para su desarrollo social y económico al impulsar el progreso científico y tecnológico, abordar desafíos globales y mejorar la calidad de vida. Su aplicación se extiende a diversas disciplinas y sectores, lo que demuestra su relevancia continua en un mundo en constante evolución.

Como en anteriores reuniones, en este simposio expertos y noveles de una gran diversidad de ramas de la ciencia expondrán y discutirán sobre los más recientes avances y descubrimientos en los campos de la Cristalografía y el Crecimiento Cristalino.

Jordi Benet Buchholz (ICIQ, Tarragona)
Eduardo C. Escudero-Adán (ICIQ, Tarragona)

Programa Científico Detallado

Martes 16 de enero

13:30 – 14:30	Registro ICIQ Avinguda dels Països Catalans, 16, 43007 Tarragona
14:30 – 15:00	Acto Bienvenida Organizadores XXXI Simposio GE3C: Jordi Benet-Buchholz y Eduardo C. Escudero Adán
	Santiago García Granda (Presidente de la Unión Internacional de Cristalografía) Luis Viña (Presidente de la Real Sociedad Española de Física) Antonio M. Echavarren (Presidente de la Real Sociedad Española de Química) Armando Albert de la Cruz (Presidente del Grupo Especializado de Cristalografía y Crecimiento Cristalino) Emilio Palomares (Director del Institut Català d'Investigació Química)
Entrega de Premios Moderadores: Jordi Benet-Buchholz y Sol López Andrés	
Premio Xavier Solans Bruker 2023	
15:00 – 15:30	Conferencia premiado: **Álvaro Vílchez-Cózar** Tuning the activity of cobalt 2-hydroxyphosphonoacetates-derived electrocatalysts for water splitting and oxygen reduction: Insights into the local order by pair distribution function analysis
Presentación de Empresas Patrocinadoras de la reunión	
15:30 – 15:45	Empresa: Bruker • Conferenciante: **Carsten Lenczyk** Bridging the gap between Electron and X-ray Diffraction
15:45 – 16:00	Empresa: Rigaku • Conferenciante: **Khai-Nghi Truong** XtaLAB Synergy-ED: 3D ED/MicroED made easy
16:00 – 16:15	Empresa: Anton Paar • Conferenciante: **Marius Kremer** Modern non-ambient X-ray diffraction for the investigation of minerals, metals and industrial materials of any type
16:15 – 16:30	Empresa: Malvern Panalytical • Conferenciante: **Javier Bolivar** Towards automated high-thoughput screening in materials chemistry
16:30 – 17:00	Pausa Café
Entrega de premios del GE3C	
17:00 – 17:15	Insignia de Oro GE3C
17:15 – 17:30	Premio Sagrario Martínez Carrera 2023
Conferencia a cargo de los Premios Sagrario Martínez Carrera 2022	

17:30 – 18:00	Guillermo Mínguez: Solvent-free synthesis of Metal-Organic Frameworks: a route towards elusive materials
18:00 – 18:30	Felipe Gándara: Desentrañando la Red: El Papel Crucial de la Química Estructural y la Cristalografía en la Química Reticular

Mesa Redonda: Mujeres y Cristalografía.
Moderadoras: María José Sánchez Barrena y Josefina Perles

18:30 - 19:30	Mesa Redonda
19:30 – 21:00	Cena

Miércoles 17 de enero

Sesión 1: Cristalografía de Proteínas y Más Allá
Moderadores: Inés G. Muñoz y José Antonio Gavira

9:00 – 10:00	Ponente invitada: **Aitziber López Cortejarena** Crystal Assembly Design through Protein Engineering and Contact Modulation Strategies
10:00 – 10:20	**Immaculada Pérez-Dorado**: Pursuing the enzyme N-myristoyl-transferase as drug target in human disease, deciphering its catalytic mechanism and interactome
10:20 – 10:40	**Isabel Uson:** Predictions and experiments in structure determination
10:40 – 11:00	**Alberto Marina:** Un nuevo mecanismo de represión en fagos que se comunican por el sistema arbitrium
11:00 – 11.30	Pausa Café
11:30 – 11:43	**Alice Grieco:** Serial synchrotron crystallography to decipher NQO1 dynamics at the active site during the formation of the NADH-reductive competent interaction
11:43 – 11:55	**Fernando Ceballos-Zúñiga Ulla**: Unraveling the role of the EccC5DUF domain in the ESX5 secretion in Mycobacterium tuberculosis
11:55 – 12:05	**María Rivera Moreno:** Towards a more resilient agriculture: Re-engineering ABA receptors
12:05 – 12:18	**Miguel Daniel Mozo:** Unveiling a Novel pH Sensing Module in Plant Proteins: Implications for Vacuolar Antiporter Regulation
12:18 – 12:30	**Uxía Pérez De José:** Structural Characterization of PdaA, an N-deacetylase from Clostridium difficile
12:30 – 12:43	**Alejandra Alba:** Crystal optimization and structural characterization of metallo-β-lactamase CAU-1 from Caulobacter crescentus
12:43 – 13:00	**Ángela Fernández García:** Crystallographic analysis of a short unspecific peroxygenase and molecular characterization of the substrate binding site
13:00 – 14:00	Pausa Comida Reunión Abierta GE3C/Comité Español de Cristalografía

Sesión 2: Grandes Instalaciones para Estudios Estructurales (esponsorizado por AUSE)
Moderadores: Laura Cañadillas Delgado y Guillermo Mínguez Espallargas

14:00 – 15:00	Ponente invitada: **Judith Juanhuix** Review of the crystallography beamlines at the ALBA synchrotron light source and future perspectives within the ALBA-II major upgrade project
15:00 - 15:25	**Gastón Gabarino**: New opportunities on the studies of condensed matter systems under extreme conditions at the ESRF-EBS
15:25 - 15:50	**Iván Da Silva:** Crystallographic studies at ISIS Neutron and Muon Source facility
15:50 - 16:05	**María José Sánchez Barrena:** Exploiting the most from synchrotron fragment-screening data for the discovery of protein-protein interaction regulatory compounds with therapeutic potential in neuronal disease
16:05 – 16.35	Pausa Café
16:35 - 17:00	**Pablo Bereciartua:** Resonant Elastic X-ray Scattering at beamline P09
17:00 - 17:25	**Iurii Kibalin:** Elucidating Individual Magnetic Contributions in Bi-Magnetic Fe3O4/Mn3O4 Core/Shell Nanoparticles by Polarized Powder Neutron Diffraction
17:25 - 17:40	**Stanislav Savvin:** XtremeD: new Spanish CRG diffractometer for extreme conditions
17:40 - 17:55	**José Manuel Martín García**: Towards deciphering the structure and dynamics of biological and non-biological molecules using time-resolved serial crystallography
18:30 – 20:30	Actividad Social: Visita guiada de Tarraco: la Tarragona romana

Jueves 18 de enero

Sesión 3: Cristalografía de Ciencias Químicas y de la Vida
Moderadores: Lourdes Infantes San Mateo y Jordi Benet-Buchholz

9:00 – 9:40	Ponente invitado: **Martin Schmidt** Nanocrystalline Organic Compounds: Structure Determination by Global PDF Fit
9:40 – 10:05	**Sergi Plana:** Full structure determination and refinement of an organic dye with triclinic symmetry by means of three-dimensional electron diffraction
10:05 – 10:30	**Jordi Cerón-Bertrán:** Salt or co-crystal? Monitoring a co-crystal screening with Electron Diffraction
10:30 – 10:45	**Mónica Benito:** Halogen Bonding in Pharmaceutical Cocrystals
10:45 – 11:00	**Sebastián Suárez:** Unlocking the Colorful World of Spiro-Rhodamines: rational design and characterization of switchable molecules
11:00 – 11:30	Pausa Café
11:30 – 12:10	Ponente invitada: **Carolina Von Essen**

	Absolute Structure Elucidation through the Crystalline Sponge Method: Challenges and Insights
12:10 – 12:35	**Elna Pidcock**: More than just visualization with Mercury
12:35– 12:48	**Jacinto López:** Adaptive structural plasticity in pMHC drives pathogenic T cell recruitment in autoimmune disease
12:48 – 13:00	**Javier Merino:** A drug discovery approach to drought resistance in crops
13:00 – 14:00	Sesión de Posters
14:00 – 15:00	Pausa Comida

Sesión 4: Ciencias de Materiales para la Sostenibilidad
Moderadores: Inés Puente Orench y Felipe Gándara Barragán

15:00 – 16:00	Ponente invitada: **Montserrat Casas Cabanas** Advancing Battery Materials through Operando and High Throughput X-ray Diffraction techniques
16:00 – 16:30	**María Retuerto:** Ru-Mixed Oxides as efficient and durable electrocatalysts for PEMWE anodes
16:30 – 17:00	**Víctor de la Peña-O'Shea**: New advances in the development of multifunctional catalysts for the Photo(electro) catalytic solar chemistry
17:00 – 17.30	Pausa Café
17:30 – 17:43	**Francesc Gispert-Guirado:** Application of parametric equations to phase transformation in NiTi shape memory alloys from synchrotron data
17:43 – 17:56	**Santiago Garcia-Granda**: Pink MgCoxNi1-xSiO4 (0 ≤ x ≤ 1) and CaMg0.5Cox Ni0.5-xSi2O6 (0 ≤ x ≤ 0.5) solid solutions: towards more sustainable pigments
17:56 – 18:09	**Clara López-García:** MOF-413 and Ga7Ni-TCPP: Two new multimetal MOFs obtained by the use of messenger building units
18:09 – 18:22	**Luis León-Alcaide:** Clip-Off Chemistry in Heterometallic Iron-Zinc ZIF-8
18:22 – 18:35	**Álvaro Vílchez-Cózar:** Carbon paper supported cobalt phosphide electrocatalysts for water splitting
18:35 – 18:48	**Abraham Sánchez-Caballero**: Study of mixed molybdates of lanthanum and praseodymium, La5.4-xPrxMo1-yNbyO12-δ, for H2 separation membranes
18:48 – 19:00	**J. M. Vila Fungueiriño:** Transmission electron microscopy study of porous metal-organic frameworks (MOFs)
19:00 – 20:00	Asamblea General GE3C
21:00	Cena – Restaurante El Barquet

Viernes 19 de enero

Sesión 5: Cristalografía Inorgánica y Mineralogía Moderadores: Sol López Andrés y Vicente José Esteve Cano	
10:00 – 11:00	Ponente invitada: **Mª de los Ángeles Fernández González** El polimorfismo del carbonato de calcio precipitado en condiciones ambientales: la influencia de la presencia de aniones tetraédricos en medio acuoso
11:00 – 11.30	Pausa Café
11:30 – 11:50	**Gerardo Gil De Cos:** Understanding a Ferroelectric Hysteresis cycles in La2-xErx(MoO4)3 solid solutions
11:50 – 12:10	**Josefina Perles:** ¡No imagines los cristales! Comprender las estructuras con modelos 3D y realidad virtual
12:10 – 12:30	**Gwilherm Nénert:** Polymorphism and re-entrant phase transition in NaSrPO4
12:30 – 12:50	**Eva Nieto Piñero:** Molibdita nano y microcristalina: Estudio y potencial de los materiales 2D.
12:50 – 13:30	Entrega de Premios y Ceremonia de Clausura
13:30 – 15:00	Comida / Comida para llevar

Información Conferenciantes Plenarios

Prof. Atiziber López Cortajarena

Prof. Aitziber Cortajarena earned her Ph.D. in Biochemistry from the Universidad del País Vasco in 2002. Then, she worked on protein design in the group of Dr. Lynne Regan at Yale University, USA, as a Postdoctoral Fellow and Associate Research Scientist. She joined IMDEA Nanociencia in 2010 and started her independent research in nanobiotechnology. In 2016, she joined CIC biomaGUNE as Ikerbasque Research Professor. Currently, she leads the Biomolecular Nanotechnology group and is Scientific Director at CIC biomaGUNE.

Her research focuses on protein engineering toward the generation of functional nanostructures and bioinspired materials for applications in nanobiotechnology and nanomedicine.

Abstract:

Crystal Assembly Design through Protein Engineering and Contact Modulation Strategies

Ordered protein-based biomaterials are highly desirable due to their applications in templating, coating, sensing, bioelectronics, catalysis, etc. This has recently spurred the development, among others, of novel 2D crystalline materials. However, *de novo* design of 2D materials is labour-intensive, and these materials are primarily designed as support scaffolds, as the entirety of the designed structure is required for the maintenance of structural integrity. In contrast, during protein crystallization, proteins naturally establish contacts with their neighbouring protein units, creating macroscopic three-dimension scaffolds, i.e. crystals.

We have explored strategies that rely on re-engineering interactions within the innate crystal contacts. On one hand, we demonstrate the potential to generate diverse crystalline protein frameworks by tuning the innate metal coordination preferences, guiding protein assembly for engineered consensus tetratricopeptide repeat (CTPR) proteins. Our findings illustrate that multiple crystal lattices can be obtained from the same protein, solely through the direction of metal ions, and without the need for protein surface engineering. On the other hand, we have developed strategies to create ordered protein-based biomaterials by re-engineering protein-protein interactions that maintain the crystalline lattice of 3D protein crystals. By strategically eliminating residues involved in the crystal contacts in CTPR proteins, we direct the protein to assemble into a 2D monolayers or 3D tubular structures. Overall, crystal contact engineering offers a rapid and attractive approach for designing ordered protein assemblies.

Prof. Judith Juahuix

Judith Juanhuix is Head of Life Sciences Section at the ALBA synchrotron, and beamline responsible of the new microfocus macromolecular crystallography beamline XAIRA.

After short period working on granular metallic alloys by X-ray spectroscopy, she focused on the structure and function of living muscles studied by small-angle X-ray diffraction (SAXS), and later on the structural basis of the complement proteins of the inmune system by macromolecular crystallogrpahy (MX), using different European synchrotron light sources. She was appointed as responsible of the BL13-XALOC beamline at the start of the ALBA Synchrotron Light Source project, and brought it from design to user operation. She has been studying the use of scavengers to reduce radiation damage and the effect of irradiation-induced oxidative stress in the functionality and structure of aldo-keto reductases. Dr. Juanhuix is currently in charge of designing, managing and building the new microfocus beamline at ALBA synchrotron dedicated to macromolecular crystallography, BL06-XAIRA, which is foreseen to enter into user operation along 2024, together with the coordination of the activities of the Life Sciences section. She is now involved in the ALBA-II project, the major upgrade of ALBA towards a 4th generation synchrotron facility.

Abstract:

Review of the crystallography beamlines at the ALBA synchrotron light source and future perspectives within the ALBA-II major upgrade project

The ALBA synchrotron light source has been instrumental in the development of the Spanish scientific community by offering an ever-wider range of X-ray techniques in a large variety of scientific fields, often connected to direct industrial applications. From the seven beamlines operating at the start of the user operation in 2012, ALBA and is currently servicing 11 beamlines, and three more are in the process to become operational in the near future.

Crystallographic techniques are offered in 5 beamlines, namely, MSPD, NOTOS, XALOC, XAIRA and 3Sbar. The MSPD beamline is dedicated to crystallography of material in powder form, and includes two experimental stations for high pressure/micro diffraction and high-angular resolution/high-throughput standard powder diffraction. NOTOS, in operation since 2023, aims to cover specific needs in chemistry, catalysis, energy science, nanomaterials and environmental science for structural studies in the short-

(XAS) and long-range order (XRD). XALOC beamline, already undergoes upgrade of some key instrumentation, copes with a variety of high-throughput macromolecular crystallography (MX) experiments. BL06-XAIRA, the new microfocus MX beamline currently in the commissioning phase, is designed to deliver high quality data from micron-sized and/or poorly diffracting crystals. Finally, 3Sbar allows simultaneous surface X-ray diffraction and photoemission experiments at 1 bar gas pressures to probe the electronic and atomic structures during surface chemical reactions and catalytic operando reactions.

Long-term plans include the major upgrade of ALBA to a 4th generation facility, ALBA-II, which includes the partial substitution of the accelerator system, the upgrade of the existing instrumentation and the addition of three new cutting-edge beamlines. We will review the current instruments of ALBA, focusing on the most recent ones, and will discuss the future perspectives offered by the new services and infrastructure proposed in ALBA-II project.

References

[1] C. Biscari, E. Aigner, K. Attenkofer, J. Casas, S. Ferrer, O. Matilla, J. Nicolas, R. Pascual, F. Pérez, M. Pont, A. Sánchez (2023), ALBA Synchrotron and its future. Eur. Phys. J. Plus (2023) 138:405.

Prof. Martin Schmidt

Martin U. Schmidt studied chemistry at RWTH Aachen University (Germany), and finished his PhD thesis on crystal structure prediction of molecular compounds in 1994. From 1995 to 2002 he was employed in the company Hoechst AG (later Clariant) in Frankfurt, where he worked on crystal engineering of industrial organic pigments. Since 2002, he is professor at Goethe University in Frankfurt. His research is focussed on the crystal structures determination of nanocrystalline organic compounds, especially pharmaceutical ingredients and organic pigments, including method developments.

Abstract:

Nanocrystalline Organic Compounds: Structure Determination by Global PDF Fit

The pair-distribution function (PDF) describes the probability to find two atoms with an atom-atom distance r (like a histogram of interatomic distances). The PDF contains intramolecular as well as intermolecular distances. The PDF is summed over all atom-atom pairs, and is weighted by the scattering power of the two atoms. It is normalised to an average atom density. Correespondingly, a PDF value of zero denotes an average probability; values above and below zero represent more and less frequent distances, resp.

Experimentally, the PDF is obtained by Fourier transformation of a powder diffractogram, carefully measured with a large 2q range, and good counting statistics especially at high 2qvalues.

The PDF can be obtained for crystalline, nanocrystalline and amorphous samples.

For organic compounds, e.g., pharmaceuticals, the PDF is used, e.g., to investigate the local structure (molecular arrangement) of nanocrystalline and amorphous compounds, to determine the domain sizes (ordering lengths), or to compare the local structures of amorphous, nanocrystalline, and crystalline samples. For all these tasks, laboratory powder data are usually sufficient.

In our group, we develop a method for the crystal structure determination of nanocrystalline organic compounds by a global fit to the PDF [1,2]. For this task, synchrotron data are required. The global PDF fit starts from scratch with a large set of random crystal structures with random lattice parameters, random molecular positions and orientations in different space groups. The structures are fitted to the experimental PDF in a multi-step procedure using a combination of our program FIDEL ("Fit with deviating lattice parameters", [3]) and TOPAS. As an example, the crystal structure of Pigment Yellow 83, $C_{36}H_{32}Cl_4N_6O_8$, was re-determined by a global PDF fit. Using a sample with a domain size of 60 nm, the correct crystal structure could be reproducibly obtained with a good fit and a high accuracy. From a nanocrystalline sample with a domain size of 10 nm only, an approximate structure could be obtained.

[1] S. Habermehl, C. Schlesinger, M.U. Schmidt: "Structure determination from unindexed powder data from scratch by a global optimization approach using pattern comparison based on cross-correlation functions", Acta Cryst. 2022, B78, 195–213, doi.org/10.1107/S2052520622001500.

[2] S. Habermehl, C. Schlesinger, M.U. Schmidt, D. Prill: "Comparison of atomic pair distribution functions using cross-correlation functions", German Patent Application No. 10 2020 004 292.9 (2020).

[3] S. Habermehl, P. Mörschel, P. Eisenbrandt, S.M. Hammer, M.U. Schmidt: "Structure determinations from powder data without prior indexing using similarity measure based on cross-correlation functions", Acta Cryst. 2014, B70, 347-359, doi.org/10.1107/S2052520613033994.

Carolina Von Essen

Carolina von Essen pursued her chemistry studies at RWTH Aachen University in Germany and successfully obtained her PhD in metal-organic chemistry in 2016. Following that, she undertook a postdoctoral research program focused on metal-organic chemistry and single crystal X-ray diffraction at the University of Jyväskylä in Finland, working with Prof. Kari Rissanen. In 2022, Carolina joined Merck KGaA in Germany as a senior scientist, where she played a key role in supporting the commercialization of the crystalline sponge method, a groundbreaking technology for elucidating compound structures in minute quantities. Since 2022, she has been in charge of leading the crystallography laboratory within Merck KGaA's analytical department.

Abstract:

Absolute Structure Elucidation through the Crystalline Sponge Method: Challenges and Insights

In 2013, Makoto Fujita published a new technique commonly known as "crystalline sponge method" (CS-XRD), which enables crystal structure determination without crystallization in nano- to few microgram analyte quantities.[1] Even information on the absolute configuration of chiral centers can be provided.[2] The CS-XRD uses pre-existing single crystals of porous metal-organic frameworks [(ZnX2)3·(tpt)2·x(solvent)]n (X=Cl; tpt=2,4,6-tris(4-pyridyl)-1,3,5-triazine), which can absorb organic molecules in its pores and make them observable by conventional single crystal X-ray diffraction. Via diffusion, the analyte is absorbed into the porous CS and regularly aligned by non-covalent interactions [3,4]. As a result, the repetitive positioning of the analytes in each pore of the framework serves for structural analysis via X-ray diffraction.

Various literature proves the method's broad applicability. For example, the combination of CS-XRD with MS or NMR data offers a great opportunity for scientists in drug metabolism and pharmacokinetics to assess the structure of metabolites produced in low amounts from in vitro studies.[5,6]

The presentation centers on absolute structure elucidation with the Crystalline Sponge method, highlighting the associated challenges and specific details.

References:

[1] Inokuma Y, Yoshioka S, Ariyoshi J, Arai T, Hitora Y, Takada K, Matsunaga S, Rissanen K, and Fujita M (2013) X-ray analysis on the nanogram to microgram scale using porous complexes [published correction appears in Nature (2013) 495:461–466]. Nature 501:262.

[2] Zhou H, Han JT, Nöthling N, Lindner MM, Jenniches J, Kühn C, Tsuji N, Zhang L, List B (2022) Organocatalytic Asymmetric Synthesis of Si-Stereogenic Silyl Ethers *J. Am. Chem. Soc.*, 144, 23, 10156–10161.

[3] Inokuma Y, Ukegawa T, Hoshino M, and Fujita M (2016) Structure determination of microbial metabolites by the crystalline sponge method. Chem Sci (Camb) 7:3910–3913.

[4] Sakurai F, Khutia A, Kikuchi T, and Fujita M (2017) X-ray structure analysis of n-containing nucleophilic compounds by the crystalline sponge method. Chemistry 23:15035–15040.

[5] Rosenberger I, von Essen C, Khutia A, Kühn C, Urbahns K, Georgi K, Hartmann RW, Badolo L (2020) Complete Structural Elucidation of Gemfibrozil Metabolites by Crystalline Sponges, Drug Metabolism and Disposition 48: 587-593.

[6] Rosenberger I, Jenniches J, von Essen C, Khutia A, Kühn C, Marx A, Georgi K, Hirsch AKH, Hartmann RW, Badolo L (2022) Metabolic Profiling of S-praziquantel: Structure Elucidation Using the Crystalline Sponge Method in Combination with Mass Spectrometry and Nuclear Magnetic Resonance.

Montserrat Casas Cabanas

Montse Casas-Cabanas is an Ikerbasque research associate and the scientific coordinator of the Electrochemical Energy Storage Area at CIC energiGUNE.

Her research interests focus on the design of next generation battery chemistries and the understanding of phenomena that occur in energy storage devices through a multidisciplinary approach, with a focus in crystal chemistry. She employs cost-efficient synthetic processes, with a focus on sustainability and recyclability, in combination with scattering, imaging, and spectroscopic techniques to develop fundamental understanding in structure-property correlations. She is recognized in the field for her contributions to the study of electrode reaction mechanisms using operando experiments and, more specifically, in the study of the impact of structural disorder and defects in the electrochemical performance, for which she pioneered the development of the FAULTS software, which is being increasingly used by the materials community.

She is actively involved in the MESC+ (Materials for Energy Storage and Conversion) Erasmus Mundus master course, the Alistore-ERI network of excellence and Battery 2030+ initiative. She was elected in 2021 Technical Advisor of the Batteries European Partnership Association (BEPA) Working Group 1 “Advanced Materials and Manufacturing” and is now Technical Leader of the “New Emerging Technologies” group in the Batteries Europe (BE) technology and innovation platform.

She has been recently awarded with the 2021 Young Researcher award from the Spanish Royal Society of Chemistry.

Abstract:

Advancing Battery Materials through Operando and High Throughput X-ray Diffraction techniques

D. Saurel, M. Reynaud, O. Arcelus, J. Rodríguez-Carvajal, N.A. Katcho, F. Fauth, J. Serrano-Sevillano, M. Jáuregui, M. Galceran, M. Casas-Cabanas*

** Presenting or corresponding author: mcasas@cicenergigune.com*

Operando X-ray diffraction experiments have gained widespread popularity as a potent tool for monitoring internal processes during battery cycling, offering valuable insights into fundamental electrochemical redox mechanisms and aging phenomena in battery materials. However, the acquisition of high-quality, representative, and actionable data from operando measurements necessitates meticulous control of various experimental parameters. This includes aspects such as cell configuration, electrode preparation, goniometer geometry, data acquisition protocols, and data interpretation methodology.

In this presentation, we aim to discuss some critical aspects essential for effective data acquisition and utilization, such as cell design, experimental setup, sample and experiment preparation, on the success of operando experiments.1 This will be illustrated through several case studies to showcase the effectiveness of operando experiments in unraveling the electrochemical signatures of various battery materials.

On the other hand, the huge amount of diffraction data generated by high-throughput screening experiments as well as by operando studies at large user facilities calls for new software tools able to radically accelerate the analysis and process data in real time, instead of the traditional post-experiment pattern-to-pattern analysis. The FullProfAPP software, built on the grounds of the current version of the FullProf program, and designed to process, refine and visualize large collections of powder diffraction patterns will be introduced.

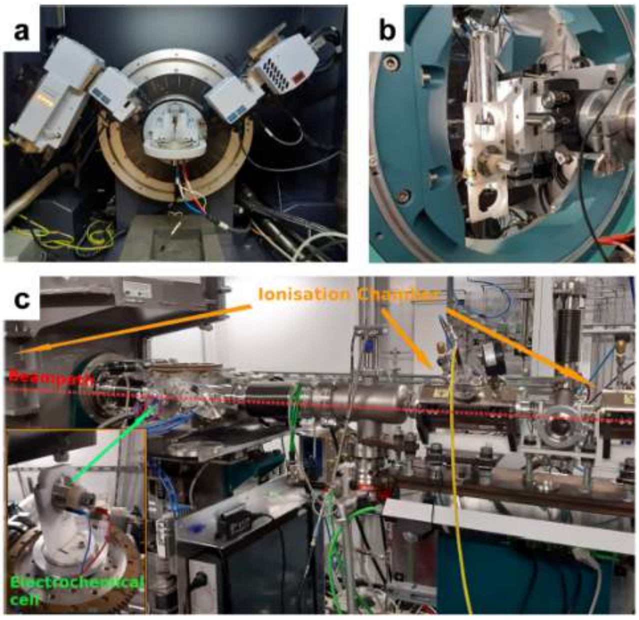

Figure 1. Images of the electrochemical cell placed in (a) Lab-scale PXRD Bragg-Brentano diffractometer, (b) in a three-cell motored stage for transmission mode HRPXRD at ALBA synchrotron's MSPD beamline, and (c) mounted in the flange ready to be introduced in the XAS chamber of the ALBA synchrotron's CLAESS beamline.1

References

1. D. Saurel, A. Pendashteh, M. Jáuregui, M. Reynaud, M. Fehse, M. Galceran, M. Casas-Cabanas, *Chem. Methods* **2021**, 1(6), 249-260.
2. O. Arcelus, J. Rodríguez-Carvajal, N.A. Katcho, M. Reynaud, A.P. Black, D. Chatzogiannakis, C. Frontera, J. Serrano-Sevillano, M. Ismail, J. Carrasco, F. Fauth, M.R. Palacin, M. Casas-Cabanas, *submitted.*
3. https://cicenergigune.com/en/fullprof-app

Ángeles Fernández González

Ángeles Fernández González es licenciada en Ciencias geológicas (1992) y doctora en Geología (1996) por la Universidad de Oviedo, donde actualmente es catedrática de universidad en el área de Cristalografía y Mineralogía. Ha llevado a cabo su actividad docente en diversos grados, licenciaturas, estudios de máster y doctorados relacionados con su especialidad. Ha dirigido cuatro tesis doctorales y numerosos trabajos de fin de grado, licenciatura y máster y ha sido la directora del programa de doctorado en Geología y del máster en Recursos geológicos e ingeniería geológica de su Universidad. Como investigadora, desarrolla su actividad en el campo de la mineralogía experimental y pertenece al grupo de investigación de la Universidad de Oviedo Síntesis, estructura y aplicación tecnológica de materiales (SYSTAM). En este marco ha participado y dirigido proyectos de investigación de ámbito autonómico y nacional. También ha estado involucrada, como investigadora, en proyectos financiados por la Comisión Europea. Los resultados de su investigación han sido publicados en las principales revistas científicas indexadas de su especialidad y difundidos entre la comunidad científica en numerosos congresos. Combina la docencia y la investigación con actividades de divulgación científica que desarrolla la Unidad de cultura científica de la Universidad de Oviedo y ha dirigido sus programas de formación continua de Extensión universitaria. En la actualidad es presidenta de la Sociedad española de mineralogía.

Abstract:

El polimorfismo del carbonato de calcio precipitado en condiciones ambientales: la influencia de la presencia de aniones tetraédricos en medio acuoso

El estudio de la precipitación de los carbonatos de calcio y de las transformaciones polimórficas que tienen lugar después de la precipitación se ha convertido en una línea clásica de la mineralogía experimental. El innegable interés mineralógico y petrológico del estudio de estos fenómenos se ha visto renovado por la relevancia que tienen los carbonatos como proxies paleoclimáticos y paleoambientales, y como biominerales y biomateriales de múltiples aplicaciones.

En la precipitación del carbonato de calcio a partir de disoluciones acuosas, la presencia de diversos iones en el fluido puede jugar un papel fundamental en cuanto a la selección de polimorfo que precipita y la secuencia de transformaciones polimórficas que se suceden tras la precipitación. Por ejemplo, la presencia de aniones tetraédricos SO_4^{2-}, SeO_4^{2-}y CrO_4^{2-} favorece la estabilización de vaterita y retrasa su transformación en calcita. Este efecto puede deberse a fenómenos de superficie, pero también debe considerarse que su incorporación en las estructuras cristalinas de los distintos polimorfos tenga una influencia significativa.

Diversos trabajos de carácter experimental en los que se han utilizado distintas técnicas de crecimiento cristalino en disolución acuosa en condiciones ambientales, muestran que vaterita y calcita incorporan en los momentos iniciales, tras la precipitación, cierta proporción significativa de estos aniones; pero si se mantienen en contacto con el agua, sufren un

proceso de purificación y en los estados finales del envejecimiento, cuando el sistema se estabiliza, únicamente permanece una calcita purificada. Por tanto, la secuencia de Ostwald se completa dejando a los aniones extraños en la disolución. Por otra parte, la precipitación de aragonito se ve fuertemente inhibida y la morfología cristalina de la calcita alterada, con un alargamiento del romboedro característico en la dirección paralela al eje principal y con el desarrollo de abundantes caras vecinales.

La modelización molecular revela que la entrada de cualquiera de los aniones considerados en la estructura del aragonito implicaría deformaciones importantes alrededor del defecto y en varias esferas de coordinación, que son extremadamente desfavorables desde el punto de vista energético. Por el contrario, la baja densidad de la vaterita respecto a los otros polimorfos y el desorden posicional de los aniones carbonato en su estructura, permiten incorporar aniones extraños sin que haya una deformación importante de la estructura cristalina. De hecho, de acuerdo con los cálculos realizados, cierta proporción de estos iones en la varita la estabilizan con respecto a la fase pura. La calcita representa un comportamiento intermedio: la deformación que implica la entrada de aniones extraños es moderada y lo que significa desde el punto de vista energético, es más leve que en el aragonito.

Abstracts Empresas Patrocinadoras

Martes, 16 de enero 15:30 – 15:45

Bridging the gap between Electron and X-ray Diffraction

Dr. Carsten Lenczyk*, Dr. Tobias Stürzer*, Dr. Jürgen Graf

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Structure determination on ever smaller and more weakly diffracting crystals is one of the biggest challenges in crystallography. Traditionally, in-house X-ray crystallography covers sample sizes down to a lower limit of approximately 50 µm.[1] Consequently, electron diffraction is receiving a lot of attention, as it promises structure determination on significantly smaller samples. However, while micro-ED can cope with samples in the nm range up to approximately 1 µm, the refined structure models are less accurate compared to X-ray data.[2] Furthermore, the preparation of suitable sub-µm samples is often a challenge, whereas few micrometers sized crystals would be readily available. Therefore, equipment for X-ray structure determination closing the gap for samples between 50 to 1 micrometer in size would be highly desirable.

Exciting developments and latest innovations in X-ray source and detector technology enable the crystallographer to bridge this gap. Crystal sizes in the sub-10 µm range are now routinely accessible by modern instrumentation, while at the same time retaining the convenience and accuracy of single crystal X-ray structure determination. This will be highlighted by single crystal X-ray diffraction data collected on three micro crystals and compared to recently published MicroED Data on the same.[3]

[1] Gruene et al., *Angew. Chem. Int. Ed. Engl.*, **2018**, 57, 16313–16317.

[2] Simoncic et al., *Acta Cryst. E*, **2023**, E79, 410–422.

[3] Bruhn et al., *Front. Mol. Biosci.*, **2021**, 8, 1– 16

Martes, 16 de enero 15:45 – 16:00

XtaLAB Synergy-ED: 3D ED/MicroED made easy

Khai-Nghi Truong,[1] Robert Bücker,[1] Christian Göb,[1] Christian Schürmann,[1]
Jakub Wojciechowski,[1] Michał Jasnowski,[2] Mathias Meyer,[2] Fraser White[1]

[1] Rigaku Europe SE, Neu-Isenburg, Germany

[2] Rigaku Polska, Wrocław, Poland

Since its launch in 2021, the XtaLAB Synergy-ED has produced many structures, with over 400 unique structures from Rigaku labs alone. The majority of those structures have been conducted at ambient temperature, lately with low temperature, particularly cryo-transfer, showing considerable usefulness for preservation of sensitive samples both those sensitive to vacuum and those sensitive to electron beam damage.

Thanks to its compatibility with the existing ecosystem of holders available for TEM instruments, the XtaLAB Synergy-ED is able to provide structural scientists with access to several experiment types already used in X-ray crystallography.

Cryo-transfer specimen holders such as the Gatan ELSA enable the protection of samples[1] before introduction to the vacuum, allowing the study of solvates and other vacuum-sensitive species, in addition to allowing exploration of phase behaviour. Some results from samples for which not only cryogenic conditions, but cryo-transfer proved essential will be discussed.

In addition, the Hummingbird Scientific MEMS biasing/heating holder offers the possibility to *increase* temperature, allowing for exploration of the phase behaviour of materials such as porous materials. Recent results using single crystal data from electron diffraction on a MOF system will be compared to results previously reported from SC-XRD and PXRD.

[1] Truong *et al.*, *Symmetry* **2023**, *15(8)*, 1555.

Martes, 16 de enero 16:00 – 16:15

Modern non-ambient X-ray diffraction for the investigation of minerals, metals and industrial materials of any type

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Modern powder X-ray diffraction (XRD) systems must nowadays be able to meet the challenges faced by multi-user and multi-application facilities. Instruments must be capable not only of routine XRD measurements, but also have to offer advanced capabilities such as measurements under non-ambient conditions (varying temperature, pressure, gas atmosphere, humidity, …) which can drastically change material properties.

The recently launched XRDynamic 500 automated multipurpose powder X-ray diffractometer from Anton Paar has set new standards in terms of data quality, automation and efficiency for laboratory powder diffractometers. The core of XRDynamic 500 is the TruBeam™ concept that comprises a large goniometer radius and evacuated optics units, automatic change of the beam geometry and all optics components, and automated instrument and sample alignment routines. All of these features combine to deliver outstanding data quality that can be measured with high efficiency in a straight-forward manner. The high level of automation means that you can perform measurements on one or many samples with different geometries and instrument configurations in one batch with no user intervention needed.

XRDynamic 500 can also be equipped with different non-ambient attachments to perform measurements under non-ambient conditions. These attachments are perfectly integrated into the hard- and software (plug-and play mode, integrated control unit, built-in connections) and guarantee best-in-class convenience for your non-ambient XRD studies.

To highlight the potential of XRDynamic 500 and non-ambient XRD in general, we will present key instrument features and benefits in addition to recent application data on non-ambient XRD. Examples include in-situ structural changes of bentonite samples and materials used for technical applications (Fig. 1), how salt mineral compositions change under the influence of gas and humidity, and the study of the tempering temperature on the properties of steel.

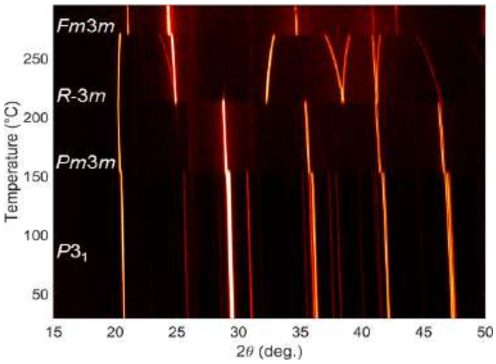

Figure 1: Temperature-induced phase transitions of $RbNO_3$ (Weidenthaler & Ternieden, 2022).

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Martes, 16 de enero 16:15 – 16:30

Towards automated high-throughput screening in materials chemistry

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Discovering new materials relies on the ability to run automated synthetic laboratory in combination with artificial intelligence. Recently, the Aeris Malvern Panalytical compact XRD diffractometer was illustrated in a newly designed autonomous solid-state synthesis of inorganic materials (https://www.nature.com/articles/s41586-023-06734-w).

Since then, newly available features recently added to our Aeris and Empyrean diffractometers will help in further supporting those breakthroughs. As data generation is nothing without proper data treatment, we will present additionally the latest news about our desktop (HighScore) and mobile (HSVu) software analytical tools.

Martes, 16 de enero 15:00 – 15:30

Premio Xavier Solans Bruker 2023

Tuning the activity of cobalt 2-hydroxyphosphonoacetates-derived electrocatalysts for water splitting and oxygen reduction: Insights into the local order by pair distribution function analysis

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Electrode materials generally exhibit complex heterostructures wherein both amorphous and crystalline phases may coexist [1]. Advanced techniques, such as Pair Distribution Function (PDF) analysis, may offer valuable structural insight into the local order and domain sizes of the active phase present in these materials.

Herein, cobalt pyrophosphate- and phosphide-based electrocatalysts were prepared from the corresponding metal (R,S)-2-hydroxyphosphonoacetates by pyrolysis in N_2 and 5%-H_2/Ar at different temperatures (500 – 800 °C) [2]. Their electrocatalytic performances toward the hydrogen and oxygen evolution reactions (HER, OER) and oxygen reduction reaction (ORR) were compared with those resulting from the N-doping and P-enrichment of the electrocatalysts. In addition, differential PDF (d-PDF) analysis of the spent electrocatalysts revealed that, regardless the amorphous or crystalline nature of the metal pyrophosphate/phosphides obtained, all of them transformed into biphasic cobalt oxy(hydroxydes) under tested OER conditions. Conversely, d-PDF demonstrated that most effective electrocatalysts for HER and ORR maintained their stability during the experimental conditions.

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Martes, 16 de enero 17:30 – 18:00

Premio Sagrario Martínez Carrera 2022

Solvent-free synthesis of Metal-Organic Frameworks: a route towards elusive materials

Guillermo Mínguez Espallargas

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Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have emerged in the last 30 years as revolutionary molecular materials with applications in societal and industrially relevant domains such as storage of fuels (hydrogen and methane), capture of gases (e.g. greenhouse gases), separation, drug delivery and catalysis, among others.[1] Recent advances in this area in the past decade has resulted in an explosive growth in their preparation, characterization, and study, with more than 100.000 MOFs reported. The common property for all these open crystalline frameworks is their permanent porosity constructed from the assembly of inorganic sub-units and organic linkers, providing an assortment of topologies and different architectures that can be intended by chemical design.

Herein we will present an uncommon synthetic approach, very versatile, for the preparation of elusive porous materials, based on the absence of solvents. With this approach, we will first present the iron(II) analogue of ZIF-8, which shows properties that are not observed in the zinc(II) derivate.[1] Then, we will extend this approach for the preparation of multivariate ZIFs, which is typically limited due to the absence of control of topologies when a mixture of ligands/metals is used.[2,3] We will show also its applicability to prepare iron(II) glasses, achieved through a series of solid-state transformations that result in a meltable iron-based zeolitic imidazolate framework (ZIF).[4] And finally, we will use this methodology for the inclusion of catalytically active Pd(II) centres in a highly robust MOF.[5]

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Martes, 16 de enero 18:00 – 18:30

Premio Sagrario Martínez Carrera 2022

Desentrañando la Red: El Papel Crucial de la Química Estructural y la Cristalografía en la Química Reticular

Felipe Gándara

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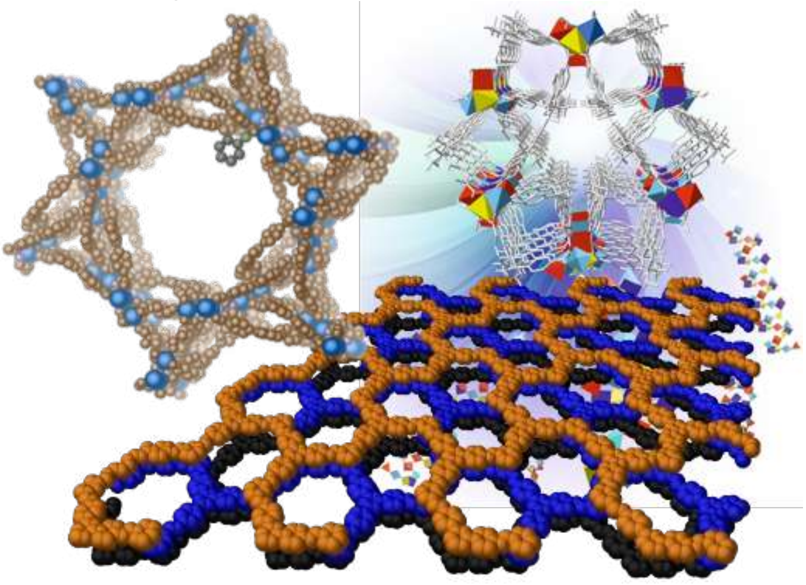

La química reticular abarca aquellos compuestos formados por unidades de construcción moleculares que se enlazan a través de uniones covalentes, propagándose en dos o tres dimensiones y formando estructuras periódicas. Las redes metal-orgánicas, MOFs, y orgánicas covalentes, COFs, son dos clases de materiales reticulares, que en la actualidad encuentran aplicación en numerosos campos tales como almacenamiento de energía, captura de contaminantes, liberación controlada de fármacos, o catálisis heterogénea. La gran versatilidad de estos materiales emana del grado control topológico, y composicional que ofrecen a través de la selección de sus unidades de construcción. Por ello, el análisis estructural y cristalográfico es fundamental en el desarrollo de este campo. En esta presentación, mostraré ejemplos que demustran la relevancia de la cristalografía aplicada al estudio de MOFs y COFs, tales como el diseño de nuevos MOFs basados en elementos de grupos principales,[1] el desarrollo de MOFs de mayor complejidad mediante combinación de múltiples metales,[2] o la investigación estructural de distintas familias de COFs mediante procesos de simulación estructural y difracción de rayos de polvo.[3]

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Abstracts Comunicaciones Orales

Sesión 1

Miércoles, 17 de enero 10:00 – 10:20

Pursuing the enzyme N-myristoyl-transferase as drug target in human disease, deciphering its catalytic mechanism and interactome

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N-myristoyltransferase (NMT) is an enzyme mediating lipidation of hundreds of proteins in all eukaryotic cells(1-3). This lipidation is a co/post-translational modification consisting of the transference of a myristoyl moiety from myristoyl coenzyme A (Myr-CoA) to the N-terminal glycine of substrate proteins(1-3). NMTs are thought to be essential in all organisms and thus, they have attracted interest as a drug targets in multiple diseases such as cancer and viral infections, and they are validated drug targets for the treatment of parasite infections such as malaria(4-8). However, progress in the field of human NMT biology has been undermined by non-selective and now invalidated compounds, raising questions about previous studies using these drugs. In this sense, a complete understanding of NMT catalysis and substrate selectivity would greatly benefit therapeutic development. The work presented here provides high-resolution snapshots of the entire catalytic mechanism of the human NMT1, from initial to final reaction states, based on high-resolution structures of the enzyme co-crystallised with Myr-CoA and peptide substrates(9). Our studies provide unforeseen details about how NMT1 reaches a catalytically competent conformation to enable substrate lipidation, which reveals new vectors for the improvement of existing NMT inhibitors of pharmacological interest(9). This mechanism also sheds light into the enzyme substrate selectivity, a valuable information for the study of the human-NMT interactome. In this line, we provide the crystallographic characterization of the novel photocross-linkable and clickable myristic acid analog X10, as efficient substrate for human NMT1 and new probe to label NMT substrates in cell culture(10). These results feature the application of this probe as a new tool to study the human-NMT substrate proteome, and uncover new interactions relevant in disease(10).

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Miércoles, 17 de enero 10:20 – 10:40

Predictions and experiments in structure determination

Josep Triviño1, Elisabet Jiménez1, Iracema Caballero1, Ana Medina1, Albert Castellví1, Massimo D. Sammito1, Kay Diederichs2 and Isabel Usón1,3*

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Protein structure prediction from sequence has been a milestone and beyond the structural biology community, researchers in every branch of the life sciences are consulting such models1. The current success of artificial intelligence on a long-standing quest, showcases a power for harnessing knowledge that will go deeper by steering particular questions.

While AlphaFold predictions are useful hypotheses about protein structures, experimental information remains essential for creating an accurate model2. Predictions have been incorporated in our structural determination methods3, demand a redefinition of how we integrate prior knowledge in experiment interpretation4 (figure 1a) and open new opportunities to gain a dynamic view by using experimental structures to establish the background of a prediction or impose boundary conditions (figures 1b, 1c).

The broad scale search for structural and genomic information preceding a prediction simultaneously retrieves knowledge on all possible contacts and states a sequence may fulfill in time or under different conditions. Our method systematically deconvolves the signal from multiple states.

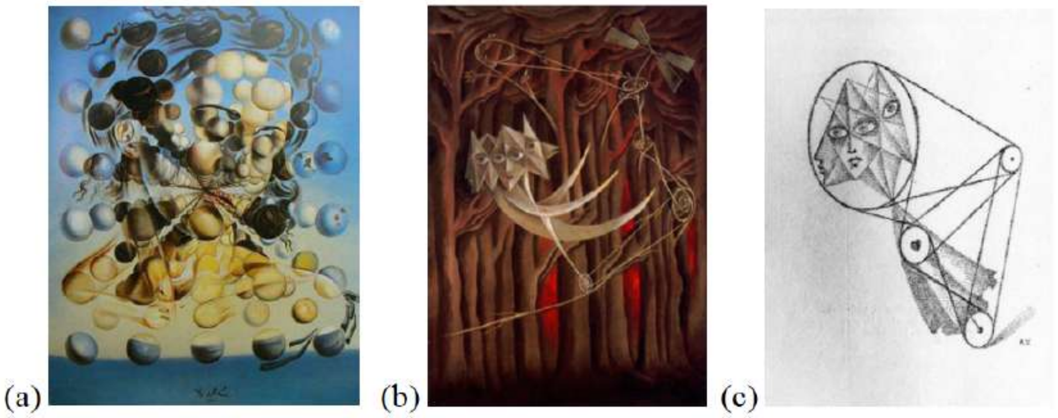

Figure 1. Our methods: ARCIMBOLDO_SHREDDER SPHERES (a) solves the phase problem systematically verifying the model and VAIRO (b) informs AF predictions with experimental structures, setting boundary conditions to target particular states within a dynamic.

Acknowledgements

We thank Martin Alcorlo and Juan A. Hermoso from IQF-CSIC; Fernando Govantes from

UPO and Tea Pavkov-Keller from U. Graz for collaborations around the cases discussed in this talk.

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Miércoles, 17 de enero 10:40 – 11:00

Un nuevo mecanismo de represión en fagos que se comunican por el sistema arbitrium

Elena Cabello-Yeves[a,b], Francisca Gallego del Sol[a,b], Aisling Brady[c,d], Cora Chmielowska[c], Javier Mancheño-Bonillo[a,b], Sara Zamora-Caballero[a,b], Alonso Felipe-Ruiz[a,b], Shira Bendori Omer[e], Manuela Torres-Puente[a], Avigdor Eldar[e], Wilfried JJ Meijer[f], Nuria Quiles-Puchalt[c,g], José R. Penadés[c], Alberto Marina[a,b]*

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Arbitrium es nuevo mecanismo de quorum sensing que utilizan bacterio(fagos) y otros elementos genéticos móviles de Bacilota para comunicarse via péptidos. En fagos de la familia SPbeta, donde arbitrium se descubrió, este sistema es utilizado para coordinar la decisión entre lisis y lisogenia (1,2). En estos fagos, la implementación de este sistema de comunicación en su ciclo vital ha requerido de un novedoso mecanismo de represión que los diferencia del prototípico presente en lambda (3,4). En la comunicación dissecionaremos a nivel estructural y funcional este mecanismo basado en un operon seis genes que hemos denominado "SPbeta phages repressor operon" (sro) y que cuenta no con uno sino con dos represores maestros, SroE y SroF (4). Interesantemente, SroF muestra un plegamiento típico de recombinasa al igual SroD, otro represor auxiliar, formando SroDEF el módulo de represión necesario para el establecimiento y mantenimiento de la lisogenia. Las otras tres proteínas del operón, SroABC, son más variables en los fagos de esta familia y forman el módulo transductor que es requerido para conectar el sistema de comunicación arbitrium con la actividad del módulo de represión (4). En este proceso, las proteínas del módulo de transducción bajo el control del arbitrium regulan un sistema toxina/antitoxina de la bacteria hospedadora que es clave para la decisión entre los ciclos lítico y lisogénico (5). Los datos presentados mostrarán el intrincado y especializado sistema de represión empleado por los fagos de la familia SPbeta necesario para la decisión de su ciclo vital en función de la densidad de población de fagos y hospedadores.

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Miércoles, 17 de enero 11:30 – 11:43

Serial synchrotron crystallography to decipher NQO1 dynamics at the active site during the formation of the NADH-reductive competent interaction

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The human NAP(P)H quinone oxidoreductase 1 (hNQO1) is a FAD-dependent oxidoreductase that catalyzes the two-electron reduction of quinones to hydroquinones. HNQO1 is essential for the antioxidant defense system, stabilization of tumor suppressors, and activation of quinine-based chemotherapeutics, and over-expressed in several tumors. In an attempt to decipher new structural insights into the flavin reductive half-reaction of the catalytic mechanism of hNQO1, we have carried out one of the first room temperature serial crystallography (SX) experiments using a fixed target approach at new ID-29 beamline of the ESRF to determine the first structure of the hNQO1 in complex with NADH. We have captured the hydride donor in two different positions within the four active sites making the hNQO1-NADH asymmetric unit. Noticeably, a molecule of the donor is present only at one active site in each of the two homodimers, while no density is detected for the coenzyme in the active site. This fact agrees with the negative cooperativity previously described for the NADH-reductive half reaction. The use of microcrystals has been key to apply the room temperature SX technique to study this mechanism, since their crystal packing differs to that in large crystals. Consequently, the catalytic site is more accessible and different conformations among chains within the asymmetric unit can be detected for cofactors, side chains and ligands at the active site. Furthermore, molecular dynamics simulations of free NQO1 and in complex with NADH agree with such experimental observations. Altogether, the results presented here pave the way for future time-resolved studies, both at XFELs and synchrotrons, of the dynamics of hNQO1 upon binding to NADH as well as during the FAD cofactor reductive half-reaction. This knowledge will allow us to reveal unprecedented structural information of the relevance of the dynamics during the kinetic mechanism that determines the function of hNQO1

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(submitted to Protein Science)

Acknowledgements

The European Union NextGenerationEU/PRTR (Grant number CNS2022-135713) and the Ayuda de Atracción y Retención de Talento Investigador from the Community of Madrid (Grant numbers 2019-T1/BMD-15552 and 2023-5ABMD-28921).

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Miércoles, 17 de enero 11:43 – 11:55

Unraveling the role of the $EccC_5^{DUF}$ domain in the ESX5 secretion in *Mycobacterium tuberculosis*

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Mycobacterium tuberculosis (*Mtb*) is the agent responsible of the human tuberculosis (TB), responsible of more than 1 million deaths/year [1]. Current treatments to combat TB remains ineffective, and they are associated with high toxicity, which is aggravated by emerging antibiotic resistances [1]. Key to its pathogenesis, *Mtb* secretes a wide range of virulence factors essential in infection and cell cycle. To do so, the *Mtb* produces up to five ESX/Type VII secretion systems, named from ESX1 to ESX5. ESX5 is mainly present in slow-growing pathogenic mycobacteria. It mediates the secretion of effectors involved in nutrient uptake, intracellular colonization and modulation of immune system response [2]. Importantly, ESX5 is essential for *Mtb* viability thus emerging as a potential drug target [2].

The ATPase $EccC_5$ is a pivotal component of the ESX5 pore complex providing the secretion driving force via nucleotide hydrolysis. It consists of two N-terminal transmembrane helices (TM) and two extra helices (stalk) connected to a first domain of unknown function ($EccC_5^{DUF}$), which is followed by three ATPase domains belonging to the FtsK/SpoIIIE family ($EccC_5^{ATPase1\text{-}3}$). Recent structural studies focused on ESX5 and ESX3 secretion systems have revealed $EccC_3$-$_5^{DUF}$ as ATPase-like fold domains with potential ATPase activity [3]. Here, we present our structural and functional characterization of *Mtb*$EccC_5^{DUF}$ domain using X-ray crystallography together with other biophysical and *in silico* analysis, which supports the absence of ATPase activity by this domain. Our results have enabled us to proposed a role of *Mtb*$EccC_5^{DUF}$ during the secretion process that highlights its potential interest as drug target.

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Miércoles, 17 de enero 11:55 – 12:05

Towards a more resilient agriculture: Re-engineering ABA receptors

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The binding of phytohormone abscisic acid (ABA) to the PYR/PYL/RCAR family of ABA receptors triggers plant response to abiotic stress, especially drought. Therefore, harnessing genetic strategies to modulate ABA receptors activity holds great biotechnological relevance. The biophysical and crystallographic analyses of these proteins have prompted the characterization of different regions of PYR/PYL as potential targets for the modulation of plant response to drought stress. These include the dimerization interface and different areas of the ABA binding pocket, such as a ‘latch’ loop involved in the stabilization of ABA and a hydrophobic 'tunnel' connecting the pocket to solvent.

We have assessed point and combined mutations in these regions, being able to design, among others, a constitutively active receptor, which cannot be activated by ABA. Critical amino acids within the tunnel region and latch loop have also been pinpointed, significantly affecting ligand affinity. Additionally, certain mutations in the dimerization interface could facilitate dimer dissociation, resulting in more active proteins upon ligand binding. The key advantage of these mutated receptors lies in the possibility to modulate them exogenously, with binding of specific molecules, other than ABA. This would trigger stress tolerance when applying such molecules to plant receptor, thus activating resilience mechanisms only when needed.

In this respect, we recently identified a molecule, nicotinic acid (vitamin B3), as an ABA antagonist, being a potential organic agrochemical [1]. Based on this finding, we now aim to unveil novel molecules capable of activating our mutated ‘tailoired’ receptors. This way, it would be possible to create drought tolerant crops and modulate them with eco-friendly molecules, adressing climate change challenges.

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Miércoles, 17 de enero 12:05 – 12:18

Unveiling a Novel pH Sensing Module in Plant Proteins: Implications for Vacuolar Antiporter Regulation

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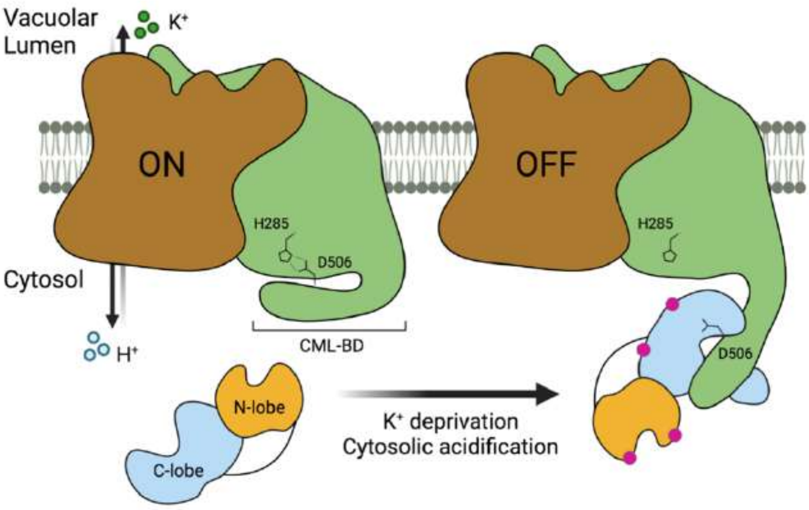
Understanding the intricate regulatory mechanisms governing **plant response to abiotic stress** is crucial for unraveling the complexities of these cellular processes. In this regard, Ca^{2+} ions often emerge as central messengers in these regulatory pathways, with Ca^{2+}-binding proteins being known to play a key role in the regulation of the antiporters involved in the maintenance of ion homeostasis during abiotic stress.

In this study, we have explored a calmodulin-like protein, uncovering **unexpected pH sensing properties** beyond its canonical role as a Ca^{2+} sensor. Importantly, the revelation of these novel properties stemmed from the determination of its **crystal structure**, unveiling a previously unknown mechanism governing its pH sensitivity. Our study connects the pH sensing capabilities of this protein to the modulation of its target antiporter activity, revealing a **second layer of regulation** that sheds light on this previously uncharacterized regulatory axis in plant cellular homeostasis. In this regard, the integration of experimental data with predictive approaches has allowed us to propose an **integrative model** which explains the relevance of Ca^{2+} and pH in the regulation of the target antiport activity.

Crucially, our discoveries have transcended the laboratory, as collaborative groups working with plants have validated our model through experimental evidence ***in vivo***. These joint efforts have not only confirmed the existence of the novel pH sensing module but have also provided additional layers of understanding regarding its physiological relevance.



Miércoles, 17 de enero 12:18 – 12:30

Structural Characterization of PdaA, an N-deacetylase from Clostridium difficile

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Clostridium difficile is a Gram-positive bacteria capable of forming spores. Spores are multilayered structures containing a peptidoglycan layer (cortex) that differs from the peptidoglycan of the bacterial wall.

Among the main differences between the cortex and the bacterial wall of C. difficile are structures called muramic-δ-lactams. The formation of these structures requires the involvement of an amidase (CwlD), which cleaves the peptide attached to muramic acid. Subsequently, N-deacetylation of muramic acid is facilitated by an N-deacetylase named PdaA. PdaA, classified as an N-deacetylase within the family 4 carbohydrate esterases, diverges from the typical metalloenzyme configuration. While most proteins in this family exhibit a metal-binding triad (Asp-His-His), PdaA substitutes the aspartic acid residue with an alanine residue.

In order to deepen the molecular basis of this enzyme, Extensive crystallization experiments were performed to solve the 3D structure of PdaA. Anomalous data processing and biophysical techniques allowed the identification of a zinc atom in the active site of the protein coordinated by the two conserved Histidines of the triad.

Details on the structure of PdaA, the structure of an inactive mutant and the structure with an analogous substrate will be shown in detail in the presentation.

Miércoles, 17 de enero 12:30 – 12:43

Crystal optimization and structural characterization of metallo-β-lactamase CAU-1 from *Caulobacter crescentus*

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Increasing resistance of some bacterial pathogens to β-lactam antibiotics is a major threat to public health. The mechanism of action of this type of antibiotics targets the bacterial cell wall, an essential structure formed by peptidoglycan (PG). Transpeptidases enzymes, known as penicillin-binding proteins (PBPs) are necessary in this PG biosynthesis. These enzymes are the target of β-lactams, which induce a cycle of cell lysis when inhibited by these antibiotics.

Resistance to β-lactams can be due to various reasons, the most common being the presence of β-lactamases. These enzymes catalyze the hydrolysis of the β-lactam ring, generating products that can no longer inhibit PBPs. There are 4 classes of β-lactamases (A, B, C and D), all except class B have a nucleophilic serine in the active site, responsible for the cleavage of the antibiotic. Members of class B are zinc-dependent metalloenzymes (MBL) that, unlike the previous ones, do not bind covalently to the antibiotic [1].

The study of MBLs is especially interesting because they are normally chromosomally encoded enzymes and because they do not respond to inhibitors developed for serine-β-lactamases.

Herein, we have carried out the production, cristallization and structure determination of the MBL CAU-1 from the bacterium *Caulobacter crescentus*, whose three-dimensional structure was not known until now. The final objective is to perform a complete structure-function analysis in this protein and use it as a model to understand MBLs in more depth.

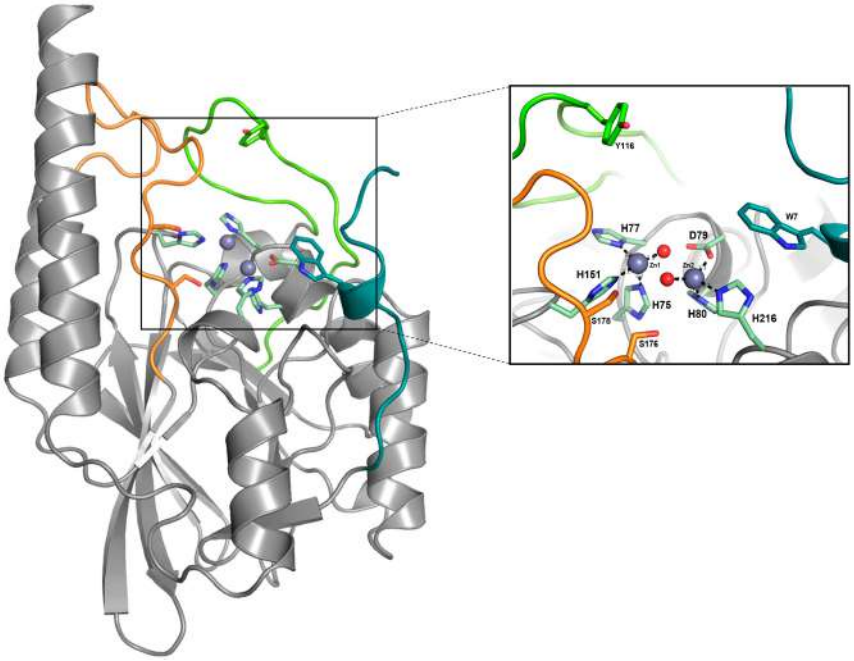

Figure 1. 3D structure of metallo-β-lactamase CAU-1 with a zoom to its active site.

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Miércoles, 17 de enero 12:43 – 13:00

Crystallographic analysis of a short unspecific peroxygenase and molecular characterization of the substrate binding site

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In the last decade, fungal unspecific peroxygenases, UPOs (EC 1.11.2.1) have been studied as potential industrial biocatalysts due to their dual peroxidative and peroxygenative activity, using hydrogen peroxide as oxygen source. These extracellular enzymes have high stereoselectivity and could be considered the ideal biocatalyst for oxyfunctionalization chemistry. Following our previous work on the first laboratory-evolved peroxygenase expressed by yeast *(Ramírez-Escudero et al, 2018*) and the *Aae*UPO A77L variant (*Gómez de Santos et al, 2023*), a short unspecific peroxygenase has been crystallized and characterized at a molecular level. Hence, we examined the substrate binding site in soaking experiments with a panel of peroxidative and peroxygenative substrates, as alkanes, fatty acids and steroids. Although this peroxygenase shows dynamic substrate trafficking, most substrates are trapped in a conserved binding mode which is defined through interactions to some hydrophobic residues constituting the heme funnel. A deeper knowledge on the structural characteristics, combined with a multidisciplinary approach including docking predictions, will lead to the application of these enzymes in pharmaceutical and chemical industries.

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Sesión 2

Miércoles, 17 de enero 15:00 – 15:25

New opportunities on the studies of condensed matter systems under extreme conditions at the ESRF-EBS

Gaston Garbarino[a]*, Mohamed Mezouar[a], Michael Hanfland [a], Anglika Rosa[a],
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In the last decades, we have witnessed an unprecedented surge in high-pressure research that has greatly improved our fundamental understanding of materials under high compression. The X-ray investigations of matter under extreme conditions has become one of the major activities at the ESRF and other 3rd generation synchrotron sources. The array of techniques includes X ray diffraction, Inelastic X-ray Scattering, Nuclear Inelastic Scattering, X ray absorption and emission spectroscopy, X ray magnetic circular dichroism, X-ray Compton scattering, X-ray magnetic scattering, among many others. As a direct consequence, many scientific breakthroughs have been achieved across fields ranging from fundamental physics to Earth and planetary sciences, chemistry and materials research, and extending into biophysics/biochemistry including questions concerning life and biological function under extreme conditions. Since August 2020, the new ESRF-EBS (extremely brilliant source) opened to the user community a new generation of synchrotron light source with unprecedented characteristics. In particular, the crystallography beamlines dedicated to the studies of materials under extreme conditions (ID15B and ID27) benefit enormously of the beam focusing capabilities and the coherent fraction.

In this presentation, the new capabilities available on ID15B and ID27, very recently reconstructed, will be presented. Also, the strengthen of the user support capabilities on the High-pressure laboratory allow to prepare the most challenging crystallographic studies under extreme pressure ($P<2$Mbar) and temperature ($3K<T<6000K$) conditions.

We will discuss particular scientific problems regarding the studies of condensed matter systems in function of high pressure and at low temperature. Finally, the possibilities of collaborations and discussions on possible future beamtime access will be introduced.

Miércoles, 17 de enero 15:25 – 15:50

Crystallographic studies at ISIS Neutron and Muon Source facility

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The Crystallography Group is responsible for the operation of a total of seven neutron diffraction instruments at the ISIS Neutron and Muon Source facility, located at the Rutherford Appleton Laboratory (UK). These are used to characterise both the local and average nuclear and magnetic structures of a wide range of different materials.

Overall, there are three main areas of the diffraction technique supported by the group and they can be described as single-crystal, powder, and total scattering diffraction. In each of these three techniques, ISIS has a unique set of instrumentation which can support the user community needs, as the scientific programme within the Crystallography Group covers a broad range of disciplines, including for example Bioscience, Chemistry, Cultural Heritage, Earth and Planetary Science, Materials Science, and Physics.

Some examples of different science cases, which are only possible to be studied at a large-scale facility like ISIS, will be presented, showing the different capabilities of the crystallography instruments.

Miércoles, 17 de enero 15:50 – 16:05

Exploiting the most from synchrotron fragment-screening data for the discovery of protein-protein interaction regulatory compounds with therapeutic potential in neuronal disease

Daniel Muñoz-Reyes[a], Daren Fearon[b], Warren Thompson[b], Charlie Tomlinson[b], Sara Pérez-Suárez[a], Mathew Golding[b], Kate Fieseler[b], Max Winokan[b], Matteo Ferla[b], Frank von Delft[b] and María José Sánchez-Barrena[a*]

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NCS-1 is a calcium signaling protein implicated in a wide range of functions in the central nervous system. It is involved in learning, memory, neuroprotection and axonal regeneration processes, as well as in pathological conditions, thus constituting an interesting pharmacological target. NCS-1 recognizes in a selective manner several proteins related with G-protein signaling: the molecular chaperone Ric-8A and the dopamine D2 and cannabinoid CB1 receptors, all of them related with neurodevelopmental disorders and neurodegeneration. In the recent years we have demonstrated that NCS-1 is a druggable target, and that it is possible to regulate the interaction with Ric-8A using small molecules. We intend to find other druggable sites within the large NCS-1 protein-protein interaction surface to regulate specifically the interactions with dopamine D2 and cannabinoid CB1 receptors. Here, we will present how we are getting the most from our previous and recent data to obtain compounds with the desired activity. First, we performed a fragment screening at XCHEM (DLS, UK). Fragment hits have been merged and linked, using AI- assisted methods and the Chemist Assisted Robotics (CAR) system, to generate bigger compounds with enhanced affinity. With the aim of obtaining the desired activity, we have introduced filters with structural information on previous protein/ligand and protein-protein structures to guide the fragment growth. A second round of soaking experiments with the bigger compounds is being performed. Finally, I will discuss how relevant these experimental structural data could be for AI-assisted drug discovery programs, regardless the fragment growth success, to create machine learing training protocols.

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Miércoles, 17 de enero 16:35 – 17:00

Resonant Elastic X-ray Scattering at beamline P09

Pablo J. Bereciartua[a]*, Sonia Francoual[a], Christian Plueckthun[a], Yongsheng Zhao[a], Juan Rodríguez-Carvajal[b], Frédéric-Emmanuel Picca[c]

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Resonant Elastic X-ray Scattering (REXS) is a powerful technique used to investigate a wide range of phenomena both in solids and thin films [1-3]. The particular combination of diffraction and spectroscopy features of this experimental approach allows the study of different charge, spin, and orbital orderings.

The beamline P09 [4] at PETRA III (DESY) is dedicated to REXS technique, and one of the main research topics of the beamline is the application of this technique to the study of magnetic structures. This is achieved by combining different experimental capabilities implemented at P09, like a small incident beam, a high photon flux, a full control of the incident polarization and the possibility of analyzing X-ray polarization. Moreover, an ongoing project at the beamline is the development of MagStREXS, a crystallographic software to analyze magnetic structures based on REXS diffraction data. Actually, the analysis of magnetic data collected in REXS experiments is very intricate and the lack of any tool to facilitate such calculations slows down and even prevents the achievement of proper results. The aim of MagStREXS is to facilitate the analysis of this type of data to the non-specialist in the field.

In this talk an overview of the main features of REXS technique will be presented, together with the different experimental possibilities implemented at beamline P09 for the application of this technique to the study of magnetic structures. Finally, the program MagStREXS and the main features implemented until now will be also presented, together with some examples of magnetic structures investigated with this software in the field of strongly correlated systems.

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Miércoles, 17 de enero 17:00 – 17:25

Elucidating individual magnetic contributions in bi-magnetic fe3o4/mn3o4 core/shell nanoparticles by polarized powder neutron diffraction

I.V. Golosovsky, I.A. Kibalin*, A. Gukasov, A.G. Roca, A. López-Ortega, M. Estrader, M. Vasilakaki, K.N. Trohidou, T.C. Hansen, I. Puente-Orench, E. Lelièvre-Berna, J. Nogués

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Heterogeneous bi-magnetic nanostructured systems have sustained interest during the last decades owing to their unique magnetic properties and wide range of derived potential applications [1]. The most common technique to study the magnetic properties of these materials is magnetometry. However, magnetization measurements usually cannot discern between different contributions of the diverse magnetic components.

Polarized neutron diffraction is sensitive to the local susceptibility tensor at each magnetic site [2], and has been extensively used with single crystals [3, 4]. Recent progress in software development in Rietveld analysis of powder patterns measured with polarized neutrons [5] makes this technique accessible for a large number of interesting compounds that cannot be prepared in the form of a single crystal [6, 7]. We demonstrate here that polarized neutron powder diffraction (PNPD) is a valuable tool to acquire unique information, difficult or impossible to retrieve with other techniques, from bimagnetic nanostructured systems.

In the talk, a comprehensive study of Fe3O4/Mn3O4 core/shell nanoparticles using PNPD will be reported. The results show that while at low fields the Fe3O4 and Mn3O4 magnetic moments averaged over the unit cell are antiferromagnetically coupled, at high fields they are oriented parallel to each other (Fig.1). This magnetic reorientation of the Mn3O4 shell moments is associated with a gradual evolution of the field induced changes of the local magnetic susceptibility from anisotropic to isotropic. These results open new avenues to obtain valuable information on the individual magnetic properties of each phase in multi-magnetic nanostructured materials through the quantitative refinement of PNPD. For more details, see [8].

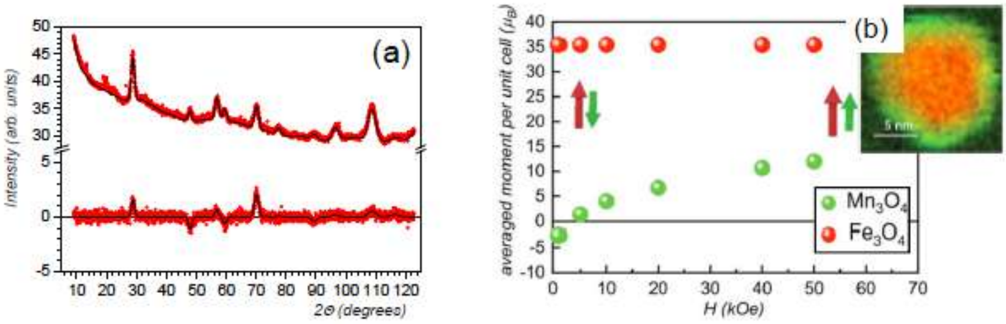

Fig.1: (a) Refinement of the sum (top curves) and difference (bottom curves) of the spin-up and spin-down pattern at 5 kOe. b) Dependence of the Fe3O4 (red symbols) and Mn3O4 (green symbols) moments averaged over the unit cell. Insert shows the Fe (red) and (green) Mn L-edge electron energy loss spectroscopy mapping of a Fe3O4/Mn3O4 of about 15 nm in size.

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Miércoles, 17 de enero 17:25 – 17:40

XtremeD: new Spanish CRG diffractometer for extreme conditions

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Powder and single crystal neutron diffraction under extreme temperatures, pressures and magnetic fields is becoming increasingly important [1] as it often unveils exotic phenomena arising from altered interatomic distances and interactions. Neutrons are indispensable in this regard as they naturally permit to locate light species in the crystal structure, tell apart chemical elements with similar atomic number or isotopes, study long- and short-range magnetic ordering, etc.

XtremeD is a new Collaborative Research Group (CRG) instrument entering into operation in 2024 at the Institute Laur-Langevin (ILL), Grenoble, France and managed by the SpINS initiative at the University of Zaragoza, Spain under the auspices of the Spanish National Research Council (CSIC). Because of the small sample volumes typically used under extreme conditions, the instrument is designed to maximize neutron flux and improve neutron detection efficiency (Fig.1). Currently, XtremeD is available for the proposal submission both through the ILL and SpINS proposal calls. The instrument can host the majority of the ILL sample environment equipment with particular focus on high-pressures (up to 20GPa) and magnetic fields (up to 15T).

The instrument capabilities and results obtained during the hot commissioning phase will be discussed

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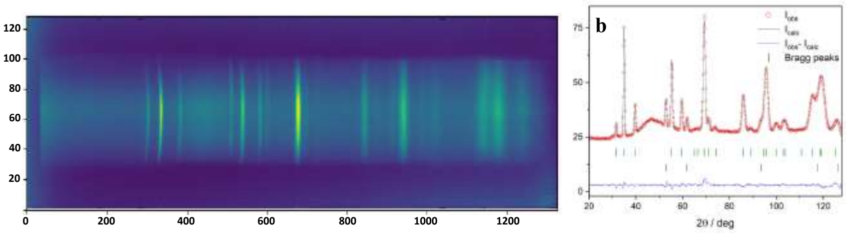

Fig. 1. Paris-Edinburgh press on XtremeD: (**a**) raw 2D detector image of Fe_2O_3 powder pattern collected at T=300K and P=2.7 GPa; (**b**) Rietveld refinement of the same pattern.

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Miércoles, 17 de enero 17:40 – 17:55

Towards deciphering the structure and dynamics of biological and non- biological molecules using time-resolved serial crystallography

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Department of Crystallography and Structural Biology, Institute of Physical Chemistry Blas Cabrera, Spanish National Research Council (CSIC), Madrid, Spain

Despite X-ray crystallography is the main way of uncovering the 3D structures of biomacromolecules, traditionally, it has been viewed as a static technique, with limited applicability to study protein dynamics. However, this scenario began to change some years ago with the development of new light sources, the X-ray free electron lasers (XFELs), which has brought about a resurgence of room temperature crystallography through so- called time-resolved serial femtosecond crystallography (TR-SFX). Also, the high intensity of state-of-the-art synchrotron sources, combined with ultrafast detectors, has enabled similar experiments in the form of time- resolved serial synchrotron crystallography (TR-SSX). Overall, in the past few years TR-SX has become a powerful technique to study reaction mechanisms *in real time*. In my group, we use TR-SX to study the structure and dynamics of biological and non-biological molecules. In my talk, I will present the TR-SFX technique, and the most recent results obtained for the beta-lactamase C (BlaC) enzyme from *Mycobacterium tuberculosis*. This work builds on possibilities unleashed by mix-and-inject TR-SFX at XFELs. We have triggered an enzymatic reaction by mixing an inhibitor with enzyme microcrystals to report, in atomic detail and at room temperature, how BlaC is inhibited by sulbactam. Our results reveal ligand binding heterogeneity, ligand gating, cooperativity, induced fit, and conformational selection, detailing how the inhibitor approaches the catalytic clefts and binds to the enzyme covalently. I will also present, briefly, some of the other projects we are working on both at XFELs and synchrotrons including the penicillin binding protein 2a (PBP2a) of *Staphyloccocus aureus*, the flavoproteins FNR and Fld of *Anbaena* and FPR of *Brucella Ovis* (collaboration with Milagros Medina and Marta Martínez Júlvez (University of

Zaragoza)), and the MOFs MUV-15 (collaboration with Carlos Martí Gastaldo (ICMOL)) and BiFe (collaboration with Felipe Gándara (ICCM-CSIC) and Víctor de la Penya (IMDEA Energía)).

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Acknowledgements

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Sesión 3

Jueves, 18 de enero 9:40 – 10:05

Full structure determination and refinement of an organic dye with triclinic symmetry by means of three-dimensional electron diffraction

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The use of electron diffraction to crystallographically characterize all kinds of materials has gained some attention in recent years due to, first, the wide availability of fast and sensitive detectors, and second, the appearance of commercial electron diffractometers. During this last decade, a large number of structural analyses from different compounds have been already carried out with the help of three-dimensional electron diffraction (3D ED) data that were not possible with the current X-ray methods [1]. In this context, the use of a transmission electron microscope as an electron nano-diffractometer has proved to be advantageous when diffraction data from single nanocrystals are required [2]. By means of a self-developed software for the automated and reliable acquisition of 3D ED data [3], several crystals of the organic dye disperse red 1 (DRED1) were analyzed to determine and fully refine the crystal structure solely based on electron diffraction data. Six datasets were evaluated revealing a triclinic crystal system. Several processing tools were then used to solve *ab initio* the structure in *P-1* and reveal all the 46 non-hydrogen atoms from the electrostatic potential map. Finally, a refinement that takes into account the dynamical theory of diffraction was applied to enable the proper description of the H-bond network of the crystal structure.

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Jueves, 18 de enero 10:05 – 10:30

Salt or co-crystal? Monitoring a co-crystal screening with Electron Diffraction

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Co-crystals, as multicomponent solid substances, offer a compelling avenue for tailoring the physicochemical properties of active compounds, particularly in the realm of pharmacological applications. This talk will provide a brief introduction to co-crystals, highlighting their significance. Emphasis is placed on the methodologies employed by Crysforma - ICIQ for the synthesis and characterization of novel co-crystals for the Pharmaceutical industry. The presentation showcases state-of-the-art analytical techniques, including 3D-ED, illustrating their instrumental role in characterizing co-crystals and elucidating their compositions through insightful examples. In particular 3D-ED is a powerful technique that allows revealing the structure in difficult cases, allowing directly or indirectly the determination of the position of the acid hydrogen (salt vs co-crystal, Figure 1).

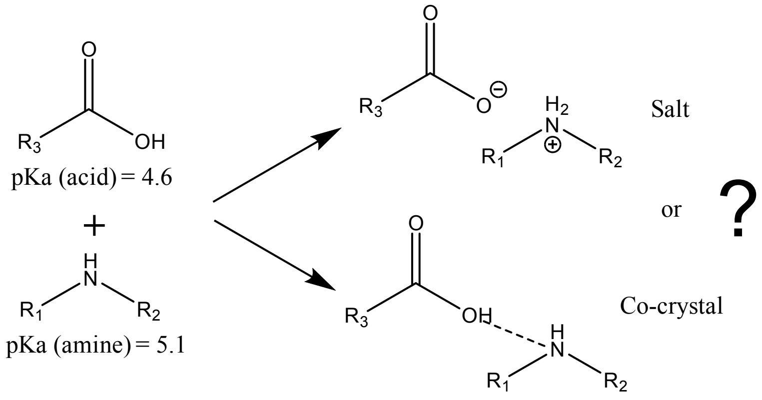

Figure 1

Jueves, 18 de enero 10:30 – 10:45

Halogen Bonding in Pharmaceutical Cocrystals

Mónica Benito[a*], Antonio Frontera[b], Elies Molins[a]

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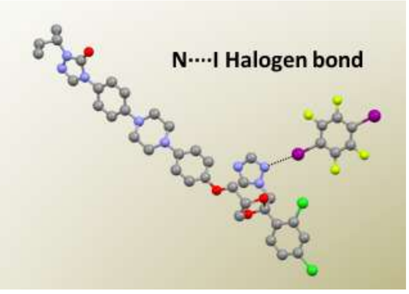
Cocrystals have emerged as relevant players in crystal engineering and specially in pharmaceutical industry in the last years. Moreover, in supramolecular chemistry, halogen bonding has attracted considerable interest and is an alternative tool to hydrogen bonding thanks to its high directionality, tuneability and hydrophobicity.[1] In this work we present the use of halogen bonding for the preparation of cocrystals containing active pharmaceutical ingredients (APIs). Three conazole molecules with antifungal properties, used as halogen bond acceptors, and the well-known perfluororated coformer 1,4-diiodotetrafluorobenzene were selected for the green synthesis of new cocrystals in which the N···I interactions govern the different arrangements observed in their crystal structures.



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Jueves, 18 de enero 10:45 – 11:00

Unlocking the Colorful World of Spiro-Rhodamines: rational design and characterization of switchable molecules

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Spiro-rhodamines (SRAs) are photochromic molecules that exhibit a switching equilibrium between an optically inactive isomer (colorless and non-fluorescent) and a highly colored and fluorescent compound.[1] This unique property of SRAs has paved the way for numerous applications beyond the traditional use of rhodamine derivatives in imaging and cell labeling.[2] Moreover, the differences between the two isomers provide a rich platform for various applications in diverse fields. For instance, the reversible switching between spiro and open forms offers opportunities in the development of molecular switches, optoelectronic devices, and stimuli-responsive materials.[3] Additionally, SRAs demonstrate potential in data storage and information encoding, acting as molecular switches for encryption and next-generation storage technologies.[4]

In this study, we investigate the structure-dynamics-function relationship and the novel properties arising from light-induced changes in spiro-rhodamines (SRAs). By carefully designing a family of SRAs with different substituents, we explore their potential for precise modulation of the isomeric transformation in response to external stimuli. We characterize the equilibrium between the isomers (see Figure 1) in solution and solid state using a comprehensive set of techniques, including fluorescence measurements as time corretated single photon counting, transient absorption spectroscopy, single-crystal X-ray and neutron diffraction, atomic force microscopy coupled with infrared spectroscopy, and computational calculations. Furthermore, we evaluate the changes occurring upon irradiation of the corresponding close isomer with ultraviolet light and document the observed differences within the synthesized family. These findings highlight promising prospects for the future applications of SRAs in various fields, owing to their distinct properties and controlled isomeric behavior.

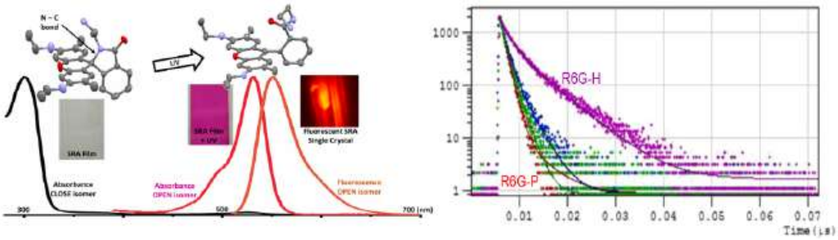

Figure 1 – Spectroscopic and structural results of SRAs switching equilibrium.

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Jueves, 18 de enero 12:10 – 12:35

More than just visualization with Mercury

Pablo Martinez-Bulit[a], Elna Pidcock[a]*

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Mercury[1] is a component of the Cambridge Structural Database (CSD)[2] suite of software, originally designed to allow the easy and intuitive viewing of small-molecule crystal structures. Over the years, since its release, it has grown into a tool which allows searching of the CSD as well as advanced analysis of loaded structures.

In this presentation we will highlight recently added features to Mercury that allow you to: calculate particle shape and examine the nature of the surfaces of the particle for rugosity and presence of functional groups (see Figure 1); determine pore size and volumes in cage-like structures; interrogate hydrogen bonding in the structure to assess geometry and likelihood; search for structural motifs and calculate and display powder patterns. We aim to provide examples of the use of Mercury to demonstrate how to maximise the value of your crystal structures.

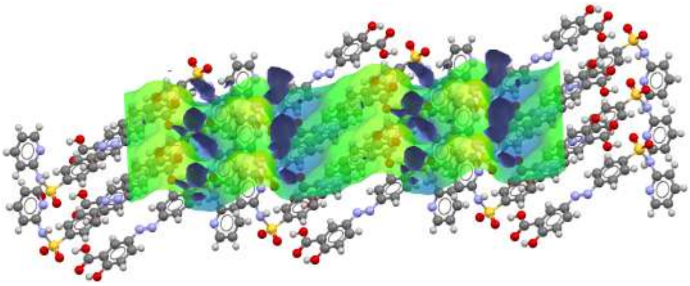

Figure 1. A surface showing rugosity and potential positions for hydrogen bond donor groups.

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Jueves, 18 de enero 12:35 – 12:48

Adaptive structural plasticity in pMHC drives pathogenic T cell recruitment in autoimmune disease.

Jacinto López-Sagasetaa*, Elena Erausquina, Pau Serrab, Daniel Parrasb, Pere Santamariab,c

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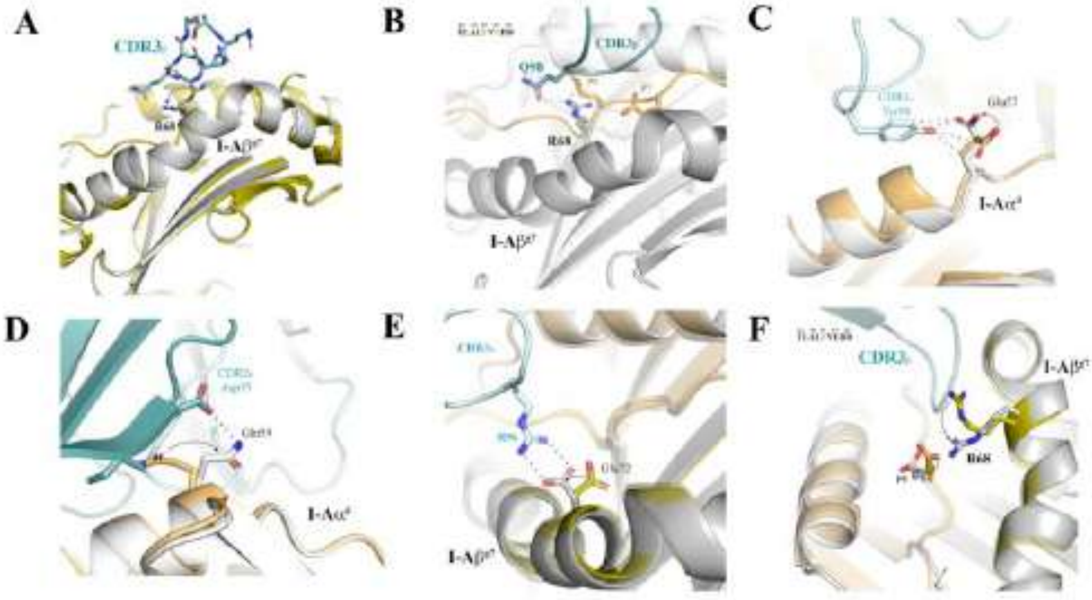
The NY4.1 T cell clone was originally isolated from pancreatic islet-infiltrating lymphocytes from non-obese diabetic (NOD) mice. We have recently shown that the NY4.1 T cell receptor (4.1-TCR) recognizes pancreatic beta cell-derived hybrid insulin peptides (HIPs) in the context of the Major Histocompatibility Complex class II (MHC-II) molecule I-Ag7. In TCR-transgenic NOD mice, recognition of these peptide-MHCII (pMHC-II) complexes triggers the activation and recruitment of NY4.1-CD4+ T cells into pancreatic islets, leading to rapid destruction of pancreatic beta cells and overt type 1 diabetes within the first few weeks of life.

We present the crystal structure of a HIP peptide/I-Ag7 complex at 1.80 Å resolution, as well as the structure of this pMHCII bound to the 4.1-TCR at 2.6 Å resolution. Comparison of the two structures reveals a previously unrecognized mode of interaction between a pMHC-II and its cognate TCR, whereby TCR engagement entails exquisite conformational motions in I-Ag7 and the HIP that are essential for binding.

This observation suggests that some pMHCII complexes are malleable and that some TCRs trigger conformational motions on their cognate pMHCIIs to optimize binding.



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Jueves, 18 de enero 12:48 – 13:00

A drug discovery approach to drought resistance in crops

Javier Merino Gracia[a], María Rivera Moreno[a], Rupesh Chikhale[b], Lourdes Infantes San Mateo[a], Armando Albert de la Cruz[a]*

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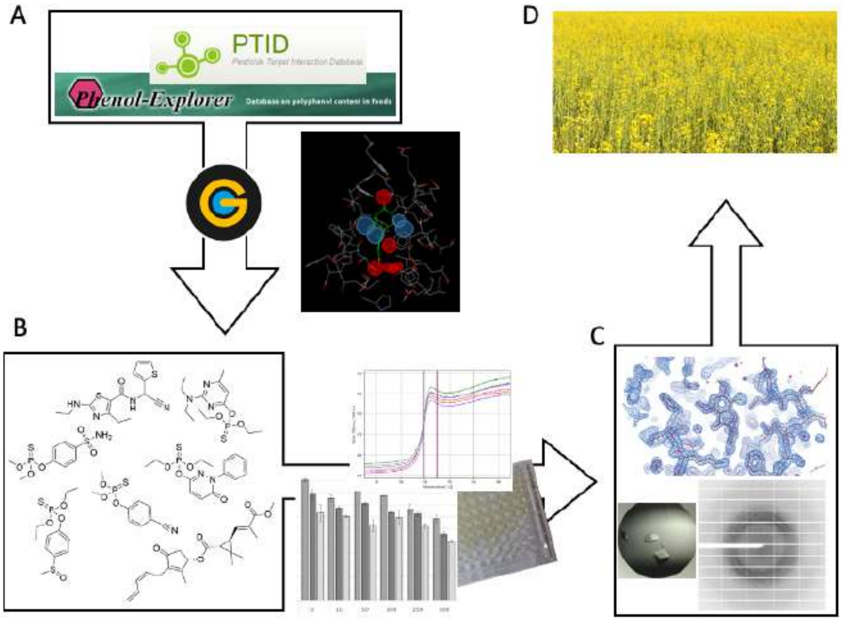
Climate change is increasing the ocurrecne and probability of adverse weather phenomena, including intense floods and prolonged droughts. In response to these environmental stresses, plants must adapt. The phytohormone Abscisic acid (ABA), sensed by cytosolic receptors, serves as a crucial hub for triggering resistance responses in plants against these abiotic challenges. The manipulation of these physiological mechanisms to enhance the resilience to external stressors, is emerging as a viable biotechnological solution for addressing these adverse phenomena in crops of agricultural interest. Previous explorations in our lab and others have combined genetic interventions with agrochemical approaches targeting ABA receptors, yielding promising results (1,2).

Here, we describe the application of a drug discovery pipeline aimed at identifying compounds capable of activating the ABA signalling pathway some crop species (see fig.1). By using the CSD's genetic algorithm GOLD, an *in-silico* search was conducted across agrochemical and natural product databases to pinpoint potential candidates (fig.1A). Subsequent biochemical tests were performed on selected molecules to assess their capacity for inducing an ABA-like response, narrowing down the candidates through various biophysical methods (fig.1B). A naturally derived molecule, displaying moderate activity, has emerged as a primary candidate. Through structural analyses, we found discrepancies between the observed conformation and our initial docking experiments (fig.1C), revealing unexpected binding pose within the binding pocket. An exploration on the CSD's uncovered an induced selection towards uncommon conformations of the lead candidate, which explain the low activity profiles. However, strategic chemical modifications have enhanced its performance, paving the way for potential applications in the field (fig.1D).

In summary, the integration of chemi- and bioinformatics methods accelerates the identification of biotechnologically relevant molecules, bypassing the need for expensive biological experiments. This study exemplifies such an approach with the identification of a fungal molecule with potential applications inenhancing crop resistance to water scarcity.



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Sesión 4

Jueves, 18 de enero 16:00 – 16:30

Ru-Mixed Oxides as efficient and durable electrocatalysts for PEMWE anodes

M. Retuerto[1],*, D. Galyamin[1], J. Torrero[2], I. Rodríguez[1], P. Ferrer[3], D. Gianolio[3], L. Pascual[1], D. García Sanchez[2], A. S. Gago[2], J. A. Alonso[4], F. Calle-Vallejo[5], S. Rojas[1]

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Green hydrogen plays a crucial role in the energy transition from carbonized to a sustainable economy. Electrolyzers are a key electrocatalytic technology for this purpose, and among them low-temperature PEM water electrolyzers (PEMWE) are one of the most promising ones. Water electrolysis comprises two half reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The OER results in higher overpotentials than HER, therefore, more efforts are focused on the development of OER catalysts. The overpotential depends mainly on the nature of the electrocatalysts at which the reaction takes place. The most active OER electrocatalysts, working in the acid media of PEMWE, are based on Ir and Ru oxides, which are very expensive and scarce, especially Ir. In order to decrease their loading, mixed oxides are been studied as an alternative.

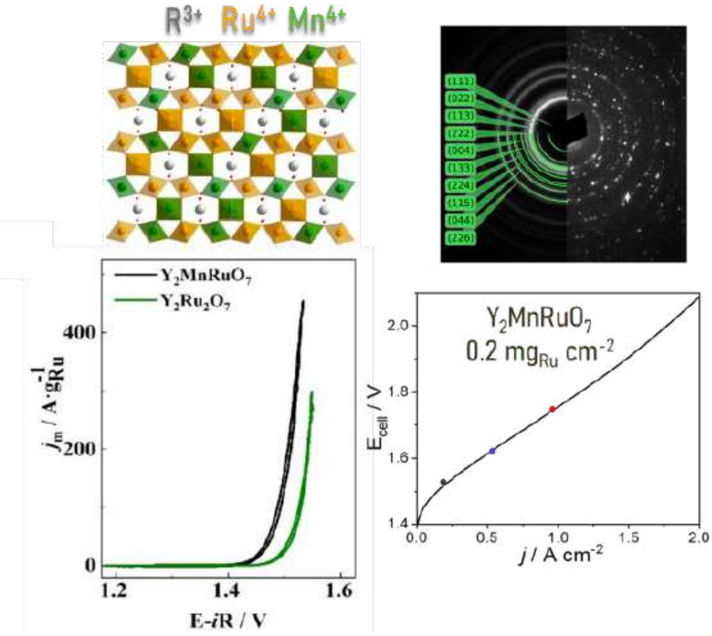

Figure: Upper panel: Y2MnRuO7 crystal structure; Lower panel: OER activity for Y2MnRuO7 and Y2Ru2O7; PEMWE test.

In our work we study the catalytic performance of Ru based mixed oxides. The OER performance was first evaluated using the RDE approach in 0.1 M HClO4. Some of those Ru-mixed oxides display very good OER performance. For instance, the pyrochlore Y2MnRuO7 displays 1.5 V at 10 mA cm-2 for 40 h, and lasts 5000 cycles up to 1.7 V at the same current density. Only pyrochlores with double quantity of Ru have shown similar durability but less catalytic activity; since most Ru phases dissolve in the acid electrolyte during the harsh conditions of the OER. Therefore, this catalyst achieves the a very promising OER performance with low Ru content. The catalyst was characterized by techniques including XAS, XPS and IL-TEM. The experimental and theoretical results demonstrate that the catalyst suffer for surface reconstruction during the first reaction cycles, and it is the RuMnOx surface the responsible of the high activity and significant durability of the pyrochlore.

Acknowledgement. We acknowledge the European Union’s Horizon 2020 research and innovation programme for the grant agreement No 862253 (PROMET-H2). Also, the Spanish Ministry of Science and Innovation for the projects TED2021-131033B-I00, PID2019-103967RJ-I00 and PID2020-116712RB-C21.

Jueves, 18 de enero 16:30 – 17:00

New advances in the development of multifunctional catalysts for the Photo(electro) catalytic solar chemistry

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The search for new photoactive materials able to efficiently produce solar fuels is a matter of growing interest due to the current global energetic crisis. In response to this situation, the generation of solar fuels has appeared as a sustainable alternative. In last years, extensive efforts have been made to develop efficient catalytic systems capable of harvesting light absorption and reducing CO_2 especially when using water as the electron donor.

Herein, we report different strategies and modifications of photocatalysts to increase process performance. Among them, an interesting approach to improve charge separation in photocatalytic systems is the use of heterojunctions. In this line, the combination of different semiconductors with noble metal nanoparticles or organic semiconducting polymers leads to a separation of the photogenerated charge carriers to increasing their life time, facilitating charge transfer to adsorbed molecules.

Organo-inorganic hybrid materials show a dramatic reactivity improvement in CO_2 photoreduction, enhancing methane selectivity. Reaction pathways are not well defined for this reaction and several uncertains are still unsolved. To explain this behavior a combination of in-situ NAP-XPS, FTIR, TAS spectroscopies and theoretical tools has been used, showing a more efficient light absorption and charge transfer in the hybrid photocatalyst compared with bare materials.

Jueves, 18 de enero 17:30 – 17:43

Application of parametric equations to phase transformation in niti shape memory alloys from synchrotron data

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The full phase transformations in NiTi samples has been first modeled with parametric equations from in-situ high energy X-ray synchrotron radiation diffraction data. The phase evolution has been studied and compared from 4 different approaches: by individually refining the Rietveld scale factors (1st approach) and using parametric equations of them (2nd approach) with the TOPAS software. Likewise, both the Austenite to R-phase and the Austenite to Martensite transformations has been treated as the distortions of two supercells defined with the ISODISTORT software with a set of strain and displacive modes. Both strain and displacive modes have been refined individually (3rd approach) and finally they have been also parameterized for modelling the supercell distortions, i.e. the distortion from the parent structure (A) to the distorted structure (R and M) (4th approach). The results show that parameterization reduces the number of parameters refined and allows following the phase evolution until its total transformation. Significant differences can be observed between the behaviour of the two transformations: the A→R transformation happens in a wide temperature range whereas the A→M transformation happens in a very narrow temperature range that the experimental setup cannot follow accurately. The method proposed allows a better estimation of the characteristic temperatures of the martensitic transformation from X-ray data even with R phase is involved.

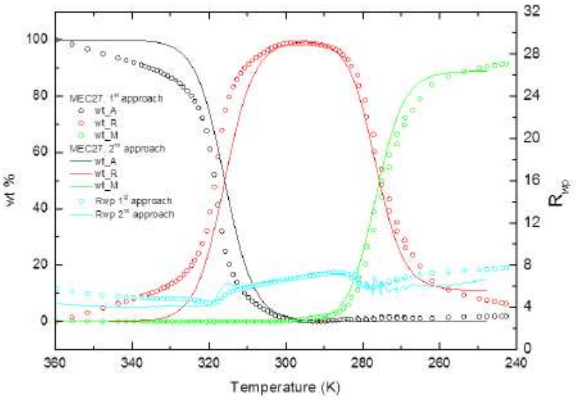

Figure 1 Left axis, Quantitative phase analysis of sample MEC27 of A, R and M phases. Dots: results obtained by refining independently the scale factors of each phase of the diffractograms taken at several temperatures (1st approach). Continuous line: results obtained by parametrically refining the scale factors (2nd approach). Right axis, calculated Rietveld agreement factor at each temperature.

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Jueves, 18 de enero 17:43 – 17:56

Pink $MgCo_xNi_{1-x}SiO_4$ ($0 \leq x \leq 1$) and $CaMg_{0.5}Co_xNi_{0.5-x}Si_2O_6$ ($0 \leq x \leq 0.5$) solid solutions: towards more sustainable pigments

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In this study, two series of solid solutions, $MgCo_xNi_{1-x}SiO_4$ ($0.0 \leq x \leq 1.0$) with olivine structure(1) and $CaMg_{0.5}Co_xNi_{0.5-x}Si_2O_6$ ($0 \leq x \leq 0.5$) with diopside structure(2) were prepared via the chemical co-precipitation method to minimise the toxic and expensive amounts of cobalt and nickel. The evolution of their color with composition and temperature will be explained by the structural characterization of these fired materials.

Co(II) and Ni(II) are randomly distributed in the $MgCo_xNi_{1-x}SiO_4$ ($0.0 \leq x \leq 1.0$) solid solutions. The occupation of Co(II) ions in M1(4a) was found higher than in M2(4c) sites. Average distances shorter than 2.12 Å in the coordination of Co(II) in these materials explain the reason for the pink $MgCo_xNi_{1-x}SiO_4$ ($0.25 \leq x \leq 1.0$) solid solutions and the blue or violet in Co_2SiO_4.

In $CaMg_{1-x}Co_xSi_2O_6$ solid solutions, the mean M1(4e)-O (M1) = Mg, Co) distances are also shorter than 2.12 Å and their variation with x, explains the pink or red colour of compounds containing octahedral Co(II) ions.

These solid solutions can be used as ceramic dyes when they are dissolved in glazes and the colour in enamelled samples is depending on x. Intense green and blue colorations are developed when these pigments are dissolved in the commercial glaze.

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We gratefully acknowledge the financial support provided by Spain´s Agencia Estatal de Investigación, PID2020-113558RB-C41.

Jueves, 18 de enero 17:56 – 18:09

MOF-413 and Ga7Ni-TCPP: Two new multimetal MOFs obtained by the use of messenger building units

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Metal-organic frameworks (MOFs) are materials comprised of metal atoms and organic linkers arranged in a periodic framework.[1] It is possible to obtain materials with new or enhanced properties by different combinations of multiple metal elements into the same framework,[2] however, the one-pot incorporation of specific metal combinations into the structure is a major challenge because the lack of control of metal ratio and distribution.[3]

Recently, we reported a novel synthetic approach to obtain multimetal MOFs with specific combinations of metal cations, through the use of heterometallic molecular complexes as precursors,[4] which through a linker exchange process allows us to incorporate specific metal atom combinations into MOF building units. We consider them as messenger building units (mBU) because of their ability to preserve specific atom combinations during MOF assembly process. Through the application of this methodology, we synthesized different MOFs with selected Ga:Ni combinations, and we demonstrated that it could be extended to different linkers and metal combinations. Recently we have obtained two new materials by using this methodology by using organic linkers with different connectivities: MOF-413 and Ga7Ni-TCPP.

MOF-413 has been characterized by single crystal X-ray diffraction, and its formula determined to be $[Ga_2Ni(\mu_3\text{-}O)(BTB)_2(PivO)(DMA)]\cdot[DMA]_x$, where BTB, PivO and DMA nomenclature corresponds to 1,3,5-Tris(4-carboxyphenyl)benzene, pivalate and dimethyl ammonium respectively. MOF-413 crystallizes in the orthorhombic system, space group *Pnma*, and it exhibits a flexible structure, consisting of two interpenetrated networks.

Ga7Ni-TCPP was obtained as a polycrystalline solid, so it was characterized by combination of different techniques such as powder X-ray diffraction, electron microscopy and X-ray photoelectron spectroscopy. Its formula determined to be $Ga_7NiF_8(H_2TCPP)_4$, where H_2TCPP corresponds to tetrakis (4-carboxyphenyl) porphyrin, and it crystallizes in the orthorhombic system, space group *Cmmm*. The catalytic and photocatalytic activity of Ga7Ni-TCPP MOF has been studied in different reactions such as olefin hydrocarboxylation and Aza-Henry reaction respectively.

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Jueves, 18 de enero 18:09 – 18:22

Clip-Off Chemistry in Heterometallic Iron-Zinc ZIF-8

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Clip-off chemistry in metal–organic frameworks (MOFs) is a pioneering manner to tune the physical properties of these porous materials.[1] This innovative strategy to modify the connectivity in MOFs is based on the use of a selective bond-breaking reaction to remove a controlled segment of the reticular network. This reticular design can be used to create open metal sites, defect engineering, and new morphologies, or to carry out pore structure engineering.[2] The latter usage is especially interesting due to the possibility of creating hierarchical structures by removing metal ions or linkers. This is achieved by randomly breaking some of the metal–ligand coordination bonds due to their low chemical or thermal stability.

ZIFs are an important subclass of MOFs formed by tetrahedral metal centers (typically Zn^{2+} or Co^{2+}) linked by imidazolate ligands. The archetypical member of this family is $Zn(mim)_2$ (mim = 2-methylimidazolate), commonly known as

ZIF-8. We have recently reported the solvent-free preparation of the Fe^{2+} analogue of ZIF-8, namely MUV-3,[3] which is highly unstable toward exposure to water. Thus, we reasoned that the combination of stable Zn^{2+} centers with unstable Fe^{2+} centers in the same structure could yield a bimetallic Fe-Zn-ZIF-8 with M–mim–M coordination bonds of different reactivity toward water molecules due to their different chemical behavior.[4] We demonstrate that Fe centers can be removed selectively without affecting the backbone of the structure that is supported by the Zn atoms (Figure 1). This allows us to create mesopores within the highly stable ZIF-8 structure. The strategy presented, combined with control of the amount of iron centers incorporated into the structure, permits porosity engineering of ZIF materials and opens a new avenue for designing novel hierarchical porous frameworks. The application of clip-off chemistry on the coordination bond between the metal and the ligand is relatively unusual in MOF systems and is applied here for the first time in ZIFs.

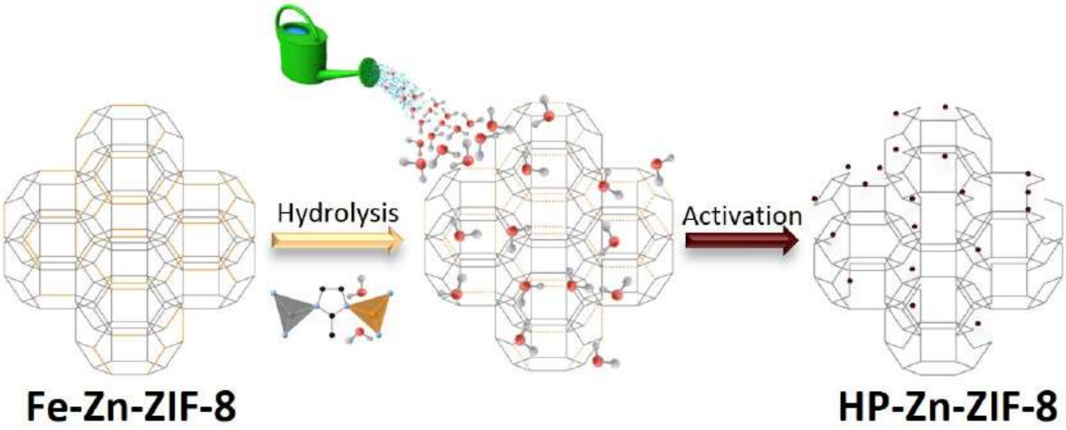

Figure 1. Schematic representation of the clip-off approach used to create a hierarchical structure in the backbone of ZIF-8.

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Jueves, 18 de enero 18:22 – 18:35

Carbon paper supported cobalt phosphide electrocatalysts for water splitting

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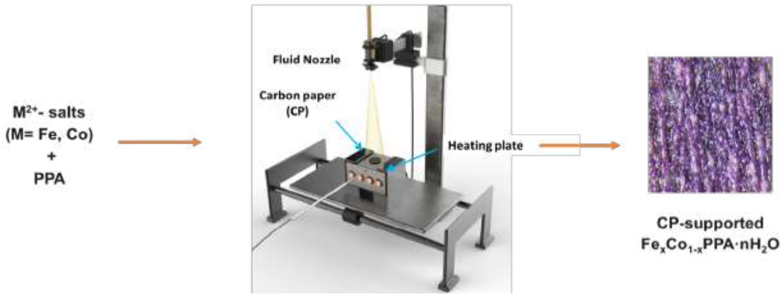
Metal phosphonates are a subclass of coordination polymers that can be used as precursors of transition metal phosphide-based electrocatalysts, alternative to those others based on precious metal electrocatalysts (Pt, RuO_2, etc) [1]. In this work, we report the synthesis and crystal structures, solved from X-ray powder diffraction, of two cobalt carboxyphosphonates, derived from the phosphonopropionic acid (PPA), with the formula $[Fe_xCo_{1-x}(HO_3PCH_2CH_2COO)_2(H_2O)n$; n = 0, 2 and x = 0, 0.2]. Carbon paper (CP) supported cobalt phosphide electrocatalysts were prepared in two sequential steps: (i) dispersion of the obtained metal phosphonates over the CP surface through a spray-drying process (Scheme 1), and (ii) pyrolysis of the deposited precursor in 5%-H_2/Ar at 750 °C. Preliminary results of their electrocatalytic activities toward oxygen and hydrogen evolution reactions (OER and HER, respectively) indicate that this new methodology allows to improve the water-splitting activity compared with that of the CP-supported Co-phosphide electrocatalysts deposited by conventional drop-coating technique [2].



Scheme 1. Preparation of CP-supported cobalt carboxyphosphonates by spray-drying.

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Jueves, 18 de enero 18:35 – 18:48

Study of mixed molybdates of lanthanum and praseodymium, La5.4-xPrxMo1-yNbyO12-δ, for H2 separation membranes.

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This research explores the impact of praseodymium and niobium doping on the La5.4-xPrxMo1-yNbyO12- _series (x= 1.35, 2.7, 4.05, 5.4; y= 0, 0.1) as materials with mixed proton-ionic conductivity suitable for hydrogen separation membranes with two main objectives: i) enhancing the electronic conductivity through praseodymium doping, and ii) increasing oxide ion vacancies to improve the ionic conductivity via niobium doping [1].

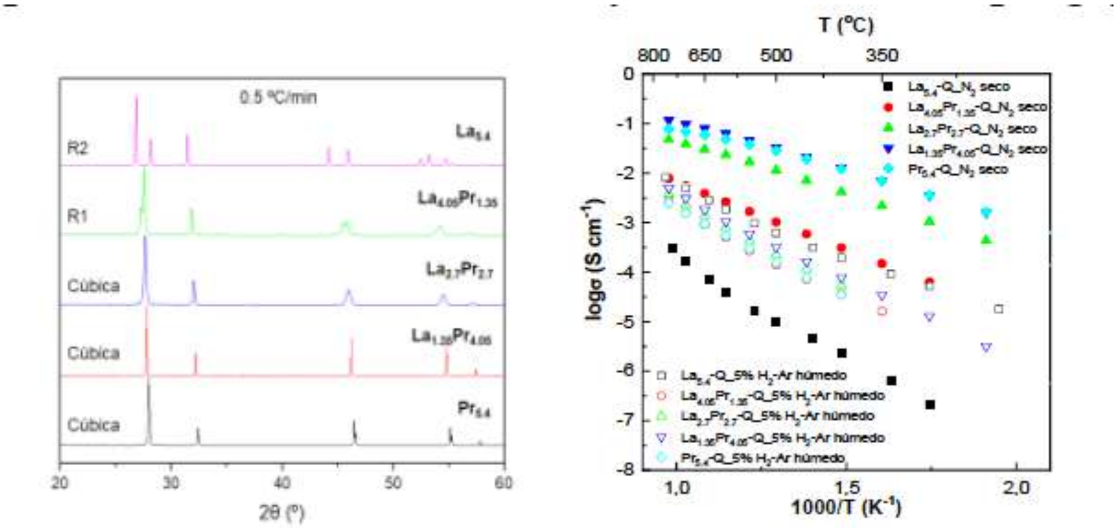

Figure 1. X-ray diffractograms of La5.4-xPrxMo1-yNbyO12- _are presented on the left, accompanied by the Arrhenius diagram illustrating the conductivity on the right.

Material synthesis involves the freeze-drying method, and characterization includes X-ray diffraction (Rietveld method), X-ray photoelectron spectroscopy, scanning and transmission electron microscopy and complex impedance spectroscopy. The symmetry of the materials (cubic or rhombohedral) is influenced by synthetic conditions and composition, compositions with higher praseodymium content exhibit a consistent cubic fluorite-type structure. Optimal conductivity is observed in a nitrogen atmosphere for compositions with high praseodymium content due to the presence of the Pr4+/Pr3+ pair. In a reducing atmosphere (wet 5%H2-Ar), conductivity significantly decreases due to the reduction of Pr4+ to Pr3+.

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Jueves, 18 de enero 18:48 – 19:00

Transmission electron microscopy study of porous metal-organic frameworks (MOFs)

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Metal-Organic Frameworks (MOFs) are an emerging family of crystalline and porous micro/nanomaterials composed of a extended network comprising metallic centres coordinated to organic ligands.[1] MOFs feature high porosity, crystallinity, and chemical tunability at multiple length scales what allows to use them in many different technological applications such as gas storage/separation, catalysis, drug delivery, chemical sensing or water treatment. [2]

The recent progression in transmission electron microscopy (TEM) and its application to MOF structure–property relationships have improved how to design their synthesis according with the application to be targeted.[3] However, MOF's structure is usually very sensitive to the electron beam employed in TEM so low-dose, cryogenic and specific image detector must be employed to prevent structural damage or artifcats.

In this word we present an electron microscopy characterization by TEM, Scanning TEM and Energy-Dispersive of X-ray (EDX) of different types of MOFs. As an example, the synthesis of UiO-66-NH_2 crystals smaller than 100 nm (Figure) is modulated through the use of halides (Cl^-, Br^- and I^-) but keeping the crystalline structure and functional properties as biocompatible carriers. The porosity and thickness of nanoMOFS is also study in the MOF family PCN-224 to be employed as core-shell nanocomposites to deliver metal nanoparticles.

We discuss the use of TEM in combination with other structural and characterization techniques (XRD, TGA, BET) to optimize the synthesis conditions and to protect the quality of MOFs.

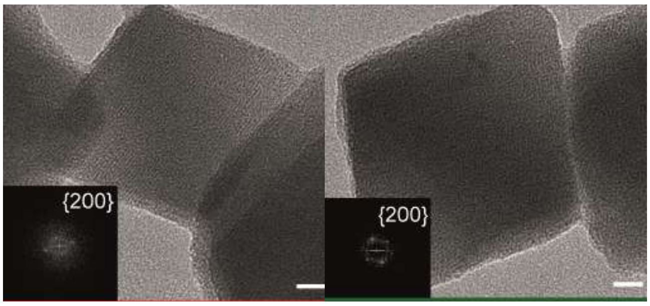

Figure 1. TEM images of (left) UiO-66-NH_2:Cl– and (right) of UiO-66-NH_2:Br. The insets show their corresponding FFT. Scale bars correspond to 10 nm.

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Sesión 5

Viernes, 19 de enero 11:30 – 11:50

Understanding a Ferroelectric Hysteresis cycles in La2-xErx(MoO4)3 solid solutions

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The solid solution La2-xErx(MoO4)3 is a family of compounds that crystallize in the ferroelectric phase of gadolinium molybdate. Some members of this family are considered to be improper ferroelectrics (I.F.). The profile of the ferroelectric hysteresis cycles performed on these materials (I.F.) shows, in general, an unsaturated cycle (known as "banana") with small polarization values, which could be attributed to dielectric losses in the material.

In this work, a comprehensive analysis is presented, to differentiate between proper ferroelectrics, improper ferroelectrics and linear dielectrics, through the analysis of hysteresis cycles, current density and Positive-Up-Negative-Down (PUND) method. The synthesis of the three solid solutions of La2-xErx(MoO4)3 with x = 0.85, 1 and 1.15 has been carried out by solid state reaction from the mixture of the powder reactants La2(MoO4)3 and Er2(MoO4)3 in the corresponding stoichiometric proportions, after compacting the powder and subjecting them to their respective heat treatments. The purity of the three synthesized phases is confirmed by X-ray powder diffraction (XRD). The results obtained confirm that the three solid solutions show a ferroelectric behavior, being La0.85Er1.15(MoO4)3 the one with the highest polarization value (Fig.1). These results show the usefulness of the analysis to discriminate ferroelectric and non-ferroelectric behaviors.

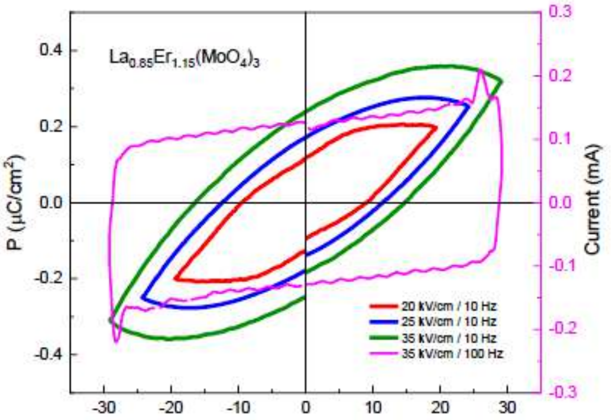

Figure 1. Hysteresis cycle and current density loops at room temperature (293 K) at 10 and 100 Hz, respectively, under the application of different electric fields for a sintered La0.85Er1.15(MoO4)3 pellet.

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Viernes, 19 de enero 11:50 – 12:10

¡No imagines los cristales! Comprender las estructuras con modelos 3D y realidad virtual

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Dentro de un proyecto de innovación docente realizado en el Grado de Química de la Facultad de Ciencias de la Universidad Autónoma de Madrid en el curso 2022-23, se diseñaron y llevaron a cabo diversas actividades para facilitar a los estudiantes de segundo curso el aprendizaje de las características estructurales de numerosas sustancias sólidas que se tratan en las asignaturas de Química Inorgánica I y II.

En esta comunicación se detallarán las herramientas, materiales y tecnologías que los alumnos utilizaron para visualizar en 3D numerosos sólidos de manera virtual, así como para construir modelos con kits de bolas y varillas (Figura 1, izquierda).

Figura 1. Actividades llevadas a cabo con los alumnos de 2° Curso de Grado en Química. Izquierda: uso de modelos físicos y virtuales en el aula. Derecha: sesión práctica en el laboratorio de DRX Monocristal SIdI-UAM.

El uso didáctico de modelos 3D físicos[1] y virtuales[2-6] permitió que los estudiantes asimilaran conocimientos y conceptos de las asignaturas del grado como los tipos de empaquetamiento, el polimorfismo, la esfera de coordinación o las clases de isomería. Se ha comprobado que estos conceptos a menudo resultan complicados de entender mediante las metodologías docentes clásicas (imágenes 2D en libros o en presentaciones en pantalla en el aula).

Una parte importante del proyecto fue el acercamiento de los estudiantes a la técnica experimental más utilizada en caracterización estructural, la difracción de rayos X, con una sesión realizada en el Laboratorio de DRX de monocristal de la UAM (ver Figura 1, derecha). En dicha sesión se analizaron los cristales obtenidos por los propios alumnos en las prácticas de las asignaturas, lo que supuso una introducción singular a esta técnica cuyo estudio no está actualmente incluido en ninguna asignatura del plan de estudios.

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Viernes, 19 de enero 12:10 – 12:30

Polymorphism and re-entrant phase transition in NaSrPO$_4$

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The crystal chemistry of $A^{I}B^{II}XO_4$ (A^{I} = alkali ion, B^{II} = alkali-earth ion, X = P,V, As) is very rich and has been widely investigated [1]. We have been investigating the crystal structures [2,3] and magnetic properties of some compositions within the $A^{I}B^{II}XO_4$ series [4]. The research activity related to these materials is motivated by their ferroelectric, ferroelastic properties and possible applications for LEDs [1,5]. Within the rich $A^{I}B^{II}VO_4$ sub-family (X = V), we have found the larnite structure with NaSrVO$_4$ [3]. In this contribution, we are investigating its counter phosphate composition.

We present the synthesis, crystal structure and polymorphism of NaSrPO$_4$. Surprisingly, this material exhibits a complex structure (31 atoms in the asymmetric unit-cell) at RT and 4 phase transitions as function of temperature. One Na atom is under bounded and we believe responsible for the rich polymorphism as function of temperature (see Fig. 1). Additionally, NaSrPO$_4$exhibits a re-entrant phase transition before reaching a hexagonal paraelasticphase at high temperature.

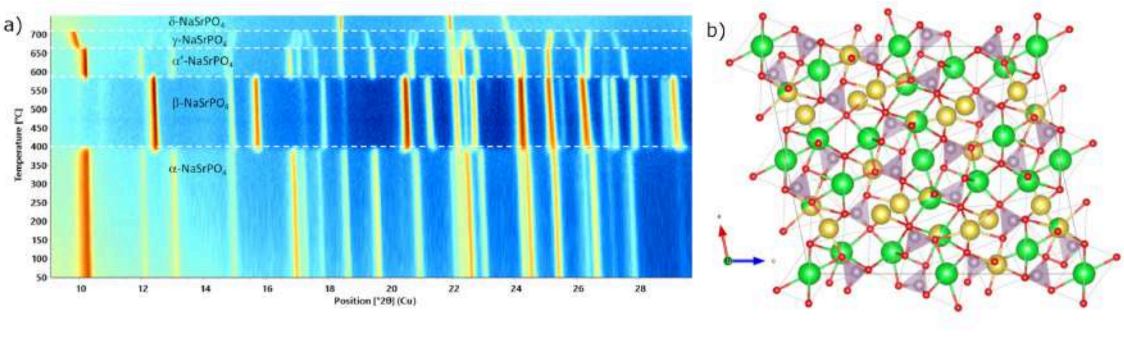

Figure 1: (a) Temperature phase diagrma of NaSrPO$_4$. (b) Crystal structure of the a re-entrantpolymorph.

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Viernes, 19 de enero 12:30 – 12:50

Molibdita nano y microcristalina: Estudio y potencial de los materiales 2D

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Los óxidos de metales de transición 2D (TMO), son atractivos debido a algunas ventajas específicas. Se trata de semiconductores, pero son menos contaminantes y ofrecen un gran potencial para ajustar sus propiedades electroópticas variando su estequiometría. En particular, MoO_3 es transparente y muestra una banda prohibida amplia (>3 eV).

Además, el α-MoO3 ortorrómbico posee la conocida estructura cristalina en capas de MoO3 que ofrece la posibilidad de crear morfologías bidimensionales (2D). [1] En este contexto, 2D MoO3 ha mostrado propiedades extraordinarias, como la propagación anisotrópica de polaritones,[2] y es un material ideal para aplicaciones electrónicas de alta potencia y optoelectrónica de longitud de onda corta.

Actualmente, la mayor parte del trabajo en semiconductores 2D todavía se realiza utilizando pequeñas escamas obtenidas de monocristales exfoliados mecánicamente; sin embargo, no hay duda de que será ventajoso depositar grandes estructuras 2D ya que esto tendrá un tremendo impacto tanto para la manipulación como para la integración. de estos materiales [3].

En contexto, mostramos la preparación exitosa de películas láminas de espesor nanométrico formadas por cristales 2D de MoO3 mediante un proceso basado en deposición por láser pulsado en. Posteriormente, las películas se recocen en aire hasta 250° C mientras se sigue su caracterización estructural, composicional y óptica.

Cuando la temperatura alcanza los 250°C comienza un claro cambio en la estructura y las propiedades ópticas, relacionado con la formación de monocristales de α-MoO3 rectangulares fácilmente observables mediante microscopía óptica. Se ha confirmado una caracterización completa de la morfología, estructura y estequiometría mediante análisis de difracción de rayos X (Fig. 1), espectroscopia Raman, AFM y microscopía electrónica de transmisión, entre otros.

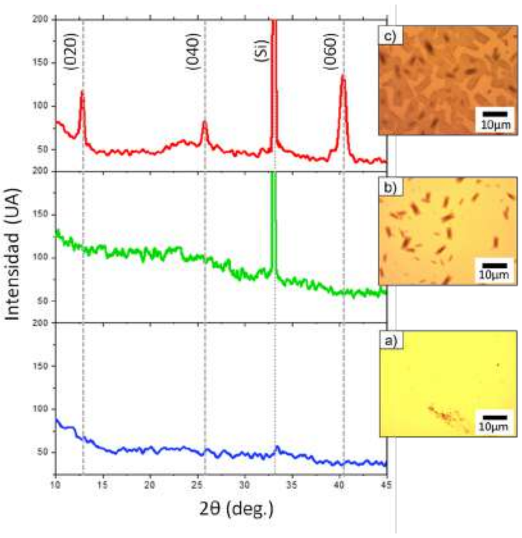

Figura1: Espectros de difracción de rayos X de las muestras a lo largo del calentamiento térmico desde la recién depositada (azul), tras una hora de tratamiento térmico a 250°C (verde) y tras cuatro horas de tratamiento térmico a la misma temperatura (rojo).

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Abstracts Pósters

Póster 1

Structural evidences of native-like aggregated species in the acylphosphatase family

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Acylphosphatase (AcP, EC 3.6.1.7) is a small model protein conformed by a ferredoxin-like fold, profoundly studied to understand protein folding and aggregation processes [1]. Numerous studies focused on the aggregation and/or amyloidogenic properties of AcPs used as model system suggest the importance of edge-β-strands in the process [2]. In this work, we show the monomeric and intertwined dimeric structures of *Escherichia coli* AcP (EcoAcP). Our domain-swapped EcoAcP structure represents the first 3-D structural evidence of native-like aggregated species for any AcP reported to date, providing clues on molecular determinants unleashing aggregation [3].

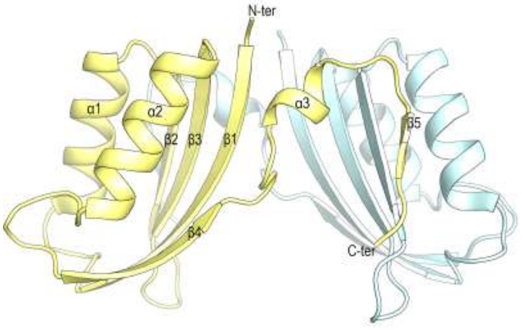

Figure 1. Intertwined EcoAcP dimer, where the C-terminal β-strand (β5) is swapped between two protomers.

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Póster 2

Targeting IPK metabolism via Crystal fragment screening.

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Inositol Polyphosphates (InsP) are a group of molecules essential for 79ellular function. They participate in processes such as cell signaling, protein stabilization and regulation, metabolic coordination of growth processes, cellular homeostasis, etc. Additionally, their role is crucial in cancer and certain metabolic pathologies like type II diabetes [2]. The synthesis and regulation of InsPs are mediated by enzymes with kinase and phosphatase activities. Among the former, there is a family of proteins with conserved structures, the InsP kinases or IPKs, responsible for the production of essential InsPs and, consequently, the regulation of their functions in the cell [1,2].

Our research group studies the molecular mechanisms underlying the phosphorylation and synthesis of different InsPs mediated by IPKs, focusing on designing small molecules capable of interfering with their function. The IPKs exhibit a two-lobed folding, N- and C-terminal, involved in nucleotide recognition. A third lobe inserted into the C-terminal provides specific elements for InsP recognition. We have produced multiple IPK crystals for fragment screening using compound libraries at the Xchem facility (Diamond Light Source synchrotron), allowing us to find promising molecules targeting both the ATP and InsP binding sites. Currently, we have about 50 'hits' (Figure 1) that are being analyzed for designing new molecules able to specifically inhibit the IPK family and with improved affinities.

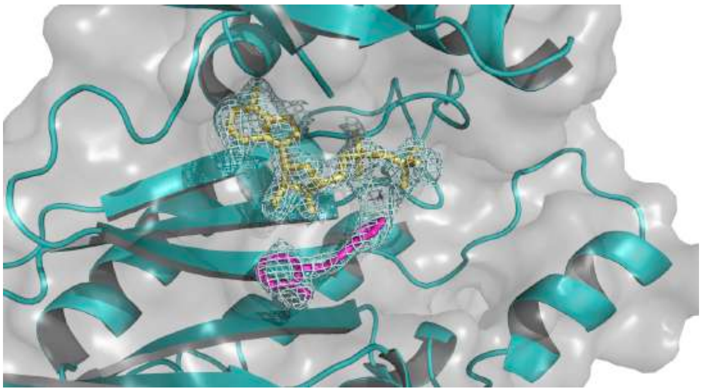

Figure 1. Structure of an IPK in complex with the nucleotide and a new ligand.

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Póster 3

Neutron diffraction studies of proper magnetic and structural incommensurability on a metal-organic coordination polymer

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In the present communication we describe of the structural and magnetic phase transitions of $(CH_3NH_3)[Ni(COOH)_3]$ perovskite-like metal–organic compound.[1] Below the magnetic order temperature the magnetic structure can be described by an unprecedented incommensurate magnetic phase. It crystallizes in the orthorhombic *Pnma* space group at room temperature, and below 84 K the appearance of new reflections close to the main reflections suggests the occurrence of an incommensurate phase. The new reflections can be indexed with a wave-vector with an incommensurate component along the *c*-axis ($\mathbf{q} = 0.1426(2)c^*$). The nuclear structure was determined using the super-space group formalism on the *Pnma*(00)0*s*0 space group. This incommensurate phase remains unchanged with the decreasing of temperature up to ca. 2 K.

The magnetic susceptibility data show that $(CH_3NH_3)[Ni(COOH)_3]$ compound exhibits an antiferromagnetic behaviour below 34 K with an small ferromagnetic component derived from an spin-canting.[2] Single crystal and powder neutron diffraction have been used in this work to confirm the long range magnetic order, and the coexistence of nuclear and proper magnetic incommensurability below [see fig 1].

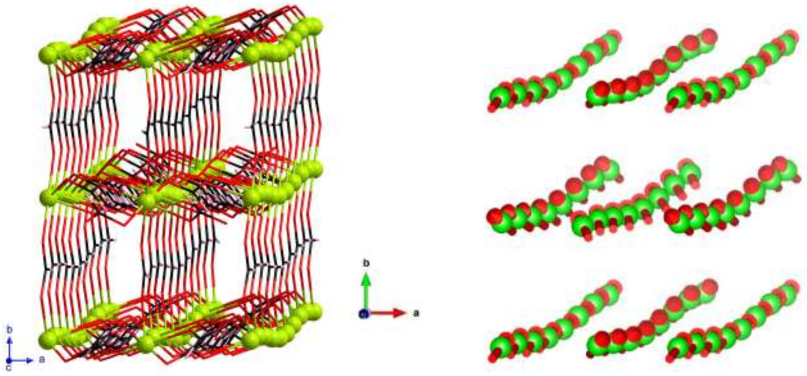

Figure 1. Left. View of $(CH_3NH_3)[Ni(COOH)_3]$ modulated structure at 40K. Right. View of the refined magnetic moments of Ni(II) in the *Pn'ma'*(00)0*s*0 magnetic super space group.

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Póster 4

Procesos de intercambio de electrones en complejos nitruro polimetálicos de titanio

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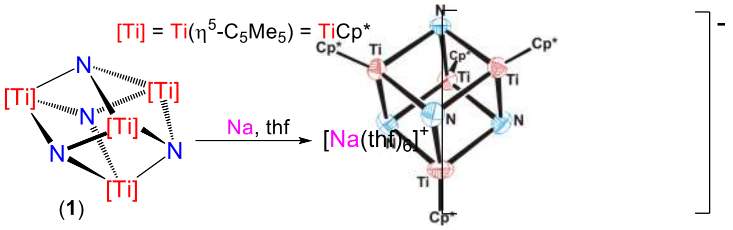
Las especies nitruro polimetálicas de los metales de transición se proponen como intermedios en la fijación biológica e industrial de dinitrógeno. Esta activación supone el intercambio de varios electrones entre la molécula de N_2 y el catalizador, por lo que es interesante estudiar los procesos de reducción y oxidación en los que intervienen estos sistemas multimetálicos.

En este contexto, nuestro grupo está investigando la reactividad del metalocubano $[\{Ti(^5-C_5Me_5)(_3-N)\}_4]$ (**1**) con diferentes agentes reductores. Así, la adición de $[K\{C_5Me_5\}]$, en presencia de un éter corona, da lugar a la incorporación de un electrón al sistema polimetálico y la formación de un compuesto iónico,[1] mientras que la utilización de los complejos hidruro $[M(^5-C_5H_5)(CO)_3H]$, M = Mo, Cr,[2] o dos equivalentes de aminoborano[1] implica la hidrogenación de uno de los grupos nitruro. En esta comunicación, se presenta la reactividad de **1** y otros azametalocubanos similares de titanio con distintos reductores, como arena de sodio (Esquema), y la caracterización estructural de los productos de reducción que se obtienen.



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Póster 5

Study of Adaptive Behavior of a New Bismuth Metal-Organic Framework During the Interaction with Guest-Molecules by Single Crystal X-ray Diffraction

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The use of bismuth as a metal center for the preparation of metal-organic frameworks, MOFs, is scarce as compared to other metal elements, despite the potential of this element in terms of chemical and structural versatility. The design of new bismuth-based MOFs is of high interest, both from fundamental and applied point of view. On one hand, the large and variable coordination number of bismuth results in multiple possible coordination modes with organic linkers to create different types of inorganic secondary building units (SBUs). On the other hand, its natural abundance, low toxicity, and Lewis acidity offer great potential for the use of bismuth MOFs in different applications. Here, we present the synthesis and characterization by single-crystal X-ray diffraction of a new Bi-MOF named BiPF-7, with presence of different adsorbed molecules in its porous framework. The structure of BiPF7 consists of two different inorganic SBUs made up of two bismuth cations, and with a 3:1 stoichiometry. These SBUs are connected through the organic linker 4,4',4'',4''-methanetetrayltetrabenzoic acid (MTBA). A single crystal X-ray diffraction study has been carried out at the X-ray diffraction facility of the Materials Science Institute of Madrid, with a Bruker Venture D8 diffractometer equipped with three (Cu, Mo, Ag) diamond-type microfocused sources and a

Photon III detector. Through this study involving the analysis of crystals with presence of different guest species, it was found that the presence of specific molecules near one of the SBUs leads to a concerted atomic response in the second SBU, where there is a lengthening of the distance between the metal atoms and a rearrangement of the coordinated water molecules, this process being reversible (Figure 1). Therefore, this new porous material has been shown to have a high adaptability involving structural changes in it that do not directly intervene in guest bonding.

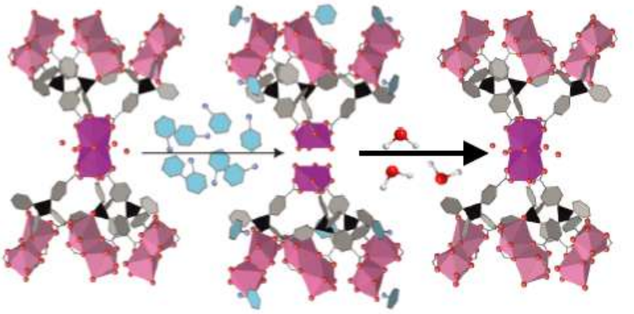

Figure 1. The adaptability of BiPF-7 during the uptake of guest molecules is enabled by the structural changes that take place in SBUs (highlighted as purple polyhedra) that are not directly involved in the binding.

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Póster 6

Proton conductivity properties of novel tin(II) phosphonates

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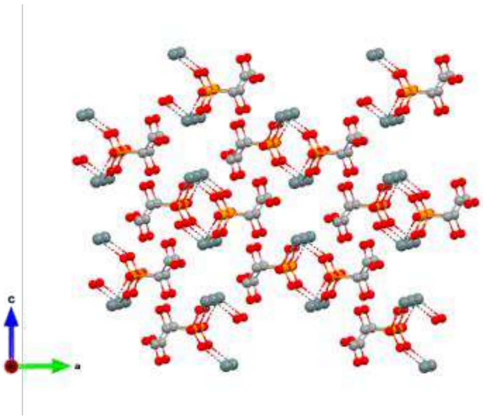
Metal phosphonates (MPs), a subclass of coordination polymers, may exhibit acidic groups such as P-OH, SO3H, COOH, N+-H, etc. Combining these features with interesting metals make them highly appealing in the field of fuel cells and electrolysers as potential proton conductors [1,2].

In this communication, we report the synthesis, characterization, and proton conduction properties of a series of Sn2+ hydroxyphosphonoacetates with a different water content, obtained at RT, 80 °C and 150 °C. The anhydrous 150 °C-synthesized phase crystallizes in the monoclinic system, s.g. P 21/n. Its crystal structure, solved ab initio from laboratory powder X-ray diffraction data, is composed of distorted pyramidal Sn2+ polyhedra connected through the oxygen atoms from the phosphonate, hydroxyl, and carboxylic groups of the ligand (Figure 1). The proton conductivity was found to increase with the water content. A study of the possible effect of hydrated amorphous phases on proton conductivity is underway.

Figure 1. View of the crystal structure of SnC2H3O6P (SnHPAA)



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Póster 6

Multivariate metal-organic frameworks as adsorption materials in analytical applications

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Metal-organic frameworks (MOFs) are crystalline coordination polymers composed by a metal center (or metal cluster) coordinated by organic ligands. The geometry and structure of the crystal lattice vary depending on the selection of these secondary units. The MOF design process allows the creation of a wide variety of different materials. This heterogeneity does not end there. In fact, since 2010, more complex compounds called multivariate MOFs (MTV-MOFs) have been described. MTV-MOFs are formed by a metal center combined with two or more types of ligands. These materials allow for greater spatial structural diversity, as well as some heterogeneity, without altering the topology of the crystal. These changes seek a higher degree of functionality in the characteristics of the material, even improving the properties of the original structure. MOFs have been used for the extraction of analytes with interesting properties or with potential harmful effect on society (e.g. drugs, pollutants...) from environmental, biological, and food matrices samples.

In this study, Al(III) MTV-MOFs have been prepared using two different ligands, fumarate and mesaconate, which produce the well-known MIL-53(Al)-FA and CIM-80(Al) MOFs, respectively. The former has the structure of MIL-53 with rectangular pores, and it may exhibit a breathing phenomenon, while CIM-80(Al) has the MIL-68 structure with triangular and hexagonal pores. The objective of this work is the preparation of MTV-MOFs with different mesaconate:fumarate rates, and the evaluation of the ligand influence on the crystalline structure and the adsorption properties of the resulting MOF. The resulting materials were properly characterized, and the adsorption kinetics of the MOFs towards the extraction of different organic pollutants from water are also evaluated, thus gaining insights about the performance of this type of MOFs for their use in analytical applications.

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