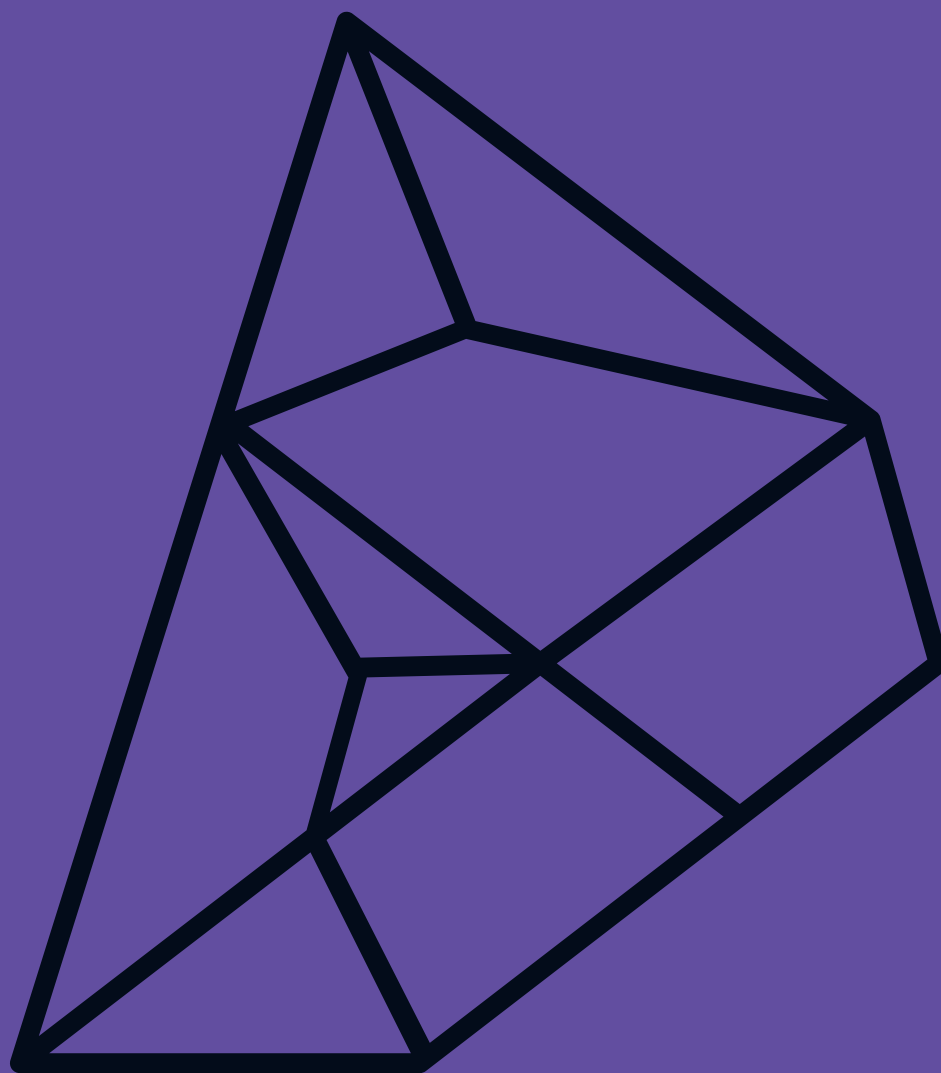

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XXIX SIMPOSIO DEL GRUPO ESPECIALIZADO
DE CRISTALOGRAFÍA Y CRECIMIENTO CRISTALINO

2021

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19-22 de enero de 2021*

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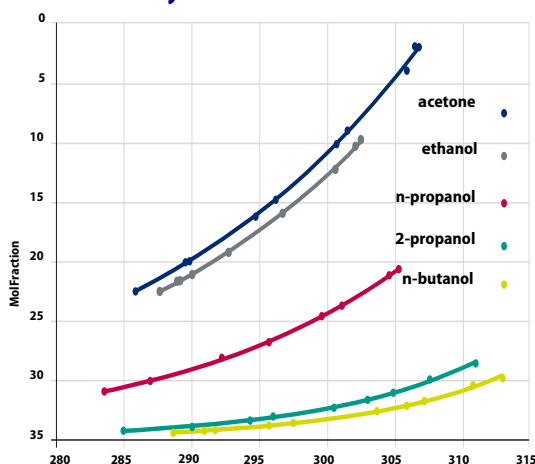
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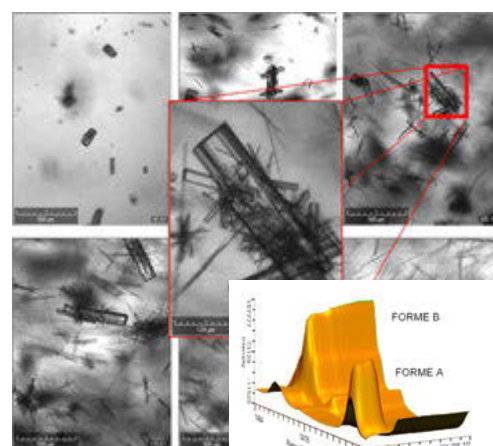
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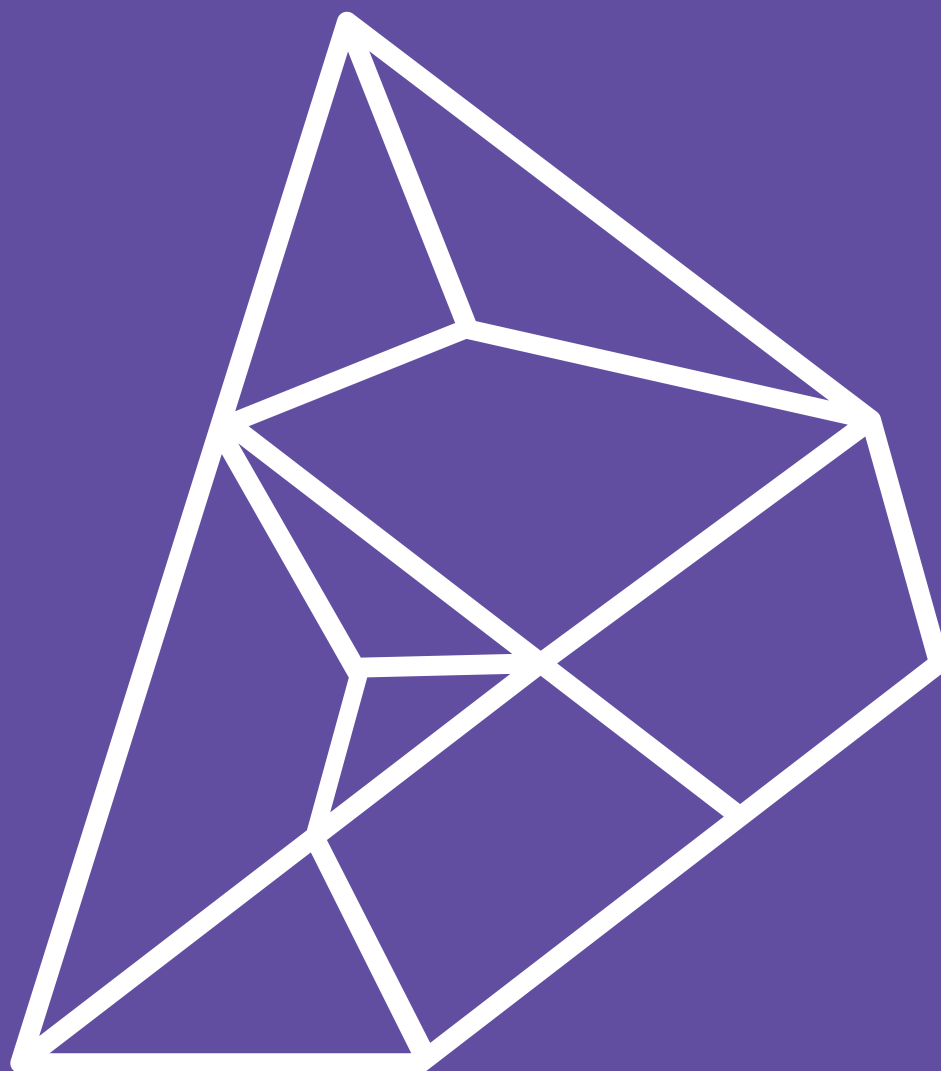
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FROM MULTIFUNCTIONAL MOLECULAR CRYSTALS TO HYBRID ELECTRONIC DEVICES

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Abstract: Using a molecular approach, crystal engineering allows the design of functional materials exhibiting electrical, magnetic or optical properties of interest. Some successful examples are the molecular conductors and superconductors, the molecule-based magnets, or the molecular materials exhibiting non-linear optics. Since these materials are made by assembling molecules, a hybrid approach that mixes two or more molecules in the same crystal may provide in a further step the possibility of creating multifunctional materials with coexistence or even coupling of properties, a possibility that is difficult or impossible to achieve in inorganic solids.

In this talk I will illustrate in the first part some possibilities offered by this hybrid approach. In a second part, I will show that this approach can also be used to fabricate molecular-based devices of interest in electronics, spintronics or information technology.

Key words: Multifunctional Molecular Crystals, Hybrid Electronic Devices

Reference:

Coronado, E. (2020). Molecular magnetism: from chemical design to spin control in molecules, materials and devices. *Nature Reviews Materials*. 5, 87-104.

3D ELECTRON DIFFRACTION ACROSS NANOCRYSTALLOGRAPHY

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Abstract: 3D electron diffraction is a rapidly developing technique which is able to provide single crystal diffraction data suitable for structure solution on nanocrystals. All the different ways for collecting 3D ED data will be discussed with a specific focus on how to tune the method depending to the sample characteristic. It will be shown how, as soon as the sample become more beam sensitive, the data collection method should change to favor speed instead of precision and completeness. Thanks to the development of fast and very sensitive single electron detectors that are radiation hard, it is possible to collect a wide angular range of reciprocal space in less than one minute and with total electron doses of few electrons per Å⁻². This has extended the field of application of 3D ED to very sensitive samples like organics nanocrystals and proteins. During the lectures specific examples of structures solved using 3D ED will be shown. These examples will cover topics of inorganic materials science, like nanoparticles of perovskite structure or zeolites, but also organic samples with possible pharmaceutical applications.

Key words: Nanocrystallography, 3D electron Diffraction

GAS CLATHRATES IN THE SOLAR SYSTEM AND THEIR ASSOCIATED GEOLOGICAL ACTIVITY

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Abstract: The goal of this conference is to show the significance of clathrate hydrates in both, the habitability and the geological evolution of the planetary bodies of the solar system. Special attention is paid to their presence in the ice moons of the giant planets, where the habitable zone is below the surface and high pressure and low temperature conditions dominate (Prieto-Ballesteros et al. 2015).

The study of these minerals is mainly performed by laboratory experiments, in which planetary conditions are simulated, computational modelling, and examination of terrestrial analogues. Results of these investigations reveal important planetary implications such as: 1) Clathrate hydrates could play a key role in the cycle of elements of these moons, such as carbon. The formation of the H₂O crystalline framework of these minerals allows retain molecules like methane in planetary crusts (Izquierdo et al. 2020). 2) The formation of clathrate hydrates in planetary endogenous aqueous systems influences the evolution of cryomagmatic fluids, which can eventually reach the surface, depending on the geochemical and geophysical characteristics of the ice moon (Bonales et al. 2013, Muñoz-Iglesias et al. 2014). 3) The catastrophic dissociation of clathrate layers within ice moons can be easily linked to volume changes in the crust, and subsequently to processes forming particular geological structures such as chaotic terrains (Muñoz-Iglesias et al. 2019).

Key words: clathrate hydrates, ice moons, cryomagmatism, solar system chaotic terrains

Acknowledgments: This work was supported by the Spanish MINECO projects ESP2017-89053-C2-1-P and PID2019-107442RB, and the AEI project MDM-2017-0737 Unidad de Excelencia “María de Maeztu”.

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DRUG DISCOVERY: THE POINT OF VIEW OF A CRO

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Abstract: The discovery of new drugs is a long and risky process that requires the preparation and evaluation of thousands of compounds in a series of design-synthesis-biological assay iterations. Biology plays a crucial role not only in regard to the discovery of a target and its role in the disease, but also in aspects related to the design of new compounds. Collaboration between structural biology and organic synthesis experts in the early stages of discovery through the use of computer tools and development of structural models is critical for the successful declaration of new candidates. This talk describes briefly the process of discovery and the role of structural biology as a differentiating element.

Key words: Drug Discovery, Organic Synthesis, Hit to Lead, Lead Optimization



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LA EFICACIA DE LOS INHIBIDORES DE LA ALDOSA REDUCTASA SE VE AFECTADA POR EL ESTRÉS OXIDATIVO INDUCIDO BAJO LA IRRADIACIÓN DE RAYOS X

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Resumen: La aldosa reductasa humana (hAR, AKR1B1) ha sido estudiada como diana terapéutica des del 1980 por su rol en las complicaciones secundarias de la diabetes. Desde entonces, ya se conoce la existencia de una isoforma forma activada de la enzima localizada en células de pacientes diabéticos. Dicha forma activada muestra una marcada insensibilidad para los inhibidores probados en ensayos clínicos y se especula que su existencia podría ser la causante de que muy pocos fármacos hayan podido superar todas las fases clínicas y ser comercializados. En este estudio, se prueba la conversión de la hAR nativa hacia su forma activada mediante la irradiación de la enzima con rayos X, simulando en su entorno condiciones de estrés oxidativo comparables a las que se generan en una célula. Tras la irradiación, la actividad de la proteína se vio incrementada hasta un 150% y la potencia de cuatro de los inhibidores de hAR más conocidos decayó antes de que el daño por radiación global aparezca. El comportamiento catalítico de la forma activada reportado en la bibliografía también se puede reproducir con la enzima irradiada, obteniendo valores de K_M mucho más grandes que para la forma nativa y valores constantes para la k_{cat} . Consistentemente, la tétrada catalítica no mostró ninguna modificación para la forma irradiada, como así demuestran los experimentos de cristalografía llevados a cabo. La única diferencia estructural relevante catalíticamente que se observa ha fue la conversión de la Cys298 hacia serina y alanina. Para dar respuesta a todos estos cambios estructurales, se ha propuesto un mecanismo que se inicia en la captura electrónica y que acaba dando como resultado la forma activada de la hAR. Como corolario, el trabajo sugiere que el diseño de inhibidores de hAR no debe ser basado en la forma nativa de la proteína, sino que puede ser basado en la forma activada obtenida con la irradiación de rayos X. Además, dado que las

especies reactivas producidas bajo condiciones de irradiación son las mismas que las producidas bajo estrés oxidativo, el método de irradiación descrito se debería poder aplicar también a otras proteínas relevantes bajo ambientes de estrés oxidativo.

Palabras clave: aldose reductase, daño por radiación, estrés oxidativo, diabetes

Referencia:

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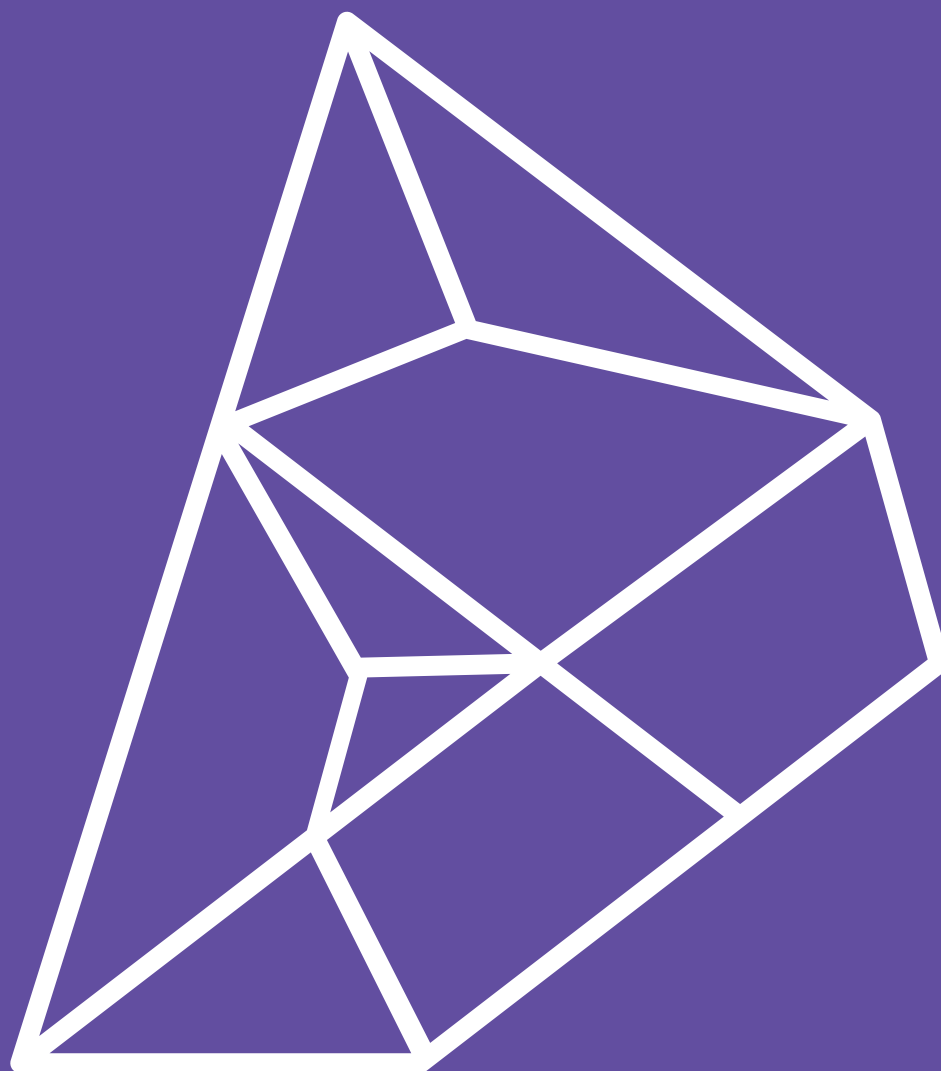
MS1- Aproximaciones del siglo XXI a la determinación estructural

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TOTAL NEUTRON SCATTERING AND THE STRUCTURE OF DISORDERED MATERIALS

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Abstract: The technique of total scattering uses the total scattered signal and not only the coherent elastic one. This is the main difference with the diffraction technique that only analyses the elastic coherent contribution and which is widely used in crystallography. In this talk, this technique will be introduced in a pedagogical way, focusing on the neutron scattering, which is particularly useful for the determination of the structure of disordered systems. These systems cover a large variety of materials, like gases, liquids, glasses, amorphous or even partially disordered materials, like nanoparticles, presenting short-range order. The total scattering technique gives information on correlation functions containing information on correlation distances, which for disordered materials overlap avoiding a clear interpretation of the experimental data. In some circumstances, the use of the isotopic substitution allows the extraction of particular correlation distances. Examples of application will be given to illustrate the usefulness of this technique.

Key words: Total Neutron Scattering, Disordered Systems, Short-Range Order, Isotopic Substitution, Pair Distribution Function

Acknowledgments: If authors wish to acknowledge funding bodies and other parties, the acknowledgments may be placed in a separate section at the end of the text, before references.

References: please follow the examples below

Cuello, G. J. (2008) Journal of Physics: Condensed Matter 20 (24), 244109.

DETERMINATION OF ABSOLUTE STRUCTURE OF INORGANIC AND ORGANIC STRUCTURES WITH 3D ELECTRON DIFFRACTION

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Abstract: The success of electron crystallography as a standard tool for structure determination was strongly supported by the use of precession-assisted 3D electron diffraction (3DED). The visible gap between the quality of structure models based on X-ray diffraction and electron diffraction is mainly due to the implementation of the kinematical approximation in the refinement step because in the case of electron diffraction, measured reflection intensities strongly deviate from kinematical intensities due to dynamical effects like multiple scattering.

We developed a data reduction and refinement routine applying the dynamical theory of diffraction, with which very accurate structure models can be determined, including the identification of partially occupied hydrogen positions, reliable displacement parameters and the absolute structure. This method works essentially for any class of materials, including minerals, zeolites, intermetallic compounds and pharmaceutical compounds.

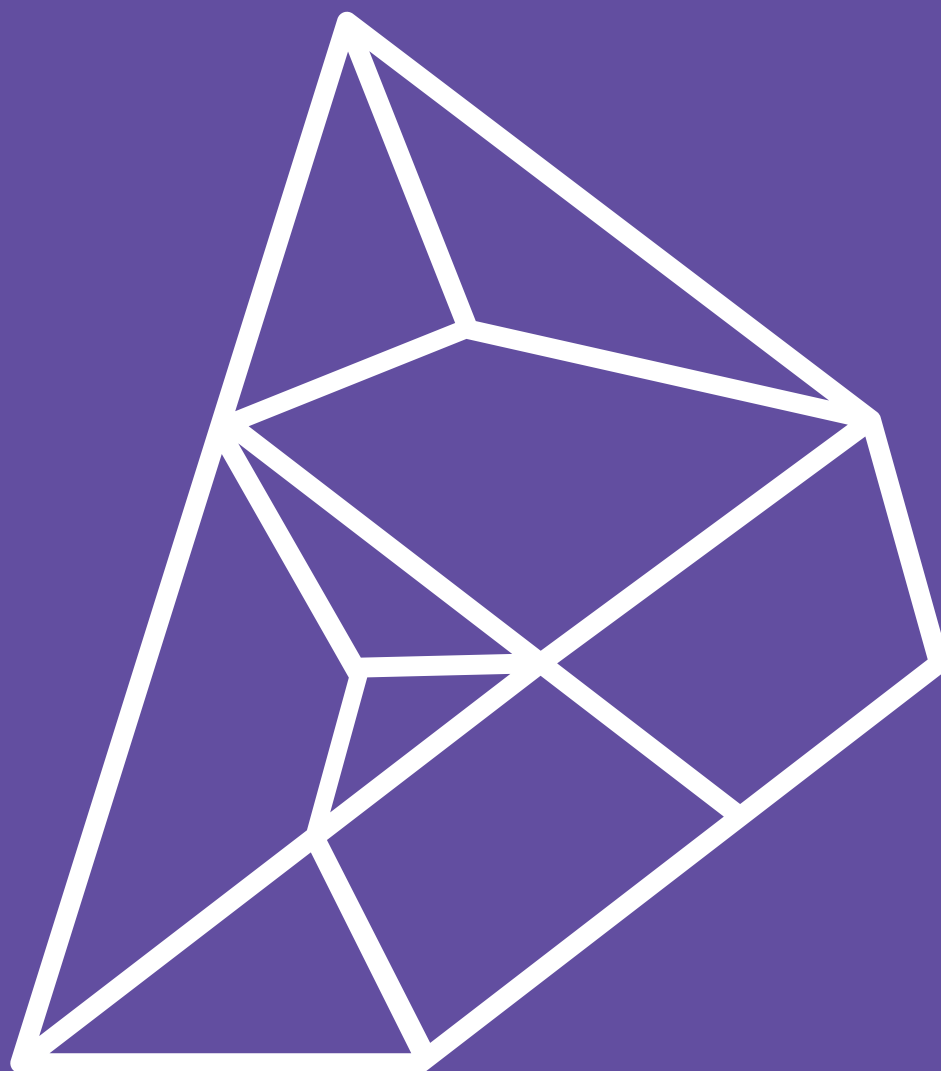
The method was tested on different data sets and measurement routines collected with different transmission electron microscopes around the world and thus is ready to be implemented in any electron crystallography laboratory. Especially the determination of the absolute structure from diffraction data is very useful in scientific and industrial applications, which can only be identified if the dynamical diffraction theory is used.

Key words: absolute structure, dynamical structure refinement, 3DED, MicroED

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ELECTRON DIFFRACTION AND NANOCRYSTALLOGRAPHY: A DEVICE DEDICATED TO THE CRYSTALLOGRAPHY COMMUNITY

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Abstract: After the Science nomination for “Breakthrough of the year 2018”,^[1,2] 3D-Electron Diffraction (3D-ED) using the continuous rotation method and X-ray crystallographic software, is gaining a lot of attention. In the past year many achievements using electron diffraction techniques have been made in the fields of organic molecules, polymorphism, material sciences, geological sciences, natural products, energetic materials, bio-molecules and many others.^[2,3] Such experiments are done in a (modified)-Electron Microscope. Though the realization of such experiments still requires plenty of expertise and efforts and it can not be applied on daily bases. Pioneers in the field of Electron Diffraction,^[4] all agree that a dedicated device for the realization of such experiments, would be of great advantage to the crystallographic community. Though such a device doesn’t exist (up to now) at all. Therefore, it is a necessity that such a device could be made available for the realization of this exciting field of nano-crystallography. Eldico Scientific AG will present a new device which is dedicated exclusively for such purposes. The device, an Electron Diffractometer, is built and optimized for diffraction experiments. Furthermore, it uses exclusively the crystallographic approach (continuous rotation method) and crystallographic software. Experimental examples of the importance of such technique will be showcased too.

Key words: Electron Diffraction, nano-crystallography, electron diffractometer, Eldico Scientific,

Acknowledgments: The authors wish to acknowledge and are grateful for the scientific work and scientific collaboration with Dr. Tim Grüne, Dr. Mauro Gemmi, and Dr. Ute Kolb. The experimental examples presented here are done in collaboration with all of them.

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MICRO-ED: A NEW CHAPTER IN STRUCTURE DETERMINATION OF SMALL MOLECULES AND MACRO-MOLECULES

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Abstract:

During the last few years cryo electron microscopy (cryo-EM) and Single Particle Analysis (SPA) have grown from techniques able to produce low-resolution structures of protein complexes (aka blobology) to tools capable of achieving atomic and quasi-atomic resolution for complexes that nobody could ever solve. This change of paradigm, that lead among other things to the Nobel prize in Chemistry in 2017 (R. Henderson, J. Frank and J. Dubochet), goes under the name of resolution revolution.

In the last year another technique has risen to prominence in field of cryo-electron microscopy: micro-ED. It consists in collecting tilt series in diffraction mode of quickly rotating microcrystal in an electron microscope. Micro-ED holds the promise to produce very quickly high-resolution structure of macro-molecules and small molecules out of crystals in the nanometer range or crystalline precipitate. In this presentation we will show the revolutionary potential of microED^{1,2,3} and we will illustrate which equipment do you need to be successful with both well-established SPA application, and innovative microED technology.

Key words: microED, CetaD,

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SERIAL CRYSTALLOGRAPHY: A DECADE AT FOREFRONT IN STRUCTURAL BIOLOGY

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Abstract: Exceptionally brilliant, femtosecond-pulsed X-ray sources, the X-ray free-electron lasers (XFELs), have brought a new way of conducting crystallography by probing nano/micrometre-sized crystals in a serial fashion. Since the first XFEL, the Linac Coherent Light Source (LCLS), started operation in 2009, the serial femtosecond crystallography (SFX) technique has opened up a new era in structural biology with new and exciting opportunities for the determination of static structures as well as the structural dynamics of macromolecules. The SFX technology has also cultivated new methods for crystallization, and assessment of nano/microcrystals, sample delivery, and data processing.

In addition to its use at XFELs, the serial crystallography (SX) approach can also be done at synchrotron radiation sources and have gained popularity in the past few years up to the point that it can now be a viable alternative to scarce X-ray free electron laser sources. Monochromatic and pink beam experiments have demonstrated the feasibility of serial data collection using micro-crystals at numerous microfocus beamlines at the most powerful synchrotron radiation sources in the world. Upcoming developments in beamline optics, detector technology and synchrotron sources by itself will enable the use of even smaller micro-crystals (<1 μm), the use of larger macromolecules as well as the possibility of conducting mix-and-inject time-resolved studies.

I will be presenting the greatest advances and exciting discoveries in the past 10 years in the emerging technology of SFX at XFELs as well as outline the frontiers of this technology at synchrotron radiation sources.

Key words: X-ray free electron lasers, serial femtosecond crystallography, nano/microcrystals, synchrotrons

Acknowledgments: Programa de Atracción y Retención de Talento de la Comunidad de Madrid (Ref. 2019-T1BMD-1552).

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SYNTHESIS AND PROPERTIES OF NOVEL LANTHANIDE CARBOXYPHOSPHONATES

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Abstract: Metal phosphonates are essentially acidic solids featured by groups such as P-OH, -COOH, etc. The presence of bound and lattice water favors the formation of H-bond networks, which make these compounds appropriate as proton conductors, attractive for proton exchange membranes (PEMs) of Fuel Cells.¹ Moreover, these properties can be enhanced by appropriate modification of the synthesis conditions.²

We report here, general characteristics of three new series of isostructural compounds resulting from the combination of the polyfunctional 5-(dihydroxyphosphoryl) isophthalate acid with lanthanide ions. All compounds were synthesized under hydrothermal conditions and their crystal structures were solved from powder X-ray diffraction data using synchrotron radiation. In contrast with Series III compounds, which exhibit a layered structure, Series I and II present pillared frameworks. All these compounds contain water molecules that contribute to the formation of H-bond networks. Upon exposure to ammonia vapour, from an aqueous solution, solid state transformations are observed which are accompanied of an enhancement of their proton conductivity properties.

Key words: metal phosphonates, coordination polymer, proton-conductivity.

Acknowledgments: This research was supported by MAT2016-77648R and PID2019-110249RB-I00 research grants (Spain) and University of Malaga under Plan Propio de Investigación.

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UNRAVELLING THE LOCAL STRUCTURE OF CATALYTIC FE- OXO CLUSTERS STABILIZED ON THE MOF-808 USING ADVANCED SYNCHROTRON TOOLS

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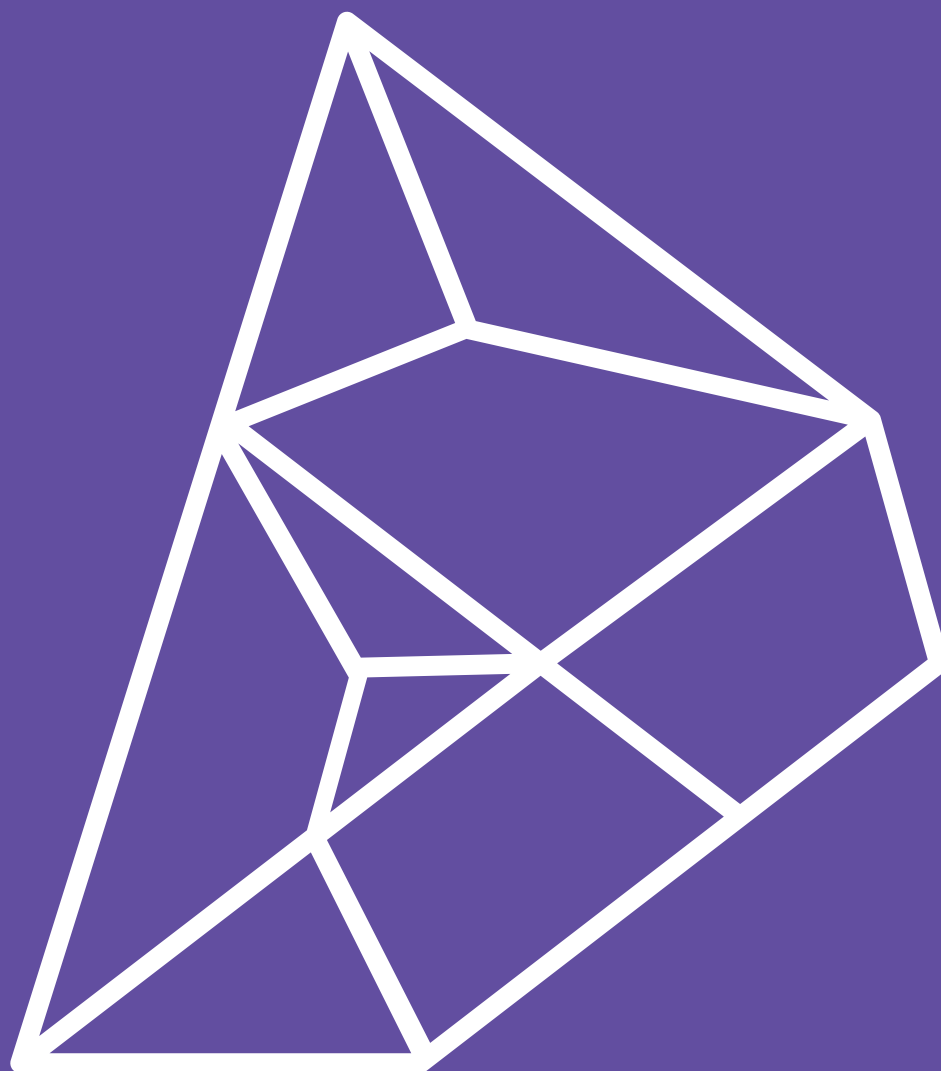
Abstract: Zr(IV) metal organic frameworks (MOFs) materials present a high thermal and chemical stability in water, allowing the applicability in aqueous-based degradation of toxic chemicals processes. However, several processes including the presence of a redox activity metal. In this contribution, we present the solvothermal incorporation of iron-oxo clusters in MOF-808 material at local scale. Detailed synchrotron characterization including pair distribution function (PDF) analyses of X-ray total scattering data and Fe *K*-edge X-ray absorption spectroscopy (XAS) together with density functional theory (DFT) computational modelling are applied to understand the local structural nature of the added redox active iron clusters within MOF-808.

Key words: Metal-organic frameworks, Pair Distribution Function, MOF-808, bisphenol A

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CHARACTERIZATION OF INTERMETALLIC COMPOUNDS IN ALUMINUM-STEEL LASER WELDS BY DIFFRACTION-BASED ELECTRON MICROSCOPY TECHNIQUES

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Abstract: The welding of dissimilar materials such as aluminum and steel is increasingly gaining importance as a strategy to obtain lightweight multi-material assemblies maintaining high toughness and resistance [1]. However, brittle intermetallic compounds (IMCs) are formed at the interface of the joints, and therefore it is necessary to control formation and growth of such compounds in order to optimize the mechanical behavior of the dissimilar joints [2]. The η (Fe_2Al_5) and the θ ($\text{Fe}_4\text{Al}_{13}$ or FeAl_3) phases are the most common IMCs found in aluminum-steel joints [3]. Nevertheless, when Si-based filler materials are used, the presence of ternary Fe-Al-Si has also been reported [4].

In the present work, dissimilar joints of 6061 aluminum alloy and S235 structural steel were generated by means of laser welding using Al-Si-based filler materials. The joints were subsequently characterized by electron diffraction-based techniques, namely electron backscatter diffraction (EBSD), electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). Sample preparation is of extreme importance, and it was necessary to resort to advanced techniques such as Ar ion polishing for EBSD and Focused Ion Beam (FIB) for the TEM analysis.

The EBSD experiments allowed for the identification of a layer of η phase crystals that grow directly at the top of the steel, followed by another layer of smaller θ crystals. Although the presence of a ternary Fe-Al-Si was indicated by previous XRD experiments, its detection via EBSD remained elusive, probably due to its lower occurrence compared to the binary phases and its relatively small grain size. Finally, the SAED and HRTEM analysis of a FIB lamella obtained at the joint interface, allowed for not only the unequivocal identification of the η (Fe_2Al_5) and θ ($\text{Fe}_4\text{Al}_{13}$) phases but also revealed the presence of a ternary $\text{Fe}_4\text{Al}_{17.5}\text{Si}_{1.5}$ phase.

Key words: Dissimilar welding, Intermetallics, EBSD, TEM.

Acknowledgments: This work was partially supported by the Government of Spain (CDTI. CIEN: IDI-20150692), and by Xunta de Galicia (ED431C 2019/23, ED481A 2017/307, ED481D 2017/010, ED481B 2016/047-0).

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COMBINING SINGLE CRYSTAL MONOCHROMATIC AND LAUE DIFFRACTION TO ELUCIDATE INCOMMENSURATE STRUCTURES

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Abstract: The ability of the metal-organic frameworks (MOFs) to combine within the same framework different physical properties have attracted a huge interest in last years. These compounds are a promising approach to obtain multiferroic materials. This is the case of $[\text{CH}_3\text{NH}_3][\text{Co}(\text{COOH})_3]$ perovskite-like metal-organic compound, that presents electric and magnetic order below 15 K.[1] Its electrical behaviour is closely related with several structural phase transitions involving incommensurate structures upon cooling down, that comprise not only the occurrence of small distortions in the 3 dimensional anionic $[\text{Co}(\text{HCOO})_3]^-$ framework but also the reorganization of the $[\text{CH}_3\text{NH}_3]^+$ counterions in the cavities of the structure. This reorganization give rise to an alteration of the hydrogen bond network that modifies the electrical properties. In order to determine properly these changes in the hydrogen bond network, single crystal neutron diffraction measurements are mandatory.

In order to explore the sequence of nuclear phase transitions, we performed neutron Laue measurements on CYCLOPS instrument from RT up to base temperature. After this reciprocal space survey, and with the objective to accurately analyse the temperature dependence of the structural variations, we collected full data sets on the monochromatic D19 diffractometer at selected temperatures. The combination of Laue and monochromatic neutron diffraction has been crucial to determine the structural models on each structural phase, and connect the changes in the crystal structure with the electric behaviour of the sample.[2]

Key words: Neutron diffraction, Laue measurements, Incommensurate structure, Metal-Organic Framework, Structure-properties relationship.

Acknowledgments: The authors acknowledge the neutron beam time provided by ILL at D19 and CYCLOPS instruments.

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D1B EL DIFRACTOMETRO DE NEUTRONES DE LA COMUNIDAD CIENTÍFICA ESPAÑOLA

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Abstract: D1B es un difractómetro de neutrones dedicado al estudio de la estructura nuclear y magnética de materiales policristalinos. Está ubicado en el Instituto Laue Langevin en Grenoble (Francia). Desde el año 1998 es un instrumento gestionado por el CSIC y su homólogo en Francia el CNRS.

Además de informar de las diferentes vías de acceso para realización de experimentos en D1B se presentarán varios ejemplos de estudios realizados recientemente.

Key words: Instrumentación avanzada. Difracción de neutrones.

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MYLAR/KAPTON-BASED MICROCHIPS FOR PROTEIN CRYSTALLIZATION AND *IN SITU* ATOMIC RESOLUTION STRUCTURE DETERMINATION

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Abstract: Sample handling and manipulation for cryo-protection remain up to date critical factors for X-ray structural determination (Broecker *et al.*, 2018). While several microchips for macromolecule crystallization have been proposed during the last two decades to partially overcome manipulation issues, increased background noise, originating from the scattering of chip fabrication materials, limits the attainable resolution of diffraction data (de Wijn *et al.*, 2019). Here we present the conception and use of low-cost, X-ray transparent microchips, for *in situ* crystallization by counterdiffusion technique (Gavira, 2016) and direct data collection. The chips are fabricated by a combination of either OSTEMER-Kapton or OSTEMER-Mylar, materials that produce sufficiently low scattering background to permit atomic resolution diffraction data collection at room temperature. The 3D structural models of lysozyme, thaumatin and glucose isomerase were determined at resolutions close to 1.0 Å. The potential of in-line data merging and scaling of the multiple crystals (Basu *et al.*, 2019) grown along the microfluidic channels is also presented and discussed.

Key words: microfluidics; counter-diffusion; protein crystallization; RT data collection.

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF LOW-VALENT TITANIUM COMPLEXES STABILIZED WITH ALUMINUM/BORON HYDRIDE FRAGMENTS

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Abstract: Low-valent early transition metals are receiving increasing attention due to their implication in catalytic processes involving bond-forming reactions. Recently, we have reported the synthesis of several monocyclopentadienyltitanium(III) dihalide compounds (see references). The treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with lithium tetrahydridoaluminate(III) in toluene at room temperature led to the dinuclear titanium(III) complexes $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}(\mu\text{-X})\}_2]$. The chloride derivative reacted with Lewis bases, as isocyanides or ammonia, to afford titanium(III) adducts.

In this communication, we will describe the synthesis and structural characterization of new low-valent half-sandwich titanium complexes stabilized with aluminum or boron hydride fragments. These compounds have been prepared by reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{Me}$) with LiEH_4 ($\text{E} = \text{Al}, \text{B}$) or $\text{BH}_3(\text{thf})$, and their structures have been elucidated by a combination of theoretical and experimental methods, including X-ray diffraction determinations. As example, the treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ with LiAlH_4 in tetrahydrofuran leads to the hydride-bridged heterometallic complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-H})\}_2\{(\mu\text{-H})_2\text{AlCl}(\text{thf})\}_2]$ (see Figure 1a). Density functional theory calculations reveal an open-shell ground state with a titanium-titanium bond and therefore can be described as a titanium(II) species. The theoretical analyses also show strong interactions between the Ti-Ti bond and the empty *s* orbitals of the aluminum atoms (see Figure 1b). In contrast, the reactions of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ with the milder reductant LiBH_4 produce titanium(III) complexes stabilized with tetrahydridoborato ligands.

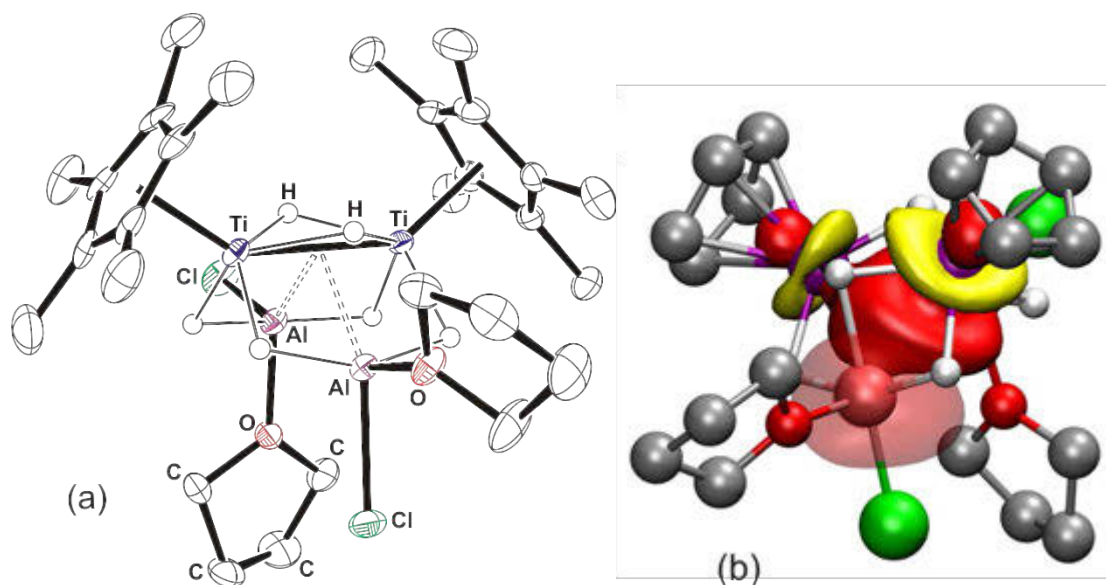


Figure 1. a) Perspective view of the complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-H})\}_2\{(\mu\text{-H})_2\text{AlCl}(\text{thf})\}_2]$. b) Donor/acceptor NBO (Natural Bond Orbital) interactions between “ $\text{Ti}_2 \rightarrow \text{Al}$ ”. Solid and transparent orbitals represent electron donor (full) and acceptor (empty) orbitals, respectively.

Key words: aluminum, boron, density functional calculations, reduction, titanium

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USO DE CATIONES ALQUILARSONIO COMO MOLÉCULAS SONDA PARA EL ESTUDIO DE ZEOLITAS

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Abstract: Las zeolitas son materiales microporosos cristalinos de gran interés no solo desde el punto de vista académico sino también desde el industrial por sus propiedades y múltiples aplicaciones. Estas propiedades dependen en gran medida de su composición química pero también de su estructura. En la actualidad, la International Zeolite Association (IZA) ha aceptado 242 estructuras diferentes [1], cada una de ellas con características específicas y una estructura cristalina particular. La obtención de una u otra estructura está muy influenciada por los agentes directores de estructura (ADE) orgánicos utilizados durante la síntesis.

Aunque los ADE más típicos consisten en cationes de alquilamonio, en los últimos años también se han descrito moléculas que contienen átomos de fósforo o de azufre en lugar de nitrógeno. Recientemente, nuestro grupo describió también el empleo de cationes de alquilarsonio, donde el nitrógeno es remplazado por un átomo de arsénico, que conducen efectivamente a la formación de una estructura zeolítica [2].

El uso de As en el ADE aporta algunos beneficios adicionales, ya que permite la incorporación de átomos pesados que pueden actuar como sonda para diferentes estudios de los materiales obtenidos. Su gran densidad electrónica, en comparación con la del nitrógeno, permite su fácil localización incluso empleando equipos de difracción de rayos X de polvo de laboratorio; hasta la fecha, la localización de los cationes alquilamonios suele requerir el uso de técnicas de monocristal o el empleo de métodos complejos. Además, esta sustitución de N por As permite el uso de otras técnicas avanzadas de caracterización, como la resonancia magnética nuclear MAS-NMR de ⁷⁵As en la muestra sólida, o espectroscopia de absorción de rayos X (XAS) en el borde K del As, para analizar la ubicación y propiedades de la molécula dentro de la red zeolítica y su evolución en condiciones no estándar.

Key words: Zeolita, alquilarsonio, difracción, XAS, RMN

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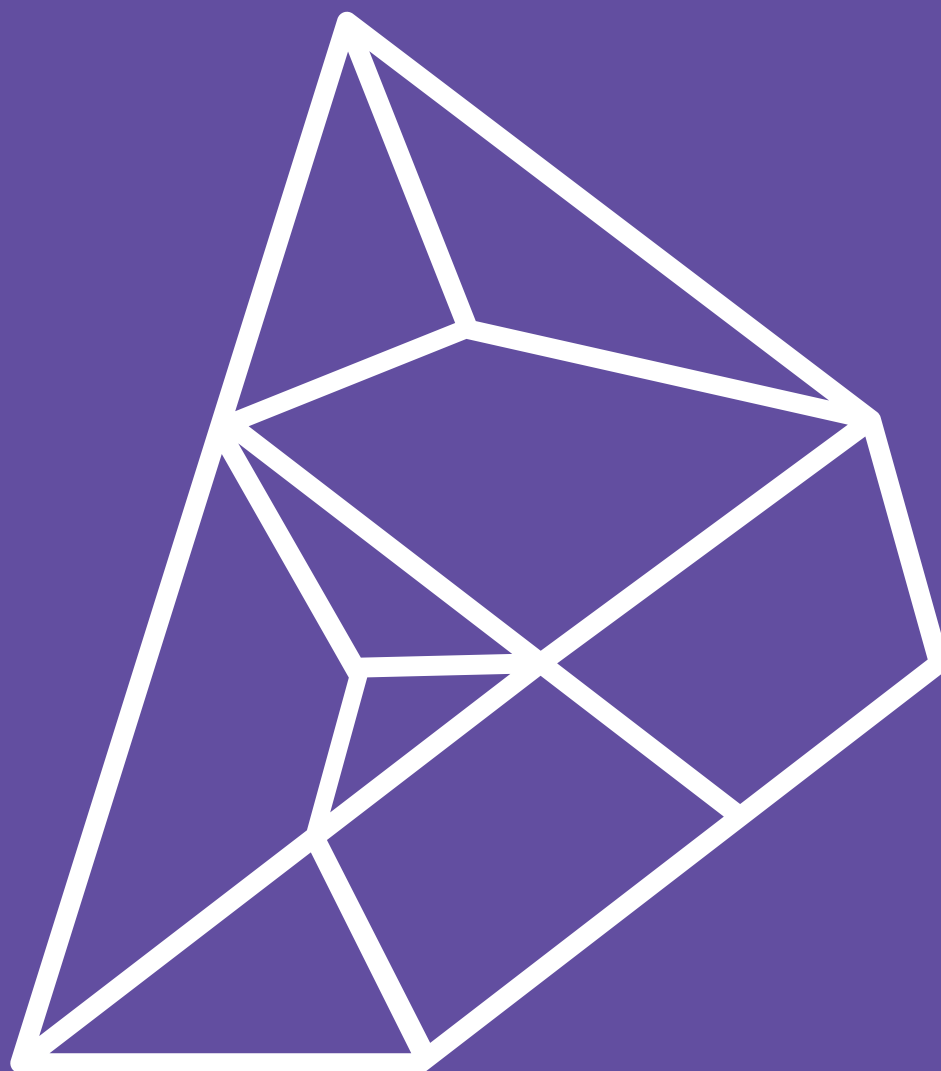
MS2- Organizaciones metalo-orgánicas y otros materiales funcionales

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STIMULUS-RESPONSE NANO COORDINATION POLYMERS WITH MOLECULAR RECOGNITION: FROM NANO-CARRIERS TO 3D PRINTABLE COLLOIDS AND AEROGELS

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Abstract:

Coordination polymers (CPs) are highly versatile compounds with designable architectures and properties, based on the rational selection of their building blocks, i.e. metal ions and organic ligands. (1) Interestingly, it has been observed that an important factor determining their processability is their synthetic procedures. (1) In fact, their high insolubility in the most of the reaction mediums makes them easily nano-processable by bottom-up approaches. (2, 3) In addition, the dynamic nature of the coordination bonds used to held together the metal ions within the organic ligands in the PC structure, add them the ability to rearrange, exchange or eliminate molecules from the metal centers coordination environment and also the organic ligands lead new functionalities and material flexibility. Therefore, CPs are also very useful in the manufacture of dynamic structures, that allow their use as sensors in response to a stimulus (currently call “smart materials”), (4) which can be obtained also as colloids or gels using different synthetic conditions. (4)

Furthermore, the use of modified nucleobases as ligands adds to the CPs molecular recognition capability, due to the formation of selective hydrogen bonds with other molecules.

With all these in mind, in this talk, we are going to discuss about the properties and potential use of (nano)materials based on 1D coordination polymers functionalized with nucleobases. In this sense, the starting non-porous CPs can be produced into nanosized materials, with different morphologies, carefully selecting the synthetic conditions, but also in interesting phases as: low toxic water stable colloidal suspensions, hydro-gels and/or highly porous and ultralight aerogels. These forms are suitable platforms for the interaction of the nucleobases moieties located along the CPs with different nucleobases derivatives and drugs. We are

currently testing them in applications such as nanocarriers of oligonucleotides at cellular level, (5) or materials to form 3D printed composites useful as robust and manageable sensors (4), among others.

Key words: Nano-Coordination Polymers, 3D printing, nanosensors, molecular recognition, metal-organic gels.

Acknowledgments: Spanish Ministerio de Economía y Competitividad (MAT2016-75883-C2-2-P, MAT2016-77608-C3-1-P, SAF2014-56763-R).

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ADDRESSING ARRANGEMENTS OF MULTIPLE METAL CATIONS IN MOFS OF HIGHER COMPLEXITY

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Abstract:

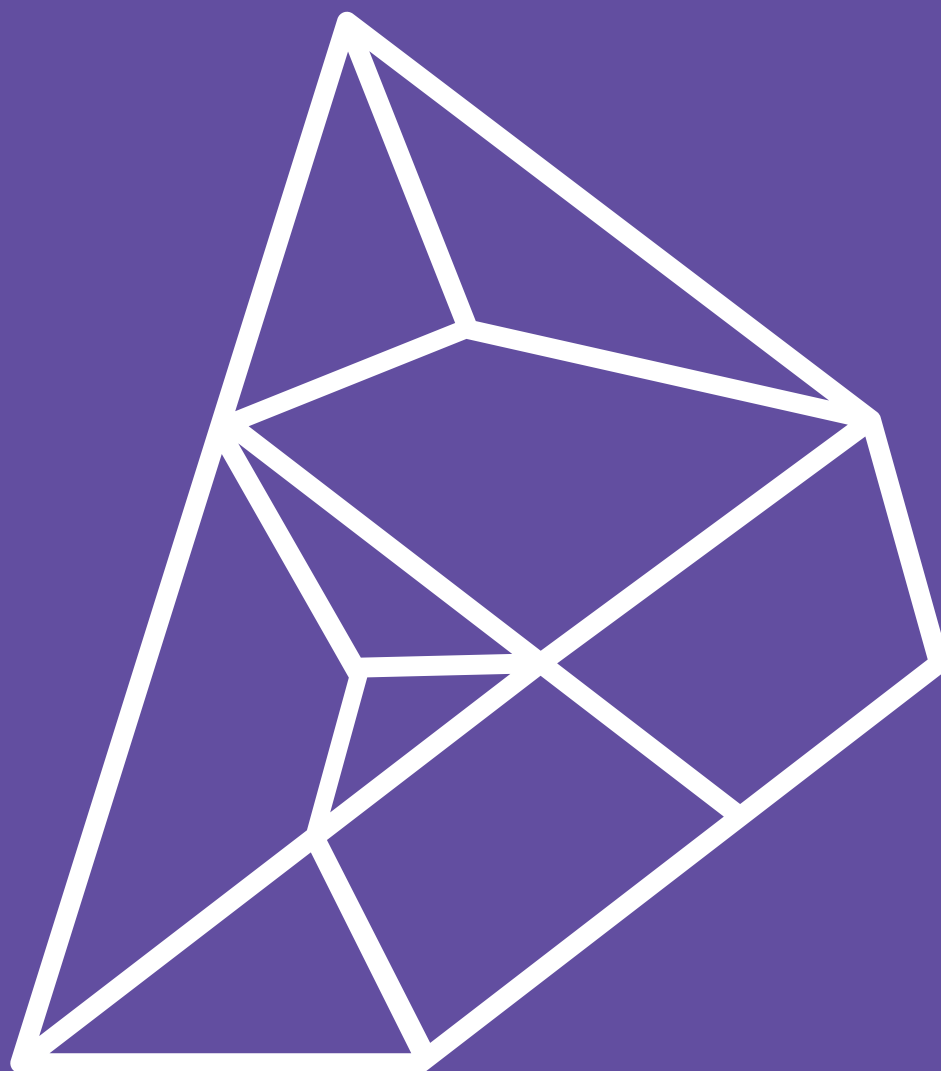
In recent years, the development of metal-organic frameworks, MOFs, that incorporate multiple metal elements within their structure has continued to receive increasing attention because the possibility to combine various metal cations results in new or enhanced properties and behaviors. However, to fully exploit a new level of complexity offered by multi-metal MOFs, it is still required to gain a higher level of control on the incorporation and disposition of the different cation combinations.

Bearing this in mind, we have studied several MOF families composed of the combination of multiple metal cations from a synthetic and structural perspective. We found that the adjustment of the initial metal combinations has a key impact on the distribution of the cations within the MOF secondary building units, which can be exploited to obtain different types of atomic arrangements and sequences. Moreover, we found that for certain metal combinations, different elements might have a prevailing effect on crystallization mechanism, which is manifested on compositional but also on morphological features of the crystals. Additionally, when using multi-metal MOFs as precursors to obtain other classes of catalytically active solids, the different types of possible initial metal arrangements are decisive in the process of programming and translating new chemical compositions.

Key words: Reticular Chemistry, MOF crystallization, crystallography

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A NEW INTERPENETRATED MOF BASED IN THE HIGHLY STABLE HIERARCHICAL MUV-2

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Abstract: Metal-organic frameworks (MOFs) are a class of porous crystalline hybrid materials constructed from metal ions or clusters and organic ligands via coordination bonds. Research on MOFs has increased interest because of their structural and functional tunability as well as their high potential applications in gas storage, separation, and catalysis, among others.¹ Flexible or “breathing” MOFs are very interesting materials since they can exhibit large changes in their cell volumes upon external stimuli such guest inclusion, temperature or pressure.²

We have recently reported a highly stable tetrathiafulvalene(TTF)-based MOF, namely **MUV-2** (MUV: Materials of University of Valencia), which shows a hierarchal structure with both mesoporous and orthogonal microporous channels.³ This MOF exhibits a reversible swelling behaviour (up to 40% of the volume cell) upon polar solvent adsorption which directly impacts on planarity of the flexible TTF linkers modifying its oxidation potential.⁴ One limitation of porous materials is interpenetration, also referred as catenation, a common phenomenon observed in MOFs, especially those presenting large pores, where one or more frameworks can grow occupying the void space in order to stabilize the resulting structure which can modify, for example, the morphology, porosity and other functional properties. In a flexible MOF, tuning the breathing behaviour through interpenetration is a very interesting phenomenon in order to modulate and control some of their functional, but this has been scarcely investigated.

Herein we present the crystal structure of **MUV-2-i**, that is the interpenetrated analogue of the hierarchical and flexible **MUV-2** (Figure A). Interestingly, the large flexibility exhibited by **MUV-2** upon polar solvent adsorption is considerably reduced in the interpenetrated form which can be explained by short S···S interactions between adjacent TTF-based ligands ensuring more rigidity to the framework. In addition, porosity of **MUV-2-i** is significantly decreased in comparison to **MUV-2** as shown by the reduced free volume in the crystal structure. We observe a significant quenching of the breathing phenomena characteristic of **MUV-2**. Thus, upon immersion to a solvent that opens the structure in **MUV-2** (e.g. pyridine), the powder X-ray diffraction (PXRD) pattern of **MUV-2-i** reveals that the

principal peak is slightly shifted (Figure B). Finally, the calculated free space of **MUV-2-i** is 55 % which is significantly lower than the non-interpenetrated **MUV-2** (82 %) in agreement with BET calculations from N₂ adsorptions (Figure C).⁵

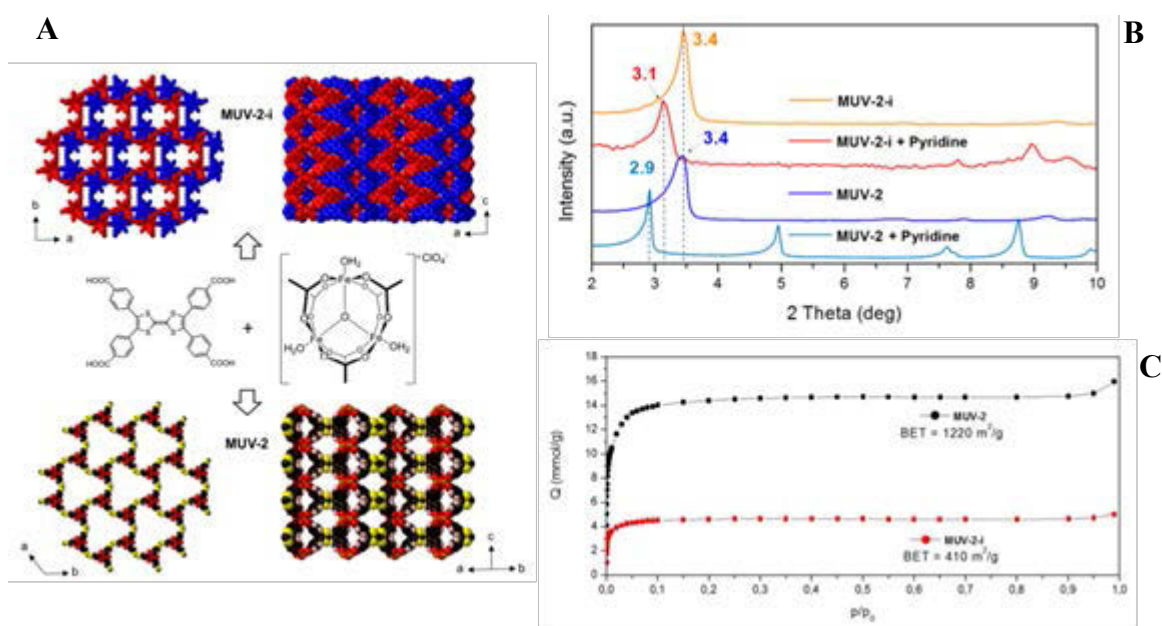


Figure A. Chemical structures of the ligand of the $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]\text{ClO}_4$ secondary building unit used in the synthesis of **MUV-2-i** and **MUV-2**. Schematic representation of the crystal structures of **MUV-2-i** and **MUV-2** along the c-axis and perpendicular view of the structure. **B.** PXRD patterns for as-synthesised **MUV-2-i** and **MUV-2** and after soaking with pyridine at room temperature. **C.** Nitrogen adsorption isotherms at 77 K on **MUV-2** and **MUV-2-i**.

Key words: MOFs, interpenetration, mesoporous, flexibility, adsorption.

Acknowledgments: The work has been supported by the European Union (ERC-2016-CoG 724681-S-CAGE) and the Spanish MICINN (CTQ2017-89528-P).

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CHASING THE LOCAL STRUCTURE OF PALLADIUM LOADED INTO LAYERED CATALYTIC COVALENT ORGANIC FRAMEWORKS¹

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Abstract: Layered covalent-organic frameworks (2D-COFs), composed of reversible imine-linkages and accessible pores, offer a versatile platform for chemical modifications towards the development of catalytic materials.²⁻⁵ Notably, nitrogen-enriched COF materials have been proved as good candidates for binding palladium species.^{6,7} Understanding the local structure of reacting palladium sites bonded to the COF pores is key to rationalize interactions between active sites and porous surfaces. By combining advanced synchrotron characterization tools, such as Pair Distribution Function (PDF) analyses and X-ray Absorption Spectroscopy (XAS), with periodic computational Density Functional Theory (DFT) modeling, we resolve the precise atomic structure of catalytic palladium sites attached to local-defects within an archetypical imine-linked and β -ketoamine 2D-COF system.⁸⁻¹⁰ This material has been synthesized using an in-situ method as a gel, under which imine hydrolysis and metalation reactions are coupled. We demonstrate that in-situ formed local defects within imine-linked 2D-COF materials are highly reactive towards palladium metalation, resulting in active materials for Suzuki-Miyaura cross-coupling reactions.

Key words: Layered Covalent-Organic Frameworks, Pair Distribution Function, Density Functional Theory modeling, Cross-Coupling catalysis

Acknowledgments: We thank the Spanish Ministry of Science, Innovation and Universities (RTI2018-096138-A-I00 and RTI2018-101049-B-I00) and the Comunidad de Madrid for funding through the TALENTO grants (2017-T1/IND5148 and 2017-T1/AMB-5264). A. E. P. -P. and F. Z. acknowledge financial support from the Spanish Ministry of Science and Innovation, through the “María de Maeztu” Programme for Units of Excellence in R&D (CEX2018-000805-M). The authors acknowledge the computing facilities of CSUC for providing resources that contributed to the research results reported within this paper. This work was supported by a public grant overseen by the French National Research Agency (ANR) as part of the “Investissements d’Avenir” program (reference: ANR10-EQPX45). We acknowledge SOLEIL ROCK synchrotron radiation beam-line (proposal 20180480). The authors would like to thank Diamond Light Source for rapid-access beamtime and to Dr. Dean S. Keeble to perform X-ray total scattering experiments (proposal CY22812). Part of this research were carried out at P02.1 beamline at DESY (proposals I-20170717 EC and I-20190208 EC), a member of the Helmholtz Association (HGF). We would like to thank Dr. Michael Wharmby for assistance during the experiment at P02.1. The research leading to this result has been supported by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020”. I. R. -M. acknowledges a FPI-UAM 2019 fellowship from Universidad Autónoma de Madrid. P.A. acknowledges the financial support from “Ayudas para Contratos Predoctorales para la Formación de Doctores” Program of MINECO (Grant BES-2017-070838).

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GUEST-, LIGHT- AND THERMALLY-MODULATED SCO IN [Fe^{II}₂] SUPRAMOLECULAR HELICATES: SINGLE-CRYSTAL-TO SINGLE-CRYSTAL MECHANISMS INVOLVED.

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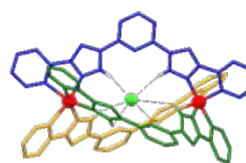
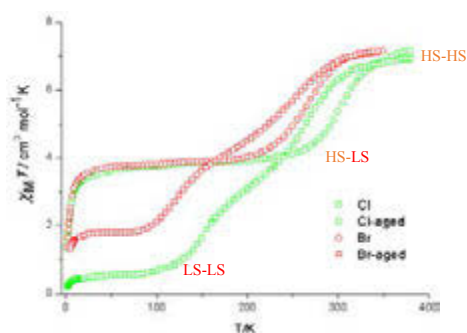
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Abstract: A new bis(pyrazolylpyridine) ligand (H₂L) has been prepared to form functional [Fe₂(H₂L)₃]⁴⁺ metallohelicates. Changes to the synthesis yield four derivatives, X@[Fe₂(H₂L)₃]X(PF₆)₂·xCH₃OH (**1**, x=5.7 and X=Cl; **2**, x=4 and X=Br), X@[Fe₂(H₂L)₃]X(PF₆)₂·yCH₃OH·H₂O (**1a**, y=3 and X=Cl; **2a**, y=1 and X=Br, called *aged complexes*). Their structure and functional properties are described in detail by single-crystal X-ray diffraction experiments at several temperatures. Helicates **1a** and **2a** are obtained from **1** and **2**, respectively, by a single-crystal-to single-crystal mechanism. The three possible magnetic states, [LS–LS], [LS–HS], and [HS–HS] can be accessed over large temperature ranges as a result of the structural non-equivalence of the FeII centers. The nature of the guest shifts the SCO temperature by roughly 40 K. Also, metastable [LS–HS] or [HS–HS] states are generated through irradiation.



Key words: Spin Crossover (SCO), single-crystal-to-single-crystal (SCSC) mechanism, host-guest chemistry, metallohelicates.

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NOVEL NICKEL-TRIAZINE MOF AS EFFICIENT WATER SPLITTING PHOTOCATALYST

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Abstract: Most of the reported MOF structures are based on carboxylate and/or N-donor ligands, remaining phosphonate-based MOFs (P-MOFs) poorly explored (ratio P-MOFs: carboxylate-MOFs $\approx$ 1:12; according to WoS). In addition, from the limited number of reported P-MOFs, only 1/3 are porous architectures. On the other hand, among the most interesting catalyzed reactions, water splitting using sun irradiation appears as a challenging process to generate solar fuels^[1]. Although several MOFs have been investigated as photocatalysts in hydrogen evolution reaction (HER)^[2], no examples of crystalline P-MOFs have been proposed yet.

Considering the above mentioned, we here present a novel robust porous P-MOF (denoted IEF-13; from IMDEA Energy Framework) based on the redox active Ni²⁺ and the tritopic phosphonate ligand 4,6-tris[(phosphonomethyl)phenyl]-1,3,5-triazine, which possesses photo- and electro-active properties. Moreover, we originally evaluate IEF-13 as photocatalyst.

The novel porous IEF-13 was successfully and purely prepared by a simple hydrothermal method. From structural resolution, IEF-13 crystallizes in the triclinic space group *P*-1 based on bi-octahedra nickel nodes and phosphonate ligand. Remarkably, this material exhibits coordinatively unsaturated nickel(II) sites, free acidic groups, and microporosity accessible to CO₂. IEF-13 is very robust, being thermally (up to 450 °C) and chemically stable in different aqueous (pH =1-10, hydrothermal conditions) and organic solutions. The band gap of the material was estimated (E_g = 2.83 eV) by UV-Vis spectroscopy. Further, IEF-13 exhibits photocurrent whose intensity increases upon increasing the polarization voltage in the positive region and with the presence of methanol, in agreement with its semiconductor nature.

Due to its robustness and optoelectronic properties, IEF-13 was tested as photocatalyst in HER without co-catalyst, being able to produce around 2200 and 1700 μmol of H₂·g⁻¹ using a Xe lamp and a solar simulator, respectively, which are values comparable with the reported ones for other MOFs using co-catalysts. Note here that the material was re-used several times keeping more than 90% of its catalytic activity. Finally, IEF-13 photocatalyst was also active in overall water splitting experiments, reaching a H₂ production comparable with others MOFs in presence of co-catalysts (175 μmol ·g⁻¹)^[3].

Key words: Metal-organic framework, phosphonates, photocatalysis, water splitting.

Acknowledgments: This work was supported by Raphuel project (ENE2016-79608-C2-1-R, MINECO-AEI/FEDER, UE), and the Ramón Areces Foundation project H⁺MOFs. PH acknowledges the Spanish Ramón y Cajal Programme (2014-15039).

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PREPARATION OF RESPONSIVE MoS_2 -MOF HYBRID MATERIALS

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Abstract: Metal-Organic Framework materials are hybrid crystalline porous materials that have shown great potential in multiple areas such as gas separation, catalysis, and biomedicine, among others. Despite often presenting superior performances, the advances of MOFs toward commercialisation and their implementation into functional devices remain limited due to their characteristic poor processability. In this line, the miniaturisation of MOFs in the form of nanoparticles has opened new venues allowing their combination with other functional materials. Most hybrid systems based in MOFs consist of combinations with soft polymers (Kalaj et al., 2020), whereas fewer studies have focused on the influence over functional 2D structures. Indeed, the use of flexible MOFs result particularly interesting in building hybrid structures since their responsive behavior upon different stimuli such as temperature, solvent molecules or gas pressure (Schneemann et al., 2014) may be capable of modulating the final properties of the hybrid material (Zhu & Xu, 2014).

Herein we present the formation of a composite material based on the combination of an archetypal nanostructured flexible MOF, MIL-88A (Chalati et al., 2011), with exfoliated nanosheets of 1T- MoS_2 (Figure 1). Retention of the MOF breathing capacity in the hybrid material is monitored by means of X-ray powder diffraction. The resulting material presents improved sorption capacity for particular gases, as a result of a favoured opening of the flexible MOF in the composite.

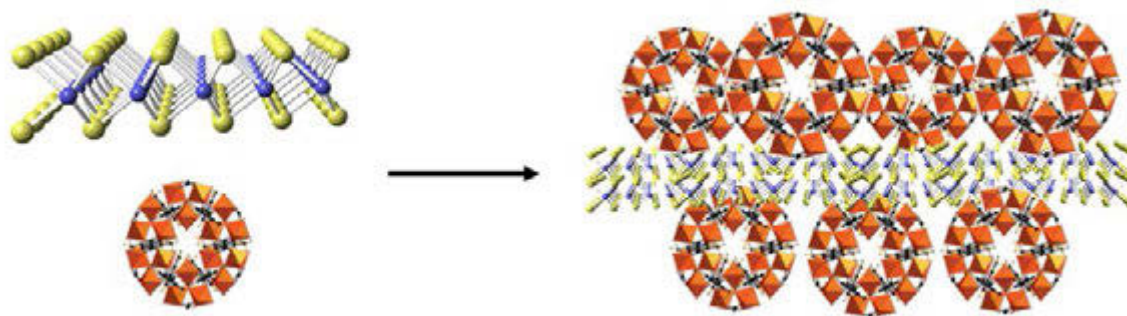


Figure 1. Schematic representation of the formation of the MoS_2 -MIL-88A composite.

Key words: Metal-Organic Frameworks, Transition-Metal Dichalcogenides, hybrid 2D materials

Acknowledgments: The main author would like to thank the Spanish Ministry of Science, Innovation, and Universities (FPU grant FPU19/00474). This work has been supported by “la Caixa” Foundation (LCF/BQ/PI19/11690022) and Generalitat Valenciana (SEJI/2020/036).

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THERMAL TREATMENT CONTROLLED BY X-RAY DIFFRACTION TO GENERATE DESIRED MOLECULAR COMPOUNDS

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Abstract: Metal Organic Framework (MOF) or Coordination polymers in general, in which the metallic centers are linked by pseudohalure ligands (N₃, NCS, NCO, among others) are very useful to design molecular magnetic systems. Depending on the coordination of the ambidentate pseudohalide, the final generated compound could show ferromagnetic or/and antiferromagnetic interactions. In the case of the NCS pseudohalure, ferromagnetic interactions are generally generated by NCS bridging ligands (EO (μ -1,1-NCS, μ -3,3-SCN) and/or EE (μ -1,3-NCS)), and antiferromagnetic interactions by NCS terminal ligands.

Focused on the study of magnetostructural relations, this work shows a synthesis method, based on thermal treatment and controlled by X-ray diffraction, to generate the desired molecular systems. The combination of Bpe (1,2-bis(4-pyridyl)ethene) with NCS and divalent cations (M= Mn, Fe, Co y Ni) leads to the preparation of new molecular compounds with formula [M(NCS)₂(Bpe)₂], where a NCS ligand acts as a terminal ligand and a Bpe ligand is the link between the metallic centers. Through the appropriate thermal treatment of the [M(NCS)₂(Bpe)₂] system, the [M(NCS)₂(Bpe)] system is generated, where the metallic centers are linked by bridging NCS ligands. The transformation from [M(NCS)₂(Bpe)₂] to [M(NCS)₂Bpe] (M= Mn, Fe, Co y Ni; Bpe= 1,2-bis(4-pyridyl)ethene) can be observed by X-ray diffraction (Figure 1). These structural transformations induce a different magnetic behaviours in these compounds.

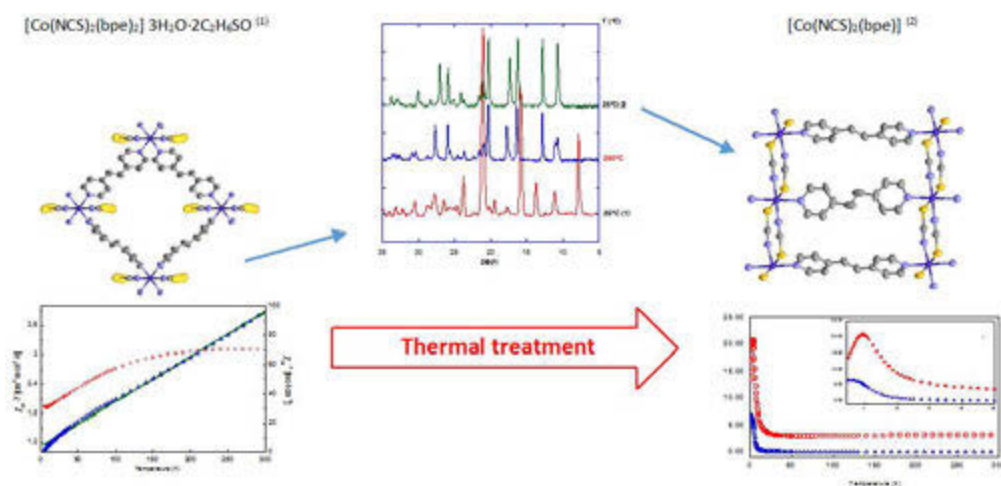


Figure 1. Thermal process of the $[\text{Co}(\text{NCS})_2(\text{bpe})_2] \cdot 3\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_6\text{SO}$ to $[\text{Co}(\text{NCS})_2(\text{bpe})]$ transformation.

Key words: Metal Organic Framework, Coordination Polymers, X-ray Diffraction, Magnetic Interactions, Heating Synthesis Method

Acknowledgments: This work was supported by Basque Government (IT1301-19) and Spanish Ministerio de Ciencia e Innovación (PID2019-106644GB-I00).

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TOWARDS MAGNETIC AND LUMINESCENT MOFS BASED ON LN(III) IONS

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Abstract: During the last two decades MOFs (metal-organic frameworks) investigation has become of great attention for both the academia and the industry.¹ The structural diversity present in MOFs has significantly expanded the application of these new materials, which broadens from gas storage and separation, catalysis, biomedicine delivery, to chemical sensing.²

In this context, the following work presents the synthesis and characterization of a family of three dimensional MOFs based on Ln(III) ions and 3-amino-4-hydroxy benzoic acid multitopic ligand. With the aim of determining future possible applications, magnetic, adsorption and photoluminescence properties of our materials have been studied.³

Key words: lanthanide, metal-organic framework, single-molecule magnets, adsorption capacity and solvent tunable emission.

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TRANSITION METAL HYDROXYPHOSPHONOACETATES AS PRECURSORS OF ELECTROCATALYSTS

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Abstract: Coordination polymers (PCs) are widely studied due to their applicability in many fields [1]. Among them, metal phosphonates are attractive materials due to their great structural and functional diversity, as proton conductors and/or precursors of electrocatalysts [2], alternative to the high-cost commercial catalysts based on noble metals [3], for both, PEMFCs and electrolytic systems.

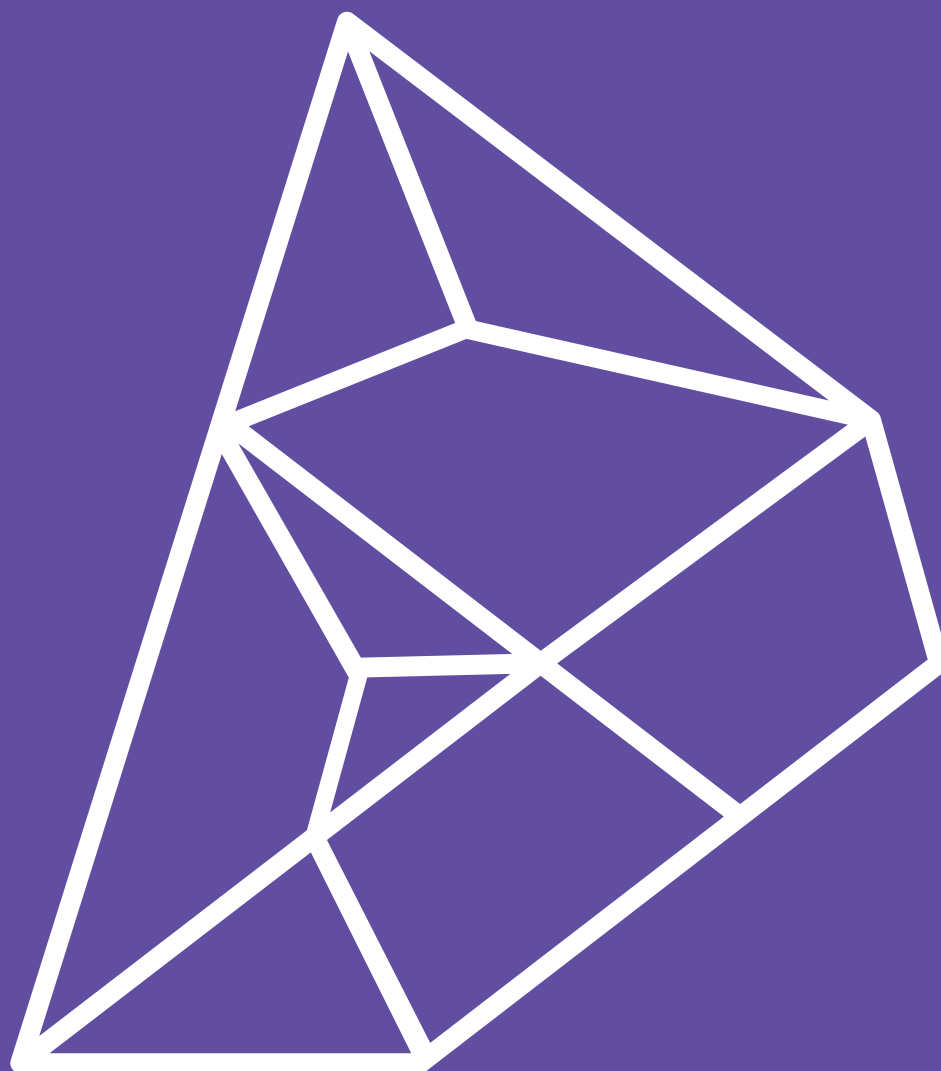
In this research-work, we report the synthesis, characterization and electrochemical properties of several coordination polymers derived from (R,S)-2-hydroxyphosphonoacetic acid (HPAA) with transition metals ($M^{II} = \text{Fe, Co, Mn, Ni}$) as well as their solid solutions. The precursor PCs decompose, upon heating in different conditions, to the corresponding metal oxalate solid solutions, which are then used as intermediate materials for obtaining new Non-Precious Metal Electrocatalysts (NPMCs), by pyrolytic treatment at different temperatures under N_2/H_2 atmospheres. The electrochemical behavior of these compounds, regarding to the Oxygen Evolution and Reduction Reactions (OER and ORR, respectively), show that the structural features are of considerable importance as to their electrocatalytic activities.

Key words: Coordination Polymers, Metal Phosphonate, Electrocatalyst, Oxygen Evolution Reaction, Oxygen Reduction Reaction.

Acknowledgments: This research was supported by MAT2016-77648R and PID2019-110249RB-I00 research grants (Spain)

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A ZINC METAL-ORGANIC FRAMEWORK CONSTRUCTED BY A MIXED-LIGAND STRATEGY FOR DETECTION OF EMERGING CONTAMINANTS IN WATER

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Abstract: Emerging contaminants are chemical substances characterized by a perceived or veridical threat to the environment or human health with a lack of published health criteria. Between then, personal care products (PCPs) are organic compounds which have already shown toxic effects in humans and other living organisms.

Micro- and mesoporous materials are widespread studied for separation and purification purposes. Among these porous materials, metal-organic frameworks (MOFs) are of great interest because these compounds could be designed to precisely tailor their structures and pores, and consequently, they can offer an accurate control of the adsorption capacity and selectivity of contaminants.

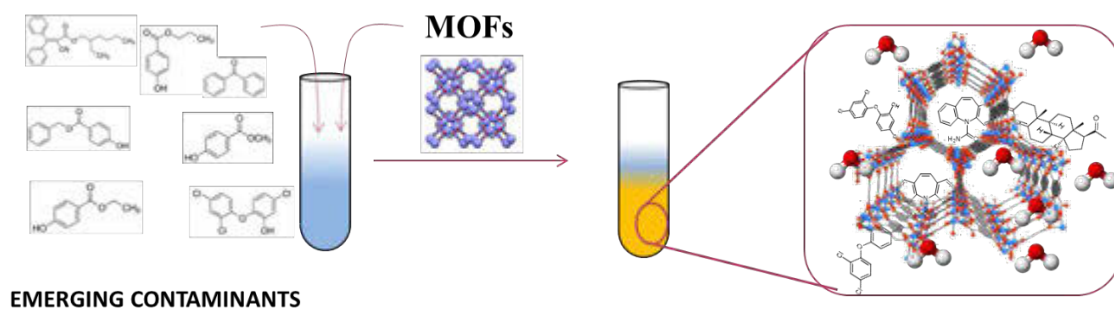


Figure 1. Scheme of the process

Here, $[\text{Zn}_2(\text{tz})_2(\text{bdc})]\cdot\text{solv}$ (CIM91) MOF compound is obtained through solvothermal self-

assembly of the triazolate and carboxylate ligands and Zn(II) nitrate salt. This compound has been used to the analytical determination of different personal care products (PCPs) in water. Crystals with enough quality to be study by single crystal X-ray diffraction of dimethylformamide and acetone solvates (CIM91@dma and CIM91@acetone) could also be isolated. The inclusion of solvent in MOFs materials is a highly specific form of guest-host interaction. The study of the MOF-solvent interactions is used to give insights on the nature of the possible interactions MOF-target contaminants. The understanding of these interactions is critical for the rational design of efficient MOF-based adsorbents for environmental purposes. This approach to understand the host-guest interactions will be very helpful not only for understanding analytical extractions but also for applications of MOFs in detection, removal, storage or delivery processes.

Key words: metal-organic frameworks; crystal structure, microextraction procedures; emerging contaminants

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COPPER(I) COORDINATION POLYMERS WITH AROMATIC THIOAMIDES

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Abstract: In recent years, research in coordination polymers has increased as an interface between synthetic chemistry and crystal engineering, generating a solid base for understanding how molecules/ions can assemble giving rise to programed (multi)functional architectures¹. In particular, those based on Cu(I) are relevant because of their structural diversity and physicochemical properties². On the other hand, organosulphur ligands such as thioamides are very versatile ligands due to the presence of nitrogen and sulphur donor sites, showing interesting chemical and structural properties upon combination with metal ions³.

Herein, we present the synthesis and structural characterization of novel coordination polymers of formula $\{[\text{CuIPyTBA}]_n \cdot n \text{ S}\}$ (S= acetone in **1**; 1/3 THF in **2**) obtained upon direct reaction of 4-pyridinethiobenzamide (PyTBA) with CuI in acetone or THF, respectively, in the presence of a saturated KI water solution. A similar reaction between CuBr and PyTBA in acetone leads to $\{[\text{CuBrPyTBA}]_n \cdot n \text{ acetone}\}$ (**3**). The three coordination polymers are isostructural, and form a 2D grid structure consisting of Cu_2X_2 (X = I, Br) units joined by PyTBA pyridinic N and S atoms of two different ligands, with voids occupied by the solvent molecules. We noticed that when the powder obtained in the direct reaction between CuI, KI and PyTBA is recrystallized in hot acetonitrile, a triply interpenetrated 3D polymeric structure with formula $[\text{CuIPyTBA}]_n$ (**4**) is formed. Interestingly, when **4** is immersed in acetone, it leads to a mixture of **1** and **4**, while heating the mixture a reversible transformation to **4** is observed. The desolvated-solvated transformation has been studied.

Key words: Copper iodide, 4-pyridinethiobenzamide, coordination polymers, X-ray diffraction.

Acknowledgments: MAT2016-77608-C3-1-P; MAT2016-75883-C2-1-P.

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HETERO-BIMETALLIC METAL–ORGANIC FRAMEWORK CU-MOF-808

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Abstract: The incorporation of local defects within Metal-Organic Frameworks (MOFs) by introduction of cation metals is an emerging synthetic route for modifying the secondary building units (SBUs)¹. This chemical tunability is very useful to add new properties into the material for ultimate applications. Different approaches have been developed in order to incorporate metal sites within a given MOF: use of organic ligands with additional metal binding sites (metalloligands), post-synthetic metal exchange, or the one-pot-synthesis of multi-metal MOFs.² In this work, we show the post-synthetic incorporation³ of catalytic copper(II) sites in the MOF-808,^{4,5} as well as the advanced characterization of the local structure using synchrotron methods such as Pair Distribution Function (PDF) analyses⁶ and Extended X-ray Absorption Fine Structure (EXAFS).

Key words: MOF-808, local structure, EXAFS, PDF.

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INSIGHT INTO THE CRYSTALLIZATION MECHANISM OF A BIMETALLIC METAL-ORGANIC FRAMEWORK

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Abstract: Over the past decades, in the quest for innovative multifunctional materials, the attention has gravitated towards metal-organic frameworks^[1] (MOFs) due to their hallmark features: robust crystalline structure, tailored permanent intrinsic porosity and versatile chemical composition. These features make them widely used in many applications, such as adsorption or catalysis,^[2] and they depend to a large extent on the metal ions of the MOF. When incorporating various metal ions into a framework, its properties are enhanced,^[3] however this field still remains fairly unexplored as compared to single-metal MOFs, one reason being the difficulty in controlling the metal combinations during the crystallization process.

Bearing this in mind, we carried out a study of the influence of an array of factors on the crystallization process of a series of bimetallic lanthanide-based frameworks. Firstly, after analyzing different combinations and ratios of metal elements, we have found that some cations have a prevailing effect on the crystallization mechanism, which is manifested on the morphological features of the resulting crystals. Furthermore, this competitive crystallization mechanism is also influenced by the selection of the solvent employed in the synthesis, which results in different distributions of the metal cations within the crystals.

Key words: metal-organic frameworks, porous materials, lanthanides

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NEW MULTIMETAL METAL-ORGANIC FRAMEWORKS FROM GROUP 13 ELEMENTS

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Abstract: Incorporating multiple metal elements within a same metal-organic framework (MOF)¹ allows the obtaining of materials with new or enhanced properties. However, in most cases, the introduction of multiple metal elements in a same MOF takes place with lack of control over their disposition. In this work, we report the structural characterization of two new heterometallic MOFs based on group 13 elements, denoted MOF-413, and MOF-1071. Through the adjustment of the synthetic conditions and initial metal precursors, we have been able to obtain heterometallic MOFs where we can control the position and amount of the different metal cations. The specific organic linkers used in this work were 1,3,5-tris(4-carboxyphenyl)benzene (H₃BTB) and benzene-1,3,5-tricarboxylic acid (H₃BTC), which have been combined with gallium and nickel, and gallium and indium, respectively. The afforded materials have been characterized with single crystal X-ray diffraction, and their formula determined to be [Ga_{3-x}Ni_x(μ₃-O)(BTB)₂(Piv)(DMF)]·[DMA]_x for MOF-413, and [In₅Ga(BTC)₈]·[DMA]₆ for MOF-1071, where the Piv nomenclature corresponds to a pivalate ligand [(CH₃)₃CCO₂], and DMA is dimethyl ammonium. Single crystal X-ray diffraction analysis of the new MOFs have been performed for both materials. MOF-413 crystallizes in the orthorhombic system, space group *Pnma*, and it exhibits a flexible² three-dimensional structure, consisting of two interpenetrated networks. MOF-1071 belongs to the $I\bar{4}$ tetragonal space group, and it consists of a three-dimensional network, with a previously unreported (3,4)-connected topology.

Key words: MOFs, heterometallic materials, crystallography

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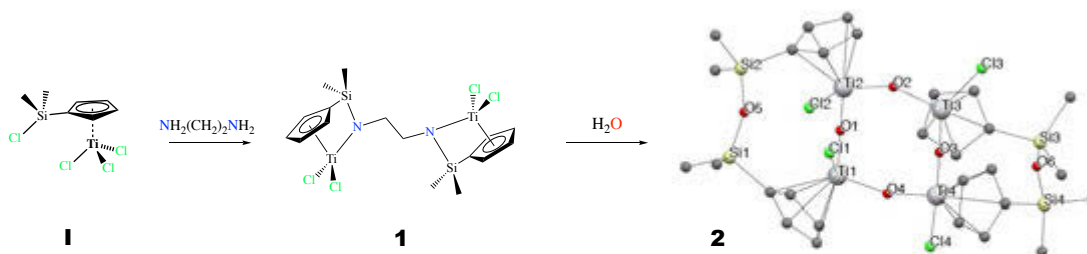
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SYNTHESES, CHARACTERIZATIONS, AND SINGLE-CRYSTAL X-RAY STRUCTURE OF $[(\text{TiCl})_2\{(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}\}(\mu_2\text{-O})]_2(\mu_2\text{-O})_2$

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Abstract: Here we describe a new approach to the synthesis of $[(\text{TiCl})_2\{(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}\}(\mu_2\text{-O})]_2(\mu_2\text{-O})_2$ (**2**). Although the complex **2** have been previously reported by Noh and coworkers,¹ this was not fully spectroscopic characterized, and its crystallographic structure had not been reported. In this work, we describe an alternative synthetic strategy to prepare **2** that has allowed to obtain monocrystals suitable to be analyzed by X-ray diffraction. Complex **2** was prepared by the controlled hydrolysis of the dinuclear complex $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta\text{NCH}_2\}\text{Cl}_2]_2$ (**1**)².



The complex **2**, $\text{C}_{28}\text{H}_{39}\text{Cl}_4\text{O}_6\text{Si}_4\text{Ti}_4$, crystallizes in a triclinic system and space group P_1 , as a racemic mixture. The complex **2** core is constituted by a flat eight membered metallacycle, Ti_4O_4 , in which titanium and oxygen atoms alternate. Contrary what is normal for this kind of cores, the values of the Ti-O-Ti angles are different two to two (150° - 176°) due to the presence of the Si-O-Si bridges. In addition, the Ti-O bonds are significantly shorter (1.76 -1.84 Å) than a typical single bond Ti-O, indicating a certain multiple character for such bonds. The cyclopentadienyl rings are located alternately above and below with regard the core plane. Considering that the cyclopentadienyl ring occupies a single coordination position, each titanium atom features a distorted "piano stool" structure.

The chirality and the high stability of **2** are very interesting features from a catalytic point of view, as the oxidation of prochiral substrates using as oxidant aqueous solution of H_2O_2 .

Key words: Air stable titanium complexes

Acknowledgments This work was supported by MINECO RTI2018-094840-B-C31 and CAM (fellowship PEJD-2019-PRE/IND-14122).

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VAPOUR-PHASE DEPOSITION OF CU-CARBOXYLATE MOF THIN FILMS

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Abstract: The integration of MOFs in microelectronics requires the development of robust thin film deposition methods [1]. Thus far, the reported procedures for the deposition of MOF thin films involve the self-assembly process between linkers and metal salts in a solvent. However, this approach is incompatible with microelectronics fabrication due to possible contamination and corrosion of pre-formed circuitry. We have recently reported the MOF-CVD method as a vapour phase deposition protocol of MOF thin films [2]. The process is based on metal precursor deposition and subsequent precursor-to-MOF conversion in a reactive atmosphere. This proof-of-concept has been demonstrated for the iconic ZIF-8 framework.

Herein, we have further expanded the scope of MOFs which can be deposited as thin films by the MOF-CVD method: the prototypical HKUST-1 (CuBTC) [3] and the isostructural CuBDC and CuCDC frameworks [4].

Uniform, crystalline and porous films are obtained from the reaction of CuO precursor and the vaporized linker in a reactive atmosphere. Interestingly, the MOF thin films grow with an out-of-plane orientation.

Key words: Metal-Organic Frameworks, Thin Films, Vapour phase deposition, Oriented MOF films

Acknowledgments: This work was supported by the European Research Council (ERC) under the grant agreements n° 716472 –VAPORE– and 771834 –POPCRYSTAL–.

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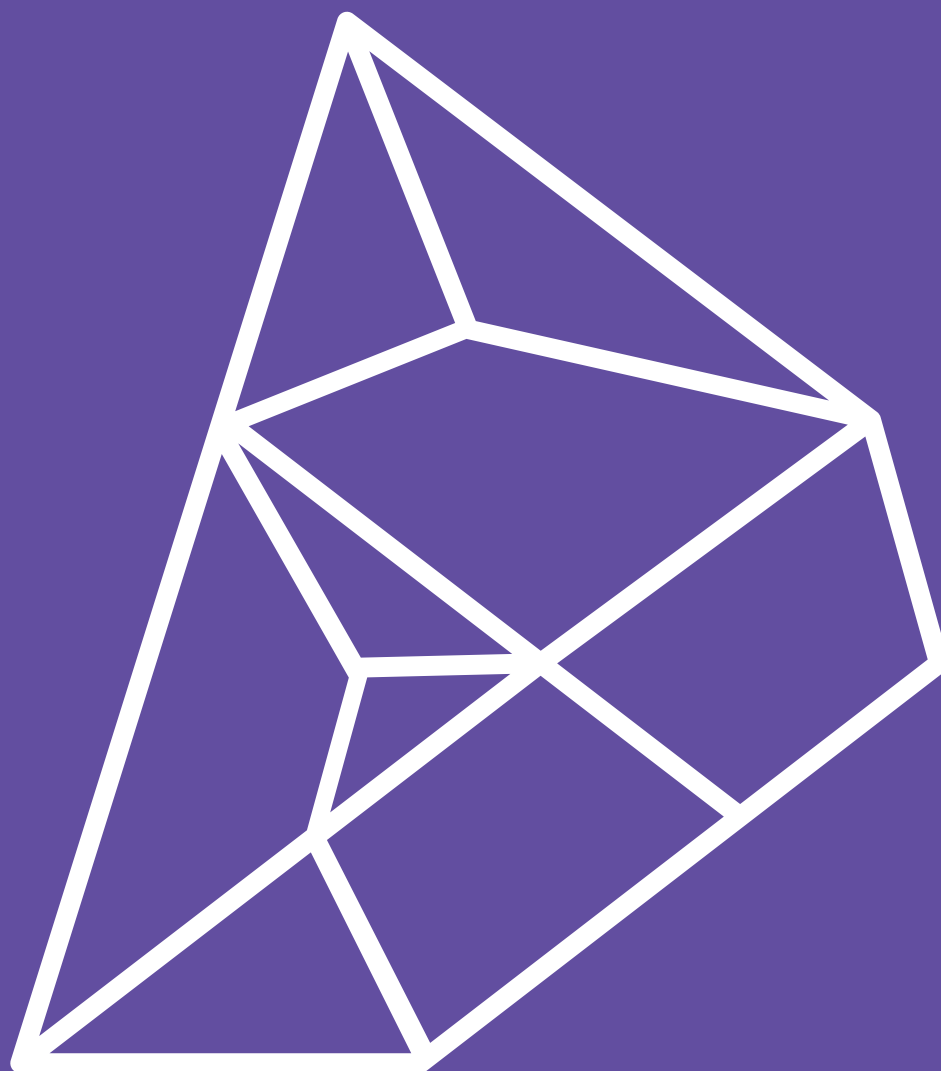
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HIGH PRESSURE CRYSTALLOGRAPHY & CHEMISTRY: AN INTRODUCTION

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Abstract: Pressure is an often underappreciated thermodynamic variable. Often crystal structures are examined over a range of temperatures, but why not pressure as well? High pressure diffraction is often thought of as an exclusive domain of physicists and geologists, but more recently chemists are discovering the utility of exploring pressure. In this presentation I will introduce the audience to the technique of high pressure crystallography as well as a number of examples relevant to the chemistry community.

Key words: high-pressure, crystallography under pressure, chemical crystallography

NEUTRON DIFFRACTION MATTERS

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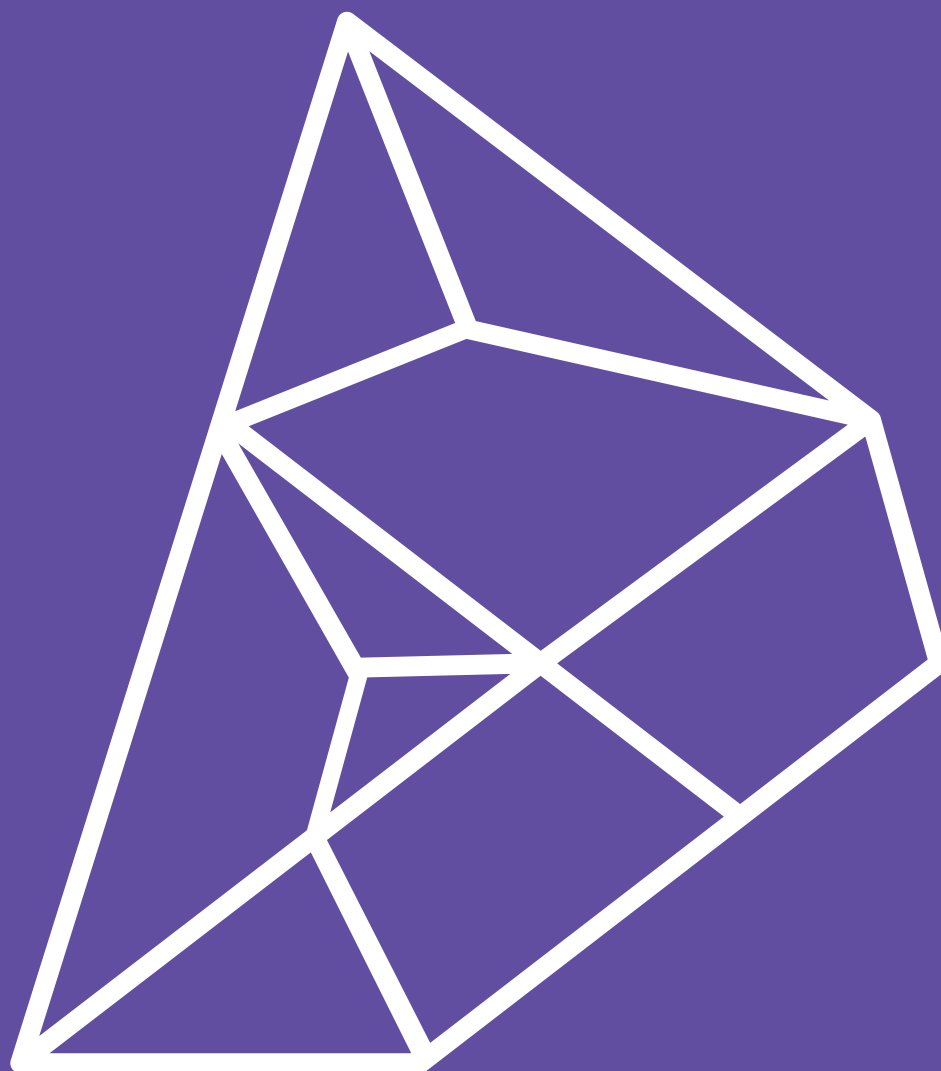
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Abstract: Diffraction methods are essential experimental techniques for the study and development of new materials as they provide a detailed knowledge of the structure of solids at the atomic or molecular level. There is a clear complementarity between Neutron and X-ray diffraction; while X-rays locate the atomic electrons, neutrons determine the position of nuclei as well as give information on microscopic magnetism.

The unique properties of the interaction of neutrons with matter play a crucial role in resolving the arrangements of magnetic moments in complex magnetic systems or locating light atoms in intricate structures, eventually through isotopic substitution. The study of smart magnetic materials is an archetypal field of research with neutron diffraction, but the range of problems related to materials science is rather wide and in recent years, the research on energy materials has strongly increased. Many of the physical phenomena associated with the properties of energy related materials are connected to chemical bonding and the movement of light atoms. These materials include hydrogen storage materials, solid-oxide fuel cells (SOFC's), electrolytes and battery materials as well as thermoelectrics or hybrid solar perovskites.

Some examples of recent work, mainly carried out at the ILL, will be presented demonstrating the valuable insights that neutron diffraction can provide in the understanding of the relationship of crystal and magnetic structures of materials with their physical properties.

Key words: Neutron Diffraction, Microscopic Magnetism, Physical Properties.



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A NOVEL BIFUNCTIONAL COORDINATION POLYMER EXHIBITING SMM AND PHOTOLUMINESCENT PROPERTIES BY COMBINING TRANSITION METALS

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Abstract: Coordination polymers (CPs) are considered very promising compounds in the field of molecular materials thanks to their large versatility of their crystal structures and wide variety of applications that these compounds can present, such as adsorption and separation of gases or heterogeneous catalysis [1]. In some cases, it is even possible the coexistence of two physical properties in the same compound to achieve multifunctional materials. Plausible combinations could be conductive/optical, magnetic/conductive and magnetic/optical, among others [2]. In addition, its great design capacity and the fact of being able to predict the resulting topologies of the crystalline structures based on a rational selection of the building blocks, metal ions and organic ligands, allows us to design these compounds towards the desired objectives [3]. In this work, the combination between cobalt(II) ion and 2-aminonicotinate organic ligand leads to the formation of a chiral 2D layered CP pillared up by means of supramolecular interactions. The synthesized compound shows a long-range magnetic ordering among the paramagnetic centers of the crystalline structure displaying a weak ferromagnetism, which derives in a spin-glass behavior. In order to break the interactions between the metallic centers, we performed a diamagnetic dilution by the partial replacement of Co(II) for Zn(II) without modifying the crystal building with two objectives in mind: on one hand, to isolate the metallic centers and break the long-range magnetic order, so that the single-molecule magnet (SMM) behavior emerges. On the other hand, d^{10} ions such as Zn(II) are widely used for building luminescent-CPs. Therefore, the inclusion of such ions in the structure imbues the compound with an additional photoluminescent property.

Key words: Coordination polymers, multifunctional materials, single-molecule magnets, photoluminescence.

This work has been funded by the University of the Basque Country (GIU 17/13); the Basque Government (GV/EJ) (IT1005-16, IT1310-19); the Junta the Andalucía (FQM-394, FQM-195) and the Spanish Ministry of Science, Innovation and Universities (MCIU/AEI/FEDER, UE) (PGC2018-102052-A-C22, PGC2018-102052-B-C21).

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ANALYSIS OF BUILDING MATERIALS BY SYNCHROTRON X-RAY IMAGING

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Abstract: Building materials have complex hierarchical microstructures. The largest components are coarse aggregates with dimensions larger than a few centimetres and the smallest ones are the calcium silicate hydrate (C-S-H) gel nanoparticles with sizes smaller than 5 nm. To fully understand the main properties of cement binders and optimize their performances, a sound description of their spatially-resolved contents is compulsory. Furthermore, cement manufacturing is responsible for about 7% of the anthropogenic CO₂ emissions and hence, to decrease the CO₂ footprint, in a sustainable and cost-effective way, is a top priority. To gain a deeper insight into the microstructures of building materials, synchrotron X-ray ptychographic nanotomography and absorption-based microtomography have been employed.

Here we will present three examples of our approach blending quantitative powder diffraction with synchrotron X-ray imaging. Firstly, we will show our comparative work on belite and Portland cement pastes cured at varying temperatures [1]. Synchrotron tomographic data taken at TOMCAT allowed understanding the different hydrating behaviour of both cements. Secondly, ptychographic nanotomographic data taken at cSAXS showed the hydration of CaAl₂O₄ with curing temperature [2]. Ptychographic data have permitted to characterise the conversion of the aluminate hydrates which is key for durability. The very good contrast in the electron density tomograms will be discussed as well as the porosity induced after the conversion reactions. Finally, we will report our work on Portland cements [3]. The densities and spatial distribution of calcium silicate hydrate (C-S-H) gel and amorphous iron-siliceous hydrogarnet components will be described.

Key words: synchrotron tomography, Rietveld analysis, ptychography

Acknowledgments: This work has been supported through BIA2017-82391-R and UMA18-FEDERJA-095 research grants, which are co-funded by FEDER.

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CRYSTAL AND MAGNETIC STRUCTURES AND DIELECTRIC PHASE TRANSITION OF THE NOVEL ORGANIC-INORGANIC HYBRID HALOMETALLATE COMPOUND: (QUINUCLIDIUM)[FeCl₄]

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Abstract: Hybrid organic-inorganic crystals are unique materials that have been attracting increasing interest in the last years due to their physical properties and potential applications in different fields. Among these, the development of high conductivity solid state electrolytes is one of the most explored areas, with a new focus on plastic hybrid materials.

In this communication we present the temperature evolution of the physical properties of the (quinuclidinium)[FeCl₄] compound,[1] which shows an unprecedented series of phase, structural and magnetic transitions. The complete phase diagram involves a phase transition between paraelectric-to-polar phase at 390 K, from polar phase-to-antiferroelectric around 280K and from paramagnetic-to-antiferromagnetic at 3.5 K. Above RT, the occurrence of the paraelectric-to-polar phase transition involves a plastic phase (Fig. 1) with a giant increase in the real part of the dielectric permittivity (reaching a maxima of 10⁵, value that is notably larger than any other hybrid compound previously reported; Fig. 2). The intermediate phases were resolved by single-crystal X-Ray and neutron diffraction (D19). Below 3.5 K, long-range magnetic order was observed. We were able to solve and refine the magnetic structure using single-crystal and powder neutron diffraction data from D19 and D1B. The magnetic model consists on a globally antiferromagnetic structure with the antiferromagnetic moments non-compensated along the *c*-axis (Fig. 2). The role of neutrons was crucial for this study, as it allowed us to locate the hydrogen atoms within the unit cell for the intermediate phases, which is not possible by X-Rays. The hydrogen positions are extremely important in the development of research of these kind of compounds, as their structure is built up by an intricate weak bonding network of electrostatic and non-covalent interactions that include hydrogen bonds and van der Waals forces. Furthermore, neutrons permitted us to solve the magnetic structure, which is not feasible by X-Ray diffraction.

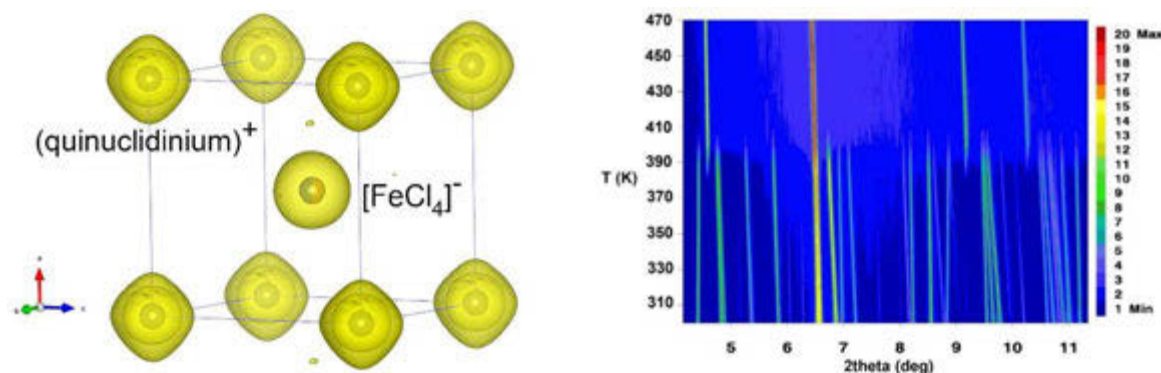


Fig. 1. (left) Calculated Fourier maps on the plastic phase derived from the refinement of the experimental data at 470 K. (right) Temperature evolution of the synchrotron powder diffraction of the (quinuclidinium)[FeCl₄] compound from RT to 470 K.

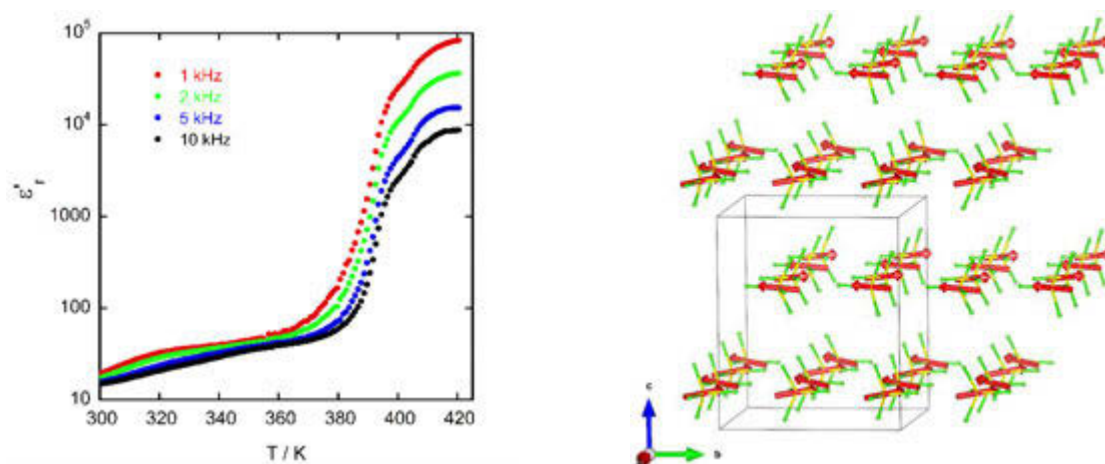


Fig. 2. (left) Relative permittivity as a function of temperature for different frequencies, in the range 300-420 K. The measurements were taken applying an amplitude of 1 V to cold-press pelletized samples. (right) Magnetic structure of (quinuclidinium)[FeCl₄] at 1.8 K. Color codes: yellow, iron; green, chloride; red, magnetic spin. The organic cations have been omitted for the sake of clarity.

Key words: plastic crystals, ferroelectric, hybrid materials, neutron diffraction, magnetic structure.

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LAYER GROUPS BRILLOUIN ZONE DATABASE ON THE BILBAO CRYSTALLOGRAPHIC SERVER

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Abstract: Operating since 1997, the *Bilbao Crystallographic Server* (www.cryst.ehu.es) (Aroyo *et al.* 2006, 2010) is a free web server that grants access to specialized databases and tools for the resolution of different types of crystallographic, structural chemistry and solid-state physics problems. Due to the growing interest in the field of materials with layer and multilayer symmetry, the number of programs dedicated to the study of these types of materials in the server has grown considerably in the recent years. Therefore, the aim of this contribution is to report on the current state of the server emphasizing on the recently developed computer tools for the study of materials with layer group symmetry.

The section dedicated to *Subperiodic groups* gives access to the layer groups crystallographic database and to more sophisticated programs to identify the layer symmetry of periodic sections or to describe the electronic structure and surface states of crystals. Recently, the layer groups Brillouin-zone database has been implemented in the server. This new database includes Brillouin-zone figures and tables of the wavevectors for all layer groups that form the background of the classification of the irreducible representations of all 80 layer groups. Layer-groups representations are extremely useful in numerous physical problems such as band-structure calculations, lattice dynamics and phase transitions. Based on the group-subgroup relation between layer and space groups, the data of the new database was derived from the space-groups wavevector database (Aroyo *et al.* 2014) available in the *Bilbao Crystallographic Server*. The symmetry properties of the wavevectors are described by the *reciprocal-groups approach* and this classification scheme is compared with the classification of Litvin & Wike (1991). In addition to this, a new computer tool for the complete characterization of the wavevectors has been developed.

Key words: Bilbao Crystallographic Server, layer groups, Brillouin-zone database

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MULTIFERROICITY AND MAGNETIC PHASE TRANSITIONS IN THE GREEN PHASE $\text{Gd}_2\text{BaCuO}_5$

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Abstract: In most of the spin-induced multiferroics, the ferroelectricity is caused by inversion symmetry breaking by complex spin structures of the transition metal ions. In this communication, we report the importance of interplay of $4f$ - $3d$ magnetic interactions in inducing ferroelectricity in the centrosymmetric ($Pnma$) green phase compound $\text{Gd}_2\text{BaCuO}_5$ [1]. With decreasing temperature, a long-range incommensurate ordering of both Gd^{3+} and Cu^{2+} spins at $T_N = 11.8$ K occurs with the modulation vector $\mathbf{k} = (0, 0, g)$ and a lock-in transition to a strongly non-collinear structure with $\mathbf{k}_c = (0, 0, \frac{1}{2})$ at $T_{loc} \sim 6$ K. Both spin structures induce electric polarization consistent with the polar magnetic space groups $P2_1ma1'(00\gamma)0s0s$ and P_c2_1ca , respectively. Based on the topology of magnetic interactions, we suggest that the ferroelectricity in both commensurate and incommensurate phases is driven by a complex interplay of two-spins and single-spin contributions from magnetic ions located in non-centrosymmetric environments. Our study demonstrates that the green phase family of compounds may serve as a new playground for studying the multiferroic phenomena, where the interplay of $4f$ - $3d$ interactions demonstrates an alternative route to find new magnetoelectric materials.

In this communication, we summarize the measured physical properties of $\text{Gd}_2\text{BaCuO}_5$. We will illustrate the process of solving the magnetic structure using the program FullProf [2]. For that, the recent implementation of magnetic superspace symmetry analysis [3] and full powder pattern simulated annealing have been crucial to distinguish different models.

Key words: multiferroics, magnetic neutron diffraction, simulated annealing

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PARAMAGNETIC BIOINSPIRED AEROGEL, FROM NANOPROCESSING COPPER(II)-URACIL COORDINATION COMPOUNDS, USEFUL IN BIOLOGICAL AND ANALYTICAL APPLICATIONS

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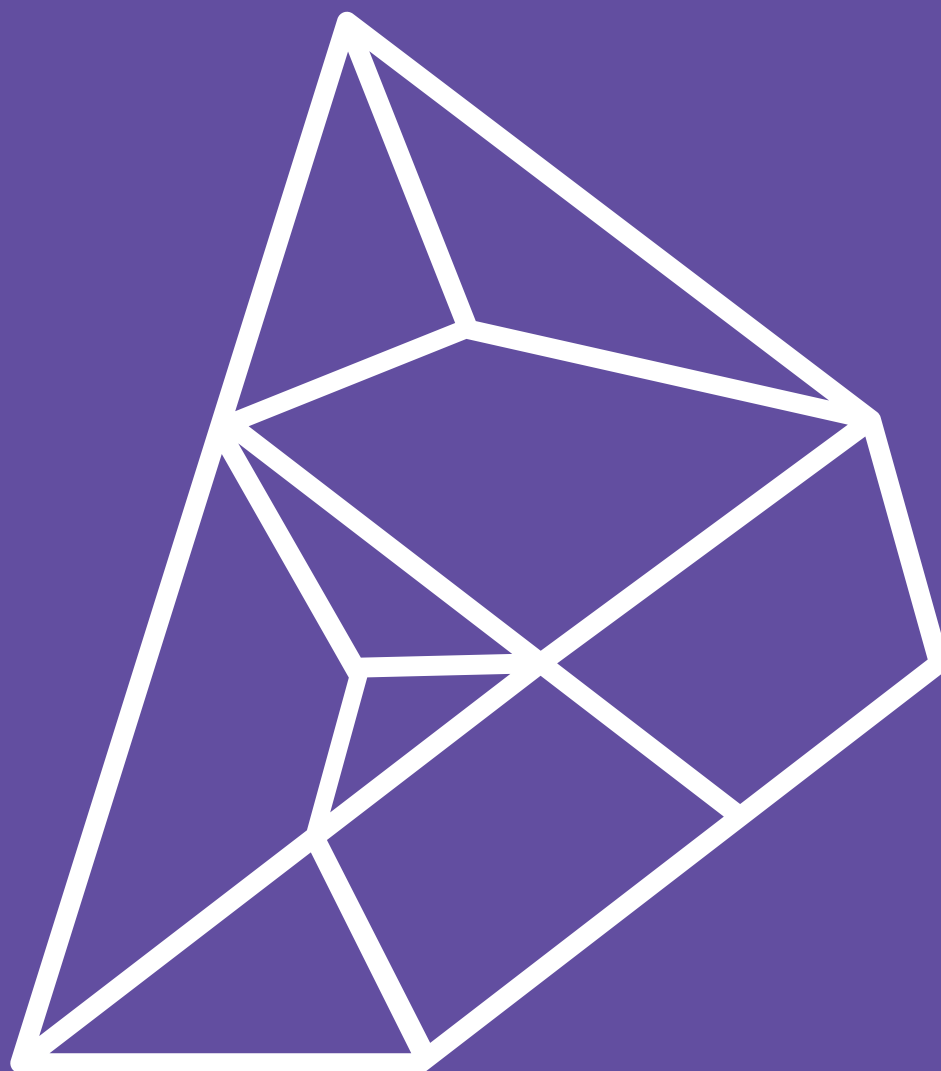
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Abstract: The combination of metal ions and nucleobases as ligands allows to synthesis new coordination compounds based on Cu(II) with modified uracil and 4,4'-bipyridine. Uracil as ligand can generate amazing structures with self-assembly and molecular recognition that help to create interesting supramolecular architectures such as the formation of gels. By direct reaction in water, it is possible to obtain the $[Cu(UPrO)_2(4,4'-bipy)_2(H_2O)]$ complex. This paramagnetic compound can also lead to the formation of a novel 1D coordination polymer $[Cu(UPrO)_2(4,4'-bipy)]_n \cdot 2.66nH_2O$, only heating it in dried methanol, and can be nanoprocessed via top-down to form a Metal-Organic Gel (MOG). The exhaustive study about conditions indicates that the presence of acetic acid in small quantities, temperature around 45°C, sonication, and traces of sulphate anion are crucial in the gel formation producing a drastic change in compound's morphology, from hexagonal-plates microcrystals to nanofibers around 26 nm of width and 12 nm of height. Its drying with supercritical CO₂ enables us to obtain the corresponding paramagnetic Metal-Organic Aerogel (MOA). This material, endowed with porosity that it previously lacked, is capable of sorbing I₂ and release it in a controlled way both in a gaseous state and in an aqueous solution. This fact together with a controlled delivery of copper ions and its nanometric size could make it useful for disinfecting applications as antibacterial agents. Otherwise, the manufacturing of this MOA, which preserve molecular recognition capacity, has made possible to create a HPLC column using it as stationary phase as proof-of-concept, being promising for bioanalytical applications.

Key words: Coordination polymers, Metal-Organic Gels and Aerogels, nanoprocessing, porosity.

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COEXISTENCE OF PROPER MAGNETIC AND STRUCTURAL INCOMMENSURABILITY ON $[\text{CH}_3\text{NH}_3][\text{Ni}(\text{COOH})_3]$ COMPOUND

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Abstract: In the present communication we describe of the structural and magnetic phase transitions of $[\text{CH}_3\text{NH}_3][\text{Ni}(\text{COOH})_3]$ perovskite-like metal–organic compound.¹ Below T_N the magnetic structure can be described by an unprecedented incommensurate magnetic phase. The structural and magnetic characterization has been performed through variable-temperature single-crystal and powder neutron diffraction. The title compound 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 $Pnma(00\gamma)0s0$ space group. This incommensurate phase remains unchanged with the decreasing of temperature up to ca. 2 K. The magnetic susceptibility data show that $[\text{CH}_3\text{NH}_3][\text{Ni}(\text{COOH})_3]$ compound exhibits an antiferromagnetic behavior below 34 K.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 T_N .¹

Key words: Incommensurate structures, Coordination polymers, Magnetic structures.

Acknowledgments: We are grateful to the Institut Laue Langevin for the allocated neutron beam-time through projects 5-41-947 and CRG-2369. We especially thanks to Dr. Nebil A. Katcho for provide the Int3D single crystal integration software. The Czech Science Foundation through project no. 18-10504S supports developing of the JANA software.

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INT3D: A DATA REDUCTION SOFTWARE FOR SINGLE CRYSTAL NEUTRON DIFFRACTION

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Abstract: In this communication we will present the software Int3D, a data reduction application for single crystal neutron diffraction. Int3D was initially developed to perform the data reduction for the D19 instrument of the Institut Laue Langevin (ILL), a large solid angle single crystal neutron diffractometer. However, it has been designed to be easily extended to any diffractometer operating with a 2D detector, and we are currently adapting the software to the D9 and D10 single crystal diffractometers of the ILL.

Int3D consists of a graphical user interface (GUI) through which the users can visualise, interact with and process their raw data to obtain the integrated intensities of the reflections collected during the experiment. It allows to perform all the required tasks of the data reduction: the peak search, the determination of the orientation matrix, the integration of the reflection intensity and the refinement of the cell and instrument parameters.

The interface is written in PyQt. The visualization tools are built from Silx (<https://www.silx.org/>) and VTK (<https://vtk.org/>) libraries. This allows fast and efficient 2D and 3D data visualization, which is extremely useful to validate the different steps in the data reduction process. Crystallographic calculations are written in Fortran (CrysFML library, <https://code.ill.fr/scientific-software/crysfml>). Forpy is used to pass data at runtime between the GUI and the Fortran programs running in the background, coupling the visualization with the crystallographic calculations (<https://github.com/ylikx/forpy>). A full demo of a data reduction process performed with Int3D can be found here (<https://youtu.be/dOxVcku10dM>)

Key words: single crystal neutron diffraction, data reduction, graphical user interface

Acknowledgments: This work was supported by the FILL2030 initiative, a European Union project within the European Commission's Horizon 2020 Research and Innovation program under grant agreement N 731096

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE PEROVSKITE-TYPE OXIDES $\text{SrCo}_{0.5-x}\text{Fe}_x\text{O}_3$ ($x=0.25, 0.50, 0.75$) DOPED WITH La, Pr AND Sm

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Abstract: Perovskite-type oxides show interesting properties that make them very versatile materials for multiple applications. Perovskite $\text{SrCo}_{0.50-x}\text{Fe}_x\text{O}_3$ ($x = 0.25, 0.50, 0.75$) has been synthesized by the ceramic and lyophilization method and a detailed study of its structure by means of X-ray diffraction has been carried out. Furthermore, our sample was doped with small amounts of La, Pr and Sm in Sr position.

In addition, UV-Vis diffuse reflectance spectra analysis was obtained and the bandgap for these semiconductors was determined by means of a Tauc plot. On a Tauc plot, $(\alpha h\nu)^{1/2}$ is represented versus the photon energy, where α is the absorption coefficient, calculated from the reflectance spectra by using the Kubelka-Munk model, h is the Planck constant and ν the photon frequency.

Key words: perovskite, XRD, ceramic, doped oxides

Acknowledgments: The authors are thankful to SEGAI (Servicio General de Apoyo a la Investigación) for the measurements

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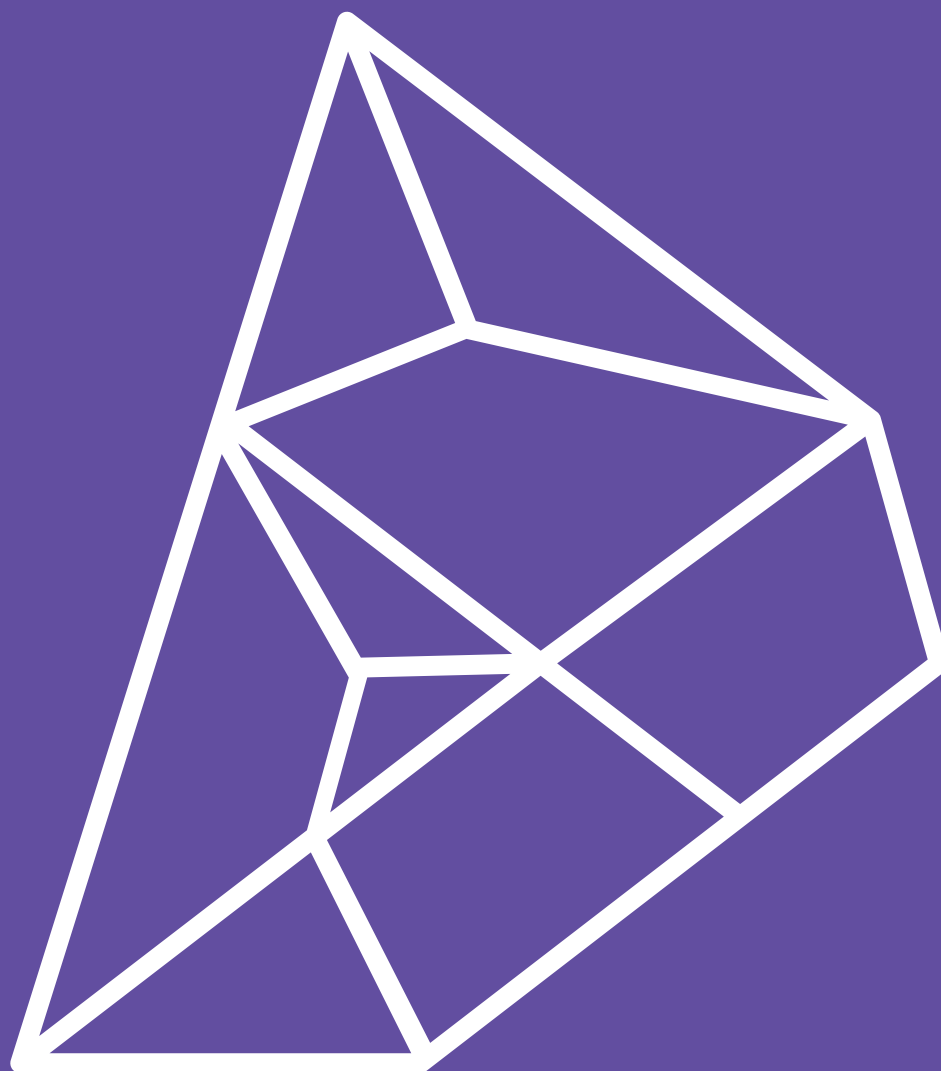
MS4- Crecimiento cristalino en diferentes entornos: desde la célula al espacio

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ON THE CRYSTALLIZATION OF CHIRAL PHARMACEUTICAL BINARY SYSTEMS

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Abstract: This scientific work presents a study of the solid state behaviour of the multicomponent system formed by the chiral active pharmaceutical ingredients (APIs) (+/-)-tramadol and *R/S*-naproxene [1]. In an initial part, the “in situ” crystallization of these molecules using a CO₂-laser (OHCD-Laser System) will be described [2]. The capillary used to perform these crystallizations is considered as a small crystallization reactor mounted on a single X-ray diffraction system in which different actions, normally applied at laboratory scale, can be performed. In order to avoid the known limitations requiring a single-component sample with a sharp melting point, solvents can be added diluted or concentrated to the capillary combined with the help of crystal seeds, polymers or other compounds with the aim to modify the crystallization conditions. In the used capillary, multi-component crystallizations of the APIs under controlled conditions, delivers different solids such as a salt of (+)-tramadol & *S*-naproxene, a co-crystal 1:2 of (-)-tramadol & *S*-naproxene or a conglomerate formed by both APIs. Goal of these controlled crystallizations is the generation of high quality single crystals for the measurement of neutron diffraction data and high resolution data for charge density analysis. Final objective is the study of weak interactions in the crystal packing and in general the solid state properties of these binary APIs.

In a second part, the enantiomeric resolution by crystallization of *rac*-tramadol with *S*-naproxene as resolving agent at industrial scale is presented [3]. After an optimization of the crystallization in solution using different solvents and conditions, yields above 40% and an optical purity >99%ee could be reached. Final objective in the resolution of these enantiomers is the fine-tuning of a deracemization methodology similar to the Viedma Ripening (Viedma) of the Temperature Cycling (Coquerel & Flood) using the CO₂-laser with the aim to obtain yields above 90% [4].

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CAN MOLECULAR FLEXIBILITY CONTROL CRYSTALLISATION?

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Abstract: Molecular flexibility has a profound impact on the number of possible ways molecules can pack in the solid state. The phenomenon of *Conformational Polymorphism* has been well-studied (Cruz-Cabeza, 2014) and recognised to be very common in complex pharmaceuticals (Cruz-Cabeza, 2015).

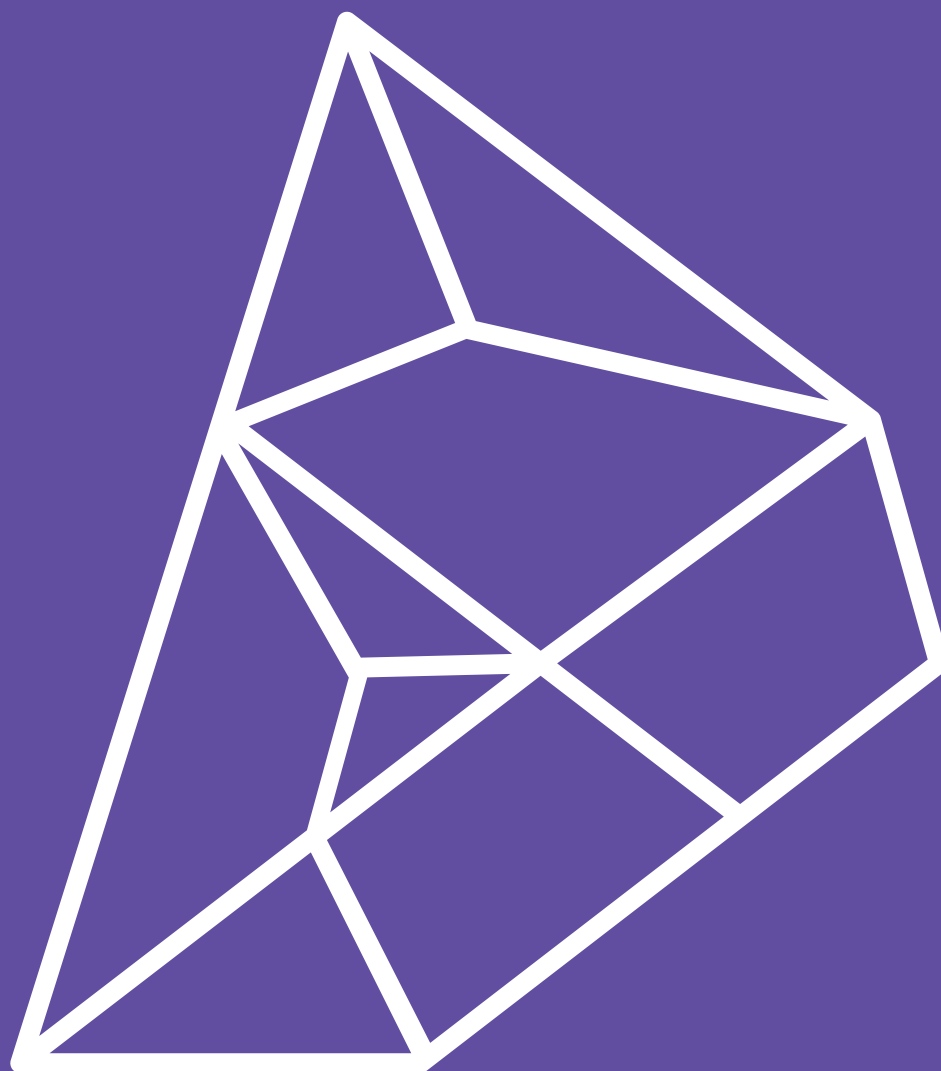
Perhaps what is less well understood is how molecular flexibility impacts crystallisation. In previous works, we studied the nucleation and growth kinetics of a number of rigid benzoic acid derivatives (Cruz-Cabeza, 2017). We have now studied the nucleation and growth kinetics of a number of flexible benzoic acid derivatives asking the fundamental question “Can Molecular Flexibility Control Crystallisation?” (Tang, 2021). Our kinetic data shows that when the energy barriers for conformational change are small, molecular flexibility is not rate controlling in crystallisation. Aromatic stacking was found, again, to be the key controlling step in the kinetics of crystallisation (Tang, 2021).

Key words: Crystal Growth, Crystal Nucleation, Molecular Flexibility, Aromatic Stacking

Acknowledgments: AJCC thanks the Royal Society for an Industry Fellowship in AstraZeneca. AJCC also thanks her colleague Prof. Roger Davey for support and helpful discussions.

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CRYSTALS SEARCH TO UNDERSTAND A PYROPHOSPHATASE FUNCTION

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Abstract: We pursue the crystallization of a phosphatase able to hydrolyse inositol pyrophosphates (PP-InsPs), key signalling and energetic molecules necessary for processes as intracellular phosphate homeostasis, telomere length regulation or apoptosis. In addition, this phosphatase hydrolyses polyphosphates (polyPs), essential for oxidative stress and pH resistance, representing an unique connection point for both PP-InsPs and polyPs metabolisms¹.

In this work, we are following an approach to gain insights into this phosphatase function and its catalytic mechanism. In our hands, the wildtype only produced crystals in presence of a variety of substrates or analogues (either inositol or polyphosphates based) and with good quality at pH 4.5. This allowed us to obtain a nice resolution protein structure and valuable data about interesting aspects of substrates recognition. However, we still lack essential information since the enzyme is not active at acidic pHs and this probably precludes in our crystal complexes two aspects: 1) a proper inositide conformation selection, due to high symmetry of the inositide ligands, and 2) a proper Mg ions configuration for catalysis. Next, we designed site directed mutagenesis, activity and thermal denaturation experiments to select protein constructs able to crystallize without substrates and at different pHs suitable for enzymatic activity. After an extensive work in that direction, we are currently boarding the crystallographic study of different protein mutants that are bringing us closer to our goals. We also plan the study of mutants and protein ligands that break the inositide or inositide recognition symmetry therefore promoting crystallization by capturing just one ligand conformation.

Key words: Inositol pyrophosphates, phosphatase, polyphosphates, protein crystallization.

Acknowledgments: This work was supported by grant BFU2017-89913-P from the Spanish Ministry of Economy and Competitiveness. Crystal data collection was performed at BL13-XALOC beamline from ALBA Synchrotron Radiation Source.

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ENCAPSULATION AND CONTROLLED RELEASE OF BIOACTIVE MOLECULES IN METAL-ORGANIC FRAMEWORKS

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Abstract: Essential oils (EOs) are aromatic liquids extracted from plants largely employed in food industry as natural antimicrobial or antioxidant agents and environmentally friendly catalysts. Their broader applicability is however limited by their poor processability as EOs typically present low stability and are volatile. One strategy to protect these delicate molecules relies in their encapsulation to enhance molecule stability, although a prolonged action and a controlled release is also desired (Hong & Park, 1999).

In this context we propose the use of nano-structured Metal-Organic Frameworks (MOFs) as robust EOs carriers. MOFs are crystalline porous materials formed by the assembly of organic linkers and metal nodes. Their modulable chemical properties and porous nature have facilitated their application in biologically related fields (Horcajada et al., 2012), demonstrating great ability to dictate and control molecule release. Furthermore, the miniaturization of MOFs in the form of nanoparticles has also favoured an enhanced bioactivity while improving their chemical and colloidal stability, facilitating the processing of the material (Giménez-Marqués et al., 2016).

Herein we present the preparation of a composite MOF-EO material based on the Fe-trimesate mesoporous MOF MIL-100(Fe). The obtained EO@MOF composite is characterized with high payloads and with control over the delivery kinetics, obtaining a large retention under specific simulated conditions and promoting a desired durable antimicrobial effect.

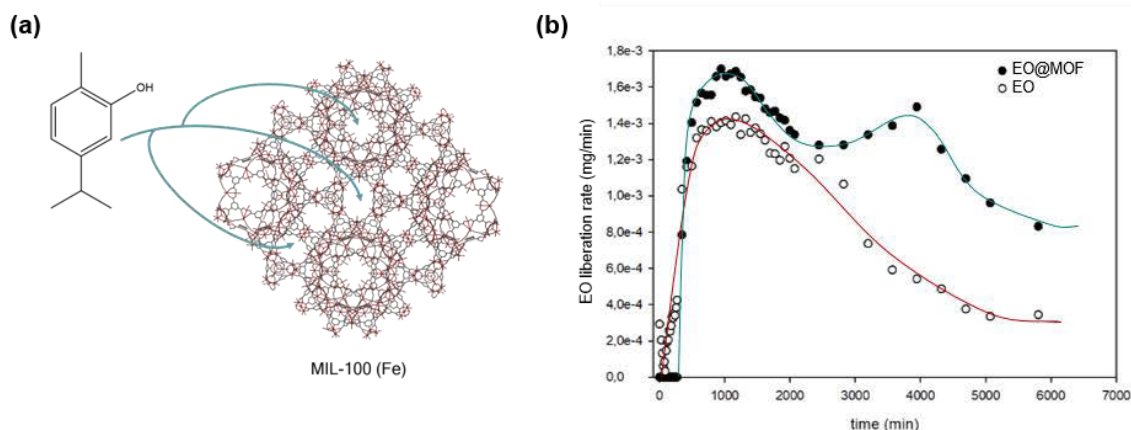


Figure: (a) Schematic representation of the composite EO@MOF. (b) EO kinetic liberation profiles as free molecules vs. encapsulated in the composite material.

Key words: MOF, controlled release, biocomposite, antimicrobial agent, improved stability.

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IN SITU MONITORING OF MINERAL PRECIPITATION SEQUENCE FROM ACOUSTICALLY LEVITATED DROPLETS OF LAKE MAGADI BRINE, EAST AFRICAN RIFT VALLEY

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Abstract: Lake Magadi is a saline soda lake in East African Rift Valley (Kenya). Perennial saline hot and warm springs fed the lagoons of lake Magadi. These springs discharging into the lagoons evolve into lake Magadi brines enriched in Na^+ , CO_3^{2-} , Cl^- , HCO_3^- and SO_4^{2-} . Evaporative concentration, mineral precipitation and fractional dissolution are thought to be the main processes responsible for the saline and soda chemistry of the lake. As a result of evaporation, different minerals precipitate in the lake. Understanding the kinetics of mineral precipitation have a paramount importance to understand the geochemical evolution of the brines. Therefore, we have envisaged an experimental study of the precipitation sequence of evaporating brines from lake Magadi. We have performed in situ X-ray diffraction of levitated droplets of the brine to monitor the mineral precipitation sequence during evaporation. A droplet of the brine was injected into an acoustic levitator and in situ X-ray diffraction were performed until complete evaporation of the droplet in the μSpot beamline at BESSY II synchrotron (Helmholtz Centre Berlin for Materials and Energy, Berlin, Germany). A monochromatized (Si 111) X-ray beam with a wavelength of 0.72929 Å and a beam size of 100 μm was used. Scattered intensities were collected with a two-dimensional X-ray detector (Eiger9M, CCD 3072 $\times$ 3072). Trona was the first mineral to precipitate. Halite precipitation began shortly after trona whereas thermonatrite was the last phase to appear. The results are compared with video monitored precipitation sequences and in situ Raman spectroscopy and ex-situ FESEM and EDX analysis. The combination of these techniques is a powerful tool for revealing actual precipitation sequences during evaporation of brines that are near saturation with respect to multiple minerals. We highlight in this work X-ray diffraction levitation experiments, and discuss the power of this technique in understanding the geochemistry of evaporative environments.

Key words: Lake Magadi, soda lake, trona, evaporation, mineral precipitation kinetics

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MANIPULATION OF TINY CRYSTALS FOR SERIAL CRYSTALLOGRAPHY

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Abstract: Since the first X-ray free electron laser fired up in 2009, the serial femtosecond crystallography (SFX) technique has revolutionized the field of structural biology with exciting and unprecedented results, allowing structural biologists access to previously restricted scientific areas. SFX has also cultivated new methods for nano-crystallogenesis, sample delivery and data processing. The success of SFX experiments strongly depends on the ability to produce large amounts of a homogeneous size distribution of well diffracting nano/micro-crystals. Over the past few years, our group has developed several micro-crystallization methods including the batch method, the free interface diffusion (FID), and the free interface diffusion centrifugation. These methods have been applied successfully in numerous SFX experiments. A brief introduction to these methods and the most common detection and characterization techniques (SONICC, the reversibility of crystallization method, DLS, TEM, and powder diffraction) of nano/micro-crystals will be presented.

Due to the nature of SFX in which each crystal is destroyed by an intense, ultra-short X-ray pulse, nano/micrometer sized crystals have to be constantly replenished between XFELs pulses¹. In early SFX experiments, the nano/microcrystals were delivered into the X-ray beam by the gas dynamic virtual nozzle (GDVN). Despite the success of the GDVN, which has been used for many SFX experiments, it has a serious limitation, the high sample consumption. Complete data sets using the GDVN can require up to 10 mL (sometimes even more) of crystal suspensions, typically containing on the order of 10^9 – 10^{11} crystals/mL. To overcome sample consumption problem, new approaches such as high-viscous media injectors, micro-fluidic devices, electrospinning injectors, and fixed targets have been developed. All these methods will be briefly discussed during my talk.

Key words: X-ray free electron lasers, serial crystallography, nano/microcrystals, sample delivery.

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NEW MULTIFUNCTIONAL DIVALENT METAL-COORDINATED SULFOPHOSPHONATES: STRUCTURES AND PROTON CONDUCTIVITIES

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Abstract: Metal phosphonate-based coordination polymers are structurally versatile multifunctional compounds that may contain a number of acidic groups such as P-OH; SO₃H, COOH, N⁺-H, etc. These features may result in the formation of extended H-bond networks and confer proton-conducting properties to the solids.¹

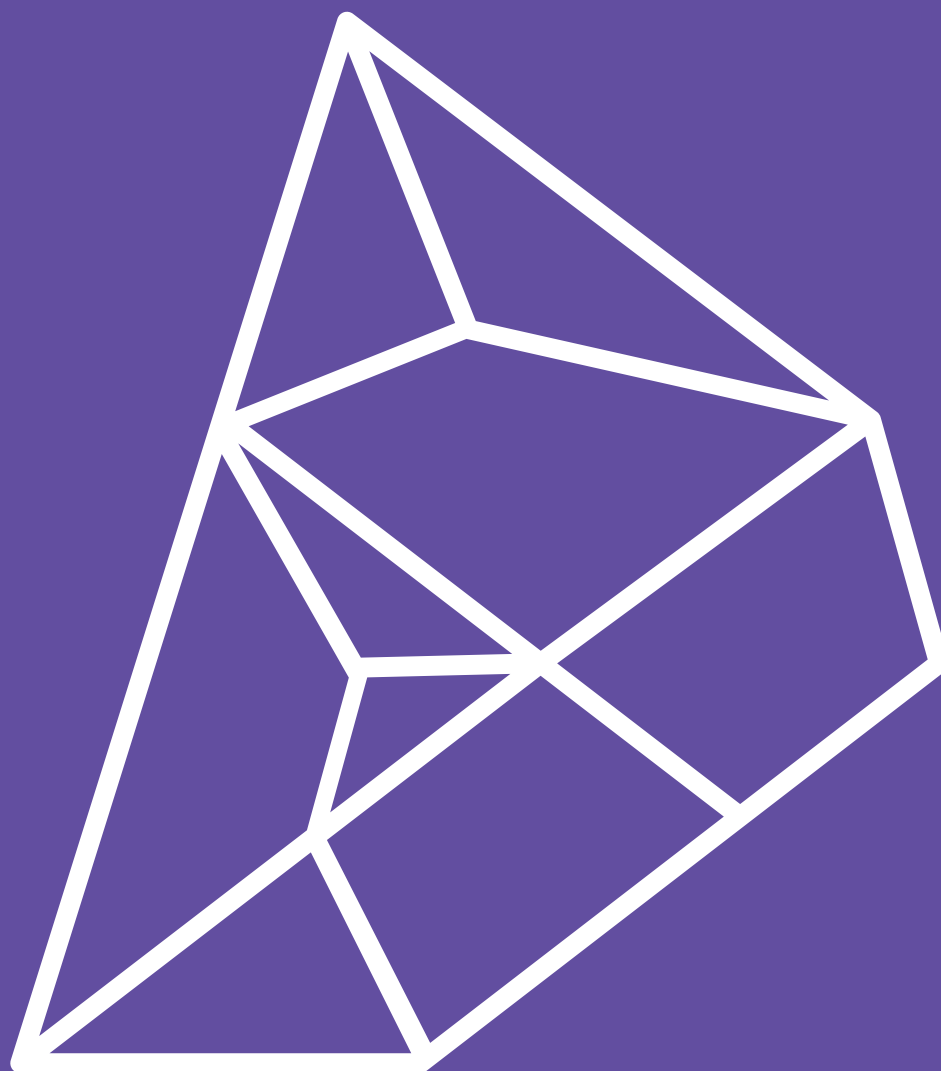
In this work, the crystal structures resulting from the combination of the amino-sulfophosphonate ligand (H₂O₃PCH₂)₂-N-(CH₂)₂-SO₃H with different divalent transition metal ions (Mn²⁺, Zn²⁺ and Cu²⁺) are reported. Optimal synthesis conditions were implemented by microwave methodology and high through-put screening. The crystal structure of the Mn(II) derivative was solved *ab initio* from synchrotron powder X-ray diffraction data. Copper derivatives required the presence of auxiliary ligands (1,10-phenanthroline, 2,2'-bipyridine or 4,4'-bipyridine) for their crystallization, being their crystal structures solved by single-crystal data. The different arrangement of the sulfonic groups determines a wide variety of metal-ligand coordination modes and frameworks, from 0D to 2D, what lead to a wide range of proton conductivity values depending on the formation of efficient H-bond networks.

Key words: coordination polymers, sulfophosphonates, proton-conductivity

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CRYSTAL ENGINEERING OF NANO/MICRO STELLATIONS

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Abstract: Characteristics of functional crystalline materials exhibiting unique features both at the nano and microscales are ultimately connected to their pathways of synthesis, which determine features such as their size, morphology, defects, surface protection, internal polarity and self-assembly behaviour. In particular, the combination of nano and microscales within a particular crystalline material can bridge advantages of nanocrystals and practical implementations in terms of catalysis. In this framework, the crystal engineering of intricate crystals with peculiar geometries, defects and surface properties necessitates to be explored and developed, which in turn will necessarily require novel synthetic strategies.

Here, we present singular geometries of NiO stellated crystals, characterized by interpenetrated crystalline facets protruding from the facets of Siamese twins (Figure 1). As fluids of reaction, we chose highly ionic molten salts, specifically molten hydroxides, whose especial feature in terms of large polarity, among other, allow for the growth of NiO stellated polyhedra in the absence of ligands protecting their surface.¹ Indeed, stabilization of charged {111} and related faces typical of these stellations must stem from the interaction with the ionic media. Likewise, concave faceted (nano) perforations at both the (micro) edges and the faces (Figure 1 c-d and d-f, respectively) are the result of crystal sculpturing in highly ionic media. Importantly, by tuning the polarity of the media we had control over the dimensions of the NiO stellated crystals from the nano- to the meso- and micro-scales (Figure 1 a-b, c-d, e-f, respectively).

Overall, we report the ligand-free crystal engineering of original shapes of NiO crystals via a simple synthetic method. Next, we will perform studies of their i) mechanism of formation and ii) catalytic performance. In all the cases, it is envisioned that the absence of organic molecules at their naked surface will be a catalytic asset.

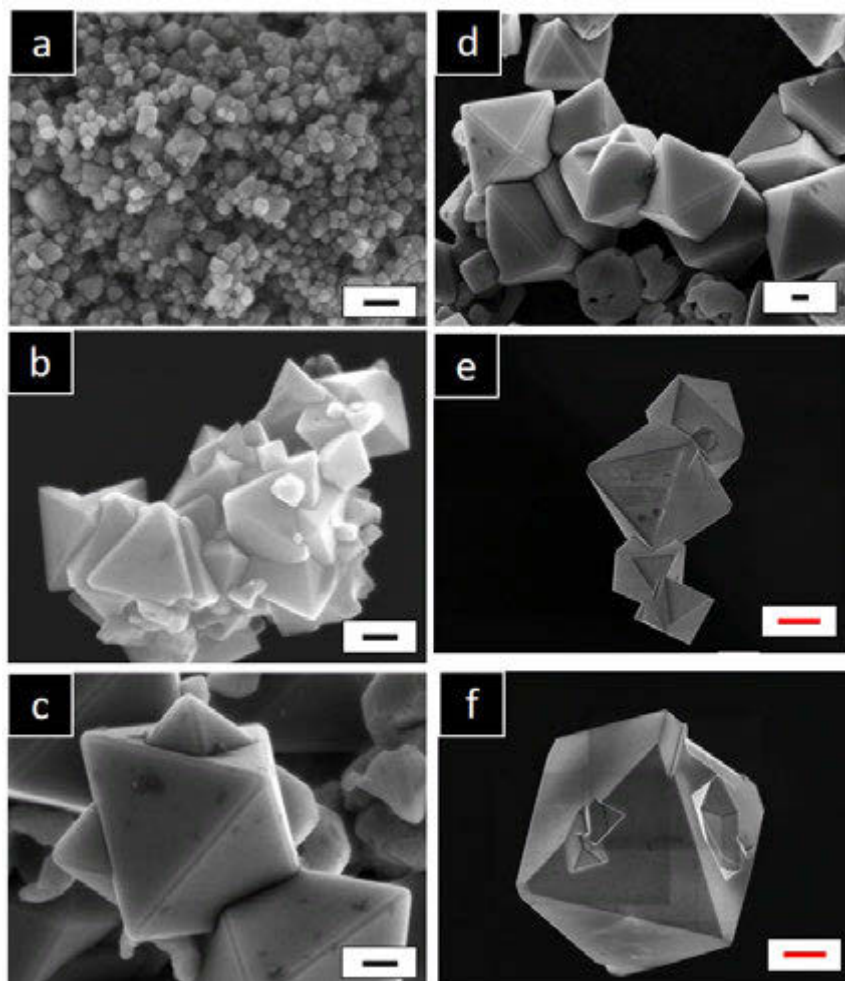


Figure 1. SEM images of stellated NiO (a) nanoparticles (~60 nm), (b) meso particles (~150 nm), (c-d) sub-micron particles (~600 nm) and (e-f) microparticles (~2500 nm). Scale bars are (a-d) 100 nm and (e-f) 1000 nm.

Key words: crystal engineering, stellated growth, stellated crystals, nickel oxide, microparticles.

Acknowledgments: This work was supported by the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement n° 600391.

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CRYSTAL GROWTH UNDER ELECTRIC FIELDS

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Abstract: The study of crystallization conditions on crystalline morphology and structure is of great scientific interest since they help a better compression of the mechanisms that regulate crystal growth. Among the conditions that can affect the crystalline habit are mentioned in the bibliography, as well as the obtaining techniques used, the degree and temperature of supersaturation of the mother solution and the applied electric field. However, not many bibliographic references are found when the crystal growth is carried out from aqueous solutions by isothermal evaporation under the action of electric fields at different intensity. In this line, in this work the first results of the crystallization of two compounds of the family of double potassium lanthanide sulphates are presented: $K_3Sm(SO_4)_3$ and $K_3Gd(SO_4)_3$ obtained by isothermal evaporation at temperatures between 70 and 80 °C under the application of electric field intensities up to 15 kV/m, studying the effect of the electric field on the promotion of new crystalline phases due to these materials have polymorphism. It is also analysed, from a theoretical point of view, how the incorporation of the electric field term in the expression associated with the variation of the Gibbs free energy affects the formation of the nucleus and therefore the formation of the crystal.

Key words: Crystal growth, Electric field, aqueous solutions, isothermal evaporation, polymorphism

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CRYSTALLIZATION OF TERBIUM-DOPED APATITE NANOPARTICLES BY THERMAL DECOMPLEXING OF CALCIUM-CITRATE-PHOSPHATE-CARBONATE SOLUTIONS

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Abstract: The preparation of luminescent nanoparticles is of great interest for applications in drug delivery and bioimaging techniques. Biomimetic nanocrystalline apatites display ideal biocompatibility properties due to its similarity to bone apatites, in which they are used as a calcium reservoir. The structure of this calcium phosphate phase allows an easy substitution of Ca^{2+} ions, in this study it will be replaced with Tb^{3+} ions to provide luminescence. We propose the synthesis of Tb^{3+} -doped apatite nanocrystals by thermal decomplexing of $\text{Ca}^{2+}/\text{Tb}^{3+}$ -citrate-phosphate-carbonate solutions [1,2]. We varied the $\text{Tb}^{3+}/\text{Ca}^{2+}$ molar ratios, using $[\text{Tb}^{3+}]$ from 0,001M to 0.02 M, and $[\text{Tb}^{3+}]+[\text{Ca}^{2+}]=0.1\text{M}$ in the mother solutions, and different maturation times (4h, 24h, 96h, 7 days). The precipitates were characterized by XRD, Raman and FTIR spectroscopies, DLS and ζ potential, SEM, TEM, HRTEM, SAED, EDX and Luminescence spectroscopy. Results show the precipitation of doped needle-shaped apatites with nanosized dimensions only when $[\text{Tb}^{3+}] \leq 0,01\text{M}$ irrespective of the maturation time, and the presence of citrate adsorbed on the nanocrystals, a feature of bone apatites; when $[\text{Tb}^{3+}]$ increases they change from nanocrystals to microcrystals, and, in addition, a nanocrystalline terbium phosphate (hexagonal phase) started to appear in the precipitate at some concentrations and time points. Maximum relative luminescence intensities (R.L.I.) of the nanocrystals were about 300 and luminescence lifetimes $\tau \sim 2.1\text{ms}$, while for samples prepared at higher $[\text{Tb}^{3+}]$, the maximum R.L.I. was about 840, and $\tau \sim 2.4\text{ms}$. To finish this study, cytotoxicity/biocompatibility tests of these samples are underway. We conclude, the thermal decomplexing method is a bioinspired technology allowing the preparation of biomimetic and luminescent apatite nanocrystals, for potential applications in nanomedicine.

Key words: Apatite, Terbium, Luminescence, Nanocrystals

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ON THE SHAPE OF THE NAICA GIANT GYPSUM CRYSTALS

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Abstract: The giant gypsum crystals found in Naica, Mexico, are the one of the biggest crystals found on Earth and probably the most spectacular group of giant crystals known today. Surprisingly, the shape of these crystals has been reported to be different from the common gypsum habits (García-Ruiz et al., 2007; Otálora and García-Ruiz, 2014; Van Driessche et al., 2010; Van Driessche et al., 2011). These studies have explained the size of the crystals in terms of temperature and nucleation frequencies, but the unique shape of these elongated crystals with dominant $\{1k0\}$ faces and the smaller $\{010\}$ faces has been less explored (Otálora et al., 2015). Such morphological study requires a deep knowledge on the specific step energies that control the relative growth rates of the different forms of gypsum crystals, mainly the $\{010\}$ and $\{120\}$. Using the previous morphological observation and our new knowledge on the specific step energy of the steps parallel to $\{010\}$ (obtained by Atomic Force Microscope, Criado-Reyes et al., 2020) and these estimated for the steps parallel to $\{120\}$, we discuss an integrated model for the morphology of the giant gypsum Naica crystals. This model is based on three key observations:

- 1- Exchange of predominant nucleation rates of faces $\{010\}$ and $\{120\}$ depending on the bulk supersaturation.
- 2- Development of the $\{1k0\}$ forms by step bunching on $[001]$.
- 3- Acceleration of the $\{-111\}$ growth rate due to the re-entrant angle of the $[100]$ contact twin.

Key words: Gypsum, Giant crystals, crystal growth, gypsum twin, dislocations, growth mechanisms.

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REDOX REACTIONS CATALYZED BY MINERAL SURFACES IN AN EARLY MARS ENVIRONMENT

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Abstract: The production of hydrogen peroxide (H₂O₂) from water oxidation catalyzed by mineral surfaces is a very attractive hypothesis invoked to locally explain the presence of oxidized mineral phases in absence of oxygen in an Early Mars environment. Here we used cyclic voltammetry (CV) to perform experiments under anoxic conditions as a way to determine the sequence of redox reactions involving the formation of free radicals during adsorption of water at mineral interfaces. This would be a useful information to be used in geochemical codes attempting to model the crystallization kinetic in early Mars scenarios. CV experiments were performed with Pt/mineral-Np's/ Nafion®/ electrodes in N₂ purged solutions vs. Ag/Cl 3M KCl and applied to determine the redox reactions resulting from water adsorption on pyrite and clay mineral surfaces, in both cases in anoxic conditions. The electrodes were built on the surface of screen printed Pt by immobilizing pyrite Np's (Gil Lozano et al 2017) and the clay mineral nontronite (Yuan et al 2018) in a Nafion® membrane (Di Giovanni et al. 2016). This procedure is advantageous to determine the redox products at the interface for various reasons: (1) nanoparticles offers higher reactive surface, compared to single crystal plates. (2) The use of Nafion® produces an adequate backbone that -when used in solution- provides a rapid hydration mechanism, due to the side chains terminated on sulfonic acid. This procedure allow-us to analyze the redox behavior of the adsorbed aqueous species at the crystal interface because the low oxygen permeability of Nafion limit the passage of O₂(g) and negatively charged ions through the membrane. Consequently, if detected, anodic oxygen oxidations (OOR) reflect the behavior of adsorbed H₂O, OH⁻ or H₂O₂ at the crystal interface and not the solution reactions. Preliminary results show that the characterization of the redox properties of structural Fe in clay minerals is particularly challenging since they are affected by its bonding environment which can be likely related to the structural and compositional differences. In the case iron disulfides (pyrite or marcasite), the efficiency of the interface reactions to form reactive oxygen species could be connected with bulk's microstructural aspects, like oriented attachment growth. This process may generate different terminations of the crystal faces in the form of kinks or terraces, then modifying the number of defects available for water splitting at pyrite interface.

Key words: water splitting 1, surface reaction 2, Mars 3, Pyrite and Nontronite 4, cyclic voltammetry 5.

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SANS STUDY OF THE PYRITE MICROSTRUCTURE IN CRYSTALS GROWN BY ORIENTED ATTACHEMENT

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Abstract: Despite its good semiconductor properties, pyrite crystals show low and poorly reproducible efficiency. This irregular response is usually attributed to intrinsic surface-states. However, in addition to the interfacial defects, mesocrystals of pyrite may form via a self-assembly mechanism with intermediate aggregation states in the bulk crystals which can provoke important differences on its reactivity and semiconducting efficiency (Gil-Lozano et al, 2017). In order to characterize the spatial distribution of the pyrite crystals at the nanometric scale we have performed Small Angle Neutron Scattering experiments (SANS). We used single-crystal plates as samples and the experiments were undertaken in air, without solvent. They were cut parallel to [100] direction. The 2-D detector images showed two completely different types of patterns consisting of: (1) Bragg-like scattering patterns, suggesting an “ordered” microstructure or (2) isotropic scattering from a disordered distribution of defects. The existence of periodic patterns affecting to the spatial distribution of the “scatterers” is rather unusual in SANS and demonstrate that some of the pyrite-single crystals has a broad Bragg-type peaks indicative of partial ordering. The eight-pointed star patterns observed in these cases are consistent with the diffraction in the normal directions to the pyritohedron faces, whose modulated growth, results in the well-known striations of the the pyrite surfaces, running parallel to the direction [100]. The growth process of pyrite single-crystals may proceed through oriented attachment (OA) of nanocrystals, (Zhu et al. 2015) when the growth units share a common crystallographic face, usually {100} and {210}. This mechanism may create interstitial defects or quantum wells along certain directions, influencing their electrochemical behavior. The experiments reported here open the possibility of use SANS spectra, to characterize the polycrystalline-to-monocrystalline conversion through OA in pyrite crystals to improve their electrochemical performance and reactivity.

Key words: oriented attachment (OA) 1, SANS 2, Pyrite 3, microstructure 4.

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USE OF PREFERRED ORIENTATIONS FOR DETERMINING THE CRYSTALLINE HABIT OF POWDER SAMPLES.

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Abstract: Crystallization in different conditions, may produce crystals with alternative habits. When the distinct facets show anisotropic surface chemistry, several physicochemical properties of importance in its pharmaceutical performance can be affected: wettability, flowability, surface area, dissolution, or bioavailability (Shell, 1963). For that reason, determining the crystalline habit can be an important point on the study of active pharmaceutical ingredients.

Powder diffraction theory assumes a random distribution of the crystallites to produce a pattern. However, in practice, crystallites tend to arrange themselves according to their habitus: flat crystallites tend to be stacked and needle shaped tend to line up in the needle direction. Preferred orientation in the specimen influences the intensities of various reflections so that some are more intense and others less intense, compared to what would be expected from a completely random specimen (Pecharsky & Zavalij, 2005).

Empyrean diffractometer allows to perform measurements both in transmission and reflection geometry. The effect of preferred orientation differs between the two geometries with planes horizontal to the sample chamber being strong in transmission while planes perpendicular to the sample chamber being strong in reflection (USP 35, 2012). This phenomenon can be used to identify the preferentially exposed facets of the material on the sample holder to obtain valuable information about the crystalline habit.

Key words: X-ray powder diffraction, Preferred orientations, Crystal habit.

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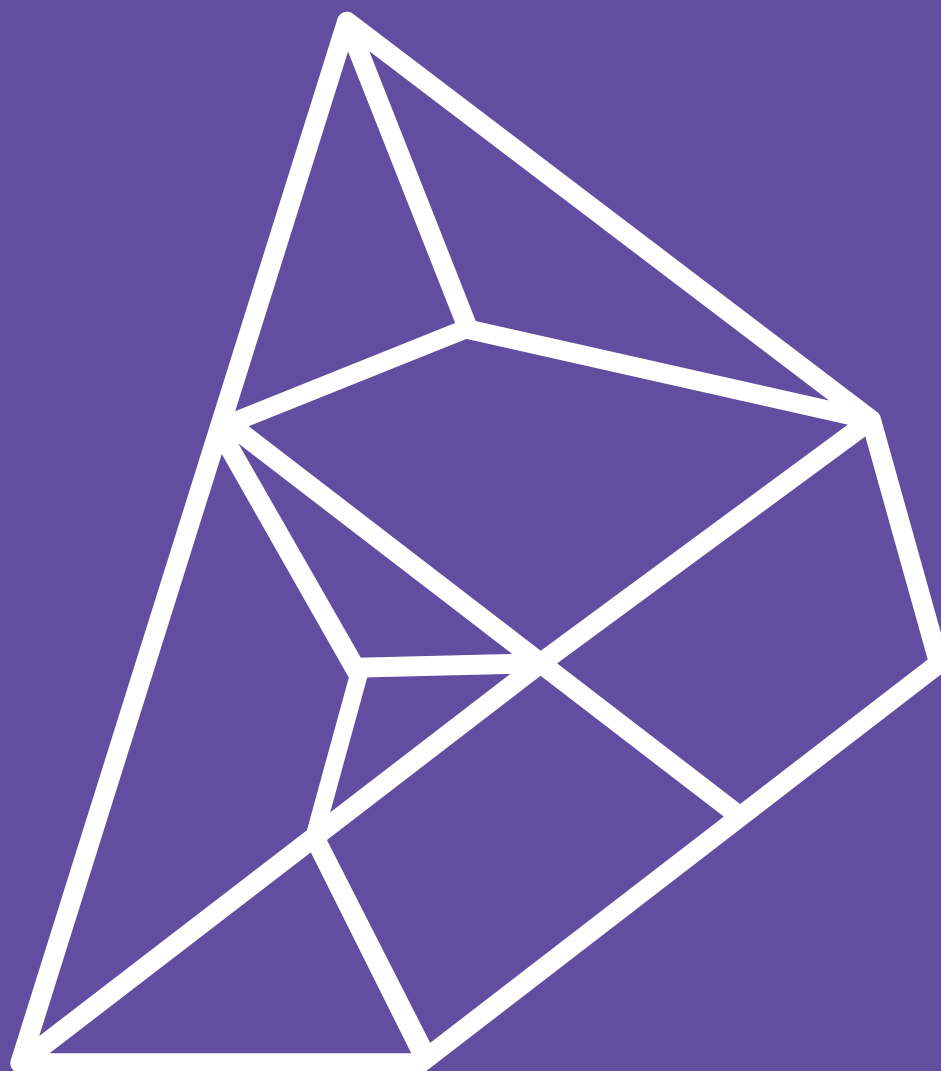
MS5- Estructura y propiedades de materiales: desde nuevos minerales a biomateriales

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DESORDEN Y DEFECTOS EN MATERIALES PARA BATERÍAS

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Abstract: La imperfección es una característica universal en los materiales cristalinos que puede llegar a tener un gran impacto en sus propiedades macroscópicas. Los defectos puntuales (de intercambio, intersticiales o vacantes), de apilamiento, los intercrecimientos, etc. se encuentran en todos los materiales funcionales, en mayor o menor medida. El reto consiste en caracterizar el desorden de forma cuantitativa, establecer correlaciones con las propiedades, y finalmente controlar su ubicación y cantidad mediante la síntesis y/o procesamiento de los materiales, ofreciendo nuevas oportunidades para la ingeniería de materiales.

Los materiales para el almacenamiento de la energía no son una excepción. En las baterías la energía se almacena mediante reacciones de oxidación/reducción, que frecuentemente ocurren en el estado sólido e implican la intercalación/desintercalación de la especie móvil (por ejemplo los iones de litio en una batería Li-ion). Estas reacciones suelen resultar en transformaciones estructurales cuya reversibilidad es clave para la ciclabilidad de la batería. Entender el rol de desorden y defectos es fundamental para el diseño de los mejores materiales.

En esta presentación se mostrarán varios ejemplos de materiales para baterías en los que varios modelos microestructurales y distintas herramientas (Rietveld, FAULTS, etc.) aplicadas a las técnicas de difracción de rayos X (difracción de polvo y de bajos ángulos - SAXS-) han permitido ofrecer una ventana accesible para la observación y parametrización de desorden y defectos para elucidar su rol en las propiedades electroquímicas.

Key words: Baterías, Desorden, Defectos

POROUS METAL-ORGANIC ASSEMBLIES FOR ENERGY RELEVANT ORGANIC VAPOUR SEPARATION

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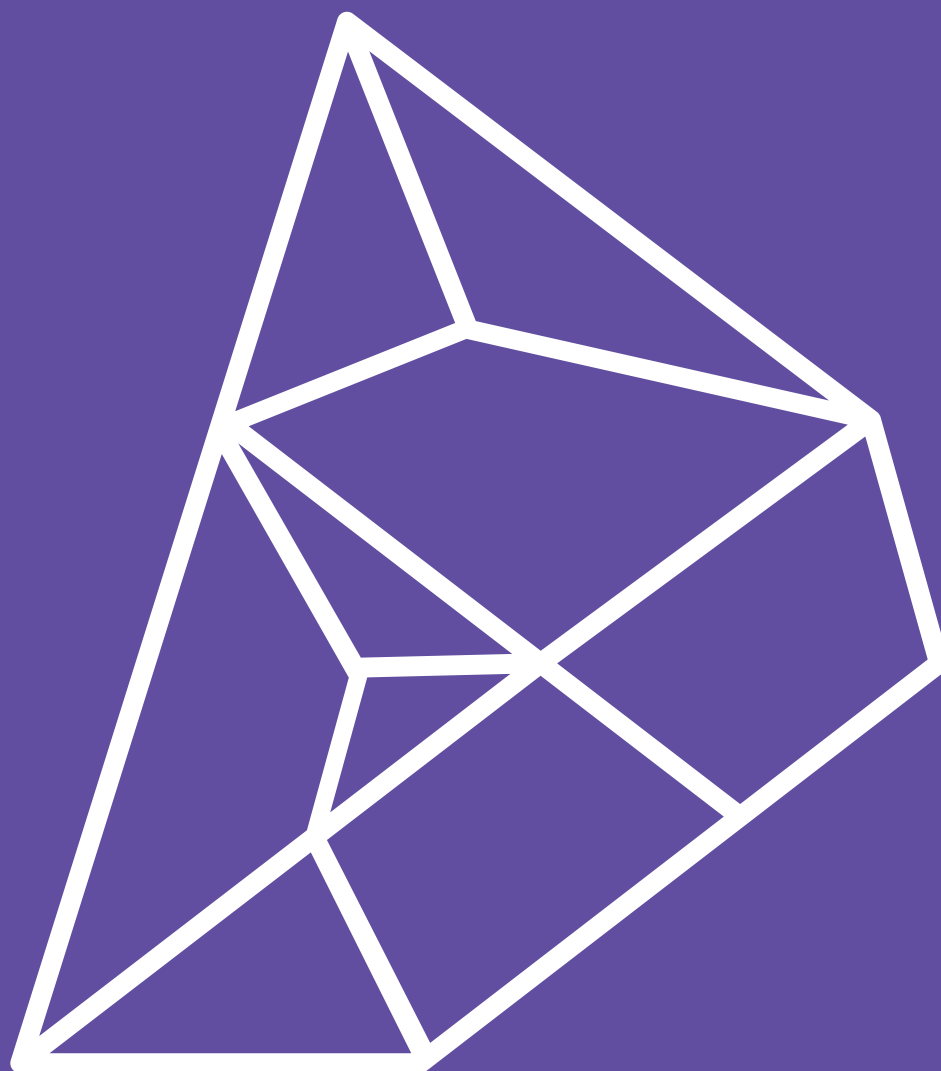
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Abstract: Selective separation of gases/vapours with similar physicochemical properties involves energetically costly distillation processes. Alternative separation processes based on shape-selective molecular sieving, taking place on porous frameworks (or membranes), are less energy demanding but require an optimal balance between selectivity and diffusion kinetics (permeability).

In this report, we focus on the low energy separation of organic vapour fuels possessing very similar boiling points. To achieve this goal, we have focused on designing porous materials with improved diffusion kinetics for efficient low energy separation processes. The optimization of the gas diffusion kinetics on the porous structure of metal-organic assemblies have been achieved using the following strategies: i) reduction of the diffusion path by formation of hierarchical pores; ii) improvement of gas diffusivity on soft-porous materials and iii) pore functionalization on constricted porous networks. To prove these concepts, we have studied the resolution of hexane isomers mixtures, relevant to RON enhancement of gasolines and the separation of cyclohexane/benzene which are considered liquid organic hydrogen carriers (LOHCs) in the future hydrogen economy.

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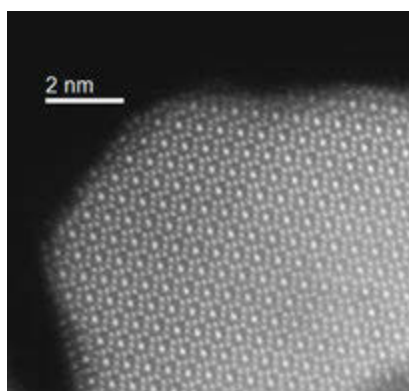
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ANTIPHASE BOUNDARIES IN TRUNCATED OCTAHEDRON-SHAPED ZN-DOPED MAGNETITE NANOCRYSTALS

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Abstract: The presence of antiphase boundaries with local ferromagnetic coupling is herein related to the magnetic performance of truncated octahedron-shaped zinc-doped magnetite nanocrystals. Atomic resolution STEM imaging reveals the presence of these antiphase boundaries perpendicular to the [111] direction of the spinel structure of the nanocrystals. Magnetic characterization and DFT calculations indicate a local ferromagnetic order, originating from Fe–Fe enrichment at these individual lattice defects in the nanocrystals, as the underlying cause of the magnetic response measured.



Key words: antiphase boundaries, ferromagnetism, antiferromagnetism, crystallographic defects, spinel structure

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CRYSTALLINE MAGNETIC 2D MOF NANOSHEETS VIA LIQUID EXFOLIATION

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Abstract: Since the isolation of graphene, the study of new 2D layered materials has become one of the main fields of research. Typically, this research involves inorganic materials, although more recently other graphenoid materials have been developed, including 2D coordination polymers and metal–organic frameworks (MOFs) [1].

Recently, our group has reported the preparation of MUV-1-X (MUV = Material of the University of Valencia), a family of layered coordination polymers of formula $[\text{Fe}(\text{bimX})_2]$ (HbimX = benzimidazole functionalized in the 5-position with X = H, Cl, Br, or CH_3), which are magnetically ordered at low temperatures. These crystalline materials are formed by tetrahedral Fe(II) centres linked via benzimidazolate bridges, and consist on neutral layers separated by weak interactions. We have recently shown the possibility of exfoliating this material using dry methods [2].

In this work, I will present the liquid exfoliation of **MUV-1-X** (see Fig. 1) [3]. Different delamination and sedimentation conditions have been studied in detail, demonstrating the production of nanosheets of good quality with lateral sizes of several microns and heights of only few nanometers. Selected-area electron diffraction shows the high crystallinity of the exfoliated flakes.

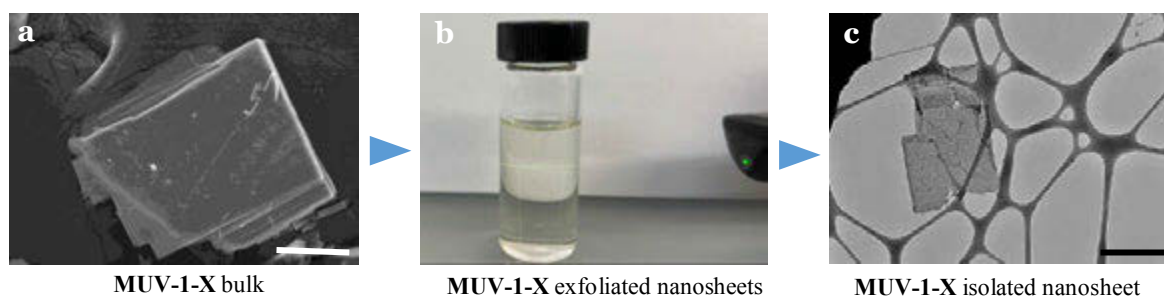


Fig. 1 (a) SEM image of a crystal of **MUV-1-X**, (b) Tyndall effect in a solution of **MUV-1-X**, (c) TEM image of **MUV-1-X** nanosheet. SEM scale is 100 μm . TEM scale is 2 μm .

Key words: 2D, MOF, exfoliation, layered.

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EFFECT OF MOLECULAR COMPOUND FORMATION ON MISCIBILITY PROPERTIES OF TRIACYLGLYCEROL SYSTEMS

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Abstract: The phase behavior of triacylglycerol (TAG) mixtures contribute to the physical properties of natural fats and oils. In this sense, three main types of mixing states exist in lipid blends: eutectic, solid solution and formation of molecular compounds (MCs). The present work aims to enlighten the influence of MC formation on miscibility properties of lipid systems through the study of the stable phase diagrams of binary and ternary mixtures of a tri-saturated TAG (PPP or 1,2,3-tripalmitoyl glycerol), and two saturated-unsaturated mixed-acid TAGs (POP or 1,3-dipalmitoyl-2-oleoyl glycerol, and OPO or 1,3-dioleoyl-2-palmitoyl glycerol). These component TAGs are widely present in natural fats and oils, such as palm oil, palm kernel oil and lard. To elucidate the phase behavior of PPP:OPO, PPP:POP and PPP:POP:OPO (POP:OPO forming MC crystals at equimolecular composition) systems, mixtures at different molar mass intervals of the former TAGs were first subjected to thermal incubation to attain thermodynamic stabilization. Then, differential scanning calorimetry (DSC) and laboratory-scale X-ray diffraction (XRD) were used for their thermal characterization and polymorphic identification. All three systems under study exhibited highly asymmetric eutectic behavior due to different thermal properties and molecular arrangement between component TAGs. However, remarkable differences arose from the ability of mixed-acid TAGs and the MC to integrate in the crystal lattice of PPP. In more detail, POP exhibited a noteworthy solubility in PPP, whereas a decrease in solubility was observed when OPO was employed, and MC exhibited an intermediate solubility between the two component TAGs. These results show how the occurrence of MC may affect the mixing behavior in complex lipid systems, which may be of special interest for the development of new functional lipid materials.

Key words: Triacylglycerol, molecular compound, crystallography, phase behavior

EGGSHELL MEMBRANE TEMPLATE FOR CONTROLLED PRECIPITATION OF CALCIUM PHOSPHATE VIA VAPOUR DIFFUSION

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Abstract: Biomimetic strategies aim to improve the properties of synthetic nano-crystalline apatites. These approaches focus on replicating the way biological systems control the precipitation of biominerals (Barthelat F., 2007). Previous nucleation experiments using vapour diffusion sitting drop (VDSD) crystallization methodology optimized a microenvironment for controlled precipitation of calcium phosphates (CaP) (Gómez-Morales et al., 2016). On the other hand, heterogeneous nucleation on a biological organic surface, like eggshell membranes (ESM), may control the microstructural properties during the mineral precipitation. In this study, we used this approach to prepare novel CaP/ESM biomimetic materials using the VDS method. The methodology consisted on the reaction of $\text{Ca}(\text{CH}_3\text{COO})_2$ and $(\text{NH}_4)_2\text{HPO}_4$ microdroplets deposited in ESM sections that react with CO_2 and NH_4 resulted from decomposition of NH_4HCO_3 solution placed in the reservoir of a *crystallization mushroom*. The experiments were carried out in different reaction times: 1, 3, 5, 7, 15 and 30 days, at room temperature and 37°C (physiological condition). Samples were characterized by SEM, XRD, FTIR-ATR and Raman techniques. Additionally, cytotoxicity and osteogenic differentiation assays on human mesenchymal stem cells are underway to evaluate the biocompatibility and potentiality of the novel materials in bone tissue engineering. FTIR spectra of the mineralized membranes displayed several absorption bands, at 560 cm^{-1} (O-P-O ν_2) and 1030 cm^{-1} (P-O $\nu_1\text{ PO}_4^{3-}$), associated to different vibrational modes of calcium phosphate mineral phases (Rey et al., 2014). Furthermore, Raman spectra showed an intense band at 961 cm^{-1} ascribed to apatite $\nu_1\text{ PO}_4^{3-}$ groups. XRD patterns displayed a broad peak approximately at $2\theta = 31^\circ$ associated to nano-crystalline apatite precipitation (Drouet, 2013). SEM images showed the mineral distribution and the crystal morphologies developed over the membrane surfaces. We conclude the proposed synthetic route produced biomimetic CaP/ESM materials with composition and properties resembling those of mineralized tissues, with potential for clinical use.

Key words: eggshell membrane, calcium phosphate, vapour diffusion, biomimetic.

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FUNDAMENTAL INSIGHT INTO PHOTOELECTROCATALYTIC HYDROGEN PRODUCTION WITH A HOLE-TRANSPORT BISMUTH METAL-ORGANIC FRAMEWORK

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Abstract:

Solar fuels production is key in the development of sustainable energy conversion technologies, where H₂ production by means of light represent one of the most crucial challenges to produce renewable fuels. In this field, metal-organic frameworks are being investigated in order to improve the activity because of its possibility to incorporate different photoactive building blocks. Nevertheless, to design more efficient materials its decisive to identify the reaction intermediates involved in the process.

In this work, we report the synthesis and deep characterization of a new MOF structure called IEF-5 (Imdea Energy Framework-5) formed by bismuth and a linker with hole transport ability, dithieno[3,2-b:2',3'-d]thiophene-2,6-dicarboxylic acid (DTTDC). We have completed a full study at different times scales (from fs to ms) by combining several techniques of time-resolved spectroscopies, as laser flash photolysis and core hole clock measurements, with theoretical studies to really understand the behaviour of the material to finally determine the effect of the competitive reactions on the H₂ production process. We have established the mechanism of the H₂ production (Figure 1) which involves the formation of a radical anion as intermediate in the reaction of photogenerated holes with an electron donor. The obtained result shed new light on the employment of new materials, specially MOFs, for solar fuels production.

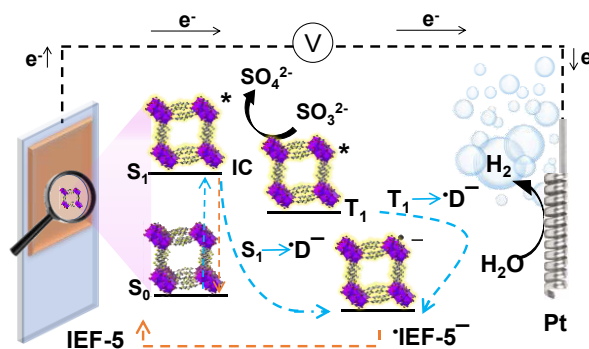


Figure 1. Scheme of photo(electro)catalytic H₂ production mechanism.

Key words: Metal-organic framework, charge transfer, hydrogen production, excited states.

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RIETVELD REFINEMENT OF BROWN AERINITE IN PYRENEAN SPECIMENS BY $tts-\mu$ XRD

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Abstract: Historically, aerinite is a blue pigment used in many romanian paintings of the Pyrenean zone between the XI-XIV centuries. Its characteristic blue color varies from dark to pale-blue. However, one double question still remains open: ‘Must aerinite be always blue?’ or ‘Is it always blue simply because it can only be clearly identified when it is blue?’ To clarify this point, the synchrotron through-the-substrate microdiffraction ($tts-\mu$ XRD) technique has been used (Rius *et al.*, 2011). This technique allows the simultaneous visualization of a thin-section under polarized light and the measurement of diffraction patterns at target points previously identified either by SEM-EDX, by EMP analyses or from BSE images. During the inspection of a polished thin-section of a specimen coming from Tartareu (Lleida), a small area containing brown submicrometric fibers was detected next to a region containing pale-blue aerinite (Rius *et al.*, 2009). The SEM-EDX analysis of this brown region suggested an aerinite-related composition with somewhat higher Fe content, and with Mn partially replacing Ca. Due to the significant compositional difference, synchrotron $tts-\mu$ XRD data were collected to verify that the brown fibers were indeed aerinite. The measured $tts-\mu$ XRD data confirmed that these fibers constitute the first finding of brown aerinite. To better understand the details of the crystal structure the corresponding Rietveld refinement was undertaken ($a=16.936(2)$, $c=5.223(1)$ Å, $V=1297.4(3)$ Å³, $P3c1$) (Crespi *et al.*, 2019). Compared to the more common blue variety, this new variety has longer a unit cell parameter (~ 0.06 Å) and nearly unchanged c value. The refinement was greatly facilitated by complementary accurate EMP data of the same zone.

Key words: aerinite; $tts-\mu$ XRD; synchrotron; polished thin section; EMP analyses

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TYPE I COLLAGEN-APATITE FIBRILLAR NANOCOMPOSITES FOR BONE TISSUE ENGINEERING

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Abstract: The current interest in collagen mineralization has increased in recent years in order to recreate and produce biological structures intended to bone tissue engineering. We have developed a base-acid neutralization method to simultaneously self-assemble and mineralize type I collagen (Col) with nanocrystalline apatites (nAp). The method is aimed to produce bioinspired Col-based nanostructured materials with varying extent of nAp mineralization, mimicking the different layers of osteochondral structures. Two variants of the method have been tested: base-acid titration (BAT), a solution of Ca(OH)₂ was added dropwise to a stirred Col-H₃PO₄ solution, and direct mixing (DM), the Ca(OH)₂ was added by fast dripping. BAT experiments yielded fibrils mineralized with either nAp or amorphous calcium phosphate plus a precipitate composed of nAp, brushite, and calcite, while DM led to Col/nAp fibrils plus nAp powder. The adding of Eu³⁺ and Tb³⁺ in DM experiments produced luminescent biocomposites for applications in bioimaging. Samples did not present cytotoxicity on human mesenchymal stem cells (hMSCs) and they were capable by themselves of inducing osteogenic differentiation in hMSCs, particularly those produced by DM, and more notably the Tb³⁺-doped biocomposites.

Key words: apatites, collagen mineralization; mesenchymal stem cells, cytotoxicity; osteogenic differentiation

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VALIDACIÓN DEL PROCESO DE SECADO EN FORMULACIONES EN SUSPENSIÓN DE MEBENDAZOL PARA CUANTIFICACIÓN POLIMÓRFICA MEDIANTE EL MÉTODO DE RIETVELD

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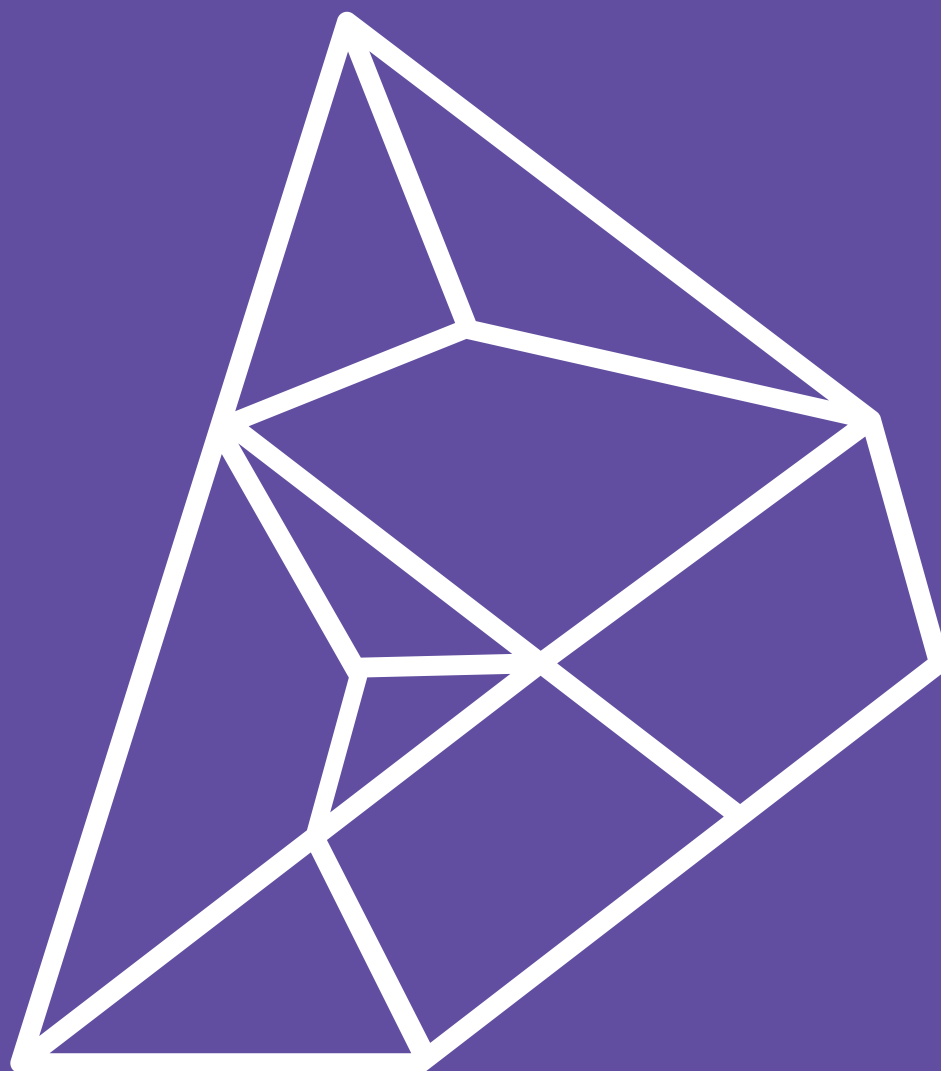
Abstract: El proceso de secado de muestras en suspensión es un paso crítico durante el análisis de cuantificación de las formas polimórficas que pueden presentar los Insumos Farmacéuticos Activos (IFAs) en un producto final o medicamento. El proceso de secado es necesario para realizar la cuantificación polimórfica usando la técnica de análisis por Difracción de Rayos X en polvo (DRXP). Sin embargo, es un proceso que puede producir modificaciones debido a la alteración de propiedades fisicoquímicas, particularmente el polimorfismo. Como ya es conocido el polimorfismo impacta en etapas críticas como la disolución, la procesabilidad y el efecto terapéutico de los productos acabados^{1,2}. Mebendazol (MBZ) es un IFA de amplio espectro, indicado en el tratamiento de parasitosis³ y que presenta polimorfismo⁴. El objetivo de este trabajo fue validar el procedimiento de secado de MBZ en suspensiones (método no provoca modificación en la relación polimórfica de las muestras) a través de diferentes tratamientos de las muestras y realizar la determinación de la cuantificación polimórfica de las formas A y C de MBZ usando DRXP y método de Rietveld. Se prepararon mezclas compuestas por 30% de MBZ-A y 70% de MBZ-C (p/p) en una solución de 0,5% (p/v) de concentración de Lauril Sulfato de Sodio (LSS) por sextuplicados y analizadas en dos grupos. Cada muestra y la solución estuvieron en contacto durante 10 minutos. Seguidamente las muestras del grupo 1 fueron filtradas y analizadas inmediatamente en el difractor (Bruker D8 Advance). Las muestras del grupo 2 terminado el filtrado se almacenaron a 40 ° C durante 6 horas y posteriormente analizadas por DRXP. La cuantificación de fases se usó dos tipos de metodologías, una modelo de Estructuras Fijas y el modelo de Cuerpo Rígido. El programa usado el Método de Rietveld (MR) fue TOPAS académico v6⁵. A partir de los resultados obtenidos de la cuantificación de polimorfos usando DRXP e MR fue evaluado la exactitud y la precisión del método de secado^{6,7}. La exactitud de la metodología propuesta se evaluó mediante el cociente entre los resultados obtenidos de los dos grupos de muestras, observándose valores de las medias ponderadas, próximos al valor de referencia. En el análisis estadístico, se puede observar que no hubo diferencias estadísticamente significativas (Intervalo de Confianza, $p < 0.5$) tanto en la comparación de los resultados de los métodos de tratamiento de la muestra (Teste t), como también los dos tipos de modelamiento de cuantificación (Prueba F Sndecor). En cuanto a la repetibilidad y precisión intermedia entre los dos métodos de tratamiento de la muestra, se observó que los valores de Coeficiente de variación (CV) varían entre 3,3%–1,2% indicando precisión de los resultados obtenidos. La exactitud y precisión de la metodología propuesta evidenciaron que el proceso de secado propuesto no impacta ni modifica los resultados en la cuantificación de fases de muestra. Por tanto, resulta un proceso de secado confiable para realizar estudios de polimorfismo en suspensiones farmacéuticas, como con MBZ.

Key words: Validación, polimorfismo, MBZ, Rietveld; suspensión, cuantificación

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BLACK RARE EARTH HEXAGONAL PEROVSKITES RMnO_3 (R = Y, La) WITH OPPOSITE SOLAR REFLECTANCE RESPONSE

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Abstract: Rare earth distorted perovskite RMnO_3 (R = Y, La) are attracting considerable theoretical and technological interest by virtue of their unusual magnetic and electronic properties ('colossal' magnetoresistance in LaMnO_3)¹ or as heat reflecting blue pigments for energy-saving coatings (exceptionally high NIR reflectance in In doped YMnO_3)². Both perovskites shows black color and crystallize in hexagonal system. YMnO_3 in acentric space group $P6_3cm$ with Mn^{3+} in trigonal-bipyramidal coordination and Y^{3+} 7-fold coordinated; the unit cell contracts 66% with temperature to a $P63/mmc$ form with Y^{3+} in octahedral coordination. LaMnO_3 obtained in air atmosphere is actually the rhombohedral $\text{LaMn}^{\text{III}}_{0.72}\text{Mn}^{\text{IV}}_{0.28}\text{O}_{3.14}$ ($R-3c$); in inert atmosphere the centric orthorhombic LaMnO_3 is synthesized. The rhombohedral phase shows a double-exchange magnetic mechanism between Mn^{3+} -O- Mn^{4+} . In this communication hexagonal perovskites RMnO_3 (R=Y,La) have been synthesized by solid state in air and characterized by XRD, chromatic parameters, band gap measurement and UV-Vis-NIR diffuse reflectance. The UV-Vis-NIR spectrum of YMnO_3 shows the absorption bands associated to $\text{Mn}^{3+}(\text{d}^4)$ in crystal field splitting of the d-orbital energies in trigonal bipyramidal coordination, with a band gap obtained by Tauc method of 1.36 eV and with exceptionally high NIR reflectance for a black material (39%). In the case of LaMnO_3 the UV-Vis-NIR spectrum of YMnO_3 shows in the Kubelka Munk spectrum a single broad band centered at 600 nm (band gap 1.38 eV) associated to the intervalence charge transfer that gives a practically full solar range spectral absorbance (R=4%).

Key words: distorted perovskite, diffuse reflectance, solar absorption.

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CARACTERIZACIÓN CRISTALOQUÍMICA DE LODOS UTILIZADOS EN LA OBTENCIÓN DEL “TINTE NEGRO”

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Resumen: En este trabajo se estudia el lodo ferruginoso que utilizan pueblos de diferentes culturas para estampar y teñir tejidos de negro. El procedimiento de estampado, consiste en dibujar con ese lodo sobre un lienzo impregnado de taninos, de manera que el hierro del lodo reaccione con el tanino y los trazos dibujados se tornen negros.

La reacción que tiene lugar es compleja, primero se forma galato ferroso, $\text{Fe}(\text{C}_7\text{O}_5\text{H}_2)$ (a partir del ácido gálico de los taninos y del Fe^{2+} del lodo) que reacciona con el oxígeno para dar galato férrico. Éste, en presencia de iones Fe^{3+} libres, pierde los carboxilos para dar pirogalato férrico, $\text{Fe}_2(\text{C}_6\text{O}_3\text{H}_3)_2 \cdot 4\text{H}_2\text{O}$, un complejo insoluble de color negro.

Dado el carácter artesanal del proceso nunca se han identificado en profundidad los lodos involucrados. En esta ocasión se analizan tres muestras diferentes (Perú, México, Mali) que tienen en común su proceso de formación, que tiene lugar en zonas pantanosas y cálidas. La caracterización mineralógica, química y morfológica se ha realizado mediante difracción de rayos X (muestra total y agregados orientados) y microscopía electrónica de barrido con EDX.

Los minerales de la arcilla identificados (caolinita y esmectita) presentan contenidos ínfimos de hierro, por lo que no pueden ser responsables de la formación del pigmento negro. Este elemento, debe proceder de otros minerales presentes en los lodos. Se ha realizado el mismo tratamiento a dos muestras de Río Tinto (Huelva), una extraída del lecho del río y la otra de una balsa colmatada y desecada. La primera reacciona con los taninos, mientras que la segunda no lo hace, pese a tener una elevada proporción de minerales de hierro en su composición. Estos datos apoyarían las hipótesis que sugieren la reducción férrico-ferroso en condiciones anóxicas, y la acción de factores entre los que las bacterias y la presencia de sulfuros disueltos podrían jugar un papel decisivo.

Palabras clave: Pirogalato férrico, Lodos ferruginosos, Taninos, Pigmento negro.

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CRYSTALLIZATION BEHAVIOR OF COCOA BUTTER IN FRESH CACAO BEANS TO UNDERSTAND GERMINATION CONDITIONS

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Abstract: The present study aims at observing the crystallization and polymorphic behavior of cocoa butter (CB) in fresh cacao beans with DSC and X-ray diffraction techniques with both synchrotron and lab-scale radiation source. Underlying idea of this study was to relate the necessary conditions of germination of cacao beans to the crystallization of CB, which are present in oil-in-water emulsion droplets, called lipid bodies having 1~2 micron-meter diameters. Different cooling and heating conditions, with rates of 15, 2, 0.5 and 0.1°C/min, were applied to fresh cacao beans and compared to bulk CB. The results showed lower crystallization temperatures of CB in fresh cacao beans at all the experimental conditions. In addition, simpler polymorphic behavior, based on the occurrence of more stable forms, was observed in fresh cacao beans. The thermal behavior of fresh and dried cacao beans with different geographical origins was also analyzed. This study indicates that the germination conditions of cacao beans are extended to low-temperature environmental areas by lowering the T_c values of CB than those of the bulk oil. The results were consistent with the germination behavior of fresh cacao beans at different temperatures.

Key words: Crystallization, polymorphism, cocoa butter, DSC, synchrotron radiation X-ray diffraction

CRYSTALLOGRAPHIC CONTROL CHARACTERIZATION DURING MINERAL REPLACEMENT USING INTEGRATED 2D-X RAY DIFFRACTION PATTERNS

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Abstract: Two-dimensional X-Ray diffraction (2DRXD) patterns contain very useful information for the microstructural characterization of polycrystalline materials (e.g. crystal domain, relative crystal size and degree of orientation). The number or density of crystals contributing to specific reflections in the Debye rings within the 2D-XRD pattern vary depending on the size and distribution of the crystals. Moreover, the preferred crystal orientation presented in a polycrystalline sample can be adequately described by pole figure integration. These pole figures display the three-dimensional distribution on specific crystallographic directions of the grains composing a polycrystalline sample. Pole figures can be efficiently registered using an area/bidimensional detector coupled to a single-crystal diffractometer with particular equipment goniometers configuration (i.e. reflection mode). To collect the data necessary to integrate the pole figures, it is necessary to obtain a series of frames while rotating the sample around the phi axis. The combination of the pole figures, using 2D plot computer software, allows us to identify specific crystallographic orientations in the phases presented in a polycrystalline material (Rodríguez-Navarro et al., 2006). This methodology has been applied in the microstructural characterization of the crystallographic control occurring during mineral replacement reactions (Álvarez-Lloret et al., 2010; Ruiz-Agudo et al., 2016). We identified several epitaxial relationships during the mineral substitution via dissolution-precipitation reactions between calcium carbonates, sulfates and phosphates phases. An accurate analysis of the microstructural characteristics appearing during these mineral transformations is a key factor since these mechanisms may determine their physicochemical properties and their potential use for technological and / or industrial applications.

Key words: X-ray diffraction, mineral replacement, crystallographic control, two dimensional pattern.

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INDUCED NUCLEATION OF APATITE NANOPARTICLES ON GRAPHENE AND GRAPHENE OXIDE NANOFLLAKES

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Abstract: Hybrid biocompatible nanocomposites combining wished complementary physical and biological properties have attracted great attention in the field of bone tissue engineering (BTE) [1]. The preparation of nanocomposites of either graphene (G) or related carbonaceous materials and calcium phosphate (apatite) nanoparticles by direct nucleation of the calcium phosphate on the nanoflakes surface, instead of simple mechanical mixing of both components, represents an innovative approach in combining the mechanical and bioactive properties for BTE applications [2,3]. In this work, the nucleation experiments have been performed by the sitting drop vapour diffusion method (SDVD) [4]. The G flakes have been obtained by sonication-assisted liquid-phase exfoliation (LPE) technique of graphite using Lysine, Arginine, Aspartic Acid, and Citrate as dispersing biomolecules, while a commercial aqueous Graphene Oxide (GO) dispersion has been used for the nucleation essays in presence of the same biomolecules. Additionally, a set of nucleation experiments has been performed in presence of luminescent Tb³⁺ ions. Mineralogical, spectroscopic, microscopic and luminescence characterization has been carried out by the techniques XRD, FTIR, Raman, FESEM, TEM, and fluorescence spectroscopy. Results indicate that G and GO flakes induce the heterogeneous nucleation of needle-shaped apatite nanocrystals on their surfaces, irrespective of the biomolecule used, whereas an increment of amorphous calcium phosphate is observed when using citrate and Tb³⁺ ions. To finish this study, cytotoxicity/biocompatibility, cell proliferation, and osteogenic differentiation of human mesenchymal stem cell tests are underway.

Key words: Nanocomposites, Graphene, Graphene Oxide, Apatite, mesenchymal stem cells

Acknowledgments: This work was supported by grant nº PGC2018-102047-B-I00 (MCIU/AEI/FEDER/UE)

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LUMINESCENT CYCLOPLATINATED SYSTEMS BASED ON THE 2-PHENYLBENZOTHAZOLE LIGAND: RELATIONSHIP BETWEEN STRUCTURE AND OPTICAL PROPERTIES

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Over last few decades phosphorescent cyclometalated Pt^{II} complexes have received expanding interest due to their potential utility in optical devices, photochemistry, sensors or biological imaging¹. In many occasions the light emitting behaviour of molecular solids, rigid media and concentrated solutions of these complexes differ from their dilute solutions because the occurrence of easy stacking of molecules. In particular, the coordination of flat and delocalized ligands favors Pt···Pt and/or $\pi\cdots\pi$ intermolecular interactions, able to produce extended linear chains and oligomeric nanostructures, which display a rich polymorphism in solid state with alterations in their optical properties.² These interactions are sensitive to external stimuli and some of these compounds present mechanochromic or vapochromic behaviour.

In this work we describe new Pt^{II} compounds based on the 2-phenylbenzothiazole (pbt) fragment as cyclometalated group and bidentate auxiliary ligands L^X, type [Pt(pbt)(L^X)] [L^X: PPh₂(*o*-PhCOOH) **2**, PPh₂(*o*-PhSO₃H) **3**, PPh₂{(CH₂)₂COOH} **4**, picolinic acid **5** and 3-aminopicolinic acid **6**], prepared from the DMSO precursor [Pt(pbt)Cl(DMSO)] **1**.

X-ray diffraction studies show structures self-assembled by hydrogen bonding and/or $\pi\cdots\pi$ intermolecular interactions. Interestingly, **6** shows two solid phases, depending on the crystallization solvent, which display different colors (red and black) and distinct emissions and **5** is mechanochromic. To insight into the nature of the optical properties, theoretical analysis have been carried out at DFT/TD-DFT level for selected complexes and for **5**, a dimer model (**5**₂) has been studied to examine the Non-Covalent Interactions (NCI).

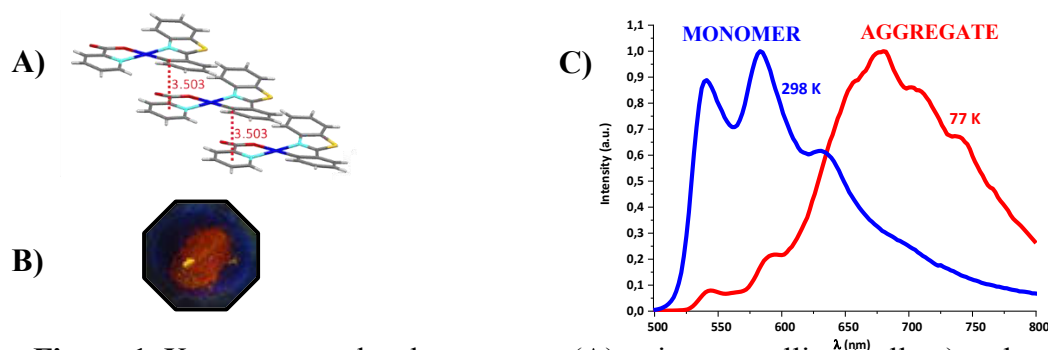


Figure 1. X-ray supramolecular structure (A), microcrystalline (yellow) and ground (orange) solid (B) and emission spectra in CH₂Cl₂ (298 K and 77K) (C) of **5**

Key words: Luminescent, Platinum, Cyclometalated, Aggregation.

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MODULATION AND CRYSTALLIZATION OF CHIRAL SPIROBIFLUORENES

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Abstract: Chiroptical responses have been an essential tool for structure elucidation over the last decades due to their exceptional sensitivity to geometry and supramolecular interactions. The typical higher accuracy of chiroptical responses, compared to other methods, have recently drawn the attention of the scientific community. Several studies have been accordingly devoted to the development of chiroptical systems through individual, collective or induced chirality in different states of matter. However, the potential of everyday chiroptical applications still remains unexplored. In this respect, we showed that allenes serve as a versatile chiral axes not only for the construction of controlled three-dimensional molecular shapes, but also their appropriate functionalization leads to chiroptical surfaces. Nevertheless, allenes easily undergo photoisomerization; limiting their further exploration. Seeking for a more robust chiral axis, we have recently targeted spirobifluorenes and demonstrated their reliability for the formation of highly stable systems presenting remarkable chiroptical responses. With these proof-of-concept studies in hand, we hereby present modulation of spirobifluorenes as a milestone toward chiroptical applications. The crystallization of the synthesized compounds not only confirms their structures, but also it gives rise to enantiomeric resolution.

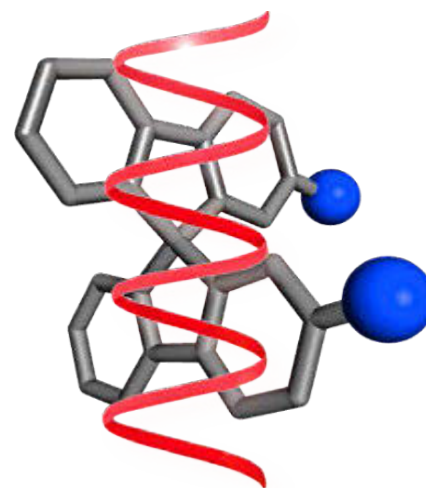


Figure 1: Chiral spirobifluorenes.

Key words: Chirality, Chiroptical Responses, Spirobifluorenes, Crystallization, Chiral Resolution.

Acknowledgments: This work was financially supported by [Xunta de Galicia] (ED431F 2016/005 and GRC2019/24), [Instituto de Bioingeniería en Red para el Envejecimiento Saludable, IBEROS] (0245_IBEROS_1_E), predoctoral fellowship [Xunta de Galicia] (ED481A-2017/302) and research contract “Ramón y Cajal” [the Spanish Ministerio de Economía y Competitividad, MINECO] (RYC-2012-10364).

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"SANDWICH" SUPRAMOLECULAR STRUCTURE OF AN AZAMACROCYCLIC LIGAND

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Abstract: Non-covalent interactions such as hydrogen bonds, π,π -stacking and/or C-H $\cdots\pi$ interactions are the main driving forces behind many self-assembly processes important for the design of new functional solid materials.¹ Water molecules can play a space filling role in supramolecular assemblies or can be a part of the self-assembled architecture themselves.² Here we report a 18-membered hexaaza-macrocyclic ligand that crystallizes in the *Pbcm* space group. It presents a markedly stepped conformation and the plane containing the pyridine rings of the macrocyclic backbone intercept that described by the four amine nitrogen atoms [rms = 0] at 69.97(8)°. The ligand forms hollow tubular structures of molecular dimensions, similar to nanotubes, along the *b* axis, giving rise to layers of macrocyclic ligands separated by water molecules (Figure 1).

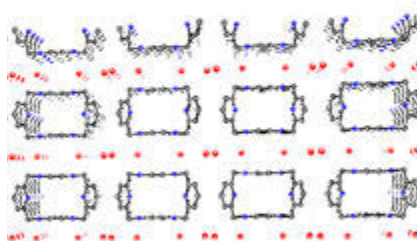


Figure 1

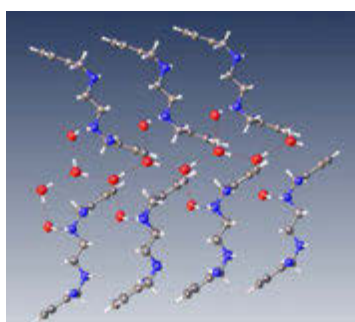


Figure 2

Two different coordination modes can be found for the water molecules: these participating in pyramidal three (O2W) or trigonal three (O1W) hydrogen bonds. O2w acts as H-bond acceptor to O1w and in turn behaves as H-bond donor joining two different macrocyclic ligands through the N2 amine atoms along the *c* axis. The O1w behaves as H-bond donor to O1w[#] and H-bond acceptor to other O1w molecule in a zigzag fashion, giving rise a 1-D infinite chain along the *b* axis (Figure 2). Also, O1w behaves as H-bond donor to O2w.

Key words: macrocyclic ligand 1, supramolecular assemblies

Acknowledgments: The authors thank CACTI (Universidade de Vigo) for the X-ray measurements.

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SISTEMAS CU-PDC COMO PRECURSORES DE BIO-MOFS: SÍNTESIS, CARACTERIZACIÓN Y ESTUDIO BIBLIOGRÁFICO

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Abstract: La Ciencia de Materiales se dedica a la creación y mejora de materiales, en una búsqueda constante en la que se desea obtener materiales multifuncionales y respetuosos con el medioambiente. De esta forma, los SCFs (Solid Coordination Framework) y los MOFs (Metal Organic Framework) resultan ser compuestos de coordinación sólidos muy interesantes, debido a sus excepcionales características, como los poros que pueden presentar sus estructuras internas. Esta característica, en particular, aporta potencial para diversas aplicaciones, como la adsorción de gases de efecto invernadero, la catálisis heterogénea, el almacenamiento de energía o incluso el suministro controlado de fármacos. Por otra parte, cuando se usan ligandos de origen biológico se pueden obtener bio-SCFs y bio-MOFS cuyas aplicaciones se extienden al área de la Medicina.

En este trabajo se presenta un precursor bio-MOF: el compuesto $(DMAH)_2[Cu(PDC)_2]$, (donde $DMAH^+$ es dimetilamonio y PDC^{2-} es piridín-2,5-dicarboxilato). El compuesto $(DMAH)_2[Cu(PDC)_2]$ se ha caracterizado mediante las siguientes técnicas: espectroscopía infrarroja (IR), difracción de rayos X (DRX) en monocristal y análisis termogravimétrico (TG).

Para completar el trabajo se ha realizado una revisión bibliográfica sobre los compuestos en estado sólido con el ligando PDC, cuya discusión se ha centrado en los compuestos basados en Cu^{II} .

Key words: Bio-MOF, PDC

Agradecimientos: Los autores agradecen a la UPV/EHU (GIU 18/197) la ayuda concedida.

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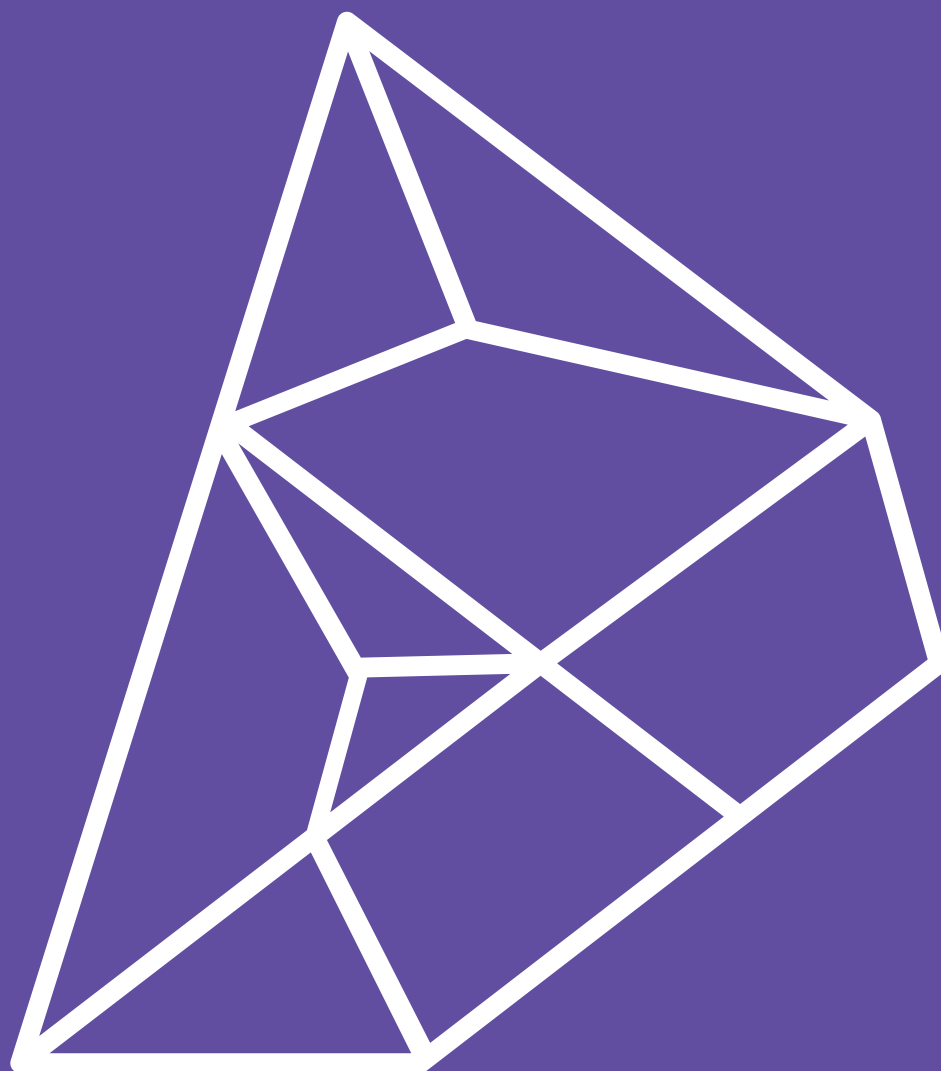
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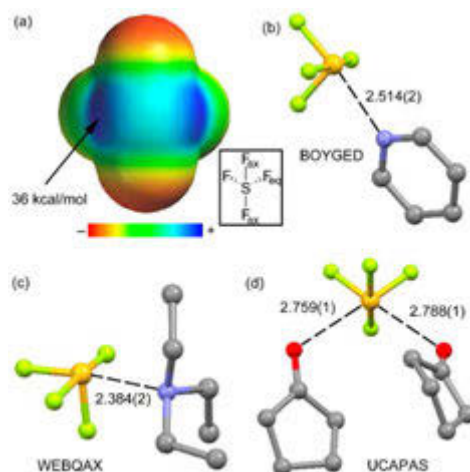


UNEXPECTED CHALCOGEN BONDS IN TETRAVALENT SULFUR COMPOUNDS

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Abstract: In this communication a combined analysis of a CSD (Cambridge Structural Database) search with theoretical calculations (RI-MP2/def2-TZVP level of theory) is presented to study the importance of polarizability in chalcogen bonding interactions. It is well known that chalcogen bonds are stronger for less electronegative chalcogen atoms, i.e., S < Se < Te, and in the presence of electron-withdrawing substituents at the chalcogen. Herein, I present experimental (X-ray structures retrieved from the CSD) and theoretical evidence (RI-MP2/def2-TZVP) that the chalcogen bond acceptor (Lewis base) has a preference in some cases for the σ -hole that is opposite to the more polarizable group instead of the more electron withdrawing one, as confirmed by Natural Bond Orbital (NBO) and Bader's theory of "atoms-in-molecules" computational tools.



Key words: CSD, chalcogen bonding, supramolecular chemistry, DFT calculations

Acknowledgments: We thank the MINECO/AEI (projects CTQ2017-85821-R and CTQ2017-90852-REDC, FEDER funds) for financial support.

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Franconetti, A., Quiñonero, D. Frontera, A. and Resnati, G. (2019). Unexpected chalcogen bonds in tetravalent sulfur compounds. *Physical Chemistry Chemical Physics*, 16 (2), 11313-11319.

INTERACTIONS, STRUCTURE AND PROPERTIES OF DISCRETE METAL CLUSTERS

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Abstract: Solvent, temperature, packing forces, counterions, hydrogen bonds and π - π interactions are several factors that can be essential for the final arrangement, conformation, and even the configuration of the compounds. Therefore, these issues must be considered in materials design, as they can modify the stability as well as the optical or magnetic properties of the molecules. All these aspects are analyzed with examples of the discrete metal cluster species $[\text{Mo}_2\text{Cl}_4(\text{R-py})_4]$ (R-py = alkyipyridines), $[\text{Ru}_2(\text{DPhF})_3(\text{O}_2\text{CMe})(\text{OH}_2)]^+$ (DPhF = *N,N'*-diphenylformamidinate) and $[\text{Ag}\{\text{Pd}(\mu\text{-SC}_6\text{F}_5)(\mu\text{-dppm})\text{Pd}\}_4(\mu\text{-SC}_6\text{F}_5)_4]^+$ (AgPd8 , dppm = bis(diphenylphosphino)methane Figure 1,) that display 4, 2.5 and single metal-metal bond order, respectively.

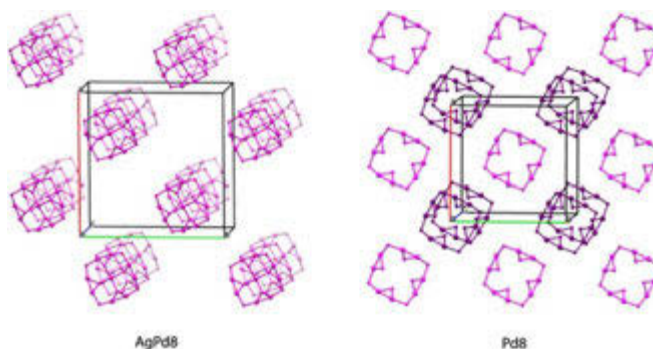


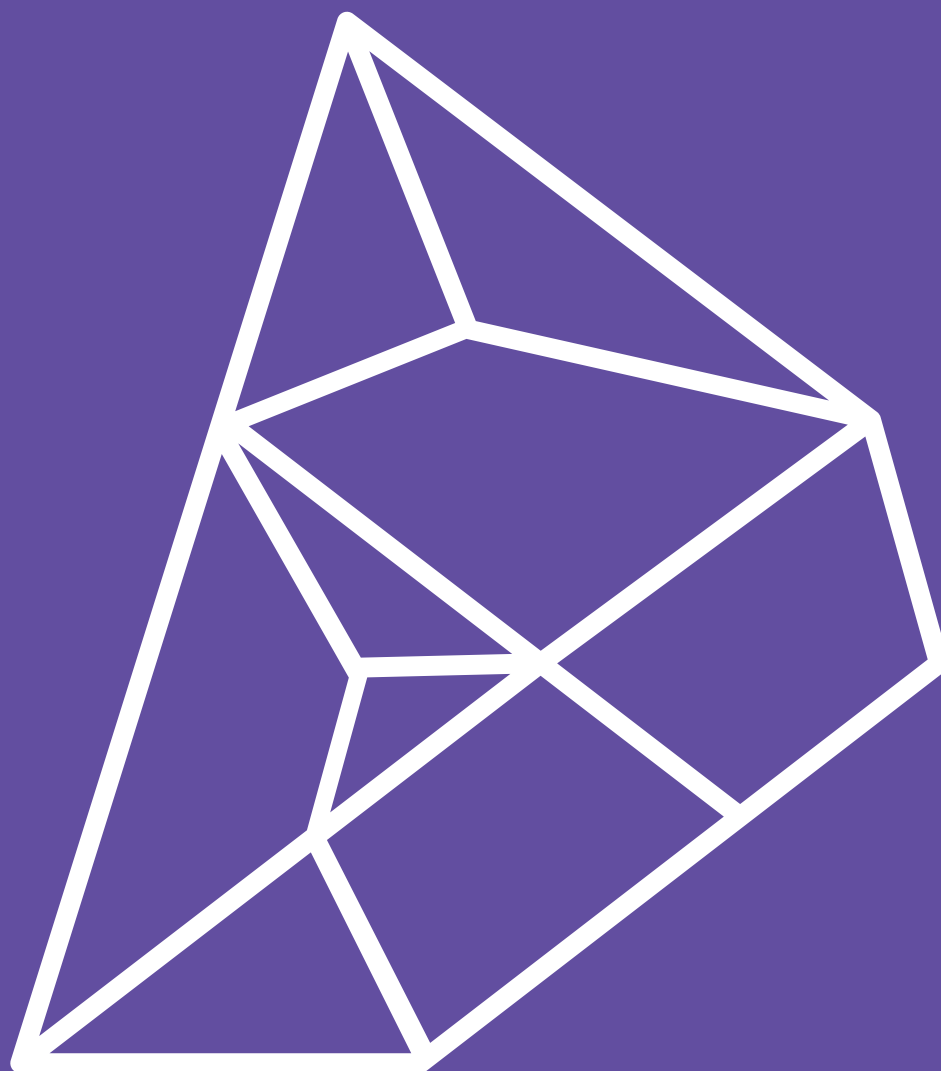
Figure 1. Comparative view of the molecular packing in $[\text{Ag}\{\text{Pd}(\mu\text{-SC}_6\text{F}_5)(\mu\text{-dppm})\text{Pd}\}_4(\mu\text{-SC}_6\text{F}_5)_4]^+$ (**AgPd8**) and $[\{\text{Pd}(\mu\text{-SC}_6\text{F}_5)(\mu\text{-dppm})\text{Pd}\}_4(\mu\text{-SC}_6\text{F}_5)_4]$ (**Pd8**) where only the cores have been depicted.

Key words: weak interactions, metal clusters, optical properties, magnetism

Acknowledgments: S.H. is grateful to the Comunidad de Madrid (project B2017/BMD-3770-CM) for financial support.

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COMPUESTOS METALOSUPRAMOLECULARES BASADOS EN BROMURO DE COBRE(I/II) Y EL LIGANDO BMTTE

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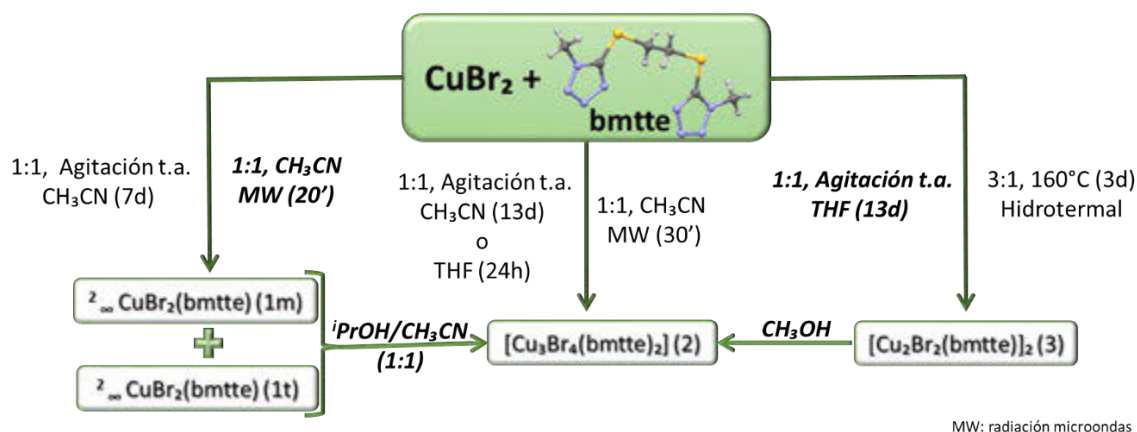
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Abstract: El anillo tetrazol se encuentra en una amplia gama de compuestos con aplicaciones biomédicas (antibacteriana, antifúngica, antitumoral...) [1]. Este tipo de actividad se basa en su estabilidad y baja toxicidad en el organismo debido a su cualidad de bioisómero con los grupos cis-amida y carboxílico.

En este marco se ha sintetizado el ligando 1,2-bis[(1-metil-1H-tetrazol-5-il)sulfanil]etano (bmtte) [2] y se ha investigado su reactividad frente a bromuro de cobre(II) en diferentes condiciones obteniendo los complejos cristalinos mostrados en el siguiente esquema:



Palabras clave: complejos de bromuro de cobre, ligandos tetrazol, difracción de rayos X, polímeros de coordinación, polimorfismo.

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IN SITU PHOTOSWITCHING OF SPIRORHODAMINES ISOMERS IN SOLID-STATE

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Abstract: Currently, the functional materials with structures switchable by stimuli such as heat, the addition of cations, changes of pH, pressure, or light are the objects of innumerable studies. They are ideal models to investigate the relation between structure-function and new properties derived from that change. In this work, we studied a family of spirorhodamines (SRAs) in solid-state photochemical reactions. These are photochromic molecules with a switching mechanism based on the differences in the electronic ground state between isomers.[1] This mechanism involves changes in the molecule structure and is thermally reversible (Figure 1).[2,3] Here, assuming the hypothesis that in the solid phase, the residence time in the optically active isomer is associated with its structural characteristics, a family of compounds was synthesized by modifying their R-substituents.

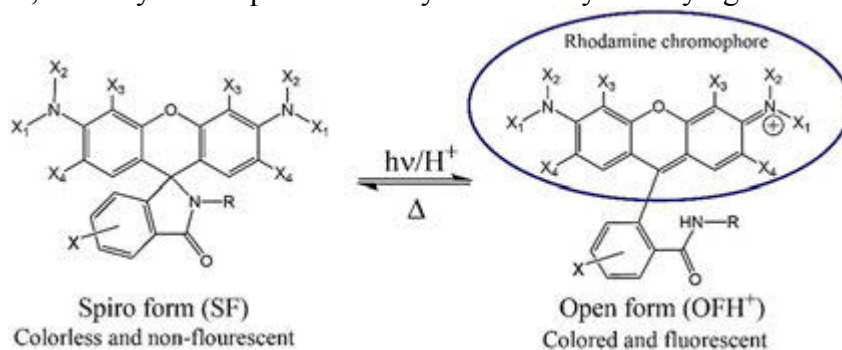


Figure 1: General structure of spirorhodamines. The equilibrium responsible for the appearance of colour is also shown. The forward reaction can be photo-induced with UV light, or by proton addition.

These equilibria were characterized in solid-state by reflection, absorption and emission fluorescence spectroscopy, single-crystal X-ray diffraction,[4] atomic force microscopy coupled to infrared spectroscopy,[4] and computational calculations. For each compound, was evaluated the changes produced after irradiating the corresponding closed isomer with ultraviolet light. Promising differences were found between the derivates from SRAs, allowing us for the rational design of these compounds as light and pH sensing devices.

Key words: photoswitching, spirorhodamines isomers, solid-state, single-crystal X-ray diffraction, functional materials.

Acknowledgments: This work was supported by Universidad de Buenos Aires, Argentina. The authors would like to thank the economic support of the Brazilian Synchrotron Light Laboratory.

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INTERACCIONES METIL...M ALCALINO EN DERIVADOS ALUMINATO CON LIGANDOS OXIMATO

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Abstract: El aluminio es el metal más abundante en la corteza terrestre y muestra un comportamiento químico muy atractivo. Así pues, es bien conocido el amplio rango de reactividad de los compuestos a base de aluminio en áreas como la catálisis o la síntesis orgánica. [1] Un tipo muy interesante de especies de aluminio son los llamados complejos de aluminato donde el átomo de aluminio se une a través de un ligando puente a un metal más electropositivo, como un metal alcalino. Se han descrito derivados aluminato con diversos ligandos puente, particularmente con ligandos O- y/o N- dadores. En nuestro grupo hemos preparado derivados con ligandos fenoxo y fenoxo-imino. [2] Recientemente hemos extendido los estudios a ligandos oximato. Este tipo de especies rara vez se ha explorado para la preparación de aluminatos, de hecho, solo se ha descrito un ejemplo.[3]

Utilizando la metodología empleada con frecuencia en nuestro grupo,[2] inicialmente tratamos la oxima con una base de metal alcalino y un precipitado sólido insoluble. La adición de AlMe_3 a este sólido conduce a la formación de los nuevos derivados de oximato **1** y **2** que presentan estructuras en estado sólido sin precedentes. Se observa un resultado diferente para los compuestos de sodio y potasio. En el primer caso, se forma el derivado $[\text{NaAlMe}_3(\text{OR})]_2$ (**1**) como único producto de la reacción (figura 1). Sin embargo, cuando el potasio es el metal alcalino, la especie final aislada **2** es un agregado de los derivados $[\text{KAlMe}_2(\text{OR})_2]_2$ y $[\text{KAlMe}_3(\text{OR})]_2$ que se combinan generando una cadena (figura 2). Estas cadenas están dispuestas en capas a través de interacciones $\text{Me}\cdots\text{M}$ en el empaquetamiento cristalino.

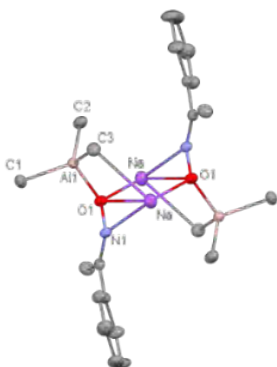


Figure 1 $[\text{NaAlMe}_3(\text{OR})]_2$

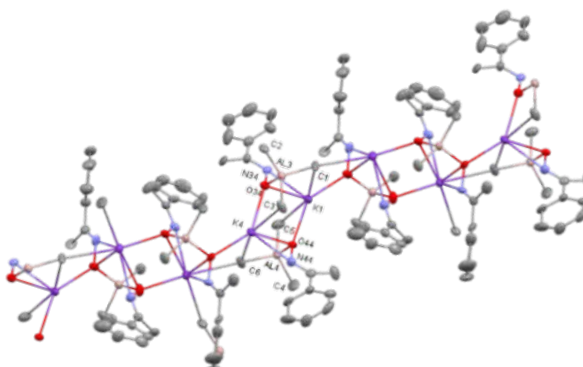


Figure 2 $[\text{KAlMe}_2(\text{OR})_2]_2 \cdot [\text{KAlMe}_3(\text{OR})]_2$

Key words: Oximato, compuesto heterometálico, interacciones Me...M, aluminato

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NEW HALOPERIDOL PHARMACEUTICAL SALTS: A SYSTEMATIC STUDY ON THE IMPACT OF COUNTERIONS ON SOLID-STATE PERFORMANCE

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Abstract: Haloperidol (HAL) is a conventional antipsychotic drug widely used as tranquilizer, included on the list of World Health Organization essential medicines for basic health care. According to the Biopharmaceutics Classification System (BCS), HAL belongs to the Class II drugs, which has poor aqueous solubility [1]. Crystal engineering has provided an efficient approach for tuning physicochemical properties of active pharmaceutical ingredients (APIs), and therefore has a direct application in the pharmaceutical industry. APIs can exist in the form of polymorphs, salts, cocrystals, hydrates, or solvates, and may exhibit distinct physical properties compared with the parent API. For instance, salt formation is a widely used strategy to improve the solubility and solid-state properties of ionizable drugs [2].

In order to better understand the relationships among the API, the selected counterions and the resultant salt form, crystalline salts were synthesized using haloperidol and a series of closely related (di)carboxylic acid counterions. Nine pharmaceutical salts were prepared by mechanochemical methods and characterized by thermal, spectroscopic and diffractometric techniques. Their crystal structures have been determined and DFT studies performed to evaluate the role of intermolecular interactions on the improvement of physicochemical properties. Stability studies at accelerated conditions as well as their solubility determination contributed to complete the whole picture of these new multicomponent molecular materials. Structure-property relationships in the expanded HAL structural landscape will be discussed in this work.

Key words: Pharmaceutical salts, Haloperidol, mechanochemistry, Crystal structure

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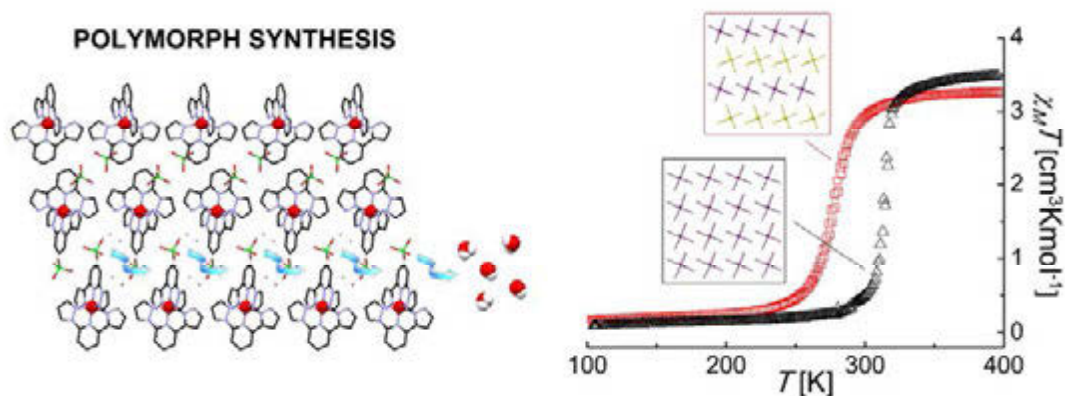
SOLID-STATE TRANSFORMATIONS: A GATE TO POLYMORPHISM IN SPIN CROSSOVER MOLECULAR MATERIALS

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Abstract: Polymorphism is a crystallographic phenomenon with important industrial applications and great scientific relevance. However, predicting the crystallization of specific polymorphs is a phenomenal challenge. Usually, polymorphs are obtained, selectively, by modifying the variables of the crystal growth process, after the accidental discovery. A novel approach uses the single-crystal-to-single-crystal (SCSC) removal of crystallization solvents from a molecular lattice, furnishing polymorphs of the solvent free-molecular material [1]. The solvents co-crystallized originally, play the role of template during the process of crystallization, while their gentle extrusion leads then to the new polymorph of the parent lattice. For some years, we have designed families of Fe(II) coordination complexes of the type $[\text{FeL}^1\text{L}^2]^2+$ (L^1 and L^2 , *tris*-imine ligands) exhibiting spin crossover (SCO) and prone to exchange small molecules with the environment, coupled to crystallographic and spin transitions [2,3]. These materials hold promise as sensors of small species, which are captured by the lattice, while signalled by changes to the properties of the host material [4]. The single crystal X-ray diffraction analysis of these compositional changes *in operando* (while they are taking place) provides detailed insights into the mechanism of these solid-state processes [5]. We present here that some of these materials are a useful platform for the synthesis of polymorphs, using the SCSC extrusion of lattice solvent molecules (Figure). This constitutes a useful resource to study the dependence of the phenomenon of SCO exclusively on the crystal lattice. In the present case, the SCO temperature and the cooperativity of the process exhibits a strong dependence from the polymorph [6]. This method of obtaining polymorphs of SCO materials may constitute a useful avenue for studying the influence of the crystal lattice on the key parameters of this molecular switching phenomenon.



Key words: Polymorphism, single-crystal-to-single-crystal, spin crossover

Acknowledgments: The authors acknowledge MINECO (CTQ2015-68370-P, MAT2017-86826-R) and the Generalitat de Catalunya (Prize ICREA Academia 2018).

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THERMOCHROMIC POLYMORPHS FOR SMART MATERIALS

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Abstract: Smart materials which switch their optical spectroscopic properties (*i.e.*, color, fluorescence) upon physical external stimulation (*i.e.*, pressure, temperature) arouse enormous interest and have found applications in fields as varied as sensing, construction, recording, display technologies or rewritable paper¹.

Polymorphism offers an excellent opportunity to establish optimal relationship between structure-properties and drives to the design of this smart materials. Crystallographic packing strongly influences exciton migration and light emitting properties of optically active materials. This high dependence of the final properties of the materials from the organization of the molecules at the nanometer level, offers many opportunities to synthesize materials which can respond to external stimuli by varying their supramolecular arrangement.²

In this context, the benzothiadiazole (BTD) is one of the preferred moieties in the quest for efficient light emitting compounds.³ This electron deficient heterocycle presents high fluorescence quantum efficiencies and has a strong propensity to adopt quinoid conformations, thus facilitating charge transfer between attached substituents and enabling the tuning of its emission properties. Herein we present a new BTD-derivative, which crystallizes in two different polymorphs with different light emission properties and interesting mechano and thermochromic behaviour.⁴ Powder X-ray diffraction indicates that in both polymorphs molecules adopt a lamellar packing, being the main difference between the two structures the different interlayer spacing. Single crystal analysis of one of the polymorphs allows us to identify weak interaction planes, which presumably facilitates the polymorphic transformation through mechanical or thermally induced sliding processes.

The polymorphic transformation and the origin of the switchable fluorescence has been rationalized through a spectroscopic and theoretical study. This study suggests that the different colors observed are due different intermolecular aromatic interactions owing to the displacement of the molecules with respect to the layer normal. Interestingly, blending this molecule with a biodegradable polymer such as polyvinylalcohol gives rise to a thermal activated reversible switchable fluorescent system, which entitles this material as an attractive candidate for technological applications, such as thermal sensors, security inks or rewritable paper.

Key words: Polymorphs, Thermochromics, Fluorescent, Supramolecular, Smart-Material

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UNDERSTANDING HYDROGEN/DEUTERIUM ISOTOPIC EXCHANGE IN METAL COMPLEXES THROUGH FLP.

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Abstract: Development of new catalysts to transform solar into chemical energy, through hydrogen generation from water, is one of the main challenges to fight climate change and to walk towards a sustainable development. Activation of the O-H bond of water is a key process, whose limitations are generally related to moisture sensitivity. In this work, we had investigated a family of rhodium complexes, which remarkably activates H₂ and H₂O in a reversible manner via a novel ‘*Frustrated Lewis Pair*’ (FLP) pathway.

In FLP systems, the coexisting Lewis acid/Lewis base pair exhibits cooperativity behaviour. To this purpose, a new family of rhodium complexes containing *N,N'*-bis(*p*-Tolyl)-*N''*-(2-diphenylphosphanoethyl)guanidine bound to a Cp^{*}Rh(III) fragment have been synthesized. Structural analysis had revealed the formation of the FLP by the κ^3 -*N,N',P fac* coordination of the phosphano-guanidine ligand to metal, and the existence of a strongly strained four-membered Rh-N-C-N metallacycle. Coexistence of sp³ and sp² nitrogen atoms within it makes viable the cleavage of the Rh–N(sp²) bond, and therefore the accessibility to the FLP for the activation of polar and non-polar bonds.

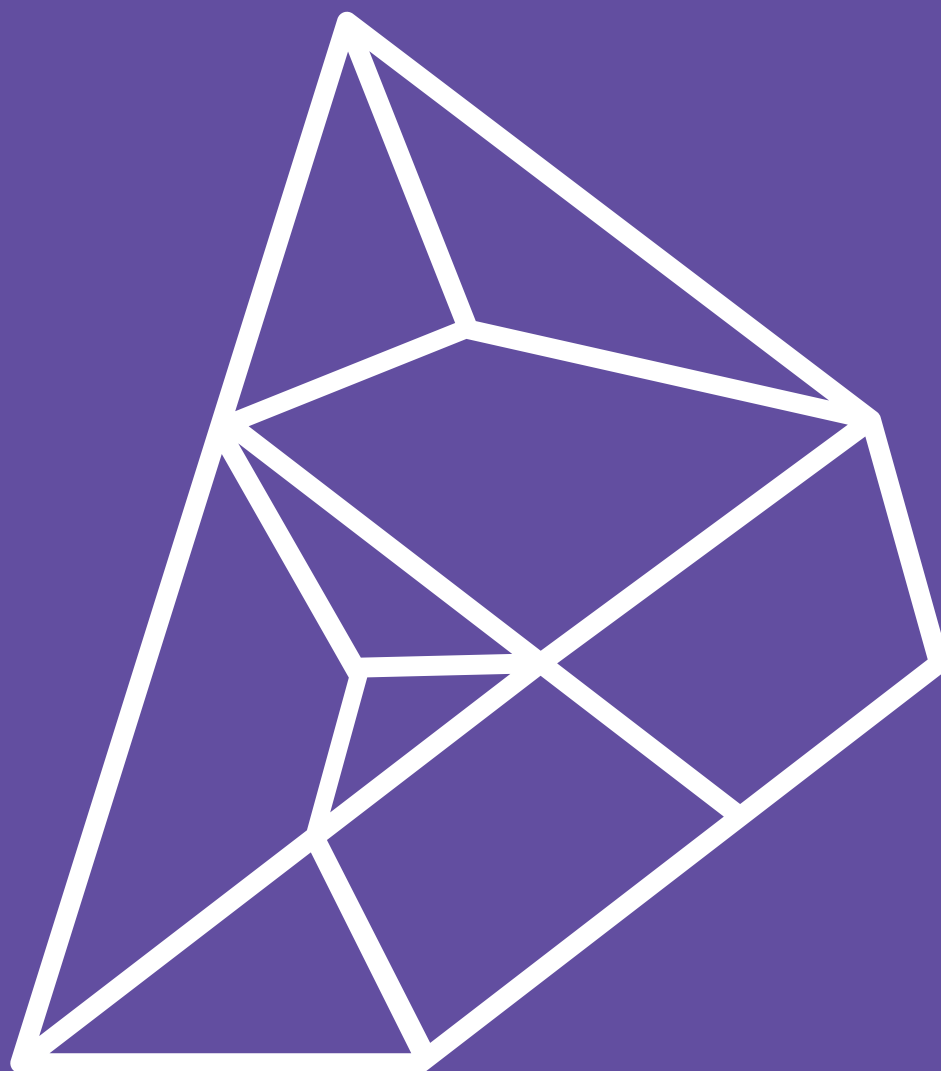
In particular, the use of deuterated water gives rise to a facile hydrogen/deuterium isotope exchange, at a pentamethylcyclopentadiene ligand, through sequential C(sp³)-H bond activation. Single crystal low temperature neutron-diffraction experiment allowed us to determine the specific deuterated positions and to ascertain the hydrogen/deuterium exchange mechanism. The results agreed with the deuteration of all the methyls groups of the cyclopentadiene ligand, together with a partial deuteration of the amine group.

Key words: Structure, H/D isotopic exchange, neutron diffraction, FLP

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BETAINES IMIDAZOLIUM-2-AMIDINATES AS NOVEL LIGANDS FOR MAIN GROUP METALS

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Abstract: Imidazolium-2-amidates are a promising class of ligands whose full potential is still unveiled. These adducts of N-heterocyclic carbenes and carbodiimides (NHC-CDI) are zwitterionic molecules that exhibit a strong basicity through the amidinate group which endows them with a rich coordination chemistry, and the possibility of tuning the electronic and steric properties.¹

NHC-CDI adducts have shown a versatile behaviour, being able to stabilize nanoparticles and to form several organometallic complexes.² Furthermore, recently we have discovered their capacity to activate C-Cl bonds via a metal free pathway, broadening the scope of research to organocatalysis.³

In this work, we have explored the coordination of ICyCDI(*p*-Tol) (L) to main group metals such as Zn, Al and Mg. The formation of the adducts [ZnEt₂L] and [MgBu₂L] was achieved by the direct reaction of the alkyl metal with the ligand. For aluminium, the analogous derivative [AlMe₂L]⁺ was generated via the reaction with the protonated ligand (L·HBPPh₄) and the alkyl aluminium.

As well, the complex [ZnL₃](BPh₄)₂ was prepared using a combination of these strategies. The generation of the same cation [ZnL₃]²⁺ had also been achieved by the direct reaction between L and ZnCl₂.³ In this case the compound [ZnL₃][ZnCl₄] was formed, and in comparison to [ZnL₃](BPh₄)₂ an important difference in the coordination modes of the ligand in the inner sphere is observed.

Key words: betaines, coordination chemistry, zinc, aluminium, magnesium.

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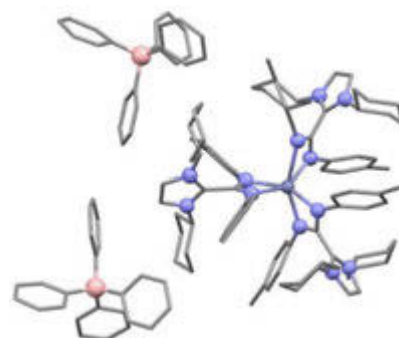


Figure 1. [ZnL₃](BPh₄)₂

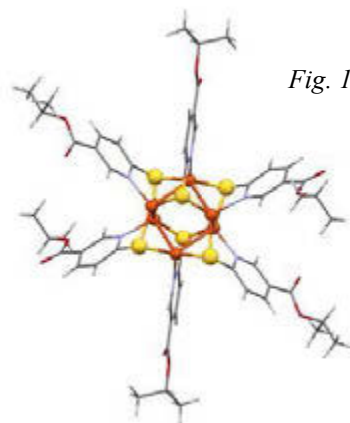
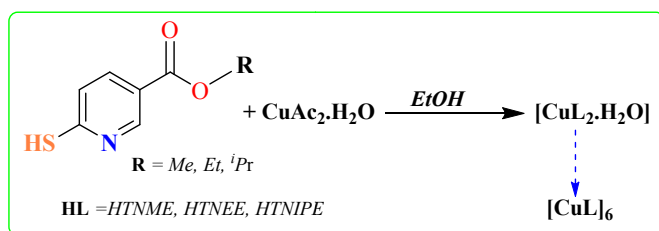
COMPUESTOS DE COBRE DERIVADOS DE 2-MERCAPTOPYRIDINA

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Resumen: Como parte de nuestra investigación sobre la interacción de cationes metálicos con moléculas biológicamente activas, estudiamos el comportamiento químico frente a cobre(II) de ligandos tipo 2-mercaptopyridina y derivados. El interés biológico de estos compuestos se debe a su actividad antibacteriana y antitumoral además de su relevancia biológica en metaloproteínas¹. Los compuestos obtenidos [CuL₂·H₂O], HL= HTNME, HTNEE, HTNIPE (Esquema 1), fueron caracterizados por espectroscopia IR y espectrometría de masas. De las aguas madres cristalizaron los compuestos hexaméricos de cobre(I), [CuL]₆ (Fig. 1).



Palabras clave: 2-Mercaptopyridina, Ácidos tionicotínicos, Complejos de cobre

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COPPER(I) BOROHYDRIDE COMPLEX WITH BIS[(2-DIPHENYLPHOSPHINO)PHENYL] ETHER. STRUCTURE INVESTIGATION BY SINGLE-CRYSTAL X-RAY DIFFRACTION AND DFT CALCULATIONS

Jesús Castro¹, Valentina Ferraro^{*2} and Marco Bortoluzzi²

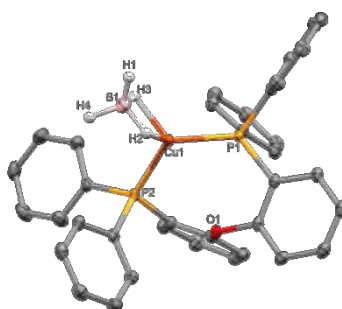
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Abstract: the borohydride anion is characterized by a rich coordination chemistry because of the variable denticity and the possibility of behaving as terminal or bridging ligand. The copper(I) complex $\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})$, where DPEphos is bis[(2-diphenylphosphino)phenyl] ether, was recently synthesized from CuCl using NaBH_4 as borohydride source. The product crystallized from dichloromethane/ethanol (space group $P\bar{1}$). The asymmetric unit contains two non-equivalent molecules, both exhibiting κ^2 coordination mode of the borohydride ligand, as suggested also by IR and ^1H NMR spectra. The same Cu(I)-BH_4 interaction was already observed for the related bis(triphenylphosphine) complex. The Cu-H distances are comprised between 1.67(3) and 1.75(2) Å, while the B-H distances are in the 1.07(2) – 1.20(2) Å range. The H-Cu-H angles for the two non-equivalent molecules are 62.7(12) and 66.3(10)°. DPEphos behaves as chelating ligand, with bite angles of 111.663(16) and 116.190(17)°. The Cu-P distances are between 2.2300(4) and 2.2776(5) Å. Bond lengths and angles of the first coordination sphere were compared with those obtained from DFT geometry optimizations, carried out using hybrid and range-separated functionals with variable percentage of Hartree-Fock exchange.



Key words: borohydride, copper(I), DPEphos, SC-XRD, DFT

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HYDROCHLOROTHIAZIDE-CAFFEINE MULTICOMPONENT PHARMACEUTICAL SYSTEM: THE SOLVENT ROLE

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Abstract: Active pharmaceutical ingredients (APIs) with poor solubility and bioavailability often lead to failure in clinical assays (Kuminek G, Kavanagh ON). Multicomponent solid forms are an strategy that allows modulating APIs' physico-chemical properties without modifying their therapeutic effect, therefore, overcoming the mentioned problem (Harris KDM, Schultheiss N).

To enhance the solubility of hydrochlorothiazide (HCT)-diuretic BCS class IV drug, a new cocrystal and its methanol solvate were obtained. Different "Generally recognised as safe" (GRAS) molecules were used as coformers in a preliminary screening, in which caffeine (CAF) was shown to form the new mentioned phases. Synthesis was performed by liquid assisted grinding (LAG) and solution techniques. Solid state characterization was performed by X-Ray diffraction, thermal analysis and spectroscopic techniques. Single crystal X-Ray diffraction was used to determine the crystal structures and, with the help of density functional theory (DFT) studies, structure property relationships were stabilised, which explained the different behaviour observed in the new multicomponent forms. Solubility studies of the new multicomponent forms show an enhancement of solubility when compared with the API, at 7.4 pH value. Finally, stability studies at high humidity and temperature conditions show that the methanol solvate transforms into the corresponding cocrystal, while the cocrystal and the API suffer no alterations in the time of study under the same conditions.

Key words: pharmaceutical cocrystals; hydrochlorothiazide; solubility; mechanochemistry.

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INFLUENCE OF HALOGEN BONDING IN C-Cl ACTIVATION REACTIONS

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Abstract: Halogen bonding (XB) is a type of non-covalent interactions that present similarities to hydrogen bonding, as such it is also highly directional and has an important electrostatic component. In this interaction a halogen atoms is share between the donor species, that present an electropositive region, and an acceptor species which is usually a Lewis base. Very frequently the acceptor group contains heteroatoms, such as oxygen, nitrogen or sulphur, which share its pair of electrons with the halogen atom. Even though the discovery and theorization of these non-conventional bonding was approached at the end of the last century, it was not until the first decade of this century that research in this field became popular. As such, this kind of noncovalent interactions have been intensely studied in a wide variety of areas such as crystal engineering, biology or supramolecular chemistry. Nevertheless, its influence in reactivity and catalysis have been less studied, although there are widely known processes like bromination of alkenes where XB interactions take part.[1]

In our previous studies we have shown the influence of the XB in M-X (Cl, Br) substitution reactions. [2] We have extended this work to organic species; in this case the halide abstraction mediated by XB interactions has been detected in a reaction that led to the activation of C-Cl bonds to generate new C-E bonds. The evident influence of XB in the reactivity, either in metal complexes or in organic molecules, gives a dynamic picture for this interaction and expands even further its applications.

Key words: Halogen bonding, C-Cl activation, dichloromethane.

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LUMINESCENT SEVEN-COORDINATED EUROPIUM(III) AMIDOPHOSPHATE COMPLEX. STRUCTURE INVESTIGATION BY SINGLE-CRYSTAL X-RAY DIFFRACTION

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Abstract: Molecules containing the [O=P] fragment behave as good O-donor ligands towards trivalent lanthanide ions and can be included in the coordination sphere of luminescent complexes. Triphenylphosphine oxide is the most common example, and several visible- and NIR-emitting lanthanide complexes are reported. Hexamethylphosphoramide is another [O=P]-donor molecule able to afford luminescent lanthanide species, for instance Eu(III) nitrate-complexes exhibit photo- and triboluminescence. Recent advances in this field include derivatives with modified phospho-

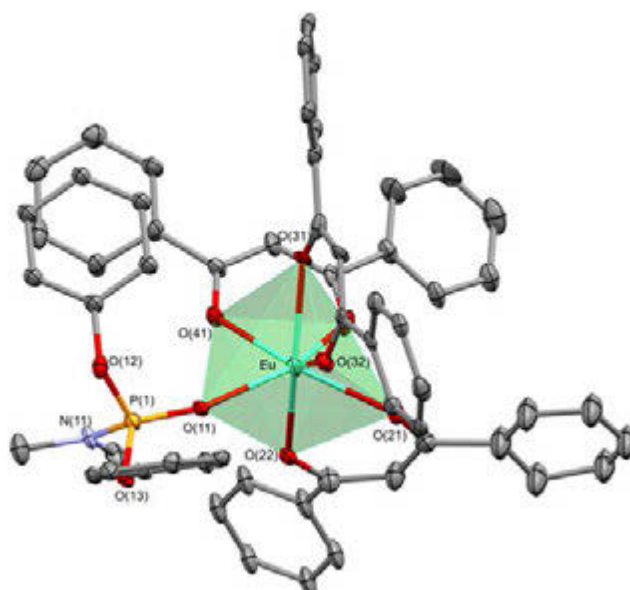


Figure 1. [Eu(dbm)₃{O=P(OPh)₂(NMe₂)}

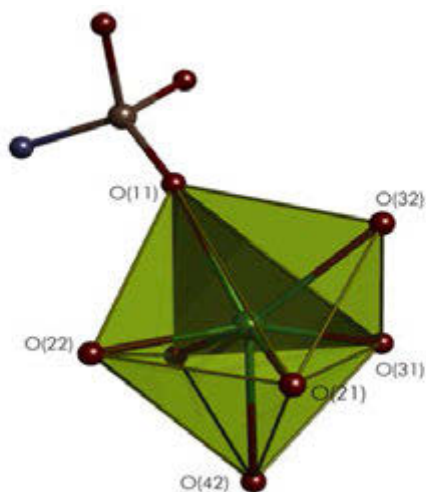


Figure 2. Coordination sphere.

ramides, arylphosphonic diamides and diazaphospholidine-2-oxides [Bortoluzzi, M., et al. (2020); Bortoluzzi, M., et al. (2019)].

Amidophosphates are another family of [O=P]-donor species not yet considered for the synthesis of luminescent complexes. The reaction of EuCl₃ with dibenzoylmethanate (dbm) and diphenyl N-dimethylamidophosphate, O=P(OPh)₂(NMe₂), afforded the seven-coordinated complex [Eu(dbm)₃{O=P(OPh)₂(NMe₂)}]. The compounds

crystallized in the triclinic system $\bar{P}$ (Figure 1). An important disorder was found in one of the dbm ligands, especially on the phenyls rings. Two positions were modelled for each ring, with occupancy factors of 0.55(1):0.45(1), but the figure shows only the most populated positions. The Eu-O(dbm) bond lengths are comprised between 2.298(9) and 2.338(8) Å, while the Eu-O(amidophosphate) distance is slightly longer, 2.380(8) Å. The Eu-O=P angle, 162.5(5)°, indicates bent coordination mode. The inner coordination sphere is close to the capped octahedron (Figure 2).

The complex is bright red luminescent by excitation with near-UV and violet light thanks to the antenna-effect from the coordinated ligands. The emission spectrum shows the transitions from the 5D_0 resonance level to the 7F_J manifold, the most intense band centred at 612 nm for $J = 2$. The high $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ ratio, around 19, and the separation in Stark sublevels of the $^5D_0 \rightarrow ^7F_1$ transition confirm the low symmetry of the complex. The luminescence lifetime, 241 μ s, corresponds to an intrinsic quantum yield around 28%.

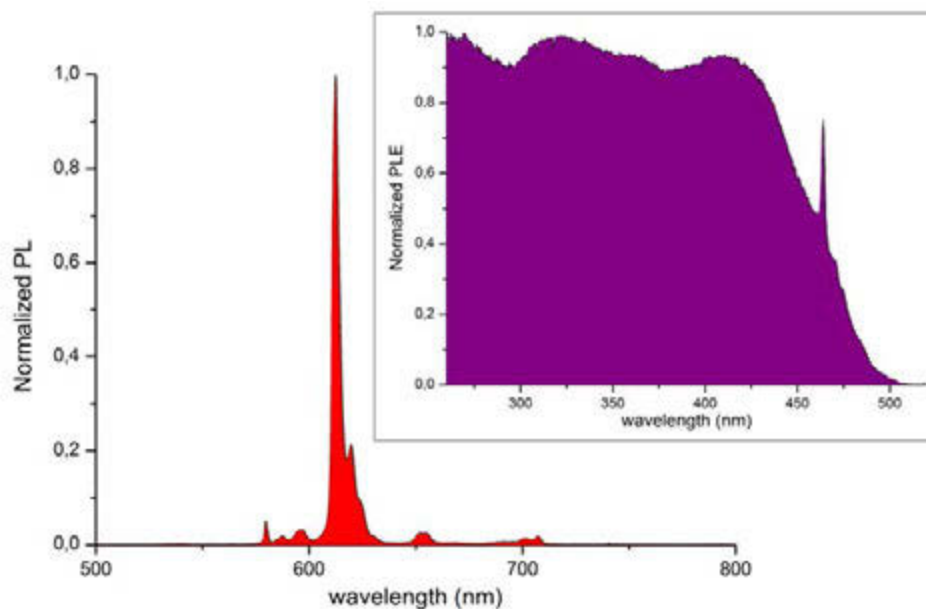


Figure 3. Normalized PL and PLE spectra for the compound.

Key words: amidophosphates, europium(III), β -diketonates, SC-XRD

Acknowledgments: CACTI (University of Vigo) is gratefully acknowledged for X-ray data collection. We acknowledge Università Ca' Foscari Venezia for financial support.

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NEW PHARMACEUTICAL SALTS WITH NON-STEROIDAL ANTI-INFLAMMATORY DRUGS (NSAIDS) WITH IMPROVED PERFORMANCE

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Abstract: Non-steroidal Anti-inflammatory Drugs (NSAIDs) are among the most widely used pharmacological agents for the control of mild to moderate pain in the world. However, NSAIDs present some problems that affect their solubility, stability and interaction with the target receptor. There is great interest in the pharmaceutical industry to find strategies to solve these problems and to improve the properties.

In the last few years, interest in multi-component solid forms have increased due to the possibility of obtaining materials with new properties [1]. Crystallisation strategies, supported by solvent and solid based techniques, have also received attention regarding the research and development of methodologies for the screening of multi-component solid forms [2]. In this work sulindac, ibuprofen, (dex)ketoprofen and diclofenac were selected as model of NSAIDs for developing molecular salts on the basis of their structural similarities using piperazine as counterion. Liquid-assisted grinding (LAG) was used as mechanochemical tool for synthesis, leading to the formation of new polycrystalline materials. The obtained forms were characterised by spectroscopic, thermal and diffractometric techniques. Stability and solubility studies were also conducted to evaluate the advantage they offer over the corresponding NSAIDs molecules.

Key words: NSAIDs, Molecular salt, Mechanochemistry.

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NOVEL SALTS AND COCRYSTALS OF 9-ETHYLADENINE

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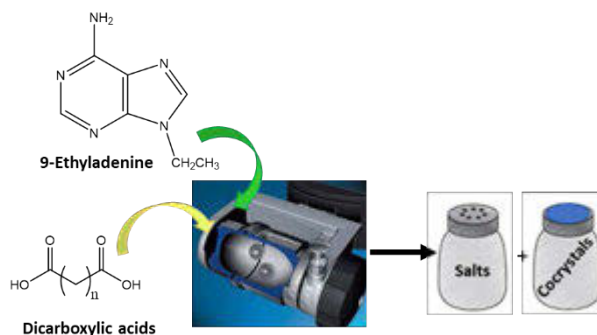
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Abstract: In this communication, we report the use of liquid-assisted grinding along with solution methods for the preparation of new salts and cocrystals containing the modified nucleobase, 9-ethyladenine, and several dicarboxylic acids with different alkyl chain lengths. The prepared compounds have been fully characterized by ATR-FT-IR, thermal methods (TGA-DSC) and powder and single crystal X-ray diffraction. Moreover, by combination of DFT and QTAIM calculations we have analyzed the relationship between the salt/cocrystal form, the coformer used or even the length of the alkyl chain through their interaction energies [1].

Finally, we would like to remark that the binding modes observed for the prepared multicomponent compounds could be used as new models for the recognition of nucleobases with proteins *via* side chains of amino acids such as for example the two essential dicarboxylic amino acids, glutamic and aspartic acid.



Key words: crystal engineering, 9-ethyladenine, mechanochemistry, QTAIM.

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SINTESIS Y REACTIVIDAD DE $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)(\text{L})]$ Y $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\text{L})_2]$

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Resumen: La química de los metales de transición conteniendo ligandos como los arildiacenuro ArN_2 , diaceno $\text{RN}=\text{NH}$ o hidrazina RNHNH_2 , sigue siendo objeto de numerosos estudios ¹, debido a la similitud de estos derivados con los intermedios en la fijación del nitrógeno. Por otra parte, estos compuestos presentan diferente reactividad y propiedades estructurales dependiendo del ligando soporte utilizado.

En esta comunicación presentamos las propiedades espectroscópicas y estructurales de los nuevos diazoderivados obtenidos mediante reacción de los compuestos semi-sandwich $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)(\text{L})]$ y $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\text{L})_2]$, $\text{L} = \text{PPh}_2\text{OCH}_2\text{Ph}$, con un exceso del correspondiente diazoalcano en presencia de NaPF_6 . La reactividad del diazo derivado $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\text{N}_2\text{C}(\text{C}_{12}\text{H}_8)\}\text{L}_2][\text{PF}_6]$ (Figura 1) frente al nucleófilo PPh_3 da lugar al derivado $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{N}_2\text{L}_2][\text{PF}_6]$ y $[\text{PPh}_3(\text{C}_{13}\text{H}_8)][\text{PF}_6]$ (Figura 2)

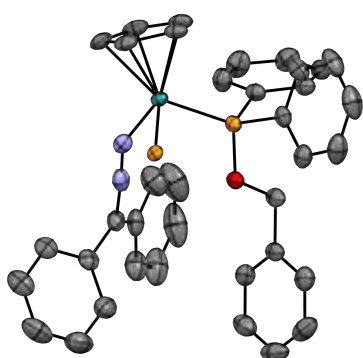


Figura 1

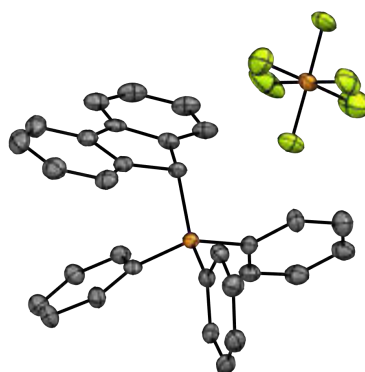


Figura 2

Palabras clave: Rutenio, ciclopentadienilos, diazoderivados

Agradecimientos: Ministerio de Ciencia e Innovación (PID2019-110218RB-100 y CTQ2017-90802-REDT)

Referencias: Albertin, G., Antoniutti, S., Castro, J., Sibilla, F. "Pentamethylcyclopentadienyl osmium complexes that contain diazoalkane, dioxygen and allenylideneligands: preparation and reactivity" *Dalton Trans.* 2019, 48, 3116-3131.

²Albertin, G., Antoniutti, S., Bortoluzzi, M., Botter A., Castro, J., "Pentamethylcyclopentadienyl Half-Sandwich Diazoalkane Complexes of Ruthenium: Preparation and Reactivity" *Inorg. Chem.* **2016**, 55, 5592-5602.

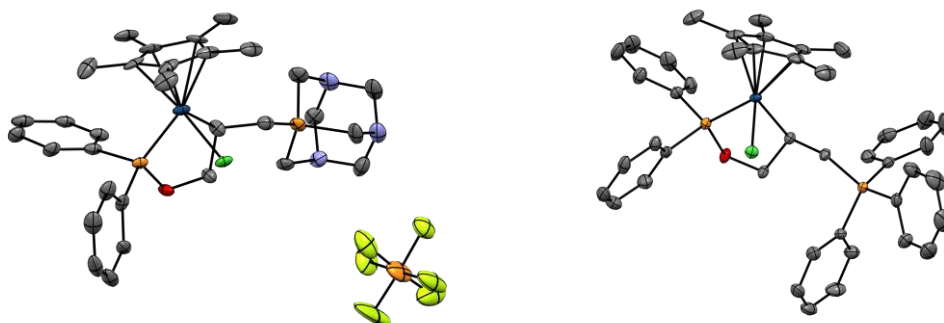
SINTESIS Y REACTIVIDAD DE COMPLEJOS DE IRIDIO(III) CON ALILDIFENILFOSFINITO

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Resumen: El interés por los ligandos alquenilfosfinito se debe a que son capaces de estabilizar especies intermedias gracias a su habilidad para generar vacantes en el centro metálico, y de ser capaces de coordinarse diastereoselectivamente al metal como un ligando quelato $\kappa^3(\text{P,C,C})$.¹ Este modo de coordinación permite que el doble enlace $\text{C}=\text{C}$ sea susceptible de ataques nucleófilos dando como resultado complejos con ligandos $\kappa^2(\text{P,C})$.

En la presente comunicación se describe la síntesis y la estructura cristalina del nuevo complejo de Ir(III) conteniendo el ligando alildifenílfosfinito $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)\{\kappa^3(\text{P,C,C})\text{Ph}_2\text{POCH}_2\text{CH}=\text{CH}_2\}][\text{PF}_6]$ así como la reactividad frente a diferentes nucleófilos $[\text{Nu} = \text{PPh}_3, \text{PPh}_2\text{Me}, 1,3,5\text{-triaz}-7\text{-fosfatriciclo}[3.3.1.1]\text{decano(PTA)}]$, que dan lugar a la formación de nuevos compuestos $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)\{\kappa^2(\text{P,C})\text{Ph}_2\text{POCH}_2\text{CHCH}_2(\text{Nu})\}][\text{PF}_6]$.



Palabras clave: Iridio, fosfinito, PTA.

Agradecimientos: Ministerio de Ciencia e Innovación (PID2019-110218RB-100 y CTQ2017-90802-REDT).

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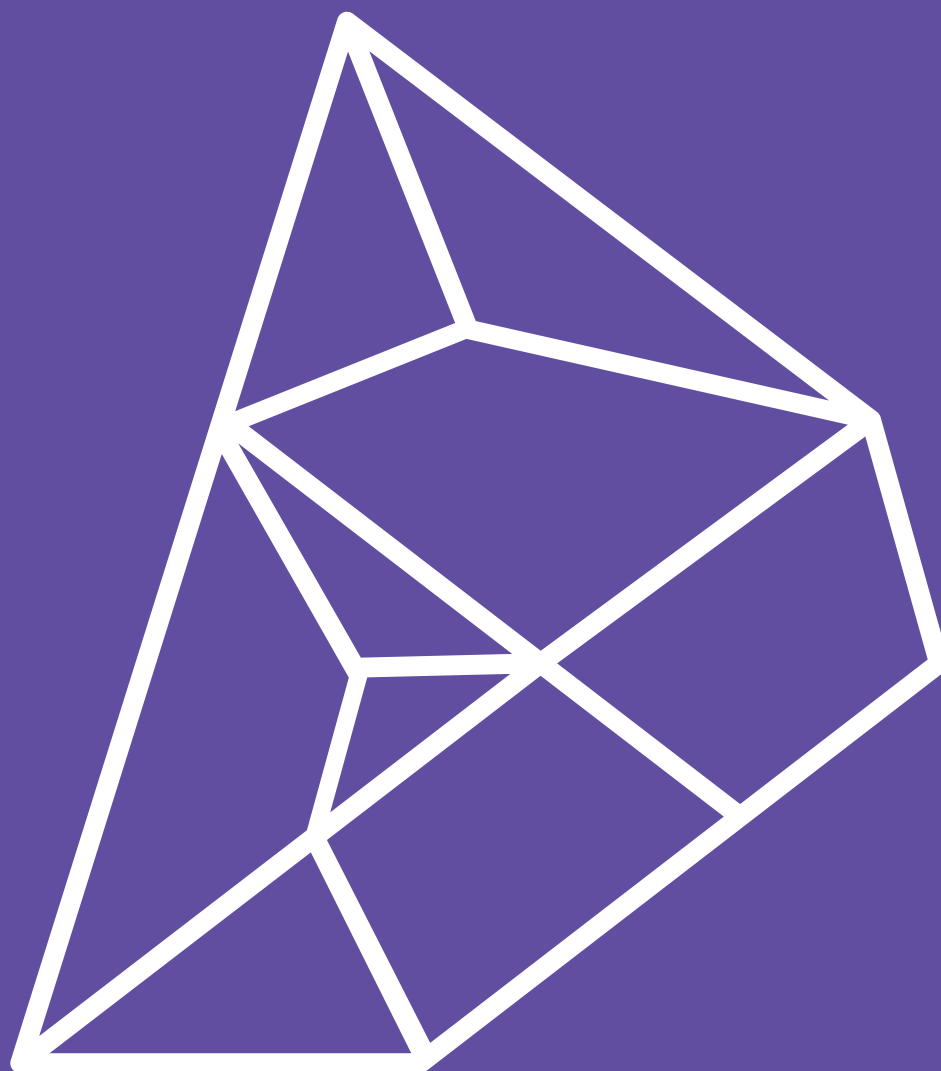
MS7- Cristalografía actual de macromoléculas

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STRUCTURES OF T7 BACTERIOPHAGE PORTAL AND TAIL SUGGEST A VIRAL DNA RETENTION AND EJECTION MECHANISM

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Abstract: Double-stranded DNA bacteriophages package their genome at high pressure inside a procapsid through the portal, an oligomeric ring protein located at a unique capsid vertex. Once the DNA has been packaged, the tail components assemble on the portal to render the mature infective virion. The tail tightly seals the ejection conduit until infection, when its interaction with the host membrane triggers the opening of the channel and the viral genome is delivered to the host cell. Using high-resolution cryo-electron microscopy and X-ray crystallography, here we describe various structures of the T7 bacteriophage portal and fiber-less tail complex, which suggest a possible mechanism for DNA retention and ejection: a portal closed conformation temporarily retains the genome before the tail is assembled, whereas an open portal is found in the tail. Moreover, a fold including a seven-bladed β -propeller domain is described for the nozzle tail protein.

Key words: viral DNA packaging, T7 bacteriophage, portal protein, X-ray crystallography, cryo-EM

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Cuervo, A., Fàbrega-Ferrer, M., Machón, C., Conesa, J.J., Fernández, F.J., Pérez-Luque, R., Pérez-Ruiz, M., Pous, J., Vega, M.C., Carrascosa, J.L. and Coll, M. (2019) Structures of T7 bacteriophage portal and tail suggest a viral retention and ejection mechanism. *Nature Communications*, 10 (1), 3746

COMBINING CHEMICAL AND BIOPHYSICAL STRATEGIES TO DEVELOP PROTEIN-PROTEIN INTERACTION REGULATORY COMPOUNDS WITH THERAPEUTIC POTENTIAL

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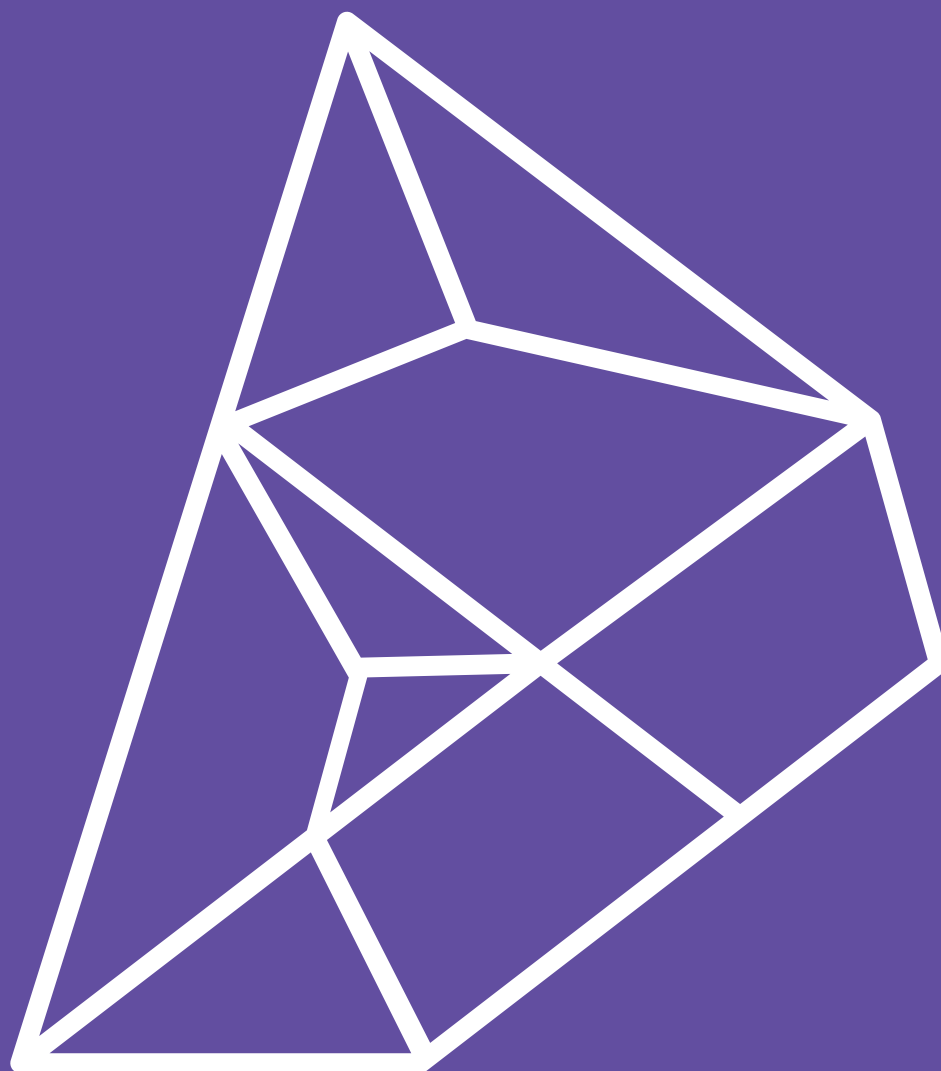
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Abstract: The protein complex formed by the Ca^{2+} sensor neuronal calcium sensor 1 (NCS-1) and the guanine exchange factor protein Ric8a co-regulates synapse number and probability of neurotransmitter release, emerging as a potential therapeutic target for diseases affecting synapse function, such as neurodevelopmental disorders and neurodegeneration [1]. In the recent years, the structural basis of the NCS-1/Ric8a interaction have been studied at molecular and atomic level. This has been critical to develop structure-based virtual screenings to find hit candidates that inhibit complex formation [2, 3]. Additionally, we have applied Dynamic Combinatorial Chemistry (DCC) approaches to find other regulatory molecules [4]. A catalyzed protein-directed DCC working at low temperatures and operating under physiological parameters has been developed to allow NCS-1 to find the best ligands in situ. Ultrafast NMR identified the reaction intermediates of the acylhydrazone exchange, tracing the molecular assemblies and getting a real-time insight into the essence of DCC processes at physiological pH. Additionally, NMR, X-ray crystallography and computational methods were employed to elucidate structural and mechanistic aspects of the molecular recognition event. This multidisciplinary approach lead us to find a compound stabilizing the NCS-1/Ric8a complex with therapeutic potential in Alzheimer’s disease.

Key words: Calcium signaling, protein-protein interaction, small-molecule regulator

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AGAROSE, THE GEL TO TAILOR YOUR PROTEIN CRYSTALS

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Abstract: The growth of protein crystals in gel has proved to date to be the cheapest means to produce protein crystals of high quality similar to those obtained under microgravity conditions (Gavira et al., 2020; Robert & Lefauchaux, 1988; Snell & Helliwell, 2005). Gels create a stable environment for crystals to grow in convection-free conditions avoiding sedimentation and the formation of aggregates and increasing crystals uniformity. The use of agarose has allowed progress in the limitations of crystal size and quality and even to obtain protein crystals inaccessible by other techniques (Sica et al., 1994).

In this work we have exploited the nucleation inducing ability of agarose gels in diffusion-dominated environments. Crystal size was successfully tuned in a wide range of agarose, protein and precipitant concentrations. The impact of gel content on crystal size resulted to be independent of the specific protein, allowing the mathematical prediction of crystals size and pointing out the exclusivity of the physical interactions between the gel and the protein to explain the observed behaviour. The versatility of the technique and the fine-tuning of the nucleation flux was demonstrated by crystallizing five different model proteins using two different techniques, batch and counter-diffusion. In addition, the potential of agarose to be used as a growth and delivery medium for serial crystallography applications has been proven by preparing unidimensional micro-crystals slurries in 0.1 % (w/v) gel.

Key words: protein crystallization, gel, nucleation, batch, counter-diffusion.

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DISCOVERY AND BIOCHEMICAL AND STRUCTURAL CHARACTERIZATION AT ATOMIC RESOLUTION OF THE NOVEL THERMOPHILIC ESTERASE ESTD11

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 Sánchez⁶,
 Aurelio Hidalgo⁶, José Berenguer⁶, María Isabel Gonzalez-Siso³, Jacobo Cruces⁴,
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Abstract: A novel esterase, EstD11, has been discovered in a hot spring metagenomic library. It is a thermophilic and thermostable esterase with an optimum temperature of 60°C and it maintains more than 50% of its activity after one hour of incubation at 70°C (García Marnotes, n.d.). A detailed substrate preference analysis of EstD11 was done using a library of chromogenic ester substrate that revealed the broad substrate specificity of EstD11 with significant measurable activity against 16 substrates with varied chain length, steric hindrance, aromaticity and flexibility of the linker between the carboxyl and the alcohol moiety of the ester.

The tridimensional structures of EstD11 and the inactive mutant have been determined at atomic resolutions. Structural and bioinformatic analysis, confirm that EstD11 belongs to the α/β -hydrolase family (David et al., 1992; Kourist et al., 2010), (Arpigny & Jaeger, 1999), (Holmquist, 2005). The canonical α/β -hydrolase domain is completed by a cap domain, composed by two subdomains that can unmask of the active site to allow the substrate to enter. Seven crystallographic complexes were solved with different substrates and reaction products that allowed us identification of the hot-spots in the active site underlying the specificity of the protein. Crystallization and/or incubation of EstD11 at high temperature

provided unique information on cap dynamics and a first glimpse of enzymatic activity in vivo. Very interestingly, we have discovered a unique Met zipper lining the active site and the cap domains that could be essential in pivotal aspects as thermo-stability and substrate promiscuity in EstD11.

Key words: Crystal structure, Thermophilic esterase, α / β -hydrolase fold, Enzyme-substrate complex.

Acknowledgments: We thank the staff from ALBA synchrotron facilities for help during crystallographic data collection. This work was funded by the UE through the HotDrops Project (FP7- PEOPLE-2012-IAPP, project number 324439). Additionally, this work was supported by the BFU2017-90030-P grant to J.A.H. from the Spanish Ministry of Science and Innovation.

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DOMAIN SWAPPING IN A CHIMERIC CONSTRUCTION OF THE C-SRC/ABL SH3 DOMAIN

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Abstract: Amyloid is the leading cause of many neurodegenerative diseases. However, the mechanism at the molecular level of the amyloid aggregation is unknown. In the case of amyloids, the study of the molecular basis of protein misfolding processes is complicated due to the difficulties to obtain structural information at an atomic level. Nevertheless, another misfolding process that produces oligomers which can be crystallized is the 3D domain-swapping (3D-DS). We used the SH3 domain of the c-Src tyrosine kinase as a model to study misfolding processes, as it forms intertwined dimers and amyloid fibres. In this domain, the n-Src loop acts as a hinge loop, which facilitates the opening of the domain to generate the intertwined oligomer. The formation of these misfolded structures is sensitive to the pH and the addition of some molecules. We have constructed several chimeric proteins of the c-Src SH3 domain where the loops RT and n-Src has been interchanged with those in Abl SH3 domain. Previously, the chimeric construction where both loops were interchanged resulted in an intertwined dimer where both loops, the RT and n-Src, act as hinge loops. Here, we have crystallized and solved the structure of the monomer and intertwined dimer of the chimeric construction where the RT loop of the Abl has been introduced in the c-Src. This construction forms an intertwined dimer by the opening of the n-Src loop, but the geometry of the dimer is different from previous intertwined structures of the c-Src SH3 domain. Here we compare the structure of this chimeric construction in its dimeric and monomeric forms and analyze the molecular basis of the formation of the 3D domain swapping.

Key words: 3D domain swapping, intertwined dimer, SH3 domain, amyloid

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DYNAMIC INSIGHTS INTO THE ACTIVATION OF ABA RECEPTORS AS DETERMINED BY X-RAY CRYSTALLOGRAPHY

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Abstract: Absciscic acid (ABA) is the main phytohormone involved in the adaptive crop responses to drought. ABA signaling relies on the family of PYR/PYL ABA receptors, which upon ABA binding form high-affinity ternary complexes with protein phosphatases type 2C (PP2Cs) and inhibit them. Our previous studies (Moreno-Alvero et al 2017) have overturned the dogma established, which states that ABA binding induces a conformational change in the receptor to interact with PP2Cs. Rather, we showed that for high-affinity ABA binding to PYR/PYL receptors, the PP2C co-receptors play a proactive role (Sánchez-Barrena et al., 2018; Rodríguez et al, 2019). The detailed study of the transitions from the inactive to active forms of the PYR/PYL receptors is central to understand the basis of such process. We have employed a combination of crystallographic and experimentally-based molecular dynamics simulation that provides a structural framework from the unbound form of the PYR/PYL/RCAR receptors to the complex with PP2Cs. This information could be useful for the discovery of new ABA mimicking molecules.

Key words: Protein crystallography, dynamic crystallography, plant biology

Acknowledgments: This work was funded by grant BIO2017-89523-R to A. Albert. We thank the ALBA beamlines XALOC) for access to the synchrotron radiation

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EXPRESSION, PURIFICATION AND CRYSTALLIZATION OF A BACTERIAL ZINC FINGER PROTEIN

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Abstract: *Pseudomonas aeruginosa* is an opportunistic gram-negative bacteria that can grow under a variety of conditions, such as in soil, water, and in human, animal and plant host-associated environments. By virtue of its high adaptability, *P. aeruginosa* evolved to as a nosocomial infection agent that affects immuno-compromised patients or individuals with complicated conditions, such as traumatic burns or who suffer genetic illness such as cystic fibrosis {Khan, 2018}. In these latter, *P. aeruginosa* invades the lungs {Davies, 2006}. Indeed, its high adaptability converted this microbe in a multidrug resistant pathogen {Khan, 2018}. One potential biomedical target is a DNA-binding Zn-finger repressor that regulate genes that are essential for *P. aeruginosa* viability, which has a homolog in *Escherichia coli*. We expressed such a repressor from both *E. coli* and *P. aeruginosa* in *E. coli* strains as a fusion protein with an N-terminal SUMO tag to increase the formerly detected low solubility. In this type of constructs, at the end of the SUMO protein there is the cleavage site for the SUMO protease. However, in our constructs the proteolytic cleavage was inefficient and we suspected a potential interference between the tag and the repressor. As an alternative, we added a cleavage site for the TEV protease between SUMO and repressor genes. However, the proteins were not cleavable by TEV under many different conditions (1-2mM DTT, 250-750mM NaCl, pH 6-9). One possible reason was that either SUMO cleavage site in the initial constructs, or the TEV site in the new ones, were too close to the Zn-finger protein. However, addition of two aminoacids between the protein and the TEV cleavage site did not allow cleavage. Unexpectedly, high efficient cleavage was achieved for constructs that contained a linker of six aa between the TEV or the SUMO cleavage site and the Zn-finger protein, which in turn resulted to be highly soluble. We are currently working on purification protocols for both constructs, which include affinity chromatographies that consist in a first step to isolate the fusion protein and a second to isolate Zn-finger protein upon cleavage. Crystallization will follow with protein in complex with nucleotides that activate the protein, and/or with DNA sequences. Our final aim is to pave the way for a drug

designed against this target. Therefore, the crystal structure of this essential protein will be pivotal to combat this pathogen with new strategies.

Key words: Zn-finger protein, affinity chromatography, TEV cleavage, *Pseudomonas*

Acknowledgments:

Project Funding:

Reference: **MDM-2014-0435** (1st of July 2015 – 31th of December 2019)

Title: *Appointment of the Department of Structural Biology of IBMB as a “María de Maeztu” Unit of Excellence.*

Spanish Ministry of Economy and Competitiveness.

Reference: **RTI2018-101015-B-100** (1st of January 2018 – 31th of December 2020)

Title: *Structural analysis of proteins essential for mitochondria and pathogen viability.*

R&D project, Societal Challenges State Plan, Life Sciences Subplan, Ministry of Science, Innovation and Universities.

Fellowship:

Reference: BES-2016-077079 (16th of April 2017-15th of April 2021)

Title: *Grants for pre-doctoral contracts for the training of doctors 2016.*

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ON THE MOLECULAR DETERMINANTS GOVERNING CHOLINE SULFATASE CATALYTIC PROMISCUITY

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Abstract: catalytic promiscuity, understood as the ability of an enzyme to catalyse the turnover of various, chemically different substrates, was suggested to play a key role in the evolution of new enzyme functions already in the seventies [Jensen, 1976]. The alkaline phosphatase superfamily harbours different promiscuous enzymes which have been proposed as model systems in order to understand enzymatic multifunctionality [Barrozo et al., 2015, Pabis and Kamerlin, 2016]. Choline-o-sulfatase (COSe, E.C. 3.1.6.6) is a member of this superfamily whose natural function is to hydrolyze choline-o-sulfate into choline and sulfate. The recombinant COSe from *Sinorhizobium meliloti* (SmeCOSe) has shown promiscuous towards different substrates [van Loo et al., 2018], but its binding mode has not yet been deciphered. We previously obtained the wild-type structure of SmeCOSe (PDB IDs: 6G5Z and 6G60); in order to gain insights into the substrate promiscuity of this enzyme, we have further conducted a deep structural and biophysical analysis of the SmeCOSe C54S active-site mutant, obtaining new structural models with different ligands. Also, thermal shift assay screening allowed identifying new ligands for SmeCOSe. Our results allow concluding on the molecular determinants governing the substrate promiscuity of this member of the phosphate superfamily.

Key words: choline sulfatase, enzyme promiscuity, phosphatase superfamily

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STRUCTURAL STUDIES OF A CALMODULIN-LIKE CALCIUM BINDING PROTEIN INVOLVED IN PLANT SALT STRESS TOLERANCE

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Abstract:

World food supply is rapidly becoming a serious concern due to climate change and population growth. Finding new strategies to improve crop performance in abiotically stressful situations is key to cater for a society with increasing demands of food production¹, and since many adaptive and regulatory mechanisms in plants such as ionic homeostasis control or homeostasis of lipid and protein levels take place in the vacuoles and cell membranes, targeting this localization is a reasonable, practical strategy to combat cell stress reduction.

Calcium ions function as fundamental messengers in many of these regulatory pathways; hence, understanding the molecular mechanisms underlying plant Ca²⁺ homeostasis may help overcome the food demand problem.² CML18 is a calmodulin-like protein which interacts with the sodium/hydrogen exchanger NHX1 regulating vacuolar ion compartmentalization in a Ca²⁺ and pH dependent manner. This process allows for a rapid detoxification of cytoplasmic Na⁺ resulting of drought and saline stress.³

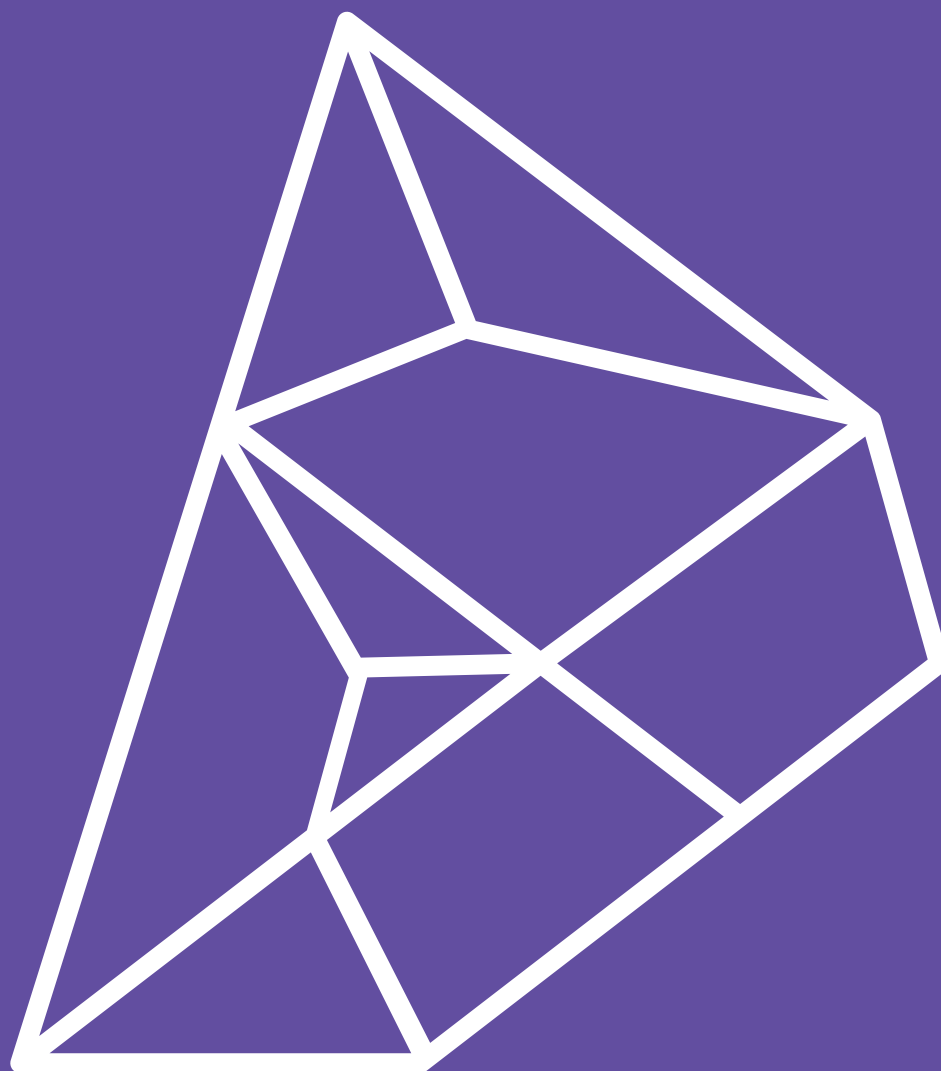
In this work, we have purified to homogeneity and crystallized CML18. Furthermore, optimization of these protein crystals have allowed us to resolve, for the first time, the structure of CML18 to a 3Å resolution. Analysis of the structure will allow us to gain insight on the basis regulating ion homeostasis and Na⁺ compartmentalization between the vacuole and the cytoplasm. Further studies on the subject will be directed towards the biochemical characterization and determination of the Ca²⁺ and NHX1-binding properties of CML18, and towards obtaining the structure of the NHX1/CML18 complex.

Key words: Calmodulin-like proteins, Ca²⁺ binding, plant ion homeostasis, salt stress.

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pH DRIVEN CONFORMATIONAL CHANGES IN THE FOLDING NUCLEI OF THE FYN SH3 DOMAIN REVEALED BY HIGH RESOLUTION CRYSTAL STRUCTURES

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Abstract: The SH3 of the Fyn tyrosine kinase (Fyn-TK), together with the c-Src SH3, is one of the modular domains which folding mechanism is better characterized. Both domains share up to 80% of their sequence (~60 residues). Previous crystal structures of the c-Src SH3 domains allowed us to characterize the formation of intertwined dimers through three-dimensional domain swapping (3D-DS) where the n-Src loop acts as a hinge loop^{1,2}. However, up to date, the Fyn SH3 does not form intertwined dimers. To determine the molecular interactions that favour the 3D-DS, we have determined the structures of the chimeric constructions of the Fyn and c-Src SH3. Here, we show the characterization of a Fyn mutant, L112V-S114N-S115T-E121L-R123H, where residues at the n-Src and distal loop have been changed by those present in the c-Src sequence. We have determined how these mutations affect the stability and structure of the protein. The atomic-resolution structures of the Fyn SH3 and its complex with a high-affinity synthetic peptide (Fyn-SH3/VSL12) were obtained from crystals in a wide range of pH (3.0-6.0) and presence and absence of low molecular weight PEGs. The addition of PEG at acidic pHs promotes the formation of intertwined structures in the c-Src SH3, but no 3D-DS was observed in the Fyn SH3. These structures show changes in the conformation of the distal loop. These changes also affect the hydrogen bond between Ser124 and Glu107, which is critical in the folding transition state of the protein. As the pH increase, Glu107 can be modelled in double conformation. In the structures at pH 6.0, the hydrogen bond between glutamate and serine side chain is mediated by a water molecule. These are the first structures of the Fyn SH3 domain where these structural features are described.

Key words: SH3, crystal structure, 3D domain-swapping, pH

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STRATEGIES TO STABILIZE AND PURIFY PROTEINS WITH HIGH TENDENCY TO AGGREGATE

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Abstract: Protein aggregation is one of the major bottlenecks during heterologous protein expression in *Escherichia coli*. Our objective is to solubilize, purify and crystallize a human protein located at the mitochondrial inner membrane. The N-terminal domain of this protein expands through the intermembrane space, whereas the C-terminal domain faces the mitochondrial matrix. Based on structure prediction, we designed a number of genetic constructs of either domain for expression. From all attempts, only one construct that includes a fragment of the N-terminal region was soluble during cell lysis in the appropriate buffer identified by extensive buffer screening. The production yield was high (at the order of mg/mL), and it eluted from the immobilized metal affinity column highly pure. However, this fragment showed a high tendency to aggregate, which impaired further characterization. This led us to explore different methods to prevent aggregation, which included differential scanning fluorimetry (DSF). Yet, the high tendency to aggregate yielded inconclusive results, which conducted us to further explore stabilization alternatives. Successful attempts are presented and discussed.

Key words: protein domain, high-scale protein production, protein stability, purification, aggregation.

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THE STRUCTURE ANALYSIS OF ARABIDOPSIS EXTENDED SYNAPTOTAGMIN 1 REVEAL THE BASIS OF ITS REGULATION AT MEMBRANE CONTACT SITES

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Abstract: Cell function requires the maintenance of membrane lipid homeostasis as changes in cellular environment unbalance this equilibrium. The non-vesicular lipid transfer at endoplasmic reticulum (ER) and plasma membrane (PM) contact sites (CS) is central to restore it. Extended Synaptotagmins (E-Syts) are ER proteins that play a central role in this process as they act as molecular tethers with PM and as lipid transfer proteins between these organelles. E-Syts are constitutively anchored to the ER through a N-terminal hydrophobic segment and bind to the PM via C-terminal C2 domains. In plants, E-Syts regulate the ER-PM communication by the activity of their two C2 domains in response to abiotic stresses. In order to shed light into this issue, we have combined macromolecular crystallography, small angle x-ray scattering, structural bioinformatics and biochemical data to analyze the regulation of plant extended synaptotagmin 1 (SYT1).

Key words: Abiotic stress; Extended Synaptotagmins; Lipid transport; Membrane contact sites.

Acknowledgments: This work was funded by grants from Agencia Estatal de Investigación (AEI, Spain) and Fondo Europeo de Desarrollo Regional (FEDER, European Union) (BIO2017-89523-R to A. Albert). A. Albert thanks ALBA and Diamond Light Source (beamlines XALOC and B21) for the access to the synchrotron radiation source.

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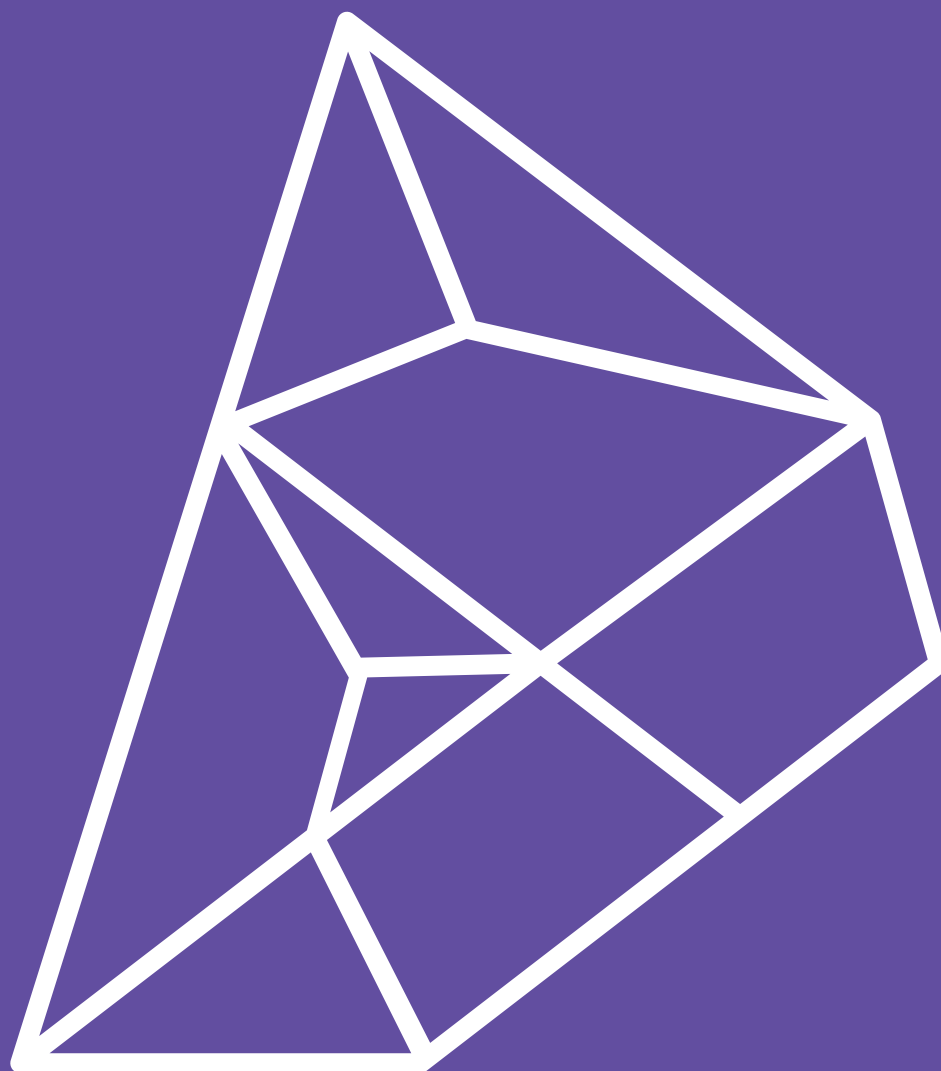
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CINCO DOCUMENTALES CIENTÍFICOS REALIZADOS DESPUÉS DE LA II GUERRA MUNDIAL

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Resumen: Se presentan cinco documentales pertenecientes al Museo de la Geología de la Universidad Complutense de Madrid (UCM). Durante muchos años estuvieron olvidados, en un armario del antiguo Departamento de Cristalografía y Mineralogía de la Facultad de Ciencias Geológicas de la UCM. Los rollos originales, en formato 8 mm, no pudieron visualizarse en un primer momento al no disponer de un proyector adecuado. Sin embargo, sus títulos prometían contenidos tan sugerentes que se impuso su digitalización. Esta fue financiada por la Unidad de Gestión del Patrimonio Histórico de la UCM.

Si nos atenemos a la definición de documental dada por el productor y director Paul Rotha como *“película de interés específico sobre temas científicos, culturales o sociológicos”*, se constata que efectivamente pertenecen a este género cinematográfico. Los cinco documentales: *“La estructura elemental de la materia”*, *“Tierra incógnita”*, *“Amianto... cuestión de tiempo”*, *“Alpha brass dislocation movements”* y *“Growth of the twins in tin singel”*, se pueden clasificar en tres grupos:

1) Los dos primeros pertenecen a la serie cinematográfica de Philips “Electrones mágicos”. Ambos fueron encargados por Philips a dos productoras diferentes: AFIFA Berlin-Wiesbaden y Verity Films Ltd (asociada a Guild), respectivamente. AFIFA fue cerrada por el gobierno alemán en 1956, con lo que *“La estructura elemental de la materia”* tiene que ser anterior a ese año, y *“Tierra incógnita”* aparece en la filmografía de Verity con fecha de 1948.

Entre los créditos figuran algunos personajes conocidos, tanto en el mundo de la investigación como del cine. Entre los asesores científicos destaca el Dr. G.D. Rieck, cristalógrafo y profesor de físico-química de la Eindhoven University of Technology. Los créditos por animación se otorgan al cineasta Fritz Brunsch y al estudio de animación británica WM Larkins. La breve pieza musical incluida en el primer documental se atribuye al compositor austriaco Rudolf Perak y la de *“Terra incógnita”* pertenece a

Malcolm Arnold (más conocido como autor de la banda musical de “El puente sobre el río Kwai”). Además, las películas se realizaron en diferentes laboratorios de prestigio (Universidad Técnica de Delft, Philips de Eindhoven y Real Observatorio de Edimburgo).

En estos documentales se tratan, desde un punto de vista muy didáctico, los aspectos más relevantes de la espectrografía y la difracción de rayos X en el primero, y de la óptica, la naturaleza de la luz y la radiación electromagnética en el segundo. Plantean conceptos muy básicos de la teoría ondulatoria, como propagación de ondas e interferencias, y los fundamentos de la difracción y sus posibilidades; empleando para ello recursos muy ingeniosos, animaciones, modelos de agua y de bolas, dioramas, etc., que solo tienen que envidiar a los actuales por la calidad de las imágenes, tristemente deterioradas por el tiempo y las pésimas condiciones en que se han conservado. Ambas películas constituyen un claro ejemplo de cine de divulgación científica, realizado para comunicar al público hallazgos y conocimientos.

2) El tercero, “*Amianto... cuestión de tiempo*”, se clasifica como un documental científico-sociológico. La trama se desarrolla en la ciudad de Asbestos que debe su nombre a que se ubica junto a la mina de crisotilo o asbesto blanco más grande del mundo, la Mina Jeffrey (Quebec, Canadá). Esta mina, descubierta en 1872, proporcionó a los habitantes de Asbestos, empleos estables y seguros durante generaciones. La Mina estuvo gestionada por la compañía Johns-Manville, que también figura como productora de la película.

En este documental se publicitan las bondades del asbesto, sus extraordinarias cualidades y paralelamente, la alta calidad de vida de los habitantes de Asbestos, completamente ligada a la actividad de la Mina. Podría tratarse de una propaganda favorable, realizada entre los años 50-60 del siglo veinte, durante el período en que la compañía fue sometida a las primeras demandas, por los casos de asbestosis y otros daños pulmonares sufridos por muchos de sus empleados. En el Archivo de la UCM se conserva un documento, fechado en 1960, según el que Johns-Manville hace entrega de la película al Museo de Ciencias Naturales, para ser exhibida en privado, con fines educativos y de divulgación.

En 1982 la compañía se declaró voluntariamente en bancarrota, al no poder enfrentarse a los miles de demandas por lesiones relacionadas con el asbesto. La Mina se clausuró en 2001 y la ciudad de Asbestos quedó arruinada, pasó de disfrutar de un excelente nivel de vida a ser considerada la ciudad más peligrosa de Canadá. Sin embargo, llama la atención que el gobierno de Canadá no prohibió la “fabricación, uso, importación y exportación de asbesto y productos que lo contengan” hasta 2018, lo cual da idea de la gran importancia que ha tenido este material en la economía del país.

3) Los dos últimos documentales constituyen un ejemplo de cómo los medios audiovisuales pueden posibilitar a los científicos el acceso a un conocimiento más profundo de la realidad. Son verdaderos instrumentos de investigación que permiten visualizar fenómenos difícilmente perceptibles para el ojo humano, por ser demasiado pequeños, o grandes, o muy rápidos o muy lentos. En este caso se trata del movimiento de una dislocación en una muestra de latón alfa, y del crecimiento de una macula en un monocristal de zinc, respectivamente.

Ambas copias fueron realizadas por la productora Crawley Films Limited para la televisión canadiense. Tanto ésta como las correspondientes a los dos primeros documentales descritos, se fundaron al inicio de la II Guerra Mundial, se mantuvieron

activas durante ésta y experimentaron un gran auge al final de la misma, período que coincide con la realización de las películas presentadas aquí.

Palabras clave: Espectrografía, Difracción, Rayos X, Microscopía electrónica.

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KRYSTALA: UNA WEB SOBRE EL MUNDO MINERAL

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Abstract: **Krystala**, un nuevo portal temático creado por el autor y la Fundación Descubre, dedicado al mundo inorgánico, es decir un portal sobre el mundo de los cristales, los minerales y los materiales inorgánicos y su interfaz con la vida. Va dirigido a una audiencia muy variada, porque es un portal eminentemente formativo, orientado a profesores y estudiantes, y en general a todos aquellos ciudadanos que quieren conocer mejor el papel que juega la ciencia en nuestra vida cotidiana. El portal es ya de acceso público y puede ser visitado en krystala.fundaciondescubre.es/

Una de las características de **Krystala** es que todo su contenido es realizado, revisado y/o recomendado por corresponsales temáticos y regionales, todos ellos profesionales de reconocido prestigio. La probabilidad de encontrar en Krystala, noticias falsas o malintencionadas, aproximaciones esotéricas, o especulaciones paracientíficas es prácticamente nula.

Krystala aspira a ser un portal de ámbito latinoamericano y por tanto su lengua vehicular es el castellano o español. No obstante, una de las fronteras que **Krystala** aspira a borrar es la idiomática. Por lo tanto, se solicitan y aceptan artículos, videos y cualquier tipo de material científico y/o artístico, escrito o hablado en otras lenguas. El único criterio de selección será la calidad determinada por un comité editorial.

El proyecto pretende contribuir a borrar también la frontera entre ciencia y humanidades publicando selectos materiales artísticos inspirados o relacionados con la ciencia. No solo videos, fotografía o prosa, sino también pintura, escultura, arquitectura o poesía.

El portal contiene varias categorías principales. *Mundo Krystala* es una categoría que contiene tres grandes bloques temáticos. Uno dedicado al futuro, con contenidos dedicado a los avances mas importantes en estas ciencias y a entrever el futuro y el impacto sobre la naturaleza y la sociedad. Otro dedicado al pasado, a la historia de la ciencia, y un tercer bloque dedicado al arte de inspiración científica. Tres grandes salas constituyen la categoría *Museo Krystala*, una de ellas dedicada a los Cristales Gigantes, otra llamada

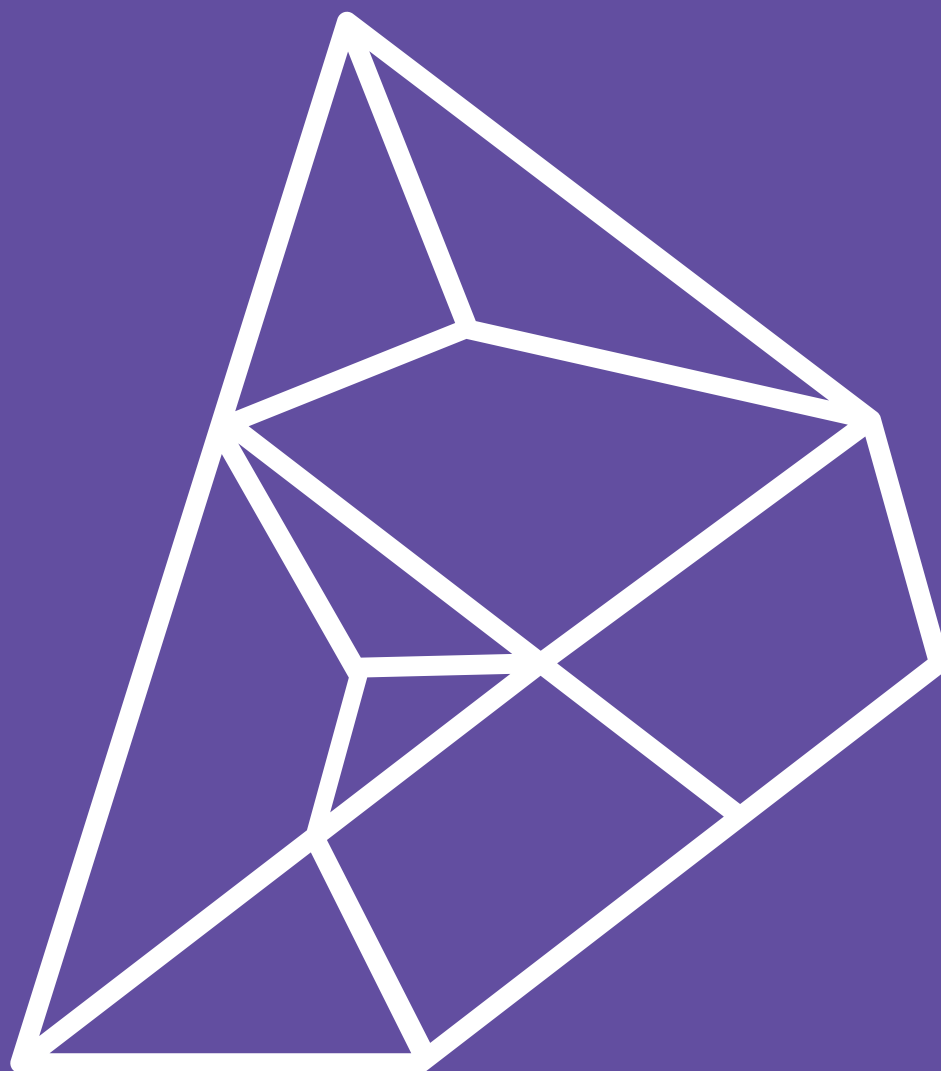
Belleza Mineral, que consiste en una selección de fotografías documentadas de piezas singulares de colecciones públicas y privadas, y que incluye también escenarios geológicos y materiales clásicos o avanzados. La tercera sala nos lleva a conocer mejor los museos de ciencia del mundo, con entrevistas a sus directores y/o curadores.

El portal también dedica un apartado a la exposición “*Cristales. Un mundo por descubrir*”, un contenido que ofrece un paseo ilustrado por esta ciencia que está disponible en una versión general y otra exposición proactiva para colegios, institutos de enseñanza media y universidades, que pueden solicitarse en la misma web.

Krystala ofrece también un espacio dedicado a la “Cristalización en la Escuela”, con todos los materiales y la información para participar y saber más sobre famoso concurso de cristalización en el participan desde hace diez años estudiantes de Educación Secundaria de toda España y de otros países del mundo. Este concurso reta al alumnado a realizar proyectos de investigación relacionados con la cristalografía para incentivar su espíritu investigador y aprender el estilo de conducta de los científicos.

Para sustentar el carácter formativo y divulgativo, el portal cuenta finalmente con una “Sala de Cine” que ofrece a la comunidad educativa títulos relacionados con esta ciencia. También existe un apartado destinado a recursos en el que se combina material didáctico, imágenes, vídeos, software y todos los recursos necesarios para profundizar en el mundo **Krystala**, junto con un diccionario temático de términos relacionados con el mundo inorgánico.

Agradecimientos: Krystala ha sido posible gracias al apoyo de la Fundación Descubre y de la Consejería de Transformación Económica, Industria, Conocimiento y Universidades. El autor agradece también al personal de la Fundación Descubre las tareas administrativa, editorial y la gestión de comunidad.



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LA ESTRUCTURA ELEMENTAL DE LA MATERIA

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Abstract: “La estructura elemental de la materia” es el título de una película perteneciente a la serie cinematográfica de Philips “Electrones mágicos”. El rollo original, en formato 8mm, pertenece al Museo de la Geología de la Universidad Complutense de Madrid y forma parte de una colección de cinco películas, entre las que se ha encontrado otra de la misma serie que lleva por nombre “Tierra incógnita”.

Ambas películas fueron producidas por AFIFA Berlin-Wiesbaden. Esta productora, fundada en Berlín en 1921, se mudó a Wiesbaden en 1949, donde instaló un estudio en el que se produjeron numerosas películas alemanas, algunas de ellas encargadas por empresas, como es el caso de la citada serie, que fue encargada por Philips. En 1956 la compañía cinematográfica fue liquidada por el estado, así que parece obvio que las películas se realizaron en la década 1949-1959.

Entre los créditos de la película figuran algunos personajes conocidos tanto en el mundo de la investigación como del cine. Entre los asesores científicos destaca el Dr. G.D. Rieck, cristalógrafo y profesor de físico-química de la Eindhoven University of Technology (Países Bajos). Los créditos por animación se le otorgan al cineasta Fritz Brunsch, la breve pieza musical se atribuye al compositor austriaco Rudolf Perak, etc.

La duración de la película es de 35,47 minutos. En ella se tratan, desde un punto de vista muy didáctico y divulgativo, los aspectos más relevantes de la espectrografía y la difracción de rayos X. Desde conceptos muy básicos de la teoría ondulatoria, como propagación de ondas e interferencias, a los fundamentos de la difracción y sus posibilidades; empleando para ello recursos muy ingeniosos, animaciones, modelos de agua y de bolas, etc., que solo tienen que envidiar a los actuales la calidad de las imágenes, tristemente deterioradas por el tiempo y las pésimas condiciones en que se han conservado.

Palabras clave: Espectrografía, Difracción, Rayos X.

Agradecimientos: La digitalización de esta película ha sido financiada por la Unidad de Gestión del Patrimonio Histórico de la Universidad Complutense de Madrid.

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