1st National Crystallographic Meeting

Aveiro Portugal
13 - 14 June 2019

Book of Abstracts

WELCOME MESSAGE

Dear Colleagues,

Under the auspices of the recently created Crystallography Group of the Portuguese Chemical Society (SPQ), and on behalf of the Organizing Committee, it is our pleasure to invite you to attend the First National Crystallographic Meeting which will be held in the 13th and 14th of June 2019 in Aveiro.

Diffraction techniques, in concurrence with Crystallography, have been a growing area of research in Portugal in the last decades. The national connection to the International Union of Crystallography (IUCr) was maintained for several years by the Portuguese Physics Society and, very recently it was ensured by SPQ so to guarantee the international projection and visibility of our national scientists.

This First National Crystallographic Meeting aims to bring together all scientists, from different areas of knowledge, working in Crystallography in Portugal, using not just laboratory instruments but also large international facilities such as synchrotron or neutron sources. We aim to create a forum for discussion and exchange of innovative ideas and prospects for the future of Crystallography in the country.

The attendance of students is strongly encouraged. Besides an interesting scientific program which is currently being prepared, a rich social program is being planned for all conference participants and accompanying persons.

We very much look forward to welcoming you in Aveiro.

COMMITTEES

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GENERAL INFORMATION

Registration

The registration fee includes:

- Admission to all the Meeting's scientific sessions
- Conference materials
- Coffee breaks
- Conference lunch and dinner

Poster and oral presentations (technical information)

Plenary sessions will have 30 minutes plus 10 additional ones for discussion.

Oral session will have 12 minutes plus 3 additional ones for discussion

All speakers should check with the Organization at least one hour prior to the beginning of their session to test and deliver the presentation.

The dimensions of the poster presentations should not exceed A0 (84 cm x 118 cm).

Please note that the Organization will not be responsible for the posters that are left in the panels after the session.

Official language

The official language of the Workshop is English. No simultaneous translation will be provided.

Badges and Security

It is essential that you wear your personal badge at all times while in the Workshop venue and during all the Events, as it is the official entrance pass to scientific sessions and other activities.

VENUE MAP

The location of all conference and poster session will be at the Department of Communication and Art, building 40.

Reach the university campus from Aveiro train station

Aveiro railway station is located at about 15 minutes walking distance or 5 minutes taxi ride from the University Campus or 10 minutes bus (line 4) which departs from outside the railway station.

Reach the university campus by car

From the north using the A1 motorway or from the east using the A25: Take the A1 motorway headed to Lisbon. Exit the A1 in the direction of Aveiro and take the A25. There are two exits to the city from the A25, first "Aveiro-Norte" and some kilometers further on, the "Aveiro" exit. This second exit is the best for reaching the University of Aveiro campus.

From the south using the A1 motorway: Take the A1 motorway in the direction of Porto, exit the motorway at "Aveiro-Sul/Águeda" (exit 15) and follow the EN235 road directly to the University Campus. From the south, using the A8 and A17 motorways: Exit the motorway at "Aveiro-Sul" and follow the EN235 road directly to the University campus.

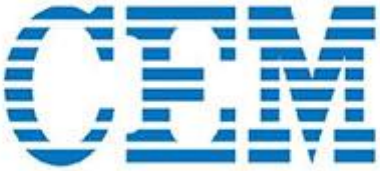
SCIENTIFIC PROGRAMM

Time	Thursday (13 June)
11h00	**REGISTRATION**
13h30	**OPENING SESSION** with the Conference Chairs, **Prof J Faria** (Vice-President of SPQ), **Prof J Coutinho** (Pro-Rector of the University of Aveiro) and **Prof A Silvestre** (Director of the Chemistry Department of the University of Aveiro)
	Chair: Filipe A. Almeida Paz
14h00	**PL1 - A Fitch -** "High resolution powder diffraction beamline ID22 at ESRF"
14h30	**PL2 - A Linden -** "Data refereeing and editing in chemical crystallography. The Acta Cryst C experience"
	Chair: Maria Teresa Duarte
15h00	**OC1 - P Brandão -** "Bioactive vitamins-metal compounds: Design, synthesis, structure and their application as anticancer drugs and NO delivery"
	OC2 - C S B Gomes - "Coordination complexes bearing aryl-BIAN ligands: structural diversity analysis"
	OC3 - M Susano - "Semi-Empirical Calculations and Experimental Structural Studies of the Bis(2,2'-bipyridine)-tris(nitrato)-lanthanide(III) Series"
	Malvern PANalytical
16h00	**Coffee Break**
	Chair: Maria João Romão
16h45	**PL3 - R Boer -** "Structural biology at the ALBA synchrotron"
17h15	**OC4 - P Matias -** "Improving the O2 resistance of a [NiFeSe] hydrogenase"
	OC5 - C Mota - "The crystal structure of an oxygen-tolerant and highly efficient W-formate dehydrogenase"
	OC6 - P T Borges - "Structure of mutants from Escherichia coli Flavodiiron-type nitric oxide reductase"
18h00	**OC7 - M Archer -** "Cryo-EM structure of glycosyltransferase AftD involved in mycobacterial cell wall synthesis"
	OC8 - F Trovão - "Molecular Recognition of a Thomsen–Friedenreich Antigen Mimetic Targeting Human Galectin-3"
	Selection of the next Meeting Venue and Election of the Conference Chair
19h30	**CONFERENCE DINNER** *Location* : University Restaurant

Time	Friday (14 June)
	Chair: Rosário Soares
10h00	**PL4 - Braz Fernandes -** "In situ studies of materials processing"
	OC9 - R F Mendes - "Enhanced Proton Conductivity in Layered Coordination Polymers"
	OC10 - A N Salak - "Conversion polymorphism in high-pressure stabilized ABO3 phases"
11h00	**OC11 - WJ Xu -** "Structure determination of molecular perovskite from powder XRD data"
	Coffee Break
	Chair: Ricardo Faria Mendes
11h45	**OC12 - S Quaresma -** "Novel azelaic acid BioMOFs"
12h00	**OC13 - I C B Martins -** "Under the hood of crystallization: a multi-faceted approach towards structural characterization of multicomponent small drug molecules"
	OC14 - B A Nogueira - "Polymorph screening and characterization of new crystallographic structures of hydantoin derivatives"
12h30	**LUNCH (12h30 - 14h15)** *Location* : University Restaurant
	Chair: Vânia André
14h15	**Bruker**
	Rigaku
	Qlabo
15h00	**Coffee Break & Poster Session**
	Chair: José António Paixão
16h45	**PL5 - J Rodriguez-Carvajal -** "Crystallography with Neutrons: crystal and magnetic structures"
17h15	**CLOSING CEREMONY**

INSTITUTIONAL SUPPORT

SPONSORS



INDEX

Plenary Sessions Page

Oral Presentations

COMPANY PRESENTATION Page

POSTER

PLENARY PRESENTATIONS

High resolution powder diffraction beamline ID22 at ESRF

A. Fitch

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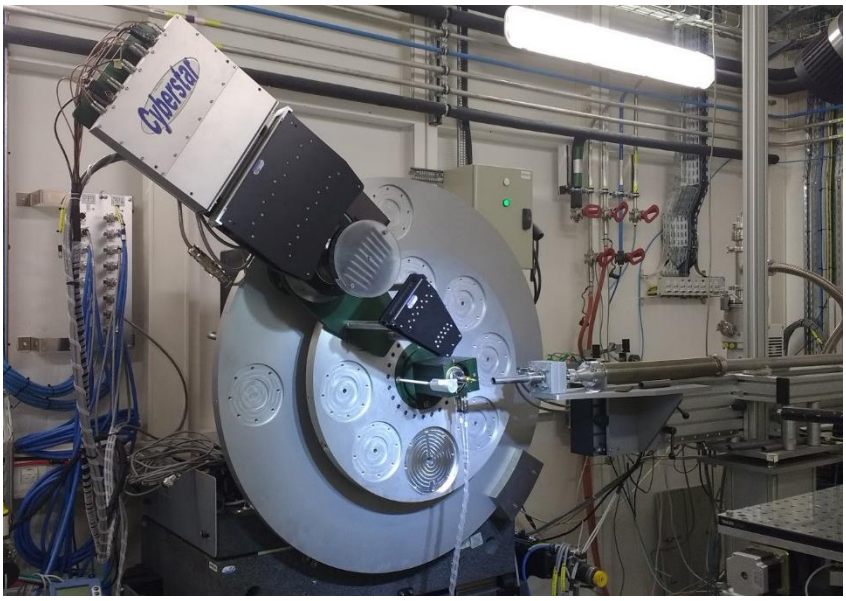
The European Synchrotron Radiation Facility in Grenoble has operated a high resolution powder diffraction beamline since May 1996. Originally built on bending magnet BM16 and upgraded in 2002 when moved to insertion device ID31, the beamline was refurbished again in 2014 and is now located at ID22, with an in-vacuum undulator source. The beamline produces very high resolution powder diffraction patterns at relatively hard photon energies, with routine operation in the range 25 – 40 keV, (λ = 0.5 – 0.3 Å), thus allowing the use of capillary specimens without worries about sample absorption for a wide range of sample types. In 2015 a Perkin Elmer XRD 1611 medical-imaging detector was installed to provide data to high Q (25 – 30 Å^{-1}) for PDF analysis at energies up to ≈70 keV. In 2017 a new high-resolution powder diffractometer, based on air-bearing technology, replaced the original machine that had operated reliably for more than 20 years. The instrument has a range of sample environments, allowing samples to be investigated routinely at temperatures in the range 4 K to 1600°C, or under different atmospheres in the range 0 to 80 bar for gas adsorption studies in MOFs and other porous samples. A sample-changing robot allows the mounting of up to 75 capillary samples, and can work with sample environments over the temperature range 80 K to 950°C, all under programmable computer control. The beamline is highly versatile and will accept all sorts of experiments needing high resolution powder diffraction or PDF analysis. This will be illustrated with selected examples.



ID22 high resolution powder diffractometer

The ESRF storage ring is currently being replaced with a low-emittance ring of the new generation, promising even brighter X-ray beams. User operation restarts in August 2020, with the next proposal deadline on 1 March. On ID22, as well as benefitting from the new source, we will upgrade our in-vacuum undulator and detector. We anticipate return of the X-ray beam with commissioning, industrial and in-house operation of the upgraded facilities in the second quarter of 2020.

Data refereeing and editing in chemical crystallography; the Acta Cryst C experience

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The IUCr journals have a continuous history of archiving data in one form or another; in the early days, tables of observed and calculated structure factors were published as part of the paper. The utility of such data was rather limited; considerable effort was required to convert the archived record into something that could be used. Most other publishers eventually turned their back on the archiving of structure factors, relegating this duty to the authors, which has undoubtedly led to the unfortunate loss of very many data sets. The advent of CIF and then electronic validation of CIF content during the 1990s was a valuable step forward, which facilitated easier archiving and more consistent evaluation by reviewers and co-editors. Even then, IUCr Journals remained almost the only publisher using structure factors during reviewing until the CCDC began accepting them about 10 years ago. The advent of area detectors diffractometers in the 1990s gave us raw frame data which contains much information beyond that which is routinely extracted. Access to such data has been helpful during some reviews, but was only asked for in special circumstances, mainly because of logistics. The capacity and accessibility of digital archives are now reducing the hurdle to reviewing and preserving raw data. In the IUCr Journals experience, authors often show resistance when new requirements are introduced. Busy authors will embrace the FAIR principles if the repositories, and the deposition, access and data extraction procedures are as routine, transparent and automatic as possible.

Structural biology at the ALBA synchrotron

Roeland Boer[1,*], I. Crespo[1], N. Bernardo[1], Judith Juanhuix[1], F. Gil[1], X. Carpena[1], D. Garriga[1], B. Calisto[1]

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Publication-grade structural information of biological samples is now almost exclusively dependent on large facilities which provide the machines necessary for collecting high quality data. These include high-brilliance beamlines suitable for protein crystallography, which are now found at all synchrotron facilities around the world. Other high-end equipment, such as high-resolution cryo-electron microscopy and high magnetic field nuclear magnetic resonance equipment, are also usually installed in purpose-built facilities accessible to international users.

This contribution discusses the current and future technological and scientific solutions that the ALBA synchrotron can offer to structural biologists. These include several applications that will be available in the near future. For example, an electron microscope facility at ALBA will be installed in the coming years, consisting of a 200 kV TEM microscope for screening single particle cryoEM grids. In addition, a microfocus beamline called XAIRA is currently in the design phase and will be available for single crystal diffraction experiments within a few years. This beamline will offer a 1x3 um beam with a flux of 10^{13} ph/s, thanks to a unique design of the monochromator which allows fast interchange between a multilayer and Si(111) crystal surface.

At the moment, XALOC is the only macromolecular diffraction beamline at ALBA. XALOC has been designed to deal not only with easily automatable X-ray diffraction experiments of micrometer-sized crystals, but also with more complex ones that include a variety of crystal sizes and unit-cell length dimensions, crystals with high mosaic spread, and/or poorly diffracting crystals. The aim for a reliable all-in-one beamline is equaled by the aim to maximize ease-of-use and automatization. Remote data collection is supported, and many users collect data from their home institution routinely. The beamline allows in situ diffraction in plates as well as in capillaries. Fast automatic data processing is available. At 12.65 keV, the flux of the beamline is $2x10^{12}$ ph/s. Currently, up to 144 samples can be stored in the automated sample changer, which supports both SPINE as well as Unipuck crystals. Continuous access to the beamline allows access within a few weeks. To illustrate the use of synchrotron radiation, in particular at the XALOC beamline, we will present the results of an in-house project studying the structures of proteins involved in bacterial conjugation of Gram-positive bacteria.

In situ studies of materials processing

F.M. Braz Fernandes* [a], A. Velhinho[a], R.M.S. Martins[b], R.J.C. Silva[a], K.K. Mahesh[a], A.S. Paula[c], S.V. Correia[a], J.P. Oliveira[d], P. Rodrigues[a], E. Camacho[a], R. Magalhães[a], P. Inácio[d], T. Santos[d], N. Schell[e]

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In situ studies of fabrication processes of metallic alloys were carried on at ESRF (ID15, ID19, BM-20) and DESY (HEMS-P07) covering the following processes: metal matrix composites casting, thin film sputtering, thermomechanical processing, welding and functionally graded materials. Main achievements in the following topics are illustrated in the current presentation:

- evaluation of wetting characteristics in FGMMC,[1]
- stacking sequence of thin film formation as a function of deposition parameters and substrate, [2,3]
- cold / hot working and subsequent recrystallization processes, [4,5]
- in service behaviour of endodontic files during rotation / flexion, [6]
- welding of shape memory alloys, [7]
- localized heat treatments for functionally graded wires / strips. [8]

These examples cover situations that may be found for applications in automotive industry, MEMs, dentistery (ortho- and endodontics), civil engineering, aeronautics.

Acknowledgements

- POCI-01-0145-FEDER-016414 (FIBR3D), co-financed by Programa Operacional Competitividade e Internacionalização and Programa Operacional Regional de Lisboa, through Fundo Europeu de Desenvolvimento Regional (FEDER) and by National Funds through FCT - Fundação para a Ciência e a Tecnologia,
- CENIMAT/I3N funded by COMPETE 2020, through FCT, under the project UID/CTM/50025/2013,
- UNIDEMI funded via the project PEst-OE/EME/UI0667/2014,
- Parts of this research were carried out at beamline P-07-HEMS at DESY, a member of the Helmholtz Association,
- project CALIPSOplus from the EU Framework Programme for Research and Innovation HORIZON 2020.

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Crystallography with Neutrons: crystal and magnetic structures

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Crystallography with neutrons is a complement to normal X-ray crystallography (conventional or synchrotron sources). It is normally used when one wants to determine precisely the position of light atoms (hydrogen, lithium...), for solving atom distribution between several Wyckoff sites, or for determining and refining magnetic structures. In this talk I will present the advantages and drawbacks of using neutrons for doing crystallography from the point of view of the fundamental physical properties of neutrons and their interaction with matter. A summary of the existing techniques and instruments at ILL will also be presented as well as the existing projects for improving current instruments and the new diffractometer XtremeD dedicated to the study of powder and single crystal under extreme conditions of pressure and applied magnetic field. Special emphasis will be given on the chemical crystallography instruments of the diffraction group: D19 and the Laue Diffractometer CYCLOPS that allow rapid data acquisition on single crystals of size around 1 to 2 mm^3.

In the second part of my talk I will present the advances in data reduction of these two diffractometers describing the programs Int3D and ESMERALDA Laue Suite showing examples of the precision we can obtain in the refinement of crystal structure with data collected on D19 and CYCLOPS.
Concerning magnetic structures the recent advances in the treatment of incommensurable magnetic structures, using the superspace formalism now implemented in FullProf, will be presented and summarized. Two examples of the data treatment using the symmetry utilities of ISODISTORT in combination with FullProf (powder diffraction) will be discussed.

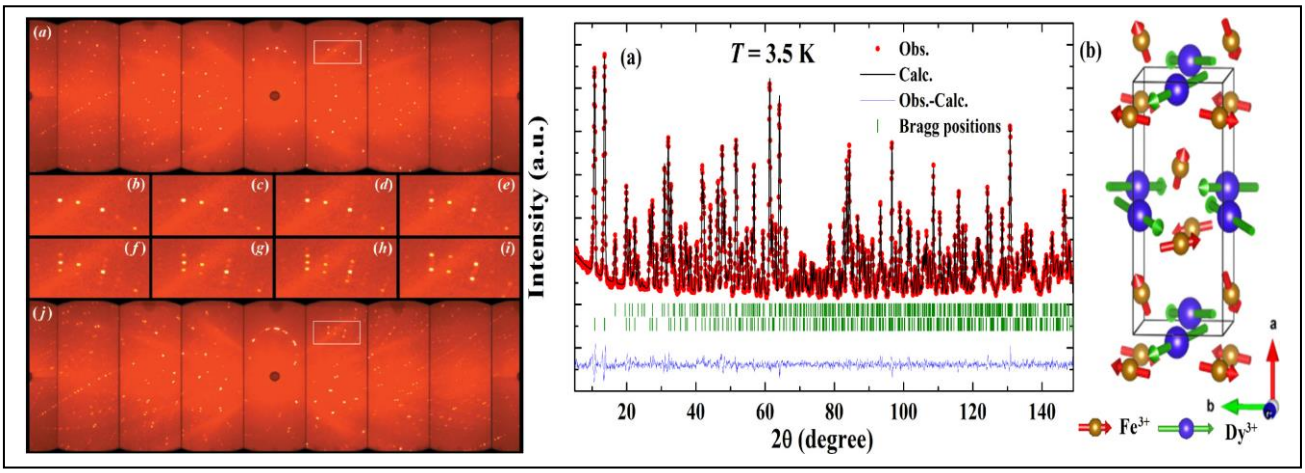

Figure: (left) Series of snapshots at different temperatures taken on CYCLOPS for studying the phase transition on the compound $[CH_3NH_3][Co(COOH)_3]$[1] (right) Refinement of the crystal and magnetic structure of the compound $DyFeWO_6$ using symmetry modes within Shubnikov magnetic space groups[2].

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ORAL PRESENTATIONS

Bioactive vitamins-metal compounds: Design, synthesis, structure and their application as anticancer drugs and NO delivery

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This work highlights the importance of vitamins as organic bio-ligands in the design and synthesis of metal complexes and metal organic frameworks (MOFs) for biomedical applications. Vitamins contain a wide variety of binding modes making them an attractive class of building blocks for the construction of metal complexes and extended MOF compounds, which can result in diverse topologies showing excellent properties. Vitamins themselves are active molecules in different biological processes, and the combination with metals might be of both scientific and pharmacological interest. In addition, vitamins are naturally abundant and easy to produce, allowing industrial low costs. Because of all these characteristics, the use of vitamins could be a great challenge to develop new biologically active and environmentally friendly metallo-drugs and Bio-MOFs[1-3]. With an attempt to emphasize the structure and biological activity of such vitamins metal complexes as well as vitamin-MOFs, we will explore the synthesis of different vitamins (mainly B_1, B_3, B_6, B_9, C) metal (mainly Fe, Cu, Co, Ni, Mg, Ca, Zn) compounds and their application in cancer therapy as well as NO delivery systems. Recently we prepared several vitamin B_1 derivatives and B_3 copper complexes showing anticancer activity,[4,5] and two isostructural Co and Ni vitamin B_3 MOFs, both having the capability of storing and releasing NO in a slow and reversible manner and showing low toxicity[6]

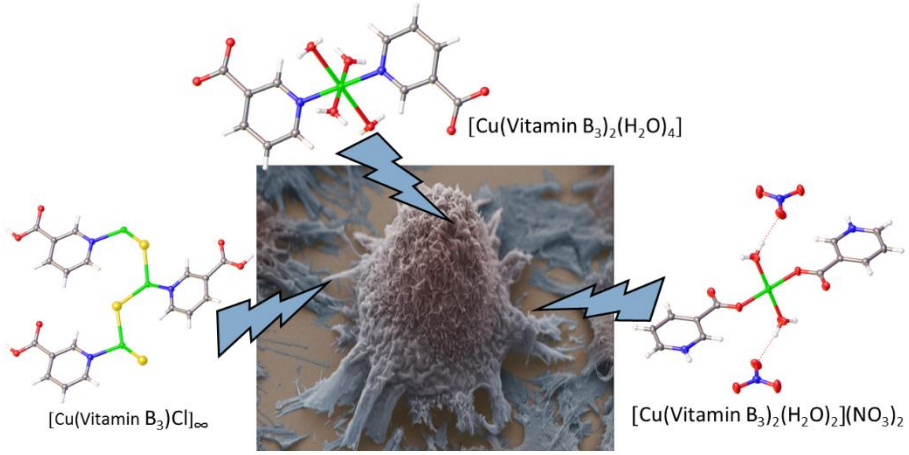

Figure 1: Vitamin B_3 copper compounds cytotoxic against human colon adenocarcinoma Caco-2 cells

Acknowledgements
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Coordination complexes bearing aryl-BIAN ligands: structural diversity analysis

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α-Diimines are versatile bidentate nitrogen chelating ligands widely employed as ancillary ligands in the field of coordination/organometallic chemistry, which are prepared by the condensation of α-diketones and anilines under acid catalysis. Their coordination to the metal center usually results in the formation of five-membered chelated rings. Designing bidentate neutral *N*,*N*-chelating ligands containing sterically demanding groups has been crucial for their use as efficient catalysts in several homogeneous catalytic reactions, particularly in olefin polymerization,[1] and copolymerization of olefins with polar monomers.[2]
We have been interested in the synthesis of Ni(II), Cu(I) and Cu(II) complexes and in their application as effective catalysts in the polymerization of ethylene,[3] cycloaddition reactions of alkynes and azides,[4] and reverse ATRP of styrene.[5]
Herein, we report the synthesis of new aryl-BIAN–Cu(I), Ag(I) and Zn(II) complexes (Figure 1), and their structural characterization by NMR and single-crystal X-ray diffraction. An analysis of their structural diversity is also presented.

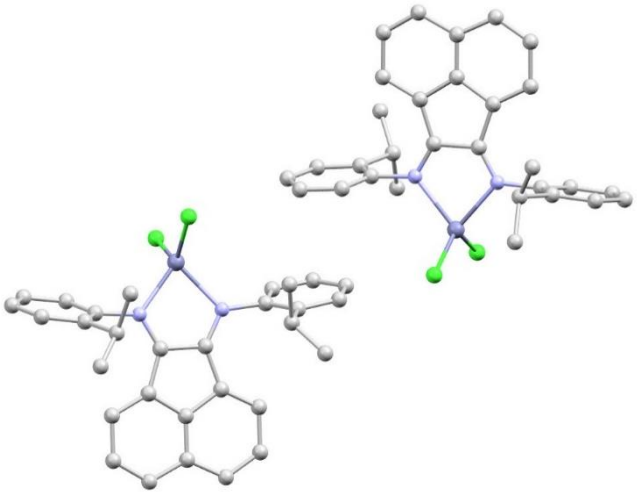

Figure 1: [Zn((*o*-^{i}Pr-BIAN)Cl_2] (*o*-^{i}Pr-BIAN = 2-iPr(C6H4)-BIAN; BIAN = bis-imino acenaphtene) molecular structure displaying two independent isomers in the asymmetric unit. Hydrogen atoms were omitted for clarity.

These complexes were tested and acted as efficient catalysts of the aerobic oxidation of benzylic alcohols (Cu(I)), in the synthesis of cyclic carbonates from epoxides and CO_2 (Zn(II)) or as antimicrobial agents (Ag(I)).

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Semi-Empirical Calculations and Experimental Structural Studies of the Bis(2,2'-bipyridine)-tris(nitrato)-lanthanide(III) Series

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Rare earth complexes have been extensively studied owing to their unique structures and their chemical, industrial, biochemical and medicinal applications[1].
The first examples of lanthanide complexes with formula $Ln(bipy)_2(NO_3)_3$ were prepared in the 1960s[2] and most of the isostructural series was recently completed by Cotton&Raithby[3]. Two of the missing members (Ln = Yb, Ho) were synthesized and characterized by us. $[Ln(bipy)_2(NO_3)_3]$ crystallizes in the orthorhombic system, in the space group Pbcn (Z = 4), without any H-bond network due to lack of H donors (Figure 1). In the series, the +3 charge of the lanthanide ion is compensated by the negative charge of the three nitrate ligands with the neutral bipyridine molecule completing the coordination sphere (a distorted sphenocorona, coordination number 10). Results indicate that as the atomic number increases and the radius decreases, Ln-N and Ln-O bond distances decrease, and the difference between the average Ln−N and Ln−O lengths also decreases, consistent with "the lanthanide contraction" (the greater-than-expected decrease in ionic radii of the elements in the lanthanide series)[4].
We have also performed semi-empirical calculations using LUMPAC[4] and the Sparkle/PM3 method to predict the molecular structure of the complexes within the series. Structural details of the entire series and the comparison between experimental and calculated structures will be presented and discussed.

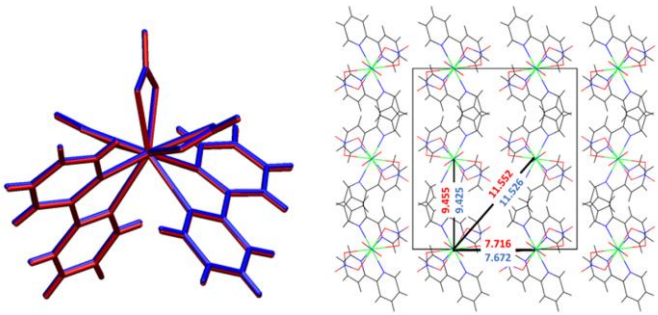

Figure 1. $Tm(bipy)_2(NO_3)_3$. Left: Superposition of the atomic arrangement around the lanthanide at 150 K (blue line) and at room temperature (red line). Right: Packing diagram viewed down the *b* axis, with distances (in Å) between neighboring metal centers, at low and room temperature (blue and red, respectively).

Acknowledgements
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Improving the O2 resistance of a [NiFeSe] hydrogenase

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The [NiFeSe] hydrogenases are a subclass of the [NiFe] hydrogenases where a selenocysteine (Sec) replaces cysteine as one of the Ni terminal ligands. They have high catalytically activities, namely for H_2 production, are more tolerant to O_2 than their [NiFe] counterparts and are less inhibited by H_2. Nevertheless, they are also susceptible to inactivation by O2: in the [NiFeSe] enzyme from D. vulgaris Hildenborough, our previous work showed this to arise from a reversible chemical oxidation of the proximal iron-sulfur cluster together with an irreversible oxidation of the terminal Ni ligand cysteine 75 to sulfinate [1].

Aiming to improve the O_2 tolerance of this enzyme, we produced variants by mutating residues in the large subunit. Three variants were crystallized, and their crystal structures determined from high-resolution data measured at the ESRF beamlines ID29 and ID30A-3 (Grenoble, FR) and the DLS beamline I04 (Didcot, UK). The effect of O_2 exposure on H_2 uptake activity was measured in solution, and an electrochemical study of O_2 and CO inhibition was undertaken. The crystal structures (**Figure 1**) showed cysteine 75 oxidation to be largely prevented or delayed in two of the variants and the electrochemical and biochemical activity assays of these variants revealed an increase in O_2 tolerance in comparison with the wild-type enzyme.

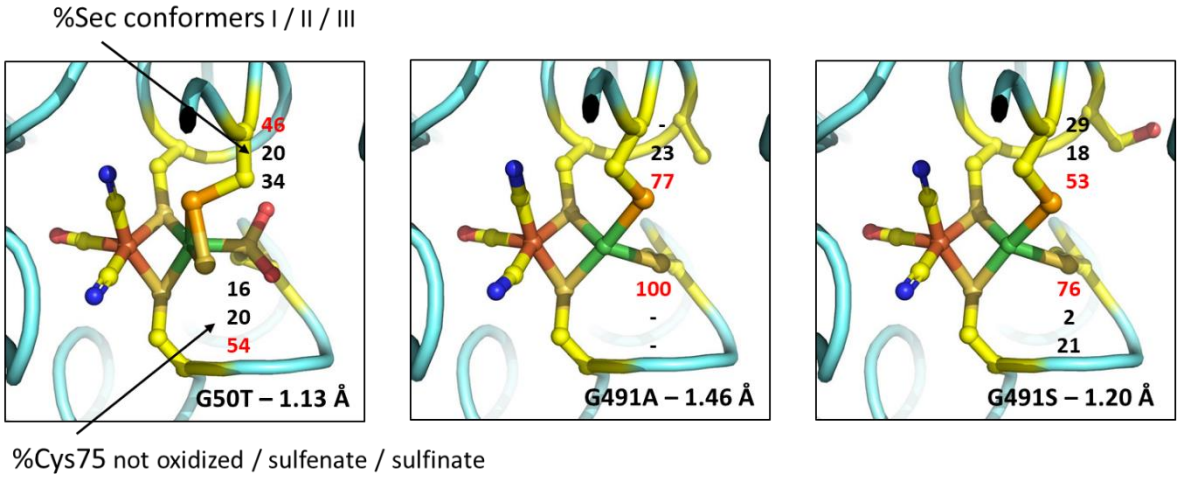

Figure 1: PyMOL representation of the active site in the three variant crystal structures showing the main structural component (red numbers). The protein chain is represented as a cyan tube and the active site residues and ligands are drawn in ball-and-stick. For clarity, only the protein side-chain atoms are represented. Atom colors are yellow for carbon, blue for nitrogen, red for oxygen, gold for sulfur, orange for selenium and brick red for iron.

Acknowledgements
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The crystal structure of an oxygen-tolerant and highly efficient W-formate dehydrogenase

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The chemical transformation of CO2, the greenhouse gas, into useful products becomes increasingly important as its atmosphere levels continues to rise because of human activity. Mo- and W-formate dehydrogenases (Fdhs) are unique prokaryote enzymes that catalyze the reversible reduction of CO2 to formate. This ability is a promising route not only for green gas sequestration but also a sustainable way to produce fuel. Formic acid is a safe, storage and delivery, option of hydrogen (53g H2/L) for cell power applications[1].
In spite of the undeniable relevance of Fdhs in new biotechnological applications, the catalytic mechanism is still unclear and controversial[2]. Until now, only 3 Fdhs crystal structures were known (Mo-FdhH and Mo-FdhN from *E. coli*, and D. gigas W-Fdh). Despite the diversity in terms of structural composition and subcellular localization, Fdhs active sites are highly conserved.
In this work we crystallized and determined the structure of FdhAB from *D. vulgaris* in oxidized and reduced forms (Figure 1). This enzyme is the main responsible for CO2 reduction in *D. vulgaris*[3]. Contrary to other Fdhs, this enzyme is oxygen-tolerant and can be purified aerobically[3]. Due to its robustness and high CO2 reduction activity, the FdhAB is a suitable model for biocatalytic applications for CO2 reduction. FdhAB is a soluble heterodimer comprising four [Fe4S4] clusters responsible for electron transfer to and from the active site. The active site presents a W hexacoordinated by four sulfur ligands from 2 MGD cofactors, a SeCys and a sulfido group. In the second coordination sphere, highly conserved His and Arg residues are also proposed to play a role in catalysis. The structural analysis of both oxidized and reduced forms allowed to identify conformational changes that disclose new features on the reaction mechanism. Finally, CO2 and proton tunnels are also proposed, allowing the engineering of new FdhAB variants towards a more efficient enzyme.

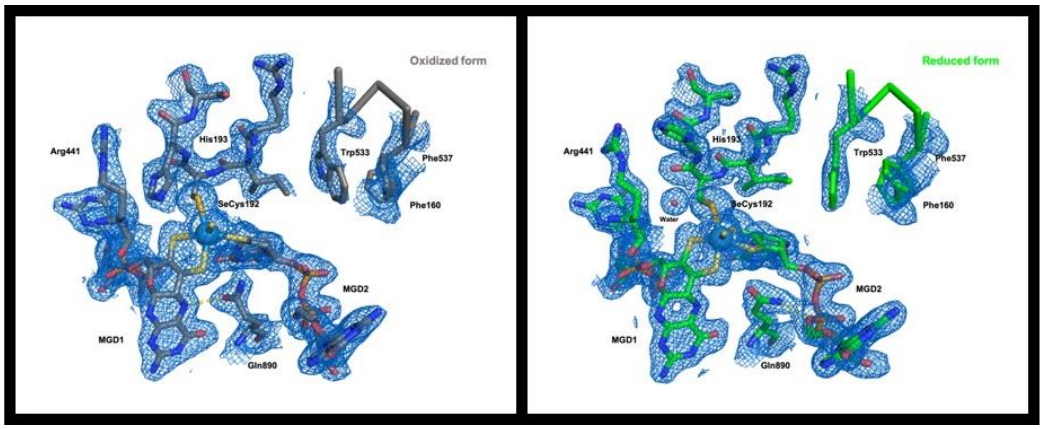

Figure 1: Active site of *D. vulgaris* formate dehydrogenase in oxidized (left) and reduced (right) forms.

Acknowledgements
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Structure of mutants from *Escherichia coli* Flavodiiron-type nitric oxide reductase

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Escherichia coli flavorubredoxin catalyzes the two-electron reduction of NO to nontoxic N_2O protecting the organism from reactive nitrogen species. Recently, based on kinetic studies[1], it was explored the possible role for K53 and Y271 residues in modulation of substrate selectivity in *Entamoeba histolytica* FDP (O_2 reductase). Therefore, to understand the structural effects of these residues, located in the diiron second coordination sphere, crystal structures of *E. coli* FDP-ΔRd mutants were determined, namely the single mutants D52K and S262Y, as well as the double mutant D52K/S262Y, in both oxidized and reduced states.
Like in other FDPs, the minimal functional unit of E. coli FDP-ΔRd mutants is composed of a “head-to-tail” dimer bringing the diiron site close to the FMN cofactor from the opposing monomer. The two irons are coordinated by conserved residues, namely, a bridging aspartate, four histidines, one aspartate and one glutamate. However, some structural differences were observed in the diiron site of FDP-ΔRd S262Y in the reduced state, similarly to the oxidized state, probably due to a high sensitivity of this mutant to radiation damage.
For the first time, molecular tunnels were identified in this family of proteins, using krypton pressurization experiments. Both side chains of residues in positions 52 and 262 from E. coli FDP-ΔRd mutants are in the vicinity of the shorter pathway, however their function in substrate selectivity still needs to be further investigated.

Acknowledgements
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Cryo-EM structure of glycosyltransferase AftD involved in mycobacterial cell wall synthesis

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Tuberculosis, one of the deadliest disease in the world persists as a major health problem for the world, responsible for over 1 million deaths each year. With the rise of fully drug resistant variants of *Mycobacterium tuberculosis*, the causative agent for tuberculosis, there is an urgent need to seek out new drug targets against this bacterium. The M*. tuberculosis* cell wall, a common target for some existing antibiotics, has a unique structure due to the presence of additional lipid-sugar moieties, arabinogalactans and lipoarabinomannan, which are essential for mycobacterium survival and virulence. Membrane-bound glycosyltransferases build these essential lipid-sugar moieties.
Here, we present the full-length membrane-bound structure of mycobacterial arabinofuranosyltransferase AftD[1,2] solved to 2.9 Å resolution using single-particle cryo-electron microscopy. The enzyme displays a conserved GT-C glycosyltransferase fold and three carbohydrate binding modules. Surprisingly, AftD is tightly associated with an acyl carrier protein (ACP). 3D structures at 3.4 and 3.5 Å resolution of a mutant enzyme with impaired ACP binding reveal a conformational change that suggests how ACP may regulate AftD function. Using a conditional knock-out constructed in *M. smegmatis*, mutagenesis experiments confirm the putative active site location and the importance of ACP binding for AftD function.

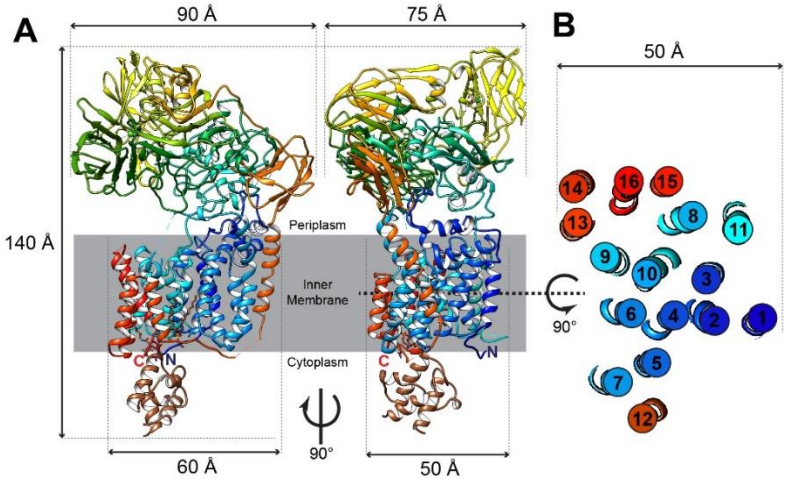

Figure 1. A) Single-particle cryo-EM structure of AftD complex, rendered in cartoon and colored in rainbow. The complexed *E. coli* acyl carrier protein and ligands are colored in brown. **B)** Transmembrane helices arrangement of AftD, viewed as a slice and magnified.

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Molecular Recognition of a Thomsen–Friedenreich Antigen Mimetic Targeting Human Galectin-3

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The Thomsen–Friedenreich (TF) disaccharide epitope represents one of the most common tumor-associated carbohydrate antigens. Its overexpression occurs in 90% of adenocarcinomas in cell membrane proteins. The binding of the TF antigen to human galectin-3 (Gal-3) is also frequently overexpressed in malignancy, which promotes cancer progression and metastasis. In this context, structures that interfere with this specific interaction have the potential to prevent cancer metastasis. A multidisciplinary approach combining the optimized synthesis of a TF antigen mimetic with NMR, X-ray crystallography methods, and isothermal titration calorimetry assays was used to unravel the molecular structural details that govern the Gal-3/TF mimetic interaction. The TF mimetic has a binding affinity for Gal-3 similar to that of the TF natural antigen and retains the binding epitope and bioactive conformation observed for the native antigen. Furthermore, from a thermodynamic perspective, a decrease in the enthalpic contribution was observed for the Gal-3/TF mimetic complex; however, this behavior is compensated by a favorable gain in entropy. The crystal structure of Gal-3/TF mimetic complex was successfully determined by molecular replacement methods using the unliganded Gal-3 carbohydrate-recognition domain (CRD) structure (PDB ID: 3ZSL) and solved to 1.1 Å resolution (PDB ID: 6G0V). From a structural perspective, these results establish our TF mimetic as a scaffold to design multivalent solutions to potentially interfere with Gal-3 aberrant interactions and for likely use in hampering Gal-3-mediated cancer cell adhesion and metastasis[1].

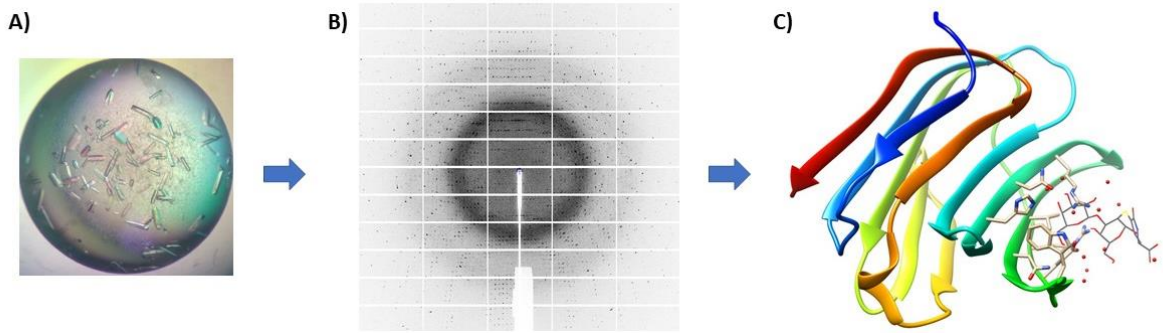

Figure 1: Overall representation of the Gal-3/TF mimetic complex solved by X-ray crystallography (PDB ID: 6G0V). A) Crystals of Gal-3/TF-mimetic complex viewed under polarized light. The average crystal size is 0.4 x 0.1 mm^2 B) X-ray diffraction image of Gal-3/TF-mimetic complex. C) Ribbon representation of Gal-3 (colored from N- to C-terminus). The TF mimetic is shown in wireframe, while neighbor residues are shown in stick representation.

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Enhanced Proton Conductivity in Layered Coordination Polymers

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Research on Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs) is currently driven towards the need to employ such materials in technological areas. Our research group has focused on the design of novel networks based on polyphosphonic acid ligands and rare-earth cations. With these building units we obtained highly robust dense networks exhibiting, in many cases, multifunctionality (*e.g.*, photoluminescence combined with catalytic activity). In this work we describe our most recent efforts to design and prepare novel crystalline layered CP materials based on gadolinium metal centres and the flexible triphosphonic acid nitrilotri(methylphosphonic acid) (H_6nmp). Two new materials were obtained by employing small changes in the experimental conditions, namely $[Gd(H_4nmp)(H_2O)_2]Cl{\cdot}2H_2O$ (**1**)[1] and $[Gd_2(H_3nmp)_2]{\cdot}xH_2O$ (x = 1 to 4) (**2**). Interestingly,**1** converts into **2** with a notable increase in protonic conductivity (Figure 1). **1** is a charged layered material counter balanced by chloride ions, with the protonic conductivity values of 1.23×10^{-5} S cm^{-1} at 98% RH at 40 ºC. At 98% RH and 94 ºC **1** exhibits a conductivity of 0.51 S cm^{-1}, being to date the highest one ever reported for a proton-conducting MOF. This increase is observed during a structural transformation into **2,** that occurs at high temperature and RH. While this remarkable conductivity is observed only after transformation and by maintaining the high humidity conditions, as-synthesized **2** also shows conductivity values of 3.79×10^{-2} Scm^{-1} at 94 ºC and 98% RH, ranked as one of the highest reported for MOFs.[2]

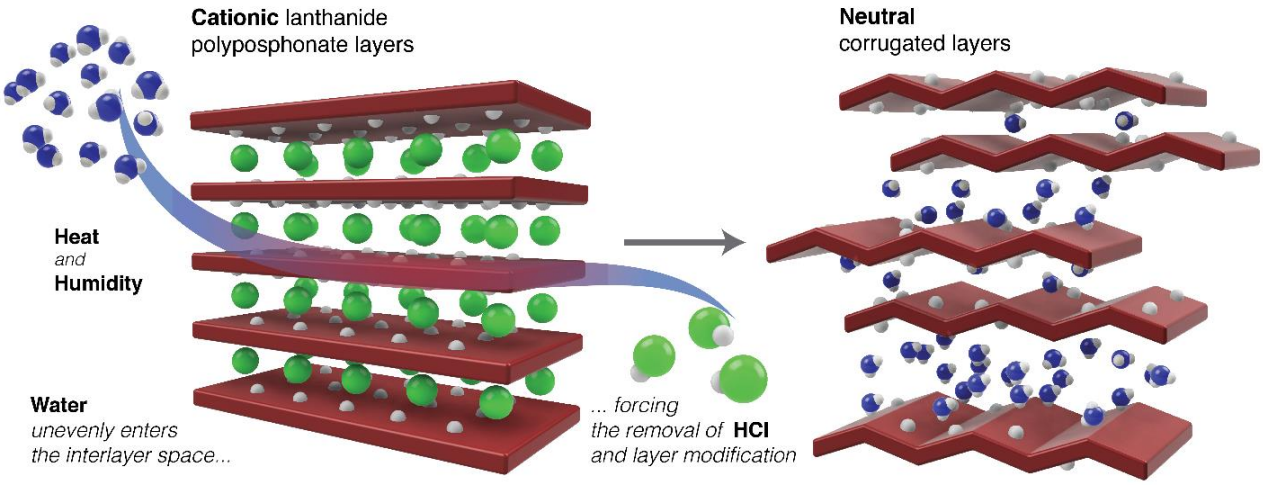

Figure 1 - Schematic representation of the structural transformation of $[Gd(H_4nmp)(H_2O)_2]Cl{\cdot}2H_2O$ (**1**, *left*) into $[Gd_2(H_3nmp)_2]{\cdot}xH_2O$ (**2**, *right*) (x = 1 to 4) at high temperature and humidity.

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Conversion polymorphism in high-pressure stabilized ABO_3 phases

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Many solid phases, which are at equilibrium under high pressure and high temperature, can be quenched to ambient conditions, where they remain kinetically stable (usually referred to as the metastable phases). Very often, these phases represent new structural polymorphs with useful and unique properties. This method, known as high-pressure synthesis, therefore, is used to obtain novel materials with improved functionalities. The methid is particularly effective to stabilize the compact structures like the perovskite one. Indeed, with the application of high-pressure synthesis, the family of perovskite materials has been substantially extended.[1,2] Organic and inorganic compounds with the perovskite structure are known to host many fascinating physical phenomena, such as high-temperature superconductivity, metal–insulator transition, ferroelectricity, multiferroic and photovoltaic properties. The flexibility of the perovskite structure to accommodate different cations and anions provides an excellent playground to design materials with controlled properties. This is particularly important to develop new multiferroics – materials that combine both ferroelectric and magnetic degrees of freedom with a prototype example of $BiFeO_3$. Using different doping/substitution strategies many multiferroics with promising characteristics have been derived from $BiFeO_3$. Regarding the Fe-site substitutions, the relative amounts of dopant necessary to change the *R*3*c* structure of the parent compound can only be incorporated into the lattice under high-pressure.

In this work, we report on systematic study of the transformations of perovskite phases and their magnetic properties in the $BiFe_{1-y}Sc_yO_3$ series. For the compositions with $y \geq 0.2$, the perovskite phases can only be stabilized under high-pressure conditions.[3] The metastable phases were subject to post-synthesis thermal treatment. As a result, we observed a set of annealing-stimulated irreversible phase transformations between the different metastable perovskite phases. In the range of compositions with *y* close to 0.3, an annealing of the as-prepared $PbZrO_3$-related *Pnma* phase leads to irreversible transformation into a rhombohedral *R*3*c* polymorph with a very unusual collinear magnetic ground state. In the vicinity of *y* ~0.5, the conversion of the metastable phases occurs through two irreversible transitions: *Pnma* → *R*3*c* upon heating followed by *R*3*c* → *Ima*2 upon cooling. The *Ima*2 polymorph is a rare example of a canted ferroelectric structure. When $y \geq 0.7$, an annealing induces a crossover from the as-prepared monoclinic *C*2/*c* phase to a polymorph with a new type of the orthorhombic structure.

We refer the annealing-stimulated irreversible transformations as ‘‘*conversion polymorphism*”[4] and demonstrate that this is a rather general phenomenon, which has been likely overlooked in many other metastable phases.

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Structure determination of molecular perovskite from powder XRD data

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The structural phase transitions in molecular perovskites or hybrid organic-inorganic perovskites (HOIPs) were revived in the past decade, by the emergence in a large number of perovskite-like compounds with various interesting properties for potential applications such as ferroelectrics, nonlinear optical (NLO) switches, and multiferroics.[1] Comparing with the well-studied perovskite oxides, molecular perovskites with larger bridges as well as organic cations give rise to an increasing complexity for structural variations. Many molecular perovskites solid can be prepared as single crystals of suitable size and quality for structural characterization by conventional single crystal X-ray diffraction techniques. However, in some cases, the single crystalline of sample cannot be maintained after drastic structural phase transition induced by external stimuli, which will increase the difficulty of obtaining structural information. This talk will presents how to solve crystal structure from powder X-ray diffraction data for two molecular perovskite ferroelectrics,[2,3] in order to understanding mechanisms of their phase transitions.

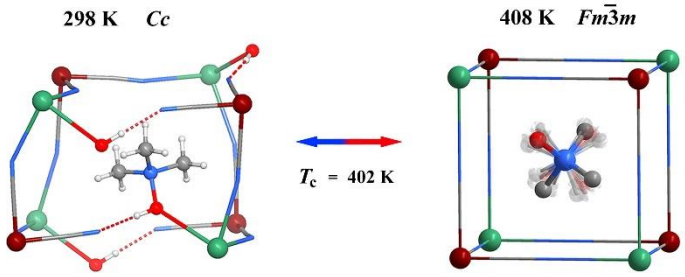

Figure 1. Thermal-induced bond-switching phase transition in a molecular perovskite $[(CH_3)_3NOH]_2[KFe(CN)_6]$.

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Novel azelaic acid BioMOFs

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The development of Metal-Organic Frameworks (MOFs) for bioapplications has gained great relevance over the last years, mainly due to their potentiality as drug carriers and/or imaging agents.
We are particularly interested in the design of novel bio-inspired MOFs, (BioMOFs) using active pharmaceutical ingredients (APIs) as ligands. When compared to MOFs, these BioMOFs present additional benefits: i) porosity is no longer required as the release of the API is achieved through the degradation of the solid; ii) the API is part of the matrix, avoiding multistep procedures to prepare the loaded material; iii) the metal can also be bioactive promoting a synergetic effect. The use of porous BioMOFs presents enhanced applications, as it can lead to the co-delivery of other APIs adsorbed in the pores.[1-3]
Herein we present novel azelaic acid BioMOFs synthesized by a simple, low-cost and environmentally friendly mechanochemical approach. Azelaic acid is an API commonly used to treat skin disorders and we disclose its coordination to several safe endogenous cations (K^+, Na^+, Mg^{2+}, Ag^+ and Ca^{2+}) (Figure 1). These novel BioMOFs were structurally characterized by a combination of different techniques (single-crystal and powder X-Ray diffraction, FTIR, DSC and TGA).
Their thermal and chemical stability was assessed under different conditions (temperature, time and humidity), relevant for cutaneous administration. Most of the structures incorporate water molecules in the metal coordination sphere, exhibiting a reversible dehydration/hydration behavior.
NMR studies indicate that the solubility of the novel frameworks is higher than the solubility of azelaic acid, except in the case of Ag-MOF.

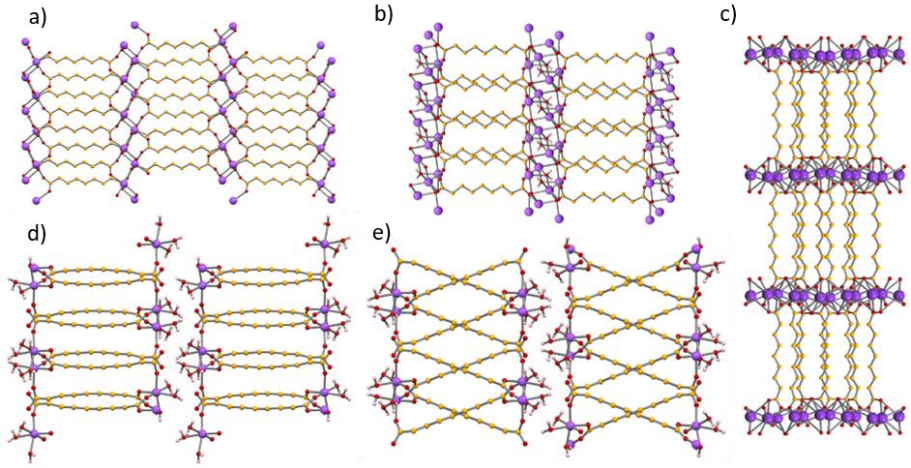

Figure 1: Molecular diagrams for **a)** AZE:Na1, **b)** AZE:Na2, **c**) AZE:K, **d)** AZE:Mg1 and **e)** AZE:Mg2

Acknowledgements
Authors acknowledge Fundação para a Ciência e a Tecnologia (FCT, Portugal) and FEDER for funding (projects PEst-OE/QUI/UI0100/2013, UID/QUI/00100/2019, and PTDC/QUI-OUT/30988/2017, PhD grant SFRH/BD/100029/2014) and "Ramon y Cajal" funding (ENE2016-79608).

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Under the hood of crystallization: a multi-faceted approach towards structural characterization of multicomponent small drug molecules

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Developing new Active Pharmaceutical Ingredients (APIs) is associated with high financial costs. As such pharmaceutical industry often focuses on tailoring the properties of "old" drug molecules. Much interest has surrounded the modification of polymorphic forms and production of API multicomponent solid forms including co-crystals, salts, co-amorphous and ionic liquids.[1-3] The different intermolecular interactions present within the different solid forms alters its physicochemical properties, such as solubility and dissolution rates.[1] Hence, understanding the atomic-level structure of the solid-state is of great importance in predicting and controlling these important properties.[4] X-ray diffraction (XRD) and Pairwise Distribution Function (PDF) in tandem with solid-state NMR (SSNMR) and Density Function Theory (DFT) calculations is an attractive and powerful approach for characterizing structure and dynamics in crystalline and amorphous solids (Figure 1).[5, 6] Particularly, this combined approach can easily resolve co-crystal vs salt ambiguities, an important distinction demanded by the Food and Drug Administration guidelines.[5, 6]
Here a number of case studies will be presented which explore the preparation and characterization of multicomponent API systems. In particular, we will highlight the importance of a multi-faceted approach and demonstrate how individual techniques do not reveal the complete story of these fascinating materials.

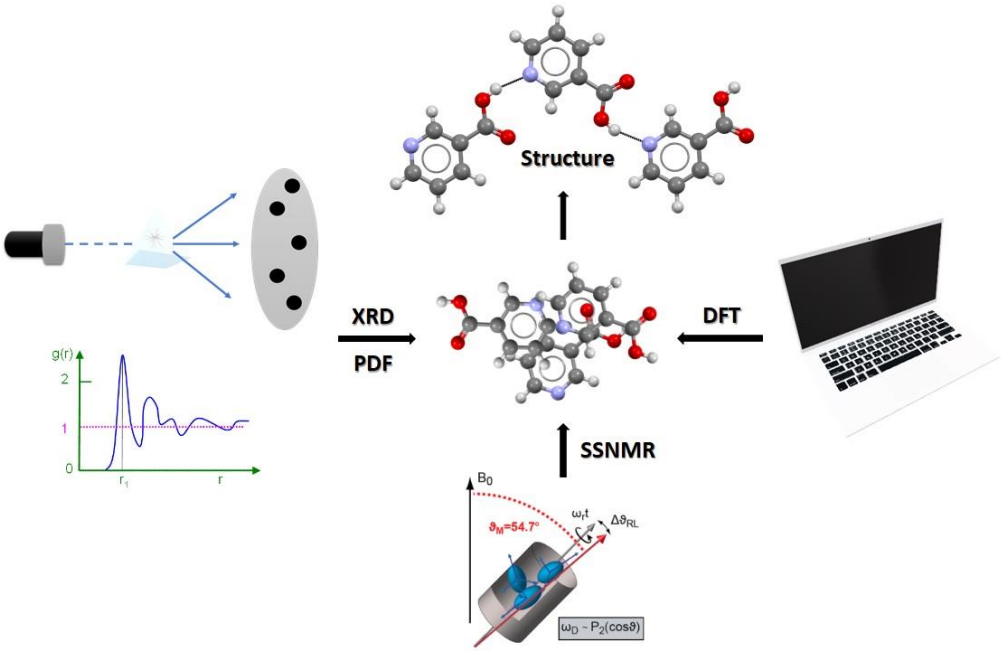

Figure 1: Schematic representation of the multi-faceted approach for the characterization of small drug molecules.

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Polymorph screening and characterization of new crystallographic structures of hydantoin derivatives

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Hydantoins have remarkable interest from the chemical and biological perspectives, and they have also been shown to receive widespread applications in medicine, agriculture, and the chemical industry. They have been clinically used as antiepileptic and antibacterial drugs and for cancer and AIDS treatments and are also used as herbicides and fungicides.
In this communication, it will be reported the polymorph screening of 1-methylhydantoin (1-MH) as well as of 5-methylhydantoin (5-MH), which were recrystallized from different solvents and by the sublimation method, originating several different polymorphs. For 1-MH, three different polymorphs were observed and characterized spectroscopically and structurally. These different polymorphs were characterized as monoclinic (polymorph I) and orthorhombic (polymorph II and polymorph III), belonging to the $P2_1/c$, $Pna2_1$ and $P2_12_12_1$ space groups, respectively. The fundamental differences between the three different polymorphs' crystallographic structures lie in the different strong hydrogen bonding (N–H···O) and, in particular, in the non-conventional C–H···O interactions.[1,2] The molecular packing and the characteristic Raman signature for the two first 1-MH polymorphs are illustrated in Figure 1.
The polymorphic screening of 5-MH originated four different polymorphs, which were characterized by infrared and Raman spectroscopies. It was also possible to determine the crystallographic structure of one of them, as a triclinic crystal system, belonging to the *P*–1 space group.[3]
The thermal behavior of both systems and the transitions between the different polymorphs were also studied and characterized.

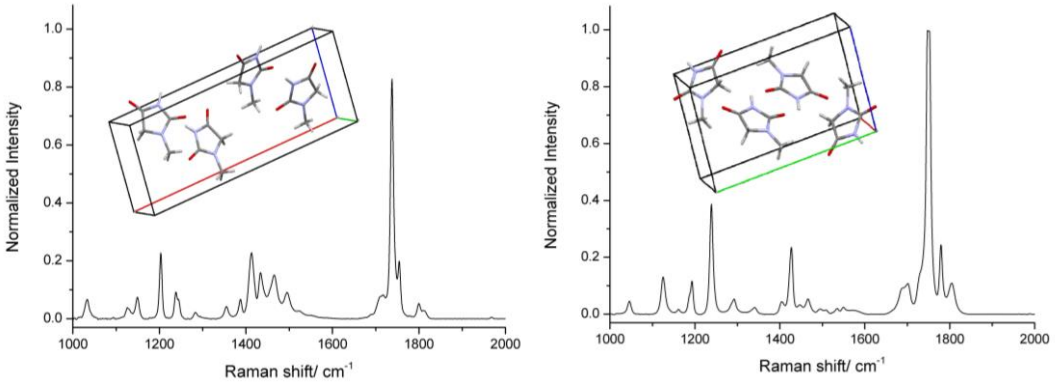

Figure 1: Molecular packing and characteristic Raman signature for the polymorphs I (left) and II (right) of 1-MH.

Acknowledgements
The Coimbra Chemistry Centre is supported by the Fundação para a Ciência e a Tecnologia (FCT), through the project UID/QUI/00313/2019.

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COMPANY PRESENTATIONS

PXRD-L Extremes

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For crystallographic applications a wide range of laboratory based Polycrystalline sample X-Ray Diffractometers are available. Extreme examples are the third generation of the Empyrean platform, and the compact Aeris diffractometer.

Empyrean, the intelligent diffractometer, redefines the concept of a multipurpose X-Ray diffraction instrument, being the first fully automated multipurpose diffractometer that allows the largest variety of measurements without any manual intervention. Newly designed MultiCore Optics featuring iCore and dCore take care of the work. It is possible now to prepare batches of samples to run overnight or over weekends, combining multiple measurement geometries to facilitate a more complete understanding of the samples, without any manual intervention. Automation also being applied to subsequent data analysis via HighScore[1] software package.

Aeris achieves same data quality as in floor-standing systems, for Bragg-Brentano geometry, with the same measuring time, on a compact diffractometer. Aeris was used to solve the crystal structure of AgCaVO4 from powder X-ray data (Figure 1) in combination with the HighScore software suite.

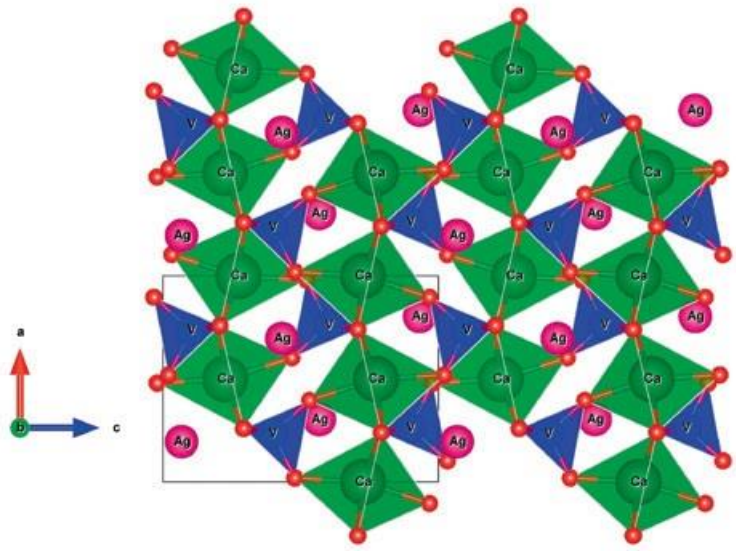

Figure 1: Crystal structure of AgCaVO4 solved from Aeris data.

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Best Data Quality from D8 QUEST and D8 VENTURE

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Modern chemical and biological crystallography continuously pushes the limits to ever smaller samples with typically weaker diffraction properties. Here we will present new software and hardware components which tremendously improve the performance of laboratory instrumentation: the new series of IμS DIAMOND sources the new PHOTON III X-ray detector family and the new IDEAL refinement routine.

- The air-cooled I□S DIAMOND microfocus sealed tube sources uses a unique diamond hybrid anode technology to produce intensities similar to modern microfocus rotating anodes. The anode consists of a diamond substrate coated with copper, molybdenum or silver. The IμS DIAMOND does not require any routine maintenance and has the same legendary life time which makes the IμS system the most popular microfocus X-ray source for more than a decade.

- The PHOTON III is a new CPAD (charge-integrating pixel array detector), which utilizes a mixed-mode approach for data collection. The ultra-sensitive PHOTON III detector can collect very weak reflections without suffering from charge-sharing or non-linearity effects common to other photon-counting detectors.

- The introduction of shutterless-mode operated, large active-area detectors has dramatically improved the accessibility of data to 0.5 Å and beyond. Today, these data are available in only one detector setting with short exposure time in excellent quality. Traditional structure refinement uses an Independent Atom Model (IAM), which beyond the establish 0.83 Å reveals electron density, which cannot be modelled appropriately. Our new IDEAL program expands the model taking bond-electron and lone pair density contributions additionally into account. The density information is derived from the INVARIOM database of *ab initio* calculations of model compounds. IDEAL is fully integrated into the APEX3 software suite.

Bruker's D8 QUEST and D8 VENTURE both take advantage of all improvements in source, detector and software technology, leading to a previously unknown level of performance and ease-of-use.

In-situ Measurement with Laboratory XRD System

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In-situ measurement technique is one of the most powerful tools for understanding the crystal phase transition behavior with changing environment of samples. Recently, the number of demands for understanding rapid reactions are increasing for researching new materials. In any case, the combination of high brilliance X-ray source, high performance X-ray mirror and detector is important.

Rigaku SmartLab® is a multipurpose, fully-automated horizontal X-ray diffractometer that allows many types of measurements and evaluations of materials ranging from powders to thin films. Rigaku's modular system and Cross Beam Optics (CBO®) system enable configuration of a wide range of optics. We propose the unique $K\alpha_1$ system with a Johansson Ge crystal for monochromatization of incident X-rays to the $K\alpha_1$. Since incident X-ray is monochromatized to $K\alpha_1$, even overlapped diffraction peaks can easily be deconvoluted. The peak positions, widths, and intensities will be determined more precisely in the diffraction patterns obtained using the $K\alpha_1$ optics than using the conventional $K\alpha$ optics. The $K\alpha_1$ unit is recommended to be used for indexing or ab initio structure analysis, which requires high-resolution data.

Also, SmartLab can adapt unique in-situ attachment as XRD-DSC, battery cell attachment, etc. In this presentation, In-situ measurement of pharmaceutical sample with XRD-DSC chamber and charge-discharge measurement of lithium ion battery will be explained.

Figure 1: SmartLab system with XRD-DSC chamber

Manifold possibilities and benefits of microwave-enhanced synthesis systems from CEM corporation

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Although the use of conductive heating as a generally implemented way for chemical transformations methodologies, microwave technology is emerging as a recognized energy source to enhance chemical synthesis performance, safety and productivity. Microwave instrumentation from the leading global provider of microwave-based solutions - CEM corporation, allows scientists to design and optimize reactions through the use of safer solvents and full control of reactions parameters, in a wide range of applications and reactions scales. From single-mode to multimode CEM's microwave synthesizers, applies to virtually all fields of synthetic chemistry, with complete power control, temperature monitoring and control, pressure management and sample containment. As an evolutionary technology CEM's Microwave Synthesis systems provides versatility and true modularity, offering a full range of accessories for new applications needs. QLABO - Equipamentos de Laboratório e Serviços, Lda. is the exclusive representative and distributor in Portugal for sales, supplies, service and warranty.

POSTERS

Thiabendazole-formic acid solvate: a crystallographic, spectroscopic and thermal study

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In this communication, we report the structure of a thiabendazole solvate, recrystallized from an acid formic solution. This new solvate was characterized by Raman spectroscopy, single crystal X-ray diffraction and differential scanning calorimetry.
Thiabendazole (TBZ) is an anthelmintic of the benzimidazole class, used to treat parasitic infections in humans. It is also commonly used as an agricultural fungicide, as a food preservative, and as a heavy metal chelating detoxification agent. Clinically, TBZ has been used as a drug to treat threadworm, cutaneous larva migrans, visceral larva migrans, and trichinosis [1].
This new TBZ solvate crystallizes in the monoclinic $P2_1/c$ space group, with 1 molecule of protonated TBZ, 1 formate anion and one neutral formic acid in the asymmetric unit cell, with a = 3.83390 (10), b = 22.1950 (6) and c = 15.3695 (4) Å. Each TBZ molecule exhibits two NH···O bonds and two weak, non-conventional H-bonds (CH···O) with the formic acid molecules. The TBZ cations are interconnected via NH···O bonds with the formate anion forming chains propagating along the c-axis. In addition, each formate anion is connected with the neutral formic acid molecule through a strong (OH···O) bond. Two CH groups of TBZ establish weak H-bonds with the bare O atom of the neutral formic acid molecule, completing two distinct motifs of H-bonding rings (Figure 1-right).

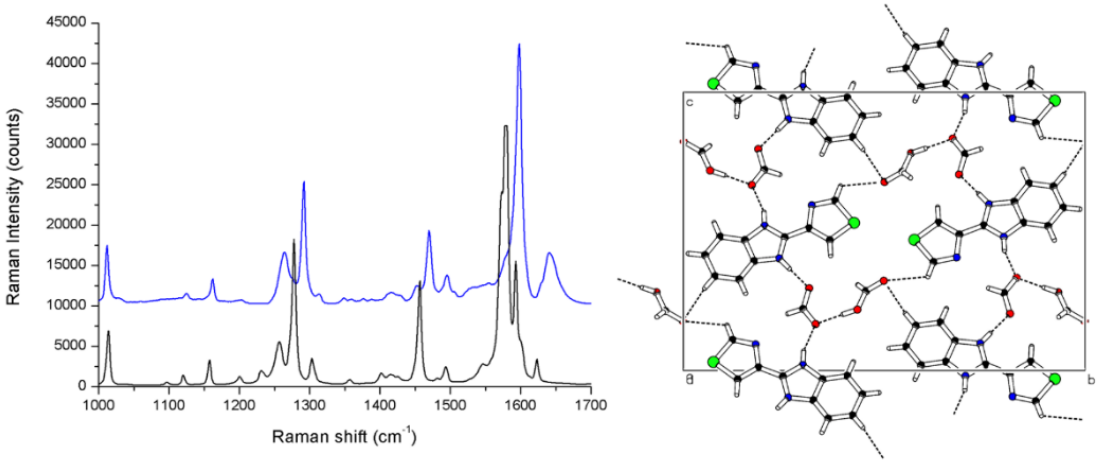

Figure 1 – Raman spectra of the thiabendazole (black) and of the new TBZ-formic acid solvate (blue) [left], and molecular packing of the TBZ-formic acid solvate [right].

Acknowledgements
The Coimbra Chemistry Centre and CFisUC are supported by the Fundação para a Ciência e a Tecnologia (FCT), through projects UID/QUI/00313/2019 and UID/FIS/04564/2019, respectively, also co-funded by FEDER/COMPETE.

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Haa1 transcription factor DNA binding domain structural analysis of two homologous proteins

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Haa1 transcription factor is the main regulator of yeast genomic response to acetic acid stress. It regulates, directly or indirectly, the transcription of 80% of the genes activated by acetic acid. Haa1 is composed by a DNA binding domain (DBD) followed by a Transactivation domain (TAD). While the DBD recognizes specific DNA sequences, in the promoter region of the transcription factor target genes, the TAD is involved in activation of other transcription factors, and may also bind to proteins co-regulating their transcription[1,2,3].

We began a DBD structural characterization of two homologous proteins, *Saccharomyces cerevisiae* and *Zygosaccharomyces bailii,* using thermal shift assays, circular dichroism, small-angle X-ray scattering (SAXS) and X-rays crystallography. Both proteins produce dimers, and showed higher a percentage of α-helices relative to anti-parallel β-sheets. Initial crystals were already obtained for both proteins, but still with very small dimensions and weak diffraction. We aim improving the actual crystals and to intend to produce their complexes with the DNA recognition motif in, order to unravel eukaryotes transcription factors mechanisms.

Acknowledgements

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Assembling bioinspired metal coordination frameworks of nalidixic acid by mechanochemistry: A clean method towards improved drugs

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The interest in metal coordination frameworks in the pharmaceutical field has been increasing as it provides an exciting structural vehicle to modify the properties of active pharmaceutical ingredients (API) without interfering with its biological role. These structures add numerous advantages to the drug due to acquired synergetic effects, enhancing its biological activity, increasing its solubility and providing a controlled drug delivery and release. To obtain a full structural elucidation of these frameworks, the use of crystallography is crucial, being the main characterization tool for these molecules. [1]

Nalidixic acid belongs to the quinolone antibiotic family – a major class of synthetic antibacterial agents – and it is used to treat urinary tract infections caused by Gram-negative bacteria. One of the drawbacks of this pharmaceutical compound is its low bioavailability resultant from a low solubility.

Direct incorporation of this drug into a framework has proven to be an efficient approach to improve its solubility and increasing its antimicrobial activity.[2] Herein we present the mechanochemical synthesis of new Ag(I), Ca(II) and Cu(II) frameworks incorporating nalidixic acid as a pharmaceutically active ligand (**Figure 1**). Mechanochemistry is an environmental-friendly synthetic technique that shown to be the most efficient pathway in this case. The novel compounds have been characterized by single-crystal and powder X-ray diffraction, fourier-transform infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis.

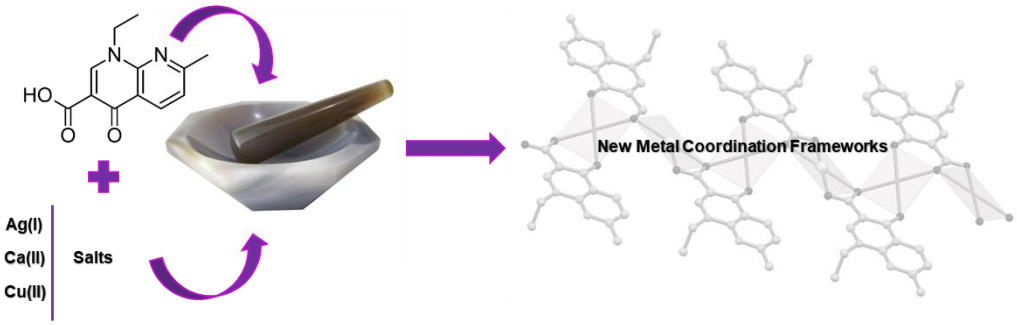

Figure 1: Mechanochemical synthesis of Nalidixic Acid coordination frameworks

Acknowledgements
Authors acknowledge Fundação para a Ciência e a Tecnologia (FCT, Portugal) and FEDER for funding (projects UID/QUI/00100/2019, and PTDC/QUI-OUT/30988/2017)

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New Lanthanide Silicate System with Visible and Near-infrared Luminescence

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A new lanthanide silicate system, $Na_2K[Ln_3Si_6O_{18}]$ (Ln = Lu, Yb/ Er, Lu/Eu, or Lu/Yb/Er), composed by microcrystals embedded in an amorphous siliceous matrix (Figure 1a), obtained by sintering at 1373 K a $Na_3K[Ln_2Si_6O_{17}]\bullet 3H_2O$ nano-crystalline precursor, is presented [1]. The crystal structure of these lanthanide silicates was solved from high-resolution synchrotron power X-ray diffraction data collected at 110 K (Figure 1b), and further supported by ^{29}Si MAS NMR and Eu^{3+} luminescence. The materials crystallize in the *P*-1 triclinic centrosymmetric space group, exhibiting a dense framework consisting of anionic hexameric $[Si_6O_{18}]^{12-}$ cyclosilicate units, and chains of two distinct $\{LnO_6\}$ octahedra. ^{29}Si MAS NMR of $Na_2K[Lu_3Si_6O_{18}]$ indicates the presence of three sharp peaks in 1:1:1 intensity ratio from the distinct crystalline Q^2 crystalline sites, and a broad bottom signal accounting to one third of the total spectral intensity attributed to the amorphous silicate phase. Moreover the 12 K luminescence spectroscopy of $Na_2K[(Lu_{0.90}Eu_{0.10})_3Si_6O_{18}]$ reveals the individual signatures of the two crystalline Eu^{3+} sites, one associated to the low-symmetry $\{LnO_6\}$ and the other to a Eu^{3+} ion on a slightly distorted inversion center, and the presence of small amounts of Eu^{3+} in the amorphous matrix. $Na_2K[(Lu_{0.75}Yb_{0.20}Er_{0.05})_3Si_6O_{18}]$ is the first example of a lanthanide silicate operative as a near-infrared ratiometric luminescent thermometer, with good sensitivity at cryogenic temperatures (<100 K). Upon excitation at 903 nm, the ratio between the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ (Yb^{3+}) and $^4I_{13/2}\rightarrow{}^4I_{15/2}$ (Er^{3+}) emissions was used for sensing temperatures in the 12-450 K range (Figure 1a), reaching a maximum thermal sensitivity of 2.6 $\%K^{-1}$ at 26.8 K (Figure 1b).

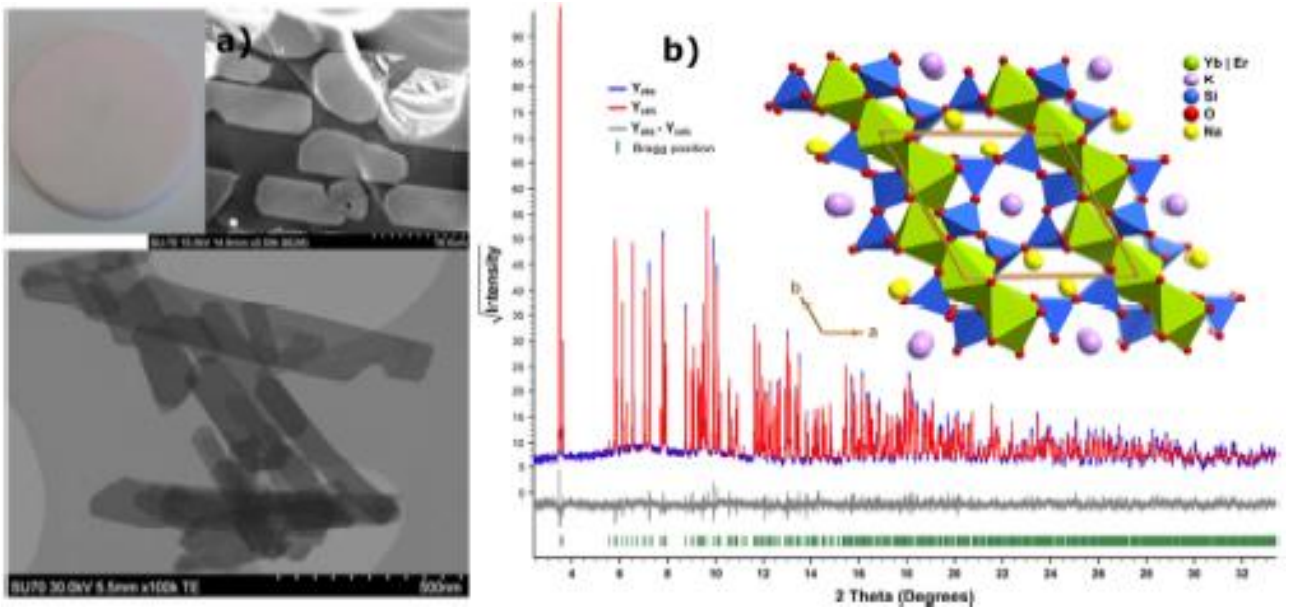

Figure 1: a) Monolith (5 cm x 0.4 cm) of the sintered material (top left) composed by $Na_2K[(Yb_{0.933}Er_{0.077})_3Si_6O_{18}]$ (**1**) embedded in an amorphous siliceous matrix, as witnessed by SEM image (top, right). STEM image of the nanocrystalline precursor $Na_3K[(Yb_{0.933}Er_{0.077})_2Si_6O_{17}]\bullet 3H_2O$ (bottom). b) Final Rietveld plot for (**1**) and a view along the [001] direction of the determined unit cell (inset).

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. This work is also funded by national funds (OE), through FCT in the scope of the framework contract (for D. A.) foreseen in the Decree-Law 57/2016, of August 29.

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Supramolecular Interactions on Sulfonamide Co-crystals: Crystallographic and Ab-initio studies

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Co-crystallization is still a booming area, especially in the pharmaceutical field, as it does not alter drug's biological activity, while improving their physicochemical properties, such as solubility, compressibility, hygroscopic stability, intrinsic dissolution rate, thermal properties and bioavailability. Predicting how Active Pharmaceutical Ingredients (API´s) interact with extra molecules to come together and form new compounds, is still a pressing search and a puzzle for researchers. In this quest the studies on supramolecular interactions, encompassing hydrogen and halogen bonds, and their hierarchical nature play a key role and can help to understand how molecules can recognize each other[1]. Another important question in the multicomponent crystal world is the salt- cocrystal paradigm [1]. Due to the possible participation of diverse functional groups of different molecules in multicomponent crystals, the design and control of crystalline solids often faces significant challenges.

In previous work of the group on multicomponent crystalline compounds of sulfadimethoxine with several co-formers[2], we observed that the preferred ones were amine derivatives. The salts obtained were based on $^{+}$N-H$_{coformer}\cdots$N$_{sulfonamide}$ charged hydrogen bonds. Also, the N-H$_{terminalamine}\cdots$O$_{sulfone}$ synthon was observed and only broken in hydrates. These results are in accordance with those obtained from other authors[3-4] on sulphonamides, in which the amide proton is the best donor and carbonyl, sulfanyl and activated aromatic nitrogen groups are the best acceptors (in this order). In order to further ascertain these results other sulfonamides (sulfacetamide, sulphanilamide and sulfaguadinine) compounds were synthetized, using 1,4-diazabicyclo[2.2.2]octane (DABCO). The new compounds were structurally characterized by single-crystal and powder X-ray diffraction and electrostatic charge distributions were determined by ab initio calculations. Results will be discussed herein.

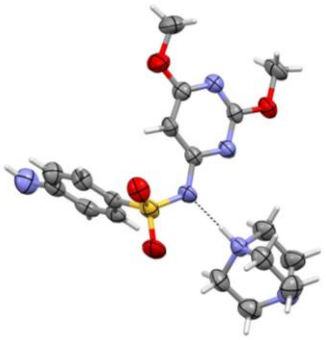

Figure 1: SDM:DABCO co-crystal

Acknowledgements
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A philatelic overview of X-rays, crystals and X-ray diffraction

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A philatelic overview from X-rays discovery and crystallography to X-ray diffraction and its application to crystal structure determination.

Picric acid detection with freebase porphyrins: a crystallographic evaluation

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The design and preparation of receptors capable of rapidly detecting chemical explosives is still a necessity in antiterrorism, national security, and environmental protection.[1] Nitroaromatic compounds (NACs) are one of the major constituents of many standard explosives.[2] Among different NACs, 2,4,6-trinitrophenol (TNP) and 2,4,6-trinitrotoluene (TNT) have received special attention because of their wide-spread use, superior explosive power and high toxicity.[3] Porphyrins are a class of compounds with high molar absorptivity and fluorescence quantum yields. Interactions between porphyrins and NACs can be achieved by way of hydrogen bonds and polarization effects.[1, 4] Several examples can be found in the literature where porphyrin are used as sensory materials for the detection of NACs.[1, 5] These properties makes them excellent candidates for trace detection of explosives, offering high sensitivity and selectivity.[6] Herein, a series of freebase porphyrins are examined for the selective detection of TNP and their affinity is revealed by spectroscopic titrations and X-ray studies. The sensing is mediated through protonation and axial connectivity where the electro-donating capabilities of the groups located at the porphyrins *meso*-positons play a crucial role in the equilibria. Furthermore, the protonation at the central core of the porphyrins further induces additional interactions, endowing an increase in the selectivity of TNP when compared with other NACs.

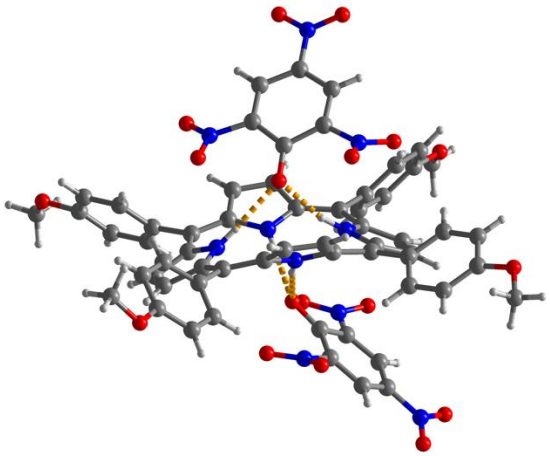

Figure 1: Crystal structure of 5,10,15,20-(tetra-4-methoxyphenyl) porphyrin interacting with two picric acid molecules.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. The research contracts of F. Figueira (REF. - 168-89-ARH/2018) is funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. RFM also gratefully acknowledge FCT for the Junior Research Position (CEECIND/00553/2017).

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4-Cyanobenzene-Ethylenedithio-TTF Radical Salts and the role of C-N…H-C interaction

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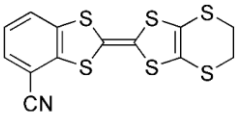
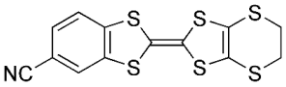
C-N···H-C interactions were found to play a significant role in electrically conducting molecular materials. This was recently described by us in salts of the dissymmetric TTF derivative *5*-cyanobenzene-ethylenedithio-tetrathiafulvalene (*5*-CNB-EDT-TTF)[1] with a 4:1 stoichiometry and two-dimensional metallic properties characterized by bilayer structure of the donors, promoted by C-N···H-C interactions, leading to a head-to-head arrangement of donor molecules in paired layers (bilayers).[2-4] The crystal engineering process that leads to the bilayer formation is serendipitous and in this context, there appears to be obvious interest to investigate whether similar interactions can take place with the CN group in a different position on the benzene ring, and therefore we decided to prepare a different isomer of this donor, *4*-cyanobenzene-ethylenedithio-tetrathiafulvalene (*4*-CNB-EDT-TTF)[5], and explore its possible salts with different anions[5,6].



4-CNB-EDT-TTF



5-CNB-EDT-TTF

Scheme: Molecular scheme for the *4*-CNB-EDT-TTF and *5*-CNB-EDT-TTF donors

Acknowledgements
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Strontium-Alendronate bio-MOF: A Multicomponent Coordination System for Osteoporosis

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Bio-Metal-Organic Frameworks (bio-MOFs) are highly ordered coordination systems constructed from metallic centres and organic linkers with intrinsic therapeutic properties. Bio-MOFs combine the pharmaceutical efficiency of distinct components used as part of the network itself and allow the delivery of large quantities of drugs.[1] The present work focuses on the development of new bio-MOFs for the treatment of osteoporosis, a disease with a significant impact on today's society. The network is designed to combine both (i) the anti-osteoporotic properties of a well-known bisphosphonate drug (alendronate, used as organic linker);[2] with (ii) the beneficial effects of strontium ions (used as metallic centres).[3]

In this work, a novel $[Sr(H_4alen)_2]$ bio-MOF was obtained through hydrothermal synthesis, under acidic conditions. Upon preparation, a complete characterization in terms of chemical composition and structure features, was achieved through X-ray diffraction (Figure 1). These properties were then corroborated by other advanced characterization techniques, such as powder X-ray diffraction, solid-state NMR, FT-IR, electron microscopy (SEM and EDS), thermogravimetric and elemental analyses. All together, these results show that $[Sr(H_4alen)_2]$ bio-MOF is a true multicomponent system, appearing as an extremely appealing and interesting approach for a more efficient treatment for osteoporosis.

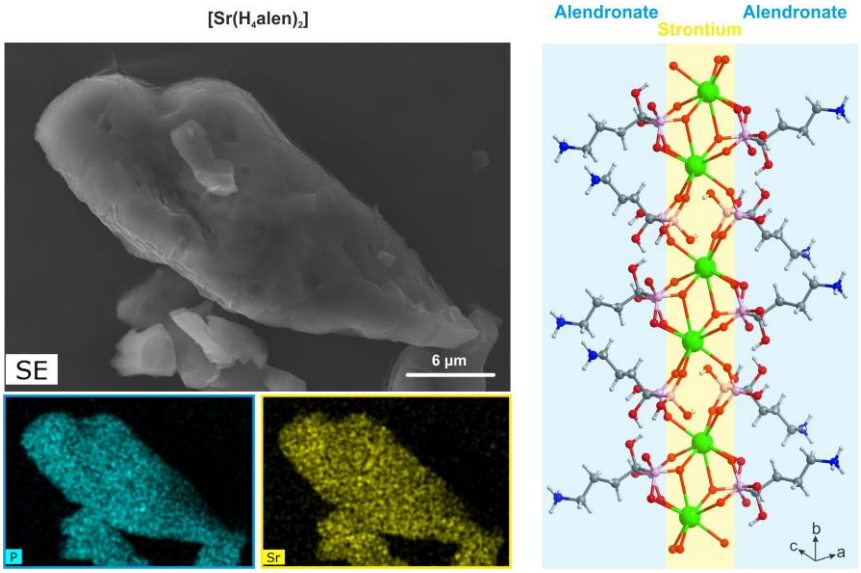

Figure 1: (Left) SEM images of $[Sr(H_4alen)_2]$ and EDS mapping showing the uniform distribution of P from alendronate linker and Sr metallic centres. (Right) Structural representation of the bio-MOF, highlighting its two components.

Acknowledgements
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Synthesis, Crystallographic and Magnetic Characterization of Monoclinic $Cu_4O(SeO_3)_3$

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$Cu_4O(SeO_3)_3$, a copper-oxo-selenite derivative belonging to the $Cu_xO(SeO_3)_{1-x}$ family containing the exotic skyrmionic chiral magnet Cu_2OSeO_3, crystallizes in two different polymorphs, with monoclinic and triclinic structures[1]. This compound was found as contaminant occurring during the synthesis of Cu_2OSeO_3, and the crystal structures of the two polymorphs are known, but their physical properties, in particular the magnetic behaviour, are poorly known. We have undertaken a study of $Cu_4O(SeO_3)_3$, including synthesis, a thorough single-crystal crystallographic study, magnetometric and specific heat measurements.
The compound can be obtained in polycrystalline form during the copper selenite decomposition in air at high temperatures [2] or by reacting CuO and SeO_2 in a typical solid-state reaction [3]. Single crystals of the monoclinic form were grown through a typical chemical vapour transport (CVT) reaction, using the polycrystalline Cu_2OSeO_3 powder previously obtained, and NH_4Cl as transport agent. A single-crystal XRD study was performed that confirmed the previously reported structure, but affording a higher precision in the structural data. This compound crystallizes in space-group $P2_1/a$, with Z=4. Figure 1 shows the unit cell of the monoclinic $Cu_4O(SeO_3)_3$ polymorph. The structure is complex and the asymmetric unit contains 16 Cu+40 O+12 Se independent atoms. The selenite anions have the typical geometry, and the transition metal atoms coordinate with O atoms featuring 3 distinct coordination geometries, 4-fold, 5-fold and 6-fold with Cu-O bonds in the range 1.884 – 2.429 Å that act as magnetic exchange pathways. The magnetometric studies show that this compound orders magnetically at low temperature, with two clear anomalies in the magnetic susceptibility data at 60 K and 13 K. The magnetic behaviour is ferrimagnetic with a small remanence observed in the magnetic hysteresis cycles, the high field saturation component attaining 0.89 μ_B/Cu atom.

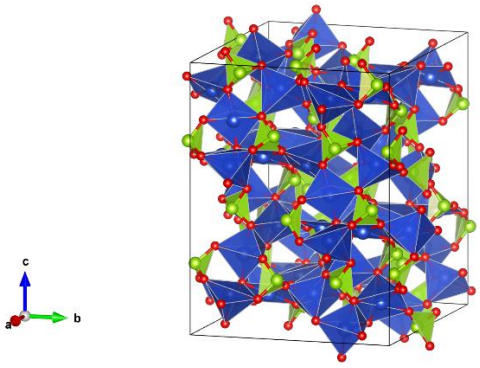

Figure 1: Structure of the monoclinic polymorph of $Cu_4O(SeO_3)_3$, depicting the coordination polyhedral of the Cu atoms in blue and those of Se atoms in green.

Acknowledgements
J.F. Malta PhD grant is supported by FCT- Fundação para a Ciência e a Tecnologia through ChemMat PhD programme. Access to TAIL-UC facility funded under QREN-Mais Centro project ICT_2009_02_012_1890 is gratefully acknowledged. This work was partially supported by funds from FEDER (Programa Operacional Factores de Competitividade COMPETE) and from FCT under the projects UID/FIS/04564/2019 and PTDC/FIS-NAN/6099/2014

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Phase transitions in undoped and Sc-substituted $BiCrO_3$ perovskite

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Perovskites produced by high-pressure synthesis have long been studied, allowing to obtain new multiferroics - materials that present at least two of the three phenomena: ferroelectricity, ferroelasticity and/or ferromagnetism. $BiCrO_3$ is a notable case, subject of studies regarding its crystal and magnetic structure[1]. $BiCrO_3$ is known to have a reversible phase transition upon annealing, from the monoclinic *C*2/*c* phase (resultant from high-pressure synthesis) to the non-polar orthorhombic *Pnma* phase above ~410 K[2,3]. In the $BiCrO_3$- based solid solutions reported so far, the *B*-site substituting cation is very similar in size to Cr^{3+}. A considerable size difference is suggested to induce new phases that are not observed in the end members. Entire series of the high-pressure stabilized $BiFeO_3$-$BiScO_3$ solid solutions where the ionic size of Sc^{3+} is by 24% bigger than that of Fe^{3+} was recently obtained[4,5]. *In situ* x-ray diffraction study of the post-synthesis thermal treatment revealed a set of annealing-stimulated irreversible phase transformations between the different metastable perovskite phases in this system[5]. Effect of the irreversible transformations (denominated as conversion polymorphism) is believed to be a general phenomenon that can be observed in other systems.

We report on synthesis of perovskite phases of the $BiCr_{1-x}Sc_xO_3$ series and detailed studies of their crystal structures and physical properties in relation to the relative amount of scandium in the materials. The compositions $BiCrO_3$ and $BiCr_{0.9}Sc_{0.1}O_3$ were synthesized under high-pressure and characterized using *in-situ* x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy, atomic and piezoresponse force microscopy, SQUID magnetometry, and dielectric spectroscopy.

It was found from *in situ* x-ray diffraction experiments performed between 300 and 623 K that the reversible *C*2/*c* – *Pnma* transformation increases from 410-420 K for $BiCrO_3$ to the range 470-520 K for $BiCr_{0.9}Sc_{0.1}O_3$. Temperature dependences of the lattice parameters and the unit cell volume of the perovskite phases were evaluated from the Rietveld refinement data. The samples microstructure was studied *ex situ* using scanning electron microscopy after each stage of the step-by-step annealing at 373, 423, 448 and 473 K. The observed microstructural changes have been attributed to a jump of the unit cell volume upon *C*2/*c* – *Pnma* transition.

Acknowledgements

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Heterogeneous nucleation of protein crystals using mesoporous MOFs

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Mesoporous Metal-Organic Frameworks (mesoMOFs) have gained some attention as protein immobilization agents. Herein, and for the first time, three model proteins (lysozyme, trypsin and albumin) were used to show that crystallization is effectively induced when the protein is immobilized inside a terbium-based mesoMOF, with this occurring for lysozyme, while trypsin and albumin were size-excluded (Figure 1).

It is shown that heterogeneous nucleation is truly remarkable in the case of lysozyme, occurring through a gradual transition from the MOFs to the protein crystal lattices. These findings suggest that the ability to fix the target protein with a molecular-scale periodicity constitutes a significant advantage of mesoMOFs over other nucleating agents.

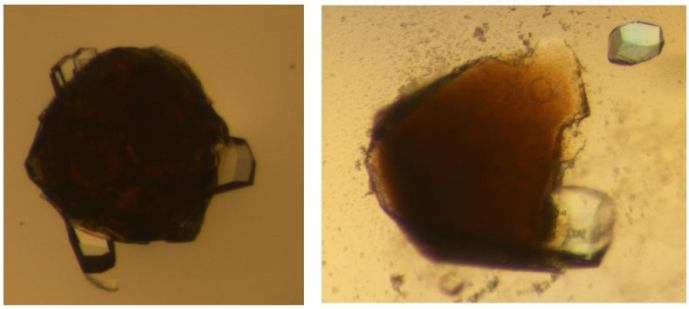

Figure 1: Lysozyme crystals grow abundantly at the surface of milimeter-size Tb-mesoMOF crystals

Acknowledgements
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Unraveling the crystal structure of a trioxolane and a tetraoxane with antiparasitic activity

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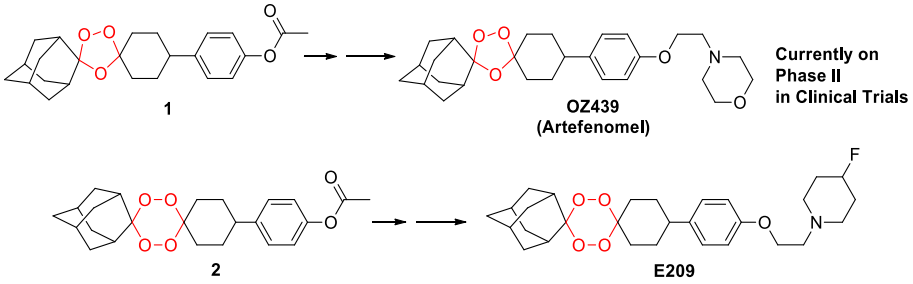
The emergence and spread of *Plasmodium falciparum* resistance to artemisinin-based combination therapies in Southeast Asia stimulated the development of new endoperoxide-type drugs.[1] Synthetic 1,2,4-trioxolanes[2] and 1,2,4,5-tetraoxanes[3,4] are particularly promising in this context, exhibiting similar anti-malarial activity to artemisinin and its semisynthetic derivatives (ARTs). This approach has yielded the ozonide **OZ439** (artefenomel)[5], currently on Phase II of clinical trials[6], and the 1,2,4,5-tetraoxane **E209**, a next-generation endoperoxide with combined pharmacokinetic and pharmacodynamic features that overcome PfK13-C580Y-dependent artemisinin resistance, the main liability of artemisinin derivatives nowadays.[4,7] We report the crystal structure, Raman spectroscopy studies and quantum-chemistry DFT calculations of a 1,2,4-Trioxolane **(1)** and a 1,2,4,5-Tetraoxane **(2)**, used as precursors in the synthesis of the antimalarial candidates **OZ439** and **E209**, respectively. A comparison of the two structures, which only differ in the pharmacophoric moiety, provides information that can contribute to the interpretation of reactivity.



Scheme 1: 4-(3-adamantanyl-1,2,4-trioxaspiro[4.5]decan-8-yl)phenyl acetate **(1)** and 4-(3-adamantanyl-1,2,4,5-tetraoxaspiro[5.5]undecan-9-yl)phenyl acetate **(2),** precursors of antimalarial candidates **OZ439** and **E209**

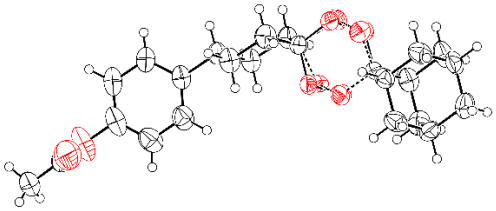


Figure 1: ORTEP plot of (**2**) showing disorder in the tetraoxane group over two alternate conformations of the ring.

Acknowledgements

The authors gratefully acknowledge Fundação para a Ciência e a Tecnologia (FCT), and FEDER/COMPETE 2020-UE, through projects UID/Multi/04326/2013, UID/FIS/04564/2019, UID/QUI/00313/2019 and PTDC/MAR-BIO/4132/2014. Patrícia Amado thanks FCT for financial support through grant SFRH/BD/130407/2017.

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Structure determination of high-pressure C_{70} phases through a joint XRD/DFT study

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Extended polymerization in ABC-stacked C_{70} fullerite at high pressure and high temperature (HP-HT) had been considered impossible to achieve, in opposite to C_{60} fullerite. Reasons invoked to explain such behavior ranged from the low molecular symmetry of C_{70} to its low chemical reactivity, when compared to C_{60}. Recently, however, we have shown that, indeed, C_{70} can form extended polymerized structures.

Two novel C_{70} phases have been discovered at 10GPa-270ºC and 7GPa-600ºC. [1,2,3] Their crystal structures were determined through a combined experimental-theoretical effort. Samples recovered from HP-HT treatments display X-ray powder patterns with poor resolution, indicating a considerable degree of crystalline disorder. Thus, the detailed crystal structures could not be determined from X-ray crystallography analysis of the powder diffraction data, although important structural information, such as, lattice constants and molecular orientations compatible with the overall observed symmetry, were retrieved. Density functional theory (DFT) modeling, in particular crystal structure optimization with constrained lattice constants and molecular orientations, was performed. These simulations have showed that the new phases involve extended polymerization of C_{70} molecules. The first structure consists of one-dimensional (1D) zig-zag polymer, while the second structure involves buckled-hexagon two-dimensional (2D) polymerized planes (see fig.1). A structural relationship between these two structures can be established, the second structure being obtained from the first one through additional bonding. [3]

Higher-level DFT modeling, employing GGA-type functionals and PAW pseudo-potentials, was performed just recently. Full structure optimizations, with non-constrained parameters, give a good agreement with previous experimentally-constrained calculations.[4]

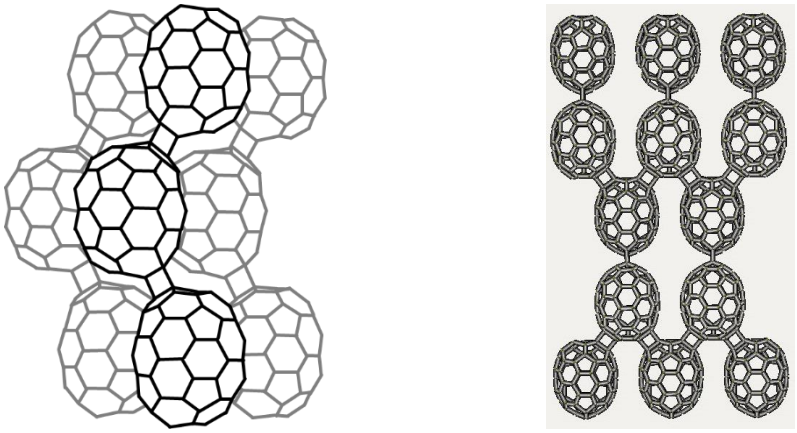

Figure 1: High-pressure C_{70} structures

Acknowledgements
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Porous metal-organic frameworks at films and membranes with potential for gas sensing

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Metal-organic frameworks (MOFs) are crystalline porous supramolecular compounds with metal atoms/clusters interconnected by organic ligands to form extended coordination networks. The versatility, high porosity, and “easy à la carte” synthesis of these compounds are key features, warranting extensive use in many technological areas, e.g. gas storage and separation, catalysis and chemical sensing. Owing to their optical properties and internal channels that provide them with an elevated porosity, porous fluorescent MOFs (FMOFs) represent an ideal choice for the fabrication of gas-sensing devices for hazardous compounds based on fluorescence.[1]

Herein, a simple method to incorporate FMOF $Zn_2(bpdc)_2(bpee)$ (bpdc = 4,4’-biphenyldicarbo-xylate and bpee = 1,2-bipyridylethene) in mixed matrix membranes (MMMs) with polydimethyl-siloxane is reported. Due to their transparency, MMMs were used as probes in transmission, and exposure to sub-ppm contents of ammonia turns on new absorption and PL bands unequivocally attributed to free bpee molecules. In this sensor the bpee ligands are effectively exchanged by ammonia, confirming a highly sensitive chemical probe with a certain selectivity degree. Furthermore, the FMOF was soft-imprinted into cellulose acetate films and their sensing properties were assessed by exposure to saturated atmospheres of 2,4-dinitrotoluene, resulting in a substantial quenching of the fluorescence after few seconds. The films exhibit good sensing ability for the detection of nitroaromatics, which was attributed to the MOF sensitivity and to the novel more efficient film processing method based on soft-imprinting.

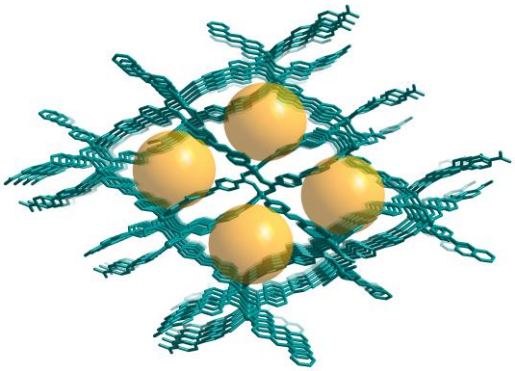

Figure 1: Schematic representation of the crystalline structure of the FMOF, Zn2(bpdc)2(bpee).

Acknowledgements
The work was co-financed by UE, FEDER and COMPETE 2020 – POCI (POCI-01-0145-FEDER-007265) through PT 2020 and by national funds through the FCT/MCTES for the research centre REQUIMTE-LAQV (UID/QUI/50006/2019), and by the European project MOFsENS (M-ERA-NET/0005/2014) and the national Project GlycGold, PTDC/CTM-CTM/31983/2017. MOFsENS (PCIN-2015-169-C02-01/02), PCIN-2015-169-C02-02 and MAD2D projects; 'Severo Ochoa' Programme for Centres of Excellence in R&D (MINECO, Grant SEV-2016-0686) and FEDER-Andalucia (Project P12 FQM-2310).

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Enhancing Biological and Physicochemical Properties of Antibiotics by Combining them in Multicomponent Crystal Lattices

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Altering and adjusting the physicochemical properties of materials recurring to crystal engineering and supramolecular chemistry has been widely applied in several research fields. However, this interdisciplinary approach has become a leading research tool in the pharmaceutical field. The design of multicomponent crystals has proved advantageous ın tailoring Active Pharmaceutical Ingredients (APIs) physicochemical properties, such as solubility, bioavailability, permeability, stability, tabletability, and melting point.[1] Having this in mind, a significant part of our research group goals has been focused on developing multicomponent forms of drugs, in particular antibiotics.
Within this project, we aimed at rejuvenated Sparfloxacin (SPX) antibiotic. SPX is a fluorinated quinolone antibiotic which is not stable in the presence of water and is barely soluble in it, therefore, its bioavailability is still limited. Besides that, SPX being a zwitterionic drug naturally offers a tradeoff between high solubility and membrane permeability. Hence, stabilizing the solid form and enhancing its bioavailability is highly important. A stable neutral form with the dual advantage of high solubility and high membrane permeability can be achieved by simply making multicomponent forms of SPX.[2]
In this context, 4-aminosalicylic acid and 3-aminobenzoic acid were chosen as possible coformers and new forms were obtained with both conventional solution or mechanochemichal synthetic procedures.
In this project not only we expect the enhancement of the physicochemical properties of SPX but also a higher antimicrobial activity, owing to a synergistic effect of the drug-drug combination within in one crystal lattice. A discussion of the structural and preliminary solubility results is presented herein.

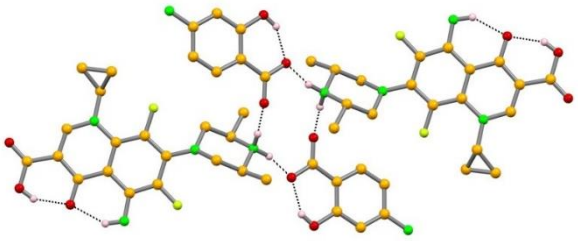

Figure 1: Supramolecular arrangement of SPAR:4ASA anhydrous molecular salt. Hydrogen atoms were omitted for clarity, except the ones involved in hydrogen bonding.

Acknowledgements
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Unravelling novel antibiotic frameworks aiming for enhanced bioactivity

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Nowadays, antimicrobial resistance to multiple drugs[0] is an important issue in public health and a huge challenge to scientists. Several strategies have been applied to augment the number of compounds with improved antimicrobial activity, such as altering the composition of already known molecules[0,0].
Quinolone antibiotics[0], such as pipemidic acid, have been used as antibacterial agents due to their broad spectrum of activity and safety profile. However, bacteria have been shown to rapidly adapt and develop resistance to these compounds[0].
In order to overcome bacterial multiresistance, the coordination of biocompatible metals with antibiotics constitutes a valid strategy to obtain alternative compounds with improved antimicrobial activity. These bio-inspired metal-organic frameworks (BioMOFs)[0] can successfully be prepared by mechanochemistry[0,0,0,0,0] - a privileged technique for molecular synthesis, in the solid state, due to its reduced reaction times, lack of solvent, selectivity enhancement and novel reactivity.
So far, the obtained metal coordination frameworks with pipemidic acid (**Figure 1**) have been analysed by X-ray diffraction techniques and will be further characterised by elemental analysis, NMR, FT-IR and UV-Vis spectroscopies. The solubility, chemical stability and degradation in biological media will be evaluated. Regarding their bioactivity, it will be assessed using selected model organisms, such as yeasts and bacteria.

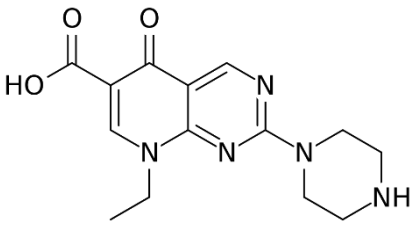

Figure 1: Pipemidic acid

Acknowledgements
Authors acknowledge Fundação para a Ciência e a Tecnologia (FCT, Portugal) and FEDER for funding (projects UID/QUI/00100/2019 and PTDC/QUI-OUT/30988/2017)

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Design, Synthesis and Characterization of Novel Thermochromic Materials

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In this communication, a structural study of a chemical system exhibiting coloured polymorphism is reported. It includes the design of new chromophore molecules, their synthesis, and polymorph screening aiming to find polymorphs displaying different colours.
Polymorphism is defined as the ability of a molecule to adopt different crystal structures that can have different physical and chemical properties. In the context of this study, the most relevant property is the colour exhibited by the different polymorphs[1,2].
Colour polymorphism is a relatively rare phenomenon. One of the few chemical systems presenting this property is the newly synthetized 2,4,6-trinitro-*N*-(m-tolyl)aniline. So far, we have obtained two different crystalline structures of this molecule, one being yellow and the second one light orange.
Raman spectroscopy and X-ray crystallography were used to characterize vibrationally the polymorphic forms and their crystalline structures, respectively. The new polymorphs are orthorhombic (form I - yellow; $Pna2_1$) and monoclinic (form II – light orange; $P2_1/c$), and were obtained after recrystallization of the compound from different solvents. In both polymorphs, a strong N-H···O intramolecular bond between the NH group and one of the three NO_2 substituents is found, but the polymorphs differ in the intermolecular H-bonding patterns, which with all probability affect the electronic delocalization of the amino and nitro substituents to the aromatic rings. Interestingly, in the monoclinic polymorph the H atom of the NH group is shared in a bifurcated H-bond.

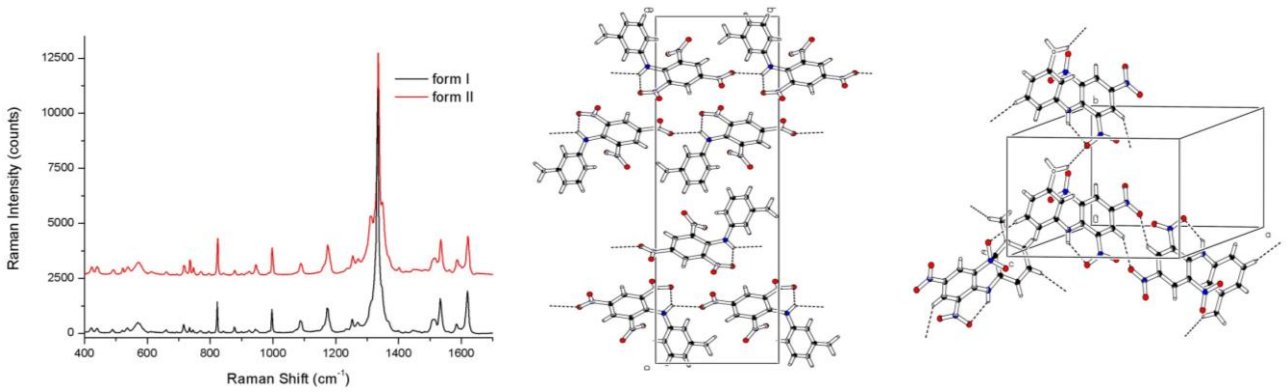

Figure 2: Raman spectra of two different polymorphic forms of 2,4,6-trinitro-*N*-(m-tolyl)aniline (*left*) and the corresponding molecular packing (form I, *middle*; form II, *right*).

Acknowledgements

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Crystal structure and growth kinetics of self-assembled diphenylalanine microtubes of different chiralities

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Chemical and physical aspects of chirality attract nowadays great research interest. For example, the chiral-induced spin selectivity effect (CISS) was used recently to manipulate electron spins transmitting through short organic molecules [1] and long supramolecular structures [2,3]. However practical applications of chirality-dependent properties still require their detailed study in various chiral supramolecular systems. Peptides are convenient building blocks for creation of various supramolecular structures, such as vesicles, nanospheres, nanotubes, nanobelts, thin films etc., via the self-assembly. The chirality runs such structures at different hierarchical levels of organization thus making them advanced functional materials for nanotechnological and biomedical applications. The simplest and most studied self-assembling dipeptide is diphenylalanine (H-Phe-Phe-OH, FF). It easily forms nanotubes and microtubes possessing high rigidity [4,5], piezoelectric [6] and pyroelectric properties [7].

Single crystal X-ray diffraction, optical microscopy and computer simulation were used here to study crystal structure and growth kinetics of FF microtubes formed from L- and D- enantiomers. We found that the microtubes of L- and D- enantiomers grown simultaneously and under identical experimental conditions, belong to different crystallographic space groups, have essential difference in sizes and demonstrate different growth kinetics. The thorough analysis showed that the observed effect cannot be attributed to the effect of enantioselective crystallization due to the solvents, substrate or impurities. Computer simulation by means of molecular mechanics methods revealed fundamental difference in interaction between structural units of microtubes of different chiralities. A physical model describing the chirality-dependent growth of microtubes is suggested.

Acknowledgements
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Design an Fe substituted niobium silicate based on its structure

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Microporous silicates have been widely used as catalysts and adsorbents due to their uniformed pore size, high surface area, large pore volume and good thermal and hydrothermal stabilities. The synthesis of new microporous silicates with mixed polyhedral frameworks can broaden the field and scope of applications of zeolite-type materials. Microporous niobium silicates are one of the few systems which are not well studied. Few studies can be found in literature.[1-4] Considering the niobium silicate $Rb_2(Nb_2O_4)(Si_2O_6)\cdot H_2O$,[4] (Figure 1) although it consists of six-ring channels in both a and b axes, its high temperature (600ºC) hydrothermal synthesis condition and expensive Rb resource limit its application explore. Since Na is much smaller than Rb, in order to stabilize the framework by Na, more cation may be required in channels. To compensate the extra positive charge from cations, the net framework negative charge need be increased, which could be achieved by replacing Nb^{5+} by M^{4+} or M^{3+} with similar ionic size. Furthermore, those metal ions need have ability to form octahedral chain. In this work Fe^{3+} was selected as an example. An Fe substituted sodium microporous niobium silicate was successfully synthesized under mild hydrothermal condition (230ºC). Its structure has been characterized by powder x-ray diffraction, SEM, EDS, TG, NMR and Raman spectroscopies.

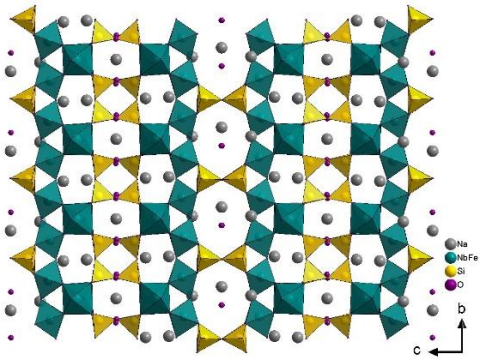

Figure 1: The structure view along *a* axis.

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