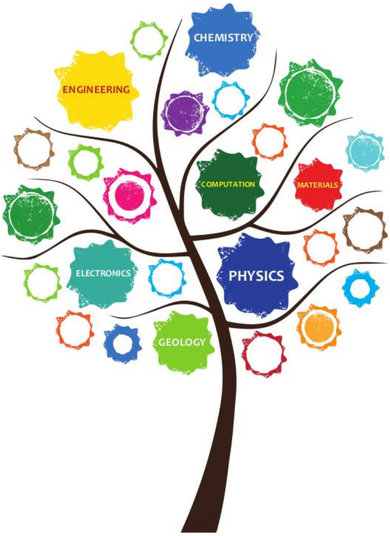
Book of Abstracts

28 - 30 June 2023, Zagreb, Croatia



Solid-State Science & Research
Zagreb, 28 - 30 June 2023

BOOK OF ABSTRACTS AND PROGRAMME

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10:30-10:45	**Stefanie Hutsch**, Ruhr-University Bochum, Germany *Mechanochemistry as Tool for Porous Organic Polymer Synthesis*	O1
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All times are in CEST (GMT+2)

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Friday, June 30

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17:00-17:15	**Pavla Šenjug**, Faculty of Science, Department of Physics, University of Zagreb *Magnetism and magnetic order in layered hybrid organic-inorganic tetrahalocuprate perovskites*	JI8

Closing ceremony and awards

Keynote lectures

K1 - Mechanochemistry is just chemistry

S. Shah, J. Crain, J. Anderson, M. Mokhtar, R. Silva, J. Mack,[1]
[1]Department of Chemistry, University of Cincinnati, Cincinnati, Ohio
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Although the history of mechanochemistry goes back centuries, with the rapid growth of articles about it, it is becoming clear that this once obscure discipline is becoming increasingly mainstream. Many of the fundamental principles that govern this technique are becoming clearer, especially with respect to organic synthesis. We recently developed capabilities for performing organic mechanochemical reactions under a variety of unique conditions. This approach offers an opportunity for strengthening the fundamental understanding of the energetics in mechanochemical systems especially for stereoselective reactions. What we have learned over the years is that many of the fundamental rules that govern solution-based reactions also govern mechanochemical reactions. During this presentation, we will unlock some of the secrets of mechanochemical processes, to have a better understanding of when these reactions behave similar to traditional solution-based reactions and when they are wildly different.

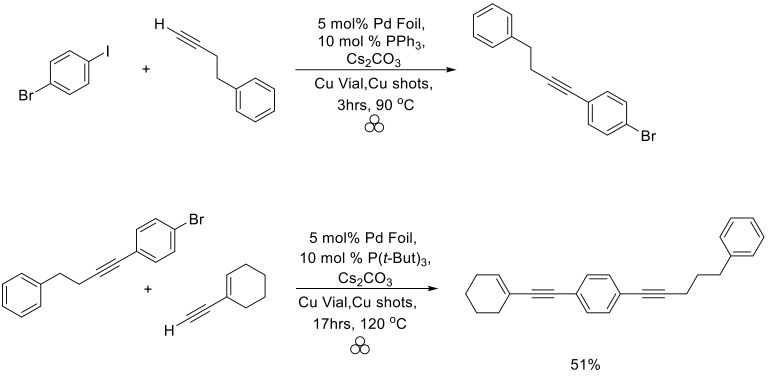

Figure 1. Novel two-step mechanochemical Sonogashira reaction.

K2 - Can we generate and transfer chirality?

A. Stroppa[1]
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Chirality is an important structural property: right-handed and left-handed chiral materials have identical chemical composition and connectivity, but they are related by mirror transformation, forming a couple of enantiomers. Chiral materials show unique features: the intrinsic non-centrosymmetry leads to optical rotation, circular dichroism (CD), second-harmonic generation (SHG), piezoelectricity, pyroelectricity, ferroelectricity, and topological quantum properties. In this talk, I will discuss the intriguing interplay between chirality and physical properties in innovative materials, ranging from twisted bilayers (non-magnetic as well magnetic) to chiral hybrid organic-inorganic perovskites.

Figure 1 Generation of chirality by twisting in bilayer graphene and corresponding spin-texture switching.

[1] K. Yananose, G. Cantele, P. Lucignano, S.-W. Cheong, J. Yu, and A. Stroppa, *Phys. Rev. B.* **104** (2021) 075407.
[2] K. Yananose, P. G. Radaelli, M. Cuoco, J. Yu, and A. Stroppa, *Phys. Rev. B.* **106** (2022) 184408.

K3 - New Advances in High-Performance Single-Molecule Magnets

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Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as molecular spintronics and high-density information storage. To realize such applications, complexes featuring large spin-relaxation barriers (U_{eff}) and high magnetic blocking temperatures (T_{B}) are required. Lanthanide ions are especially well-suited for the design of single-molecule magnets due to their large magnetic moments and magnetic anisotropy that originate from strong spin-orbit coupling of the 4f orbitals. Our approach to improve T_{B} is to pursue multinuclear single-molecule magnets where strong magnetic exchange between lanthanide centers through the employment of radical bridging and bismuth ligands, respectively, is targeted. Such ligands possess diffuse spin orbitals that can penetrate the core electron density of the lanthanide ions where the 4f spin orbitals lie buried. Here, various strategies to single-molecule magnets containing radical and bismuth ligands will be discussed (Figure 1).[1-5]

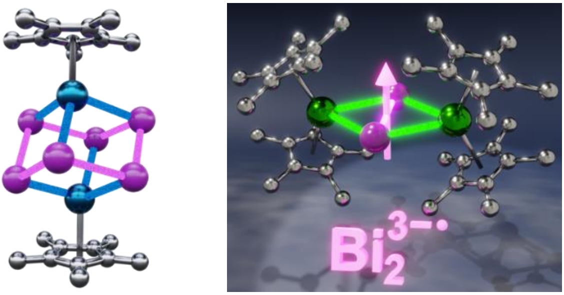

Figure 1. Structures of the $[Cp^*{}_2Dy_2Bi_6]^{2-}$ dianion (left) and the $[(Cp^*{}_2Dy)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2^{\bullet})]^-$ anion (right).

[1] F. Delano IV, E. Castellanos, J. McCracken, S. Demir, *Chem. Sci.* **12** (2021), 15219.
[2] F. Benner, S. Demir, *Chem. Sci.* **13** (2022), 5818.
[3] P. Zhang, F. Benner, N. F. Chilton, S. Demir, *Chem* **8** (2022), 717.
[4] P. Zhang, R. Nabi, J. K. Staab, N. F. Chilton, S. Demir, *J. Am. Chem. Soc.* **145** (2023), 9152.
[5] F. Benner, L. La Droitte, O. Cador, B. Le Guennic, S. Demir, *Chem. Sci.* (2023), Advance Article. DOI: 10.1039/D3SC01562A.

Invited lectures

I01 - Isotopic labeling: a valuable approach for studying reaction mechanisms in ball-milling

T. X. Métro,[1] C.-H. Chen,[1,2] I. Goldberga,[1,3] C. Leroy,[1] D. Laurencin[1]
[1]Institut Charles Gerhardt de Montpellier, CNRS, Montpellier, France
[2]Johnson Matthey Technology Centre, Reading, United Kingdom
[3]Laboratoire de Chimie de la Matière Condensée, Paris, France
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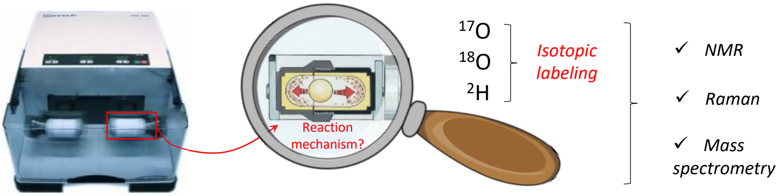
While mechanochemistry is a rapidly expanding field of synthesis, a deeper knowledge still needs to be gained concerning the actual reaction mechanisms occurring inside the milling jars. This explains why much effort is being put into (i) the design of chemical systems allowing to better understand the reactions taking place, (ii) the development of *operando* analytical methods (e.g. pXRD, Raman spectroscopy…), to follow "in real time" the evolution of a reaction medium, and (iii) the computational modeling of mechanochemical reactions. Over the past few years, we have been focusing our efforts on developing ball-milling reactions for the enrichment of molecules and materials in stable isotopes like ^{17}O, ^{18}O and ^{2}H.[1] Here, we will show how thanks to these labeled compounds, it becomes possible to perform more extensive spectroscopic analyses of ball-milling reaction media, and thereby learn more about the reactions occurring in the solid state. [2-4]



[1] https://www.misotoplab.org/publications/
[2] I. Goldberga, N. Patris, C.-H. Chen, E. Thomassot, J. Trébosc, I. Hung, Z. Gan, D. Berthomieu, T.-X. Métro, C. Bonhomme, C. Gervais, D. Laurencin, *J. Phys. Chem. C*, **126** (2022), 12044-12059.
[3] C. Leroy, T.-X. Métro, I. Hung, Z. Gan, C. Gervais, D. Laurencin, *Chem. Mater.* **34** (2022), 2292.
[4] C.-H. Chen, F. Mentink-Vigier, J. Trébosc, I. Goldberga, P. Gaveau, E. Thomassot, D. Iuga, Mark E. Smith, K. Chen, Z. Gan, N. Fabregue, T.-X. Métro, B. Alonso, D. Laurencin, *Chem. Eur. J*, **27** (2021), 12574-12588.

I02 - Correlation between disorder and defects in halfmetals and topological insulators and their functional properties

V.K. Lazarov[1], *B. Achinuq*[2], *A. Kerrigan*[1], *L. Lari*[1], *T. Hesjedal*[2], *D. Kepaptsglou*[1,3], *L. Li*[4], *K. Hamaya*[5] *and M. Weinert*[4]
[1] School of Physics and Engineering, University of York, York YO10 5DD, UK
[2]Department of Physics, University of Oxford, Oxford OX1 3PU, UK
[3]SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury WA4 4AD, UK
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Spin manipulation via spin currents generation, propagation, as well as spin injection and detection are key steps for realization of fast, non-volatile and increasingly important low power computational spintronic devices.

In this work, by employing Scanning Transmission Electron Microscopy, Electron Energy Loss Spectroscopy, Energy Dispersive X-Ray, as well as Scanning Tunneling Microscopy and Spectroscopy we will present a correlation between atomic structure and functionality of heterostructured spintronics devices, with focus on the role of interfaces, grain boundaries, point defects, and strain. First part of the talk will focus on how chemical-atomic disorder determines the spin polarization of Co based Heusler alloys, and the role of atomic structure of the interfaces for spin injection in Si and Ge. Both the experiment and modelling show that the spin injection is inherently not possible even in atomically abrupt $Co_2FeAlSi$/Si(111) systems, in difference to Co2FeAlSi/Ge(111) heterostructures which are less sensitive to both structural and chemical abruptness at the interfaces. In the second part of the talk, we will show that Heusler alloys both via atomically abrupt and crystalline interface (i.e. $Co_2FeAlSi/BaTiO_3$) as well as amorphous ($Co_2FeAlSi$/PMN-PT) can magneto elastically couple, and ultimately magnetisation control by strain can be achieved. Finally, by studying the strain associated with misfit dislocations, we will show that topological states in the Bi_2Se_3 3D topological insulator can be tailored in such a way that tensile strain leads to opening of the band gap of the topologically metallic surface states, while compressive strain push the Dirac point to lower energy.

I03 - Mechanical design and infolding of pollen grains

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Pollen carries male plant genetic material encapsulated in a hard protective shell containing flexible, soft regions—apertures. The mechanical design of the shell regulates how the pollen grain folds into itself (infolds) upon dehydration, which often occurs once it becomes exposed to the environment. The same design also guides the response of pollen grains to hydration which may lead to bursting of the pore and the leakage of the pollen proteins in the atmosphere – this process releases submicronic pollen particles, which can provoke strong allergic reactions in sensitive individuals. Infolding pathways of pollen grains are investigated by studying elastic deformations of inhomogeneous thin shells. Different pathways are governed by the interplay between the elastic properties of the hard and soft regions of the pollen shell and by the aperture shape, number, and size. We delineate regions of mechanical parameters of the pollen grain which lead to complete closure of all apertures, thus reducing water loss and presenting evolutionary viable solutions to the infolding problem [1]. We also show that the apertures, although important for the initiation of the pollen tube, also present a weak regions of the grain wall and that they are prone to bursting once the pollen grain swells enough in humid atmosphere [2].

[1] A. Božič, A. Šiber, *Proc. Natl. Acad. Sci. U.S.A.* **117** (2020) 26600.
[2] A. Božič, A. Šiber, *Biophys J* **121** (2022) 782.

I04 - Creation of magnetic photocatalysts for degradation of water pollutants

D. Ljubas, I. Gabelica, L. Ćurković
Faculty of Mechanical Engineering and Naval Architecture,
University of Zagreb, Zagreb, Croatia
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Photocatalytic oxidation process with heterogeneous photocatalysts can be effective technology in the degradation of different water pollutants. The main problem with dispersed photocatalyst in water is the need to separate them after the reaction and use them again.

In this study two different methods were applied: growth of magnetite crystals on the photocatalyst surface and creation of photocatalytic nano-film on the magnetite core [1,2]. Magnetic technology was used for separation of particles from water. Photocatalysts were successfully prepared and reused with the average recovery rate of more than 95%. They were also successfully used for degradation of different water pollutants – pesticide precursor, pharmaceutical and natural organic matter with degradation efficiency more than 90% in 60 or 120 minutes.

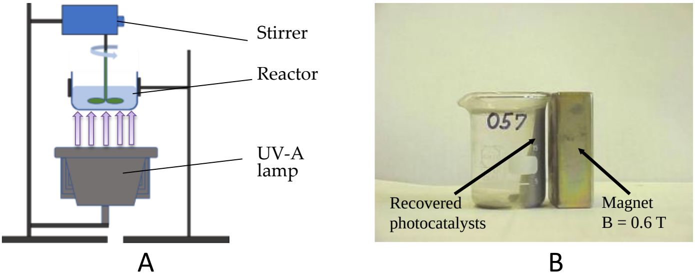

Figure 1 A-Experimental set-up; B- Recovery of magnetic photocatalysts

[1] I. Gabelica, L. Ćurković, V. Mandić, I. Panžić, D. Ljubas, K. Zadro, *Catalysts* **11** (2021) 1136.
[2] D. Ljubas, M. Franzreb, H.C. Bruun Hansen, P.G. Weidler, *Sep. Pur. Tech.* **136** (2014) 274.

I05 - Designing chiral magnetic responses by tailoring geometry of thin films: curvilinear ferro- and antiferromagnets

D. Makarov[1]

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Extending 2D structures into 3D space has become a general trend in multiple disciplines, including electronics, photonics, plasmonics, superconductivity and magnetism [1,2]. This approach provides means to modify conventional or to launch novel functionalities by tailoring curvature and 3D shape of magnetic thin films and nanowires [2,3]. In this talk, we will address fundamentals of curvature-induced effects in magnetism and discuss realizations of curved low-dimensional architectures and their characterization, which among others resulted in the experimental confirmation of exchange-driven chiral effects [4]. Geometrically curved architectures can support a new chiral symmetry breaking effect: it is essentially non-local and manifests itself even in static spin textures living in curvilinear magnetic nanoshells [5]. The field of curvilinear magnetism was extended towards curvilinear antiferromagnets [6,7], offering a novel material science platform for antiferromagnetic spinorbitronics. It was demonstrated that intrinsically achiral 1D curvilinear antiferromagnets behave as a chiral helimagnet with geometrically tunable DMI, orientation of the Neel vector and the helimagnetic phase transition [6]. Application potential of geometrically curved magnetic thin films is being explored as mechanically reshapeable magnetic field sensors for automotive applications, memory, spin-wave filters, high-speed racetrack memory devices as well as on-skin interactive flexible [8,9] and printed self-healable electronics [10].

[1] P. Gentile et al., *Nature Electronics* (Review) **5** (2022) 551.
[2] D. Makarov et al., *Advanced Materials* (Review) **34** (2022) 2101758.
[3] D. Makarov et al., Curvilinear micromagnetism: from fundamentals to applications (Springer, Zurich, 2022). https://link.springer.com/book/10.1007/978-3-031-09086-8
[4] O. Volkov et al., *Physical Review Letters* **123** (2019) 077201.
[5] D. Sheka et al., *Communications Physics* **3** (2020) 128.
[6] O. Pylypovskyi et al., *Nano Letters* **20** (2020) 8157.
[7] O. Pylypovskyi et al., *Appl. Phys. Lett.* **118** (2021) 182405.
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[9] G. S. Canon Bermudez et al, *Nature Electronics* **1** (2018) 589.
[10] R. Xu et al., *Nature Communications* **13** (2022) 6587.

I06 - Epitaxial $La_{1-x}Sr_xMnO_3$ thin films obtained by PAD – influence of temperature and Sr concentration

Marija Milanović,[1] *Jelena Vukmirović,*[1] *Danica Piper,*[1] *Pavla Šenjug,*[2] *Damir Pajić,*[2]*, Vladimir V. Srdić*[1]
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Oxide thin films with perovskite structures exhibit properties such as ferromagnetism, ferroelectricity, giant/colossal magnetoresistance effects and multiferroic behavior, making them excellent candidates for application in electronics, magnetics and sensors. $LaMnO_3$ has cubic perovskite structure which is distorted at RT into an orthorhombic structure due to strong Jahn-Teller (JT) interaction. This structure could be easily doped (with Sr^{2+}, Ca^{2+}, Ba^{2+}…) forming an interesting class of compounds where the interplay between metal-insulator and ferromagnetic-paramagnetic transitions results in a variety of fascinating properties such as colossal magnetoresistance. Vapor deposition techniques are usually the first choice for fabrication of high-quality epitaxial oxide films. However, high cost of those methods has led to development of more affordable techniques such as polymer assisted deposition (PAD).

$La_{1-x}Sr_xMnO_3$ thin films were prepared by PAD technique and deposited at different single crystal substrates in order to investigate the possibility of their epitaxial growth from a liquid phase [1]. Stoichiometric amounts of metal cations were dissolved in distilled water with the addition of water-soluble polymers EDTA and PEI used as complexation agents. The prepared solutions were spin coated onto substrates and thermally treated at different temperatures up to 900°C in order to produce thin films. Structure and epitaxial nature of the films are confirmed by X-ray diffraction analysis and transmission electron microscopy. In addition, films were investigated by magnetic measurements.

[1] J. Vukmirović, S. Joksović, D. Piper, A. Nesterović, M. Novaković, S. Rakić, M. Milanović, V.V. Srdić, Ceram. Int. **49** (2023) 2366.

I07 - Nanofabrication, Functionalization and Applications of Atomically Thin 2D Materials

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Two-dimensional (2D) materials exhibit unparalleled electronic, optical, and mechanical properties, rendering them highly versatile in numerous applications such as (opto)electronics, sensing, catalysis, energy harvesting *etc*. The integration of these materials into nanodevices such as nanopore-based nanofluidic devices and field-effect transistors (FET) unlocks a wealth of possibilities, particularly in biosensing and the manipulation of molecules and ions at the single-molecule level. The presentation will focus on the nanofabrication and applications of nanopores[1,2] and nanopore-FET[3] devices fabricated from 2D materials, including chemical functionalization methods[4,5] used to design novel hybrid materials and tailor their properties to suit specific applications.

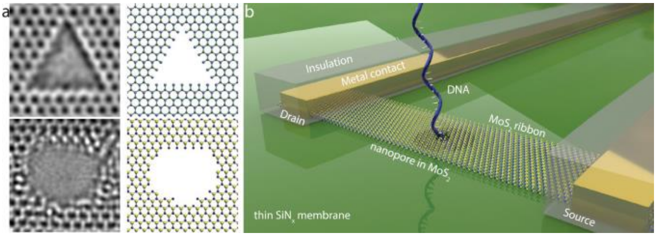

Figure 1 (a) HR-TEM images of nanopores in hexagonal boron-nitride (top) and MoS_2 (bottom). (b) An illustration of a nanopore-FET device. Adapted from [2] and [3].

[1] M. Graf#, M. Lihter#, M. Thakur#, V. Georgiou, J. Topolancik, B. R. Ilic, K. Liu, J. Feng, Y. Astier, A. Radenovic*, *Nat. Protoc.* **14** (2019) 1130.
[2] K. Liu#, M. Lihter#, A. Sarathy, S. Caneva, H. Qiu, D. Deiana, V. Tileli, D. T. L. Alexander, S. Hofmann, D. Dumcenco, A. Kis, J. P. Leburton, A. Radenovic*, *Nano Lett.* **17** (2017) 4223.
[3] M. Graf, M. Lihter, D. Altus, S. Marion, A. Radenovic*, *Nano Lett.* **19** (2019) 9075
[4] M. Lihter*, M. Graf, D. Iveković, M. Zhang, T.-H. Shen, Y. Zhao, M. Macha, V. Tileli, A. Radenovic*, *ACS Appl. Nano Mater.* **4** (2021) 1076
[5] M. Lihter*, M. Graf, D. Iveković, A. Radenovic*, *Adv. Funct. Mater.* **30** (2019) 1907860

I08 - Pair Distribution Function analysis of metal oxide nanocrystals and metal oxo clusters

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Metal oxide nanocrystals find application in solar cells, batteries, bio-imaging, etc. On the other hand, oxo clusters are building blocks in metal organic Frameworks (MOFs) with exciting catalytic properties. We focus here on group zirconium and hafnium oxide nanocrystals and metal oxo clusters of the type $M_6O_4(OH)_4(OOCR)_{12}$ (M = Zr or Hf).

First, we introduce surfactant-assisted synthesis of colloidal nanocrystals and elaborate on the chemical mechanism of the synthesis of zirconium and hafnium oxide nanocrystals. Using Pair Distribution Function (PDF) analysis in solution, we find that an amorphous phase precedes the crystalline nanoparticles.[1]

Using the same ligands as for nanocrystals, we synthesize oxo cluster with the high solubility. The results objects are amorphous and yet, we can analyze their structure using PDF analysis, see Figure 1.[2]

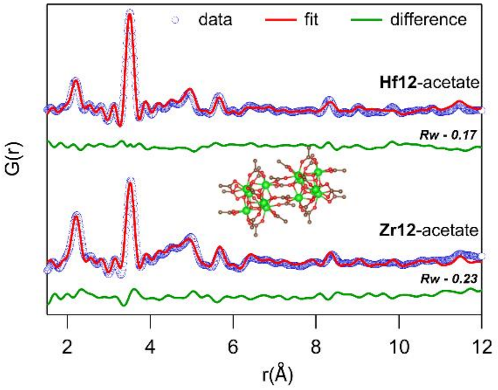

Figure 1. PDF refinement of oxo clusters.

[1] Pokratath, R, … De Roo, J., *ACS Nano.* **17** (2023) 8796.
[2] Van den Eynden, D, … De Roo, J. *Chemical Science.* **14** (2023) 573.

I09 - Investigation of Oxide Glass-(Ceramics) Employing Impedance Spectroscopy

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Solid state impedance spectroscopy (SS-IS) is a powerful, non-destructive, fast and easy-to-implement technique for studying electrical and dielectric properties of diverse materials. The overall electrical response of a material-electrode system encompasses a range of frequency-dependent microscopic processes occurring within the material itself, such as ion and/or electron transport and polarization. It also involves phenomena taking place at the interface between the material and the electrode, including charge carrier transitions and accumulation depending on the electrode type. As a result, IS finds applications across a wide spectrum of materials, spanning from ionic and mixed ionic-electronic conductors, and semiconductors, to dielectrics and insulators. By combining IS with structural-thermal characterization, we can deepen our understanding of the electrical transport in these complex materials, enabling their utilization in novel applications.

In this talk, the application of SS-IS will be illustrated through a series of case studies on various materials under different conditions with a particular focus on phosphate-based glass-(ceramics) systems with different conduction mechanisms. Systems that incorporate both mobile alkali ions and transition metal (TM) ions, such as V, Nb, Mo, W, and Fe, have been demonstrated to be highly effective as electrode materials in solid-state batteries. A further advantage is that these TMs are known to be highly selective and active catalysts in oxidation processes, rendering such conductive glasses-(ceramics) materials as good candidates for catalysis which opens up new possibilities for the application of TM-containing glassy and glass-ceramic materials.

I10 - Molecular magnets with single-electron bond between rare-earth metals

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Encapsulation of magnetic species within robust molecular containers is a natural route towards stable and processable single molecule magnets (SMMs). Air-stability, thermal stability, ability to form thin molecular layers on different substrates are among the critical issues to be addressed. Chemical and thermal stability of fullerenes makes them perfectly suitable for this goal. When fullerenes encapsulate two rare-earth metal atoms, the latter can form single-electron metal-metal bond, resulting in peculiar magnetic properties,[1] such as giant exchange coupling or very broad magnetic hysteresis. In this contribution we will overview the studies of such molecular magnets by EPR spectroscopy and magnetometry and discuss their deposition on various substrates and magnetic properties of monolayers.[2,3]

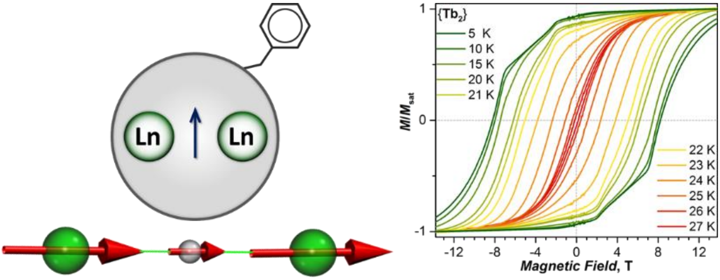

Figure 1 Molecular structure, coupling of magnetic moment, and magnetic hysteresis of $Tb_2@C_{80}(CH_2Ph)$ with single-electron Tb–Tb bond.

[1] Liu, F.; Spree, L.; Krylov, D. S.; Velkos, G.; Avdoshenko, S. M.; Popov, A. A., *Acc. Chem. Res.* **52** (2019) 2981

[2] Spree, L.; Liu, F.; Neu, V.; Rosenkranz, M.; Velkos, G.; Wang, Y.; Schiemenz, S.; Dreiser, J.; Gargiani, P.; Valvidares, M.; Chen, C.-H.; Büchner, B.; Avdoshenko, S. M.; Popov, A. A., *Adv. Funct. Mater.* **31** (2021) 2105516.

[3] Paschke, F.; Birk, T.; Enenkel, V.; Liu, F.; Romankov, V.; Dreiser, J.; Popov, A. A.; Fonin, M., *Adv. Mater.* **33** (2021) 2102844.

I11 - Spin liquids on the triangular spin lattice

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A quantum spin liquid (QSL) is an intriguing magnetic state of matter that is highly quantum entangled, yet it remains magnetically disorder even at zero temperature. In recent years, this state has been experimentally observed in a variety of geometrically frustrated materials, including the two-dimensional triangular spin lattice. For this lattice, however, perturbations away from the isotropic Heisenberg exchange are required to yield a QSL ground state.

Using a variety of complementary experimental techniques, we have recently discovered such a case in a novel rare-earth (RE) based triangular antiferromagnet neodymium heptatantalate, $NdTa_7O_{19}$, in which magnetic anisotropy is very large [1]. Contrary to other examples of QSLs on the triangular lattice, this state is characterized by sizable Ising-like spin correlations (Figure 1).

As the magnetic anisotropy in REs is strongly ion specific, RE-based heptatantalates provide a new generic framework for quantum disordered phases. Parallels will be drawn to other promising members of the family.

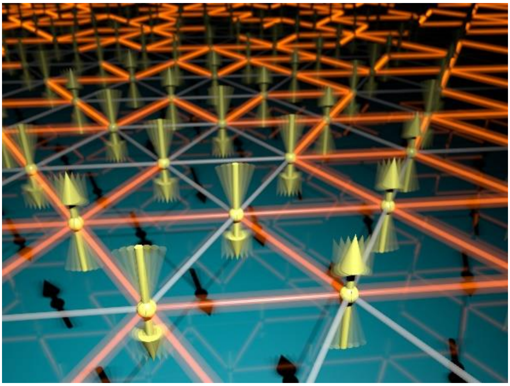

Figure 1 Visualization of the QSL state of spins (arrows) on the triangular lattice in $NdTa_7O_{19}$, where glowing bonds represent nearest-neighbor Ising correlations.

[1] T. Arh et al., *Nat. Mater.* **21** (2022) 416.

I12 - Synthesis, crystal growth, and characterisation of frustrated magnets and other quantum materials

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Most magnetic materials exhibit long-range magnetic ordering at low temperatures. However, in geometrically frustrated magnets, the topology of the lattice hinders long-range magnetic ordering down to temperatures near absolute zero, leading to competing exotic ground states such as spin glasses or spin liquids. In the first part of the talk, some geometrically frustrated compounds with K_2NiF_4 structure are presented and their synthesis, crystal growth, and magnetic properties are discussed [1–4].

The quasi-two-dimensional quantum antiferromagnet $SrCu_2(BO_3)_2$ represents the first realisation of the Shastry-Sutherland model for orthogonally interacting $S = 1/2$ dimers and serves as an important test case for understanding quantum magnetism [5]. The second part of the talk focuses on the synthesis and crystal growth of doped-$SrCu_2(BO_3)_2$ and describes the effects that different dopants have on its magnetic properties.

Due to its $4d^9$ electronic configuration and $S = 1/2$, materials based on Ag^{2+} have been considered as promising analogues to superconducting cuprates [6]. However, the chemistry of Ag^{2+} is slow to develop due to its extreme reactivity and sensitivity to moisture. The last part of the talk discusses our recent efforts to extend the chemistry of Ag^{2+} by developing new synthetic techniques which enables the exploration of new magnetic phases.

[1] M. Dragomir, P. A. Dube, I. Arčon, *et al. Chem. Mater.* **31** (2019) 7833.
[2] M. Dragomir, I. Arčon, P. A. Dube, *et al*. *Phys. Rev. Mater.* **5** (2021) 074403.
[3] B. Michon, C. Girod, S. Badoux, *et al.*, *Nature* **567** (2019) 218.
[4] M. Dragomir, Q. Ma, J. P. Clancy, *et al. Phys. Rev. Mater*. **4** (2020) 114801.
[5] Z. Shi, W. Steinhardt, D. Graf, *et al. Nat. Commun*. **10** (2019) 2439.
[6] J. Gawraczyński, D. Kurzydłowski, R. A. Ewings, *et al*. *Proc. Natl. Acad. Sci. U.S.A*., **116**, 1495.

I13 - Entropy chase in 5d^1 double perovskites

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A family of double perovskites comprises a very broad range of compounds, displaying a variety of properties and raising interest from physicists, chemists, and applied scientists. In this talk I will focus on our recent work on 5d^1 compounds, with an emphasis on Ba_2MgReO_6. Here, the magnetism arises from a single electron occupying t_{2g} orbitals under the influence of strong spin-orbit coupling, resulting in the ground state quartet. Thermodynamic measurements reveal two features, and from resonant x-ray scattering (REXS) it is possible to associate them with long-range order of magnetic dipoles developing below 18 K and charge quadrupoles below 31 K. On the other hand, careful specific heat studies reveal that in the range 2-50 K recovered entropy reaches only Rln2, indicating a doublet as a ground state. Contrary to the predominant view, we show evidence of a persisting doublet-doublet gap revealed by resonant inelastic x-ray scattering (RIXS). The puzzle of the ground-state degeneracy and its relation to the observed quadrupolar order can be resolved by invoking a dynamical Jahn-Teller distortion of ReO_6 octahedra, unscathed by both transitions, and eventually freezing out only below 1 K. This implies a novel environment for magnetic dipoles and charge quadrupoles, in which their interaction through intermediate oxygen ions is strongly renormalized due to a varying p-p orbital overlap. Our results will have a direct impact onto the understanding of double perovskite compounds in which strong covalent bonds with ligands are formed on a single site.

Junior invited lectures

JI1 - Overview of ferrocene peptidomimetics – conformational analysis, DFT study and solid state

Monika Kovačević,[1] *Ivan Kodrin,*[2] *Sunčica Roca,*[3] *Krešimir Molčanov* [3] *and Lidija Barišić* [1]

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The biological activity, conformational stability, and therapeutic application of peptides depend on their secondary structure. Therefore, the main goal in the design and preparation of synthetic peptides is to nucleate the formation of secondary structure elements. It has been shown that various ferrocene templates, when incorporated into peptides, induce the formation of hydrogen bonds, which allows the formation of turn- and β-sheet-like structures [1,2].

Here, we provide an overview of hydrogen-bonding patterns in ferrocene peptides based on detailed spectroscopic, DFT and crystallographic analyses.

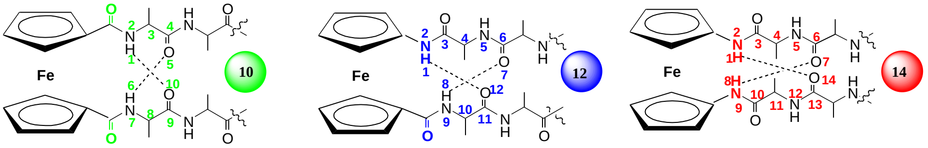

Figure 1. Types of ferrocene peptides

[1] Kovačević, M.; Kordin, I.; Roca, S.; Molčanov, K.; Shen, Y.; Adhikari, B.; Kraatz, H.-B.; Barišić, L. *Chem. Eur. J.*, **2017**, *23*, 10372.

[2] Kovačević, M.; Markulin, D.; Zelenika, M.; Marjanović, M.; Lovrić, M.; Polančec, D.; Ivančić, M.; Mrvčić, J.; Molčanov, K.; Milašinović, V.; Roca, S.; Kodrin, I.; Barišić, L. *Int. J. Mol. Sci.*, **2022**, 23, 12233.

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JI2 - Macro-karyotype model for tumor evolution

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Most tumors have abnormal number of chromosomes, which arise from mistakes during mitotic division and evolve through numerous complex mechanisms, including chromosome missegregation, cell proliferation and apoptosis (Figure 1). However, the mechanisms leading to tumor evolution from healthy cells remain unclear. Here we show, by introducing a "macro-karyotype model", that perturbed number of chromosomes in tumor cells arises predominantly from faster division of cells characterized by a specific combination of chromosomes, or together with irregular cell death [1]. This finding, strengthened by comparison of our theory with experimentally observed combination of chromosomes in different stages of tumor development, gives a direction for future experiments in identifying the key processes underlying tumor development.

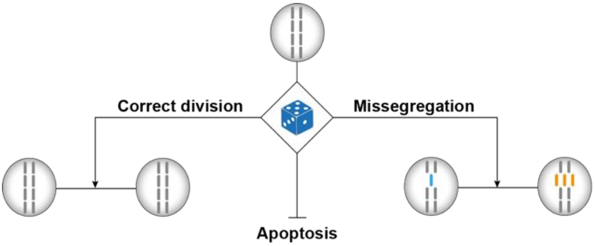

Figure 1 Processes included in our model.

[1] Ban I, Tomašić L, Trakala M, Tolić IM, Pavin N. *Biophys J*. **122** (2023) 632.

JI3 - Direct *in situ* measurement of polymorphic transition temperatures in thermo-mechanochemical reactions

J. Alić,[1] *M. Etter,*[2] *M. Rubčić,*[3] *Z. Štefanić,*[1] *M. Šekutor,*[1] *K. Užarević,*[1] *T. Stolar*[1]
[1]Ruđer Bošković Institute, Zagreb
[2] Deutsches Elektronen-Synchrotron (DESY), Hamburg
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Mechanochemistry is known for its efficiency and sustainability in polymorph screening [1]. Here we present the methodology for measuring polymorphic transition temperatures in thermo-mechanochemical reactions by *in situ* synchrotron powder X-ray diffraction and thermal monitoring [2]. We detected the onset and completion of the thermo-mechanochemical polymorphic transition temperature in mechanosynthesized 1-adamantyl-1-diamantyl ether [3], which is 27 °C lower than the corresponding differential scanning calorimetry transition temperature.

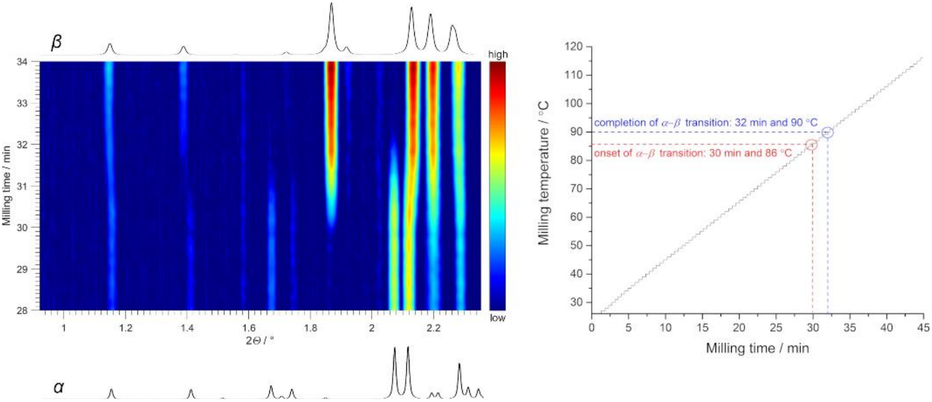

Figure 1. *In situ* monitoring of variable temperature ball milling of 1-adamantyl-1-diamantyl ether by synchrotron PXRD (λ = 0.207316 Å).

[1] T. Stolar, J. Alić, I. Lončarić, M. Etter, D. Jung, O. K. Farha, I. Đilović, E. Meštrović, K. Užarević, *CrystEngComm* **24** (2022) 6505.
[2] N. Cindro, M. Tireli, B. Karadeniz, T. Mrla, K. Užarević, *ACS Sustainable Chem. Eng*. **7** (2019) 16301.
[3] J. Alić, T. Stolar, Z. Štefanić, K. Užarević, M. Šekutor, *ACS Sustainable Chem. Eng.* **11** (2023) 617.

JI4 - Resist-free micropatterning of oriented MOF films with anisotropic optical properties

M. de J. Velásquez-Hernández,[1] M. Linares-Moreau,[1] L. A. Brandner,[1] B. Marmiroli,[2] R. Ameloot,[3] C. Doonan,[4] P. Falcaro[1].
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Integrating MOFs into miniaturized devices requires: i) control over the crystals' orientation; ii) confining the MOF crystals in pre-defined areas. Herein, we combined the heteroepitaxial ceramic-to-MOF conversion approach with the mixed-linker strategy to design a resist-free patternable oriented MOF film $Cu_2[(Br_2BDC)_{0.94}(BDC)_{0.06}]_2DABCO$.[1] Integrating the brominated dicarboxylic ligand in the reticular network makes the MOF coating sensitive to X-rays, acting simultaneously as a resist and functional porous material.[2] When exposed to deep X-rays under a photomask, the MOF film undergoes chemical damage, allowing for the selective removal of the exposed areas. A fluorescent dye (BODIPY) was immobilized within the oriented pore channels of the MOF crystals. The alignment of the dye molecules within the pores engenders a switchable anisotropic fluorescent response when rotating the polarization angle of the excitation laser.

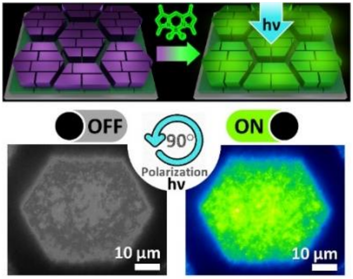

Figure 1. Oriented MOF patterns and fluorescent anisotropic response

[1] M. de J. Velásquez-Hernández, M. Linares-Moreau, R. Ameloot, C. Doonan, P. Falcaro, et al. *Adv. Mater*. (2023), 2211478.
[2] M. Tu, B. Xia, R. A. Fischer, M. de J. Velásquez-Hernández, P. Falcaro, R. Ameloot, et al. *Nat. Mater*.**20**, (2021), 20, 93.

JI5 - Cocrystals with copper(II) complexes as halogen bond donors

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Metal-organic compounds are studied in the design of halogen-bonded cocrystals [1] predominantly as halogen bond acceptors [2]. In this research, we have prepared the first known cocrystals in which imine copper(II) coordination compounds are halogen bond donors. Imines used as ligands were derived from 2,3,5,6-tetrafluoro-4-iodoaniline and salicylaldehyde – **itfasal** or *ortho*-vanillin – **itfaovan**. Synthesized complexes were cocrystallized with ditopic nitrogen-containing halogen bond acceptors: 4,4'-bipyridine (**bpy**), 1,2-bis(4-pyridyl)ethane (**bpean**) and 1,4-diazabicyclo[2.2.2]octane (**dabco**). Mechanochemical synthesis and crystallization from solution of prepared complexes with **bpean** and **dabco** resulted in 1:1 cocrystals. Crystallization from solution of complexes with **bpy** resulted in formation of dinuclear complexes with copper(II) centers bridged with **bpy** molecules, making them tetratopic halogen bond donors in cocrystals with noncoordinated **bpy** molecules. Prepared cocrystals were characterized by diffraction methods (SCXRD and PXRD). Structure analysis revealed that in all cocrystals the desired I···N halogen bond was formed between iodine atoms from metal-organic units and nitrogen atoms of acceptor molecules. Unexpectedly, cocrystals with dinuclear complexes have a high share of voids, up to 40 % of the unit cell volume.

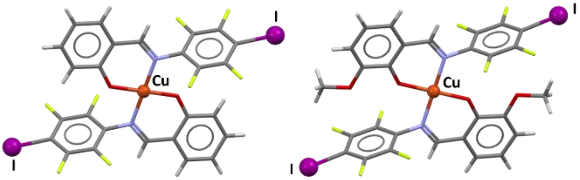

Figure 1 Halogen bond donors Cu(**itfasal**)$_2$ (left) and Cu(**itfaovan**)$_2$ (right).

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **116** (2016) 2478.
[2] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović and D. Cinčić, *CrystEngComm*, **23** (2021) 3063.

JI6 - Monometallic and bimetallic MOF-74 materials based on structural isomers as linkers

<u>K. Lisac</u>,[1]D. Mendaš,[2] V. Martinez,[1]B. Karadeniz,[1] T. Ročnik Kozmelj,[3]
I. Đilović,[4] M. Grilc,[3] E. Jasiukaitytė-Grojzdek,[3] M. Herak,[5] B. Likozar,[3] D. Žilić,[1]
K. Užarević [1]
[1]Ruđer Bošković Institute, Zagreb, Croatia, [2]Faculty of Chemical Engineering and Technology, Zagreb, Croatia, [3]National Institute of Chemistry, Ljubljana, Slovenia, [4] Faculty of Science, University of Zagreb, Zagreb, Croatia
[5] Institute of Physics, Zagreb, Croatia
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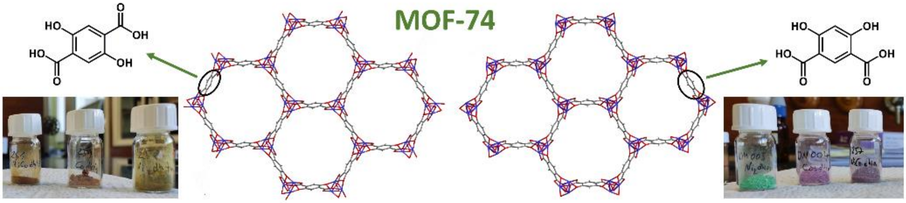
MOF-74 materials are members of the metal-organic framework (MOF) family based on 2,5-dihydroxyterephthalic acid as a linker.[1] These materials are extensively studied because of their modular design, stability, and accessibility of open metal sites. The mixed-metal MOF-74 materials are particularly interesting due to their improved magnetic and catalytic properties.[2]

Here we present a comparison of monometallic and bimetallic isostructural MOF-74 materials based on 2,5-dihydroxyterephthalic acid and its structural isomer 4,6-dihydroxyisophthalic acid as organic linkers. In this work, all MOF-74 materials studied are prepared by thermally controlled mechanochemical milling, and bimetallic MOF-74 materials are prepared by a previously presented method using specifically prepared coordination polymer precursors with 1:1 stoichiometric composition.[3] Our study shows that these two groups of isostructural materials have significantly different thermal, magnetic, and catalytic properties.



[1] N. L. Rosi et. al., *J. Am. Chem. Soc.* **127** (2005) 1504.
[2] T. Stolar et al., *ACS Appl. Mater. Interfaces* **13** (2021) 3070.
[3] G. Ayoub et.al., *Chem. Mater.* **31** (2019) 5494.

JI7 - Probing the electronic properties of titanates with NMR and ESR

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Nuclear magnetic resonance (NMR) and electron spin resonance (ESR) are powerful local probes. We will show how these techniques can be used to explore the electronic properties of two distinct titanate families – the insulating rare-earth (Ti^{3+}) titanates and the low carrier density metal (Ti^{4+}) $SrTiO_3$. The rare-earth titanates exhibit an interesting interplay between spin, orbital and lattice degrees of freedom. Their magnetic ground state can be easily manipulated through chemical substitution or external stain which influence subtle lattice distortions. Our measurements find a small orbital gap that is closely connected to the ferromagnetic ground state [1]. On the other hand, the electron-doped strontium titanate is a peculiar metal and superconductor due to extremely low densities of high-mobility carriers and the proximity to a ferroelectric quantum- critical point. We will present a $^{47,49}Ti$ NMR magnetic resonance study across the temperature-doping phase diagram of Nb- and oxygen-vacancy-doped $SrTiO_3$ which provide insight into the local electronic spin susceptibility.

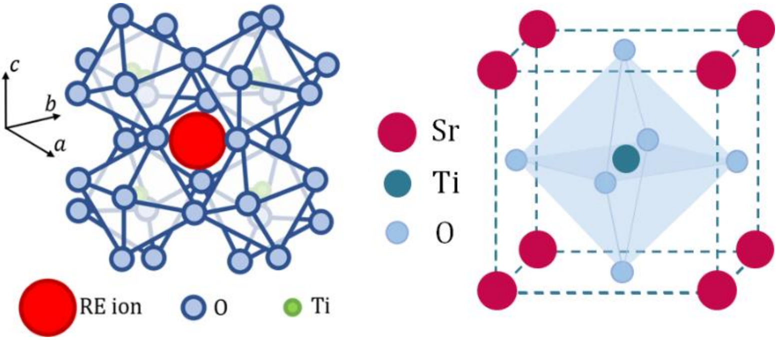

Figure 1 Structure of rare-earth titanates (left) and $SrTiO_3$ (right).

[1] A. Najev, *et al.*, arxiv:2211.12387 (2022)

JI8 - Magnetism and magnetic order in layered hybrid organic-inorganic tetrahalocuprate perovskites

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In recent years, layered hybrid organic-inorganic perovskites (HOIPs) have gained a lot of attention due to their potential as multifunctional materials. The layered structure, where the inorganic metal halide layers are separated by organic cations, offers a great freedom in the selection of its components and thus in the selection of desired properties, such as magnetic, ferroelectric, semiconducting, photonic, and multiferroic properties.[1]

In this talk, I will concentrate on the magnetic properties of series of HOIP tetrahalocuprates and give the overview of the open questions found in this field such as the origin of the observed magnetic long-range order, mechanism responsible for the ferroelectric ordering and the possibility of magneto-electric coupling.

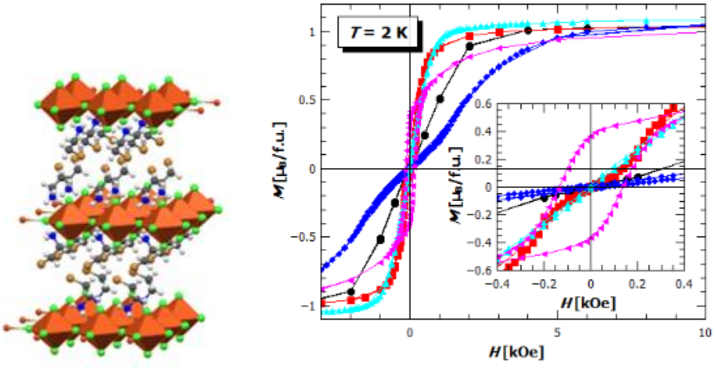

Figure 1 Left: The crystal structure of 2-bromoethylammonium tetrachlorocuprate(II). Right: Magnetization of a series of haloethylammonium tetrahalocuprates.

[1] D. Bossini et al, *J. Phys. D: Appl. Phys.* **56** (2023) 273001

Oral presentations

O1 - Mechanochemistry as Tool for Porous Organic Polymer Synthesis

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Porous organic polymers have gained considerable interest due to their flexibility, ductility, and the ability to incorporate various organic functional groups, which results in a great tunability of the material. The syntheses of porous organic polymers are based on several reaction types, such as cross-coupling reactions or oxidative polymerizations. However, these usually wet chemical syntheses suffer from the low solubility of large precursor and the use of hazardous solvents. To overcome these drawbacks and reduce the amount of waste to a minimum, their syntheses were transferred to mechanochemical approaches. The mechanochemical Scholl reaction is a great example for a solvent-free approach towards microporous material[1] and the mechanochemical Friedel-Crafts polymerization is a versatile tool to gain covalent triazine networks,[2] or porous polymers with different degrees of cross-linking.[3] This contribution highlights the great potential of mechanochemical reactions for porous organic polymer synthesis.

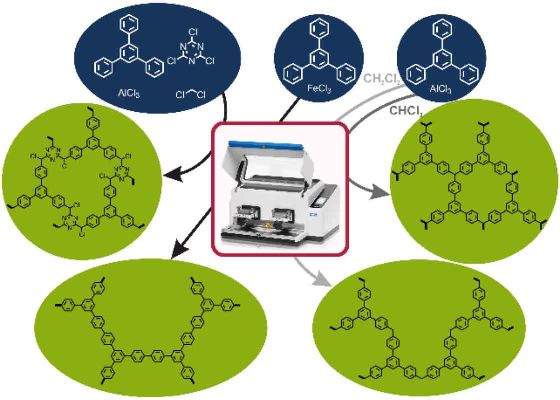

Figure 1: Examples of mechanochemical synthesized porous organic polymers.

[1] A. Krusenbaum, S. Grätz, S. Bimmermann, S. Hutsch, L. Borchardt, *RSC Adv.* **10** (2020) 25509.
[2] A. Krusenbaum, F. J. L. Kraus, S. Hutsch, S. Grätz, M. V. Höfler, T. Gutmann, L. Borchardt, *Adv. Sustainable Syst.* **7** (2023) 2200477.
[3] A. Krusenbaum, J. Geisler, F. J. L. Kraus, S. Grätz, M. V. Höfler, T. Gutmann, L. Borchardt, *J. Polym. Sci.* **60** (2022) 62.

O2 - Mechanochemical preparation of Ruddlesden-Popper type perovskites

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Understanding mechanistic details of mechanochemical processes enables the optimization of preparational procedures and conditions leading to various important classes of materials. Here, a series of liquid-assisted ball milling reactions leading to Ruddlesden-Popper type perovskites $MCuCl_{4-x}Br_x$ (M = Rb, Cs),[1] monitored *in operando* by synchrotron PXRD will be presented. The results show that the added liquids usually catalyze perovskite formation through a common, unidentified intermediate. However, adding specific strongly interacting liquids leads to stable or metastable solvates, which inhibit or even terminate the perovskite formation. This, in turn, indicates that the role of liquids is not general for all types of systems. Reaction profiles and kinetics, extracted from experimental data supported by computational simulations, will shed more light on the specific role of liquids in inorganic mechanochemical reactions, which has not been widely explored since.

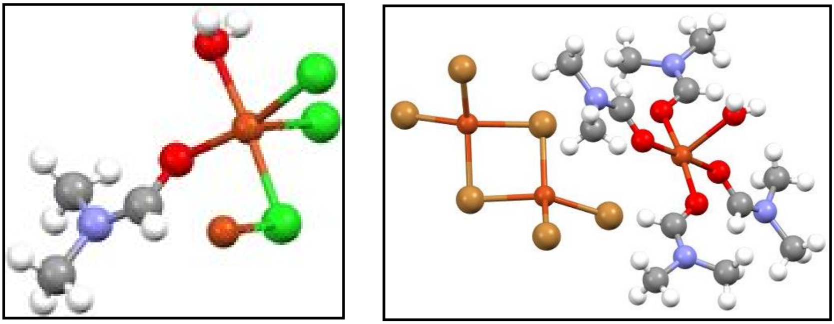

Figure 1 Solvate of $CuCl_2$ and $CuBr_2$ with DMF.

[1] Kundu et al. *J. Phys. Chem. C* **125** (2021) 4720.

O3 - Plasmon in topological nodal line semimetal

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Topological nodal line semimetals (NLSMs) that have been intensively studied lately are three-dimensional materials with linear Dirac electron energy bands crossing at dispersive nodal lines [1]. We investigated the plasmon collective mode of a dispersive topological nodal line semimetal with two-dimensional Dirac electron energy bands and the long range three-dimensional Coulomb electron–electron interaction within the random phase approximation (RPA) [2]. We analyzed the effect of the interband electron–hole excitations on the plasmon mode by evaluating the energy-loss function. Our calculations showed that the plasmon mode was optical, strongly anisotropic and hardly damped as it entered into the interband electron–hole continuum. The obtained results for the plasmon mode are consistent with earlier experimental and theoretical results for these materials [3,4].

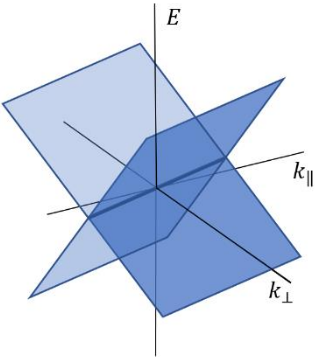

Figure 1 Electron energy bands.

[1] A. Burkov, M. Hook, L. Balents, *Phys. Rev. B*. **84** (2011) 235126.
[2] Ž. Bonačić Lošić, *Can. J. Phys.* **100** (2022) 303.
[3] M. B. Schilling, L. M. Schoop, B. V. Lotsch, M. Dressel, A. V. Pronin, *Phys. Rev. Lett.* **119** (2017) 187401.
[4] W. Zhou, A. N. Rudenko, S. Yuan, *Adv. Electron. Mater.* **6** (2020) 1900860.

O4 - Exploring the Effects of Disorder and Metastability in Insulating Thin-Film Manganites

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Z. Jagličič,[3,4] D. Rivas Góngora,[2] S. Tomić,[2] A. Hamzić,[2] F. Fischgrabe,[5]
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[2]Institut za fiziku, Zagreb, Croatia
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Manganites have been extensively researched for their colossal magnetoresistance, which results from the competition between the ferromagnetic metallic phase and the paramagnetic insulating and antiferromagnetic charge-ordered insulating phases. While the metallic phase is well understood, the insulating behavior in manganites remains a subject of active investigation.

This study focuses on investigating the dc resistivity and magnetization of thin-film $La_{1-x}Ca_xMnO_3$ samples in the antiferromagnetic charge-ordered insulating region of the phase diagram ($0.5 \leq x \leq 0.75$) at low temperatures and magnetic fields up to 16 T. We observed a remarkable impact of the applied magnetic field which suppreses the charge-order transition and the variable range hopping mechanism. Notably, an extremely high colossal magnetoresistance value of $8 \cdot 10^{11}\%$ was found for $x=0.58$. We also observed history-dependent relaxations that occur over extremely long timescales.

These phenomena are interpreted in the relatively new picture of electron localization in the presence of disorder and strong interactions. We find that nanoscale phase separation plays a crucial role in manganites, where ferromagnetic metal clusters emerge in the background of the charge-ordered/antiferromagnetic state. This study sheds light on the complex insulating behavior of manganites and may offer a possible route towards potential applications of thin-film $La_{1-x}Ca_xMnO_3$ in magnetoelectric devices.

O5 - Novel electronic materials on the verge of metallicity and ionicity

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[2]Laboratory for Quantum Magnetism, EPFL, Switzerland
[3]Laboratory of Physics of Complex Matter, EPFL, Switzerland
[4]Department of Physics, University of Fribourg, Switzerland
[5]Institute for Solid State Physics, TU Wien, Austria
[6]Institute Ruđer Bošković, Zagreb, Croatia

Cuprates and pnictides are two intensively investigated families of functional materials that are on the verge of ionicity and metalicity. Both families display a wide range of surprising behaviors, each one characterized by a different ordering tendency. Among them, high-temperature superconductivity is perhaps the most exciting and mysterious one. A constructive way to improve understanding of this phenomenon is to synthesize and investigate a new system, which displays superior crystallochemical flexibility and tunability of the valence of the transition metal ions.

I will discuss murunskite-based compounds, which interpolate between cuprates and pnictides[1]. A successful growth and characterization of the first-ever high-quality murunskite ($K_2FeCu_3S_4$) single crystals will be presented. This compound shows semiconducting behaviour in resistivity and optical transmittance, while magnetic susceptibility reveals antiferromagnetic ordering around 100 K. Spectroscopy (XPS) and Density Functional Theory (DFT) calculations concur that the sulfur 3*p* orbitals are partially open, making them accessible for charge manipulation, which is a prerequisite for superconductivity in analogy with cuprates and pnictides. Furthermore, DFT indicates that the valence band is more cuprate-like, while the conduction band is more pnictide-like. We also managed to synthesize single crystals of several chemically substituted compounds (e.g., Se,Te for S), whose transport and optical conductivity measurements will be discussed in the presentation.

[1]D.Tolj, et al, Applied Materials Today, Volume 24, 101096, (**2021)**.

O6 - Quantum vortex liquid in iron-based superconductors $FeSe_{1-x}S_x$ and $FeSe_{1-x}Te_x$

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[1]Institut za fiziku, Zagreb
[2]High-Field Magnet Laboratory (HFML-EMFL) and Institute for Molecules and Materials, Radboud University, Nijmegen
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One of the most exciting phenomena in condensed matter physics is superconductivity – the ability of a material to conduct an electric current with zero resistance and to completely expell an external magnetic field from its interior. Many such superconducting (SC) materials, besides this 'pure' SC state, posses also a mixed state, in which a material still has zero resistance, but a magnetic field partially penetrates into its interior. The area where the field enters the material is divided into separated thin tubes, at the edge of which a circular SC current flows and creates a quantized magnetic flux - magnetic vortices. Interestingly, these vortices are not randomly distributed within the material, but usually form a regular triangular lattice, known as Abrikosov lattice. In some cases the vortex lattice can be melted by strong thermal fluctuations, giving rise to an emergence of a vortex liquid, which no longer has zero resistance. Here we report our recent magnetoresistance study on iron-based superconductors $FeSe_{1-x}S_x$ and $FeSe_{1-x}Te_x$, which indicates the presence of such a vortex liquid regime even at extremely low temperatures, where only quantum fluctuations are at play [1]. Such behavior points towards the existence of a quantum vortex liquid, a very rare state that has until now been reported only in a few materials.

[1] M. Čulo, S. Licciardello, K. Ishida, K. Mukasa, J. Ayres, J. Buhot, Y.-T. Hsu, S. Imajo, M. W. Qiu, M. Saito, Y. Uezono, T. Otsuka, T. Watanabe, K. Kindo, T. Shibauchi, S. Kasahara, Y. Matsuda, and N. E. Hussey, under revision in *Nat. Commun.* (2023).

O7 - Thermomechanical Properties of Molecular Crystals from Machine Learning Potentials

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Molecular crystals are a common and important class of crystalline materials. However, modeling molecular crystals based on first principles (eg. with density functional theory) is often difficult due to the size of a typical unit cell. Therefore, high-throughput calculations for the discovery of useful properties are rare. Mechanical and thermal properties are even harder to model correctly as a standard harmonic approximation is often not accurate enough. In this presentation, we will show how machine-learned interatomic potentials can enable accurate and fast calculations of mechanical and thermal properties of molecular crystals enabling a high-throughput search for materials with the desired properties. In principle, to train machine learning potential one would need to create a sufficiently large database of molecular crystals calculated with the desired accuracy. This is also a very challenging task and we will show how to avoid this step using transfer learning and existing databases of small systems.

O8 - Base-pairing of uracil and 2,6-diaminopurine: from cocrystals to photoreactivity

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In a combined experimental and computational study, we have investigated the base-pairing of two nucleobases: the non-canonical 2,6-diaminopurine (D) and the RNA component uracil (U). Depending on the temperature and water availability in the system, D and U assemble in thermodynamically stable hydrated and anhydrated D-U base-paired cocrystals. Density functional theory (DFT) simulations were performed to assist the structural analysis. We observe that the water molecules contribute favorably to the stabilization energies in D-U cocrystal hydrate by inter-layer hydrogen bonds, while in the anhydrate cocrystal form, D and U molecules exhibit advantageous homomeric stacking interactions and hydrogen bonding. Under UV irradiation, an aqueous solution of D-U base-pair undergoes photochemical degradation, while a pure aqueous solution of U does not, thus demonstrating that base-pairing alters the photostability of U. To understand this decreased photostability of U, we combine computational techniques to model the main channel for U photodestruction, i.e., covalent photodimerization. Our simulations suggest that D may trigger the U photodimerization because of its ability to form hydrogen bonds with π-stacking dimers of U. Besides achieving this example of bio-material engineering, we show how supramolecular interactions between small biological building blocks affect photo-reactivity, as well as how molecular recognition of nucleobases may have played a role in chemical evolution.

[1] “Prebiotic base-pairing of uracil and 2,6-diaminopurine” T. Stolar, B. K. D. Pearce, M. Etter, K.-N. Nghi Truong, A. Krajnc, G. Mali, B. Rossi, K. Molčanov, I. Lončarić, E. Meštrović, K. Užarević, and L. Grisanti, *submitted*

O9 - Polymerization of aromatic C-nitroso derivatives on Au(111) surface: ellipsometry, AFM and nano-FTIR study

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Compounds with multiple aromatic nitroso groups can interact to form polymeric azodioxides. The simplest such compound is 1,4-dinitrosobenzene which polymerizes into a very stable one-dimensional (1D) polymer, classified as a potential wide-bandgap organic semiconductor [1]. The polymerization property of aromatic dinitroso compounds could be used to design azodioxy thin films on metal surfaces. We investigated the polymerization of various aromatic dinitroso compounds initiated by nitroso-terminated monolayer on Au(111) surface [2] by ellipsometry, atomic force microscopy (AFM) and nano-FTIR spectroscopy. The obtained results indicated the formation of azodioxy oligomer films and a greater tendency towards oligomerization with a longer adsorption time [3]. In addition to providing important new insights into surface-initiated interactions of aromatic C-nitroso compounds, this study also demonstrated the high sensitivity of nano-FTIR spectroscopy for the chemical identification of very thin films (Figure 1).

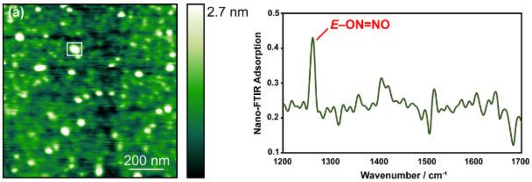

Figure 1 Topography image and nano-FTIR spectra of azodioxy oligomer film.

This work has been fully supported by Croatian Science Foundation under the project IP-2020-02-4467.

[1] L. Matasović, B. Panić, M. Bubaš, H. Vančik, I. Biljan and I. Rončević, *J. Mater. Chem. C* **10** (2022) 5433.
[2] B. Panić, M. Koprivnjak, T. Marić, K. Majerová Varga, I. Biljan, *Colloid Interface Sci. Commun.* **45** (2021) 100539.
[3] L. Nuić, B. Panić, L. K. Pereković, I. Šrut Rakić, M. Kralj, A. Mihanović, H. Vančik, I. Biljan, *Polymer* **271** (2023) 125795.

O10 - Extending the scope of protein encapsulation into ZIFs

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Among different metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs, synthesized from Zn^{2+} and 2-methylimidazole (HmIM)) are of interest for the encapsulation of enzymes since the synthesis can be carried out in biocompatible conditions.[1] This biocompatible process is called biomimetic mineralization: the metal ions accumulate on the enzyme surface and facilitate the MOF growth.[1] This means that the process can proceed only for enzymes that are negatively charged in the reaction environment.[2] This limitation can be overcome via the use of time consuming and cumbersome enzyme surface functionalization protocols.[2] Here, we report the successful encapsulation of positively charged enzymes into ZIFs via the addition of co-precipitating agents (like PVP [3] or BSA) or by adjusting the pH of the reaction. In situ small angle X-ray scattering studies were performed to investigate the different effect of these protocols on the mechanism of ZIF biocomposites formation. These new, fast and easy protocols broaden the field of application of ZIFs, since the encapsulation process can be easily achieved with both negatively and positively charged enzymes.

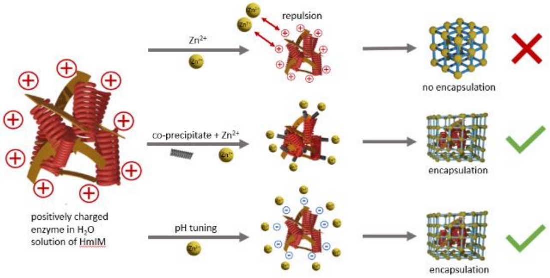

Figure 1: schematic of the strategies investigated to enable the encapsulation of positively charged proteins into ZIFs.

[1] K. Liang, R. Ricco, C. M. Doherty et al., Nat. Commun. **6** (2015), 7240.
[2] N. K. Maddigan, A. Tarzia, D. M. Huang et al., Chem. Sci. **9** (2018), 4217.
[3] K. Liang, C. J. Coghlan, S. G. Bell et al., Chem. Commun. **52** (2016), 473.

O11 - Lignin-based covalent adaptable networks (CANs): a possible replacement for fossil-based thermosets

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Thermoset polymers offer high strength and durability however, they have limited recyclability. In contrast, thermoplastics are more flexible and have greater recyclability, but they may lack strength and durability. Thus, covalent adaptable networks (CANs) emerged as interesting approach to develop reprocessable thermosets [1]. CANs possess both covalent and non-covalent bonds in their network structure, providing stability, strength and recyclability. Using lignin and its building blocks to develop bio-based CANs is an attractive option due to lignin's renewable and abundant character. Among the mostly widely studied examples of lignin building blocks are vanillin, eugenol and syringaldehyde. Hence, this work focuses on the use of vanillin and syringaldehyde to develop lignin-based CANs. The diversity of this work lies on the fact that imine [2] and acyl hydrazone bonds are built on vanillin structure and incorporated in the final structure of thermosets, allowing its recyclability at the end of its life.

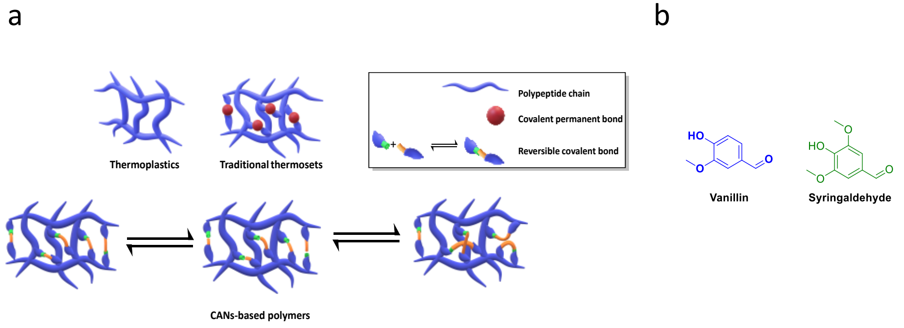

Figure 1. Reversibility of CANs bonds (a). Vanillin and syringaldehyde (b).

[1] Kloxin, C.J.; Bowman, C.N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev*. 2013, 42, 7161–7173, doi:10.1039/C3CS60046G.
[2] Lei, Y.; Zhang, A.; Lin, Y. *Polym. Chem*. 2021, **12**, 4052–4062, doi:10.1039/D1PY00623A.

O12 - From thin film deposition to composite materials of switchable coordination compound

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Bistable molecular materials with switchable properties are good candidates for developing technological applications such as sensors for information storage. The incorporation of magnetic molecular materials into real electronic devices requires some fabrication methodology of robust devices that can be handled and integrated without compromising their functionality.

Our work at first aimed to prepare thin films of a multi-responsive CN-bridged network (Figure 1), which undergoes electron transfer in response to various stimuli and shows room temperature multi-stability [1]. However, coordination assemblies as such in the crystalline form are usually brittle, easily breakable and show poor surface stability. To resolve the following problem we prepared composite material, in which particles of coordination system are embedded into an organic polymer matrix. By employing the electrospinning method we developed robust switchable material with more favourable mechanical properties and this way widening the applicational potential of molecule-based sensors.

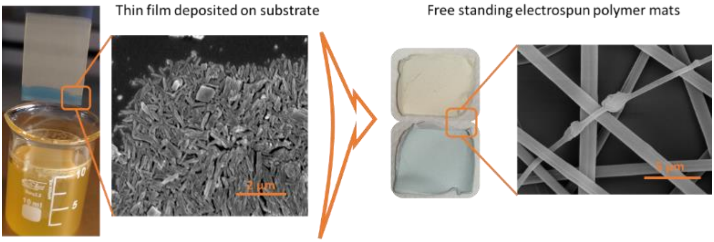

Figure 1 Macroscopic and microscopic view of the prepared thin film and electrospun mats of CN-bridged switchable network.

[1] M. Reczyński, et al., *Angew. Chem. Int. Ed.* **60** (2021) 2330.

O13 - π-hole interactions: a new playground for materials science

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π-hole interactions involving metal-bound electron donor are studied for the first time on four isomorphous co-crystals of [Cu(terpy)Cl*X*] (*X* = Br, I) and perhalogenquinone X'_4Q (*X*' = Cl, Br). Close contact between the halide *X* from [Cu(terpy)Cl*X*] and the quinoid ring has geometry similar to those observed previously for free halides [1,2]. This is an *n*→π* interaction [3] with a partial charge transfer from the halide to the quinone. Therefore, it weakens the Cu–*X* bond: in [Cu(terpy)ClI]·Cl_4Q the length of Cu–I bond is 2.844 Å, which represents an elongation of 0.18 Å.

The extreme elongation indicates charge transfer from the Cu–*X* bond to the quinone, which then has a partial semiquinoid radical character. This is corroborated by EPR spectroscopy: two signals are observed, one corresponding to Cu^{2+} cation ($g = 2.0067$), the other to a semiquinone radical ($g = 2.00263$). Degree of charge transfer between an uncoordinated iodide and Br_4Q in a previously studied system is in the range 8–11 % [3].

A weaker π-hole interaction between Cl atom of the complex and a symmetry-equivalent quinoid ring helps form π-hole-bonded chains parallel to [100]. Since the crystals grow as rods extended along the *a* axis, electrical contacts could be attached to a single crystal, allowing study of electrical properties by impedance spectroscopy. The compounds are weak semiconductors: room-temperature DC conductivity of [Cu(terpy)ClI]·Cl_4Q is 10^{-9} S cm^{-1}.

This is the first documented case of conductivity through a π-hole interaction and shows that it may find use in materials chemistry.

[1] K. Molčanov, G. Mali, J. Grdadolnik, J. Stare, V. Stilinović, B. Kojić-Prodić, *Cryst. Growth Des.* **18** (2018) 5182-5193.
[2] V. Milašinović and K. Molčanov, *CrystEngComm* **23** (2021) 8209-8214.
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O14 - On the crystal engineering of mechanically responsive crystals using facet-dependent DFT Young's moduli

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The mechanical properties of molecular crystals influence a range of bulk solid-state properties. Despite the increasing interest in the mechanical properties of molecular crystals, most of the interesting examples of elastic/plastic deformation [1] and other phenomena reported in the literature are based on empirical observations, often as a result of serendipity. While it would be desirable to use *ab initio* methods to support the discovery of such crystals, currently the most widely used modelling codes for calculating the elastic constants of crystals provide only average properties, which cannot readily be reconciled with the facet-dependent Young's moduli and hardness of crystals measured by experimentalists using the nanoindentation technique. Our group has developed a new code that interfaces with VASP and translates the DFT strain-energy data [2] into facet-dependent Young's moduli for candidate crystals at the push of a button. We have performed the largest study on charting the mechanical property landscape of molecular crystals using DFT methods. Our results indicate that in general static dispersion-corrected DFT methods are accurate to within ± 3 GPa for crystals such as amino acids that comprise very strong electrostatic intermolecular interactions, suggesting promise for the *ab initio* discovery of stiff and ultra-stiff molecular crystals. For crystals comprising weak dispersive intermolecular interactions, the accuracy of the predictions is generally poorer. Caution should be exercised when using average computed Young's moduli to infer facet-dependent properties.

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O15 - *Ab initio* prediction of structures, functional properties and solid-state reactivity of crystalline materials

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This presentation will highlight the recent developments in crystal structure prediction (CSP) of metal-organic frameworks (MOFs).[1] MOFs are renowned for exceptional diversity in functional applications, owing to the vast number of node and linker combinations, which yield materials with different crystal packing, network topology, surface properties and, ultimately, functional performance. The application of CSP to predict a series of hypergolic MOFs,[2] rapidly ignitable upon contact with an oxidizer, will be demonstrated, as the first example of using the CSP methodology to computationally design new MOF materials.

The presentation will proceed with the demonstration of how periodic density-functional theory (DFT) calculations can be used to predict the solid-state reactivity of molecular crystalline materials.[3] It will be shown that DFT calculations not only allow us to predict the thermodynamic possibility of solid-state transformations occurring, but also provide accurate values of reaction energies, as verified by the dissolution calorimetry measurements.

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[2] Y. Xu, J. M. Marrett, H. M. Titi, J. P. Darby, A. J. Morris, T. Friščić, M. Arhangelskis, *J. Am. Chem. Soc.* **145**, (2023), 3515.
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O16 - Dancing crystals - mechanically and thermally stimulated crystal movements

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An emerging number of reports describing crystals that can respond to outer stimuli with mechanical motion, consequently retaining the crystalline identity, has been observed lately.[1] With that discovery one of the greatest impediments to the incorporation of crystalline materials in advanced devices was overcome, and the path of crystal dynamics field was firmly paved. Metal-organic crystalline materials are of great interest, as metal ions in the crystal structure allow a variety of interesting properties to be achieved, such as magnetic or electric. Particularly interesting example of a responsive metal containing crystalline materials are one-dimensional coordination polymers of cadmium(II) halides with heterocyclic ligands, as they displayed a remarkable span of diverse mechanically stimulated flexible responses, from slightly to extensively elastic, elastic→plastic and extremely plastic.[2–5] All these mechanical responses could be controlled and fine-tuned by only incorporating small changes at the molecular level, which cause slight differences in the strength of intermolecular interactions that has a surprisingly large impact in achieving a certain type of mechanical output. Some of these crystals also display thermally triggered motions what makes them excellent candidates for a variety of applications in the future.

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O17 - Therapeutic Coordination Polymers (TCPs) as Controllable Drug Release Materials

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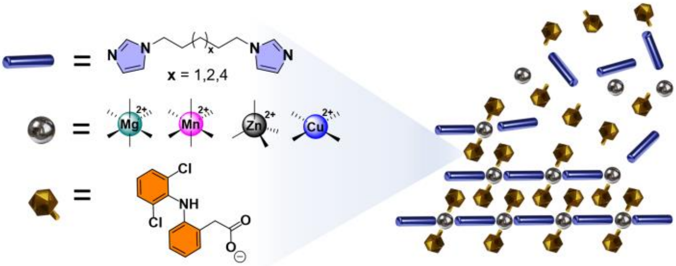
Abstract: Therapeutic Coordination Polymers (TCPs) are materials constructed from a unique combination of three principal components, i) a cationic metal center (such as Cu2+, Zn2+, Mn2+, or Mg2+), ii) an anionic pharmaceutical, such as a non-steroidal anti-inflammatory drug, and iii) alkyl bis-imidazole or bis-nicotinate organic ligands which behave as “linkers” between metal centers.[1] In this approach drug release occurs based on a controllable degradation-based mechanism for drug release. The TCPs reported have several significant advantages as controlled drug release systems, including: i) tailored drug release rates which can be modified by the choice of metal ion and organic linker with intrinsic dissolution rates spanning over three orders of magnitude, ii) a simple, scalable, one-step synthetic procedure, iii) high-drug loading between 65-70 wt. % and iv) stimuli-responsive behavior which demonstrates that TCPs can be triggered to release their payload under changes in pH or via addition of competitive metal chelators.



Scheme 1: Principal components of therapeutic coordination polymers and their degradation-based release of pharmaceuticals.

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O18 - Hydrogen-bonded organic frameworks and enzymes: a new class of biocomposites

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Enzymes can improve efficiency, selectivity, and environmental sustainability of a number of chemical syntheses. The main limitations to their widespread industrial application are their intrinsic fragility, their limited recyclability, and cumbersome products' purification. Thus, immobilization in porous solids is a strategy to enhance enzyme stability in catalysis, biomedical, and biosensing applications. In 2019, we reported the first immobilization of enzymes in Hydrogen-bonded Organic Frameworks (HOFs).[1] By adding tetra–amidinium and tetra–carboxylate tectons (BioHOF-1) in water and at room temperature, we immobilized enzymes in HOF crystals. These enzyme@HOF systems have shown superior performances in terms of protein loading capacity, wide pH range stability and protection against chemical/physical inhibitors.[2] Here, we will highlight the potential of HOF biocomposites considering aspects such as the huge variety of HOF materials and the genetic engineering of enzymes for a new generation of composites suitable for biocatalysis and biomedicine.

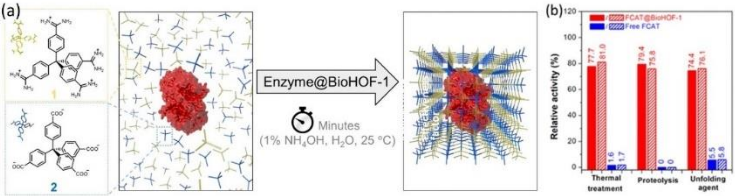

Figure 1 a) Schematic representation of the synthesis of enzyme@BioHOF-1 composites. (b) Relative activity (%) of free enzymes (FCAT) and FCAT@BioHOF-1 after exposure to chemical/physical inhibitors.

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O19 - Various strategies of synthesizing Prussian blue analogs of mixed composition into reduced dimensionality systems

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Molecular magnetic nanomaterials often combine multiple attractive properties, such as low density, high magnetic moment per unit of volume, or sensitivity to external stimuli (temperature, pressure, etc.). Although the size reduction of a final product is usually beneficial from the application point of view, synthesizing samples into a desired shape, size, and composition is often challenging.

The results for two Prussian blue analogs' families will be presented: binary systems of $Fe_4[Fe(CN)_6]_3$ and $Fe_3[Cr(CN)_6]_2$, and a series of compounds with mixed composition, $Ni_3[Fe(CN)_6]_x[Cr(CN)_6]_{2-x}$. We obtained the samples from the first group in the form of films and nanotubes by electrochemical deposition using different substrates. For the second family, we chose sequential adsorption and ion-exchange techniques to grow two different film types, and slow precipitation to create nanoparticles. We analyze the morphology of final products and present their structural, spectroscopic, and magnetic properties.

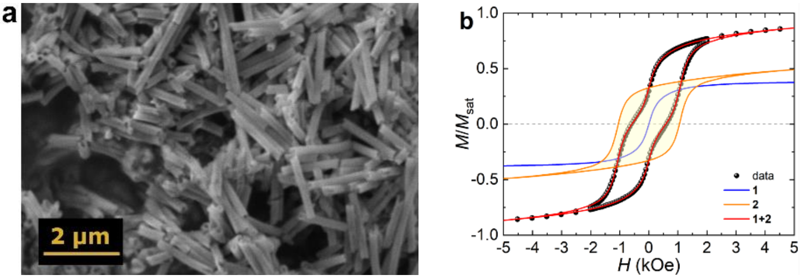

Figure 1 Double-shell nanotubes of $Fe_4[Fe(CN)_6]_3$ and $Fe_3[Cr(CN)_6]_2$: morphology (a) and magnetic hysteresis loop decomposed into base phases (b)

Acknowledgments: This work was supported by the Croatian Science Foundation (project no. HrZZ IP-2020-02-9666) and National Science Centre Poland (project no. UMO-2018/31/N/ST5/03300).

O20 - (Bi)metallic amidoboranes – synthesis, characterisation and perspective

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Monometallic and bimetallic amidoboranes are successfully prepared by mechanochemical reaction of ammonia borane (NH_3BH_3) with alkaline or alkaline earth hydrides by mechanochemistry. Here we present a new procedures for the synthesis of monometallic $NaNH_2BH_3$ [1] and bimetallic amidoboranes $M_2M'(NH_2BH_3)_4$ [2,3] (M = Li, Na; M' = Mg, Ca). They are discussed in terms of their possible utilization for hydrogen storage. Specifically, although characterized by high gravimetric and volumetric hydrogen capacity, as well as relatively low hydrogen desorption temperature, their unfavorable dehydrogenation thermodynamics prevent rehydrogenation of the products in technologically acceptable conditions.

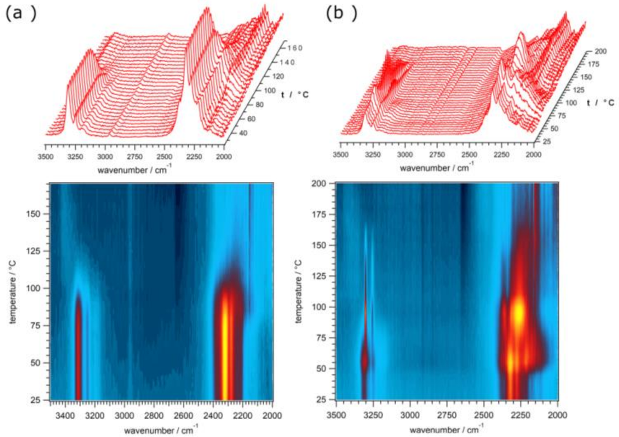

Figure 1. Temperature-dependent IR spectra of (a) $Li_2Ca(AB)_4$ and (b) $Na_2Ca(AB)_4$.

[1] I. Milanović, N. Biliškov *Int. J. Hydrogen En.* **45** (2020) 7938.
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[3] I. Milanović et al. *ACS Sustain. Chem. Eng.* **9** (2021) 2089.

O21 - Versatile usage of the complex hydride materials

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It is widely known that the traditional usage of complex hydrides is to be a reducing agent in chemical synthesis, and they attract massive attention as potential chemical hydrogen stores for on-board applications. In this contribution, we want to present other uses of this group of compounds.
Firstly, they can serve as precursors of highly-interesting refractory materials, like boron nitride or borides, upon their pyrolysis [1-3]. Secondly, borohydride systems with paramagnetic metal centres (e.g. Ln^{3+}) showed that BH_4^- anion can act as a bridge for the transfer of magnetic superexchange, similarly to familiar F^- and O^{2-} ligands [4]. Additionally, the incorporation of well-known expanded organic cations in some Ln^{3+} borohydride systems leads towards molecular nanomagnets [5], or even luminescent SMMs [6], without the use of advanced organic ligands or metalloligands. Yet, what is crucial is today's interest in using complex hydrides, especially those of light elements such as lithium, boron, nitrogen and/or carbon, considering their employment as solid-state electrolytes in Li-ion batteries [7]. Various synthesis routes will also be presented briefly [1-11].

[1] W. Wegner, K. J. Fijalkowski, W. Grochala, *Dalt. Trans.*, **49** (2020) 336.
[2] W. Wegner, T. Jaron, W. Grochala, *J. Alloys Compd*., **744** (2018) 57.
[3] R. Owarzany, K. J. Fijalkowski, T. Jaron, P. J. Leszczynski, Ł. Dobrzycki, M. K. Cyranski, W. Grochala, *Inorg. Chem*., **55** (2016) 37.
[4] W. Wegner, J. van Leusen, J. Majewski, W. Grochala, P. Kögerler, *Eur. J. Inorg. Chem*., **2019** (2019) 1776.
[5] M. Magott, W. Wegner, *Phys. Chem. Chem. Phys.*, **25** (2023) 10689.
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[11] W. Wegner, K. J. Fijalkowski, *Materials* **23** (2022) 8653.

O22 - Alkali-Metal Fluoridooxidovanadates(V)

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A Lewis acid vanadium trifluoride oxide, VOF_3, readily accepts fluoride ion(s) and forms a variety of fluoridooxidovanadate(V) anions with rich structural diversity [1–3].

In this work, reactions of VOF_3 with LiF, NaF, and KF in anhydrous HF were studied, resulting in the isolation and structural characterization of the following compounds: lithium and sodium salts of a dimeric $[V_2O_2F_8]^{2-}$ anion; potassium salts of $[VOF_4]^-$ and $[V_2O_2F_7]^-$ chain anions; as well as the complexes $[Na(HF)VOF_4]$ and $[K_9(HF)_2V_9O_9F_{36}]$ (Fig. 1) with alkali-metal coordinated by HF. In addition, the XeF_2 coordination compounds $[Li_2(XeF_2)V_2O_2F_8]$ and $[Na_2(XeF_2)V_2O_2F_8]$ were obtained from solutions of the ligand and the corresponding salt, $Li_2V_2O_2F_8$ and $Na_2V_2O_2F_8$, respectively. These complexes represent a rare example of XeF_2–Li^+ coordination and the first instance of xenon difluoride coordination to Na^+ [4].

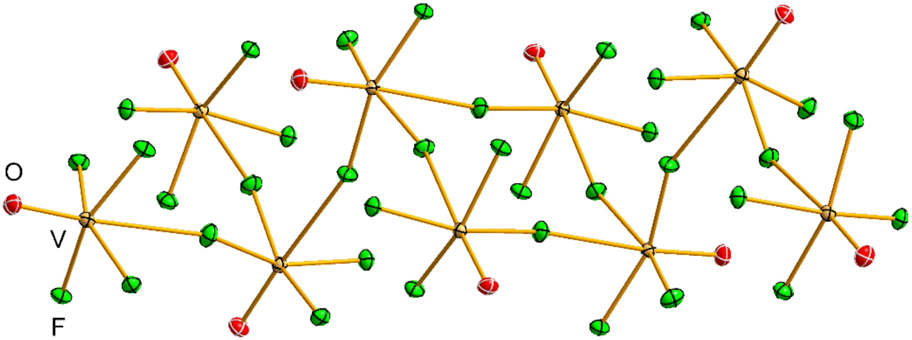

Figure 1 Large nonameric fluoridooxidovanadate(V) anion $[V_9O_9F_{36}]^{9-}$ observed in the crystal structure of $[K_9(HF)_2V_9O_9F_{36}]$ (50% probability ellipsoids).

[1] T. Kanatani, K. Matsumoto, R. Hagiwara, *Eur. J. Inorg. Chem.* (2010) 1049.
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O23 - Fabrication of 3D-oriented MOF films and patterns from oriented ceramic nanostructures

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Processing oriented metal-organic frameworks (MOFs) as thin films is a key challenge for their application to device fabrication [1]. Typical fabrication methods cannot generate precisely oriented crystals on commercially relevant scales (i.e. cm^2), which limits access to applications that require anisotropic functional properties. Recently, the fabrication of MOF films by conversion from a sacrificial ceramic template has emerged as a powerful tool to obtain MOF films with precise pore-channel orientation [1]. In particular, highly oriented Cu-MOFs can be synthesized by immersing a film of aligned $Cu(OH)_2$ nanobelts in an ethanolic solution containing organic linkers. Recently, we reported a semi-automatic method that affords a 100% yield of high-quality ceramic films, at the cm scale, for the fabrication of precisely oriented and homogenous Cu-MOF coatings [2]. Furthermore, we have demonstrated the microfabrication of 3D-oriented Cu-MOF patterns by deep X-ray lithography (DXRL, Elettra Synchrotron) [3]. By integrating a brominated dicarboxylic ligand (Br_2BDC) into Cu_2L_2DABCO (L=BDC/Br_2BDC) through a mixed-linker strategy, we achieved oriented and homogeneous films with sensitivity to radiation. The oriented crystalline micropatterns act as diffraction gratings upon illumination with a laser and display anisotropic optical properties. Such progress could facilitate the application of MOFs to molecular separators and optical devices.

[1] P. Falcaro, C.J. Doonan, M. Takahashi, et al., *Nat. Mater.* **16** (2017), 342.
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O24 - Site Selective Spin Crossover in Large Undecanuclear Cyanido-Bridged Clusters

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The intensive development of technology creates technological challenges in the miniaturisation of physical systems dedicated to the detection of specific external stimuli as well as information storage/processing. In this context particular interest in material science is focused on molecular materials, which could combine several desirable physicochemical properties to conform switchability regime and thus, to constitute the physical basis for recording, reading, and processing information [1].

The presentation will focus on results considering synthesis and physicochemical properties of large undecanuclear coordination clusters $\{Fe^{II}[Fe^{II}(bzbpen)]_6[W^{V}(CN)_8]_2[W^{IV}(CN)_8]_2{\cdot}solv\}$, representing switchable magnetic properties realized via spin crossover (SCO) phenomena stimulated by temperature or sorption/desorption of solvent [2].

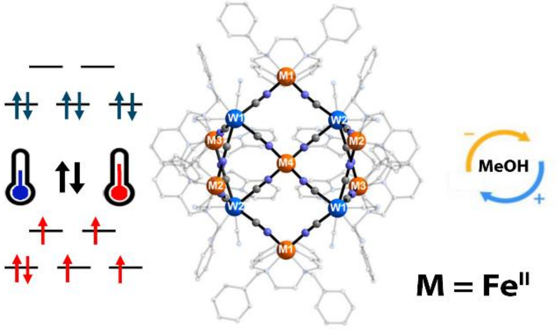

Figure 1. Coordination skeleton of $\{Fe^{II}[Fe^{II}(bzbpen)]_6[W^{V}(CN)_8]_2[W^{IV}(CN)_8]_2\}$ cluster.

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[2] L. Shi, J. Kobylarczyk, K. Dziedzic-Kocurek, J. J. Stanek, B. Sieklucka, R. Podgajny, *Inorg. Chem.* **62** (2023) 7032

Poster presentations

P01 - Influence of the movement pattern of the used milling material on the direct mechanochemical Suzuki coupling

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The application of mechanical forces to drive chemical transformations has garnered significant interest due to its potential applications in a wide range of fields.[1] However, a major drawback of this promising chemistry is the lack of information on how these mechanochemical transformations occur. Critical parameters that could affect mechanochemical reactions, such as the movement path of the milling ball, are often overlooked in typical parameter screenings. In direct mechanocatalysis, this parameter could be particularly crucial, as the reaction takes place on the surface of the milling ball - i.e., the catalyst. Therefore, we observed the flight path of milling balls at different frequencies using a high-speed camera in thin PFA vessels, with the Suzuki coupling as the model reaction.[2] By monitoring the different movement paths, we were able to identify a possible correlation between the movement path and the observed yield, which could not be explained by the frequency dependency of the reaction alone.

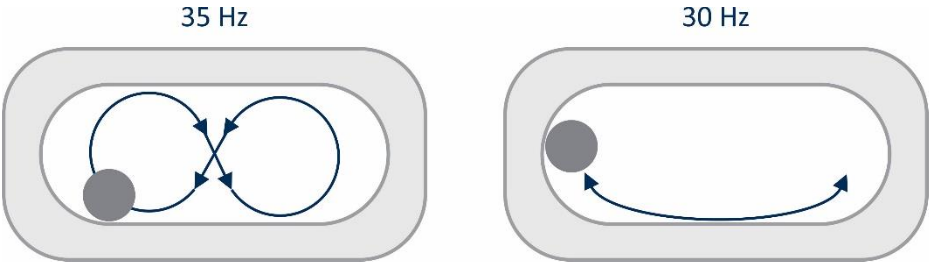

Figure 1: Trajectory of a milling ball (Ø 10 mm) observed at 35 Hz and 30 Hz in a MM500 mixer mill.

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P02 - Expanding direct mechanocatalysis towards alloyed milling tools

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In the last decade, mechanochemistry has gained the attention of organic chemists around the world. Numerous known, transition metal catalyzed reactions were conducted successfully already.

Advancing the so-called mechanocatalysis further, we presented "Direct Mechanocatalysis".[1] Here the catalyst is not a metal-salt or complex, nor a powder or bed of shaped bodies, but the milling ball itself in a ball mill.

We have recently shown this concept for the direct mechanocatalytic Suzuki and Sonogashira coupling reaction with neglectable abrasion and excellent reaction rates using milling balls made from pure Palladium.[2,3]

Our group is currently exploring cost-effective alternatives for milling tools, as the high cost of Pd as a milling material makes it unsuitable for large scale application. By alloying Pd with different transition metals that have suitable crystal structures, we aim to find the optimal Pd content for achieving the benefits of direct mechanocatalysis while reducing costs. Interestingly, we discovered that the reaction rate of a milling balls with 20% Pd is comparable to a milling ball with 80% Pd content, showing a non-linear relation between the Pd content and the yield, rather than decreasing linearly with lower Pd content. This finding establishes a direct connection between metallurgical material science and its direct application in mechanocatalysis.

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P03 - Merging Mechanochemistry with Light

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Recently, the combination of mechanochemical techniques with heating, cooling, piezo-electrics, or photochemistry gained more interest [1]. Especially, the combination with light convinces in terms of green chemistry, being one of the greenest energy sources. Yet, conventional photochemical reaction lacks in terms of sustainability for usually being performed in high dilutions. By merging mechanochemistry with a light source the advantages of both techniques can be combined. Until now, only a few publications on photo-mechanochemical reactions are available [2-5] which is mainly due by the absence of suitable equipment like reaction set-ups and translucent milling vials. Transparent vials from polymers allow the irradiation by visible light, but are opaque for higher energetic UV-light, which is indispensable for most organic photochemical transformations. For this reason, our group developed novel milling vessels made from quartz glass, that are resistant against mechanical forces as well as a suitable custom photoreactor. In this contribution show the efficiency and versatility of this novel combination of mechanochemistry and UV-light on the example of C-C coupling reaction [6].

Figure 1 Custom-build photoreactor for mixer mill (IST 500) with UVC LED units for simultaneous photo-mechanochemical reactions.

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[5] Obst, M. König, B. *Beilstein J. Org. Chem.* **12** (2016) 2358.
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P04 - Influence of milling time and thermal treatment on catalytic activity of MoS_2/graphene oxide composites

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In recent years, research has been directed toward the development of cheap, efficient, and renewable energy sources. Among them, hydrogen certainly has the main role, and the most desirable is green hydrogen. For that purpose, water electrolysis is studied and different catalysts are employed in order to make it more efficient and affordable. Transition metal dichalcogenides, among which molybdenum disulfide stands out, are widely investigated as catalysts for hydrogen evolution reaction (HER). The layered structure of MoS2 is easily modified to obtain a large number of active sites for HER. But its lack in conductivity draws the need for combining with other materials. Therefore, graphene oxide with adjustable surface chemistry and electronic properties is an excellent candidate. Combining these two materials should incorporate both enough catalytically active sites for hydrogen production and sufficient conductivity for electron transfer.

The molybdenum disulfide was obtained by hydrothermal route, while graphene oxide was prepared by modified Hummers' method. Afterward, composites were obtained by milling using a high-energy ball mill (SPEX Mixer/Mill 5100). The milling time and constituent ratio were optimized and prepared composites were analyzed as catalysts for hydrogen evolution. Additionally, in order to improve material properties, thermal pretreatment was also performed to increase the conductivity of graphene oxide.

P05 - Pd-catalyzed cyanation reaction using potassium ferrocyanide in direct mechanocatalysis

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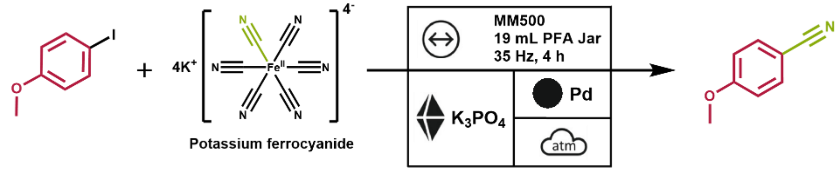
Cyano compounds are useful building blocks that are applied in a wide range of syntheses for e.g., pharmaceuticals, agrochemicals, and dyes [1]. Due to its strong electron-withdrawing property, the cyano group can be used as a versatile functional group to tune the reactivity of molecules.

Beside these advantages, the classical cyanide reaction has the critical drawback of inevitably using highly toxic cyanide sources. There have been several publications that attempt to replace the noxious cyanide agent with the much safer potassium ferrocyanide [2,3]. To the best of our knowledge, these attempts have not been reported yet using a ball mill system. To utilize this reaction in a ball mill, we use the novel concept of direct mechanocatalysis, in which the grinding material itself acts as a catalyst and no additional metal salt or supporting ligand has to be added [4,5].

Here we present our recent research on this topic, particularly in regard to comparing our current understanding of the cyanation reaction mechanism in conventional chemistry and ball mill chemistry, respectively.



Scheme 1. Proposed model scheme of cyanation reaction using potassium ferrocyanide in the ball mill.

[1] M. Neetha, C. M. A. Afsina, T. Aneeja, G. Anilkumar, *RSC Adv.* **10** (2020) 33683.
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[4] W. Pickhardt, S. Grätz, L. Borchardt, *Chem. Eur. J.* **26** (2020) 12903.
[5] S. Hwang, S. Grätz, L. Borchardt, *Chem. Commun.* **58** (2022) 1661.

P06 - Mechanochemical prebiotic synthesis of esters

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It has long been accepted that amino acids were present on the prebiotic Earth, but the pathways to their oligomerization remain unclear. This is particularly interesting considering that peptide bond formation is thermodynamically disfavored in aqueous solution. One possibility is that peptide bond formation was preceded by ester bond formation, followed by spontaneous ester-amide bond exchange [1]. Prebiotic conditions on Earth are often simulated by evaporation and rehydration cycles. However, the abundant geological changes of the early Earth, such as meteorite impacts and lithospheric activity could have provided the energy and environment necessary for prebiotic reactions. Mechanochemistry can provide a simulation of these conditions, as well as overcoming the limitations of solubility, solvation and solid diffusion [2]. Therefore, we used ball milling to perform esterification reactions catalyzed by prebiotically plausible minerals and other solid acid catalysts.

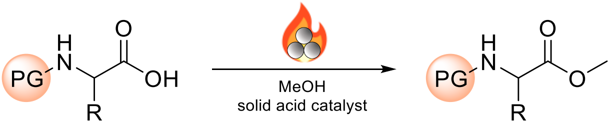

Figure 1 Solid acid catalyzed mechanochemical esterification.

[1] J. G. Forsythe, S.-S. Yu, I. Mamajanov, M. A. Grover, R. Krishnamurthy, F. M. Fernández, N. V. Hud, *Angew. Chem. Int. Ed.* **54** (2015) 9871.
[2] T. Stolar, S. Grubešić, N. Cindro, E. Meštrović, K. Užarević, J. G. Hernández, *Angew. Chem. Int. Ed.* **60** (2021) 12727.

P07 - Continuous mechanochemical Suzuki-Miyaura coupling

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The problem of waste in the chemical industry has become increasingly urgent due to rising environmental concerns, such as climate change. In particular, the synthesis of fine and pharmaceutical chemicals generates significant amounts of solvent waste. Mechanochemistry offers a potential solution to this problem. Currently, ball milling is the most common method used in mechanochemistry[1]. However, this approach is not suitable for industrial applications, as it is a small-scale batch process and scaling it up is challenging. A better option for large-scale mechanochemical processes is continuous reactive extrusion.[2] Therefore, the objective of this project is to scale up the mechanochemical molecular Suzuki cross-coupling by transforming the batch approach in a ball mill into a continuous process using an extruder. The Suzuki coupling was selected because C-C couplings are crucial in drug discovery, and Suzuki-Miyaura reactions are the second most frequently used reaction in drug discovery after amide bond formations.[3]

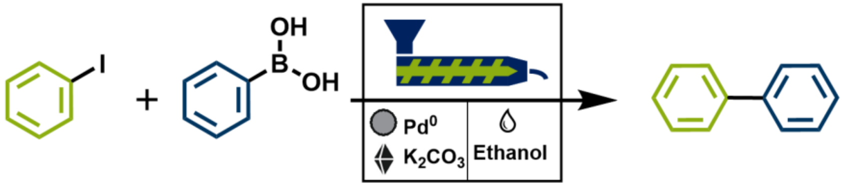

Figure 2: Reaction scheme of iodobenzene and phenylboronic acid to biphenyl using palladium as catalyst and potassium carbonate as bulk material and base.

[1] L. Takacs, *Chem. Soc. Rev*. **42** (2013) 7649.
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P08 - Hydrogen storage properties of MgH_2-Ni: catalysis vs. mechanical milling

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The effect of Ni addition (5 wt.%) in MgH_2 was mechanochemically examined for short milling times. The MgH_2-Ni system was ball-milled for 15, 30, and 45 minutes and characterized by XRD, SEM-EDS, PSD, DSC, and TPD. The uniform distribution of nickel decreases the temperature of H_2 desorption by more than 100°C in comparison with pure MgH_2. In addition, a kinetic model of the H_2 desorption was established. For the first time, it was demonstrated that two major processes (grinding and catalysis) could be examined individually. It is concluded that the catalysis of H_2 desorption by Ni particles on MgH_2 matrix is predominant effect for examined short milling times [1].

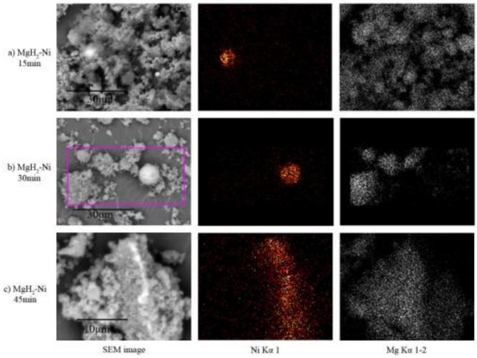

Figure 1. SEM-EDS micrographs of milled MgH_2-Ni composite.

[1] B.Babić et al. *Int. J. Hydrog.* **In Press** (https://doi.org/10.1016/j.ijhydene.2023.04.078).

P09 - Exploration of XeF_2–VOF_3 System by Mechanochemistry

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Xenon difluoride (XeF_2) readily forms compounds in which it acts as a fluoride-ion donor [1]. A subgroup of potential fluoride-ion acceptors, transition-metal oxyfluorides, has been systematically studied only for group 6 oxyfluorides of the MOF_4 type (M = Cr, Mo and W) [2,3]. Although VOF_3 has been shown to form adducts with XeF_2, namely $XeF_2 \cdot VOF_3$ and $XeF_2 \cdot 4VOF_3$ [4], the reliable synthesis of these compounds is rather challenging. This is due to the poor solubility of VOF_3 in anhydrous HF, a commonly used reaction medium and crystallization solvent in noble-gas chemistry.

To circumvent this problem, we reinvestigated the XeF_2–VOF_3 system using mechanochemistry [5]. This approach allowed a rapid and phase-pure synthesis of already known $XeF_2 \cdot VOF_3$ and new $3XeF_2 \cdot 2VOF_3$ adducts, whereas thermal reactions typically result in inhomogeneous mixtures. Single crystals obtained from reactions in the melt enabled a (re)determination of their crystal structures (Figure 1).

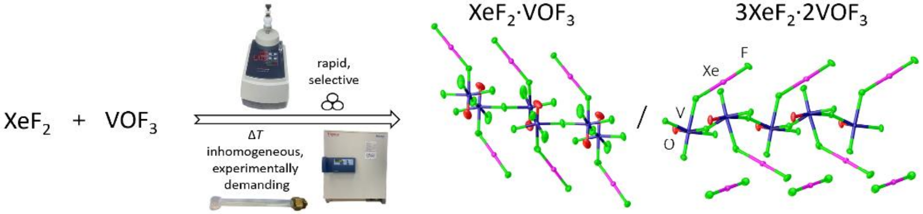

Figure 1 Synthetic approaches for the preparation of XeF_2–VOF_3 adducts and their crystal structures (50% probability ellipsoids).

[1] M. Tramšek, B. Žemva, *Acta Chim. Slov.* **53** (2006) 105.
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[4] M. Lozinšek, *Ph.D. Thesis, University of Ljubljana* (2013).
[5] T. Friščić, C. Mottillo, H. M. Titi, *Angew. Chem. Int. Ed.* **59** (2020) 1018.

P10 - Mechanochemical Adventures in Noble-Gas Chemistry

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The noble-gas chemistry started more than 60 years ago and it has become a fruitful field of many fundamental discoveries [1]. Its strong connection with fluorine chemistry, however, has limited the research of such compounds to only a few laboratories worldwide. Apart from unconventional methods and, in most cases, technically demanding procedures, such as the use of F_2 gas to passivate the equipment and anhydrous HF as a solvent, has rightly given noble-gas chemistry a reputation of a rather inaccessible research field.

In this work, we show that such extreme technical and chemical demands can be circumvented for certain systems by using simple and commercially available mechanochemical equipment [2]. Selection of a proper milling setup and milling parameters for selected reactions of XeF_2 and XeF_4 enables convenient syntheses of the corresponding adducts, salts, and cocrystals (Figure 1) [3,4]. This demonstrates that mechanochemistry can indeed be used as a facile synthetic method in the exotic field of noble-gas chemistry.

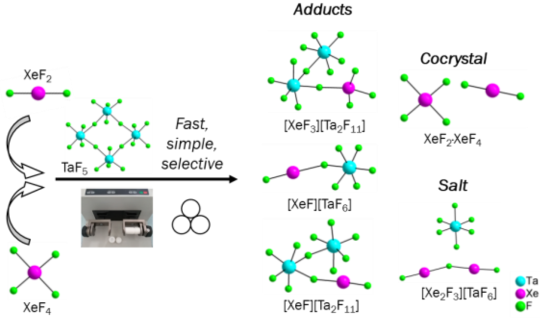

Figure 1 Mechanochemistry enables rapid and efficient syntheses of noble-gas species.

[1] G. J. Schrobilgen, Chemistry at the Edge of the Periodic Table, In: *The Periodic Table I. Structure and Bonding* (D. Mingos, Ed.), Springer, 2019, 157.
[2] T. Friščić, C. Mottillo, H. M. Titi, *Angew. Chem. Int. Ed.* **59** (2020) 1018.
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P11 - Effects of acidic additives and azobenzene substituents on solid-state cyclopalladation

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C–H bond activation is one of the simplest and most common synthetic methods to obtain cyclopalladated compounds.[1] Although the synthetic and mechanistic aspects of cyclopalladation in solution are well known, there are few studies on the mechanochemical activation of C–H bonds. Since palladacycles occur as intermediates in many palladium-catalyzed reactions, the understanding of factors affecting the reaction outcomes is essential, especially in an environmentally-friendly solid-state approach. In recent years, the strong effect of acidic additives on solution-based C–H bond activation and functionalization reactions has been reported.[2] In addition, studies from our group showed that the choice of palladium precursors and different substituents on ligand core play a crucial role on reaction kinetics.[3,4]

Continuing our previous studies of the C–H bond activation, we investigated the role of selected organic acids and electron-donating and/or electron-withdrawing groups in 4,4'-positions of the azobenzene substrates on mechanochemical ligand-directed C–H bond activation. Insight into the dynamics of the formation of azobenzene palladacycles was gained using *in situ* Raman monitoring. The results show that acidic additives and azobenzene substituents significantly increase the rate of solid-state C–H bond activation.

[1] J. Dupont, M. Pfeffer, *Palladacycles: Synthesis, Characterization and Applications*, Wiley, Weinheim, Germany, 2008.
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[4] A. Bjelopetrović, S. Lukin, I. Halasz, K. Užarević, I. Đilović, D. Barišić, A. Budimir, M. Juribašić Kulcsár, M. Ćurić, *Chem. Eur. J.* **24** (2018) 10672.

P12 - Mechanochemical activation of dasatinib to improve its oral absorption properties in the treatment of leukemia

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Dasatinib (DAS) is a second-generation tyrosine kinase inhibitor used for the treatment of Philadelphia chromosome-positive chronic myeloid leukemia and acute lymphoblastic leukemia. However, this drug is characterized by poor gastrointestinal absorption and low bioavailability due to its low aqueous solubility [1]. A promising approach to improve the properties of DAS is to modify its crystalline structure by supramolecular structural modifications, such as the preparation of a co-amorphous system. This research is focused on the application of the green co-grinding method to prepare amorphous solid dispersions of DAS in a matrix of polyvinylpyrrolidone (PVP). Several favorable events were expected: a reduction in the particle size of the drug and thus an increase in the specific surface area, better wettability, and possible intermolecular interactions between DAS and PVP, which could also improve the dissolution rate of the drug and thus its bioavailability. Amorphous solid dispersions and fluidized bed melt granulation were used to prepare tablets with strictly defined aimed properties. *In vitro* dissolution tests confirmed that this particular drug could be mechanochemically activated in terms of improving its dissolution properties.

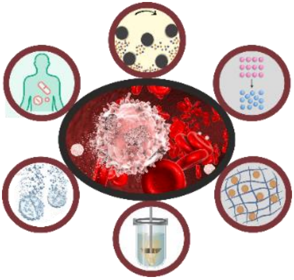

Figure 1 Mechanochemical activation of the drug to improve its properties.

[1] S. Dharani, E. M. Mohamed, T. Khuroo, Z. Rahman, M. A. Khan, *Pharmaceutics* **14** (2022) 2450.

P13 - Mechanochemical synthesis of some transition metal polycyanometallates

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The history of cyanometallate compounds started with the discovery of Prussian blue in 1704. This was followed by the synthesis of many other cyanometallate compounds which have found numerous applications [1]. A typical synthetic protocol involves solution-based synthesis which is for many such compounds well-documented [2]. However, in most cases high excess of starting cyanide source is used which, apart from safety issues, inevitably results in time-consuming and wasteful purification procedures, especially in regards to the solvent used.

In an attempt to find new and faster synthetic methods of cyanometallate compounds, we have utilized mechanochemistry [3]. Neat grinding of the (hydrated) metal salts of Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and potassium cyanide yielded the pure products in the case of $K_4[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ within minutes. In other cases, a mixture of phases was obtained. To further elucidate the intermediates formed during the reactions as well as their pathway, *in situ* Raman measurements were performed (Fig. 1).

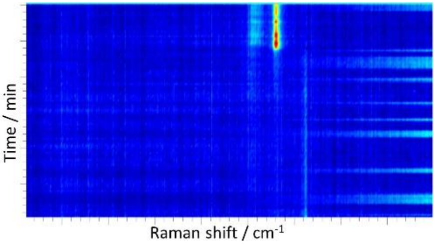

Figure 1 Waterfall diagram of *in situ* Raman spectra of milling $NiCl_2$ with KCN.

[1] K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.*, **45** (1997) 283.
[2] A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, Cambridge, 1976, pp. 6.
[3] T. Friščić, C. Mottillo, H. M. Titi, *Angew. Chem. Int. Ed.*, **59** (2020) 1018.

P14 - Fulleretic hybrid materials by liquid-directed mechanochemical templation

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Zeolitic imidazolate frameworks (ZIFs) are infinite periodic structures built from tetrahedral metal centers and imidazolate ligands. They are thermally and chemically stable, highly porous, and can form a multitude of 3D structures (topologies) with different properties.[1] Unfortunately, the solvothermal synthesis of ZIFs is inefficient and often gives mixtures of topological products. Mechanochemistry can be used to increase the yield, efficiency, and sustainability of ZIF syntheses, and molecular templates can stabilize specific structural motifs, directing the synthesis to the desired outcome and giving hybrid materials with novel properties.[2] For instance, C60 fullerene has been shown to change the vibrational properties, color, and luminescence of ZIF-8 upon encapsulation.[3]

We demonstrate that adding fullerenes and different liquid additives in the mechanochemical synthesis of zinc imidazolates can yield unexpected topological results and novel functional materials.

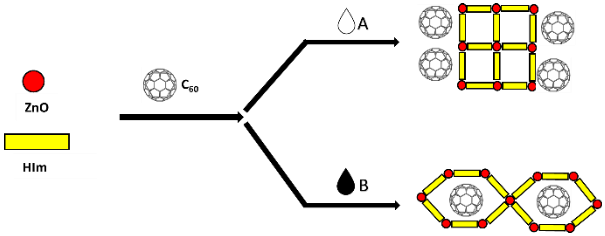

Figure 1 The effect of different liquid additives on the topological outcome of the mechanochemical synthesis of hybrid fulleretic zinc imidazolate materials.

[1] B. Chen, Z. Yang, Y. Zhu, Xia, *J. Mater. Chem. A* **2** (2014) 16811.
[2] I. Brekalo, C.M. Kane, A.N. Ley, J.R. Ramirez, T. Friščić, K.T. Holman *JACS* **140** (2018) 10104.
[3] V. Martinez, B. Karadeniz, N. Biliškov, I. Lončarić, S. Muratović, D. Žilić, S. M. Avdoshenko, M. Roslova, A. A. Popov, K. Užarević, *Chem. Mater.* **32** (2020) 10628.

P15 - Mechanochemical modification of FAU zeolite with transition metal iodides and its gas adsorption properties

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Zeolites are porous compounds usually comprised of silicon, aluminum and oxygen. Due to their porosity, zeolites excel in gas adsorption [1]. Furthermore, properties of these materials can be finely tuned by post-synthesis modification via ion-exchange which is usually carried out in solution. It has been shown entire complexes can be synthetized inside their pores, which enables various new modifications [2]. Preparation of these complexes by mechanochemistry has also been recently demonstrated [3].

To further investigate the possibilities of this synthesis method, iron, cobalt, nickel and copper iodide complexes were synthesized within FAU-type zeolite by grinding. Solid state synthesis yielded stable products within the FAU pores. The metal iodides were characterized by Raman and infrared spectroscopy and compared with the theoretical spectra generated by computational means. Gas adsorption properties of such modified FAU-type material were tested in acidic atmospheres of NO_2 and HCl.

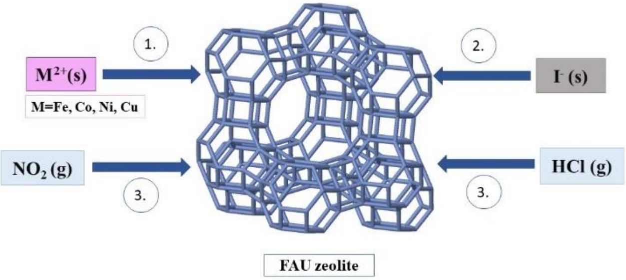

Figure 1 Synthesis of complexes within FAU zeolite pores, followed by gas adsorption.

[1] C.J. Rhodes, *Sci. Prog.* **93** (2010) 223.
[2] R. J. Taylor, R. S. Drago, J. E. George, *J. Am. Chem. Soc.*, **111** (1989) 6610.
[3] D. Šinjori, N. Jakupec, A. Palčić, A. Stanković, *Mechanochemical synthesis of polycyanometallates inside zeolite Y cavities*, 7th Symposium of Chemistry Students, 2022, Zagreb, Book of Abstracts, p. 39.

P16 - Mechanochemical path towards (synthesis of) hierarchical zeolites

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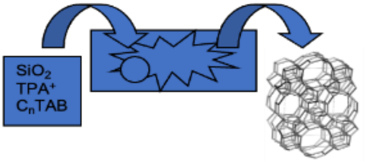
Hierarchical zeolites having additional level of porosity are one of the most utilized heterogeneous catalysts in oil refining and chemical industries [1]. Mechanochemistry is an established technique of preparing different materials advantageous over traditional solvothermal synthesis due to the reduced synthesis time and solvent exclusion [2]. In zeolite synthesis, it is mostly applied for presynthesis treatment of precursors followed by (hydro)thermal treatment [3]. Herein, we used advanced mechanochemical approach for zeolite synthesis using specially designed milling equipment, which enables heating of milling jars to desired temperature for prolonged time window. In that way, process of high temperature zeolite synthesis could be conducted completely while milling in just one step. Preliminary XRD data show that one step milling treatment of prepared hierarchical zeolite precursor systems at elevated temperature produce, in majority of cases, crystalline MFI-type zeolite. Compared to the traditional hydrothermal treatment, milling reactions were completed in much shorter time, which makes this mechanochemical zeolite synthesis approach very convenient in the terms of diminishing cost and negative influence on the environment.



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[2] T. Friščić, C. Mottillo, H.M. Titi, *Angew. Chem Int Ed.*, **59** (2020) 1018.
[3] D.N.Rainer, R.E. Morris, *Dalton Transactions*, **50** (2021) 8995.

Acknowledgment: The authors are grateful to the Croatian Science Foundation for funding this research (project ID: UIP-2019-04-4977).

P17 - Preparation of High/Pure-Silica LTA Framework Type Zeolite Materials

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High alumina LTA-type zeolite material, so called zeolite A (Si/Al = 1), is an archetype drying agent (water adsorbent) as well as ion exchanger (e.g. in water softening) [1]. Incorporating more Si in the framework, i.e. increasing Si/Al ratio, renders this kind of materials more (hydro)thermally stable and apt for catalytic application, in particular for vehicle exhaust gases purification [2,3]. Cu-LTA were found exceptionally active catalysts in NH_3-SCR even after hydrothermal aging at 900 °C, the temperature at which the commercial catalyst deforms and loses activity [4]. In the scope of this research challenges of preparing high/all-silica LTA zeolites are going to be addressed. Besides, several examples of their successful preparation will be demonstrated.

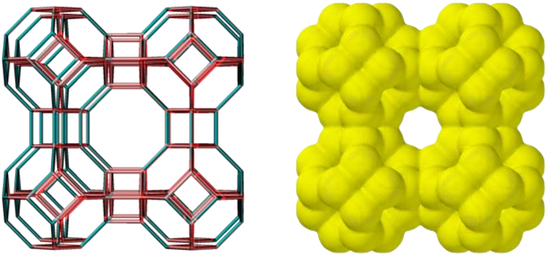

Figure 1 Graphical representation of the LTA-type zeolite framework.

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[2] Y. Bouizi, J.-L. Paillaud, L. Simon, V. Valtchev, *Chem. Mater*. **19** (2007) 652.
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Acknowledgment: The authors are grateful to the Croatian Science Foundation for funding this research (project ID: UIP-2019-04-4977)

P18 - Gas adsorption by FAU zeolite modified with mechanochemicaly synthesized polycyanometallates

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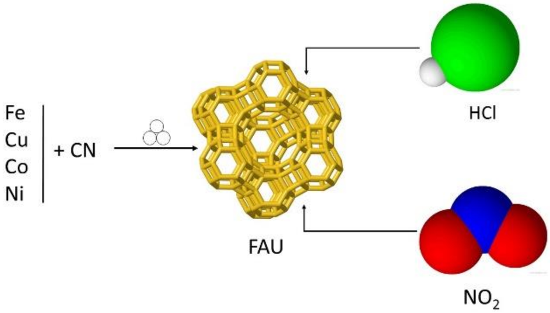
Zeolites are a class of porous materials comprised of tetrahedra linked via oxygen vertices building a framework. Due to their porosity, zeolites have been used in catalysis and gas adsorption [1]. The cavities of some zeolites, like zeolite Y, contain charge compensating cations which can be exchanged with other cations. Furthermore, coordination compounds like polycyanometallates can be synthesised inside zeolite cavities. Hexacyanocobaltate(III) ($[Co(CN)_6]^{3-}$) [2] and hexacyanoferrate $[Fe(CN)_6]^{2-}$ [3] have successfully been synthesized in zeolite cavities by solution methods.

The aim of this research was to prepare polycyanometallates of iron, copper, nickel and cobalt inside the cavities of a FAU-type zeolite *via* mechanochemical means and to test the structural stability and gas adsorption properties in acidic atmospheres of NO_2 and HCl. Stability of the zeolite crystalline structure was determined by PXRD analysis, while the presence of adsorbed gases was identified using IR spectroscopy. Analysis showed that the adsorbed gases were still present inside the structure a month after the initial exposure.



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P19 - Structural and magnetic study of MOF-74 isophthalic homologues

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Most solution syntheses of bimetallic metal-organic frameworks (MOFs) lack the ability to control the framework stoichiometry. They, therefore, result in materials with a non-homogeneous distribution of metals throughout the framework, a problem solved using mechanochemical synthetic strategies.[1] MOF-74 materials, derived from 2,5-dihydroxyterephthalic acid (**dhta**) and various divalent d-block metal nodes, represent an important class of MOFs studied for their remarkable structural features and properties.[2] Here, MOF-74 homologues based on 4,6-dihydroxyisophtalic acid (**dhia**), its *meta*-isomer, were studied to determine structural and magnetic differences from typical MOF-74 materials, synthesized with **dhta** as a linker. MOF syntheses were explored using room- and high-temperature milling, where bimetallic MOFs were prepared via different 1:1 M-dhia (M=Ni, Mn) intermediates. Prepared novel MOFs and intermediates were structurally characterized by X-ray diffraction, and the interactions of spin-active centres were studied using X-band EPR spectroscopy.

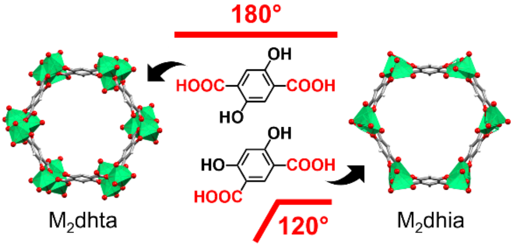

Figure 1 Structural differences between **dhta** and **dhia** and their MOF-74 homologues

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P20 - Cocrystallization of novel 4-iodotetrafluorophenoxy azobenzene ethers with bipyridyl derivatives

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Over the last 10 years azo-derivatives have been investigated in context of halogen bond formation, mainly in synthesis of new optical materials as well as materials that exhibit photomechanical properties. [1] In this work, we explored the use of two novel azo-halogen bond donors in synthesis of multicomponent crystals with bipyridyl derivatives. Two azo-derivatives **IazCl** and **IazH** (Figure 1.) where synthesized and cocrystal screening was done using five bipyridyl derivatives. Cocrystallization experiments were performed both, mechanochemically, using liquid-assisted grinding and solution-wise, using crystallization techniques. A series of five cocrystals with **IazCl** was obtained by means of solution cocrystallization. Unexpectedly, mechanochemical synthesis failed to give any cocrystals at all. Obtained cocrystals were characterized by single crystal X-ray diffraction and differential scanning calorimetry. Structural analysis revealed that that the dominant supramolecular interaction in all five cocrystals is the $\mathrm{I}\cdots\mathrm{N}_{\mathrm{pyridine}}$ halogen bond.

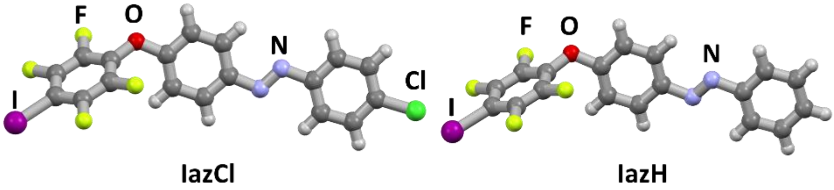

Figure 1 4-iodotetrafluorophenoxy azobenzene ethers used in this study.

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P21 - Optimization of Periodic DFT Methods for the Simulation of Halogen Bonded Cocrystals

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The halogen-bonded [1] cocrystals are of interest due to their potential application in different fields [2]. Periodic DFT methods can efficiently predict the formation and interconversion of halogen bonded cocrystals [3]. However, the choice of different methods, namely functionals and dispersion corrections, can affect the results. Hence, a benchmark study using different periodic DFT methods is needed for the efficient engineering of cocrystals with tailor-made properties.

In the present study, we have used several DFT methods of different level (LDA, GGA, Hybrid and range separated) with and without the dispersion correction. The previously reported, halogen bonded cocrystals of 1,3,5-trifluoro-2,4,6-triiodobenzene with PPh_3, $AsPh_3$ and $SbPh_3$ were taken for the study [4, 5]. Interaction energy and topological parameters (at the bond critical point) were calculated for I···P/As/Sb halogen bonds from the energy minimized crystal structures. A good correlation was obtained between the geometrical and topological parameters. These theoretical results will be validated against the multipole model obtained from the high resolution (~0.42 Å) experimental X-ray diffraction measurements.

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P22 - N K-edge RIXS of TTF-TCNQ: Theory and Experiment

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TTF-TCNQ is a quasi-1D charge transfer salt exhibiting three Peierls transitions that gradually reduce its metallic character and turns this compound into an insulator [1,2]. We decided to investigate the relation between crystal structure and the change in electronic properties using x-ray spectroscopy.

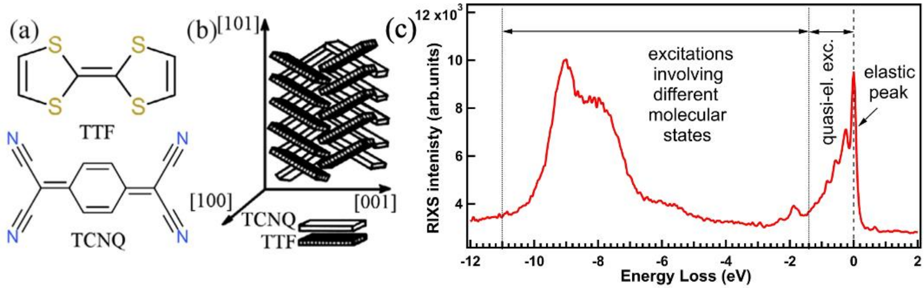

Figure 1 (a) TTF and TCNQ molecules. (b) TTF-TCNQ structure [3]. (c) RIXS spectrum of TTF-TCNQ (our work).

We performed resonant inelastic x-ray scattering (RIXS) measurements that probed excitation between molecular states and also clearly showed some lattice dynamics. Furthermore, we are simulating the cross section of the scattering process on the TCNQ molecule using *ab initio* DFT calculations in order to confront it with the results from our experimental spectra.

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P23 - Green and scalable synthesis of alkaline-dhta polymers

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The 2,5-dihydroxyterephtalic acid (**dhta**) is a tetratopic ligand widely applied in the synthesis of functional porous metal-organic frameworks, such as MOF-74, and coordination polymers. In the vast majority of these materials, **dhta** is coordinated to transition metal cations, and only a few examples involving s-block metals are known. During the synthesis of such materials, control over topology and stoichiometry remains a challenge.[1] Here we present a fast and green mechanochemical approach as a fitting solution for this problem. Ball-milling allowed the stoichiometrically controlled and fast synthesis of five novel alkaline-dhta-based coordination polymers on a gram scale. Polymers were also obtained from the solution, and their crystal structures were solved, as well as the previously unknown structure of pure **dhta**.

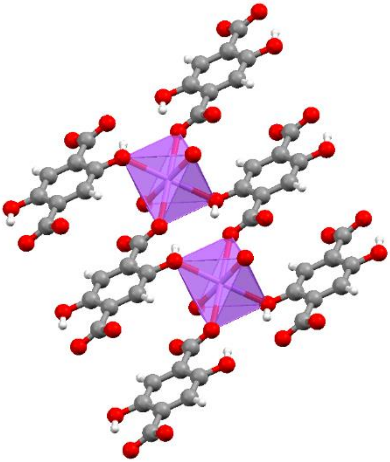

Figure 1 Polyhedral view of **Na-dhta** polymer.

[1] E. Quarez et al., *CrystEngComm* **22** (2020) 1653.

P24 - From binary to ternary halogen-bonded cocrystals using Werner coordination compound

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Due to the difficulty of balancing multiple components and controlling specific interactions in a crystal, the targeted synthesis of cocrystals containing three or more components could be very complex. Obtaining ternary cocrystals which are connected exclusively by halogen bonds represents a significant challenge, and so far very few examples of purely organic crystals have been described. [1] The aim of our research was to design ternary cocrystals using a metal-organic complex as an acceptor moiety. We synthesized the Werner coordination compound, $Ni(CH_3C_5H_5N)_4(NCS)_2$, containing two trans-isothiocyanate groups capable of forming multiple halogen bonds. To build cocrystals, a combination of selected donor molecules was used: 1,3-diiodotetrafluorobenzene, 1,4-diiodotetrafluorobenzene and 1,3,5-trifluoro-2,4,6-triiodobenzene. Four different ternary cocrystals were synthesized and compared to previously synthetizes binary cocrystals containing the same donor molecules. For both binary and ternary cocrystals, periodic density-functional theory (DFT) calculations were performed, in plane-wave DFT code CASTEP, using PBE functional with many-body dispersion (MBD*). [2] These calculations were used to compute cocrystal formation energies, as well as intermolecular interaction energies.

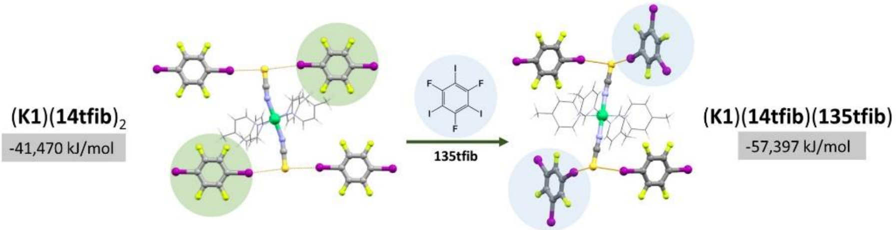

Figure 1. Cocrystals (**K1**)(**14tfib**)$_2$ (binary) and (**K1**)(**14tfib**)(**135tfib**) (ternary)

[1] H. Jain, D. Sutradhar, S. Roy, G. R. Desiraju, Angew. Chem. Int. Ed. **60** (2021) 12841.

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P25 - X-ray Charge-Density Study of Xenon Fluorides

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Noble-gas compounds are text-book species exhibiting interesting structures and bonding modalities [1–3]. The intermolecular interactions observed in the crystal structures of xenon compounds, such as XeO_3, $XeOF_2$, XeF_4 and XeF_2, have attracted substantial attention in recent years, with various theoretical investigations focused on the presence and importance of a σ-hole-based interactions [4,5]. Experimental electron-density distribution of fluorides is rarely studied, and no X-ray charge-density analysis on noble-gas compounds has been reported to this date. In this work, low-temperature single-crystal X-ray diffraction data was measured with silver X-ray source on selected xenon fluorides (Fig. 1) to high resolution, typically up to 0.3 Å. Experimental charge density was derived from multipole refinements.

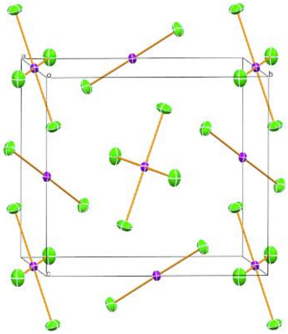

Figure 1 The X-ray crystal structure of $XeF_2 \cdot XeF_4$ cocrystal. Thermal ellipsoids are drawn at the 50% probability level.

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P26 - Elucidating interaction energies in the formation of three component cocrystal by periodic DFT

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In the design and synthesis of multicomponent molecular crystals (cocrystals) with desired properties, a comprehensive understanding of non-covalent interactions is essential. This includes interactions such as hydrogen bonding, halogen bonding, π-π stacking, and so on.[1] Analyzing the interaction energies of these interactions and identifying which interactions stabilize the lattice energies in a crystal system is crucial for modeling a cocrystal.

During the exploration of the cocrystal interconversion reaction inspired by our previous work,[2] we have observed the formation of a three-component cocrystal containing pyrazine, triphenylphosphine sulfide and 1,3,5-triidod-trifluorobenzene, containing I···N and I···C_π halogen bonding interactions regardless of where the reaction was initiated. Interestingly, this three-component cocrystal is formed by overcoming the interaction between iodine and sulfur atoms and by forming a bond between iodine and π-system of the triphenylphosphine sulfide.

In this presentation, I will compare the experimental results outcomes of milling reactions and dissolution calorimetry measurements of reaction enthalpies with periodic DFT calculations, as a way to systematically analyze and predict the effects of non-covalent interactions in the design and synthesis of new cocrystals with desired properties.

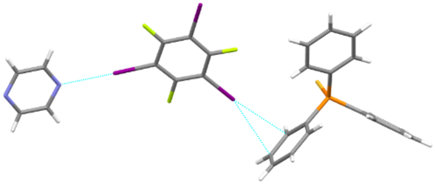

Fig: Three component cocrystal under discussion

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P27 - Study on multicentric *pancake bond* between TMPD cations in novel chloride co-crystal with 2,5-dichlorohydroquinone

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N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD or Wurster's blue) has been known as an electron donor since 19th century [1]. It can easily be oxidized into a radical cation with an interesting semiquinoid structure. Organic radicals usually form the strongest π-interactions with the energy as high as −20 kcal $\mathrm{mol^{-1}}$. Such interactions usually have non-negligible covalent character, but also they can contribute to properties of the material, like electric conductivity and magnetism. Strong π-interactions involve multiple centers so they are described as two-electron multicentric bonds and interestingly termed as *pancake bonding*.[2] Since crystals of planar organic radicals represent a great playground for studying of the *pancake bond*, here we present a crystallographic study of a novel compound, TMPD chloride salt cocrystal with 2,5-dichlorohydroquinone in which *pancake bonded* TMPD cation dimers are present. Today this phenomenon can be studied in detail by different crystallographic methods such as variable-temperature crystallography (80 – 400 K) and X-ray charge density.[3] These methods show changes in the structure caused by cooling or heating the crystal and reveal fine details of electron density between the stacked radicals. This work represents the first study of charge density between *pancake-bonded* radical cations.

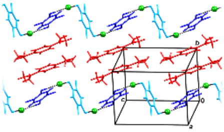

Figure 1 Crystal packing of TMPD chloride cocrystal with 2,5-dichlorohydroquinone

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[2] V. Milašonović, A. Krawczuk, K. Molčanov and B. Kojić-Prodić, *Cryst. Growth Des.* **20** (2020) 5435.
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P28 - Cocrystals of Zn(II) and Cu(II) complexes: halogen bonding with the morpholinyl fragment *vs.* chloride ligands

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Over the past decade research of halogen bonding in metal-organic cocrystals was focused mainly on systems containing neutral metal-organic units — coordination compounds with ligands containing reliable acceptor moieties such as (pseudo)halogenides — and neutral halogen bond donors [1]. In this study, zinc(II) and copper(II) coordination compounds containing both the peripherally located oxygen atom of the morpholine fragment [2] as well as chloride ligands as possible acceptor sites [3] have been prepared, with the aim of studying competition and/or cooperativity for halogen bonding. The prepared coordination compounds were cocrystallized with halogen bond donors, perhalogenated iodobenzenes, mechanochemically and by solution crystallization. Structural analysis of the prepared cocrystals revealed that in all cocrystals the molecules are interconnected with halogen bonds, and in the majority of cases both morpholine oxygen and chloride ligands are acceptors. In three cocrystals only M–Cl···I halogen bonds are present, while in one cocrystal only the morpholine oxygen acts as a halogen bond acceptor. Therefore, it is shown that morpholine oxygen can be a prominent acceptor, competitive to the chloride ligand.

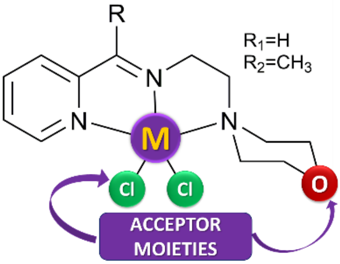

Figure 1. Structural diagram of the studied coordination compounds.

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[2] V. Nemec et al., *Cryst. Growth Des.* **20** (2020) 3617.
[3] K.Lisac, D. Cinčić, *CrystEngComm.* **20** (2018) 5955.

P29 - Surface reactions of titanium dioxide and poly(N-ethyl-vinylpyridinium) adsorption

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Titanium oxide is a material present in wide range of applications, mostly as a white pigment in food colouring, sunscreen, and paint. As a frequently used material, a lot of research has been done regarding surface characterisation, but there is very little data on thermodynamic of the surface reactions. [1,2] Furthermore, a common problem of TiO2 is its point of zero charge which is usually close to neutral pH. This property causes unstable suspensions near neutral pH values. A polyelectrolyte can be adsorbed to TiO2 surface producing the more stable suspension. Polyelectrolytes are macromolecules containing ionic groups in their subunits. Poly(N-ethyl-vinylpyridinium) cation was chosen for this research as it has absorption maximum in UV-Vis region which enables the quantitative analysis.

In this work, surface of TiO2 nanoparticles (10 nm) in aqueous medium was investigated in detail by means of dynamic light scattering, electophoretic light scattering, potentiometric acid-base titrations, ITC calorimetric titrations and UV-Vis spectrophotometry. After detailed surface characterisation, adsorption of a polyelectrolyte was investigated. Results were used to model and obtain the equilibrium constants and reaction enthalpies of surface protonation, deprotonation and polyelectrolyte adsorption on TiO2 surface.

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P30 - Use of the building block $[Fe^{III}(C_2O_4)_3]^{3-}$ in the preparation of heterometallic compounds with alkyl-ammonium cations

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Metal-organic coordination polymers due to their structural diversity, allow the introduction of two (or even more) properties leading to multifunctional materials. The oxalate group, $C_2O_4^{2-}$, has been used as one of the most versatile ligands for the preparation of this type of materials. Its various possibilities of coordination to the metal centres and the ability to mediate magnetic interactions between paramagnetic metal ions have enabled the synthesis and characterization of a large number of oxalate-based transition-metal species of different nuclearity and dimensionality, many of which exhibit a tunable magnetic framework. Most of the oxalate-based molecular magnets described so far have been obtained by the "complex-as-ligand approach"; the tris(oxalato)metalate $[M^{III}(C_2O_4)_3]^{3-}$ anion (M^{III} = Cr, Mn, Fe, Ru, Rh, or V) is used as a molecular building block, that serves as a ligand towards another metal cations. Proton conductivity has recently been considered as a new functionality of oxalate-based compounds; in general, the simplest method to introduce proton carriers is to incorporate a counterion such as hydronium (H_3O^+), ammonium [NH_4^+, $(CH_3)_2NH_2^+$,...] during synthesis, resulting in charged compounds. The counterions form hydrogen bonds with the guest water or other components of compound and form proton-conducting pathways consisting of hydrogen bonding networks [1]. To prepare heteropolynuclear oxalate compounds and incorporate alkyl-ammonium counterions as proton carriers, we utilized a procedure in which an aqueous solution of $[Fe^{III}(C_2O_4)_3]^{3-}$ containing $(CH_3)_2(C_2H_5)NH^+$ or $(CH_3)(C_2H_5)_2NH^+$ was used as a building block in reactions with manganese(II) or cobalt(II) ion, and with the addition of *N*-donor ligands. Depending on the used reactants, homo- and heterometallic compounds of arrangements were obtained and characterized.

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P31 - The Mixed Glass Former Effect: A Pathway to Enhanced Conductivity in Na_2O-ZnO-P_2O_5-Nb_2O_5 glass-(ceramics)

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Alkali phosphate-based glass-(ceramics) exhibit potential as materials for solid-state batteries which offer high safety, energy density, and long cycling life [1]. To improve their chemical durability and conductivity, intermediate and/or conditional glass-forming oxides (ZnO, Nb_2O_5) can be incorporated, strengthening the glass network and cross-linking phosphate groups via mixed P-O-M bonds (M = Zn, Nb) [2]. The mixed network enhances alkali ion transport, thereby leading to an increase in ionic conductivity, which is commonly known as the mixed-glass forming effect (MGFE) [3].

This study investigates the impact of Nb_2O_5 and ZnO addition on the physical properties of $35Na_2O$-10ZnO-$(55–x)P_2O_5$-xNb_2O_5 (x = 0–40 mol%) glass-(ceramics). Synthesis is performed via conventional melt-quenching. The amorphous nature of glasses is confirmed by PXRD analysis, and quantitative analysis is conducted on high-content Nb_2O_5 glass-ceramic sample. Thermal behaviour is examined by DTA, while (micro)structural properties are evaluated by SEM-EDS, Raman, and IR-ATR spectroscopy. Electrical transport is investigated by solid-state impedance spectroscopy across a wide frequency range (0.01 Hz–1 MHz) and temperature range (–90 °C–240 °C). Results exhibit significant enhancement in ionic conductivity, peaking at 20 mol% Nb_2O_5, confirming the MGFE. Additionally, the influence of alkali ion type on electrical conductivity is explored for the sample with the highest conductivity.

Acknowledgements: This work is supported by the Croatian Science Foundation under the projects IP-2018-01-5425 and DOK-2021-02-9665, and by the Croatian Academy of Science and Arts (HAZU), 2022.

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P32 - Computational and structural studies of flexible coordination polymers of copper(II) and cadmium(II)

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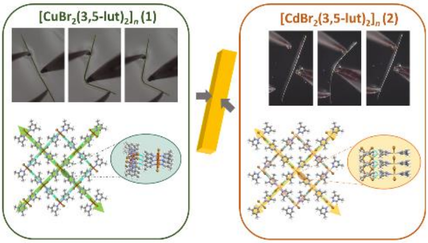
Discovery of crystals that can move under the influence of heat, light or mechanical stimuli completely changed a perception of crystals as static systems,[1] but also made them excellent candidates for a variety of applications in advanced technologies, e.g. thermal actuators,[2] or self-healing materials.[3] Recently, it has been shown that in addition to two commonly observed mechanic responses, elastic and plastic, crystals are able to present a whole spectrum of different adaptabilities to external pressure.[4] To provide a deeper insight into those interesting crystalline behaviors, herein we opted for crystals of coordination polymers of $CuBr_2$ and $CdBr_2$ with 3,5-lutidine (**3,5-lut**), [$CuBr_2$(**3,5-lut**)$_2$]$_n$ (**1**) and [$CdBr_2$(**3,5-lut**)$_2$]$_n$ (**2**). It was shown that both crystals were 2D isotropically responsive, but while **1** was purely plastic, **2** was *elastic→plastic*. Computational DFT methods were used to complement experimental findings by simulating the deformation of the unit cells along the crystallographic axes. Comparison of the fitted potential energy curves enabled us to better understand the effect of intermolecular interactions on mechanically induced flexibility.



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Acknowledgment: This work has been fully supported by the Croatian Science Foundation under the project IP-2019-04-1242.

P33 - Monomeric and dimeric cobalt(II) complexes with pyridine-2,5-dicarboxylic acid

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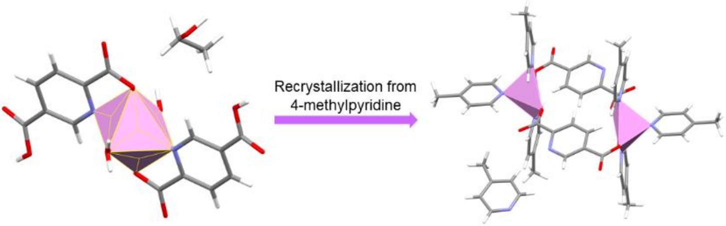
Multidentate ligands with significant coordination potential can be used as a tool for designing supramolecular structures with interesting properties [1-2]. An employment of ligands equipped with a pyridyl donor group and a pronounced hydrogen bonding functionality (carboxylic groups) may lead to the formation of supramolecular structures which can be used in various areas as materials with improved catalytic, adsorption, conductive, biomedical, electronical, optical or magnetic properties.



$[Co(2,5\text{-}pydcH)_2(H_2O)_2]\cdot C_2H_5OH$ $[Co(2,5\text{-}pydcH)(4\text{-}CH_3py)_3]_2\cdot 4\text{-}CH_3py$

Figure 1 Cobalt(II) complexes with 2,5-pydcH$_2$

In order to improve our understanding on structure-function correlation in metal carboxylate complexes, we have prepared two cobalt(II) complexes with pyridine-2,5-dicarboxylic acid (2,5-pydcH$_2$), monomeric ethanol solvate and dimeric 4-methylpyridine (4-CH$_3$py) solvate (Fig. 1). The compounds were characterized by single crystal X-ray structure analysis combined with spectroscopic and thermal analysis.

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P34 - Investigating the Properties of Flexible Copper(II) Crystals Containing 3-nitropyridine Ligands

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Flexible crystals – a rapidly growing class of materials that combine a long-range order of a typical crystal structure with a certain degree of mechanical flexibility. So far, this mechanical flexibility has been reported for a significant number of organic molecular crystals, but mechanical properties of metal–organic crystalline solids have been less understood [1]. Recently, it has been shown that coordination polymers can serve as ideal models of metal-organic systems that might result in exceptional flexible crystals [2].

In this work, we have prepared needle-like crystals of coordination polymers of copper(II) halides with 3-nitropyridine and determined the type of their mechanical response, which was subsequently quantified. Moreover, we examined the crystals' flexible responses to the applied thermal stimuli using hot-stage microscopy along with the electrical properties using impedance spectroscopy, the results of which will be discussed in detail.

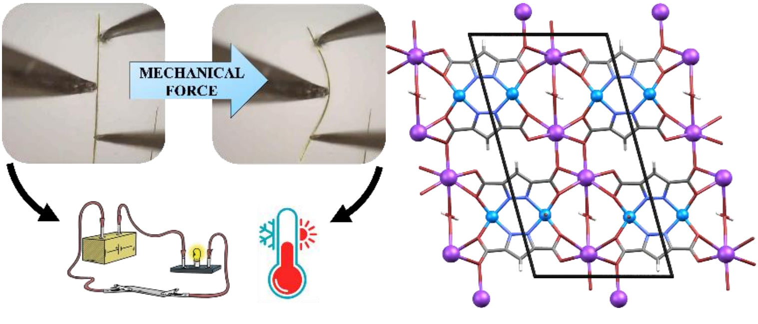

Figure 1. Properties of flexible crystals of copper(II) coordination polymers

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This work has been fully supported by Croatian Science Foundation under the project IP-2019-04-1242.

P35 - Efficiency Enhancement of $FAPbI_3$ Perovskite Solar Cells by adding a $BaTiO_3$ Layer

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In a recent research study [1], we synthesized perovskite solar cells (PSCs) with bare TiO_2, which acts as an electron transport layer with a power conversion efficiency (*PCE*) of 7%. In this study we added a layer of $BaTiO_3$ between the perovskite absorber and the TiO_2 electron transport layer and we produced a device with an experimental *PCE* of 11%. Theoretical simulations were performed using SCAPS-1D software [2]. After optimization of the PSC parameters that can affect its performance (thickness of the $BaTiO_3$ and absorber layers, doping, and defect concentration), the results indicated that the *PCE* could reach a value of 14.71%. In an ideal device, the efficiencies can even reach 20%, verifying that the BaTiO3 layer can drastically improve the PSC performance and can be used in future research as a promising material for optoelectronic devices.

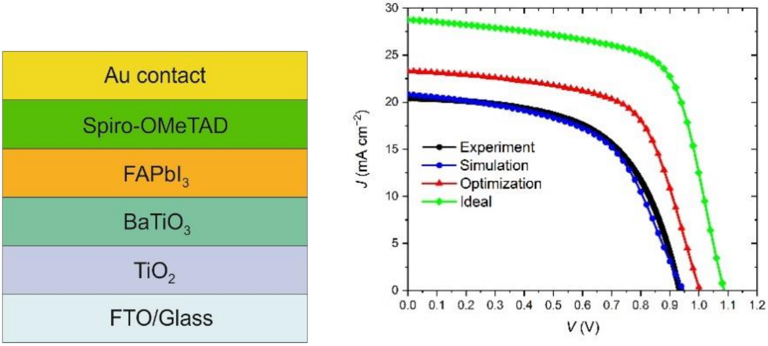

Figure 1 Solar cell structure and I-V characteristics of experimental and simulation data.

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*This work has been supported by Croatian Science Foundation, HRZZ-IP-2018-01-5246.

P36 - Advantages of crosslinking self-assembled molecular layers on metal surfaces

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Self-assembled molecular layers (SAMs) are highly ordered molecular assemblies that can be formed on various different materials, including metals. Just by exposing the metal to the solution that contains the appropriate molecules, such as fatty acids, spontaneous adsorption occurs due to their affinity for metal. SAMs are easy to prepare, can be formed on rough and irregular surfaces, and small amounts of chemicals are needed to cover large surfaces. SAMs can also be used for surface functionalization since their application can modify the chemical and physical properties of surfaces. Therefore, SAMs have many advantages that make them potentially applicable in many fields such as corrosion protection, biomedicine, catalysts, sensors, and optics [1]. The main drawback that prevents them from being widely used in practice is their instability. In order to preserve all the advantages of SAMs and to improve their stability and durability, SAMs can be crosslinked [2]. In this work, fatty acids have been used to form SAMs on copper surface. Using gamma irradiation, SAMs are crosslinked into nano-thick polymer coatings. The aim of this work is to determine the improved stability of coatings upon crosslinking. Electrochemical methods were used to study the behavior and protective properties of obtained improved nanocoatings in simulated atmospheric conditions. Surface hydrophobicity was determined with contact angle goniometry, while atomic force microscopy was used to examine topography of the surface. Results have shown that crosslinked SAMs offer longer and better protection of copper in simulated urban rain, compared to non-crosslinked SAMs.

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P37 - Synthesizing a Spatially Arranged Network of Gold Micro- and Nanoclusters on Silicon Substrate

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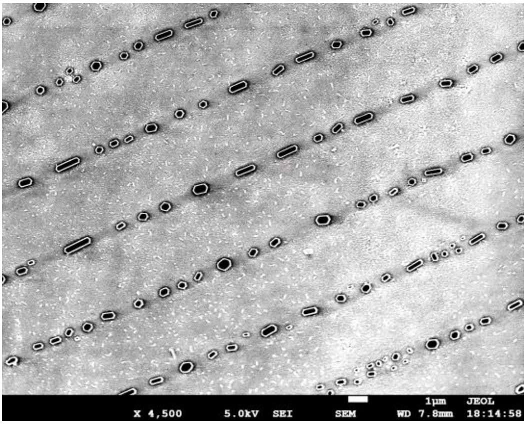
A spatially arranged network of gold micro- and nanoclusters was synthesized on thermally oxidized silicon substrates (Figure 1). The desired line pattern was acquired using photolithography and gold deposition via sputtering. Gold micro- and nanoclusters were formed after thermal annealing of the samples. We examine the behaviour of height and surface area of the gold clusters for different annealing temperatures and times. The spatially arranged network of gold clusters may prove useful in working with proteins and biosensorics.

Figure 1. SEM image of a sample after thermal annealing at 1000 °C for 1 h.



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P38 - Microwave-Assisted Hydrothermal Method with Plant Material Incorporation for Iron Oxide Nanoparticles

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Microwave-assisted hydrothermal synthesis is gaining popularity for its simplicity, shorter synthesis time, and control over conditions, enabling precise regulation of the final product's size, shape, and composition, including the integration of natural plant materials. In this study, iron oxide nanoparticles were synthesized using this method with $FeCl_3$ as the precursor in highly alkaline media. The investigation explored the effects of incorporating lemon essential oil and extract, along with different synthesis conditions (200 °C for 20 minutes and 5 minutes), on the resulting iron oxide phases. Samples with essential oil showed hematite and goethite phases, like reference samples, while those with extract exhibited pure magnetite phase. These findings are intriguing as magnetite particles are typically synthesized using Fe^{2+} and Fe^{3+} precursors in a 1:2 ratio, but only Fe^{3+} precursor was used here. The resulting product was characterized using FTIR, PXRD, and FE-SEM. In conclusion, this study presents an environmentally friendly method for synthesizing iron oxide nanoparticles, combining the microwave-assisted hydrothermal method with plant material incorporation.

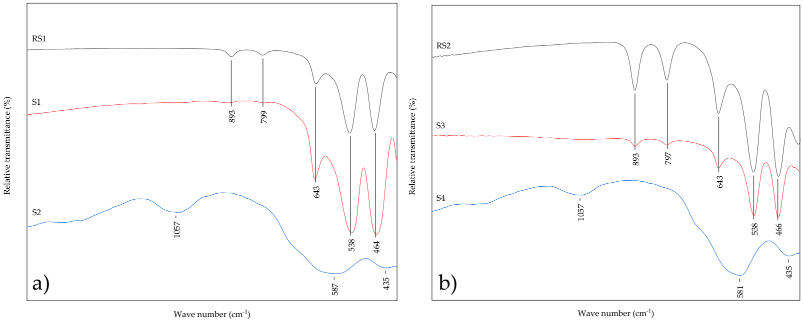

Figure 1 FTIR spectra of samples synthesized at 200 °C for a) 20 min and b) 5 min.

P39 - Hydrostatic pressure effects on electronic and crystal structures of non-centrosymmetric Eu*T*Ge_3 (*T*=Co, Rh & Ir)

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Intermetallic EuTX_3 (*T*: transition metal, *X*= Si/Ge) forms a non-centrosymmetric $BaNiSn_3$-type structure and has been attracting considerable attention due to complex magnetic structures and unique pressure phase diagram that potentially accommodates superconductivity under pressure [1, 2]. At ambient pressure, Eu*T*Ge_3 series host divalent Eu ions ($4f^7$, J=7/2) and exhibit antiferromagnetic ordering at low temperature (< 15 K), while the ordering direction depends on the selection of *T* [1]. We studied the pressure evolution of the electronic and crystal structures of Eu*T*Ge_3 (*T*= Co, Rh, Ir) by high-resolution x-ray absorption spectroscopy and powder x-ray diffraction. Our study unveiled that the pressure gradient of the Eu valence change varies depending on *T*. By applying pressure, a continuous contraction of the lattice volume was observed in both $EuCoGe_3$ [3] and $EuRhGe_3$. $EuIrGe_3$ implied a structural transition above 34 GPa.

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P40 - High-Pressure Structural Behavior of XeF_2–TaF_5 Adducts

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High-pressure investigations can open new avenues of research in already established fields. Chemical and structural changes of compounds under high pressure in the GPa range can be studied by means of a diamond anvil cell (DAC). This provides access to previously unattainable compounds and phases with exotic properties, such as new or rare oxidation states, bonding modes, or coordination numbers [1].

The high-pressure aspect of noble-gas chemistry is particularly interesting, as many intriguing but elusive phases have been proposed and a vast majority of them remain only as theoretical predictions [2,3]. In this work, we have performed an experimental high-pressure structural study of the adducts of XeF_2 and TaF_5. Single crystals were grown either from solutions in anhydrous HF or by controlled cooling of the melts [4]. Air-sensitive compounds were loaded into DAC inside of a glovebox. Special attention was devoted to the selection of a suitable inert pressure-transmitting medium. Pressure-induced structural changes, such as the dimerization of $[XeF]^+[TaF_6]^-$ shown in Fig. 1, were studied using single-crystal X-ray diffraction and Raman spectroscopy.

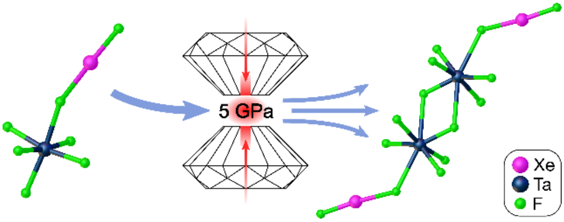

Figure 1 High-pressure induced dimerization of $[XeF]^+[TaF_6]^-$.

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P41 - Syntheses of Novel Polyfluoridotitanate(IV) and Polyfluoridostannate(IV) Salts

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TiF_4 and SnF_4 react with fluoride-ion donors of different strengths yielding a variety of compounds with monomeric, oligomeric and polymeric fluorido anions [1–3]. Despite extensive research and a wide range of synthetic approaches employed, the factors determining the nature and degree of aggregation found in these anions remain poorly understood.
Within our investigation of the XeF_2–MF_4 systems [4,5], TiF_4 and SnF_4 were reacted with XeF_2 and other selected Lewis bases. In this contribution, an overview of fluoridotitanates(IV) and fluoridostannates(IV) obtained from anhydrous HF solutions or upon thermal treatment is presented. Their rich structural diversity, ranging from MF_5^- chains and $M_2F_9^-$ ladders (M = Sn, Ti) to corrugated $Sn_4F_{17}^-$ layers (Figure 1) is highlighted and the preferential formation of the observed anions under selected reaction conditions is discussed beyond the formation of species defined solely by the initial stoichiometry.

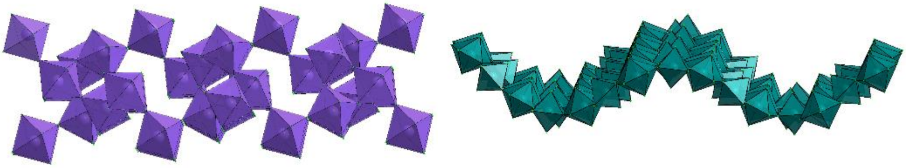

Figure 1 The $M_4F_{17}^-$ anionic layers found in noble-gas compounds $[XeF][Ti_4F_{17}]$ (*left*) and $[Xe_2F_3][Sn_4F_{17}]\cdot XeF_2\cdot HF$ (*right*).

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P42 - Structural Investigation of Silver(II) Sulfates by 3D ED

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Currently, the only fluorine-free ligand that can withstand the oxidizing power of silver(II) is the sulfate anion, SO_4^{2-}, as evidenced by the intriguing α-$AgSO_4$ [1], β-$AgSO_4$ [2], and $AgSO_4·H_2O$ [3]. The three compounds were structurally characterized by powder X-ray diffraction, with some ambiguities arising in the case of α-$AgSO_4$, as different structural models were reported [1,4,5]. In order to conclusively determine the structures, the silver(II) sulfates were examined by 3D electron diffraction (3D ED) [6]. The redetermined crystal structure of α-$AgSO_4$ (Figure 1) differs from the previously proposed models, whereas the structures of β-$AgSO_4$, and $AgSO_4·H_2O$ validate the results obtained from PXRD.

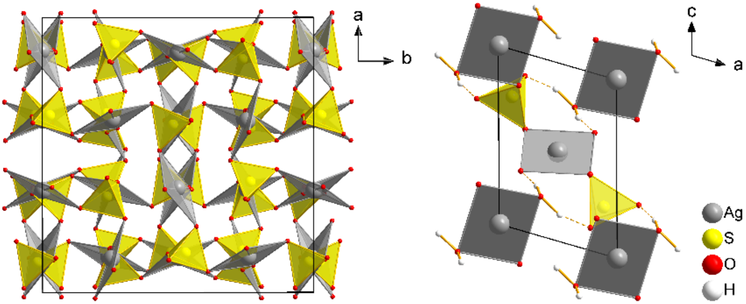

Figure 1: Crystal structures of α-$AgSO_4$ (left) and $AgSO_4·H_2O$ (right).

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P43 - Pyrophyllite modified carbon-based electrode

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The main goal is to develop electrode material for the detection of traces of pesticides in food and water in a wide range of pH values. The leading idea is to use natural clay **pyrophyllite to modify carbon paste electrode. SPEX** Mixer/Mill 5100 is used for mechanochemical modification. The changes in the structure of pyrophyllite before and after the grinding process were studied by means of PSD, XRD, FTIR, and DTA-TG [1]. The electrochemical behavior of the sensor was followed using differential pulse stripping voltammetry (DPSV). It is shown that obtained material can be used as electrodes in electrochemical sensors for pesticide detection in a wide range of pH.

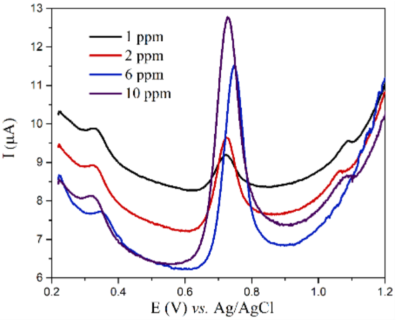

Figure 1 DPSV in Britton – Robinson buffer at pH 8

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P44 - Development and characterization of pyrophyllite based composites with silver nanoparticles

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The clay-based materials are suitable for designing hybrid clay systems as potential multifunctional carriers with higher efficacy for a variety of biological applications. In this study, pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, was mechanochemically activated using 2, 5, and 10wt% of silver in the form of $AgNO_3$. The grinding time was adjusted from 20 to 320 minutes. The collected samples were analyzed using XRD (X-Ray diffraction analysis), SEM (Scanning Electron Microscopy) with EDX (Energy Dispersive X-Ray Analysis) as well as PSD (Particle-size Distribution). The results showed that AgNPs were produced during the mechanochemical processing of this mixture and that its physicochemical characteristics are significantly influenced by the amount of silver added and the grinding time. This and further solid-state characterization of the pyrophyllite/$AgNO_3$ composite in conjunction with biopharmaceutical evaluation will allow us to investigate the potential of this system and make additional adjustments for performing controlled and targeted drug delivery.

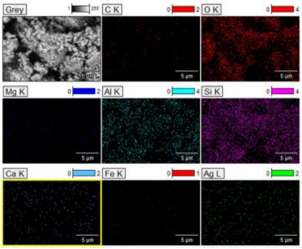

Figure 1 SEM and EDX of pyrophyllite/Ag NO_3.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia Grant No. 451-03-47/2023-01/200017

P45 - Development of two-dimensional micro hydrogen fuel cell

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Our research focuses on the development of a compact two-dimensional micro-hydrogen fuel cell using SU8 photoresist. The scope of micro fuel cells has been extensively studied [1-3] and our cell is the first proton exchange membrane hydrogen fuel cell (PEMFC) with hydrogen and oxygen channels on the same side of the electrolyte membrane. The channels with a total volume of about 2.4 mm^3 are separated by a 120 micrometer thick wall and covered with a membrane. Through experimental investigations, we have obtained promising results for the performance of the fuel cell. The reproducible polarization curve measured several times is shown in Fig. 1, and the long-term evaluation shows stability and durability. These results demonstrate the effectiveness of our two-dimensional micro-hydrogen fuel cell. The compact integration of channels on one side of the electrolyte membrane enables the future development of 2D fuel cell stacks. This research contributes to the advancement of sustainable hydrogen-based energy conversion technologies, with potential application in low power microelectronics.

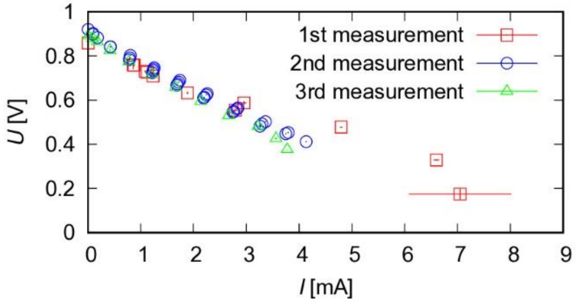

Figure 1 Polarization curve of two-dimensional micro fuel cell.

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P46 - Synthesis and structural study of three-component chiral metal-organic frameworks

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Metal-organic frameworks (MOFs) are a class of advanced materials with numerous potential applications, such as *i*) catalysys [1], *ii*) enantiomeric separation [2], *iii*) adsorption and separation of gases and other guest molecules [3]. Over 118 000 datasets in the Cambridge Structural Database (CSD) are in MOF subset, but only 26 datasets are three-component MOFs that contain copper(II), a heterocyclic base as a linker, and an amino acid or an amino acid derivative [4]. In this work, we report solution and mechanochemical syntheses and crystal structural analysis of four new three-component MOFs of copper(II) with 1,2-bis(4-pyridyl)ethene (bpe) and amino acid (L-threonine, thr; L-serine, ser; and L-homoserine; hser). Three isoreticular MOFs were obtained with all three amino acids (topological type *uki*, Figure 1), but with L-threonine another type of framework also crystallized (topological type *irl*, Figure 1).

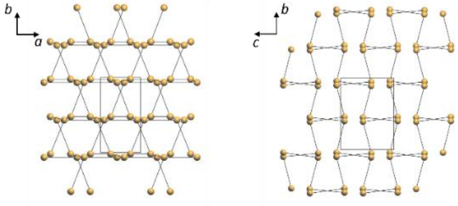

Figure 1 Two types of topologies obtained in MOFs prepared in this work: *uki* (left) and *irl* (right).

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P47 - Spectroscopic Evidence Heat Accumulation within Carnauba Wax in Mixtures with Montmorillonite

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The presented phase change materials gained attention due to their potential for high-density lateral energy storage in isothermal conditions [1, 2]. We focus on studying a biobased carnauba wax and its mixtures with nanoclay.

IR spectral evidence proved the intact molecular and atomic structure caused by chemical reactions. The band positions for 50(wax)/50(clay) and for 500 times cool-heat cycling samples were identical within the experimental error, proving the chemical stability of the system.

The variable temperature ^{13}C CP NMR spectrum of the pure wax is dominated by the resonances of the aliphatic carbons at 14.7, 24.3, 30.2 ppm and ca 33.0 ppm for the chain methylene carbons and 62.5 and 65.5 ppm for C-OH, -OCH_2- groups. The ratio between the integrals of the resonances at 33 (trans):30 (gauche conformers) ppm is 3.85:1. The predominant trans conformation suggests the presence of abundant crystalline regions in the aliphatic chains with minor amorphous domains. A slight shift of about 0.2 ppm to lower field of the initial 32.8 ppm signal as well as sharper resonances due to enhanced dynamics are detected increasing the temperature. The ratio between the integrals for the trans- and gauche conformation changes in favor of the latter (33:30 ppm=1.25:1) due to increase of the amorphous regions in the sample with nanoclay. Surprisingly, the ^{13}C CP spectra after annealing at 60 °C for 1 month reveal further disorder. The ratio between the integrals of the signals at 33:30 ppm is 1:1. It is obvious that during thermal exposure of the material, reorganization of their structure took place at the molecular level without chemical reactions, which must be taken into account when operating such materials on an industrial scale.

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P48 - Halloysite nanotubes modified with nanoparticles of cerium(IV) oxide for UV protection

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In this study, we synthesized nanomaterials based on cerium(IV) oxide and halloysite aluminosilicate nanotubes. The synthesis of nanomaterials aluminosilicate nanotubes / cerium(IV) oxide was carried out under mild conditions in aqueous solutions without stabilizers, according to the principles of "green" chemistry. We coated cerium(IV) oxide nanoparticles on aluminosilicate nanotubes to further enhance the stability and immobility of the nanoparticles. The content of cerium(IV) oxide for a number of synthesized nanomaterials was 0.5, 1, 2, 3, 4, 5 wt. %. We used halloysite aluminosilicate nanotubes. They are non-biodegradable and biocompatible, so they can be used in many applications. Nanocrystalline cerium(IV) oxide has antioxidant properties and has a low toxic effect on living organisms. We investigated aluminosilicate nanotubes and aluminosilicate nanotubes / cerium(IV) oxide nanomaterials for UV protection using UV-Vis-NIR spectroscopy. The absorption of UV radiation by the nanomaterials showed maxima at 269–305 nm with a significantly higher absorption intensity and a wider band than for the original aluminosilicate nanotubes. Cerium(IV) oxide enhanced the absorption of UV radiation by nanomaterials, the intensity of absorption correlates with the content of oxide in them. Cerium(IV) oxide nanoparticles induced a blue shift of the edge of the absorption band in the UV range, and we found that the shift was nonlinearly related to particle size.

The main hypothesis of this study is that cerium(IV) oxide nanoparticles can be a viable alternative to titanium dioxide or zinc oxide nanoparticles as inorganic UV blocking agents in UV filters. cerium(IV) oxide has relatively low photocatalytic activity and high absorption in the ultraviolet range. The use of a substrate such as aluminosilicate nanotubes can reduce the potential for absorption of nanoparticles through the skin.

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P49 - Automated differential 3ω method for thermal conductivity measurement of proton exchange membranes

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Polymer electrolyte membranes (Nafion) prepared at the Faculty of Science, University of Split were successfully implemented into hydrogen micro fuel cells with promising performance [1]. Membranes will be modified with the aim of increasing dry film electron and proton conductivity and optimizing lateral heat conductivity to improve H_2 fuel cell efficiency and longevity.
The 3ω thermal conductivity measurement technique applies to amorphous solids, crystals and amorphous thin films [2]. Micro heaters are fabricated by vacuum metallization, optical lithography and etching. AC current is sent through the heater with frequency ω which induces local heating of the substrate as a function of 2ω. Third harmonic of the voltage across the heater contains information on the thermal properties of the material in contact with the heater. Thin film of Nafion coated onto the heater is considered a parallel thermal resistance. Thermal conductivity of the film is calculated by subtraction from the previously measured conductivity of the substrate [3].

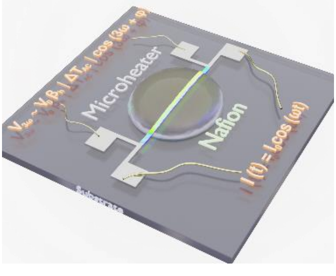
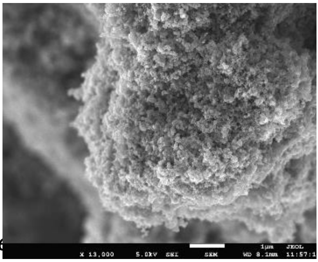


Figure 1 Nafion coated onto 3ω sensor



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P50 - Development of GO/WPA nanocomposites with ion beams for electrochemical supercapacitors

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Development of energy storage devices is a significant task in addressing present-day challenges. Among others, graphene-based supercapacitors are interesting due to versatile synthesis and modification routes. Our recent research showed potential of graphene oxide (GO) and 12-tungstophosphoric acid (WPA) nanocomposite for supercapacitor applications, where surface chemistry of GO, redox properties of WPA and structural modification of both components played a crucial role [1]. In this work further development of GO/WPA supercapacitors was investigated using ion beam irradiation as a tool for modification of structure and surface chemistry. GO/WPA composites with different mass ratios of constituents were synthesized and irradiated with low and high energy ion beams (N 40 keV and Xe 167 MeV). Surface chemistry of GO and composites was investigated with X-ray photoelectron spectroscopy which showed that higher fluences are needed for modification of functional groups in the case of composites. Galvanostatic charge discharge measurements have shown an improved capacitance of irradiated composites, which can be connected to previously observed changes induced in WPA with ion beam irradiation [2].

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P51 - Phase-memory electron spin relaxation time of vanadyl(IV) cations incorporated in MOFs measured by Carr-Purcell-Meiboom-Gill pulse sequence

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Metal-organic frameworks (MOFs) are porous coordination polymers built from metal nodes and organic linkers.[1] These materials can potentially be used in spintronics as 2D or 3D molecular spin qubits frameworks, providing required spatial ordering and separation among molecular spins.[2] The phase-memory electron spin relaxation time (T_m) of two multivariate porphyrinic Zr-MOFs, MOF-525 and PCN-223,[2] doped with 10% vanadyl(IV) cations were examined by pulse electron paramagnetic resonance spectroscopy. Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was applied as a dynamical decoupling method to extend T_m conventionally measured by Hahn-echo pulse sequence.[3-5]

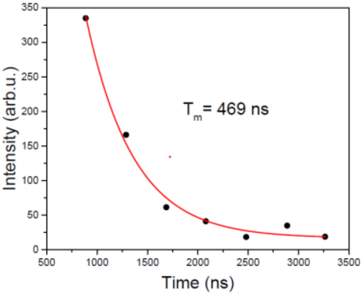

Figure 1. CPMG echo time decay of vanadyl(IV) cations in MOF-525 at 80 K. Phase-memory relaxation time (T_m) is estimated from the monoexponential fit (red line).

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P52 - Iron L-edge RIXS of multiferroic $[(CH_3)_2NH_2]Fe(HCOO)_3$

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$[(CH_3)_2NH_2]Fe(HCOO)_3$ belongs to a family of metal-organic frameworks with a perovskite like ABX_3 structure, showing a simultaneous ferroelectric and magnetic order at low temperature [1,2]. This multiferroïc behavior is achieved by combining the magnetic ordering inside the $Fe(HCOO)_3$ skeleton, while the charge ordering appears in the organic $[(CH_3)_2NH_2]^-$ part occupying interstices. In order to probe the effects of the ordering of the $[(CH_3)_2NH_2]^-$ at the 164 K ferroelectric transition on the environment of the Fe ion in the $Fe(HCOO)_3$ skeleton, we measured Fe L-edge resonant inelastic x-ray scattering (RIXS).

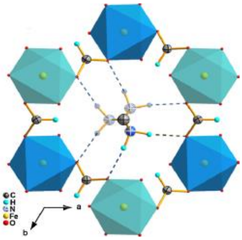

Figure 1 Possible orientations of the $[(CH_3)_2NH_2]^-$ ion inside the $Fe(HCOO)_3$ skeleton, from [3].

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P53 - Search for novel phases in Y-Ba-Cu-O family

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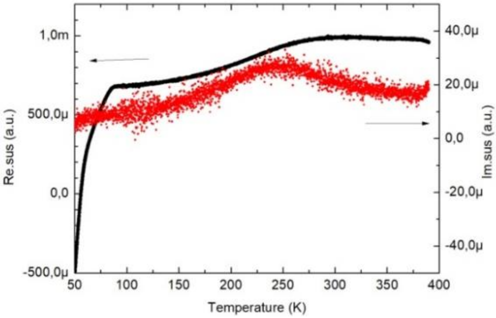
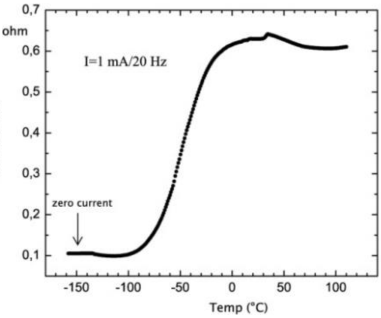
Discovery of the superconductivity 1987. at $T_c = 91$ K in $YBa_2Cu_3O_{7-x}$ (123 phase) by Chu and co-workers [1] was followed by worldwide reports claiming possible appearance of higher transition temperatures. The present author and co-worers reported resistive transition at 210 K indicated by small diamagnetism [2,3], and he proposed possible new phase in Y–Ba-Cu-O [4]. Common to all appearances was poor reproducibility of the evaluated data.

2019. author DD reused the mixed initial powders of 123 phase prepared 1987, repeated the preparation, and showed that data presented in [2,3]are correct and reproducible. The measurement of AC susceptibility (M.Prester and Dj.Drobac, IF) is shown in Fig.1, and shows two phase system, one started Meissner effect at +15 °C, and at 91 K starts a downturn coming from a 123 phase. Estimated fraction of diamagnetism at T~91 K is ~ 6-7 percent of the total diamagnetism. Electric resistivity is shown in Fig.2.





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P54 - Paramelaconite Cu_4O_3, controversies and facts

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Intermediate copper oxide Cu_4O_3 (paramelaconite) has been investigated in past decades in the mineral sample. The examinations of the structure by Frondel and O'Keeffe and Bovin (FO'KB) revealed the tetragonal unit cell containing 4 unit formulae Cu_4O_3. However, repeated XRD records on the same, as well as, as on other mineral sample don't support the structure described by FO'KB, presumably as a result of a high sample inhomogeneity. Laboratory preparations, of the pure paramelaconite indicated by FO'KB XRD structure failed in all attempts. Present author (DD) prepared the sample containing the mixture of paramelaconite and other oxides, like Ag_2O and PbO. In the meantime, the same author prepared the pure oxide indicated by the paramelaconite stoichiometry $CuO_{0.75}$, and samples exhibit all known properties of the mineral sample (antiferromagnetism, neutron scattering, spiral magnetism, DSC), but XRD reveals the structure that of CuO, giving rise to a possibly some novel type of copper oxide.

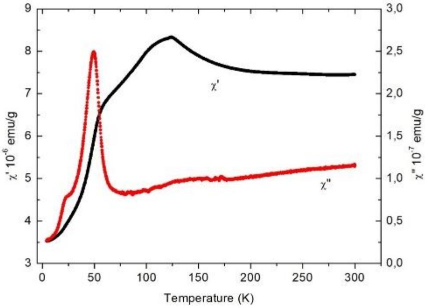

Figure 1 Temperature dependence of the magnetic susceptibility of $Cu_4O_{0.75}$ (M. Prester and Dj. Drobac).

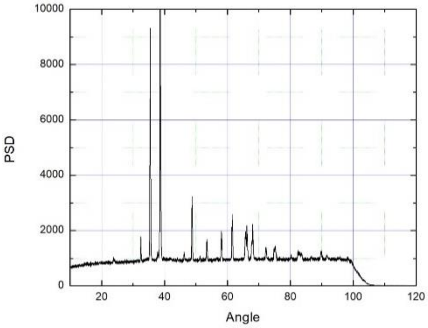

Figure 2 XRD of $Cu_4O_{0.75}$ (V. Mandić).

P55 - Anisidinium Tetrachlorocuprates(II): Structure-Related Evolution of Magnetic Order

Edi Topić,[1] *Pavla Šenjug,*[2] *Dario Barišić,*[2]
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Hybrid halometallates offer wide possibilities for the design of multifunctional materials.[1] The electric and magnetic properties of these materials are often tightly coupled with the dimensionality of their inorganic framework.[2]

Three tetrachlorocuprate(II) hybrids based on anisidine isomers were prepared and studied in the solid state *via* magnetization measurements and X-ray diffraction.[3] Depending on the geometry of the cations a discrete, defective layered and layered frameworks were obtained for the *ortho*-anisidinium *meta*- and *para*-hybrids, respectively. For layered and defective layered structures this affords quasi-2D layered magnets, thus unveiling a complicated interplay of strong and weak magnetic interactions leading to the long-range ferromagnetic order. In the case of the structure with discrete tetrachlorocuprate(II) ions interesting antiferromagnetic (AFM) behavior was established. In extension, the method for calculation of dimensionality of the inorganic framework as a function of interaction length was developed, thus providing additional reasoning for the observed relation between cation geometry and framework dimensionality, as well as their relation to the observed magnetic behavior.

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[3] E. Topić, P. Šenjug, D. Barišić, I. Lončarić, D. Pajić, M. Rubčić, *Cryst. Growth Des.* 2023, doi.org/10.1021/acs.cgd.3c00066.

P56 - Magnetic properties of fluorinated ethyl-ammonium derivatives

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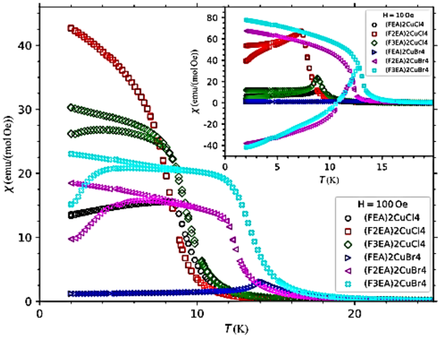
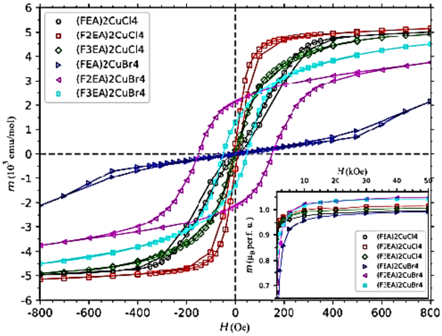
Metal-organic compounds with 2D perovskite structure have in recent times proven to be a fruitful ground in search for multifunctional materials, e.g. in domain of optical switching of magnetization and magnetoelectricity [1,2,3], thus making them suitable for applications in fast and energy efficient computer logic [4]. Here we discuss magnetic properties of six metal-organic compounds derived from parent compound EA2CuCl4. The structure consists of planes of (CuCl4)2- or (CuBr4)2- corner sharing octahedra. Ethyl-ammonium cations act as spacers between the planes, where one, two or three of the H atoms in the NH3 tail of the cation are substituted by F atoms. The resulting compounds show a variety of magnetic properties (ferromagnetic, antiferromagnetic, metamagnetic) as the substitution of H with F atoms and Cl with Br atoms affects the magnetic interactions.





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P57 - Magnetic properties of metal-organic perovskites $[C(NH_2)_3][M^{II}(HCOO)_3]$ (M = Cu, Mn and Co)

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Lately, perovskites (ABX_3) are highly popular in the science of materials, especially metal-organic perovskites containing both organic and inorganic building blocks. Hybrid organic-inorganic perovskites (HOIP) have many potentials, the most interesting being the magnetic properties they hold. Even though the magnetic properties have been tested on powdered samples, the magnetic properties have not been tested on many monocrystals due to lack of synthetic strategies. [1]

With this in mind, we have prepared a series of ABX_3 hybrid organic-inorganic Cu^{2+}, Mn^{2+} and Co^{2+} perovskites containing formate bridge on the X site and a guanidinium molecule on the A site; $[C(NH_2)_3][Cu(HCOO)_3]$ **(1)**, $[C(NH_2)_3][Mn(HCOO)_3]$ **(2)**, $[C(NH_2)_3][Co(HCOO)_3]$ **(3)**. For all compounds, the quality monocrystals large enough are obtained. The temperature dependence of magnetization M(*T*) was measured using a SQUID magnetometer in the temperature range 1,8 K–350 K. The hysteresis was also measured with the temperature being between 2 K–10 K. The Curie-Weiss law was successfully fitted on higher temperature intervals for all compounds. Depending on the crystal structure, the magnetic susceptibility was modelled for chain compounds using Fischers approach for local spins larger than ½, and Bonner-Fischer approach for local spins of ½ in the lower temperature intervals. All three compounds have magnetic phase transitions at low temperatures. Magnetic transitions are at temperatures 20 K for compounds **(1)** and **(2)** and at 25 K for compound **(3).** Analyzing the graphs lead to the conclusion that all three compounds are weak ferromagnetic materials.

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P58 - Hybrid organic-inorganic multiferroic perovskite cuprates: long range magnetic order from low-D magnetism

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The full title ought to be: “Hybrid organic-inorganic multiferroic perovskite cuprates: how long range magnetic order originates from the low-dimensional magnetism, and some notes about perspectives of their application in photonics, spintronic, memories, quantum-computing and opto-magneto-electronics.”

Some novel results of magnetic research in 2D and 3D metal-organic systems will be presented [1,2,3] and discussed in a broader context of multiferroicity and applications [4].

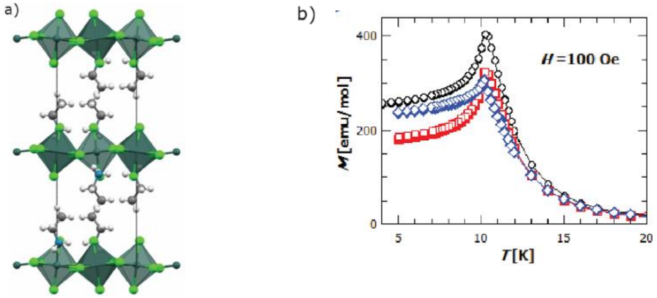

Figure 1 Layered metal-organic perovskite diethylammonium-tetrachlorocuprate(II). a) Prototype crystal structure. b) Magnetic phase transition.

[1] E. Topić, P. Šenjug, D. Barišić, I. Lončarić, D. Pajić, M. Rubčić, *Cryst. Growth Des. 2023 10.1021/acs.cgd.3c00066*.
[2] P. Šenjug et al, Materials **14** (2021) 1730.
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P59 - Magnetoresistance of single crystal rutile TiO_2

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Rutile, the stable phase of polymorphic titanium dioxide, exhibits small polaronic excitations that affect electronic transport and have potential applications in energy conversion, battery technology, solar cells, and electrical devices, as well as the biocompatibility of bone implants [1,2]. In this study, we present the magnetic field dependence of the electrical resistivity of single crystal rutile TiO_2, which is hardly found in the literature. The electrical resistivity has a minimum at 30 K and increases by six orders of magnitude when cooled down to 2 K. In the magnetic field, the electrical resistivity increases especially at low temperatures.

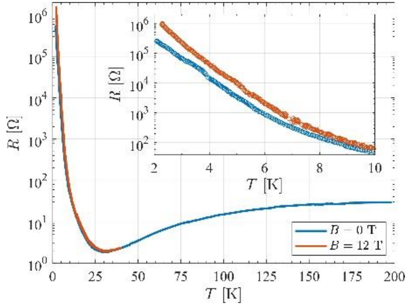

Figure 1. Temperature dependence of the resistivity of rutile TiO_2 single crystal for 0 T and 12 T.

[1] Franchini C, Reticcioli M, Setvin M, Diebold U, Nature Reviews Materials, (2021), 560-586, 6(7), (2021), 560-586, 6(7).
[2] Diebold U, Surface Science Reports, (2003), 53-229, 48.

P60 - Fabrication of solar-active materials for environmental technologies

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Bismuth vanadate ($BiVO_4$) is one of the semiconductors with perspective for solar-driven activation and usage for various environmental applications such as water purification and/or renewable energy production via H_2 evolution. However, several shortcomings of $BiVO_4$, such as short charge carrier diffusion length, poor electron transfer kinetics, and relatively fast photo-generated charge recombination may restrict its potential effectiveness.

In this study we present simple and energy efficient fabrication of $BiVO_4$ by co-precipitation using ethylenediaminotetracetic acid (EDTA), followed with the tailored thermal treatment to obtain optimum homojunction structure between monoclinic scheelite and tetragonal zircon crystal phases allowing minimization of aforementioned shortcomings. To further improve already promising photocatalytic properties of obtained isotype $BiVO_4$; e.g. 2.5 times higher diclofenac removal rate under Solar irradiation than its hydrothermal counterpart possessing pure monoclinic scheelite structure, the enrichment by reduced graphene oxide and surface-decoration by nobel and transition metal ions was performed. The structural and morphological properties of all obtained materials are inspected and compared. The analysis of semiconducting properties of enriched materials showed further minimization of charges recombination leading to increased degradation rates of studied organic pollutants (ciprofloxacin, single-benzene-ring compounds) under Solar irradiation, as well as the potential for hydrogen evolution.

P61 - High-throughput and high-resolution Raman spectrometer for monitoring of mechanochemistry reactions

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In order to overcome the limitations in temporal monitoring of mechanochemistry reactions associated with Fiber Raman Spectrometers [1], we have developed a novel f/0.8 free-space optics Raman spectrometer whose time resolution is improved by almost two orders of magnitude.

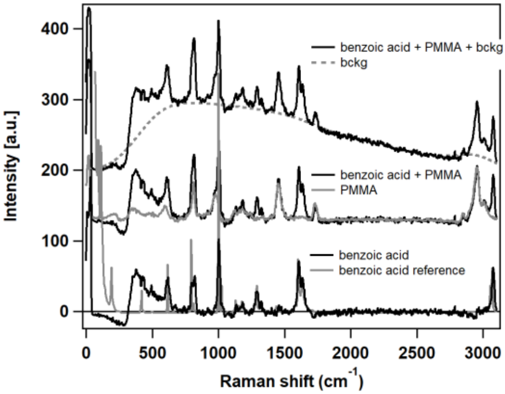

Figure 1 Raman spectra of benzoic acid in a typical PMMA milling cell compared with reference spectra (bottom panel). The upper panels demonstrate the passage from raw spectrum to the final spectra of compound of interest.

By employing a low-cost and sensitive detector, free-space optics, and advanced spectral data processing, our spectrometer achieves a significantly higher spectral resolution of 6-8 cm^{-1} compared to the typical 15 cm^{-1} resolution of FRS. This enhanced resolution allows for more accurate identification and characterization of chemical species appearing during milling. Furthermore, our spectrometer achieves a remarkable reduction in integration time, requiring less than 100 ms to capture a Raman spectrum with a good signal-to-noise ratio.

[1] S. Lukin, K. Užarević, I. Halasz, *Nat Protoc* **16**, (2021) 3492–3521

P62 - Machine learning aided *ab initio* crystal structure prediction of metal-organic frameworks

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Metal-organic frameworks (MOFs) are hybrid materials constructed of transition metal nodes connected with organic linker molecules. MOFs exhibit many exciting applications, including gas sorption and separation, catalysts, sensors, energetic martials and many more [1]. The specific application of MOFs is dependent on the choice of nodes and linkers. The development of our *ab initio* crystal structure prediction (CSP) method for predicting MOF structures and functional properties, could offer us a systematic way to design MOFs without extensive experimental screening.

The recently reported *ab initio* CSP approach [2] for MOFs, has been validated by accurately predicting the structures of several classes of MOFs. Later, we further demonstrated the capabilities of this MOF CSP method by predicting three novel copper (II) hypergolic zeolitic imidazolate frameworks (ZIFs) [3]. Crucially, our predicted ZIF structures matched the subsequently synthesized materials, demonstrating the feasibility of this materials design approach. However, the high computational cost from using periodic density-functional theory (DFT) calculations for MOF structural predictions and energy rankings can be still improved. Therefore, machine learning (ML) trained interatomic potentials are currently investigated on the highly polymorphic ZIFs. So far, ML optimized structures have shown good agreement with periodic DFT optimized structures, and experimentally matching ZIFs have also been observed. The computational cost for ML structural optimizations is a factor of 1000 less than DFT ones, marking great progress towards our ultimate goal of high-throughput *ab initio* MOF design.

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