

## MS35-O3

**CO<sub>2</sub> adsorption sites in the triangular channels of Fe<sub>2</sub>(BPEB)<sub>3</sub>: an insight by in-situ and operando high-resolution and high-energy PXRD**Simona Galli<sup>1</sup>, Carlotta Giacobbe<sup>2</sup>, Elisa Lavigna<sup>1</sup>, Angelo Maspero<sup>1</sup>

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Growing concerns on global warming stimulate research to reduce anthropogenic CO<sub>2</sub> emission and lower atmospheric greenhouse gases concentration. Till the use of greener energy sources will be practicable, CO<sub>2</sub> sequestration technologies will be the most viable strategy to mitigate global warming. Many all-inorganic adsorbents have been studied in this respect. Lately, metal-organic frameworks [1] (MOFs) have emerged as a promising alternative to inorganic materials in gas adsorption. We have recently studied the structural features underneath the remarkable CO<sub>2</sub> adsorption capacity (40.5 wt % at 298 K and 10 bar) of Fe<sub>2</sub>(BPEB)<sub>3</sub> [2] (H<sub>2</sub>BPEB = 1,4-bis(1*H*-pyrazol-4-ylethynyl)benzene), by coupling advanced experimental and computational tools [3]. *In situ* and *operando* high-resolution and high-energy PXRD experiments were run at the beamline ID22 of ESRF at 273 and 298 K, dosing CO<sub>2</sub> in the pressure range of 0-20 bar. Juxtaposing structure determination to total scattering analysis enabled us to disclose the CO<sub>2</sub> primary adsorption sites, and the host-guest and guest-guest interactions at all the investigated pressures. Molecular dynamics simulations confirmed the experimentally individuated adsorption sites and helped in characterizing the energetics of the process. Our molecular-level insight into the adsorption of CO<sub>2</sub> by Fe<sub>2</sub>(BPEB)<sub>3</sub>, a rigid host without exposed metal sites or functional groups with particular affinity to CO<sub>2</sub> on the ligand, affords important information on a debated topic, i.e.: the chemical and structural properties a host should possess for efficient CO<sub>2</sub> adsorption under rather mild conditions.

## References:

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**Keywords:** High-resolution PXRD, high-energy PXRD, CO<sub>2</sub> adsorption

## MS35-O4

**Coordination Polymers with Supramolecules as Nodes**Eugenia Peresykina<sup>1</sup>, Dr. Alexander Virovets<sup>1</sup>, Prof. Dr. Manfred Scheer<sup>2</sup>

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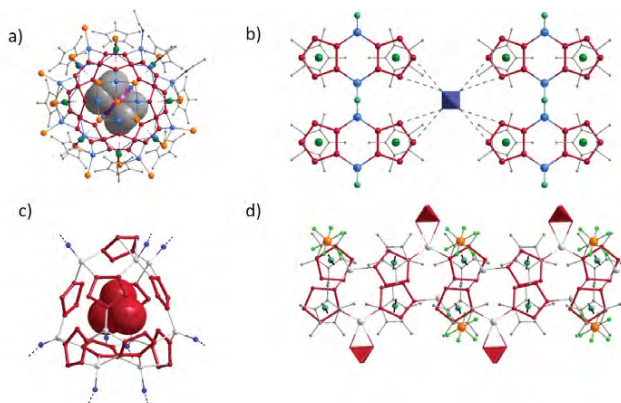
email: [peresyp@niic.nsc.ru](mailto:peresyp@niic.nsc.ru)

Since 2003, we have been investigating the use of pentaphaferrocene [Cp<sup>R</sup>Fe(η<sup>5</sup>-P<sub>5</sub>)] (Cp<sup>R</sup> = η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>, R = Me, CH<sub>2</sub>Ph, PhC<sub>4</sub>H<sub>9</sub>) as a building block in supramolecular chemistry. The phosphorus atoms of the planar P<sub>5</sub>-rings are able to coordinate to Cu<sup>+</sup> and Ag<sup>+</sup> (M<sup>+</sup>) cations resulting in either coordination polymers with M<sub>x</sub>(halogen)<sub>y</sub> fragments as nodes or in self-assembled spherical hollow supramolecules of 2.1–4.6 nm in diameter [1-3]. Both coordination polymers and supramolecules can serve as matrices or molecular containers for various small molecules. For example, we succeeded in the encapsulation of metallocenes such as Cp<sub>2</sub>Co<sup>+</sup> [2] (Fig.1a) as well as of metastable molecules such as the tetrahedral molecules white phosphorus, P<sub>4</sub>, and yellow arsenic, As<sub>4</sub> [3] (Fig.1b).

A new direction of our research is to connect giant supramolecules by organic linkers to form coordination polymers with entire supramolecules as nodes. Thus, the coordination of Ag<sup>+</sup> cations to the P<sub>5</sub>-rings results in the in situ formation of supramolecules, while the additional coordination of Ag<sup>+</sup> to N-donor atoms of N≡C(CH<sub>2</sub>)<sub>n</sub>C≡N (L<sup>n</sup>, n=5-10) (L<sup>n</sup>) flexible linker, in turn, leads to 1D, 2D and 3D coordination polymers in one-pot reactions. Depending on the experimental conditions, coordination polymers with mononuclear Ag<sup>+</sup> nodes can also be obtained. The composition and structure of the supramolecules as well as the dimensionality of the polymer can be controlled by changing the reaction stoichiometry or by adding guest molecules as P<sub>4</sub>. Thus, in the presence of P<sub>4</sub>, two new 1D-polymers were obtained, (P<sub>4</sub>)@[Cp\*FeP<sub>5</sub>]<sub>9</sub>Ag<sub>8</sub>(L<sup>10</sup>)<sub>4</sub>(SbF<sub>6</sub>)<sub>9</sub> (Fig.1c) and [(Cp\*FeP<sub>5</sub>)<sub>2</sub>Ag<sub>2</sub>(μ,η<sup>2</sup>-P<sub>4</sub>)(SbF<sub>6</sub>)]SbF<sub>6</sub> (Fig.1d). The former contains polynuclear cationic nodes of [Ag<sub>9</sub>(Cp\*FeP<sub>5</sub>)<sub>9</sub>]<sup>9+</sup> that encapsulates tetrahedral P<sub>4</sub> molecules in the central cavity.

Effective collaboration between chemists and crystallographers allowed developing effective crystallization methods, skilled crystal handling and proper single-crystal X-ray data collection techniques to perform structural studies at atomic resolution. As a result, fine details of structures containing hundreds of heavy atoms could be analysed, shedding light on the nature of host-guest interactions. In addition to the usual methodological problems as for instance severe crystallographic disorder, the structural studies are occasionally encumbered by the appearance of modulated or incommensurate structures. Financial support from the ERC grant ADG 339072 is gratefully acknowledged. Parts of these investigations were carried out at PETRA III synchrotron source at DESY, a member of the Helmholtz Association (HGF).

Fig. 1. *a*) encapsulation of  $\text{Cp}_2\text{Co}^+$  in the supramolecule; inclusion of  $\text{E}_4$  ( $\text{E}=\text{As}, \text{P}$ ) molecule into *b*) coordination polymer and *c*) into  $[\text{Ag}_9(\text{Cp}^*\text{FeP}_5)_9]^{9+}$  cage. *d*)  $[(\text{Cp}^*\text{FeP}_5)_2\text{Ag}_2(\mu,\eta^2\text{-P}_4)(\text{SbF}_6)]\text{SbF}_6$ .



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**Keywords:** coordination polymer, host-guest compounds, pentaphosphaferrocene

## MS35-O5

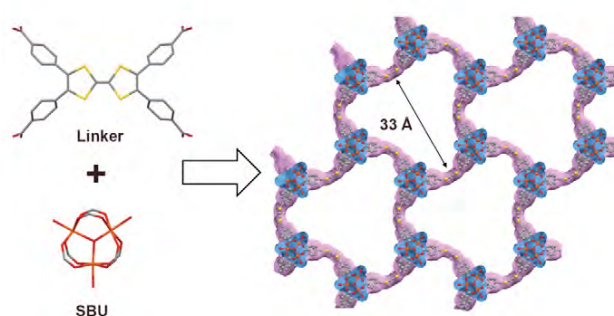
## A hierarchical metal-organic framework with breathing-dependent redox activity

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Metal-Organic Frameworks (MOFs) combining both large pores and high stability have received a lot of attention during the past years due to their high interest towards practical applications such as MIL-100 or MIL-101. Moreover, the preparation of hierarchical MOFs, presenting both micro- and mesopores, has also become a subject of great interest since micropores contribute to the bulk of the surface area whereas mesopores provide a better accesability to larger molecules to quickly diffuse, becoming very attractive for catalytic applications.[1] Herein we report the synthesis, structure determination and physical properties of **MUV-2** (MUV: Materials of University of Valencia), a highly stable tetrathiafulvalene (TTF)-based MOF with a non-interpenetrated hierarchical crystal structure with mesoporous channels (~33 Å) disposed orthogonal to microporous channels (~10 Å). The advantages of **MUV-2** respect to widely used MOFs catalyst (MIL-100 and MIL-101) will be clearly demonstrated for a reaction of large applied interest (aerobic oxidation of benzothiophenes), illustrating the advantages of having a hierarchical MOF with large mesopores and high stability.[2] In addition, **MUV-2** presents a continuous breathing behaviour upon solvent or gas adsorption, cause by the flexibility of the TTF-based ligands that show conformational changes, as unequivocally demonstrated by single crystal X-ray diffraction. The reversible swelling not only modifies the accessible space, but also the oxidation potential of the MOF.[3]



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**Keywords:** Highly-stable MOFs, breathing MOFs, hierarchical MOFs

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