

MS35-O3

CO₂ adsorption sites in the triangular channels of Fe₂(BPEB)₃: an insight by in-situ and operando high-resolution and high-energy PXRDSimona Galli¹, Carlotta Giacobbe², Elisa Lavigna¹, Angelo Maspero¹

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Growing concerns on global warming stimulate research to reduce anthropogenic CO₂ emission and lower atmospheric greenhouse gases concentration. Till the use of greener energy sources will be practicable, CO₂ 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 CO₂ adsorption capacity (40.5 wt % at 298 K and 10 bar) of Fe₂(BPEB)₃ [2] (H₂BPEB = 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 CO₂ in the pressure range of 0-20 bar. Juxtaposing structure determination to total scattering analysis enabled us to disclose the CO₂ 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 CO₂ by Fe₂(BPEB)₃, a rigid host without exposed metal sites or functional groups with particular affinity to CO₂ on the ligand, affords important information on a debated topic, i.e.: the chemical and structural properties a host should possess for efficient CO₂ adsorption under rather mild conditions.

References:

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Keywords: High-resolution PXRD, high-energy PXRD, CO₂ adsorption

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Coordination Polymers with Supramolecules as NodesEugenia Peresykina¹, Dr. Alexander Virovets¹, Prof. Dr. Manfred Scheer²

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Since 2003, we have been investigating the use of pentaphosphaferrocene [Cp^RFe(η⁵-P₅)] (Cp^R = η⁵-C₅R₅, R = Me, CH₂Ph, PhC₄H₉) as a building block in supramolecular chemistry. The phosphorus atoms of the planar P₅-rings are able to coordinate to Cu⁺ and Ag⁺ (M⁺) cations resulting in either coordination polymers with M_x(halogen)_y 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 Cp₂Co⁺ [2] (Fig.1a) as well as of metastable molecules such as the tetrahedral molecules white phosphorus, P₄, and yellow arsenic, As₄ [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⁺ cations to the P₅-rings results in the in situ formation of supramolecules, while the additional coordination of Ag⁺ to N-donor atoms of N≡C(CH₂)_nC≡N (Lⁿ, n=5-10) (Lⁿ) 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⁺ 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 P₄. Thus, in the presence of P₄, two new 1D-polymers were obtained, (P₄)@[Cp*FeP₅]₉Ag₈(L¹⁰)₄(SbF₆)₉ (Fig.1c) and [(Cp*FeP₅)₂Ag₂(μ,η²-P₄)(SbF₆)]SbF₆ (Fig.1d). The former contains polynuclear cationic nodes of [Ag₉(Cp*FeP₅)₉]⁹⁺ that encapsulates tetrahedral P₄ 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).