

FA4-MS08-O1

Porous Metal Organic Frameworks: From Synthesis to Applications. Patricia Horcajada. Institut Lavoisier, UMR CNRS 8180, Université de Versailles St Quentin en Yvelines, 45 Avenue des États-Unis, 78035 Versailles Cedex, France.

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Porous hybrid solids are fascinating solids,[1,2] due to their potential applications in catalysis, separation, gas storage, adsorption or drug delivery. If most Metal Organic frameworks (MOFs) exhibit a rigid framework, a few porous hybrid solids possess an unusual behavior with a large flexibility of their structure, resulting in changes in cell volumes depending on their pore content.[2] Our group has reported two types of flexible MOFs built either on chains of metal octahedra, i.e. the metal terephthalates MIL-53(Al, Cr, Fe) (MIL: Material Institut Lavoisier),[3] or made from trimeric inorganic sub-units, i.e. the series of iron(III) or chromium(III) carboxylates denoted MIL-88A, B, C and D and constructed from fumaric acid (MIL88-A), 1,4-BDC (MIL88-B), 2,6-NDC (MIL88-C) and 4,4'-BPDC (MIL88-D).[4] The MIL-53 solids breathe upon hydration-dehydration with a variation in cell volume around 40 % while the MIL-88 solids exhibit a giant and reversible swelling effect which leads to an increase of 85 % (MIL-88A) up to 220 % (MIL-88D) in their cell volumes, far beyond those reported before in the field of porous solids. [5]

Adsorption experiments of green house gases, polar or apolar vapours, liquids and drugs have been performed using these solids.[6] In most cases, in situ XRPD or Infra-red spectroscopy experiments have been conducted to analyse the breathing behavior of the flexible solids upon adsorption of guest molecules. Results suggest that the breathing phenomenon occurs in most cases with a rather selective behavior and that selectivity depends not only on the structure and the organic linker but also on the nature of the metal present in the nanoporous hybrid solid. These results pave the way for new applications in the field of adsorption.

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Keywords: metal-organic compounds; porous solids; adsorption

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MOFs Prepared by Solvent-Free Grinding Reactions. Stuart L. James. School of Chemistry and Chemical Engineering, Queen's University Belfast, Northern Ireland, BT9 5AG, UK.

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The preparation of chemicals and materials by simply grinding together solid reactants in the absence of solvent has obvious appeal from a green perspective. It also presents fundamental challenges to understand and predict reactivity under such conditions.

We are developing the efficient synthesis of microporous metal-organic frameworks (MOFs) by grinding metal salts and bridging organic ligands in ball mills under solvent-free conditions [1-3]. Remarkably, in some case these materials can be obtained by this method in crystalline form within minutes and in quantitative yield.

Recent results of systematic reactivity studies, as well as the preparation of complex, interpenetrated networks will be presented and discussed.

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FA4-MS08-O3

Guest Packing in Channel Coordination Polymers. Mikhail Meilikhov^a, Kirill Yusenko^a, Roland A. Fischer^a. *Inorganic Chemistry II - Organometallic and Materials*, Ruhr-University Bochum, Germany.

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The Coordination Polymers (CPs) with permanent porosity and high thermal stability are a unique class of hybrid solid state materials with bright future [1]. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. Also aiming at applications in catalysis we have introduced the solvent-free gas-phase loading of porous CPs via the adsorption of volatile organometallic all-hydrocarbon precursors [2]. There are only few examples of MOF-based absorbate structures were described in literature. Our attention here was concentrated on the packing of the guest's molecules inside the 1D channels of the host structures based on the MIL53(Al), hydrogen bonds and host-guest and guest-guest interactions were analyzed as well. MIL-53(Al), [Al(OH)(bdc)], is a member of a huge family of porous CPs based on chains of *trans*-corner sharing octahedral units {MO₆} cross-linked by bdc (terephthalic acid) which results in a 3D structure exhibiting 1D channels along the *a* axis. Terephthalic acid, methylbenzyl, dimethylbenzyls, ferrocene (Fc) [3], ferrocenealdehyd (Fca), 1,1'-ferrocenedialdehyde (Fcaa), 1,1'-dimethylferrocene (Fcee) and 1,1'-diethylferrocene (Fcmm) were selected as a test guest molecules; also structural effects of the substitute group in the guest molecule were investigated. Our structural data were compared with known literature examples [1, 4].

In Fc@MIL-53(Al) crystal structure, there are no strong guest-guest and guest-host interactions. The existing short contact of 3.12 Å between the Cp-ring and the benzene ring of the linker has to be noted. Fc molecules are oriented around perpendicularly to the channel's direction. In all Fc-derivation's structures, strong guest-host interactions between substitute groups and μ -OH-groups of the host framework are present. The guest molecules are oriented in the channel's direction. As the fact, the packing of the guest molecules depends on guest-host but not on guest-guest interactions. MIL-47(V) framework does not give a strong breathing effect like MIL-53(Al). Therefore, Fc@MIL-47(V) adsorbate structure is similar to Fcaa@MIL-53(Al) and both guest molecules are oriented in the channel's direction.

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Keywords: X-ray powder diffraction; structure determination; framework structures; guest-host structures

FA4-MS08-O4

Alkali Metal Complexes with Diphenylacetic Acid. Manuela Ramos Silva^a, Sérgio R. Domingos^b, Ana Matos Beja^a, José A. Paixão^a, Jesús Martín-Gil^c. ^aDepartment of Physics, University of Coimbra, Coimbra, Portugal. ^bMolecular Photonics Group, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Netherlands. ^cETSIA, Universidad de Valladolid, Avda Madrid 57, Palencia, Spain.

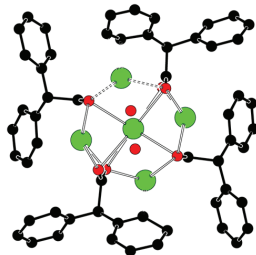
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Diphenylacetic acid (DPA) does not contain a chiral center but can induce chiral assemblies by assuming a propeller-like conformation [1].

In the Na-DPA crystal structure the carboxylate oxygen atoms and the Na⁺ ions alternate at the vertices of a distorted cube centered at the origin of the -4 axis, forming an infinite columnar structure [2].

In the Rb-DPA crystal structure, the rotoinversion axis is lost and there is the formation of a ladder climbing along an -1 axis [3].

In the K-DPA crystal structure, there is the formation of a columnar structure although some of its constituting atoms are disordered, the following figure shows the columns as viewed from the top (H atoms were omitted for clarity).



This new compound crystallizes in the centrosymmetric

space group *Cc* with cell parameters: $a = 29.0438(10)$ Å, $b = 5.959(3)$ Å, $c = 29.9002(19)$ Å, $\beta = 106.902(2)^\circ$, $V = 4951(3)$ Å³. Structural features will be presented and discussed.

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Keywords: metal complexes; diphenylacetic acid; chirality

FA4-MS08-O5

Powder Diffraction Structural Studies at Ambient and Non-Ambient Conditions on Porous Coordination Polymers. Simona Galli. Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, Como, Italy.

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The increasing industrial and environmental importance of applications such as gas storage, gas or liquid selective separation, heterogeneous catalysis, and drug delivery promoted the investigation of porous coordination polymers (PCPs) as promising materials [1-3] to overcome some of the limits of 'classical' porous species (e.g. activated carbons, metal hydrides, inorganic zeolites).

With the aim of engineering novel PCPs featuring (hydrogen, carbon dioxide, methane) gas storage or separation, our research group explored the coordination capabilities of polyazaaromatic ligands toward transition metal ions. Pioneering, remarkable results were obtained with the $M(5-X-2-pymo)_2$ materials ($M = Co, Zn, Cu, Pd$; $5-X-2-Hpymo = 5-X$ -pyrimidin-2-ole) [4-6]. Tuning either the coordination possibilities or the length of the organic spacer, led to the isolation and characterization of the $M(\text{Hoxonic})(4,4'\text{-bipy})_{0.5}$ ($M = Cu, Zn$; H₂oxonic = oxonic acid; 4,4'-bipy = 4,4'-bipyridine) and $M(\text{bpb})$ ($M = Ni, Zn$; H₂bpb = 1,4-(4-pyrazolyl)benzene) species, respectively.

Selected examples from the three families will be presented to highlight the effectiveness of powder diffraction structure solution methods applied to laboratory data, juxtaposed to thermogravimetric studies even in conditioned atmosphere, in providing a structural frame to the investigated functional properties.

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