

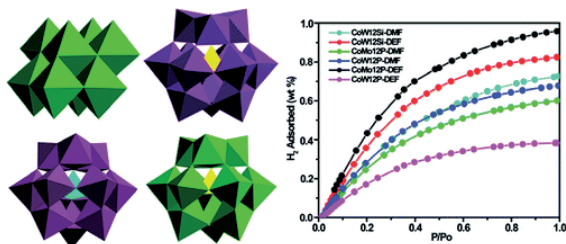
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Structure and selective gas adsorption study on POM-based ionic salts

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Seven new ionic solids built on polyoxometalate (POM) anions and $[\text{Co}(\text{en})_3]^{3+}$ cations namely, $[\text{Co}(\text{en})_3\text{Mo}_8\text{O}_{26}(\text{H}_2\text{O})(\text{Cl})](\text{DMF})_4(\text{H}_2\text{O})$ (*Co-Mo₈-DMF*), $[\alpha\text{-PW}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]\cdot 6\text{DMF}$ (*Co-W₁₂P-DMF*), $[\alpha\text{-PW}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]\cdot 6\text{DEF}$ (*Co-W₁₂P-DEF*), $[\alpha\text{-PMo}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]\cdot 5.5\text{DMF}$ (*Co-Mo₁₂P-DMF*), $[\alpha\text{-PMo}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]\cdot 6\text{DEF}$ (*Co-Mo₁₂P-DEF*), $[\alpha\text{-SiW}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]_{3/2}[\text{Cl}]_{1/2}\cdot 6\text{DMF}\cdot 3\text{H}_2\text{O}$ (*Co-W₁₂Si-DMF*) and $[\alpha\text{-SiW}_{12}\text{O}_{40}][\text{Co}(\text{en})_3]\cdot 6\text{DEF}$ (*Co-W₁₂Si-DEF*) have been synthesized from non aqueous (DMF/DEF) media and characterized by single-crystal X-ray diffraction. We attempt to understand if $[\text{Co}(\text{en})_3]^{3+}$ cations used in these reaction systems play a crucial role in controlling the assembly of these crystals. These ionic solids, after removal of the DMF or DEF molecules, are found to exhibit size selective H_2 adsorption properties over N_2 . The amount of hydrogen adsorption was influenced by POM anion types and their orientations. *CoMo₁₂P-DEF* has the highest (0.9 wt%) H_2 uptake and *CoW₁₂P-DEF* has the lowest (0.4 wt%) uptake among the series when the adsorbate pressure approached 1 atm. We believe that the successful synthesis of these seven new ionic solids and the discovery of their selective H_2 adsorption properties, as a result of the cooperative behavior between their cationic/anionic component species, will open up new vistas in the search for polyoxometalate based materials with useful absorptive properties. We are further engaged in designing porous ionic crystals with functionalized interiors for enhanced gas adsorption capacity and higher selectivity.



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Keywords: porous, salts, adsorption

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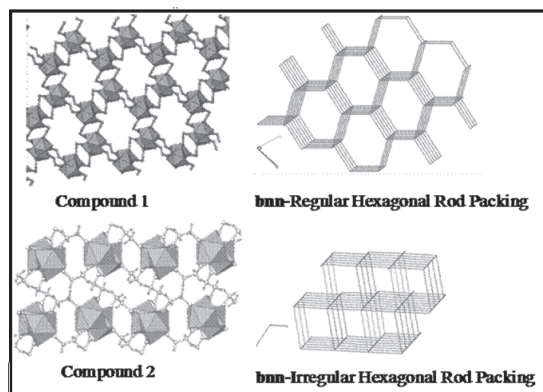
Structural influence of aromatics as templates or SDAs in MOFs crystallization

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MOFs (Metal Organic Frameworks) are crystalline organic-

inorganic polymeric networks which consist of metal ions (isolated or joined in clusters of different dimensionalities) covalently connected by organic ligands to give 1D, 2D or 3D structures. These materials are applied in several fields like gas adsorption, catalysis and controlled drug release [1]. It is well-known that during the self-assembly process, *structural directing agents (SDAs)* and *templates* are crucial for obtaining 3D porous structures. This strategy was widely used in zeolites synthesis [2]. However, the use of such agents in the synthesis of MOFs has been less explored, so a distinction between both functions is perhaps subtler in this subject. The primary template effect occurs during the synthesis process when the organic guest molecule is self-included into the host framework by non-covalent interactions acting as a placeholder, thus preventing the interpenetration of the open network. The secondary template effect is a dynamic process that takes place when appropriate guest molecules act as templates and induce reversible structure transformations [3]. In contrast, the SDAs drive the formation of a certain phase but not necessarily are included in the structure. The objective of this work is to study the structural directing or template functions of aromatic molecules (salicylic acid, acetylsalicylic acid, benzene and pyridine) in the formation of MOFs based on the succinate ligand and Ho(III) ion, exploring in turn, the effect of the *in situ* ligand generation by hydrolysis of the succinylsalicylic acid.

Under different hydrothermal synthesis conditions, two compounds with formulae $[\text{Ho}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2]\cdot 0.33(\text{C}_7\text{H}_6\text{O}_3)$ (1) and $[\text{Ho}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2]$ (2), were obtained, both belonging to the triclinic system and P1 space group. In the case of 1, it was found that aromatic molecules act as templates determining channels that represent a free cell volume of 21.5%. These molecules are hosted with partial occupation of 0.25-0.5 molecules per formula. On the contrary, in compound 2, the auxiliary organic molecules are not included in the framework allowing us to consider them as SDAs due to their presence in the synthesis mixture leads specifically to the formation of this compound, while if they are absent, a third Ho(III)-succinate phase is obtained. It has been found that the role of aromatic molecules varies from SDAs to templates as the corresponding concentration increases.



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Keywords: MOFs, templates, structure-directing agents.

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Organic-inorganic hybrids assembled from lanthanide and 1,4-phenylenebis(phosphonate)

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Organic-inorganic hybrids constitute an important class of compounds in the exploratory research area of advanced materials design. In this connection, metal phosphonates represent a particularly versatile field for investigation because of the great latitude open to the investigator. During the past two decades a lot of research attention has been devoted to the chemistry of metal phosphonates for their potential applications in ion exchange, catalysis, and in sensor devices [1-5]. The wide choice of metals and the variety of organic ligands, and since that almost any desired organic compound may be converted into a phosphonic acid by known reactions, it is thus possible to introduce phosphonate ligands with different functional groups into the hybrid structures, which suggests the possibility of rational design of structures for highly specific function, and even with unusual properties. Recently, investigations of di-, tri-, and tetra-valent metal phosphonates have yielded exciting structural diversity with interesting chemistries and applications, including porous pillared layered structures [6, 7]. However, reports on the structure and photoluminescence properties of lanthanide (Ln) arylphosphonates or aryldiphosphonates are scarce [8, 9].

Herien, we present a series of novel organic-inorganic hybrids based on trivalent lanthanide (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) and 1,4-phenylbis(phosphonate) formulated as $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ and obtained as single phases under hydrothermal conditions either by oven or microwave heat. In the praseodymium compound (Za1) single crystals have been obtained and the crystal structure determined. Za1 crystallize in monoclinic space group, C2/c, with $a = 5.6060(4) \text{ \AA}$, $b = 20.251(7) \text{ \AA}$, $c = 8.2740(6) \text{ \AA}$, $\beta = 108.52(1)^\circ$. All other compounds are isostructural to Za1 as confirmed by Rietveld refinement by using X-ray powder diffraction data. Compounds are characterized by thermal analyses (TG-MS and SDTA), elemental analysis, IR spectra, and X-ray thermodiffraction analysis. These series of compounds exhibit an unusual very high thermal stability. Eu- and Tb-based compounds exhibit, respectively, strong red and green emissions.

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Novel 3D Fluorinated-MOFs: Structure, topology and magnetic properties

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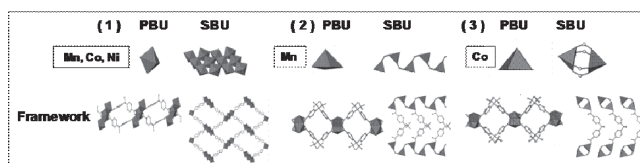
The metal-organic frameworks (MOFs) are a class of materials that are constantly attracting significant attention not only for their potential applications as functional crystalline materials, but also for their fascinating topologies and structural diversity [1]. The use of flexible and extended ligands contributes to the development of porous frameworks with diverse structural topologies, which, in turn, can lead to obtain varied properties even for the same constitutive units. On the other hand, the magnetic behavior of MOFs, which extended inorganic networks or local paramagnetic centers are linked by diamagnetic linkers that can efficiently mediate magnetic exchange, have evoked considerable interest [2]. However, in MOFs, the magnetism may be introduced through the incorporation of magnetic moment carriers such as paramagnetic metals, or open-shell organic ligands, or both [3].

In this way, we decided to proceed our studies obtaining Fluorinated Metal Organic Frameworks (F-MOFs) constructed of the flexible 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H_2hfipbb) as ligand and transition metal ions {Mn(II), Co(II) and Ni(II)}, in order to induce interesting magnetic properties. Besides, we have explored several synthesis conditions to expand the possibilities to get diverse crystal topologies expecting different magnetic properties.

Three novel compounds (1a-c) with formula $[\text{M}_3(\text{hfipbb})_2(\text{OH})_2(\text{H}_2\text{O})]$, M = Mn, Co, Ni has been hydrothermally synthesized and completely characterized. The compound 1a's structure corresponding to the P2₁/c space group, has been determined by single crystal synchrotron XRD at the ESRF- BM16 beam line, while for compounds 1b and 1c powder diffraction methods were applied in order to obtain both cell parameters and the space groups. Such study indicated the isostructural character of compounds 1a-c. Besides, another two compounds with formula $[\text{M}_2(\text{hfipbb})_2(\text{H}_2\text{hfipbb})]$, M = Mn (2) and Co (3), were hydrothermally obtained at different synthesis conditions and their structures, corresponding to the C2/c and P2₁/n space groups, respectively, were determined by conventional single crystal XRD data.

Magnetic behavior of compounds 1a-c and 3 has been studied and such results indicate that compounds 1a and 3 have antiferromagnetic interactions while 1b and 1c are ferromagnetics.

The topological study of 2 and 3, having the same composition but different crystal structure has also been performed.



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Lanthanide-organic frameworks of Bis-Gd complexes: composed by carbonate ions spacers