

Synthesis, Characterization and Application of Metal-Organic Frameworks

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Metal-organic frameworks (MOFs), also known as porous coordination polymers,¹⁻³ are porous materials in which metal-containing nodes are connected by organic bridges. A large variety of inorganic and organic components can be used to construct MOFs, and this versatility has enabled the rational design and assembly of materials having novel topologies and exceptional properties.

Luminescent MOFs are potentially useful as chemically-selective sensors.⁴⁻⁷ We have discovered a new luminescent MOF synthesized by treating Eu(III) ions with 2,2'-bipyridine-5,5'-dicarboxylic acid in *N,N*-diethylformamide (DEF). The X-ray crystal structure of the resulting material, $\text{Eu}_2(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)_3(\text{DEF})_4(\text{H}_2\text{O})_5$, shows that it is a MOF with large channels ($25 \times 15 \text{ \AA}$), and that the carboxylate groups but not the nitrogen atoms of the bipyridine units are bonded to the europium centers. Surface area measurements on the desolvated material confirm that the material shows permanent porosity. When this material is exposed to 1,3,5-trinitrotoluene (TNT) or smaller nitroaromatics, the fluorescence of this MOF is significantly quenched. In contrast, 1,1-diphenyl-2-picrylhydrazine, a larger nitroaromatic, as well as aromatic molecules lacking nitro substituents, do not cause quenching. Thus, the sensing ability of this MOF is both size- and chemoselective.

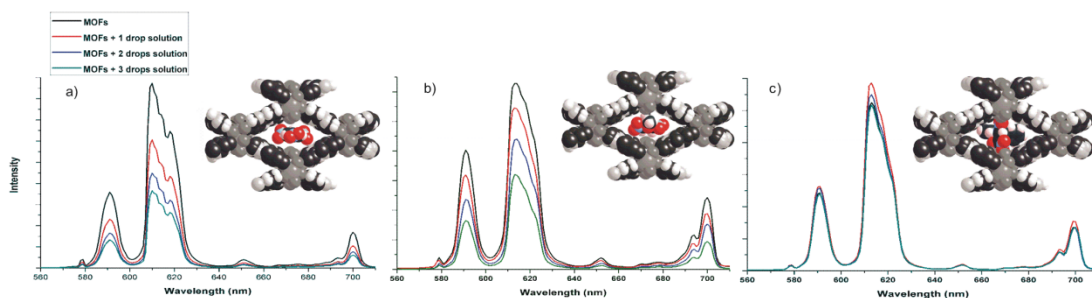


Figure 1: Different size of polynitro-aromatics fitting into the pores of EuBDC in spacing filling mode, and the corresponding fluorescence spectra upon the successive addition of TNT solution.

Treatment of Zn(II) ions with 2,2'-bipyridine-5,5'-dicarboxylic acid and formic acid gives a different MOF, $\text{Zn}_3(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)_2(\text{O}_2\text{CH})_2 \cdot 2\text{DEF}$. Crystallographic studies show that this compound crystallizes in a chiral space group $P4_12_12$ by spontaneous resolution,⁸⁻¹⁰ although the specimen we examined was a racemic twin. Two of the zinc atoms are five-coordinate, whereas the other zinc atom has an octahedral coordination environment. The chiral nano-pores, which have cross sections of $0.78 \times 1.53 \text{ nm}$, are arranged in a herringbone fashion along the *c* axis.

The ability of MOFs to withstand high pressures is necessary for many of the most interesting potential applications of MOFs.¹¹⁻¹⁵ We carried out a high pressure study of the metal

organic framework $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$ (IRMOF-1) up to 8.93 GPa, using a synchrotron radiation source and a diamond anvil cell. Both as-synthesized and desolvated samples of IRMOF-1 retained some crystallinity to 6.57 GPa (65 700 atm) and 4.32 GPa (43 200 atm), respectively. Both begin to convert to a new material even at pressures as low as 0.21 GPa; for the as-synthesized and desolvated material, this process is essentially complete at 8.33 and 5.17 GPa. The diffraction pattern obtained for the material formed by compression of the desolvated MOF suggests that pressure promotes a hydrolysis reaction; the water molecules necessary for this reaction were evidently absorbed from the atmosphere during sample handling after desolvation. Some amorphization occurs along with the formation of the new phase.

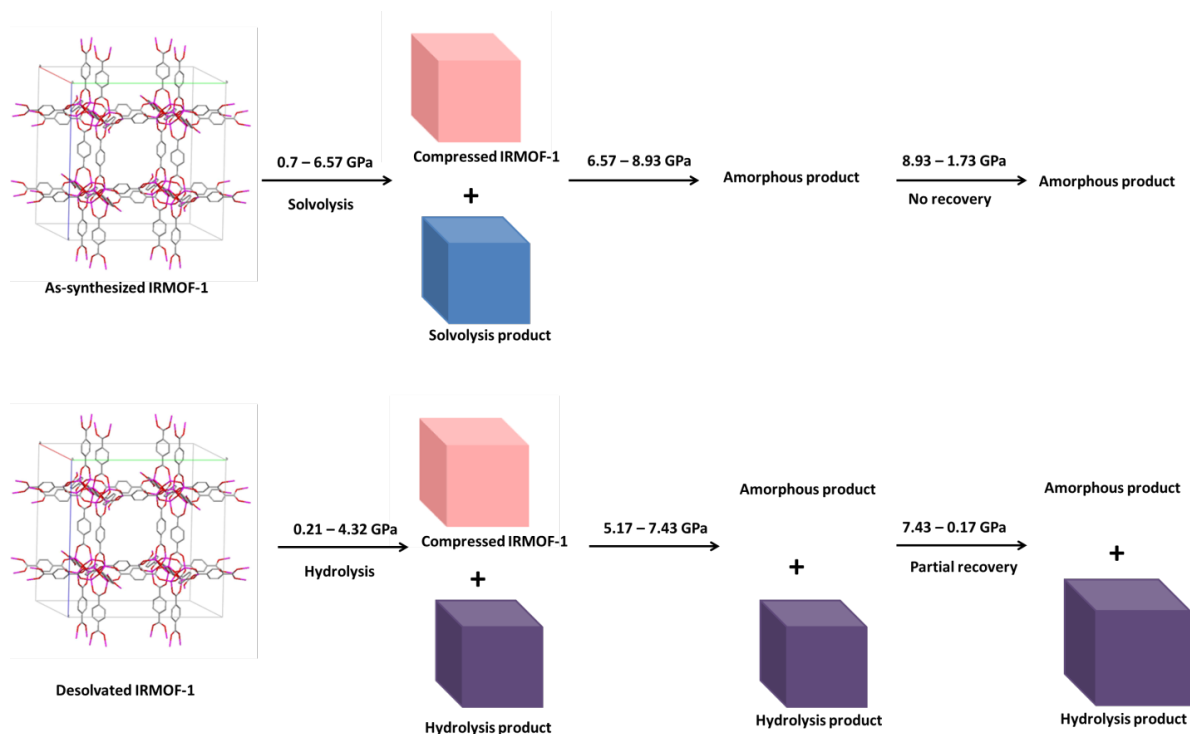


Figure 2: Structural change of IRMOF-1 with increasing pressure.

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