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Temperature and Concentration Control over Interpenetration in a Metal−Organic Material

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Self-assembled combinations of well-designed molecular building blocks (MBBs) and multitopic organic ligands have afforded a wide range of framework metal−organic materials (MOFs) that exhibit intriguing topologies and fascinating if not unique properties or combinations of properties. The property that has perhaps attracted the greatest attention is porosity, and MOFs provide platforms that offer hitherto unprecedented levels of surface area.[1] In this context, a contemporary challenge is to design MOFs that combine high free volume and low density. However, the use of readily accessible tetrahedral or octahedral MBBs to form diamondoid[2] (*dia*) or octahedral[3] (*pcu*) MOFs, respectively, brings a very strong tendency to exhibit interpenetration,[2b,3c] mitigates the free volume, and increases the density. Although the existence of interpenetration is not necessarily negative, it remains a challenge to control interpenetration of those MOFs that are topologically amenable to interpenetration. A recent paper indicated that interpenetration can be avoided through using liquid-phase epitaxy on an organic template,[4] but the factors that generally influence interpenetration remain unclear. In this communication we address such control by studying a pillared MOF, a class of MOM that has been attracting attention from a number of groups.[5] We report how systematic variation of temperature and concentration affords control over the synthesis of a noninterpenetrated form of [Cd(bipy)(bdc)]·3DMF·H_2O, **1**, and its previously reported 2-fold interpenetrated form, **2**, [Cd(bipy)(bdc)].[6]

The solvothermal reaction of 4,4′-bipyridine (bipy), 1,4-benzenedicarboxylic acid (bdc), and $Cd(NO_3)_2 \cdot 4H_2O$ in a 1:1:1 ratio in DMF/DEF (2:1 v/v) at 85 °C afforded colorless block crystals of compound **1**. The X-ray single crystal structure of **1** revealed that it is a framework sustained by dinuclear $\{Cd_2N_4O_8\}$ MBBs and bdc linkers that form sheets which are in turn pillared by bipy.[7] The topology of **1** can be described as *pcu* if each dicadmium moiety is treated as an octahedral MBB. The bdc ligands exhibit two coordination modes, and the Cd^{2+} ions of the MBBs are bridged by two chelating/bridging bis-bidentate carboxylate moieties and chelated by one terminal bis-bidentate carboxylate group. Each Cd^{2+} ion has a distorted N_2O_5 pentagonal bipyramidal coordination sphere with nitrogen atoms from two bipy ligands at the apexes and five carboxylate oxygen atoms in the equatorial positions. The resulting 3D framework exhibits 8.1 × 11.7 Å^2 square channels along the *a* direction and 12.5 × 12.5 Å^2 rhombic channels along the *c* direction occupied by disordered DMF and H_2O. The effective free volume in compound **1** is ca. 59.3% of the unit cell as calculated by the program PLATON.[8]

The bulk purity of **1** was confirmed by comparing its experimental powder X-ray diffraction (PXRD) pattern to that calculated based on the single crystal structure. Thermogravimetric analysis indicates a weight loss of 34.34% (loss of 3 DMF and 1 water solvent molecules) below 180 °C (cal. 35.36%) and a weight loss of ca. 44.89% from 380 to 460 °C.

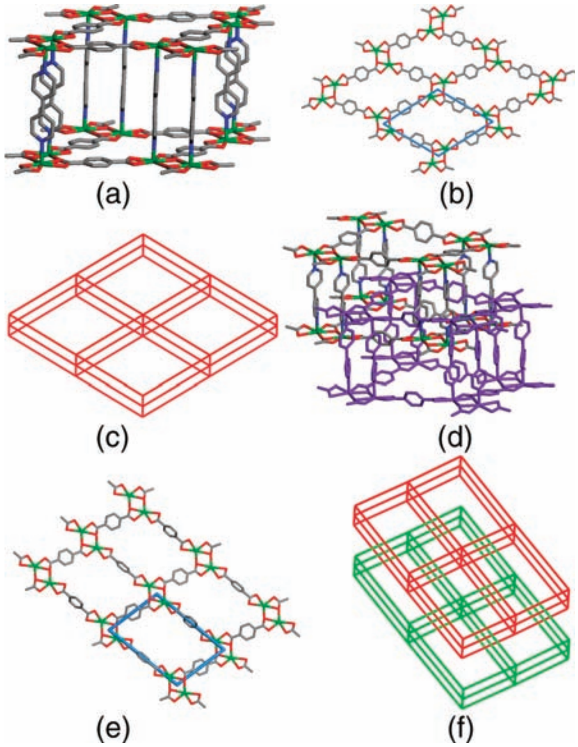

Figure 1. (a) Pillared noninterpenetrated structure of compound **1**. (b) Single [Cd(bdc)] layer in **1** viewed along the *c* direction. (c) Schematic diagram showing the primitive cubic (*pcu*) structure of **1**; (d) Pillared interpenetrated structure of compound **2**. (e) Single [Cd(bdc)] layer in **2** viewed along the *b* direction. (f) Schematic diagram showing the 2-fold interpenetration in **2**.

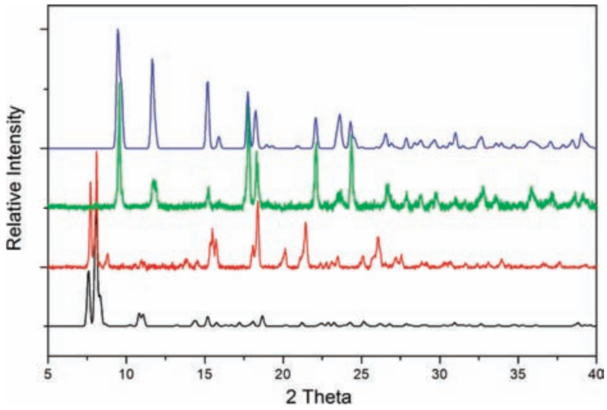

Figure 2. Powder X-ray diffraction (PXRD) patterns of **1** and **2**: calculated PXRD pattern from the single crystal structure of **1** (black); observed PXRD pattern of **1** at room temperature (red); observed PXRD pattern of **2** at room temperature (green); calculated PXRD pattern from the single crystal of **2** (blue).

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Table 1. Summary of the Products Isolated at Different Temperatures and Concentrations (? = Unknown New Phase)

	0.2M	0.1M	0.05M	0.025M	0.0125 M	0.00625M
85°C	?	1	1	1	1	?
95°C	?	1	1	1	1	?
105°C	?	1+2	1+2	1	1	?
115°C	?	2	2	1+2	1	?
125°C	?	2	2	1+2	?	?

That **1**, a compound based upon an octahedral MBB with 59.3% free volume, exists as a noninterpenetrated structure was a surprising observation in light of the fact that its 2-fold interpenetrated form, **2**, has been previously reported. To determine whether or not temperature influences interpenetration, the reaction conditions used to prepare **1** were repeated at 115 °C, a temperature at which small needle crystals of compound **2** were obtained. The structure of **2** bears the same 3D pillared neutral framework based on the same dinuclear {$Cd_2N_4O_8$} MBB, bdc linkers, and bipy pillars. However, **2** is distorted around the Cd^{2+} cations, presumably to accommodate the second network. There are two independent bdc linkers in **2**. **2** also differs from **1** as follows: one bdc has two chelating carboxylate groups whereas the other has two chelating/bridging carboxylates; the pyridyl rings of the bipy pillar in **2** are twisted by 38.6° whereas in **1** they are nearly coplanar; the cavities within the undulating sheets of **2** exhibit dimensions of 10.34×15.12 Å^2 with a corresponding bite angle of 75.9°, compared with 12.46×12.46 Å^2 and 62.6°, respectively, in the planar sheet of **1**.

That the same reactions conducted at 85 and 115 °C afforded noninterpenetrated and interpenetrated forms, respectively, prompted us to take a systematic approach to address what influence temperature and concentration might have upon interpenetration. The following observations were made and are detailed in Table 1: (1) If the concentration of starting materials is 0.1 M, lower temperatures (85 and 95 °C) afford **1** whereas a high temperature (115 and 125 °C) leads to **2**. A mixture of **1** and **2** is obtained at an intermediate temperature (105 °C). A similar trend was observed for reactions performed in the concentration range 0.1−0.00625 M; i.e., **1** tends to be favored at lower temperature. (2) When the temperature remains fixed and the concentration is changed we observed that a high concentration tends to favor **2** over **1**. The reaction at 115 °C is a typical example and is presented in Table 1. (3) At higher concentrations (0.2 M) new phases that are yet to be identified were obtained. (4) At the lowest concentration studied (0.00625 M), the phases obtained exhibited weak PXRD peak intensity yet revealed that another new phase exists.

The role of temperature in controlling interpenetration can be rationalized as higher temperatures would naturally be expected to afford more thermodynamically stable, denser interpenetrated crystal forms. The effect of concentration is also to be anticipated since lowering the concentration of starting materials would be expected to reduce the possibility of forming a sublattice in the voids of noninterpenetrated structures as they are being formed. The "concentration effect" is consistent with processes used to prepare macrocyclic compounds under dilute conditions.[9] Although the influences of temperature and concentration on interpenetration are only observed in a certain concentration range, the results described herein provide an indication that simple but efficient ways to control interpenetration in metal−organic materials are at hand. Such an ability to control interpenetration is relevant since there are advantages and disadvantages to interpenetration that depend upon the desired application: a highly interpenetrated structure might exhibit high thermal stability and selective molecular recognition, but it would have a relatively low free volume, thereby limiting applications in areas such as catalysis, encapsulation, and separation of large molecules; a noninterpenetrated structure might possess a high free volume but lower thermal stability and an absence of microchannels and cavities suitable for trapping small molecules.

In summary, a new noninterpenetrating pillared MOF, **1**, and its previously reported 2-fold interpenetrated form, **2**, were synthesized simply and cleanly by systematically changing the reaction temperature and starting material concentrations: high temperature and concentration favored an interpenetrated crystal form; low temperature and concentration favored its noninterpenetrated form. Further work is needed to see whether the observations reported herein are serendipitous or a general rule for metal−organic materials that are capable of interpenetration.

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Supporting Information Available: X-ray crystallographic files in CIF format; bond lengths and angles; detailed synthesis process, TGA curves, IR spectra, and X-ray powder patterns for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for **1**: $C_{27}H_{35}N_5O_8Cd$, Orthorhombic, *Pbam*, $a = 12.9491(5)$ Å, $b = 21.2900(6)$ Å, $c = 11.6829(5)$ Å, $V = 3220.8(2)$ Å^3, $Z = 4$, R_1 [2896 observed reflections with $I > 2\sigma(I)$] = 0.0428, $wR_2 = 0.1081$ (all data), GOF = 1.019 (133 parameters).

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