ChemComm

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Journal:	*ChemComm*
Manuscript ID:	CC-COM-05-2015-004223.R1
Article Type:	Communication
Date Submitted by the Author:	05-Jul-2015
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A Non-regular Layer Arrangement of a Pillared-layer Coordination Polymer: Avoiding Interpenetration via Symmetry Breaking at Nodes

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A coordination terpolymerization strategy is introduced to alter the connectivity within layers of a pillared-layer coordination polymer. Assembling two different dicarboxylate linkers around a metal cluster in the layer suppresses interpenetration while enabling formation of a rectangular 2D grid structure.

Microporous coordination polymers (MCPs), materials built from organic bridging linkers and metal ions or clusters, have witnessed rapid and extensive development over the last two decades. Pillared-layer MCPs possessing the metal paddlewheel secondary building unit (SBU) and both carboxylate and neutral nitrogen based linkers are one of the earliest and most-studied classes of MCPs. DMOF[1] $[Zn_2(BDC)_2(DABCO)]_n$ represents a prototype coordination polymer of this category and it is composed of binuclear Zn paddlewheel SBUs bridged by 1,4-benzenedicarboxylate (BDC) to generate 2D layers of $Zn_2(BDC)_2$ which are connected in the third dimension by 1,4-diazabicylco[2.2.2]octane (DABCO) pillars. The rational modulation of this type of pillared-layer structure has been demonstrated by many groups and can generally be categorized in two ways: a) control of the pillar dimension by replacing the DABCO with extended analogues[2,3] and/or b) altering the 2D layer with alternative dicarboxylates to vary the dimension of the 2D square grid.[2, 4-6] However, extension of the pillaring linker to 4,4'-bipyridine (4,4'-bipy), for example, promotes framework interpenetration by creating sufficient void space in a topology prone to catenation.[2, 4-7] An approach to avoid this interpenetration is substitution of aromatic core of the carboxylate linkers with alkyl[2]/alkoxy chains.[8, 9] The dangling side chains occupy void space

thus suppressing intergrowth of the frameworks,[2, 10] a strategy that also is effective for cubic MOFs.[11] However, the conformational freedom of carboxylate groups induced by the alkoxy side chains as well as alteration of the Zn coordination geometry to avoid the steric crowding between pendant functionalities can lead to formation of an unexpected honeycomb-like structure rather than the preferred pillared-layer structure in addition to reducing pore volume.[9, 12] These challenges associated with the production of a non-interpenetrated pillared-layer MCP emphasize the need for an alternative design strategy. Herein we report that symmetry breaking[13-15] at nodes can thwart interpenetration while preserving the pillared-layer structure. The strategy involves incorporation of two dicarboxylate linkers of differing lengths[16] with 4,4'-bipyridine in the presence of Zn(II).[17]

It was hypothesized that employing two different carboxylate linkers may avoid interpenetration by breaking the local fourfold symmetry[1] at the Zn paddlewheel nodes (Figure 1) by, for example, enabling the formation of a rectangular grid as opposed to the common square grid. Symmetry breaking at nodes can be explained if a low symmetry case is considered where m number of short and n number of long ditopic linkers are attached to a 4-connected Zn paddlewheel node (m+n=4) (Figure 1); this arrangement leads to a reduction of local symmetry at the node from fourfold to twofold or onefold depending on the m/n ratio and disposition of linkers. We envision that reduction of nodal symmetry originating from different linker arrangements may suppress the interpenetration of networks and serve as a complement to ligand-based symmetry breaking.[13]
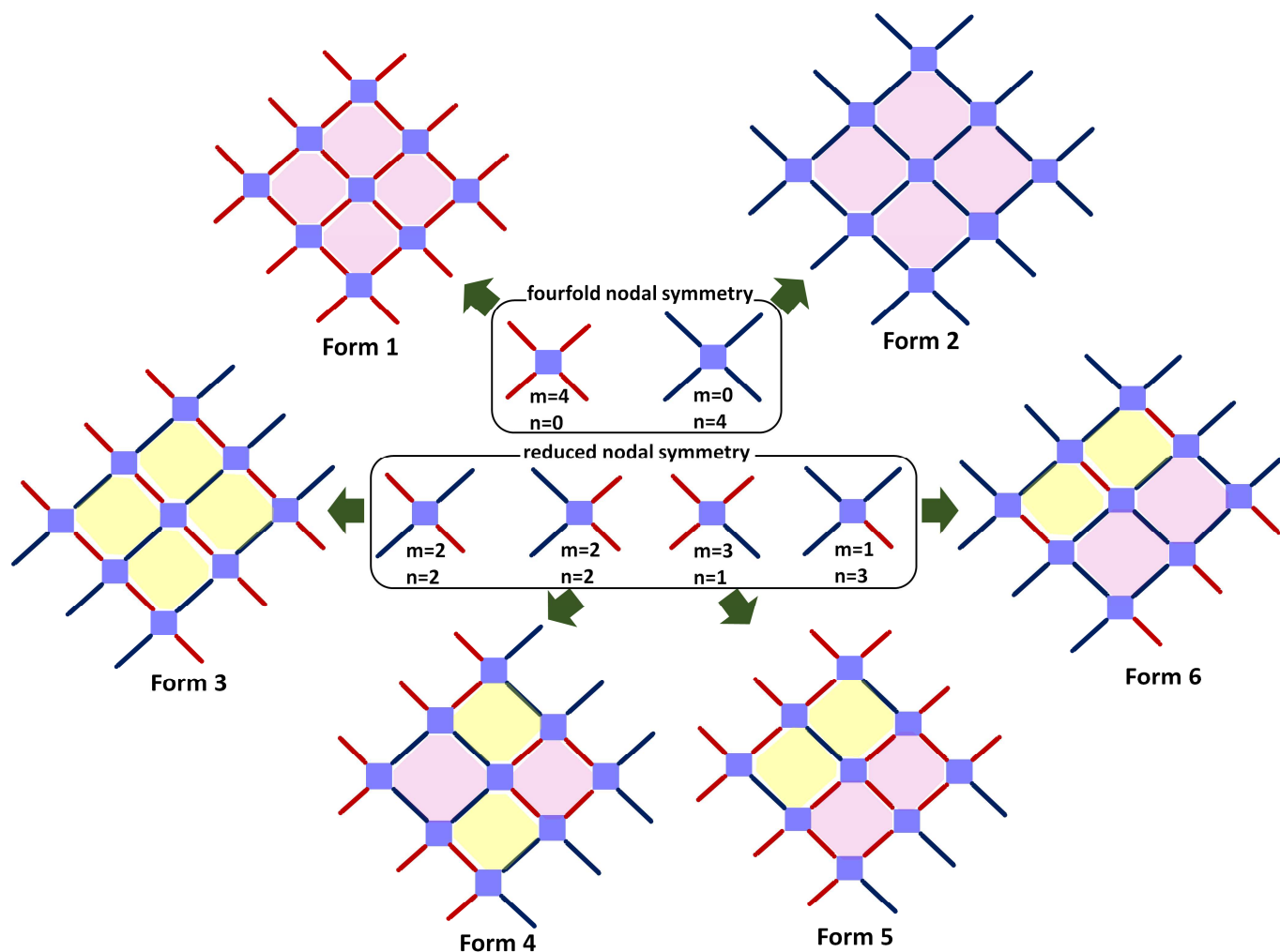
Figure 1. Possible arrangements of m short (red) and n long (blue) linkers around a 4-connected metal paddlewheel node (purple) (m+n=4) and resultant layer structures from self-repetition of these units. Square and rectangular grid sections of a layer arrangement are indicated by pink and yellow colors respectively.

In order to construct a layer composed of two dicarboxylate linkers, H_2-BDC and 2,6-napthalenedicarboxylic acid (H_2-NDC), were selected. Combining two linkers of different lengths with a 4-connected square-planar Zn paddlewheel SBU yields six potential tilings (Figure 1) that, upon self-repetition, give rise to six forms (in parentheses): four BDC around a metal paddlewheel (Form 1), four NDC (Form 2), *trans*- two BDC: two NDC (Form 3), *cis*- two BDC: two NDC (Form 4), three BDC: one NDC (Form 5), and one BDC: three NDC (Form 6). The solvothermal reaction of a mixture of H_2-BDC, H_2-NDC with 4,4'-bipy in a 1:1:1 molar ratio in the presence of Zn(II) resulted in a needle-shaped material, designated UMCM-15 (Section 1 and 2 in ESI). UMCM-15 exhibits a distinct powder X-ray diffraction (PXRD) pattern from those of $[Zn_2(BDC)_2(4,4'-bipy)]_n$ and $[Zn_2(NDC)_2(4,4'-bipy)]_n$, two well-studied members of pillared-layer family derived from a single carboxylate linker.[2, 18] ^{1}H NMR spectroscopy experiments (Section 3 in ESI) performed on acid digests of evacuated UMCM-15 indicate the presence of BDC, NDC, and 4,4'-bipy in a ratio of ~ 1:3:2 signalling a probable formation of Form 6 as described above. Several attempts to grow crystals of UMCM-15 suitable for single crystal structure determination were unsuccessful and individual crystals demonstrated diffraction out to on ~2 Å consistent with modest long range translational order. Nonetheless, indexing the PXRD pattern of as-synthesized UMCM-15 revealed a unit cell with $a = 18.63$ Å, $b =$

24.45 Å, $c = 14.02$ Å, $\alpha = 90°$, $\beta = 135°$, and $\gamma = 90°$. Based on the unit cell parameters and ^{1}H NMR spectroscopic data a model of Form 6 was constructed and geometrically optimized with the Forcite module of Materials Studio. The calculated PXRD pattern was compared to the experimental one to find good agreement thus confirming UMCM-15 is indeed Form 6.[19] A Pawley refinement was performed to obtain the final unit cell parameters: $a = 18.67 \pm 0.01$ Å, $b = 24.31 \pm 0.03$ Å, $c = 14.01 \pm 0.04$ Å, $\alpha = 89.258 \pm 0.002°$, $\beta = 135.719 \pm 0.001°$, and $\gamma = 90.789 \pm 0.002°$ (final R_p 2.80% and R_{wp} 4.39%) (Section 4 in ESI). UMCM-15 (Figure 2) consists of one BDC and three NDC linkers assembling around a Zn paddlewheel SBU to generate a 2D layer with two kinds of windows: a rectangular window of dimensions 9.2 × 7.5 Å^2 and a square one of 9.2 × 9.2 Å^2 (Figure 2b). The remaining axial positions of the metal SBU are occupied by 4,4'-bipy serving as pillars between adjacent layers of spacing 7.4 Å (Figure 2a). Noteworthy, UMCM-15 is a coordination copolymer of three linkers incorporated into a framework, an addition to an extremely rare group of coordination terpolymers.[20-22] Production of UMCM-15 also illustrates the power of the multilinker approach as a tool for creating structural diversity in the field of MCPs using commercial feedstocks.

Utilization of the symmetry breaking strategy is envisioned to promote non-interpenetration of the framework through introduction
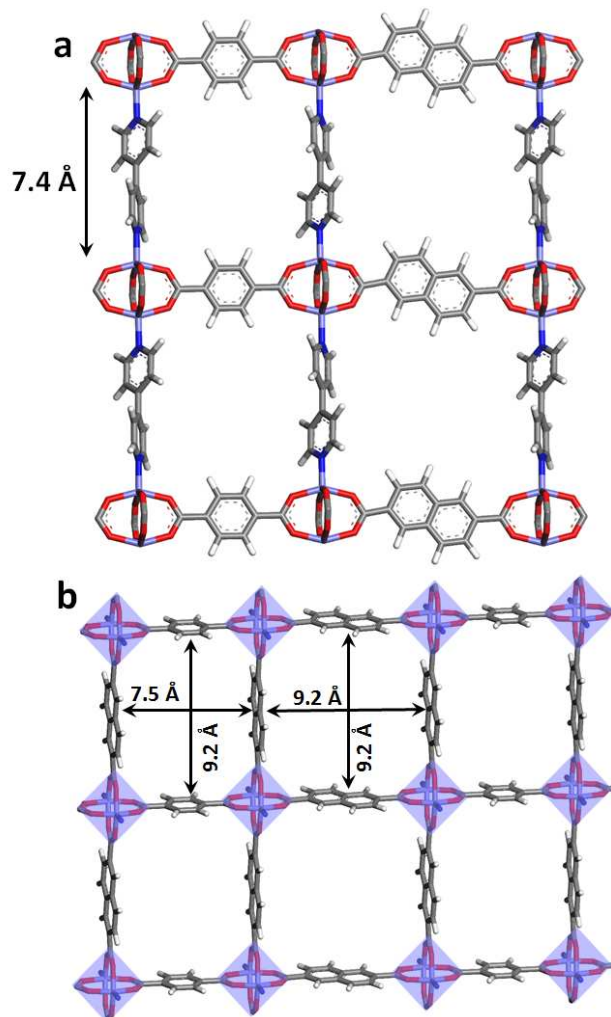
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Figure 2. a) Pillared-layer structure of UMCM-15 and b) layer arrangement of UMCM-15 showing a square and a rectangular pore window. Pore dimensions are measured with subtraction of the van der Waals radii of the atoms.

of topological complexity. Note that this strategy contrasts with the use of networks incapable of framework interpenetration because they are non-self-duals[22, 23] such as the single linker-directed MOF-177,[22] coordination copolymers UMCM-1 to UMCM-4,[24] and the pillared-layer materials UMCM-10 to UMCM-12.[19] In the present case symmetry is merely lowered so that the interpenetration must occur in a very specific fashion which, we hypothesize, slows the second network formation. In order to test for reduced interpenetration in UMCM-15, Nile red, a polycyclic organic dye was chosen which has a kinetic diameter[19] (8.6 Å) comparable to the largest pore window of the non-interpenetrated model of UMCM-15. Here it must be noted that the pillared-layer MCPs derived from a single carboxylate linker, $[Zn_2(BDC)_2(4,4'-bipy)]_n$ and $[Zn_2(NDC)_2(4,4'-bipy)]_n$, are two- and threefold interpenetrated respectively.[2] For comparison all three MCPs, $[Zn_2(BDC)_2(4,4'-bipy)]_n$, $[Zn_2(NDC)_2(4,4'-bipy)]_n$, and UMCM-15, were immersed in *N, N*- dimethylformamide solution saturated with Nile red and containing additional solid dye at room temperature for one day. Nile red, possessing kinetic diameter larger than pore dimensions, cannot penetrate the pores of interpenetrated $[Zn_2(BDC)_2(4,4'-bipy)]_n$ and $[Zn_2(NDC)_2(4,4'-bipy)]_n$ (Figure 3). By contrast, the dye molecule enters the pores of UMCM-15 indicative of more accessible void in UMCM-15 resulting from a reduced

interpenetration (see below the surface area and pore volume of UMCM-15). From the standpoint of controlling the extent of interpenetration, there are various approaches to address this challenge such as installation of sterically bulky functionalities on the organic linker,[11, 26] epitaxial growth,[27, 28] utilization of templates,[29] alteration of the reaction temperature and concentration,[30, 31] and use of reduced symmetry linkers[13, 14, 32] or non-self-dual nets.[23, 24] However, the mechanism to avoid interpenetration in this study is fundamentally distinct and is an outcome of non-uniformity of distances between metal SBUs.[16] The overall network topology for $[Zn_2(BDC)_2(4,4'-bipy)]_n$, $[Zn_2(NDC)_2(4,4'-bipy)]_n$, and UMCM-15 is essentially same as ***xah***[33] (standard presentation of the net is obtained from topological calculations performed in Topos[34]). However, the degree of interpenetration is not same in these MCPs which is believed to stem from different spacings between metal SBUs. In $[Zn_2(BDC)_2(4,4'-bipy)]_n$ and $[Zn_2(NDC)_2(4,4'-bipy)]_n$, there exists a single distance between metal SBUs in the layer which readily gives rise to a high symmetry network substructure.[13] However, UMCM-15 derived from two carboxylate linkers breaks the high nodal symmetry in the layer; this complexity ultimately eliminates the interpenetration. Note that these changes in local nodal symmetry are completely lost in a purely topological analysis; $[Zn_2(BDC)_2(4,4'-bipy)]_n$, $[Zn_2(NDC)_2(4,4'-bipy)]_n$, and UMCM-15 all have the same ***xah*** net and yet behave very differently.

Given the fact that UMCM-15 is non-interpenetrated, a higher surface area is expected than for MCPs derived from a single carboxylate linker. The N$_2$ sorption isotherm of the solvent-free material prepared by vacuum activation shows hysteresis indicating a structural change upon activation and/or sorption experiments. Nevertheless, the N$_2$ uptake and BET surface area of UMCM-15 (220-270 cc/g and 850 - 950 m^2/g) are higher than those of $[Zn_2(BDC)_2(4,4'-bipy)]_n$ (~175 cc/g and ~700 m^2/g) and $[Zn_2(NDC)_2(4,4'-bipy)]_n$ (essentially non-porous) consistent with more void space in UMCM-15 (Figure S5 in ESI) possessing a total pore volume of ~0.38 cc/g (total pore volumes of $[Zn_2(BDC)_2(4,4'-bipy)]_n$ and $[Zn_2(NDC)_2(4,4'-bipy)]_n$, are 0.28 and 0.007 cc/g
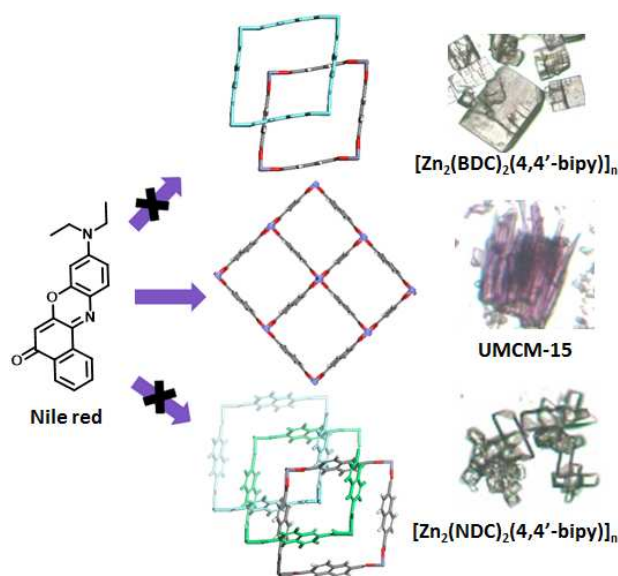

Figure 3. Schematic of size exclusion results for Nile red incorporation into the pores of twofold interpenetrated $[Zn_2(BDC)_2(bipy)]_n$, threefold interpenetrated $[Zn_2(NDC)_2(bipy)]_n$, and UMCM-15 and optical micrographs of the resulting crystals of each MCP.

respectively). Furthermore, characterization of UMCM-15 by Ar sorption followed by NLDFT fitting revealed a pore-volume weighted pore size distribution centred at ~10 Å confirming the non-interpenetrated nature of the material (Figure S6-S8 in ESI). The PXRD pattern of the material after evacuation differs from the as-synthesized material indicating the flexible nature[4, 35] of UMCM-15. Notably the material regenerates the as-synthesized PXRD pattern upon re-soaking with the solvent of synthesis (Figure S9 in ESI).

Conclusions

To conclude, breaking nodal symmetry by incorporation of three linkers into a framework offers a largely unexploited approach to the production of porous materials lacking interpenetration. UMCM-15, a coordination terpolymer derived from two carboxylate linkers, 1,4-benzene dicarboxylate and 2,6-naphthalene dicarboxylate, in the layer and 4,4'-bipyridine pillars presents a powerful demonstration of this strategy. UMCM-15 is a non-interpenetrated MCP wherein its analogous pillared-layer MCPs derived from a single dicarboxylate linker are two- or threefold interpenetrated. Employing two carboxylate linkers in the layer enables formation of a non-regular layer arrangement with a rectangular grid structure as opposed to common square grids observed in pillared-layer coordination polymers. Although breaking the nodal symmetry in UMCM-15 does not alter the overall network topology from its single carboxylate variants, it suppresses interpenetration. Furthermore, utilization of commercially available linkers, in principle, allows use of a myriad of commercial ditopic linkers to generate a rich landscape of structurally diverse materials.

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