Metal–Organic Frameworks

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Stitching 2D Polymeric Layers into Flexible Interpenetrated Metal–Organic Frameworks within Single Crystals**

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Abstract: *A 2D coordination polymer prepared with bulky diethylformamide solvates exhibits channels which allow dipyridyl bridging ligands to diffuse into the crystal lattice. The absorbed dipyridyls thread through the pores of one layer and substitute the surface diethylformamide molecules on the neighboring layers to stitch alternate layers to form flexible interpenetrated metal–orgaic frameworks. The threading process also results in exchange of the bulky diethylformamide solvates for aqua to minimize congestion and, more strikingly, forces the slippage of two-dimensional layers, while still maintaining crystallinity.*

Modifying structurally established metal–organic frameworks (MOFs) allows the introduction of desirable functionality into pores and the creation of new MOFs not available directly from metal–ligand assembly.[1] Herein, we report the synthesis of twofold interpenetrated MOFs by using ligand 'threading' through the pores in a single crystal of a 2D coordination polymer. Although interpenetration is now a widely recognized phenomenon in MOFs,[2] controlling the interpenetration manifold is still a challenge.[3] Interpenetration is undesirable for some applications because of reduced porosity.[2a,b,3a,4] However, there are positive outcomes of this structural feature in terms of gas storage capacity,[5] framework stability, and structural flexibility.[6] During our targeting of MOFs from $Cd(NO_3)_2{\cdot}4H_2O$, H_3BTB, and ehmnH[7] in DEF (H_3BTB = benzene-1,3,5-tribenzoic acid, ehmnH = ethyl 6-(hydroxymethyl)nicotinate, DEF = diethylformamide) with mixed ligands, we unexpectedly isolated a two-dimensional polymeric complex $[Cd_3(BTB)_2(DEF)_4]{\cdot}2\,(DEF)_{0.5}$ (**1a**). Complex **1a**, previously described by Walton and co-workers,[8] features a bilayered structure, wherein two honeycomb-shaped sublayers are interconnected by Cd_3 secondary building units (SBUs; Figure 1). The two honeycomb-like layers are related by a center-of-inversion to give offset hexagonal-shaped cavities in adjacent layers (see Figure S1a in the Supporting Information). Each outer Cd atom in the Cd_3 linear cluster binds to one DEF molecule.

In addition to the reported channels along the *a* axis (see Figure S1b in the Supporting Information),[8] we noticed that

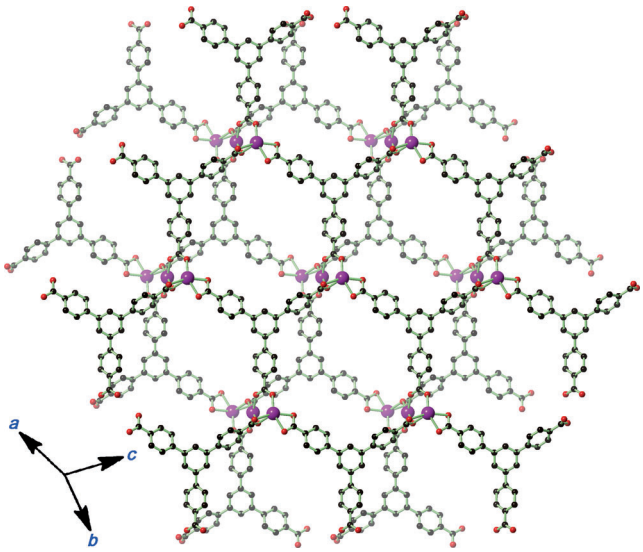

Figure 1. The double-layered structure of $[Cd_3(BTB)_2(DEF)_4]{\cdot}2\,(DEF)_{0.5}$ (**1a**) showing the layers connected by Cd_3 secondary building units. All free and coordinated solvates and hydrogen atoms are omitted. Color codes: Cd (dark magenta), O (red), C (black).

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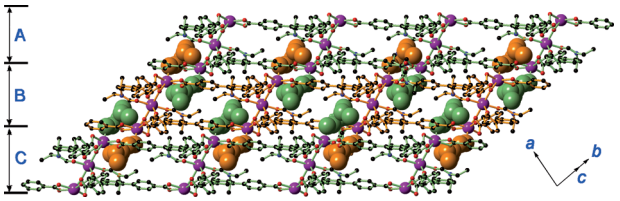
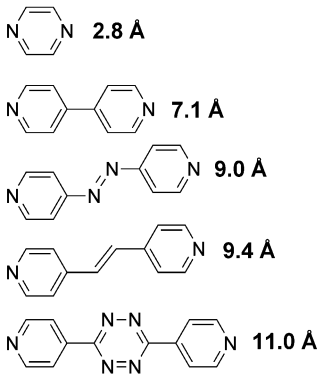


Figure 2. Three consecutive two-dimensional layers of $[Cd_3(BTB)_2(DEF)_4]\cdot 2\,(DEF)_{0.5}$ (**1a**) looking along the [0 −1 1] direction. The surface DEF molecules are presented in space-filling models (DEF molecules from the surface of layers A and C are in green and the those from layer B are in orange). All other molecules are presented as ball-stick models. Color codes for ball-stick models: Cd (dark magenta), O (red), C (black).

two DEF solvates from the surface of alternate layers (layers A and C in Figure 2) fitted snugly into the cavity of the sandwiched layer (layer B) when looking along the [0 −1 1] direction. This observation inspired us to investigate if these apical DEF molecules on the surface of alternate layers could be replaced by bridging ligands, thereby generating a 3D network. Dipyridyl ligands could potentially diffuse into the crystal lattice through the pores along the *a* axis. A successful conversion should then form twofold interpenetrated MOFs and the DEF–dipyridyl (non-aromatic–aromatic) exchange might result in a higher surface area. However, we surmised that the length of the ligands should be constrained within a certain range for bridging to occur. As the shortest Cd···Cd separation of alternate layers is 12.9 Å and Cd–N bond lengths are around 2.3 Å, a dipyridyl ligand with an N···N separation of around 8.3 Å (12.9 Å—2 × Cd-N) ought to be ideal. A search of the Cambridge Structural Database (CSD)[9] for potential ligands revealed that N···N separations for 4,4′-bipyridine (bpy, ca. 7.1 Å), 4,4′-azopyridine (azopy, ca. 9.0 Å), and *trans*-1,2-bis(4-pyridyl)ethylene (bpe, ca. 9.4 Å) would be promising.



Dipyridyl ligands with lengths ranging from 2.8 Å to 11.0 Å were tested in ligand-substitution reactions. Single crystals of **1a** were added to solutions of excess bridging ligands bpy, azopy, or bpe in $CHCl_3$ to yield $[Cd_3(BTB)_2(bpy)(H_2O)_2]\cdot(bpy)\cdot x\,CHCl_3$ (**2**), $[Cd_3(BTB)_2(azopy)(H_2O)_2]\cdot(azopy)\cdot x\,CHCl_3$ (**3**), and $[Cd_3(BTB)_2(bpe)(H_2O)_2]\cdot(bpe)\cdot x\,CHCl_3$ (**4**) after 10 days, while maintaining crystallinity throughout. There was no apparent change in the shape and color of the crystals, with the exception of crystals in the solution with azopy, which changed from colorless to red. Single-crystal X-ray analyses of **2**–**4** indicated that they are isostructural and, therefore, only **2** is discussed in detail here. The linear Cd_3 cluster units, as well as the coordination modes for the BTB ligands of **1a**, remained intact in **2** (Figure 3). The

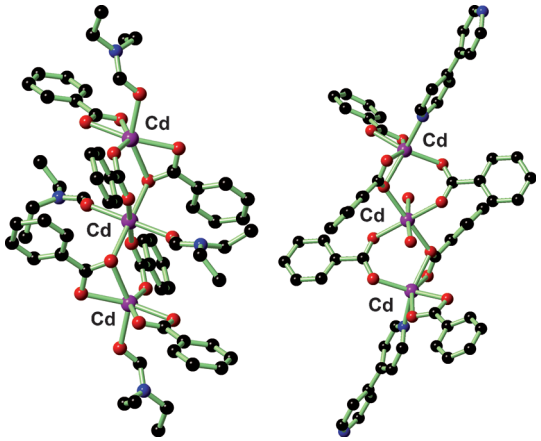


Figure 3. Comparison of the Cd_3 coordination environments of **1a** (left) and **2** (right). Color codes: Cd (dark magenta), O (red), N (blue), C (black).

apical DEF molecules of **1a** were replaced by dipyridyl ligands, as anticipated. The two DEF solvate molecules on the central Cd atoms in **1a** were also replaced by two aqua solvates. This substitution was probably triggered by the threading of bpy through the layers and driven by the thermodynamics of coordination. One free bpy ligand as a lattice solvent was stabilized by O–H···N hydrogen bonding between coordinated aqua molecules and one N atom from bpy. Alternate honeycomb-like layers supported by Cd_3 clusters and BTB were, therefore, linked by bpy to give complex **2** with twofold interpenetration (Figure 4). An expanded void space of 1786.4 $Å^3$ per cell (43.2 % of total cell volume as estimated by Platon[10]) relative to starting **1a** (391.5 $Å^3$ per cell, 19.2 % of total cell volume) was created by insertion of this bridging ligand. The void space was filled with $CHCl_3$ and free bpy solvates (see Figure S2 in the Supporting Information). Moreover, the two-dimensional layers in **2** moved with respect to each other in the *ab* plane (see Figure S4 in the Supporting Information), as evidenced by the shorter Cd···Cd separation of 11.6 Å compared to 12.9 Å in **1a**. This slippage of the plane was probably driven by coordination of Cd to the bridging bpy ligand (ca. 7.1 Å), which is shorter than the aforementioned ideal length of 8.3 Å. This result highlights the capacity of **1a** to accommodate bridging ligands of different lengths and also revealed the flexible nature of the entanglement in **2**.

The alternate two-dimensional layers were bridged by azopy and bpe ligands in **3** and **4** to give Cd···Cd separations of 13.4 Å and 13.8 Å, respectively (see Figure S3 in the Supporting Information). Even a small deviation from the Cd···Cd separation in **1a** (12.9 Å) would cause the slippage of the

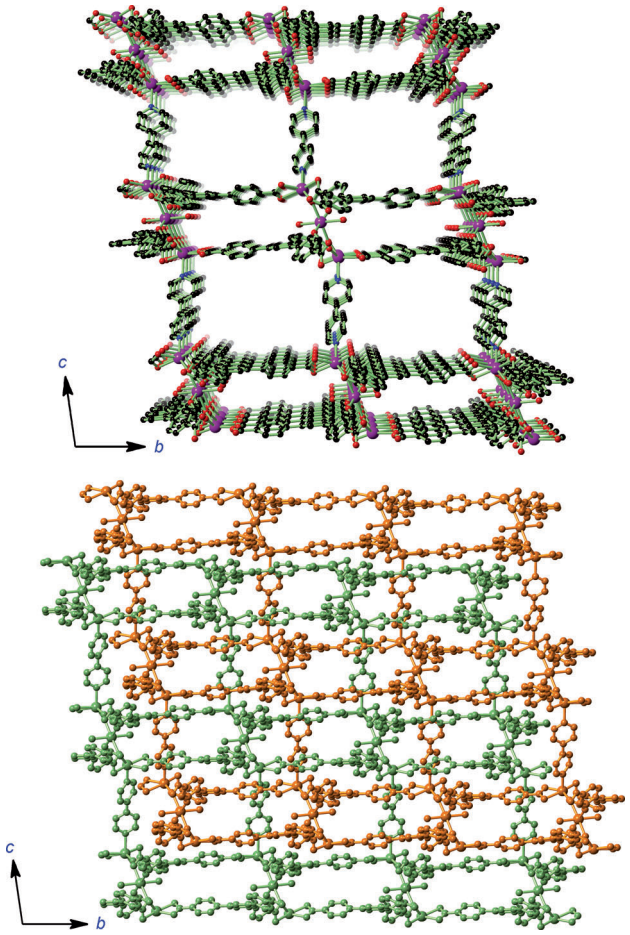


Figure 4. Structure of $[Cd_3(BTB)_2(bpy)(H_2O)_2]\cdot(bpy)\cdot x\,CHCl_3$ (**2**) showing the successful installation of bpy (top) and interpenetration (bottom). All free solvates and hydrogen atoms are omitted. Color codes for the case with bpy: Cd (dark magenta), O (red), N (blue), C (black).

layers with respect to each other (see Figure S3 in the Supporting Information). The void spaces of 1862.6 Å^3 (43.2% of total cell volume) in **3** and 1949.2 Å^3 (44.7% of total cell volume) in **4** are similar to that found in **2**. Comparing the cell parameters of **2**–**4** revealed that the *c* axis (along the bridging ligand) of **2** is shorter, commensurate with the shorter bridge (see Table S1 in the Supporting Information).

We then examined the effects of using ligands that deviate more significantly from the ideal length. A shorter pyrazine (pz) ligand (N···N separation of 2.8 Å) and a longer 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (bptz) ligand (N···N separation of 11.0 Å) were chosen. Addition of crystals of **1a** to a solution of excess pz ligands in $CHCl_3$ resulted in rapid disintegration of the larger single crystals into smaller ones. Fortunately, the quality of these small crystals was still sufficient for single-crystal X-ray diffraction analysis. Substituted two-dimensional layered complex $[Cd_3(BTB)_2(pz)_4]\cdot x\,CHCl_3$ (**5**) was observed (Figure 5).

The structure of complex **5** resembles that of **1a**, but with the DEF solvates at both the apical and central Cd atoms replaced by monocoordinated pz ligands. The cell parameters

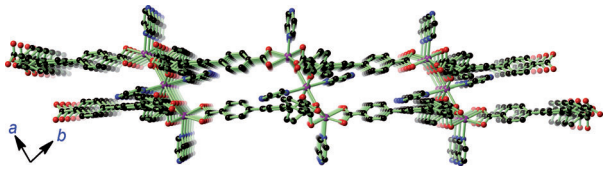


Figure 5. Two-dimensional structure of $[Cd_3(BTB)_2(pz)_4]\cdot x\,CHCl_3$ (**5**). All free solvates, disordered domains, and hydrogen atoms are omitted. Color codes: Cd (dark magenta), O (red), N (blue), C (black).

for **5**, particularly the cell angles, deviated significantly from those of **1a**, thus indicating the slippage of layers in **5** upon replacement of the solvate (see Figure S3 in the Supporting Information). A void space of 849.4 Å^3 (38.5% of total cell volume) was calculated for **5**, more than twice that of **1a**. A similar reaction of **1a** with the longer bptz ligand resulted in no apparent reaction after several days, as determined by single-crystal X-ray analysis.

The dimethylformamide (DMF) analogue of **1a**, namely, $[Cd_3(BTB)_2(DMF)_4]\cdot 2.5\,DMF$ (**1b**),[11] was also synthesized under similar experimental conditions. Complex **1b** had the same Cd_3-based double layers. Analysis of the relative positions of the Cd_3 layers revealed that the shortest Cd···Cd separation was 12.5 Å, thus rendering the linking of alternate Cd_3 layers through ligand substitution conceivable (see Figure S5a in the Supporting Information). Platon calculations on **1b** also indicated a solvent-accessible space of 1992.0 Å^3 (24.6% of total cell volume), higher than that found in **1a** (391.5 Å^3, 19.2%). Reactions of **1b** with bpy, bpe, or azopy in $CHCl_3$ under similar conditions to those used to prepare **2**–**5** gave cracked or broken crystals. The small crystal fragments resulting from these reactions did not diffract. The sharp difference in the reactivity of **1a** and **1b** may originate from the different orientations of the layers in the crystalline state (**1a** crystallizes in triclinic space group *P*-1 and **1b** in monoclinic space group *C*2/*c*), caused by the modest, but significant difference in the size between DEF and DMF. The channels parallel to the linear Cd_3 cluster direction in **1a** and **1b** are not feasible for ligand penetration (see Figure S5b in the Supporting Information). However, large channels were found along the [-1 0 1] direction (see Figure S5c in the Supporting Information) which are nearly perpendicular to the Cd_3 direction and are largely occupied by coordinated DMF solvates in **1b**. These coordinated solvent molecules appear to block the dipyridyl ligands from diffusing into the pores through this alternative route.

Thermogravimetric analyses (TGA) of as-prepared samples indicated that the frameworks of **2**–**5** are stable up to around 300 °C, after which decomposition commenced, accompanied by the loss of dipyridyl ligands (see Figure S6 in the Supporting Information). Sublimation of the trapped dipyridyl solvates in **2**–**4** was observed upon heating these samples at 210 °C under vacuum during surface area analysis experiments. The sublimed single crystals from **2** on the wall of the vacuum tube (see Figure S7 in the Supporting Information) were confirmed to be bpy by X-ray crystallography. The 3D frameworks remained intact upon removal of the solvent and free dipyridyl ligands. It is interesting to note

that the TGA decomposition temperatures for **2**–**5** are largely unchanged by prior removal of the encapsulated bipyridyl ligands (see Figure S6 in the Supporting Information). This finding suggests that the host structure could be intact upon removal of the guests.

Activated samples of **2**–**5** exhibited uptake of CO_2 at 195 K, but no adsorption of the slightly larger N_2 even at 77 K (see Figure 6, and Figure S8 in the Supporting Information).[12] All complexes exhibited a type I CO_2 adsorption

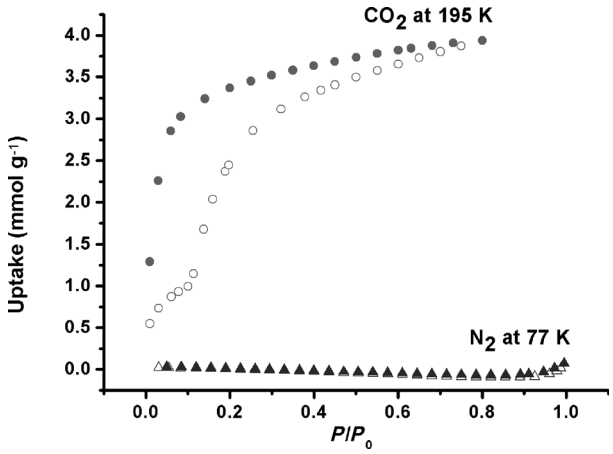


Figure 6. N_2 (77 K) and CO_2 (195 K) sorption isotherms for $[Cd_3(BTB)_2(bpe)(H_2O)_2]\cdot(bpe)\cdot x CHCl_3$ (**4**). Open symbols indicate adsorption and closed symbols desorption. P_0 is the saturated vapor pressure of the adsorbates at the measurement temperatures.

profile with steep uptake in the low-pressure region, consistent with the presence of an open channel in the degassed phase.[12] The Brunauer-Emmett-Teller (BET) surface areas calculated from CO_2 sorption data for **2**–**5** are 104 (**2**), 102 (**3**), 306 (**4**), and 58 $m^2 g^{-1}$ (**5**), which are lower than that of **1a** (504 $m^2 g^{-1}$).[8] The CO_2 adsorption isotherms for **2**–**5** also exhibit different degrees of hysteresis upon desorption, thus indicating the variable structural flexibility of the frameworks.[13] In addition, the adsorption curve for **4** also displays a gating pressure at around 74.5 mmHg, which is not found in other complexes. The hysteresis loops for **2**–**5** are closed and rejoin the adsorption branch, thus indicating that all of the adsorbate molecules can be removed from the framework.[6d] Complex **4** also adsorbed up to 87.7 $cm^3 g^{-1}$ CO_2 (3.94 mmol g^{-1}, 17.3 wt% at standard temperature and pressure), comparable with $Mn(HCOO)_2$ (105 $cm^3 g^{-1}$),[12a] Mn(2,6-ndc) (2,6-ndc = 2,6-naphthalenedicarboxylate; 66.8 $cm^3 g^{-1}$),[14] $Cu(fma)(bpe)_{0.5}$ (fma = fumarate, bpe = *trans*-bis(4-pyridyl)ethylene; 100 $cm^3 g^{-1}$),[15] and Zn(dtp) (H_2dtp = 2,3-di-1*H*-tetrazol-5-ylpyrazine; 99 $cm^3 g^{-1}$)[16] under similar experimental conditions.

Single-crystal to single-crystal conversion requires the coherent cooperation of functional groups during the rearrangement of atoms in the solid state. A handful of successful examples involving transformation in small reaction domains, prompted by light[1i,17] or heat,[2d,18] have been reported. Direct reaction of 2D polymers with bridging ligands in a single crystal to form 3D MOFs is uncommon,[1g,19] and the synthesis of interpenetrated MOFs by threading of the bridging ligand unprecedented. We have observed that the long dipyridyl ligands not only diffuse into the crystal lattice, but also penetrate through more than one 2D layer. This threading process also results in a DEF–aqua exchange to minimize congestion and, more strikingly, forces the slippage of two-dimensional layers to accommodate the bridging ligands of different lengths, while still maintaining crystallinity. Also notable was that DEF and DMF, two solvents commonly used interchangeably in MOF syntheses, could behave quite differently. Fortuitously, the bulkier DEF molecules caused the Cd_3-based double layers to form sizable channels that in turn enabled the bridging ligands to access and displace the solvent molecules. We will apply this serendipitous discovery to other crystal systems (not only MOFs) that possess replaceable solvates. The two-dimensional complex **5** is an example of the in situ substitution of 'normal' solvates in **1a** with "functional" solvates. We have also demonstrated a method to increase the porosity of an MOF in single-crystal conversions. We are currently exploring the scope of this strategy, by employing different carboxylate struts and bridging ligands to optimize crystalline materials for CO_2 capture and other applications.

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