Electronic Supplementary Information for

An N,N'-diethylformamide solvent-induced conversion cascade within a metal–organic framework single crystal

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Experimental

General

 $[Cd_3(BTB)_2(DEF)_4] \cdot 2(DEF)_{0.5}$ (MOF 1) and $[Cd_3(BTB)_2(BPEE)(H_2O)_2] \cdot (BPEE) \cdot xSol$ (MOF 2) were synthesized by our previously reported method.¹ Cd(NO₃)₂·4H₂O (\geq 99.99%, Macklin), benzene-1,3,5-tribenzoic acid (H₃BTB, >98.0%, TCl), 4,4'-azopyridine (AZOPY, ≥97.0%, Aldrich), N,N'-dimethylformamide (DMF, ≥99.8%, Aladdin) and N,N'-diethylformamide (DEF, >99.0%, TCI) were obtained from commercial sources and used without further purification. FT-IR spectra were obtained on a Bruker Vertex 70 FTIR spectrometer in transmission mode over the range 600–4000 cm⁻¹. Elemental analyses for C, H and N were conducted on a Carlo-Erba CHNO-S microanalyzer. Samples were first immersed in CHCl₃ to replace the encapsulated species with volatile CHCl₃ solvate and air-dried before analysis. Thermogravimetric analyses (TGA) were performed in an Al₂O₃ pan on a Mettler TGA/SDTA851 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ under an N₂ gas flow. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 GADDS (General Area Detector Diffraction System) micro-diffractometer equipped with a VANTEC-2000 area detector with ϕ rotation. N₂ and CO₂ adsorption isotherms were recorded using a BELSORP-max (BEL, Japan). The sample was air-dried in the fumehood and exchanged with CHCl₃ twice before transferring to the instrument for activation. The sample was heated under a vacuum of 10⁻² kPa for 24 hours. The evacuated sample tube was weighed and the sample mass determined by subtracting the mass of the empty tube. The N₂ and CO₂ isotherms were measured using a liquid nitrogen bath (77 K) and dry ice/acetone (195 K), respectively.

PeakForceTM quantitative nanomechanical mapping (PF-QNM) analysis was carried out on a Bruker Dimension Icon AFM under ambient conditions. A probe PPP-NCHR-20 was used with a nominal spring constant k = 45.72 N m⁻¹ and the tip radius R was the default value (10 nm). The deflection sensitivity was measured against a sapphire surface and the spring constant k was calibrated by the thermal tune method. A scanning size was typically 5 μ m × 5 μ m with a digital resolution of 256 pixel × 256 pixel at a scanning rate of 0.977 Hz.

The Derjaguin-Muller-Toporov DMT model was applied to calculate Young's modulus. This model assumes a deformation, which is much less than the tip radius, providing spherical contact. This model takes into account the adhesion between the tip and the surface. The DMT modulus is calculated as follows:

$$F_{tip} = \frac{4}{3}E^*\sqrt{Rd^3} + F_{adl}$$

Wherein F_{tip} is the force on the tip, F_{adh} is the adhesion force, R is the tip radius, d is the sample deformation and E* is the reduced modulus. The latter is further defined as

$$E_{s} = (1 - \nu_{s}^{2}) \left[\frac{1}{E^{*}} - \frac{\nu_{tip}^{2}}{E_{tip}} \right]^{-1}$$

Wherein v_s and E_s are the Poisson's ratio and the modulus of the sample, v_{tip} and E_{tip} are the Poisson's ratio and the modulus of the tip. Since the value of v_s is not known for most samples studied, it is taken by default to equal 0.3.

Single-crystal conversion cascades from $[Cd_3(BTB)_2(BPEE)(H_2O)_2] \cdot (BPEE) \cdot xSol$ (MOF **2**) and the characterization of MOFs **3b**, **4**, and **1**'

Single-crystals of $[Cd_3(BTB)_2(BPEE)(H_2O)_2] \cdot (BPEE) \cdot xSol (MOF 2)$ were added to DEF and the reaction monitored by periodically analyzing the single-crystal structures. Replacement of the two H₂O solvates on the central Cd^{2+} proceeded over two minutes, yielding H₂O/DEF and H₂O/BPEE statistical mixtures. Samples collected 100 120 at seconds and seconds possessed the formula $[Cd_3(BTB)_2(BPEE)_{1,8}(DEF)_{0,9}(H_2O)_{0,8}]$ xSol (denoted as MOF **3a**) and $[Cd_3(BTB)_2(BPEE)_2(DEF)_{1,1}(H_2O)_{0,4}]$ xSol (denoted as MOF 3b). The H₂O-to-DEF and H₂O-to-BPEE exchanges were completed in one hour, yielding [Cd₃(BTB)₂(BPEE)₂(DEF)₂]·xSol (MOF 4). The complete conversion from MOF 2 to MOF 1' required approximately six hours.

General characterization of $[Cd_3(BTB)_2(BPEE)_2(DEF)_{1.1}(H_2O)_{0.4}]$ ·xSol (MOF **3b**)

IR (cm⁻¹): 3349 (m), 2988 (m), 2893 (w), 1637(s), 1606 (m), 1585 (s), 1536 (s), 1382 (s), 1249 (m), 1221 (m), 1189 (m), 1142 (m), 1109 (m), 1068(m), 1015 (s), 975 (w), 893 (w), 857(s), 831 (m), 810 (m), 782 (s), 706 (s), 670 (s), 650 (w), 608 (m). Anal. Calcd (%) for C_{83.5}H_{62.9}O_{13.5}N_{5.1}Cd₃·3CHCl₃: C 50.70, H 3.24, N 3.49; found: C 49.13, H 4.39, N 2.04.

General characterization of [Cd₃(BTB)₂(BPEE)₂(DEF)₂]·xSol (MOF 4)

IR (cm⁻¹): 3350 (m), 3062 (w), 2982 (w), 2907(w), 1606 (m), 1581 (s), 1531 (s), 1383 (s), 1307 (w), 1249 (m), 1222 (s), 1188 (s), 1143 (m), 1111(m), 1069 (m), 1016 (s), 977 (m), 957 (w), 952 (w), 892 (w), 857 (s), 831 (m), 811 (m), 781 (s), 706 (s), 670 (s). Anal. Calcd (%) for C₈₈H₇₂O₁₄N₆Cd₃·3CHCl₃: C 51.24, H 3.54, N 3.94; found: C 51.36, H 3.71, N 2.18.

General characterization of [Cd₃(BTB)₂(BPEE)(DMF)(H₂O)]·xSol (MOF **5**)

IR (cm⁻¹): 3358 (m), 3065 (w), 2926 (w), 1651(m), 1607 (m), 1581 (s), 1531 (s), 1383 (s), 1312 (w), 1247 (m), 1221 (w), 1205 (w), 1186 (m), 1144(m), 1107 (m), 1069 (m), 1016 (s), 978 (m), 961 (w), 895 (w), 856 (s), 832 (m), 811 (m), 781 (s), 704 (s), 671 (s), 635 (w), 623 (w), 608 (w). Anal. Calcd (%) for $C_{69}H_{49}O_{14}N_3Cd_3$ ·CHCl₃: C 52.52, H 3.15, N 2.63; found: C 53.24, H 3.79, N 2.39.

The reaction of brown-orange-colored $[Cd_3(BTB)_2(AZOPY)(H_2O)_2] \cdot xSol (MOF$ **6**) with DEF to visualize the replacement of dipyridyl ligands by DEF

A sample of crystalline $[Cd_3(BTB)_2(AZOPY)(H_2O)_2] \cdot xSol (MOF 6)$ was divided into twelve equal parts and mixed with equal volumes of DEF, filtered, and washed with $CHCl_3$ three times at different time intervals, before drying in air. The crystal color gradually changed from red to light yellow, and ultimately white.

X-ray data collection and structure determinations

Data collections were performed on a Bruker APEX III CCD X-ray diffractometer (except MOF 1') or Bruker D8 Quest (MOF 1') with an enhanced X-ray source Mo K α (λ = 0.71073 Å). Refinement and reduction of the collected data were achieved using the program Bruker SAINT and absorption corrections performed using a multi-scan method.² Crystal structures were solved by direct methods and refined on F² by fullmatrix least-squares techniques with *SHELXTL-2013*.³

Data were collected for a sample isolated at 40 s (denoted as MOF_40s), and the two pyridyl rings in this sample were refined as rigid hexagons. The positions of the hydrogen atoms on the coordinated water were estimated by WinGX⁴ and whole molecules were subsequently refined as rigid groups with O–H = 0.83 Å and thermal parameters constrained to $U_{iso}(H) = 1.2U_{eq}(O)$.

At 100 s (MOF **3a**), the BPEE and coordinated water on the central Cd²⁺ displayed positional disorder with a relative ratio of 0.8 : 0.2 fixed for BPEE and H₂O, respectively. The DEF and coordinated water at the *trans*-position also displayed positional disorder with a relative ratio of 0.4 : 0.6 fixed for DEF and H₂O, respectively. The DEF coordinated to the flanking Cd²⁺ displayed occupational disorder with an occupancy factor of 0.5 fixed for all atoms. The CHCl₃ solvate displayed conformational disorder with a relative ratio of 0.77 : 0.23 refined for the two domains. The hydrogen atoms on the disordered water solvates were not located.

At 120 s (MOF **3b**), the DEF coordinated to the central Cd^{2+} displayed positional disorder with the coordinated water and their occupancy factors were fixed at 0.6 : 0.4 for the two components. The occupancy factor for the DEF solvent on the flanking Cd^{2+} was fixed at 0.5 to obtain reasonable thermal

factors. The hydrogen atoms on the coordinated water solvates of the central Cd²⁺ (disordered with a coordinated DEF) were not located.

At one hour (MOF **4**), the DEF molecules coordinated to the flanking and central Cd^{2+} displayed conformational disorder with relative ratios of 0.86 : 0.14 and 0.76 : 0.24 refined for the two components.

At three hours (denoted as MOF_3h), the DEF molecules coordinated to the flanking and central Cd^{2+} displayed conformational disorder with the relative ratios of 0.81 : 0.19 and 0.79 : 0.21 refined for the two components. The occupancy factor for the CHCl₃ solvent was fixed at 0.5 to obtain reasonable thermal factors.

At six hours (MOF 1'), the DEF molecules coordinated to the flanking and central Cd^{2+} displayed conformational disorder with relative ratios of 0.16 : 0.84 and 0.50 : 0.50 refined for the two components.

For data collected from the reaction of MOF **2** with DMF for two hours (MOF **5**), the occupancy factor for the dissociated DMF solvent was fixed at 0.25 to obtain reasonable thermal factors. For data collected from the reaction of MOF **2** with DMF for 14 months (MOF_DMF_14m), the location of the two hydrogen atoms on the coordinated water was suggested using the Calc-OH program in the WinGX suite.⁵ The O–H distances were to O–H = 0.83 Å and thermal parameters constrained to $U_{iso}(H) = 1.2U_{eq}(O)$.

A large amount of spatially delocalized electron density was found in the lattice of each MOF crystal examined, but acceptable refinement results could not be obtained for this electron density. The solvent contribution was then modeled using SQUEEZE in the Platon program suite.⁶

The crystal structures of MOFs **1/1'**, and **2** have been described previously.¹ The crystallographic data for MOF_40s, MOF **3a**, MOF **3b**, MOF **4**, MOF_3h, MOF **5**, and MOF_DMF_14m have been deposited with the Cambridge Crystallographic Data Center (CCDC) with numbers of 1978516–1978522. A summary of the key crystallographic data is presented in Table S1.

	MOF 1	MOF 2	MOF_40s
Remarks	2D starting MOF	3D MOF (interpenetrated)	Reaction proceeds for 40s
Formula weight	1702.63	1847.22	1608.45
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	<i>P</i> -1	<i>P</i> -1
a (Å)	10.4150(5)	16.3187(10)	16.320(5)
b (Å)	14.2887(8)	17.0365(9)	16.974(5)
<i>c</i> (Å)	14.6852(8)	18.9426(11)	19.292(6)
α (°)	69.9420(10)	88.412(2)	88.171(7)
6 (°)	82.7040(10)	70.681(2)	70.164(7)
γ(°)	88.6440(10)	62.5920(10)	62.671(6)
𝗸 (ų)	2035.77(19)	4362.9(4)	4417(2)
Ζ	1	2	2
$ ho_{ m calc}$ (g cm ⁻³)	1.389	1.406	1.209
F(000)	863	1844	1612
μ (cm⁻¹)	0.842	0.967	0.770
total refls.	33934	92676	99801
uniq. refls.	8953	15928	21854
Obsb.refls.	7440	10133	10040
<i>R</i> _{int}	0.0280	0.0678	0.1427
variables	473	862	868
R_1^{a}	0.0413	0.0873	0.0949
wR ₂ ^b	0.0530	0.2532	0.2847
GOF ^c	1.040	1.083	1.025

Table S1 Crystal data and refinement parameters for the MOFs reported herein

MOF 3a	MOF 3b	MOF 4	MOF_3h
Reaction proceeds for 100s 1758.67	Reaction proceeds for 120s 1690.08	Reaction proceeds for 1h 1894.08	Reaction proceeds for 3h 1994.22
triclinic	triclinic	triclinic	triclinic
P-1	P-1	P-1	<i>P</i> -1
16.360(7)	16.377(3)	16.400(3)	16.459(5)
17.031(7)	17.024(4)	16.980(3)	17.028(5)
19.943(9)	20.123(4)	20.488(3)	20.704(6)
89.551(12)	90.241(5)	92.380(4)	92.164(8)
69.596(11)	110.656(5)	111.486(4)	111.745(7)
62.889(9)	117.102(4)	116.958(3)	117.015(7)
4559(3)	4580.8(17)	4581.5(12)	4650(2)
2	2	2	2
1.281	1.225	1.373	1.424
1762	1702	1912	2022
0.837	0.746	0.839	0.831
98376	100338	91900	160751
17941	17387	22486	22923
11080	12520	13275	12911
0.0983	0.0700	0.1119	0.1377
992	931	1113	1230
0.1155	0.1305	0.0943	0.0848
0.2686	0.2806	0.2280	0.2304
1.134	1.127	1.048	1.043

Table S1 continued

MOF 1'	MOF 5	MOF_DMF_14m
Reaction proceeds	Immersing MOF 2 in	MOF 2 in DMF for
for 6h 1612.57	DMF for 2h 1499.58	14 months 1481.31
triclinic	triclinic	triclinic
<i>P</i> -1	<i>P</i> -1	P-1
10.5194(13)	16.713(3)	16.754(2)
14.3966(17)	16.927(2)	16.894(2)
14.7425(17)	17.944(3)	18.001(3)
69.722(3)	65.931(4)	66.663(4)
82.581(3)	77.105(4)	77.370(4)
87.555(3)	62.489(4)	62.283(3)
2076.7(4)	4107.3(11)	4138.0(10)
1	2	2
1.289	1.213	1.189
818	1500	1480
0.820	0.823	0.816
59299	33818	141382
10425	18754	20523
6992	8468	12287
0.0630	0.0935	0.1168
429	811	802
0.0637	0.0899	0.0727
0.1248	0.2295	0.1710
1.074	1.053	1.025

Table S1 continued

 $\overline{{}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|, wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]\}^{1/2}, \text{ GOF} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)\}^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is total number of parameters refined.}$

Table S2 The site occupancies in different MOFs

	Ligand rations (central Cd ²⁺)		DEF on the flank Cd ²⁺
	BPEE : H ₂ O	DEF : H ₂ O	Site occupancy (%)
MOF_40s	0:1	0:1	0
MOF 3a	0.8 : 0.2	0.4 : 0.6	0.5
MOF 3b	1:0	0.6 : 0.4	0.5
MOF 4	1:0	1:0	1

	Ligand rations (central Cd ²⁺)		DMF on the flank Cd ²⁺
	BPEE : H ₂ O	DMF : H ₂ O	Site occupancy (%)
MOF 5	0:1	1:0	0
MOF_DMF_1	0:1	1:0	0
4m			



Fig. S1 The PXRD patterns of MOF **1** (red) and MOF **1'** (blue), showing their good match with that of the simulated (black).



Fig. S2 The PXRD patterns of MOF **4** showing a good consistency among the simulated (black), assynthesized (red), and that after BET analysis (blue).



Fig. S3 The simulated (black) and experimental (red) PXRD patterns of MOF 5.



Fig. S4 The experimental PXRD patterns of $[Cd_3(BTB)_2(AZOPY)(H_2O)_2] \cdot xSol (MOF 6)$ immersed in DEF for 48h (red), showing that MOF 6 converted back to 2D MOF 1 (black).



Fig. S5 Crystals of MOF **6** immersed in DMF at different time intervals indicating that the replacement of AZOPY ligand by DMF is much slower than by DEF and that the AZOPY ligand cannot be completely removed.



Fig. S6 Photographs showing the experimental apparatus for AFM analysis.



Fig. S7 The surface morphologies of MOFs **1** (a), **2** (b), and **1'** (c) determined using an AFM height sensor in PF-QNM mode, and the elastic modulus of MOFs **1** (d), **2** (e), and **1'** (f) in DMT mode.



Fig. S8 TGA curves of MOF **4** before and after BET measurements (represented by black and red lines), demonstrating that these MOFs are generally stable below 350 °C.



Fig. S9 N_2 (77 K) and CO₂ (195 K) sorption isotherms of MOF **4**. The black squares and red circles represent CO₂ absorption and desorption, while the blue and pink triangles represent N_2 adsorption and desorption. P_0 is the saturated vapor pressure of the adsorbates at the measurement temperatures.

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