Supplementary Information

Metal-directed topological diversity of three fluorescent metal-organic frameworks based on a new tetracarboxylate strut

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2,4,4',6-tetramethylbiphenyl

Materials and Methods

All reagents were purchased from commercial sources and used without further purification. 2,4,4',6-Tetramethylbiphenyl was purchased from Jinan Henghua Sci. & Tec. Co. Ltd. Fourier-transform infrared (FT-IR) spectra (4000-600 cm^{-1}) were collected in the solid state on a Varian 800 FT-IR spectrometer. Elemental analyses (C, H, and N) were carried out on a FLASH 2000 elemental analyzer. Powder X-ray Diffraction (PXRD) measurements were performed on a D8-ADVANCE X-ray diffractometer at 45 kV, 40mA for Cu*K*α (λ = 1.5418 Å). High resolution dynamic thermogravimetric analysis (TGA) were performed under N_2 and recorded on a SDT Q600 Thermogravimetric Analyzer with a heating rate of 5 ^oC per minute. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-4500 Fluorescence Spectrophotometer.

Experimental Section

Synthesis of [1,1'-biphenyl]-2,4,4',6-tetracarboxylic acid (H_4BPTC)

The mixture of 2,4,4',6-Tetramethylbiphenyl (0.10 mol, 21.0 g), KOH (0.40 mol, 22.4 g), and 1000 mL H_2O was heated to reflux. $KMnO_4$ (1.28 mol, 201.6 g) was added in portions to the refluxing solution. Refluxing was continued until 2,4,4',6-Tetramethylbiphenyl was completely oxidized. After cooling to room temperature, the mixture was filtered and the residual manganese dioxide was washed with the solution of hydroxide sodium. The combined filtrates were acidified with concentrated hydrochloric acid. The white solid precipitate was filtered off, washed several times with water, and dried to afford H_4BPTC (yield of 62 %). EI-MS: m/z $[M-H]^-$, 329.04 (calcd for $C_{16}H_{10}O_8$, 330.04). Anal. (%) calcd. for $C_{16}H_{10}O_8$ C, 58.19; H, 3.05. Found: C, 58.12; H, 2.97. IR (cm^{-1}): 3108, 1693, 1604, 1568, 1414, 1376, 1289, 1163, 1005, 915, 783, 728, 703.

Synthesis of Zn_2(BPTC) (1):

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.75 mg, 0.1 mmol), and H_4BPTC (33.01 mg, 0.1 mmol) in 8 mL H_2O and 2ml NaOH(1mmol/ml, 0.2mmol) was sealed in a 25 mL Theflon-lined stainless steel container and heated at 180 °C for 12 days. After the mixture cooled to room temperature at a rate of 2 °C/h, colorless block crystals of **1** were obtained with a yield of 32% (based on Zn). Anal. calcd for C_{16} H_6 O_8 Zn_2 (%): C, 42.05; H, 1.33. Found: C, 42.17; H, 1.31. IR (cm^{-1}): 3055, 2930, 1605, 1532, 1368, 1182, 1004, 920, 868, 799, 768, 727, 702.

Synthesis of $[Cd_2(BPTC)(H_2O)_3]\cdot(H_2O)$ (2):

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.85 mg, 0.1 mmol), and H_4BPTC (33.01 mg, 0.1 mmol) in 8 mL H_2O and 2ml NaOH(1mmol/ml, 0.2mmol) was sealed in a 25 mL Theflon-lined stainless steel container and heated at 160 °C for 4 days. After the mixture cooled to room temperature at a rate of 2 °C/h, colorless block crystals of **2** were obtained with a yield of 46% (based on Cd). Anal. calcd for $C_{16}H_{14}$ $O_{12}Cd_2$ (%): C, 30.84; H, 2.27. Found: C, 30.96; H, 2.28. IR (cm^{-1}): 3567, 2450, 2362, 1652, 1580, 1521, 1427, 1397, 1362, 1005, 948, 921, 855, 781, 737, 707.

Synthesis of $[Pb_2(BPTC)(DMA)_4]$ (3):

A mixture of $Pb(NO_3)_2$ (99.36 mg, 0.3 mmol), and H_4BPTC (33.01 mg, 0.1 mmol) in 10mL DMA was sealed in a 25 mL Theflon-lined stainless steel container and heated at 110 °C for 7 days. After the mixture cooled to room temperature at a rate of 2 °C/h, colorless block crystals of **3** were obtained with a yield of 37% (based on Pb). Anal. calcd for C_{32} H_{42} N_4 O_{12} Pb2 (%): C, 35.29; H, 3.90; N, 5.15. Found: C, 35.35; H, 3.91; N, 5.14. IR (cm^{-1}): 3458, 2934, 1628, 1508, 1394, 1359, 1263, 1147, 1045, 1015, 961, 853, 827, 770, 709.

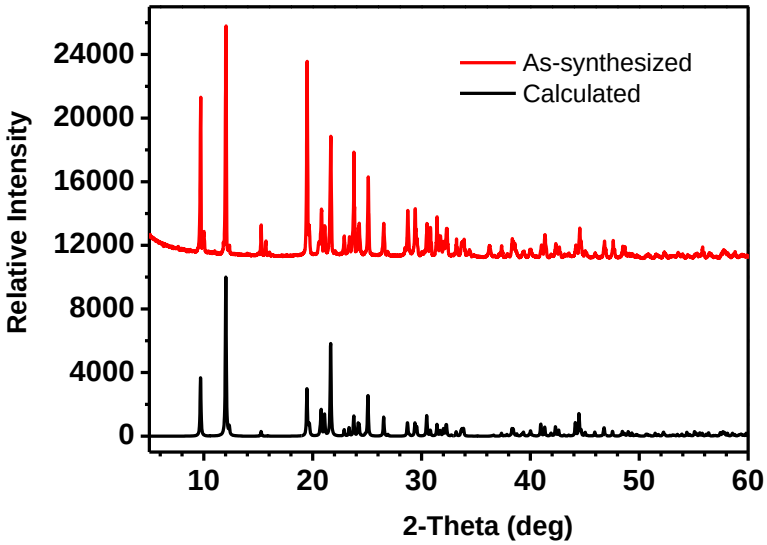

Fig. S1 PXRD patterns of calculated and as-synthesized compound **1**, confirming the purity of bulk samples.

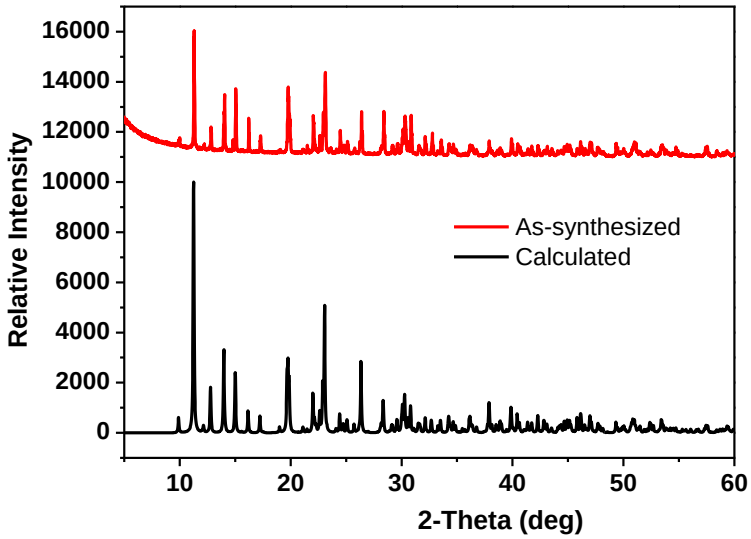

Fig. S2 PXRD patterns of calculated and as-synthesized compound **2**, confirming the purity of bulk samples.

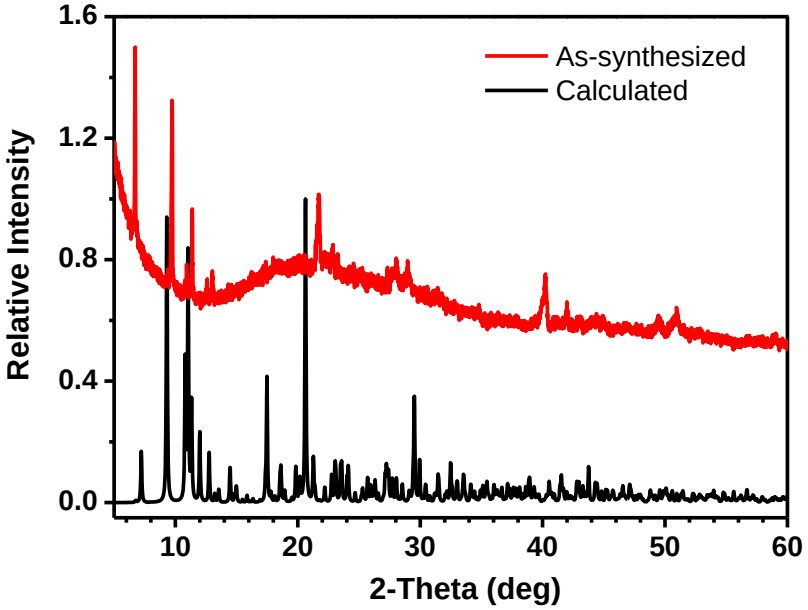

Fig. S3 PXRD patterns of calculated and as-synthesized compound **3**, confirming the purity of bulk samples.

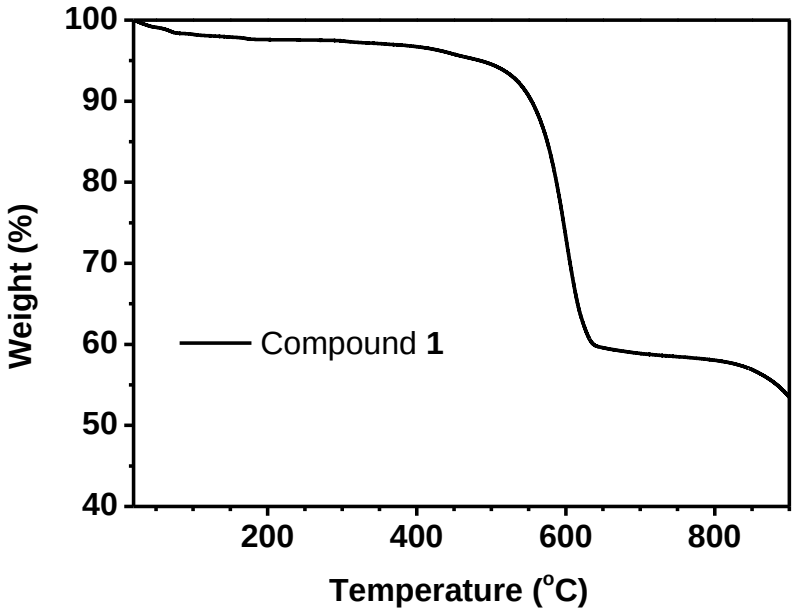

Fig. S4 TGA plot of compound **1**, which shows that **1** can be stable up to at least 400 ^{o}C. The weight loss at the beginning of plot is due to the moisture in the air.

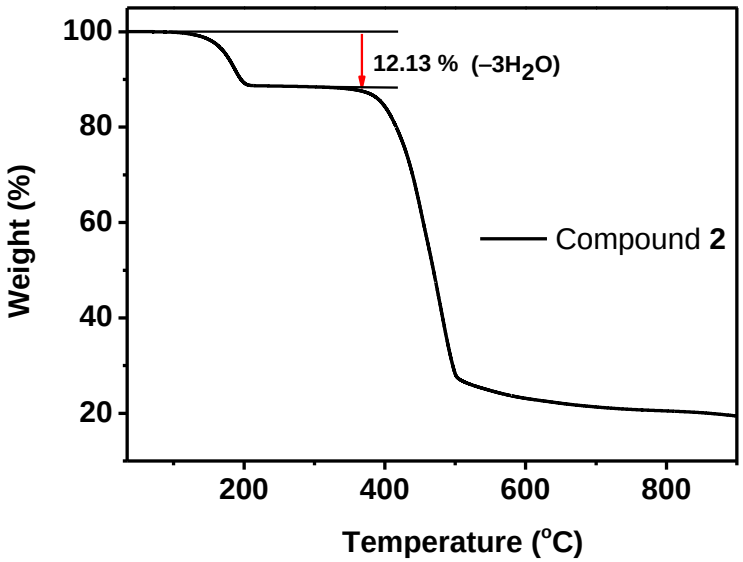

Fig. S5 TGA plot of compound **2**, which shows that **2** can be stable up to 360 °C. The weight loss of 12.13% (theoretical, 11.56%) is corresponding to the one guest and three coordinated water molecules of one unit cell. Because the strong hydrogen bonds (O8···O12 = 2.762 Å, O9···O12 = 2.814 Å, O10···O12 = 2.717 Å), free water molecules are also releasing at higher temperature.

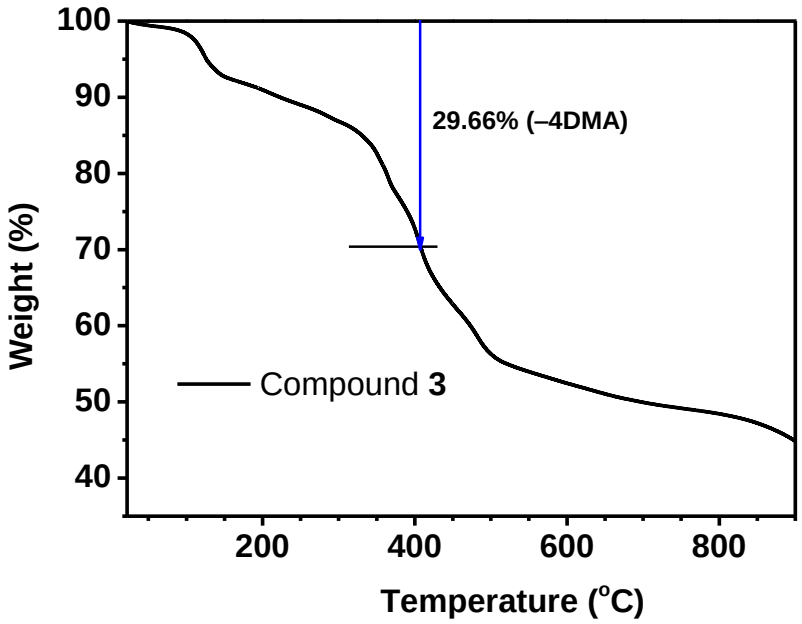

Fig. S6 TGA plot of compound **3**. The weight loss of 29.66% (theoretical, 31.96%) is corresponding to the releasing of coordinated four DMA solvent ligands in **3** of one unit cell.

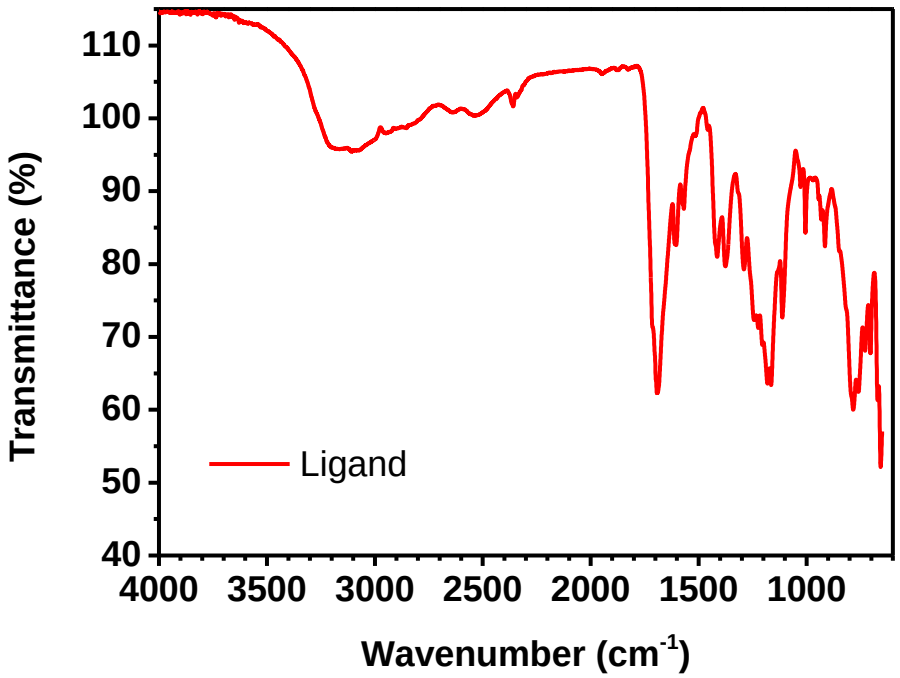

Fig. S7 FTIR spectrum of ligand H_4BPTC.

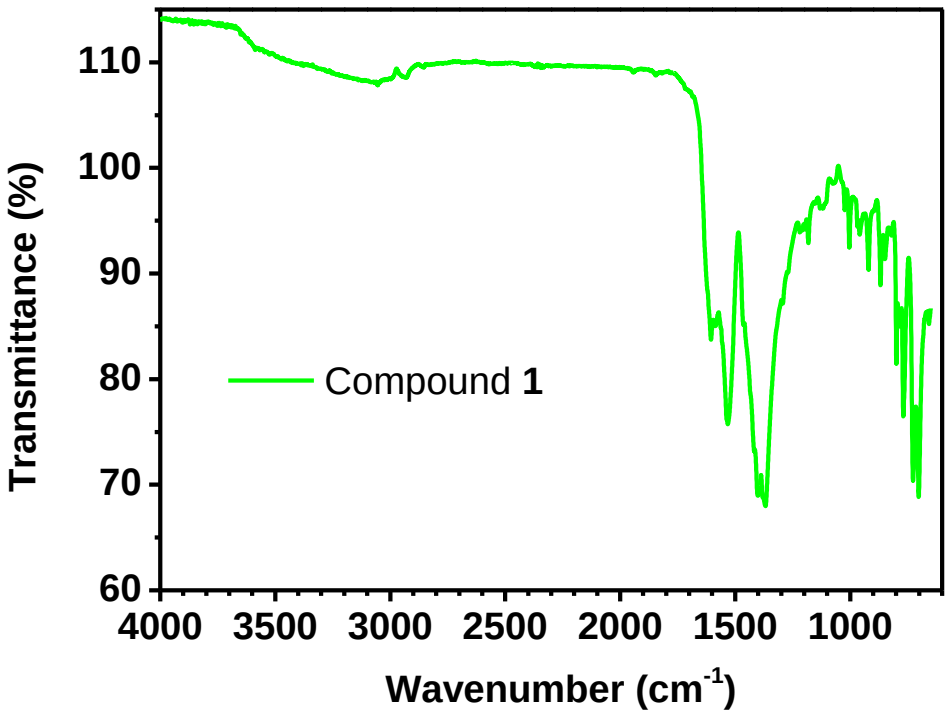

Fig. S8 FTIR spectrum of compound **1**.

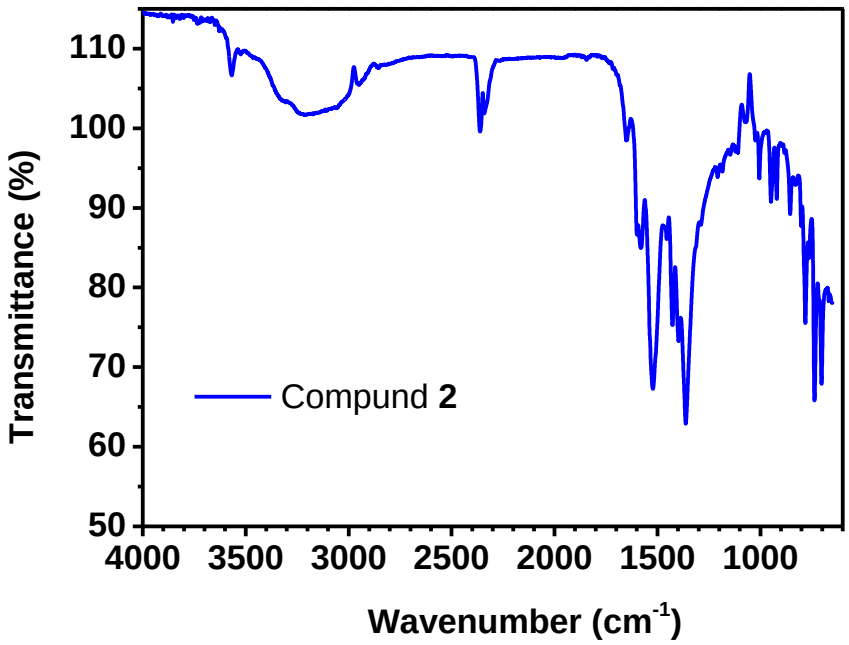

Fig. S9 FTIR spectrum of compound **2**.

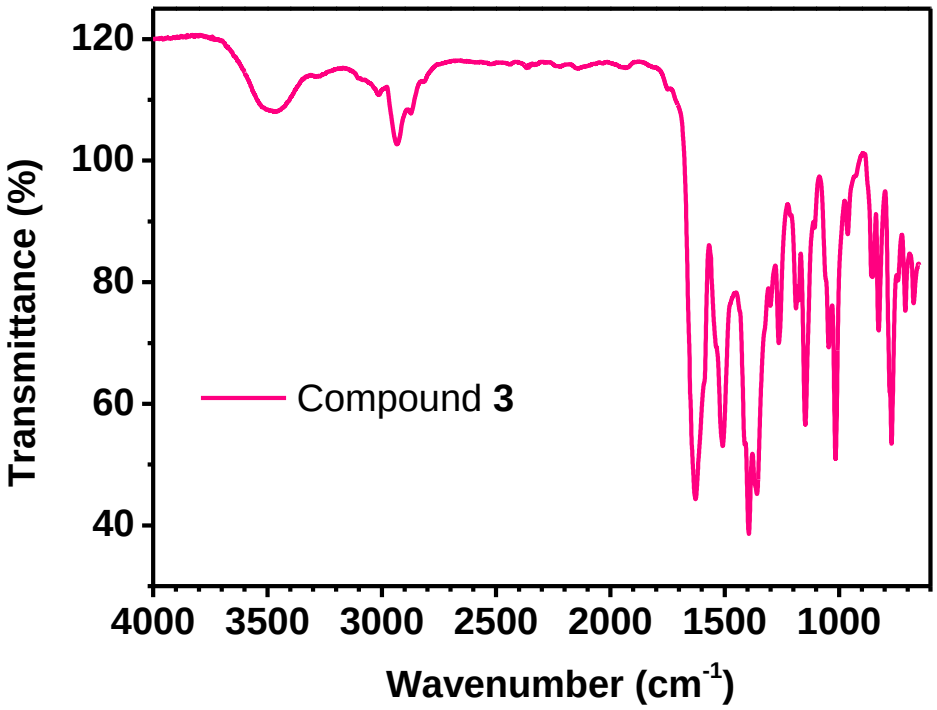

Fig. S10 FTIR spectrum of compound **3**.

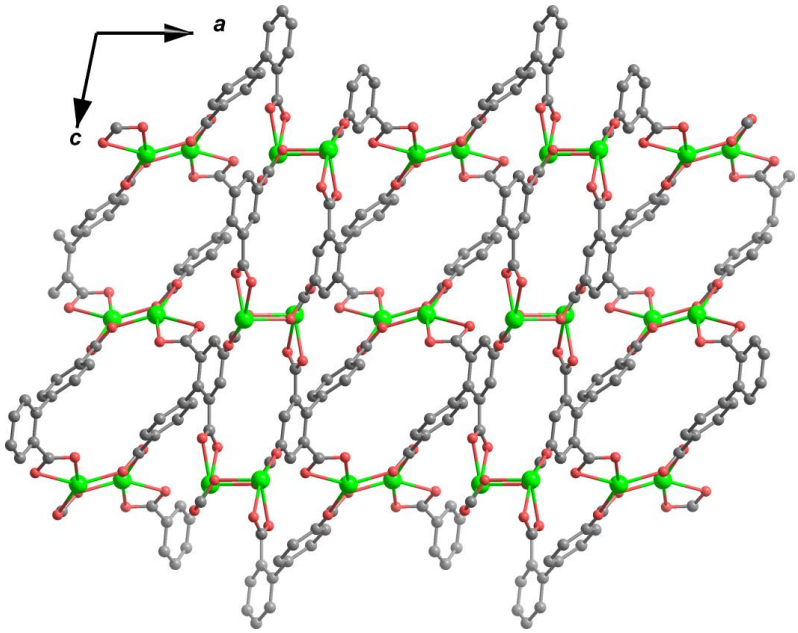

Fig. S11 The single **lvt** net in compound **2**. The coordinated and free water molecules are omitted for clarity. Colour code: green, cadmium; red, oxygen; gray, carbon.

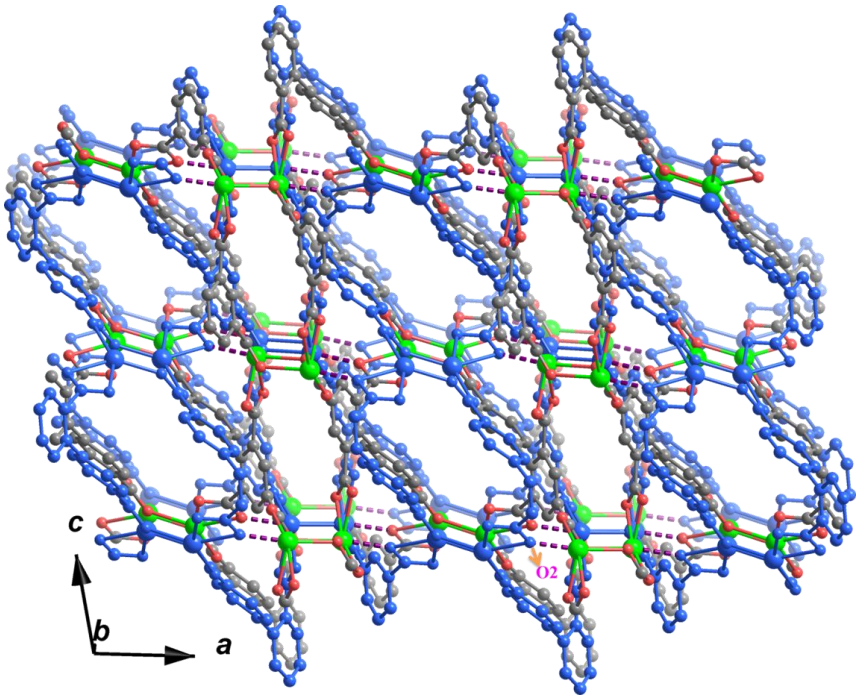

Fig. S12 The 3D structure of compound **2**, which is clearly showing the self-interpenetrated structural feature. The purple dot lines represent the Cd2 – O2 bonds and blue framework shows one single **lvt** net as in Fig. S11. The coordinated and free water molecules are omitted for clarity. Colour code: green, cadmium; red, oxygen; gray, carbon.

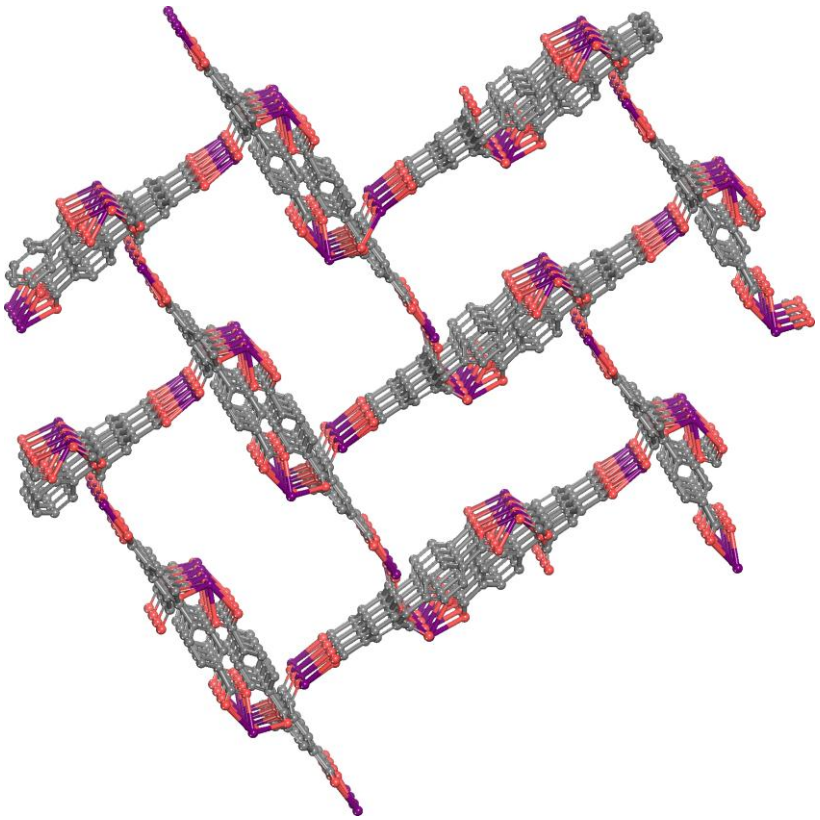

Fig. S13 Ball-and-stick representative 3D structure of compound **3** after removing the coordinated DMA ligands, showing the 1D squeezed rectangular channel along *a*-axis. Colour code: purple, lead; red, oxygen; gray, carbon.

X-ray Crystallography

Crystallographic data of **1** and **3** were collected on a Bruker SMART APEX-II CCD diffractometer and that of **2** was collected on an Oxford diffraction Gemini E diffractometer with Mo-Ka radiation (λ = 0.071073Å) at ambient temperature. The data were corrected for Lorentz-polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program.[1] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. In compound **3**, the coordinated solvent molecules of DMA are disordered and refined using constraints. Selected bond distances and band angles are given in Table S1. Crystal data and refinement conditions are shown in Tables S2–S4.

Table S1 Selected bond lengths (Å) and bond angles (°) in compounds **1-3.**

1		**2**		**3**	
Zn1-O1	1.909(2)	Cd1-O1	2.344(3)	Pb1-O1	2.418(4)
Zn1-O2	1.974(2)	Cd1-O2	2.410(2)	Pb1-O3a	2.378(5)
Zn1-O3	1.963(2)	Cd1-O7a	2.219(3)	Pb1-O4a	2.712(5)
Zn1-O4	1.933(2)	Cd1-O8b	2.220(3)	Pb1-O9	2.488(5)
O1-Zn1-O4	131.19(8)	Cd1-O9	2.323(3)	Pb1-O2	2.818(4)
O1-Zn1-O3	106.43(8)	Cd1-O10	2.280(3)	Pb1-O10	2.625(6)
O4-Zn1-O3	109.41(7)	Cd2-O2c	2.341(2)	Pb2-O2	2.634(5)
O1-Zn1-O2	109.23(8)	Cd2-O3d	2.316(3)	Pb2-O5b	2.508(4)
O4-Zn1-O2	94.96(7)	Cd2-O4	2.218(2)	Pb2-O6b	2.508(4)
O3-Zn1-O2	101.47(7)	Cd2-O5e	2.251(3)	Pb2-O7c	2.327(4)
		Cd2-O6e	2.473(3)	Pb2-O8c	2.741(5)
		Cd2-O11	2.265(3)	Pb2-O11	2.703(11)
		O1-Cd1-O10	87.39(10)	Pb2-O13	2.929(9)
		O1-Cd1-O8b	146.91(11)	O1-Pb1-O3a	82.81(16)
		O9-Cd1-O8b	93.58(11)	O1-Pb1-O4a	132.72(16)
		O1-Cd1-O9	89.39(11)	O3a-Pb1-O4a	50.94(15)
		O1-Cd1-O2	54.60(8)	O1-Pb1-O9	83.9(2)
		O1-Cd1-O7a	92.02(10)	O1-Pb1-O10	75.3(2)
		O4-Cd2-O5e	112.34(10)	O2-Pb2-O5b	77.71(14)
		O5e-Cd2-O6e	54.79(9)	O5b-Pb2-O6b	51.91(15)
		O6e-Cd2-O11	101.46(10)	O11-Pb2-O6b	73.8(3)
		O4-Cd2-O11	91.58(10)	O8c-Pb2-O6b	122.77(17)
		O2c-Cd2-O11	89.30(10)	O5b-Pb2-O8c	130.88(17)
		O3d-Cd2-O11	82.07(10)	O2-Pb2-O7c	85.11(18)
				O2-Pb2-O13	97.1(2)

Symmetry code in compound **2**: a = 1-x, y, 1.5-z; b = x, 1-y, -0.5+z; c = x, 1+y, z; d = 2-x. 3-y, 1-z; e = x, 3-y, -0.5+z.

Symmetry code in compound **3:** a = 1-x, -0.5 +y, 1.5-z; b = 1+x, y, z; c = 0.5 + x, 0.5-y, 2-z.

Table S2 Crystal data and structure refinement for compound **1**.	
Empirical formula	C_{16} H_6 O_8 Zn_2
Formula weight	456.95
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 12.213(5) Å alpha = 90 deg. b = 14.723(6) Å beta = 108.105(4) deg. c = 8.994(4) Å gamma = 90 deg.
Volume	1537.1(10) Å ^3
Z, Calculated density	4, 1.975 Mg/m^3
Absorption coefficient	3.167 mm^-1
F(000)	904
Crystal size	0.23 x 0.16 x 0.11 mm
Theta range for data collection	2.77 to 25.49 deg.
Limiting indices	-14<=h<=14, -17<=k<=17, -10<=l<=10
Reflections collected / unique	5276 / 1440 [R(int) = 0.0258]
Completeness to theta = 25.49	99.9 %
Max. and min. transmission	0.7221 and 0.5296
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1440 / 0 / 121
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR2 = 0.0496
R indices (all data)	R1 = 0.0278, wR2 = 0.0518
Largest diff. peak and hole	0.343 and -0.290 e.A^-3

Table S3 Crystal data and structure refinement for compound **2**.	
Empirical formula	$C_{16}H_{14}Cd_2O_{12}$
Formula weight	623.07
Temperature	291.15K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic，P2/c
Unit cell dimensions	a = 12.8567(3) Å alpha = 90 deg. b = 8.9378(2) Å beta = 101.613(2). deg c = 16.0555(4) Å gamma = 90 deg.
Volume	1807.17(7) $Å^3$
Z, Calculated density	4，2.290mg/mm^3
Absorption coefficient	Multi-scan
F(000)	1208.0
Crystal size	0.2mm × 0.19mm × 0.18mm
Theta range for data collection	5.88 to 52.74°
Limiting indices	$-16 \le h \le 9$, $-9 \le k \le 11$, $-20 \le l \le 20$
Reflections collected / unique	7811/ 3680[R(int) = 0.0226]
Completeness to theta = 26.32	99.77
Max. and min. transmission	1and 0.95869
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3680/4/272
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	$R_1 = 0.0301$, $wR_2 = 0.0624$
R indices (all data)	$R_1 = 0.0381$, $wR_2 = 0.0661$
Largest diff. peak and hole	0.88/-0.69 e $Å^{-3}$

Table S4 Crystal data and structure refinement for compound **3**.	
Empirical formula	C_{32} H_{42} N_4 O_{12} Pb_2
Formula weight	1089.08
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 10.1447(7) Å alpha = 90 deg. b = 13.8559(9) Å beta = 90 deg. c = 26.1423(17) Å gamma = 90 deg.
Volume	3674.7(4) Å ^3
Z, Calculated density	4, 1.969 Mg/m^3
Absorption coefficient	9.216 mm^-1
F(000)	2088
Crystal size	0.18 x 0.12 x 0.11 mm
Theta range for data collection	2.49 to 25.50 deg.
Limiting indices	-12<=h<=12, -16<=k<=16, -31<=l<=31
Reflections collected / unique	27493 / 6834 [R(int) = 0.0312]
Completeness to theta = 25.50	99.9 %
Max. and min. transmission	0.4305 and 0.2878
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6834 / 188 / 435
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0666
R indices (all data)	R1 = 0.0303, wR2 = 0.0680
Largest diff. peak and hole	0.622 and -0.509 e.A^-3

References

1. G. M. Sheldrick, *SHELXL-97*, *Program for refinement of crystal structure*, University of Göttingen, Germany, 1997.