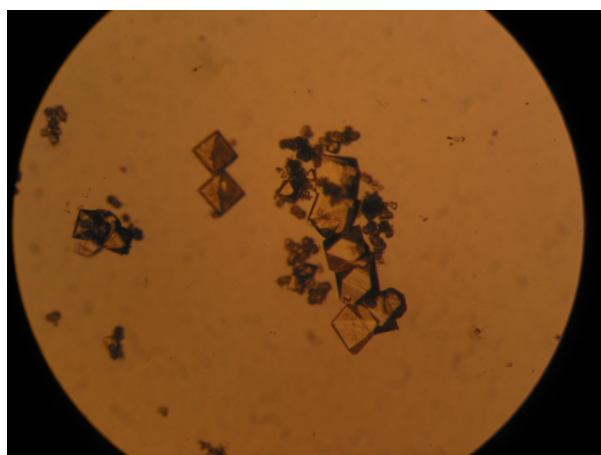Supplementary Information

Synthesis and Characterization of a Zinc Metal-Organic Framework with Chiral Nano-Pores

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Synthesis of $Zn_3(BPDC)_2(O_2CH)_2$•2DEF (1•2DEF). The chemicals were obtained from Aldrich and used as received. The synthesis was performed under solvothermal conditions. $Zn(NO_3)_3$·$6H_2O$ (0.0446 g, 0.15 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (0.0244 g, 0.10 mmol) and formic acid (0.8 mL of a 75% aqueous solution) were mixed and dispersed in DEF (5 mL). The resulting white slurry was then heated in an oven at 100 ºC for 3 weeks to afford octahedron-shaped crystals (Figure S1); the long duration of this step probably reflects the limited solubility of 2,2'-bipyridine-5,5'-dicarboxylic acid in DEF. Yield: 70%. Anal. for the as-prepared material (University of Illinois Microanalytical Laboratory): Calc. for $Zn_3(BPDC)_2(O_2CH)_2$•2DEF: C, 43.1; H, 3.42; N, 8.38. Found: C, 42.8; H, 3.13; N, 8.35. Desolvation to **1** was achieved by immersing the as-prepared crystals in chloroform (5 mL) for three days, with the solvent being changed once daily. The solid was then collected by filtration and dried in a vacuum oven at 120 ºC for 3 h.

200 μm

Fig S1. Crystals of **1•2DEF**.

Brunauer - Emmett - Teller (BET) measurements. Three-point BET ($P/P_0 = 0.1-0.3$) surface area measurements were performed on a QuantachromeNova 2200e apparatus at liquid nitrogen temperature using nitrogen as the working gas.

Powder X-ray diffraction. Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF22 rotating anode generator operating at 50kV and 40mA supplied the Cu Kα graphite monochromatized incident beam. The simulated powder diffraction pattern calculated from the single crystal X-ray data of as-synthesized **1•2DEF** matches well with the observed pattern for desolvated **1** (Figure S2).

Supplementary Information

Thermogravimetric Analysis (TGA). TGA experiments were performed on Cahn Thermax 500 Thermogravimetric Analyzer
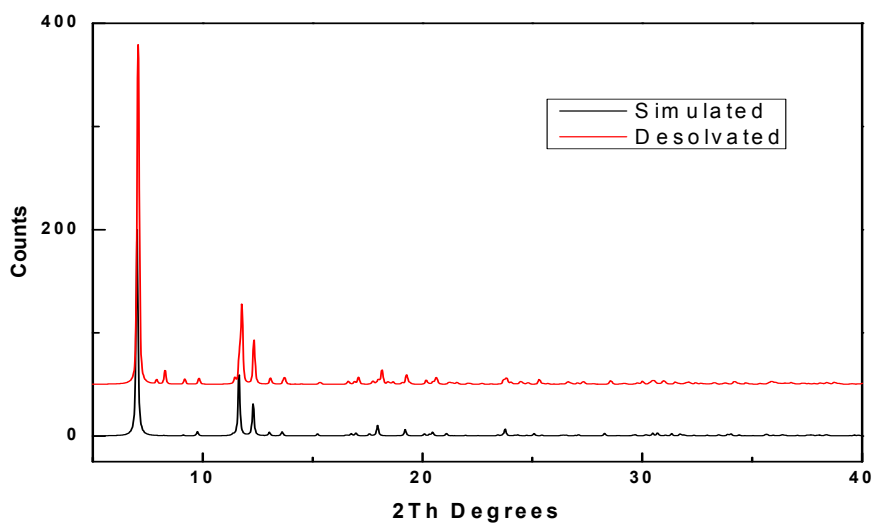
(Figure S3).

Fig S2. Powder X-ray diffraction pattern of desolvated **1** (red), and pattern calculated from the single crystal

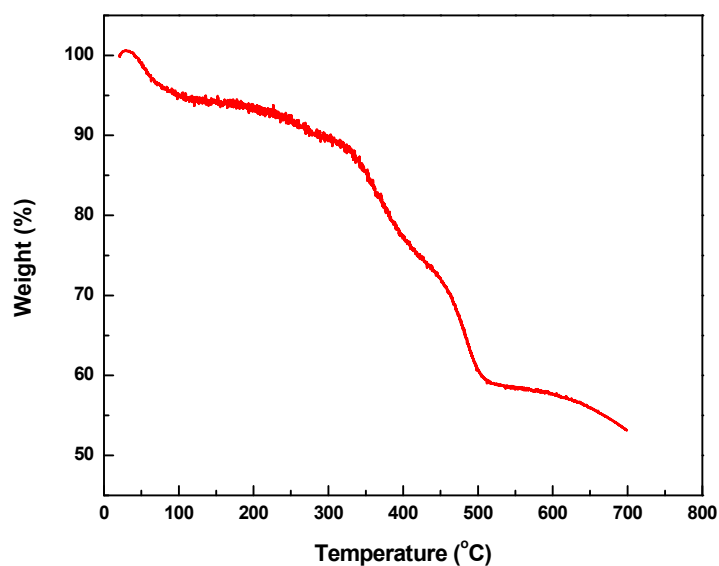structure of as-synthesized **1•2DEF** (black).

Fig S3. Thermogravimetric analysis of a freshly prepared sample of **1•2DEF.**

Supplementary Information

X-ray single crystal diffraction. The data crystal was mounted using oil (Paratone-N, Exxon) to a glass fiber. One distinct cell was identified using APEX2 (Bruker, 2010). Twenty frame series were integrated and filtered for statistical outliers using SAINT (Bruker, 2005) then corrected for absorption by integration using SHELXTL/XPREP V2005/2 (Bruker, 2005) before using SADABS (Bruker, 2005) to sort, merge, and scale the combined data. The absorption correction was done prior to the squeeze process using an absorption coefficient that included the contribution from the two diethylformamide molecules per formula unit. No decay correction was applied. The final refinements excluded the 0 2 3 and 0 1 3 reflections. The structure was phased by direct methods (Sheldrick, 2008). Systematic conditions were consistent with both of the enantiomorphic space groups $P4_12_12$ or $P4_32_12$. On the basis of 1955 unmerged Friedel opposites, the fractional contribution of the racemic twin was close to 50% (Flack, 1983 & 2000). The fractional contribution was checked before the "squeeze" process and the $P4_12_12$ component was slightly larger than the $P4_32_12$ component by ~1%. After the "squeeze" process the ratio was 0.50(4). The central portion of the $-OOC(C_{10}H_6N_2)COO-$ unit was disordered over two sites. The Zn-N distances in the disordered ligand were restrained to be similar. The bond distances and angles within the disordered molecules were restrained to be similar and the central portion of the molecule was also restrained to be approximately flat. The O3 atom was also split over two sites. The like C-O distances for this atom were restrained to be similar. Rigid-bond restraints were imposed on displacement parameters for all disordered sites, and similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of the van der Waals radii. C13 and O6 of the bound formate ligand have large displacement parameters. This is because O6 is not bound to the framework and the molecule can freely pivot about the O5-C13 axis in the solvent cavity. The highest peaks in the final difference Fourier map were in the vicinity of atom Zn2; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude and some dependence on resolution.
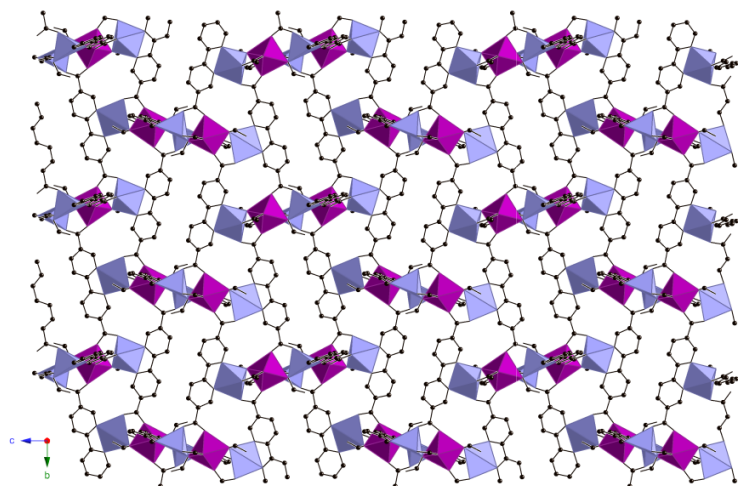
Supplementary Information

Fig S4. Representation of the structure of **1** along the *a* axis (C, black; Zn1, light purple polyhedron; Zn2, purple polyhedron; H, omitted).

Supplementary Information

Table S1. Crystal data and structure refinement for $Zn_3(BPDC)_2(O_2CH)_2 \cdot 2DEF$.

Empirical formula	C36 H36 N6 O14 Zn3
Formula weight	972.82
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Tetragonal
Space group	P4(1)2(1)2
Unit cell dimensions	a = 15.1751(3) Å α = 90°.
	b = 15.1751(3) Å β = 90°.
	c = 22.5604(8) Å γ = 90°.
Volume	5195.3(2) Å^3
Z	4
Density (calculated)	1.244 Mg/m^3
Absorption coefficient	2.111 mm^{-1}
F(000)	1984
Crystal size	0.164 x 0.072 x 0.07 mm^3
Theta range for data collection	4.12 to 67.73°.
Index ranges	-18<=h<=14, -17<=k<=18, -26<=l<=27
Reflections collected	57131
Independent reflections	4672 [R(int) = 0.0466]
Completeness to θ = 67.73°	99.4 %
Absorption correction	Integration
Max. and min. transmission	0.9322 and 0.8488
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4672 / 503 / 324
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	$R1$ = 0.0422, $wR2$ = 0.1174
R indices (all data)	$R1$ = 0.0427, $wR2$ = 0.1178
Absolute structure parameter	0.50(4)
Largest diff. peak and hole	1.109 and -0.400 e.Å^{-3}

Supplementary Information

Table S2. Selected bond distances and angles for $Zn_3(BPDC)_2(O_2CH)_2 \cdot 2DEF$.

Bond lengths [Å]		Angles [°]		Angles [°]	
Zn(1)-O(2)#1	2.006(2)	O(2)#1-Zn(1)-O(5)	103.45(10)	O(3)#3-Zn(2)-O(5)	93.4(13)
Zn(1)-O(5)	2.037(2)	O(2)#1-Zn(1)-O(4)#2	96.27(12)	O(1)#4-Zn(2)-O(5)	91.42(10)
Zn(1)-O(4)#2	2.051(2)	O(5)-Zn(1)-O(4)#2	99.14(11)	O(1)#1-Zn(2)-O(5)	93.21(10)
Zn(1)-N(1)	2.101(5)	O(2)#1-Zn(1)-N(1)	100.7(5)	O(5)#5-Zn(2)-O(5)	173.54(15)
Zn(1)-N(1B)	2.111(6)	O(5)-Zn(1)-N(1)	151.4(4)	O(3)#2-Zn(2)-O(3B)#2	12.0(10)
Zn(1)-N(2B)	2.158(6)	O(4)#2-Zn(1)-N(1)	93.1(2)	O(3)#3-Zn(2)-O(3B)#2	84.0(13)
Zn(1)-N(2)	2.176(5)	O(2)#1-Zn(1)-N(1B)	99.7(7)	O(1)#4-Zn(2)-O(3B)#2	176.8(7)
Zn(2)-O(3)#2	1.951(16)	O(5)-Zn(1)-N(1B)	153.0(6)	O(1)#1-Zn(2)-O(3B)#2	90.0(7)
Zn(2)-O(3)#3	1.951(16)	O(4)#2-Zn(1)-N(1B)	91.8(3)	O(5)#5-Zn(2)-O(3B)#2	84.2(5)
Zn(2)-O(1)#4	2.055(3)	N(1)-Zn(1)-N(1B)	1.8(8)	O(5)-Zn(2)-O(3B)#2	91.3(5)
Zn(2)-O(1)#1	2.055(3)	O(2)#1-Zn(1)-N(2B)	91.6(9)	O(3)#2-Zn(2)-O(3B)#3	84.0(13)
Zn(2)-O(5)#5	2.091(2)	O(5)-Zn(1)-N(2B)	88.3(5)	O(3)#3-Zn(2)-O(3B)#3	12.0(10)
Zn(2)-O(5)	2.091(2)	O(4)#2-Zn(1)-N(2B)	167.6(5)	O(1)#4-Zn(2)-O(3B)#3	90.0(7)
Zn(2)-O(3B)#2	2.093(15)	N(1)-Zn(1)-N(2B)	75.9(4)	O(1)#1-Zn(2)-O(3B)#3	176.8(7)
Zn(2)-O(3B)#3	2.093(15)	N(1B)-Zn(1)-N(2B)	77.4(4)	O(5)#5-Zn(2)-O(3B)#3	91.3(5)
O(1)-C(11)	1.236(5)	O(2)#1-Zn(1)-N(2)	91.9(6)	O(5)-Zn(2)-O(3B)#3	84.2(5)
O(1)-Zn(2)#6	2.055(3)	O(5)-Zn(1)-N(2)	87.4(3)	O(3B)#2-Zn(2)-O(3B)#3	91.8(14)
O(2)-C(11)	1.266(4)	O(4)#2-Zn(1)-N(2)	168.0(4)	C(11)-O(1)-Zn(2)#6	134.2(2)
O(2)-Zn(1)#6	2.006(2)	N(1)-Zn(1)-N(2)	76.7(2)	C(11)-O(2)-Zn(1)#6	128.2(2)
O(3)-C(12)	1.271(8)	N(1B)-Zn(1)-N(2)	78.2(4)	C(12)-O(3)-Zn(2)#7	155(3)
O(3)-Zn(2)#7	1.951(16)	N(2B)-Zn(1)-N(2)	0.9(9)	C(12)-O(3B)-Zn(2)#7	137.6(15)
O(3B)-C(12)	1.268(6)	O(3)#2-Zn(2)-O(3)#3	78(2)	C(12)-O(4)-Zn(1)#4	120.7(2)
O(3B)-Zn(2)#7	2.093(15)	O(3)#2-Zn(2)-O(1)#4	171.2(14)	C(13)-O(5)-Zn(1)	106.1(3)
O(4)-C(12)	1.251(4)	O(3)#3-Zn(2)-O(1)#4	97.4(12)	C(13)-O(5)-Zn(2)	131.4(3)
O(4)-Zn(1)#4	2.051(2)	O(3)#2-Zn(2)-O(1)#1	97.4(12)	Zn(1)-O(5)-Zn(2)	110.67(11)
		O(3)#3-Zn(2)-O(1)#1	171.2(14)	C(1)-N(1)-C(5)	120.1(5)
		O(1)#4-Zn(2)-O(1)#1	88.25(18)	C(1)-N(1)-Zn(1)	122.9(5)
		O(3)#2-Zn(2)-O(5)#5	93.4(13)	C(5)-N(1)-Zn(1)	116.4(4)
		O(3)#3-Zn(2)-O(5)#5	81.5(13)	C(10)-N(2)-C(6)	118.0(6)
		O(1)#4-Zn(2)-O(5)#5	93.21(10)	C(10)-N(2)-Zn(1)	127.4(5)
		O(1)#1-Zn(2)-O(5)#5	91.42(10)	C(6)-N(2)-Zn(1)	114.3(4)
		O(3)#2-Zn(2)-O(5)	81.5(13)		

Symmetry transformations used to generate equivalent atoms: #1 y-1/2,-x+1/2,z-1/4   #2 -x+1/2,y+1/2,-z+1/4
#3 y+1/2,-x+1/2,z-1/4   #4 -x+1/2,y-1/2,-z+1/4   #5 y,x,-z   #6 -y+1/2,x+1/2,z+1/4   #7 -y+1/2,x-1/2,z+1/4