Supplemental Information for

A chiral porous 3D metal-organic framework with an unprecedented 4-connected network topology

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Table S1. Crystal data and structure refinement for $[Cd\mathbf{L}_2(H_2O)_2][ClO_4]_2 \cdot 2DMF \cdot 3EtOH \cdot 5/3H_2O$ (**1**)

	1
Formula	C80 H91.33 Cd Cl6 N6 O20.67
Formula weight	1792.69
Crystal size (mm^3)	0.60 × 0.50 × 0.30
Crystal color	colorless
Crystal system	trigonal,
Space group	P321
Unit cell dimensions	a = 26.209(2) Å
	c = 12.752(2) Å
Volume ($Å^3$)	7586.1(13)
Z	3
Calculated density ($g \cdot cm^{-3}$)	1.177
F(000)	2786
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	0.436
θ for data collection (^{o})	1.83 to 23.30
Limiting indices	$-27 \le h \le 28$, $-29 \le k \le 29$, $-14 \le l \le 14$
Reflections collected	48883
Unique reflections (R(int))	7294 [R(int) = 0.0796]
Refinement method	Empirical
Absorption correction	Full-matrix least-squares on F^2
Data / restraints / parameters	7294 / 12 / 481
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0831, wR2 = 0.2268
R indices (all data)	R1 = 0.0986, wR2 = 0.2415
Flack parameter	0.04(5)
Largest diff. peak and hole ($e \cdot Å^3$)	0.907 and -0.894

$R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x\ 10^3$) for **1**.

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
Cd(1)	6989(1)	0	-10000	37(1)	C(21)	4989(5)	2102(5)	-4307(8)	66(3)
Cl(1)	6778(1)	548(1)	-3528(2)	59(1)	C(22)	4696(5)	2269(5)	-3608(7)	61(2)
Cl(2)	2870(2)	-275(2)	-1786(5)	177(3)	C(23)	4239(5)	1865(5)	-2989(8)	61(2)
O(1)	4649(4)	1463(3)	-6579(5)	68(2)	C(24)	4061(5)	1249(4)	-3080(8)	63(3)
O(2)	5419(4)	2483(3)	-4956(6)	85(3)	C(25)	3592(6)	815(4)	-2491(9)	77(4)
O(3)	7458(4)	-381(3)	-11040(5)	65(2)	C(26)	3407(10)	262(7)	-2634(19)	151(9)
O(4)	2874(9)	1929(8)	2826(16)	226(10)	C(27)	3724(7)	79(6)	-3299(14)	131(7)
O(5)	7950(20)	-890(20)	-9870(30)	213(15)	C(28)	4172(6)	480(6)	-3830(14)	106(5)
O(6)	8251(19)	-1214(18)	-7740(30)	202(13)	C(29)	4359(4)	1088(4)	-3810(8)	55(2)
N(1)	6536(3)	363(3)	-8830(5)	39(2)	C(30)	3090(5)	2124(4)	-1611(8)	61(3)
N(2)	3430(4)	2562(4)	-942(5)	51(2)	C(31)	3341(5)	1882(4)	-2302(8)	58(3)
N(3)	3027(13)	1351(16)	4088(17)	253(18)	C(32)	3946(5)	2075(5)	-2253(7)	60(3)
C(1)	6832(4)	810(4)	-8209(6)	40(2)	C(33)	4283(5)	2527(5)	-1537(7)	61(3)
C(2)	6598(4)	992(4)	-7473(6)	46(2)	C(34)	3997(4)	2735(4)	-920(6)	48(2)
C(3)	6000(3)	728(3)	-7366(6)	36(2)	C(35)	3470(20)	1940(40)	4550(20)	400(50)
C(4)	5664(4)	252(4)	-8005(6)	43(2)	C(36)	2836(17)	730(17)	4500(20)	229(14)
C(5)	5945(4)	70(4)	-8721(5)	40(2)	C(37)	2694(13)	1411(14)	3180(20)	235(19)
C(6)	5713(4)	929(4)	-6574(7)	43(2)	C(38)	7160(20)	-1710(20)	-10260(40)	186(19)
C(7)	5319(4)	1089(4)	-6959(7)	48(2)	C(39)	7710(20)	-1440(20)	-9770(40)	177(18)
C(8)	5038(4)	1290(4)	-6263(7)	47(2)	C(40)	8140(20)	-870(30)	-6580(40)	180(20)
C(9)	5160(4)	1329(4)	-5167(6)	43(2)	C(41)	8150(20)	-1310(20)	-6870(40)	163(16)
C(10)	5561(4)	1170(4)	-4793(6)	45(2)	C(43)	5380(60)	-4030(60)	690(100)	290(70)
C(11)	5714(5)	1213(4)	-3683(6)	51(2)	Cl(3)	3932(9)	-4419(9)	107(14)	201(12)
C(12)	6089(4)	1041(4)	-3313(6)	45(2)	O(9)	4025(11)	-4854(10)	398(19)	194(12)
C(13)	6310(4)	788(4)	-4007(6)	47(2)	O(10)	4411(11)	-4014(12)	-510(20)	156(17)
C(14)	6209(4)	754(4)	-5096(6)	40(2)	O(11)	3445(10)	-4612(12)	-510(20)	239(13)
C(15)	5833(3)	953(3)	-5485(6)	36(2)	O(12)	3880(20)	-4124(18)	940(20)	198(5)
C(16)	4639(6)	1558(5)	-7688(9)	73(3)	O(102)	5670(50)	-2860(50)	-420(80)	140(50)
C(17)	4278(7)	1871(7)	-7845(13)	107(5)	C(42)	5540(30)	-4460(30)	0	230(30)
C(18)	5760(6)	3244(6)	-6199(11)	93(4)	O(8)	5410(40)	-3770(50)	310(80)	180(50)
C(19)	5396(7)	2992(5)	-5322(12)	91(4)	O(101)	3333	-3333	2340(20)	167(9)
C(20)	4828(5)	1518(4)	-4432(7)	54(2)					

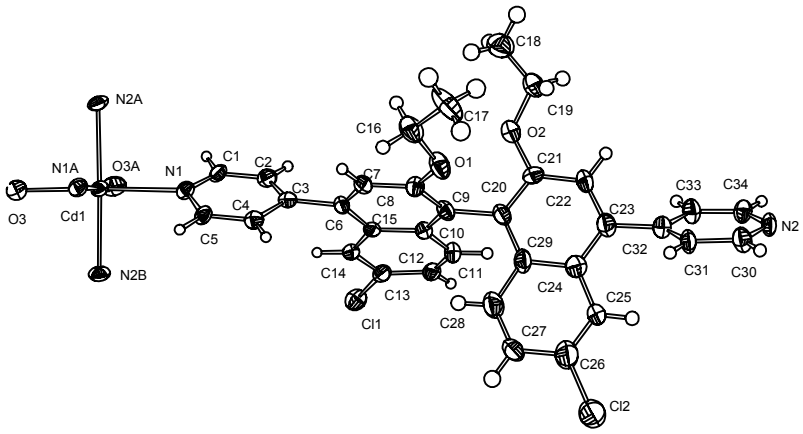

Figure S1. ORTEP representation of the symmetry expanded local structure for **1** (30% probability ellipsoids).

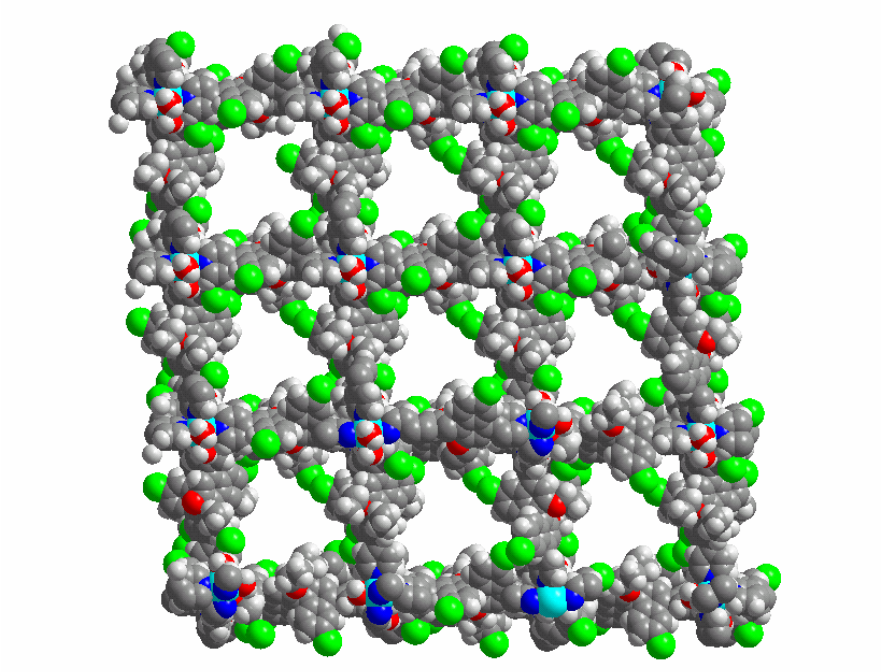

Figure S2. Packing diagram of **1**, showing the square cavities with dimensions of 20.4 × 20.4 $Å^2$.

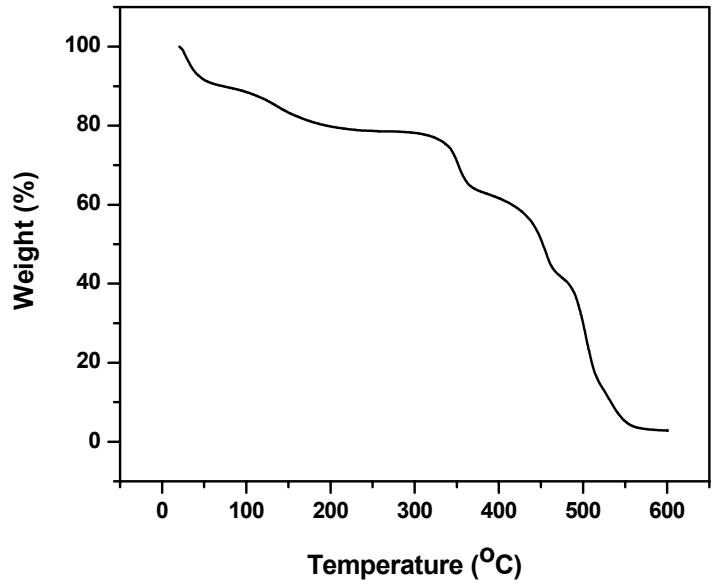

Figure S3. Thermogravimetric analyses (TGA) for **1** between 20 and 600 °C

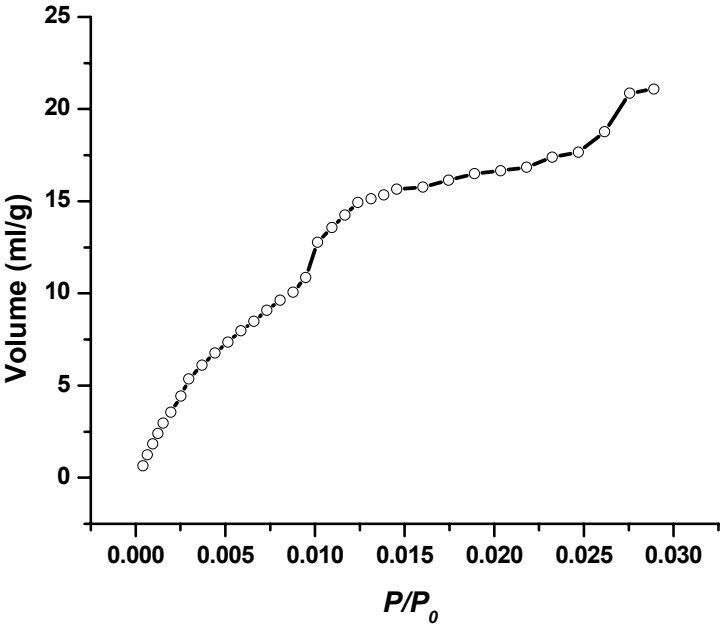

Figure S4. CO_2 adsorption isotherm for an evacuated sample of **1** at 273 K.

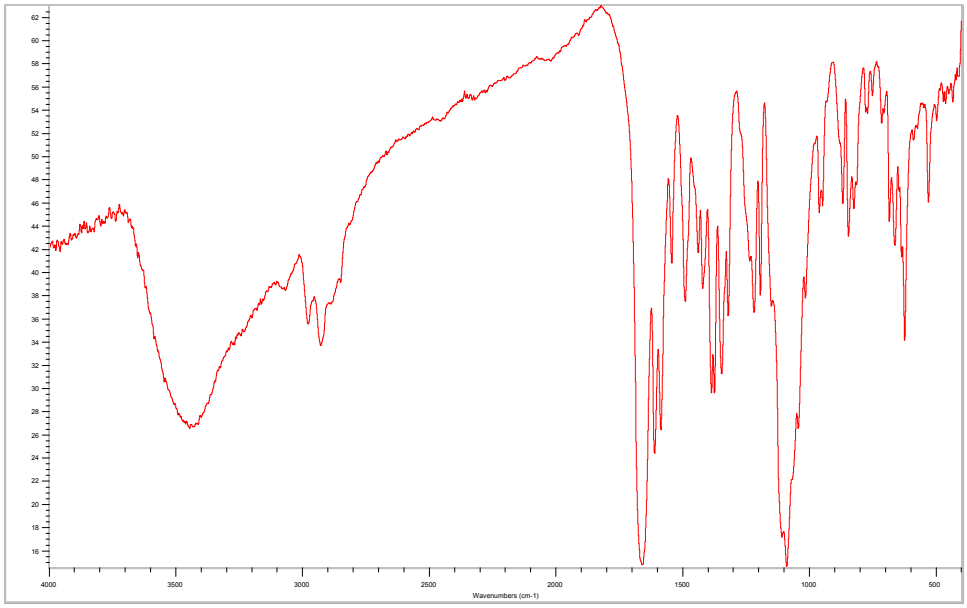

Figure S5. IR spectrum of **1**.

Enantioselective sorption of racemic 1-phenylethanol. Compound **1** (0.025 g, 0.014 mmol) was evacuated at 75 ^{o}C for 12 hours under vacuum, and then 1 mL of racemic 1-phenylethanol was added. The mixture was stirred for 12 hours and filtered. The solid was washed with EtOH several times. The remaining solid was soaked in CH_2Cl_2 and stirred overnight to exchange the 1-phenylethanol molecule guests from the porous solid. After filtration, the CH_2Cl_2 solvent was removed under reduced pressure. The ee% of the adsorbed 1-phenylethanol was determined by GC on a Supelco β-Dex 120 column.