

Supplementary Material (ESI) for Chemical Communications  
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## ***Electronic Supplementary Information (ESI)***

# **Chiral Porous Metal-Organic Frameworks from Chiral Building Units with Different Metrics**

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## 1. Synthesis of (*S,S*)-1H<sub>2</sub> and (*S,S*)-2H<sub>2</sub>

### 1.1. General consideration for the synthesis

Unless otherwise noted, all materials were obtained from commercial suppliers Aldrich and TCI, and used without further purifications. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from calcium hydride and stored over 4 Å molecular sieve. Evaporation of organic solvents was conducted using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates (Silica gel 60 F<sub>254</sub>, Merck) were visualized by ultraviolet light and/or treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products were accomplished by flash chromatography by using Merck silica gel 60 (230~400 mesh) with a mixture of *n*-hexane and ethyl acetate as eluents. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini 75 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to the methyl peak of TMS. High performance liquid chromatography (HPLC) was conducted using a Waters model 600 pumping system with a Waters model 2487 ultraviolet detector at 254nm. Infrared (IR) spectra were recorded on a Bomem 102 FT-IR spectrometer. Optical rotations were measured at the 589 nm sodium D-line with RUDOLPH AUTOPOL automatic polarimeter. Low- and High-resolution FAB mass spectra were obtained by JEOL JMS-AX505WA mass spectrometer. Melting points were measured with capillary melting point apparatus of Thomas Hoover and are uncorrected.

### 1.2. Synthesis of the ligands

#### 1.2.1. The preparation of (*S,S*)-1H<sub>2</sub>

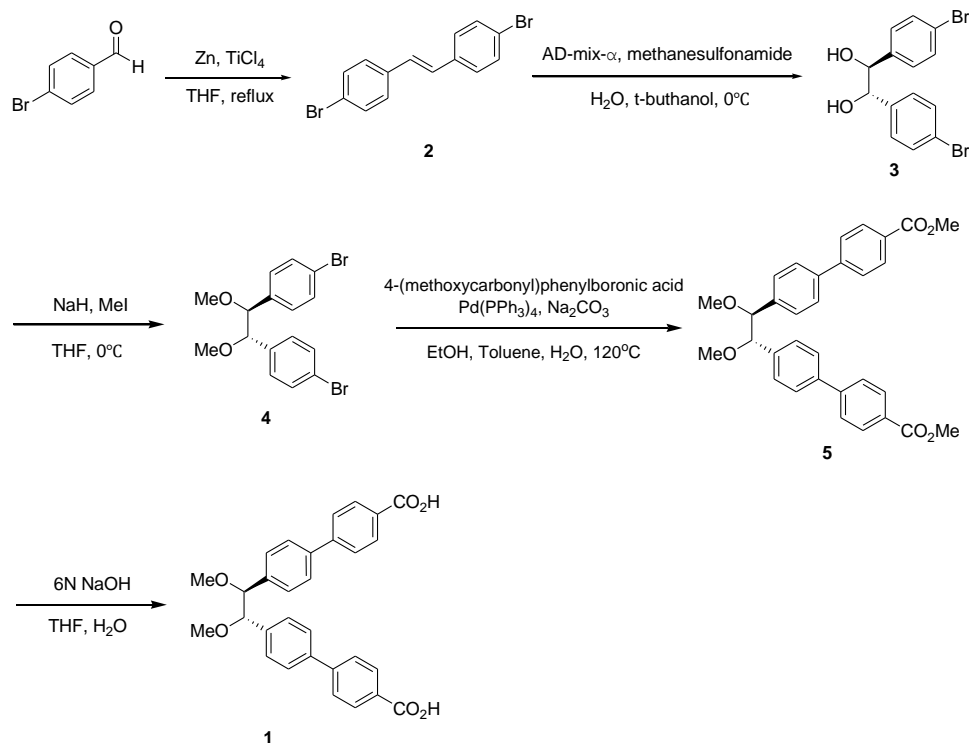
This ligand was synthesized according to the previously reported method.<sup>S1</sup>

#### 1.2.2. The preparation of (*S,S*)-2H<sub>2</sub>

##### ***Trans*-4,4'-Dibromostillbene (2)**

To a stirred suspension of zinc powder (19.9 g, 302 mmol) in THF (300 mL), TiCl<sub>4</sub> (16.5 mL, 151 mmol) was added slowly at -10 °C. Then, a solution of 4-bromobenzaldehyde (10.0 g, 54 mmol) in THF (250 mL) was added dropwise at reflux and the resultant mixture was stirred for 5 h. The reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> solution and extracted with ethyl acetate (3 x). The combined extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, and then filtered. The filtrate was concentrated *in vacuo*, and the resultant precipitates were washed with *n*-hexane to give a white solid (8.84 g, 97 %). R<sub>f</sub>: 0.62 (*n*-hexane:ethyl acetate = 5:1), mp: 183~185 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.01 (s, 2H), 7.37 (d, 4H, *J* = 8.7Hz), 7.49 (d, 4H, *J* = 8.7Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 121.62, 127.99,

128.10, 131.84, 135.88; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3,055 (br); Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{Br}_2$ : C, 49.74; H, 2.98; Br, 47.28; Found: C, 49.33; H, 2.93.



**Scheme 1: Synthesis of (S,S)-2H<sub>2</sub>**

**(S,S)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol (3)**

AD-mix- $\alpha$  (0.7g, 0.5 mmol) was stirred in two phases of *t*-butyl alcohol (2.5 mL) and water (2.5 mL) at rt. With stirring,  $\text{CH}_3\text{SO}_2\text{NH}_2$  (48 mg, 0.5 mmol) was added to the solution of AD-mix- $\alpha$  at 0 °C. To the reaction mixture was added *trans*-4,4'-dibromostilbene (120 mg, 0.5 mmol) portion by portion at 0 °C. The resultant mixture was further stirred at 0 °C for 20 h. After completion of the reaction, the mixture was quenched with a saturated aqueous  $\text{Na}_2\text{CO}_3$  solution and extracted with ethyl acetate (3 x). The combined extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$  and filtered. The filtrate was concentrated under the reduced pressure to give a pale yellow solid. The crude product was purified by column chromatography ( $\text{SiO}_2$ ) with an eluent of *n*-hex/EA=1:1. **3** (103 mg) was obtained in 75 % yield as a white solid.  $R_f$ : 0.45 (*n*-hexane:ethyl acetate = 1:1), mp: 112 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300MHz):  $\delta$  3.27 (s, 2H), 4.48 (s, 2H), 6.90 (d, 4H,  $J = 8.4\text{Hz}$ ), 7.34 (d, 4H,  $J = 8.4\text{Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75MHz):  $\delta$  78.42, 122.02, 128.62, 131.31, 138.38; FT-IR (KBr,  $\text{cm}^{-1}$ ) 3379, 3055, 2933; Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{O}_2$ : C, 45.20; H, 3.25; Br, 42.95; Found: C, 45.139; H, 3.230. HPLC (DAICEL CHIRALPAK AD-H, *n*-hexane:ethyl acetate = 9:1, flow 0.5ml/min, detection at 254nm)  $\tau_R=20.25\text{min}$  ((*R,R*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol:18.433min);  $[\alpha]_D^{17}$  (deg  $\text{cm}^3 \text{g}^{-1} \text{dm}^{-1}$ ) = -143 ( $c = 0.005 \text{ g cm}^{-3}$  in  $\text{CHCl}_3$ ).

**(*S,S*)-1,2-bis(4-bromophenyl)-1,2-dimethoxyethane (4)**

To a suspension of NaH (60% in oil, 533 mg, 13.44 mmol) in dry THF (20 mL) was slowly added a solution of (*S,S*)-1,2-bis(4-bromophenyl)-ethane-1,2-diol (**3**) (1.00 g, 2.69 mmol) at 0 °C under argon atmosphere. After completion of gas evolution in 10 min, a solution of iodomethane (0.58 ml, 9.4 mmol) in THF (1 mL) was introduced into the reaction mixture at room temperature under argon atmosphere. After stirring of the resultant reaction mixture for 24 h, the mixture was quenched with water carefully and partitioned between water and ethyl acetate. The organic extracts were combined and washed with brine, dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to give a white solid. The crude product was purified by column chromatography (SiO<sub>2</sub>, eluent; *n*-hexane:ethyl acetate = 5:1) to afford a white solid (1.08 g, 99 %). R<sub>f</sub>: 0.43 (*n*-hexane:ethyl acetate = 5:1); mp; 73°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz): δ 3.23 (s, 6H), 4.24 (s, 2H), 6.87 (d, 4H, *J* = 8.4Hz), 7.33 (d, 4H, *J* = 8.4Hz), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz): δ 57.25, 86.44, 121.76, 129.50, 131.10, 136.88; FT-IR (KBr, cm<sup>-1</sup>) 3059, 2916; Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub>: C, 48.03; H, 4.03; Br, 39.94; O, 8.00; Found: C, 48.132; H, 4.222. [α]<sub>D</sub><sup>21</sup> (deg cm<sup>3</sup> g<sup>-1</sup> dm<sup>-1</sup>) = -153 (c = 0.005 g cm<sup>-3</sup> in CHCl<sub>3</sub>).

**(*S,S*)- dimethyl 4',4''-((1*S*,2*S*)-1,2-dimethoxyethane-1,2-diyl)dibiphenyl-4-carboxylate (5)**

A mixture of (*S,S*)-1,2-bis(4-bromophenyl)-1,2-dimethoxyethane (**4**) (1.14 g, 2.86 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (330 mg, 0.29 mmol, 10 mol%), 4-(ethoxycarbonyl)phenylboronic acid (1.22 g, 6.29 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.82 g, 7.16 mmol) was stirred in EtOH (2.86 ml), Toluene (12 ml), and H<sub>2</sub>O (2 ml) at 130 °C under argon atmosphere. After stirring of the resultant reaction mixture for 6 hours at 130 °C, the mixture was filtered with celite. The crude mixture was purified by column chromatography (SiO<sub>2</sub>, eluent; *n*-hexane:ethyl acetate = 5:1) to afford a white solid (yield). R<sub>f</sub>: 0.38 (*n*-hexane:ethyl acetate = 5:1), m.p.; 125-130 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz); δ 1.39 (t, 6H), 3.31 (s, 6H), 7.15 (d, *J* = 7.9 Hz 4H); 7.46 (d, *J* = 8.7 Hz, 4H), 7.61 (d, *J* = 8.3 Hz, 4H), 8.07 (d, *J* = 8.5 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 57.57, 61.22, 76.89, 77.29, 77.72, 87.28, 127.04, 128.72, 130.26, 138.43, 139.50, 145.17, 166.71. FT-IR (KBr, cm<sup>-1</sup>); 3033, 1695. Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>: C, 76.34; H, 6.22; O, 17.40; Found: C, 76.16; H, 6.41. [α]<sub>D</sub><sup>17</sup> (deg cm<sup>3</sup> g<sup>-1</sup> dm<sup>-1</sup>) = 136 (c = 0.005 g cm<sup>-3</sup> in MC).

**(*S,S*)-4',4''-((1*S*,2*S*)-1,2-dimethoxyethane-1,2-diyl)dibiphenyl-4-carboxylic acid (6)**

A mixture of (*S,S*)-Diethyl 4',4''-((1*S*,2*S*)-1,2-dimethoxyethane-1,2-diyl)dibiphenyl-4-carboxylate (**5**) (700 mg, 1.27 mmol), KOH (428 mg, 7.62 mmol), THF (30mL) and H<sub>2</sub>O (30 mL) were stirred for 5 h at reflux. The reaction mixture was concentrated in vacuum and acidified with 1 N HCl until pH 2 was attained. The white precipitate was filtered (350 mg,

60%).  $R_f$ : 0.35 (dichloromethane:MeOH = 10:1), m.p.; 156-157 °C,  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ , 300 MHz);  $\delta$  3.24 (s, 6H), 4.83 (s, 2H), 7.35 (d,  $J = 8.5$  Hz, 4H); 7.58 (d,  $J = 8.2$  Hz, 4H); 7.67 (d,  $J = 8.3$  Hz, 4H), 7.93 (d,  $J = 8.2$  Hz, 4H).  $^{13}\text{C}$  NMR (DMSO- $\text{D}_6$ , 75 MHz):  $\delta$  57.35, 86.20, 128.64, 129.51, 130.50, 143.67, 168.33. FT-IR (KBr,  $\text{cm}^{-1}$ ); 3033, 1695. Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_6$ : C, 65.45; H, 5.49; O, 29.06; Found: C, 65.67; H, 5.19.  $[\alpha]_{\text{D}}^{17}$  ( $\text{deg cm}^3 \text{g}^{-1} \text{dm}^{-1}$ ) = 816 ( $c = 0.005 \text{ g cm}^{-3}$  in DMSO).

## 2. Preparation and characterization of Zn-(+)-1, and Zn-(+)-2.

### 2.1. Synthesis of MOFs

#### 2.1.1. Zn-(+)-1

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.020 g, 0.050 mmol) and (*S,S*)-1 $\text{H}_2$  (0.0375 g, 0.100 mmol) in DEF (7.5 mL), EtOH (2.5ml) was heated at 100 °C for 2 days. Colorless plate-shaped crystals were obtained in 52% yield. Zn-(+)-1, Elementary analysis, (%) calcd. for Zn-(+)-1  $\text{C}_{296} \text{H}_{374} \text{N}_{16} \text{O}_{95} \text{Zn}_{16}$ : C, 52.89; H, 5.61; N, 3.33; found: C, 52.24; H, 5.34; N, 3.15. FT-IR (KBr,  $\text{cm}^{-1}$ ) 3451 (br), 3072 (w), 2997 (w), 2929 (w), 2820 (w), 1665 (s), 1607 (s), 1539 (s), 1404 (s), 1303 (w), 1261 (w), 1210 (w), 1176 (w), 1084 (s), 1017 (w), 940 (w), 865 (w), 789 (m), 730 (m), 654 (w), 553 (w).

#### 2.1.2. Zn-(+)-2

A mixture of  $\text{Zn}(\text{OAc})_2$  (0.007 g, 0.010 mmol) and (*S,S*)-2 $\text{H}_2$  (0.005 g, 0.040 mmol) in DEF (2 mL) was heated at 100 °C for 1 day. Colorless block-shaped crystals were obtained in 21% yield. Zn-(+)-2, Elementary analysis: (%) calcd. for Zn-(+)-2  $\text{Zn}_8\text{C}_{200}\text{H}_{188}\text{N}_4\text{O}_{42}$ : C, 62.51; H, 4.93; N, 1.46; found: C, 62.09; H, 4.34; N, 1.34. FT-IR (KBr,  $\text{cm}^{-1}$ ) 3451 (br), 3072 (w), 2997 (w), 2938 (w), 2812 (w), 1665 (s), 1607 (s), 1530 (s), 1396 (s), 1303 (w), 1253 (w), 1210 (w), 1176 (w), 1092 (s), 1025 (w), 940(w), 865 (w), 798 (m), 739 (m), 654 (w), 545 (w).

### 2.2. Single crystal X-ray diffraction studies

#### 2.2.1. Zn-(+)-1

X-ray data for Zn-(+)-1 was collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Preliminary orientation matrix and cell parameters were determined from three sets of scans at different starting angles. Data frames were obtained at scan intervals of  $0.5^\circ$ . The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS.<sup>S2</sup> The structure of Zn-(+)-1 was solved by direct methods with the SHELXTL program.<sup>S3</sup> Considering more than 800 atoms in the asymmetric unit, only the metal atoms, and some carbon and

oxygen atoms were refined anisotropically in the structure. Guest molecules in Zn-(+)-**1** was significantly disordered and could not be modeled properly, thus the program SQUEEZE,<sup>S4</sup> a part of the PLATON package of crystallographic software,<sup>S5</sup> was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Solvent molecules were found to be coordinated to one zinc atom in each Zn<sub>4</sub>O building unit. (Two DEF molecules serve as ligands on Zn1, Zn5, and Zn9. One DEF and one H<sub>2</sub>O molecule coordinate to Zn13.) For Zn-(+)-**1**, the contributions of some 460 electrons were removed from the unit-cell contents, and as  $Z = 1$  in this case, this could/might correspond with the removal of solvent such as 7 DEF and 7 H<sub>2</sub>O molecules. Crystal data of Zn-(+)-**1** (squeezed): empirical formula = C<sub>296</sub>H<sub>374</sub>N<sub>16</sub>O<sub>95</sub>Zn<sub>16</sub>,  $Mr = 7182.12$ ,  $T = 258(2)$  K, triclinic, space group  $P1$ ,  $a = 21.701(4)$  Å,  $b = 23.071(5)$  Å,  $c = 23.286(5)$  Å,  $V = 9264(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{calc}} = 1.287$  g cm<sup>-3</sup>,  $m = 1.780$  mm<sup>-1</sup>, 34979 reflections collected, 2231 unique ( $R_{\text{int}} = 0.0681$ ),  $R_1 = 0.0710$ ,  $wR_2 = 0.2124$  [ $I > 2\sigma(I)$ ].

### 2.2.2. Zn-(+)-**2**

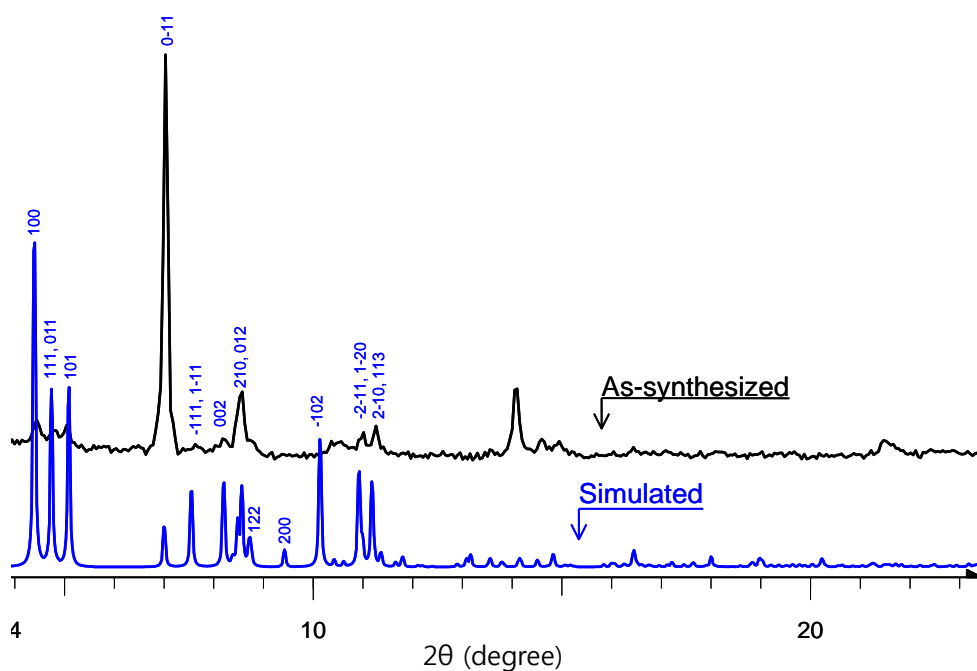
A block colorless crystal (0.12 mm x 0.05 mm x 0.04 mm) was mounted on a cryoloop under a cooling stream of N<sub>2</sub> at 100(2) K. Diffraction data were collected with synchrotron radiation using a 6B MX-I ADSC Quantum-210 detector with a silicon (111) double crystal monochromator at the Pohang Accelerator Laboratory. The ADSC Quantum-210 ADX program (Ver. 1.92) was used for data collection and HKL2000 (Ver. 0.98.699) was used for cell refinement, data reduction, and absorption corrections. The structure was solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELX program. CheckCIF/PLATON validation alerted the low resolution of X-ray data in Alert level A. The resolution of the current X-ray data is about 0.8 Å with a theta value of 27.5 degree. Considering the crystal size is relatively small (0.12 x 0.05 x 0.04), the X-ray data is good enough to reveal the most important features of the reported structure: coordination geometry, ligand conformation, and framework connectivity. In particular, the Flack  $x$  parameter has been converged to 0.0519 with esd of 0.0127, indicating the stereochemical configuration of the six chiral ligands in an asymmetric unit has been correctly assigned. However, due to a large number of atoms in an asymmetric unit, 266 non-H atoms including 8 Zn atoms, some detail information such as thermal parameters (ADP) could not be modeled clearly. It was found that many phenyl rings in the ligands tend to show dynamic or statistical disorder, producing large elongated and abnormal thermal ellipsoids. These problems were indicated in Alert levels B and C in the CheckCIF output. In small-size structures, this disorder would have been resolved. However, in our case, the current ordered

structural model can maintain the quality and important aspects of the MOF structure. Crystal data of Zn-(+)-**2**: empirical formula =  $C_{200}H_{188}N_4O_{42}Zn_8$ ,  $Mr = 3842.50$ ,  $T = 100(2)$  K, orthorhombic, space group  $P2_12_12_1$ ,  $a = 22.945(5)$  Å,  $b = 31.803(6)$  Å,  $c = 32.955(7)$  Å,  $V = 24048(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calc} = 1.061$  g cm<sup>-3</sup>,  $\mu = 1.569$  mm<sup>-1</sup>, 94172 reflections collected, 26210 unique ( $R_{int} = 0.0736$ ),  $R_1 = 0.0788$ ,  $wR_2 = 0.2107$  [ $I > 2\sigma(I)$ ].

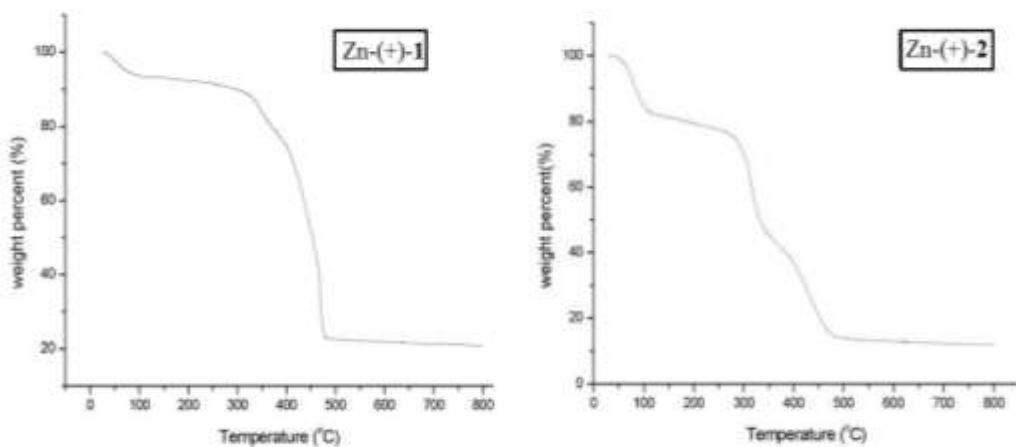
**Table S1. Crystal data and structure refinement for Zn-(+)-1 and Zn-(+)-2**

	Zn-(+)-1	Zn-(+)-2
empirical formula	C <sub>317</sub> H <sub>352</sub> N <sub>21</sub> O <sub>105</sub> Zn <sub>16</sub>	C <sub>200</sub> H <sub>188</sub> N <sub>4</sub> O <sub>42</sub> Zn <sub>8</sub>
f.w.	7182.12	3842.50
<i>T</i> (K)	258(2) K	100(2) K
wavelength (Å)	1.54178 Å	0.90000 Å
crystal system	Triclinic	Orthorhombic
space group	<i>P</i> 1 (No. 1)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No.19)
unit cell data		
<i>a</i> (Å)	21.701(4)	22.945(5)
<i>b</i> (Å)	23.071(5)	31.803(6)
<i>c</i> (Å)	23.286(5)	32.955(7)
α (deg)	63.91(3)°	90°
β (deg)	68.86(3)°	90°
γ (deg)	64.94(3)°	90°
<i>V</i> (Å <sup>3</sup> )	9264(3)	24048(8)
<i>Z</i>	1	4
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.287	1.061
Absorption coefficient(mm <sup>-1</sup> )	1.780	1.569
<i>F</i> (000)	3721	7968
Crystal size	0.20 × 0.20 × 0.05 mm <sup>3</sup>	0.12 × 0.05 × 0.04 mm <sup>3</sup>
Theta range for data collection	2.16 to 58.82°	1.37 to 27.50°
Index ranges	-24 ≤ <i>h</i> ≤ 23, -25 ≤ <i>k</i> ≤ 25, -22 ≤ <i>l</i> ≤ 25	-23 ≤ <i>h</i> ≤ 23, -31 ≤ <i>k</i> ≤ 31, -33 ≤ <i>l</i> ≤ 33
Reflections collected	57776	94172
Independent reflections	34979 [R(int) = 0.0681]	26210 [R(int) = 0.0736]
Completeness	85.6 %	97.1 %
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	34979 / 23 / 2231	26210 / 78 / 2273
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.982	0.927
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0710, <i>wR</i> 2 = 0.1965	<i>R</i> 1 = 0.0788, <i>wR</i> 2 = 0.2107
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0813, <i>wR</i> 2 = 0.2124	<i>R</i> 1 = 0.1115, <i>wR</i> 2 = 0.1906
Absolute structure parameter	0.02(2)	0.052(13)
Largest diff. peak and hole	1.057 and -0.647 e.Å <sup>-3</sup>	1.359 and -0.772 e.Å <sup>-3</sup>

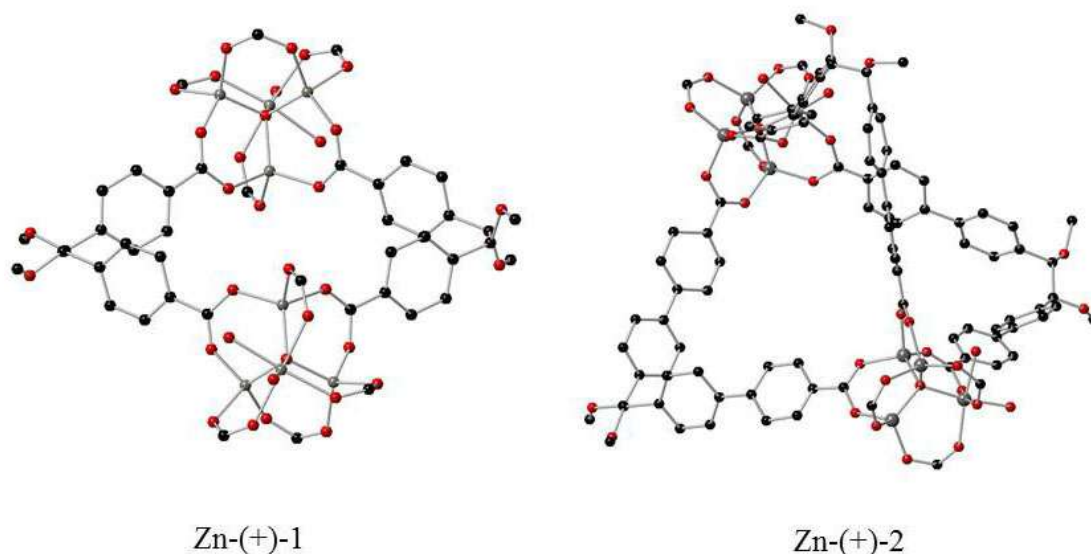




**Fig. S1.** Comparison of the experimental PXRD pattern of as-synthesized Zn-(+)-1 (black) with the one simulated from its single crystal structure (blue).



**Fig. S2.** TGA data of the as-synthesized Zn-(+)-1 and Zn-(+)-2.

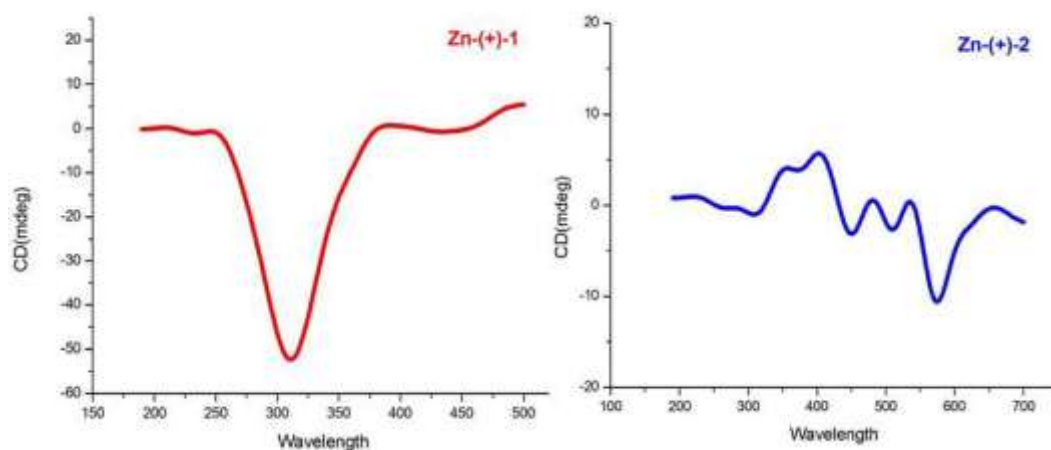


**Fig. S3.** Asymmetric units for Zn-(+)-1 and Zn-(+)-2.

### 3. Circular dichroism (CD) measurement of ligands and MOFs.

UV-Vis absorption spectra of various solutions were measured between 800 and 200 nm with a Jasco UVIDEK 650 spectrophotometer. CD spectra were recorded using a Jasco J-810 spectropolarimeter. The DRCD spectra were obtained by inserting a diffused reflectance sphere in the optical path of the instrument. This J-810 was specifically modified to allow simultaneous detection of LD (linear dichroism) as a simple way to verify one of potential artifacts.

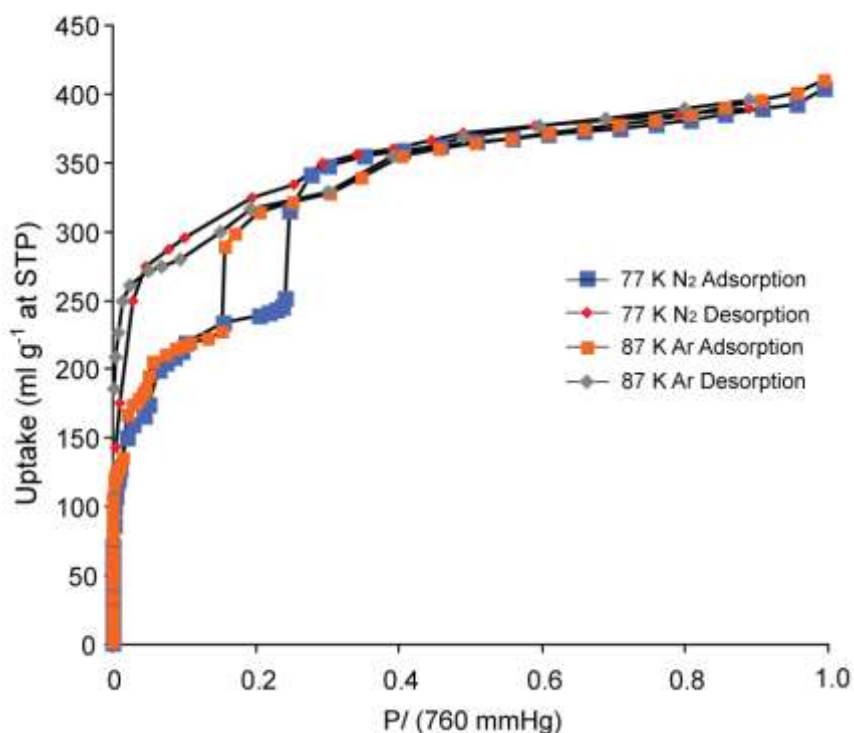
*Preparation of solid-samples of MOF;* A mixture of 30 mg of crystal and 100 mg of KBr was grounded together and compressed to form a pellet.



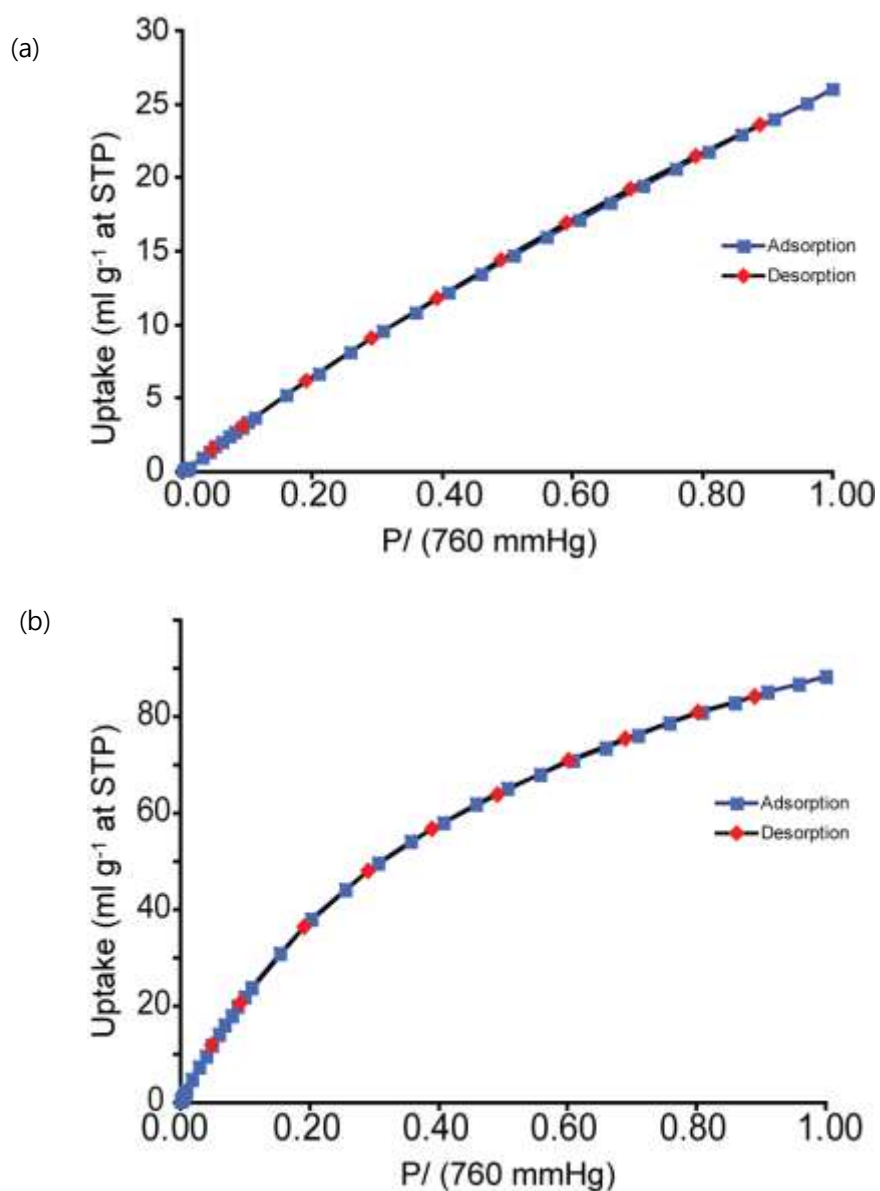
**Fig. S4.** CD spectra of Zn-(+)-1 and Zn-(+)-2.

#### 4. Gas Adsorption Measurements on Zn-(+)-1.

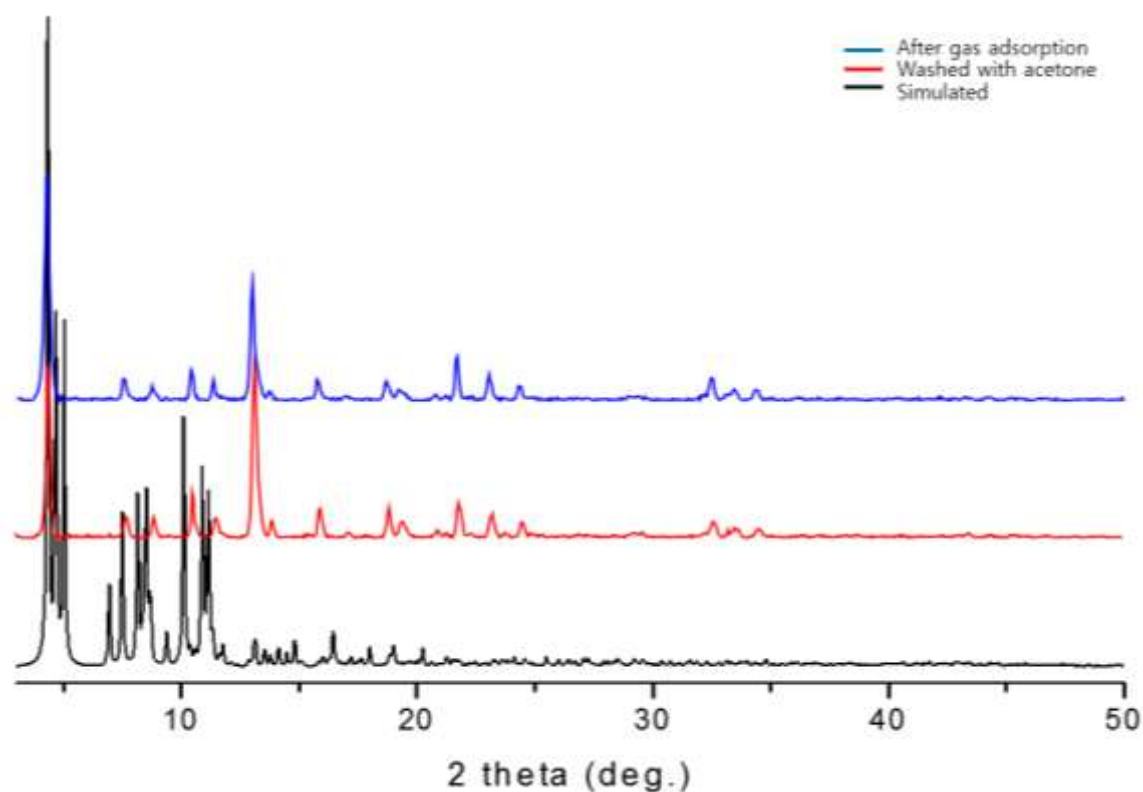
Low pressure N<sub>2</sub> adsorption isotherms were measured volumetrically on an Autosorb-1 analyzer (Quantachrome Instruments). A liquid nitrogen bath (77 K) was used for the measurements. The N<sub>2</sub> and He gases used were UHP grade. From the N<sub>2</sub> adsorption isotherms, the BET surface areas (accessible surface area) and total pore volumes of each material have been calculated. The pore volume of each material was estimated from the Dubinin-Radushkevich (DR) model with the assumption that the adsorbate is in the liquid state and the adsorption involves a pore-filling process. To estimate pore size distributions for the MOFs, N<sub>2</sub> isotherms were analyzed using nonlocal density functional theory (NLDFT) implementing a hybrid kernel for N<sub>2</sub> adsorption at 77 K based on a zeolite/silica model containing cylindrical pores<sup>S6</sup>. For porosity measurements, as-synthesized Zn-(+)-1 was immersed in acetone or acetonitrile for 24 h, during which time the activation solvent was replenished three times.



**Fig. S5. Comparison of the nitrogen adsorption isotherm at 77 K and the argon adsorption isotherm at 87 K for Zn-(+)-1.** Adsorption data for nitrogen are shown as blue squares and desorption data as red rhombuses; adsorption data for argon are shown as orange squares and desorption data as grey rhombuses; connecting lines are guides for the eye. The swelling of Zn-(+)-1 occurs at different pressures for different temperatures and gases.



**Fig. S6. Hydrogen adsorption isotherm (77 K) and carbon dioxide isotherm (273 K) of Zn-(+)-1.** Zn-(+)-1 can uptake (a) 0.79 wt% H<sub>2</sub> at 1 atm, 77 K or (b) 5.12 wt% CO<sub>2</sub> at 1 atm, 273 K. Adsorption data are shown as blue squares and desorption data as red rhombuses.



**Fig. S7.** Comparison of the experimental PXRD pattern of simulated Zn-(+)-1 (black) and after washed with acetone (red) with after gas adsorption (blue).

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