

Electronic Supplementary Information (ESI)

Homochiral 3D Metal-Organic Frameworks from Chiral 1D Rods: 6 – Way Helical Packing

Sung Min Shin,^a Dohyun Moon,^b Kyung Seok Jeong,^a Jaheon Kim,^c Praveen K. Thallapally^{d,*} and Nakcheol Jeong^{a, e*}

^a Department of Chemistry, Korea University, Seoul, 136-701, Korea.

+82-2-3290-3121; +82-2-3290-3136; E-mail: njeong@korea.ac.kr

^b Beamline Division, Pohang Accelerator Laboratory/POSTECH

San-31 Hyoja-Dong, Nam-Gu Pohang, Kyung Buk 790-784, Korea

^c Department of Chemistry, Soongsil University, Seoul 156-743, Korea.

^d Pacific Northwest National Laboratory, Richland, WA, 99352, USA

Fax: 5093717249; Tel: 509-371-7183; E-mail: praveen.thallapally@pnl.gov

^e Korea Basic Science Institute, Seoul Centre, Seoul, 136-713, Korea

Contents

1. Synthesis of (S,S)-1H₂ and (S,S)-2H₂

1.1. General consideration for the synthesis 1

1.2. Synthesis of ligands2

1.2.1. The preparation of (S,S)-1H₂

1.2.2. The preparation of (S,S)-2H₂

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

.....3

2.1. Synthesis of MOFs3

2.2. Single crystal X-ray diffraction studies4

Table S1. Crystal data and structure refinement for four representative crystals.....5

Figure S1.6

Figure S2. Asymmetric unit of four crystals.....7

3. Circular dichroism (CD) measurement of Cu-(+)-1 and Cu-(+)-2.8

1. Synthesis of (S,S)-1H₂ and (R,R)-1H₂

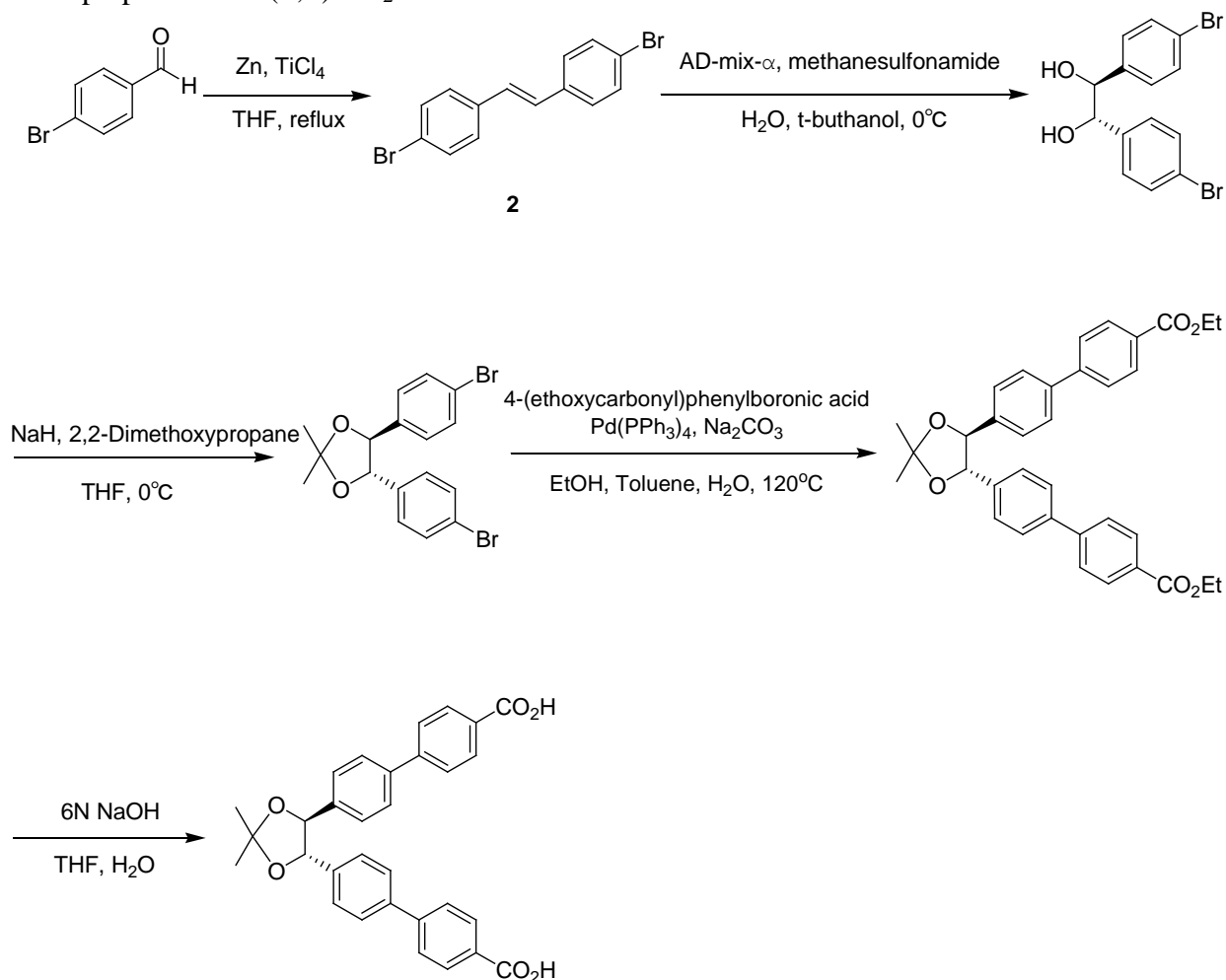
1.1. General consideration for the synthesis

Unless otherwise noted, all materials were obtained from commercial suppliers Aldrich and TCI, and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from calcium hydride and stored over 4Å 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 F₂₅₄, 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. ¹H NMR spectra were recorded on 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 589nm 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. The preparation of (*S,S*)-**1H**₂

This ligand was synthesized according to the previously reported method.¹

1.2.2. The preparation of (*S,S*)-**2H**₂



Scheme S1

Trans-4,4'-dibromostilbene (2)

To a stirred suspension of zinc powder (19.9g, 302 mmol) in THF (300 mL), TiCl₄ (16.5 mL, 151 mmol) was added slowly at -10 °C. Then, a solution of 4-bromobenzaldehyde (10.0g, 54mmol) 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 NaHCO₃ solution and extracted with ethyl acetate (3 x). The combined extracts was washed with brine, dried over anhydrous MgSO₄, 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_f: 0.62 (*n*-hexane:ethyl acetate = 5:1), mp: 183~185 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.01 (s, 2H), 7.37 (d, 4H, *J* = 8.7Hz), 7.49 (d, 4H, *J* = 8.7Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 121.62, 127.99, 128.10, 131.84, 135.88; FT-IR (KBr, cm⁻¹): 3,055 (br); Anal. Calcd. for C₁₄H₁₀Br₂, C; 49.74 H; 2.98 Br; 47.28, Found, C; 49.33 H; 2.93.

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

AD-mix- α (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, CH₃SO₂NH₂ (48 mg, 0.5 mmol) was added to a solution of AD-mix- α 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 Na₂CO₃ solution and extracted with ethyl acetate (3 x). The combined extracts was washed with brine, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under the reduced pressure to give a pale yellow solid. The crude product was purified by column chromatography (SiO₂) with an eluent of *n*-hex/EA=1:1. **3a** (103 mg) was obtained in 75 % yield as a white solid. R_f : 0.45 (*n*-hexane:ethyl acetate = 1:1), mp: 112 °C. ¹H NMR (CDCl₃, 300MHz): δ 3.27 (s, 2H), 4.48 (s, 2H), 6.90 (d, 4H, *J* = 8.4Hz), 7.34 (d, 4H, *J* = 8.4Hz). ¹³C NMR

(CDCl₃, 75MHz): δ 78.42, 122.02, 128.62, 131.31, 138.38; FT-IR (KBr, cm⁻¹) 3379, 3055, 2933; Anal. Calcd. for C₁₄H₁₂Br₂O₂, 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) $\tau_R=20.25$ min ((*R,R*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol:18.433min); $[\alpha]_D^{17}$ (deg cm³ g⁻¹ dm⁻¹) = -143 (c = 0.005 g cm⁻³ in CHCl₃).

(*S,S*)-4,5-bis(4-bromophenyl)-2,2-dimethyl-1,3-dioxolane (4)

A reaction mixture of (*S,S*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol (3) (15.6g, 42 mmol), *p*-TsOH·H₂O (319mg, 1.68mmol, 4mol%) 2,2-dimethoxypropane(7.70ml, 62.9mmol), cyclohexane (600ml, 0.07M) equipped with a Dean-stark trap was stirred at reflux. After 3h, the reaction mixture was concentrated in vacuo to give crud product as a dark oil. This was purified by column chromatography (SiO₂, eluent; *n*-hexane:ethyl acetate = 5:1) to afford a white solid (1.08 g, 99 %). R_f: 0.65 (*n*-hexane:ethyl acetate = 5:1); mp; 130 °C, ¹H NMR (CDCl₃, 300MHz): δ 1.66 (s, 6H), 4.62 (s, 2H), 7.08 (d, *J* = 8.4Hz, 4H), 7.46 (d, *J* = 8.4Hz, 4H), ¹³C NMR (CDCl₃, 75MHz): δ 27.08, 84.78, 109.76, 122.33, 128.24, 131.64, 135.40; FT-IR (KBr, cm⁻¹) 2996, 2884, 1911, 1601 cm⁻¹; Anal. Calcd. for C₁₆H₁₆Br₂O₂, C; 49.54 H; 3.91 Br; 38.78 O; 7.76 Found, C; 49.53 H; 3.90; $[\alpha]_D^{21}$ (deg cm³ g⁻¹ dm⁻¹) = 1329 (c = 0.005 g cm⁻³ in CHCl₃).

Diethyl 4',4''-((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dibiphenyl-4-carboxylate (5)

A mixture of (*S,S*)-4,5-bis(4-bromophenyl)-2,2-dimethyl-1,3-dioxolane (4) (1.5g, 3.64mmol), Pd(PPh₃)₄ (421mg, 0.37mmol, 10mol%), 4-(ethoxycarbonyl)phenylboronic acid (1.63g, 8.37mmol) and Na₂CO₃ (2.31g, 21.84mmol) was stirred in EtOH(3.64ml), Toluene(15ml), and H₂O(2ml) at 120 °C under argon atmosphere. After stirring of the resultant reaction mixture for 6 hours at 120 °C, the mixture was filtered with celite. The crude mixture was purified by column chromatography (SiO₂, eluent; *n*-hexane:ethyl acetate = 5:1) to afford a white solid (yield). R_f: 0.38 (*n*-hexane:ethyl acetate = 5:1), m.p.; 125-130 °C, ¹H NMR (CDCl₃, 300MHz); δ 1.41 (t, 6H), 4.52 (s, *J* = 6.9 Hz, 6H), 1.72 (s, 6H); 4.49 (q, *J* = 7.1 Hz, 4H), 4.83 (s, 2H), 7.36 (d, *J* = 7.9 Hz, 4H), 7.60 (d, *J* = 8.0 Hz, 4H), 7.65 (d, *J* = 8.2 Hz, 4H), 8.11 (d, *J* = 8.2 Hz, 4H). ¹³C NMR (CDCl₃, 75 MHz): 14.30, 27.14, 60.92, 85.03, 109.61, 126.83, 127.28, 129.28, 130.02, 136.63, 139.92, 144.84, 166.36. FT-IR (KBr, cm⁻¹); 3033, 1695. Anal. Calcd. for C₁₈H₁₈O₆, C; 76.34, H; 6.22, O; 17.40 Found, C; 76.16 H; 6.41; $[\alpha]_D^{17}$ (deg cm³ g⁻¹ dm⁻¹) = 136 (c = 0.005 g cm⁻³ in MC).

4',4''-((4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dibiphenyl-4-carboxylic acid (6)

A mixture of diethyl 4',4''-((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dibiphenyl-4-carboxylate (5) (700mg, 1.27mmol), KOH (mL), THF (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 (350mg, 60%). R_f: 0.35 (dichloromethane:MeOH = 10:1), m.p.; 156-157 °C, ¹H NMR (DMSO-D₆, 300 MHz); δ 1.62 (s, 6H), 4.86 (s, 2H), 7.35 (d, *J* = 8.5 Hz, 4H); 7.58 (d, *J* = 8.2 Hz, 4H); 7.67 (d, *J* = 8.3Hz, 4H), 7.93 (d, *J* = 8.2Hz, 4H). ¹³C NMR (DMSO-D₆, 75 MHz): δ 57.35, 86.20, 128.64, 129.51, 130.50, 143.67, 168.33. FT-IR (KBr, cm⁻¹); 3033, 1695. Anal. Calcd. for C₁₈H₁₈O₆, C; 65.45, H; 5.49, O; 29.06 Found, C; 65.67 H; 5.19; $[\alpha]_D^{17}$ (deg cm³ g⁻¹ dm⁻¹) = 816 (c = 0.005 g cm⁻³ in DMSO)

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

2.1. Synthesis of MOFs

2.1.1. Cu-(+)-1

A mixture of Cu(NO₃)₂·3H₂O (0.0121 g, 0.050 mmol) and (*S,S*)-1H₂ (0.0342 g, 0.100 mmol) in DMF (2.5 mL), MeOH(2.5ml), H₂O (2.5 mL) was heated at 65 °C for 7 days. Blue block crystals were obtained in 52% yield.

Cu-(+)-1, Elementary analysis, (%) calcd. for Cu-(+)-1 C₂₁H₁₈CuN₂O₇: C, 46.72, H, 5.51, N, 1.70; found: C, 46.98, H, 4.34, N, 1.65. FT-IR (KBr, 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. Cu-(+)-2

A mixture of CuCl₂·2H₂O (0.001 g, 0.006 mmol) and (*S,S*)-2H₂ (0.003 g, 0.006 mmol) in DMF (1 mL) and H₂O (0.05 mL) was heated at 85 °C for 2 weeks. Blue block crystals were obtained in 21% yield.

Cu-(+)-2, Elementary analysis: (%) calcd. for Cu-(+)-2 C₆₈H₆₂Cu₂N₂O₁₄: C, 64.91, H, 4.97, N, 2.23; found: C, 63.09, H, 4.49, N, 2.35. FT-IR (KBr, 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. Cu-(+)-1

A block colorless crystal with a suitable size (0.30 mm x 0.30 mm x 0.20 mm) was attached on a glass capillary, which was positioned in a N₂(g) stream at 273(2)K upon mounting on a Bruker SMART CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube ($\lambda = 0.71073\text{\AA}$) operated at 2,000 W power (50 kV, 40mA). The frames were integrated with the SAINT software package with a narrow frame algorithm². The final cell constants were based on the *xyz* centroids of 4,510 reflections. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS³. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package⁴. A total of 12,608 reflections were collected in the range $1.73^\circ < \theta < 28.34^\circ$ of which 4929 were independent and 7,679 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.917$ ($I > 2\sigma(I)$), $wR_2 = 0.2128$ (all data) and GOF = 1.014. The crystal belongs to the monoclinic space group C2 (No. 2) with $Z = 4$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated with the ideal geometry and included in the refinement processes. The crystal formula was used from a reasonable estimate with the aid of both elemental microanalysis (EA) and the size of the available volume in the unit cell.

2.2.2. Cu-(+)-2

A block colorless crystal with a suitable size (0.30 mm x 0.30 mm x 0.10 mm) was attached on a glass capillary, which was positioned in a N₂(g) stream at 100(2)K upon mounting on a Bruker SMART CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube ($\lambda = 0.71073\text{\AA}$) operated at 2,000 W power (50 kV, 40mA). The frames were integrated with the SAINT software package with a narrow frame algorithm². The final cell constants were based on the *xyz* centroids of 6,969 reflections. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS³. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package⁴. A total of 56,703 reflections were collected in the range $1.26^\circ < \theta < 23.29^\circ$ of which 12350 were independent and 43,551 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.1074$ ($I > 2\sigma(I)$), $wR_2 = 0.1612$ (all data) and GOF = 0.898. The crystal belongs to the hexagonal space group $P6(5)$ (No. 1) with $Z = 6$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated with the ideal geometry and included in the refinement processes. The crystal formula was used from a reasonable estimate with the aid of both elemental microanalysis (EA) and the size of the available volume in the unit cell.

1. Jeong, K. S.; Kim, Y. S.; Kim, Y. J.; Lee, E.; Yoon, J. H.; Park, W. H.; Park, Y. W.; Jeon, S. -J.; Kim, Z. H.; Kim, J.; Jeong, N. *Angew. Chem. Int. Ed.* **2006**, *45*, 8134-8138
2. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
3. Sheldrick, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data, University of Goettingen: Goettingen, Germany, 1996.
4. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

Table S1. Crystal data and structure refinement for four representative crystals

	Cu-(+)-1	Cu-(+)-2
empirical formula	C ₂₁ H ₁₈ Cu N ₀ O ₇	C ₆₈ H ₆₂ Cu ₂ N ₂ O ₁₄
f.w.	733.53	1528.28
<i>T</i> (K)	273(2)	100(2)
wavelength (Å)	0.71073	0.71073
crystal system	Monoclinic	Hexagonal
space group	C2	<i>P</i> 6(5)
unit cell data		
<i>a</i> (Å)	16.7458(7)	18.6018(16)
<i>b</i> (Å)	10.5063(5)	18.6018(16)
<i>c</i> (Å)	12.7529(6)	42.963(4)
α (deg)	90°	90°
β (deg)	112.534(2)°	90°
γ (deg)	90°	120°
<i>V</i> (Å ³)	2072.40(16)	12874.8(19)
<i>Z</i>	4	6
<i>D</i> _{calcd} (Mg/m ³)	1.429	0.974
Absorption coefficient(mm ⁻¹)	1.092	0.544
<i>F</i> (000)	916	3924
Crystal size	0.30 x 0.30 x 0.10 mm ³	0.30 x 0.30 x 0.10 mm ³
Theta range for data collection	1.73 to 28.34°.	1.26 to 23.29°.
Index ranges	-21<= <i>h</i> <=22, -14<= <i>k</i> <=14, -17<= <i>l</i> <=16	-20<= <i>h</i> <=13, -20<= <i>k</i> <=20, -47<= <i>l</i> <=47
Reflections collected	12608	56703
Independent reflections	4929 [R(int) = 0.1537]	12350 [R(int) = 0.1987]
Completeness to theta = 28.32°	99.2 %	99.8 %
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4929 / 1 / 260	12350 / 1 / 783
Goodness-of-fit on <i>F</i> ²	1.014	0.898
Final R indices [I>2σ(I)]	R1 = 0.0758, wR2 = 0.1981	R1 = 0.0704, wR2 = 0.1481
R indices (all data)	R1 = 0.0917, wR2 = 0.2128	R1 = 0.1074, wR2 = 0.1612
Absolute structure parameter	0.02(2)	0.138(17)
Largest diff. peak and hole	1.193 and -1.180 e.Å ⁻³	0.366 and -0.389 e.Å ⁻³

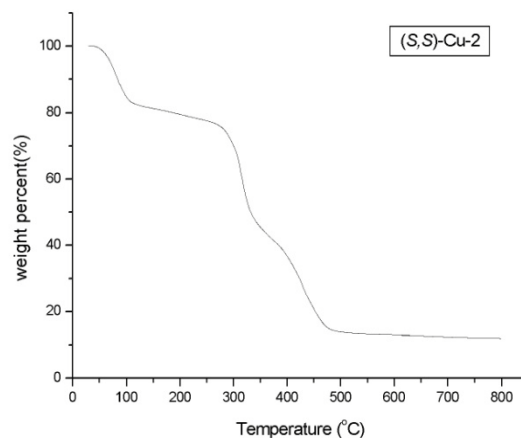
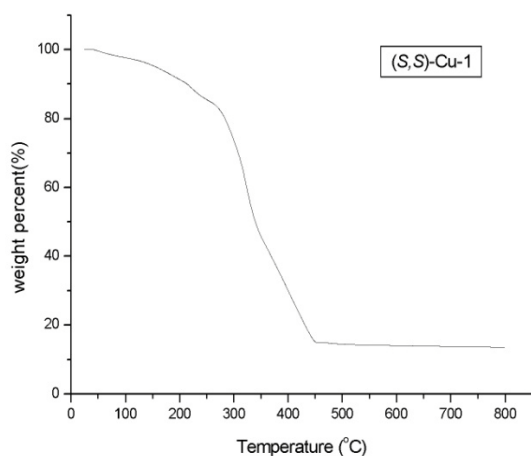
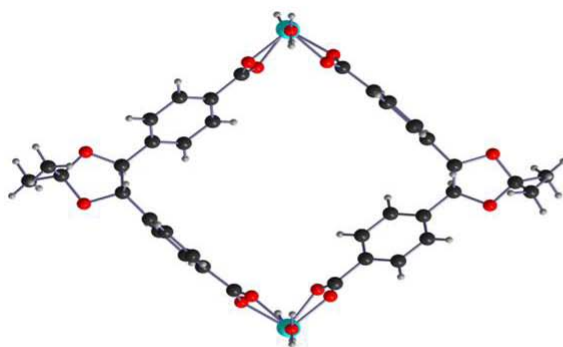
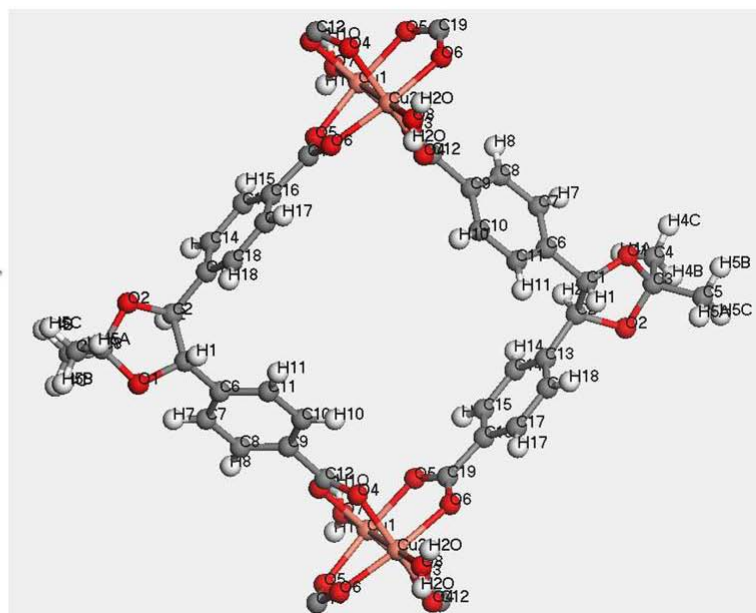


Figure S1. TGA data

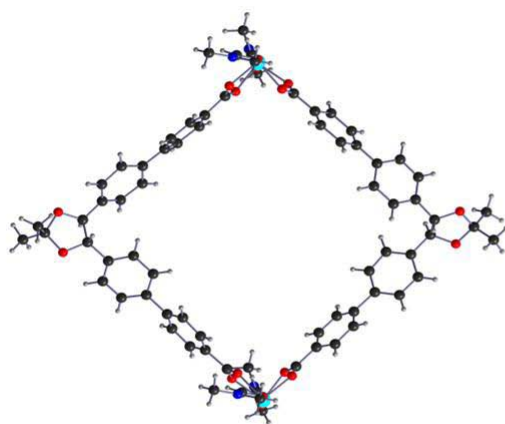
(a)



Cu-(+)-1



(b)



Cu-(+)-2

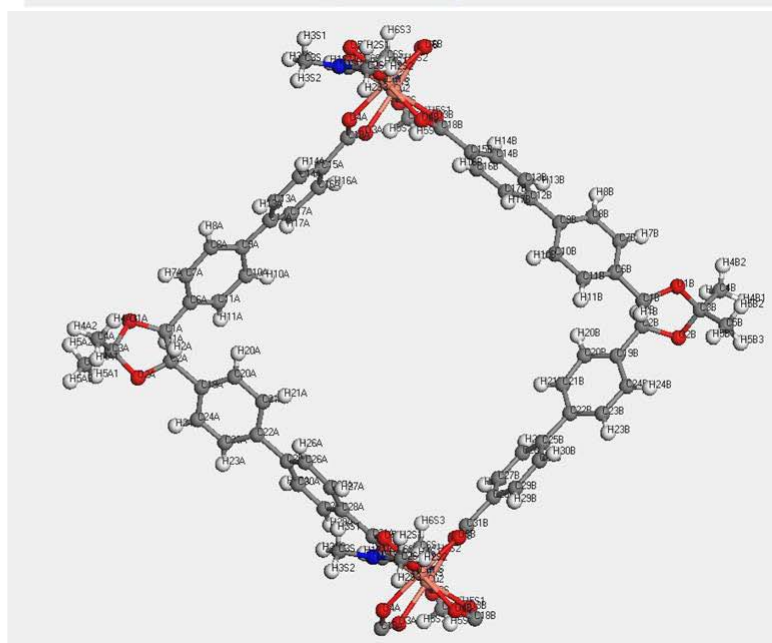


Figure S2. Asymmetric unit for Cu-(+)-1 and Cu-(+)-2

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 ligand samples in solution; The 10mg of ligand was dissolved in 1mL of methanol.

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

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

The CD spectroscopy is a very powerful technique to obtain conformational information of chiral molecules. The results of solid-state CD measurements indicate that both single crystal and the bulk crystals of Cu(+) 1 and Cu (+) 2, display similar dichroic signals corresponding to the absorptions of the UV spectra. As shown in Figure S3, the CD spectra was measured using a few crystals of Cu(+) 1 and Cu (+) 2, which that show strong signals corresponding to the absorptions of their IR spectra, indicating the crystals of Cu(+) 1 and Cu (+) 2 are chiral. On the basis of these experimental results, it may be considered that the crystallization of Cu(+) 1 and Cu (+) 2 are enantiomeric excess rather than racemic.

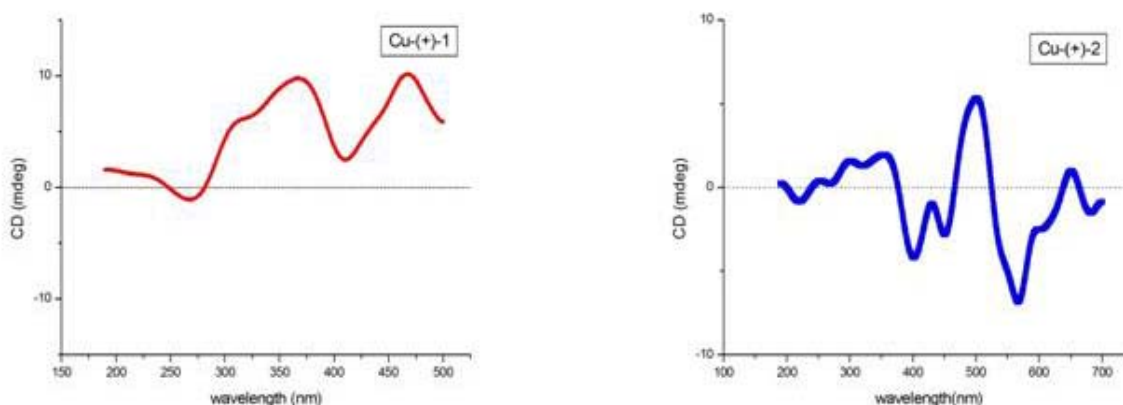


Figure S3. CD Measurement: