Electronic Supplementary Information (ESI)

Achiralization during the Preparation of Chiral MOF due to the Preferential Formation of a Pseudo-Centrosymmetric Asymmetric Unit by Conformationally Flexible Homochiral Ligands

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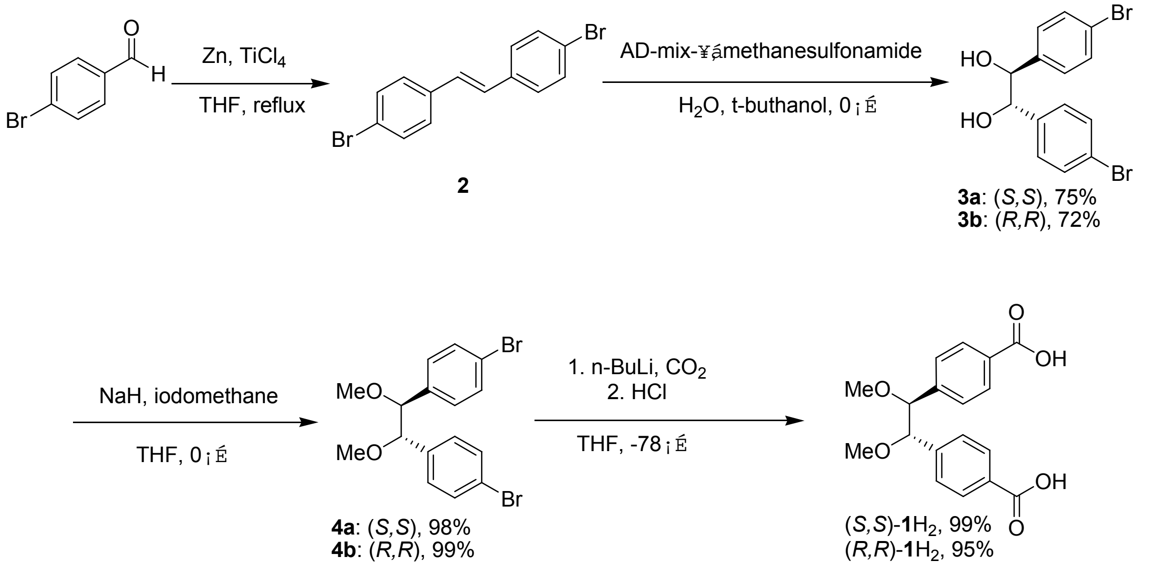
1. Synthesis of (S,S)-1H_2 and (R,R)-1H_2

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 F_{254}, 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. ^{1}H 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*)-**1**H_2 and (*R,R*)-**1**H_2

The synthesis was carried out by the following scheme.



Trans-4,4'-dibromostillbene (2)

To a stirred suspension of zinc powder (19.9g, 302 mmol) in THF (300 mL), $TiCl_4$ (16.5 mL, 151 mmol) was added slowly at -10 ^{0}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 $NaHCO_3$ solution and extracted with ethyl acetate (3 x). The combined extracts was washed with brine, dried over anhudrous $MgSO_4$, 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 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.01 (s, 2H), 7.37 (d, 4H, *J* = 8.7Hz), 7.49 (d, 4H, *J* = 8.7Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 121.62, 127.99, 128.10, 131.84, 135.88; FT-IR (KBr, cm^{-1}): 3,055 (br); Anal. Calcd. for $C_{14}H_{10}Br_2$, 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 (3a)

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, $CH_3SO_2NH_2$ (48 mg, 0.5 mmol) was added to a solution of AD-mix-α at 0 ^{0}C. To the reaction mixture was added *trans*-4,4'-dibromostilbene (120 mg, 0.5 mmol) portion by portion at 0^{0}C. The resultant mixture was further stirred at 0 ^{0}C for 20 h. After completion of the reaction, the mixture was quenched with a saturated aqueous Na_2CO_3 solution and extracted with ethyl acetate (3 x). The combined extracts was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under the reduced pressure to give a pale yellow solid. The crude product was purified by column chromatography (SiO_2) 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℃. ^{1}H NMR ($CDCl_3$, 300MHz): δ 3.27 (s, 2H), 4.48 (s, 2H), 6.90 (d, 4H, *J* = 8.4Hz), 7.34 (d, 4H, *J* = 8.4Hz). ^{13}C NMR ($CDCl_3$, 75MHz): δ 78.42, 122.02, 128.62, 131.31, 138.38; FT-IR (KBr, cm^{-1}) 3379, 3055, 2933; Anal. Calcd. for $C_{14}H_{12}Br_2O_2$, 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) τ_R=20.25min ((*R,R*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol:18.433min); $[\alpha]_D^{17}$(deg cm^3 g^{-1} dm^{-1}) = -143 (c = 0.005 g cm^{-3} in $CHCl_3$).

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

Same procedure as above, but using AD-mix-β instead of AD-mix-α, was applied to obtain **3b**. 8.2g (22.0 mmol, 72% yield) of **3b** was obtained from 10.3 g (30.6 mmol) of **2**. HPLC: τ_R = 18.43 min, 99.8 % ee; $[\alpha]_D^{18}$(deg cm^3 g^{-1} dm^{-1}) = -142 (c = 0.0052 g cm^{-3} in $CHCl_3$).

(*S,S*)-1,2-Bis(4-bromophenyl)-1,2-dimethoxy-ethane (4a)

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 (**3a**) (1.00g, 2.69 mmol) at 0 ^{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 $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a white solid. The crude product was purified by column chromatography (SiO_2, eluent; *n*-hexane:ethyl acetate = 5:1) to afford a white solid (1.08 g, 99 %). R_f: 0.43 (*n*-hexane:ethyl acetate = 5:1); mp; 73℃, ^{1}H NMR ($CDCl_3$, 300MHz): δ 3.23 (s, 6H), 4.24 (s, 2H), 6.87 (d, 4H, *J* = 8.4Hz), 7.33 (d, 4H, *J* = 8.4Hz), ^{13}13C NMR ($CDCl_3$, 75MHz): δ 57.25, 86.44, 121.76, 129.50, 131.10, 136.88; FT-IR (KBr, cm^{-1}) 3059, 2916; Anal. Calcd. for $C_{16}H_{16}Br_2O_2$, C;48.03 H;4.03 Br;39.94 O;8.00 Found, C;48.132 H;4.222; $[\alpha]_D^{21}$ (deg cm^3 g^{-1} dm^{-1}) = -153 (c = 0.005 g cm^{-3} in $CHCl_3$).

(*R,R*)- 1,2-Bis(4-bromophenyl)-1,2-dimethoxy-ethane (4b)

Same procedure as above was applied to **3b** to yield 3.19 g (7.98 mmol, 99%) of (*S,S*)-1,2-Bis(4-bromophenyl)-1,2-dimethoxy-ethane **(4b)** as a white solid from 3.00 g (8.06 mmol) of (*R,R*)-1,2-Bis(4-bromophenyl)-ethane-1,2-diol **(3b)**. Spectral data of **4b** are identical with those of **4a** except the optical rotation; $[\alpha]_D^{21}$ (deg cm^3 g^{-1} dm^{-1}) = +155 (c = 0.051 g cm^{-3} in $CHCl_3$).

(*S,S*)-1,2-Bis(4-carboxyphenyl)-1,2-dimethoxy-ethane ((*S,S*)-1H_2)

A solution of *n*-butyllithium (4.4 mL of 1.6 M solution in *n*-hexane, 7.1mmol) was added slowly to a solution of (*S,S*)-1,2-bis(4-bromophenyl)-1,2-dimethoxy-ethane (**4a**) (1.28 g, 3.20mmol) in distilled THF (32 ml) at −78□ under argon atmosphere. After stirring for 30 min at −78□, the freshly crushed dry-ice was added to a reaction mixture and then the reaction mixture was allowed to warm to room temperature. The reaction mixture was quenched with aqueous NaOH (1N 100ml) solution and then washed with ethyl acetate. The aqueous layer was extracted with an aqueous HCl solution (1 N, 100 ml) and then the organic acids were extracted with ethyl acetate (3 x). The organic extracts were combined. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was then concentrated under a reduced pressure to give a crude solid product. The residue was recrystalized from ethyl acetate (10 mL) and *n*-hexane (50 mL) to afford white solid (1.04g, 3.15mmol, 99%). R_f: 0.38 (dichloromethane:MeOH = 10:1), m.p.; 156-157 °C, ^{1}H NMR (DMSO-D_6, 300 MHz); δ 3.16 (s, 6H), 4.52 (s, 2H), 7.13 (d, *J* = 8.2 Hz, 4H); 7.80 (d, *J* = 8.5 Hz, 4H); 12.88 (br, 2H).^{13}C NMR (DMSO-D_6, 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 $C_{18}H_{18}O_6$, C; 65.45, H; 5.49, O; 29.06 Found, C; 65.67 H; 5.19; $[\alpha]_D^{17}$ (deg cm^3 g^{-1} dm^{-1}) = +63 (c = 0.005 g cm^{-3} in DMSO).

(*R,R*)- 1,2-Bis(4-carboxy-phenyl)-1,2-dimethoxy-ethane ((*R,R*)-1H_2)

Same procedure as above for (*S,S*)-**1**H_2 was applied to yield 2.35 g (7.12 mmol, 95%) of (*R,R*)-1,2-bis(4-carboxyphenyl)-1,2-dimethoxy-ethane ((*R,R*)-**1**H_2**)** as a white solid from 3g (7.49 mmol) of (*R,R*)-1,2-bis(4-bromophenyl)-1,2-dimethoxy-ethane 3.00 g (8.06 mmol) **(3b)**. Spectral data of (*R,R*)-**1**H_2 are identical with those of (*S,S*)-**1**H_2 except for $[\alpha]_D^{20}$ (deg cm^3 g^{-1} dm^{-1}) = -61(c = 0.005 g cm^{-3} in DMSO).

2. Preparation and characterization of La-(±)-1, and La-(+)-(*S,S*)-1.

2.1. Synthesis of MOFs

2.1.1. La-(±)-**1**

A mixture of $LaCl_3{\cdot}7H_2O$ (0.015 g, 0.040 mmol) and racemic-**1**H_2 (0.017 g, 0.053 mmol) in DEF (2.5 mL) and H_2O (2.5 mL) was heated at 85 ºC for 7 days. Colorless block crystals were obtained in 50% yield.

La-(±)-**1**, Elementary analysis, (%) calcd. for La-(±)-1 $C_{32}H_{45}NO_{15}La$: 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. La-(+)-(*S,S*)-**1**

A mixture of $LaCl_3{\cdot}7H_2O$ (0.015 g, 0.040 mmol) and (*S,S*)-1H_2 (0.017 g, 0.053 mmol) in DEF (2.5 mL) and H_2O (2.5 mL) was heated at 85 ºC for 2 weeks. Colorless block crystals were obtained in 45% yield.

La-(+)-(*S,S*)-**1**, Elementary analysis: (%) calcd. for La-(+)-(*S,S*)-**1** $C_{32}H_{41}NO_{13}La$: C, 48.86, H, 5.25, N, 1.78; found: C, 48.23, H, 4.75, N, 1.65. 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. La-(±)-**1**.

A block colorless crystal with a suitable size (0.50 mm x 0.30 mm x 0.30 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 (λ = 0.71073 Å) operated at 2,000 W power (50 kV, 40mA). The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. 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 SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 8,692 reflections were collected in the range 2.02° < θ < 28.19° of which 6,544 were independent and 5,276 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 $R_1 = 0.0726$ ($I > 2\sigma(I)$), $wR_2 = 0.1954$ (all data) and GOF = 1.060. The crystal belongs to the triclinic space group $P(-1)$ (No. 2) with Z = 2. 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. La-(+)-(*S*,*S*)-**1**

A block colorless crystal with a suitable size (0.50 mm x 0.30 mm x 0.30 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 (λ = 0.71073 Å) operated at 2,000 W power (50 kV, 40mA). The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. 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 SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 26,953 reflections were collected in the range 2.20° < θ < 28.32° of which 14,277 were independent and 13,152 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 $R_1 = 0.0401$ ($I > 2\sigma(I)$), $wR_2 = 0.1054$ (all data) and GOF = 1.041. The crystal belongs to the triclinic space group $P1$ (No. 1) with Z = 1. 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. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettigen: Gottingen, Germany, 1996.
3. 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

	La-(±)-1	**La-(+)-(*S*,*S*)-1**
empirical formula	$C_{32}H_{36}LaNO_{10}$	$C_{64}H_{70}La_2N_2O_{20}$
f.w.	733.53	1465.04
T (K)	273(2)	100(2)
wavelength (Å)	0.71073	0.71073
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P1$
unit cell data		
a (Å)	9.799(2)	9.7792(13)
b (Å)	11.272(3)	11.3331(14)
c (Å)	15.935(4)	15.924(2)
α (deg)	70.517(4)°	71.042(2)°
β (deg)	84.668(4)°	85.290(2)°
γ (deg)	71.302(10)	70.907(2)°
V (Å^3)	1569.1(7)	1576.7(3)
Z	2	1
D_{calcd} (Mg/m^3)	1.553	1.543
Absorption coefficient(mm^{-1})	1.419	1.412
F(000)	744	742
Crystal size	0.12 x 0.1 x 0.08 mm^3	0.15 x 0.1 x 0.05 mm^3
Theta range for data collection	2.02 to 28.19°.	2.20 to 28.32°.
Index ranges	-12<=h<=12, -14<=k<=14, -20<=l<=10	-13<=h<=12, -15<=k<=15, -21<=l<=21
Reflections collected	8692	26953
Independent reflections	6544 [R(int) = 0.0325]	14277 [R(int) = 0.0209]
Completeness to theta = 28.32°	85.0 %	98.4 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6544 / 34 / 428	14277 / 34 / 809
Goodness-of-fit on F^2	1.060	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0726, wR2 = 0.1882	R1 = 0.0401, wR2 = 0.1021
R indices (all data)	R1 = 0.0895, wR2 = 0.1954	R1 = 0.0445, wR2 = 0.1054
Absolute structure parameter		0.036(17)
Largest diff. peak and hole	1.963 and -1.237 e.Å^{-3}	1.761 and -0.644 e.Å^{-3}

Figure S1. (a) 1D rods of La-(+)-1 and La-(±)-1 (b) 3D network of La-(+)-1 and La-(±)-1, top-view (c) 3D network of La-(+)-1 and La-(±)-1, side-view

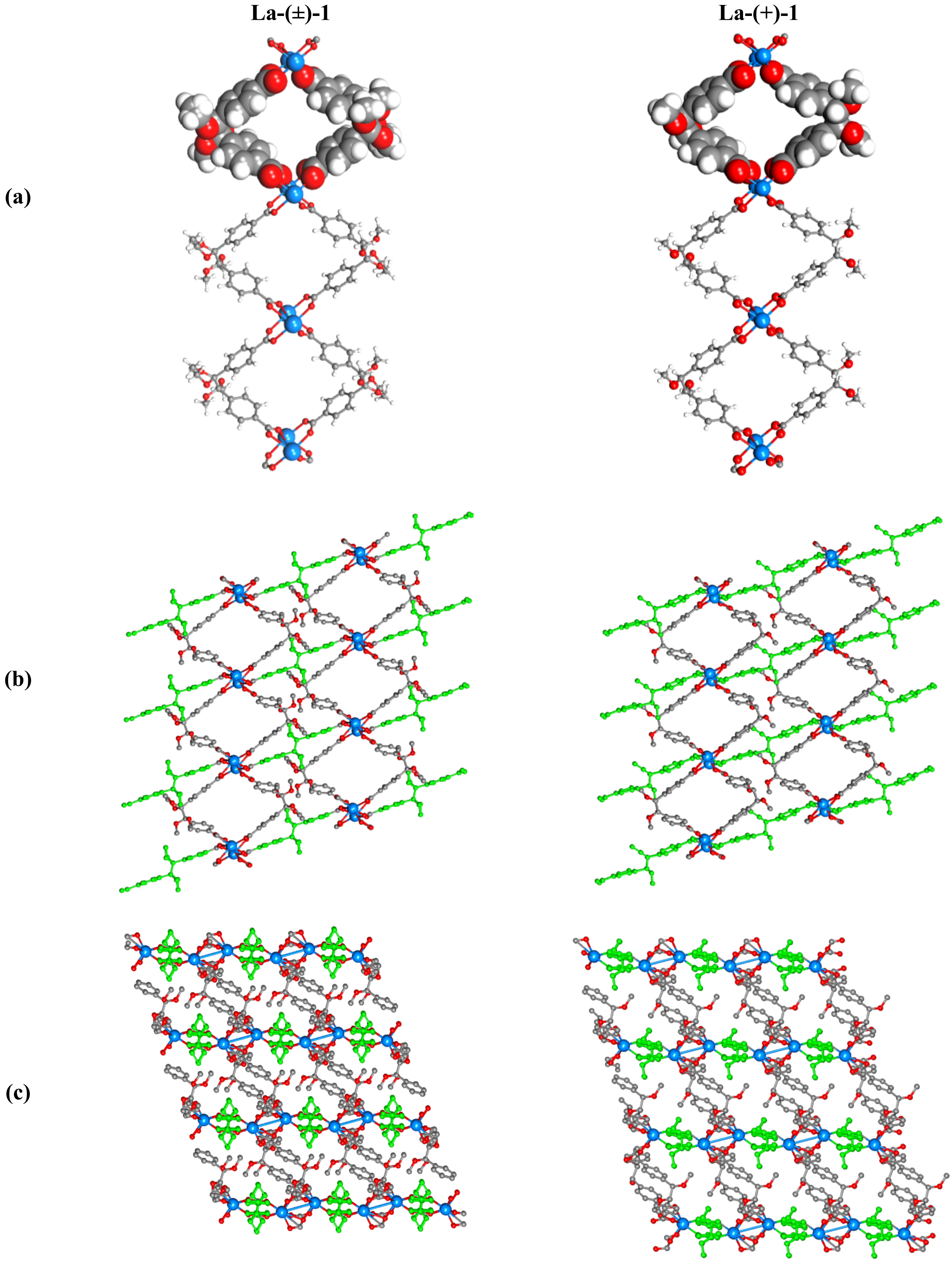
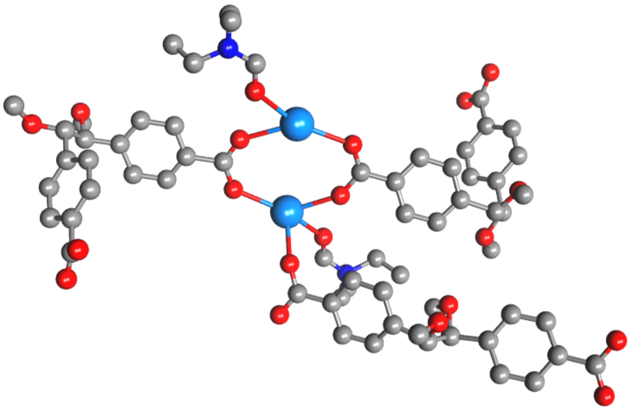
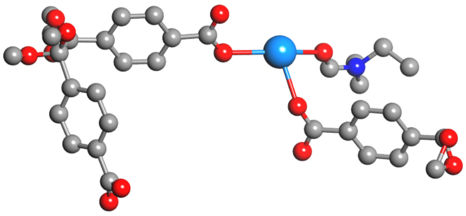


Figure S2. **Asymmetric unit of two crystals**



La-(+)-(*S*,*S*)-1



La-(±)-1

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 UVIDEC 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.

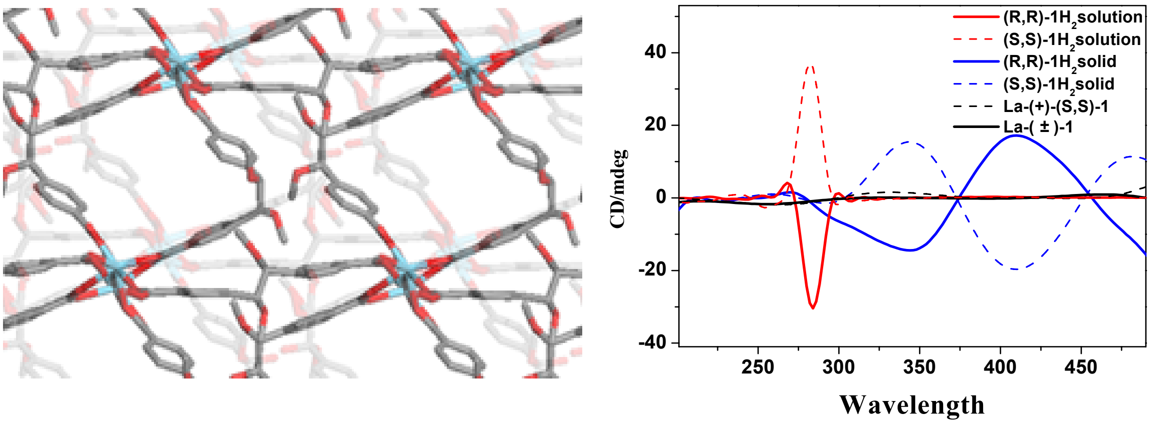


Figure S3. **CD Measurement**: (a) Superposition of La-(+)-(*S*,*S*)-**1** (top, a structure given by dark lines) and La-(±)-**1** (bottom, a structure given by dark lines) (b) solid-state CD spectra of La-(+)-(*S*,*S*)-**1** and La-(±)-**1** together with solution and solid CD spectra of (+)-(*S*,*S*)-**1**H$_2$ and (-)-(*R*,*R*)-**1**H$_2$.

4. Hydrogen Asorption Measurements.

The adsorption isotherms were measured using the standard volumetric procedure on a BELSORP-mini (BEL-Japan, INC.) equipment. Prior to measurement, the DEF guest molecules occluding the pores of La-(+)-(*S*,*S*)-**1** were exchanged with more volatile THF by immersing the crystals as-prepared in THF for 29 days. The sample was filtered, dried under low vacuum (~10^{-3} Torr) in the Schelnk line before it was loaded into the sample tube of the sorption apparatus. The dried sample was fully outgassed at 250℃ under vacuum (<1.0 x 10^{-3} torr) for 6 hr just before the measurement. The dead volume of the sample cell was automatically measured using helium gas. Pressure equilibrium points were also collected automatically by the equipment. After each measurement, the sample weight was checked by a microbalance. High purity gases (99.9999%) were used, and for hydrogen sorption measurements, both the internal parts of the instrument and the sample tube were flushed three times prior to data collection.

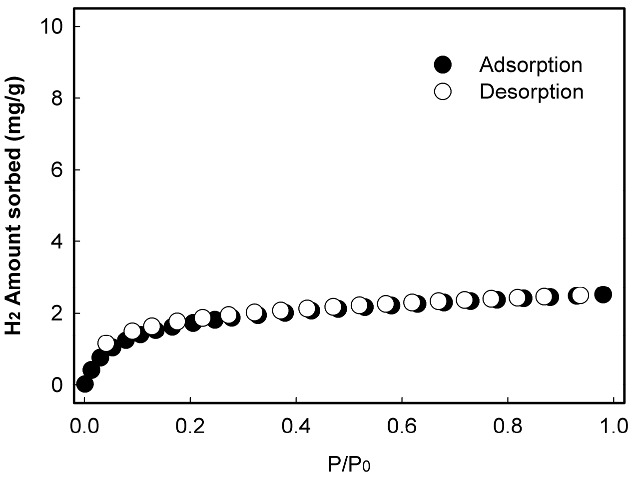


Figure S4. **Hydrogen sorption isotherms at 77K. Filled marks denote adsorption, and open ones desorption process.**