

A supermolecular building block approach for construction of chiral metal-organic frameworks

Hong Jiang,^a Kai-Jie Chen,^b Fan-Fan Zheng,^a Xu Chen,^a Yan Liu,^{*,a} and Yong Cui^{*,a,c}

^aSchool of Chemistry and Chemical Technology and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

^bDepartment of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi, 710072, China.

^cCollaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China.

Email: yongcui@sjtu.edu.cn; liuy@sjtu.edu.cn

Table of Content

1. Materials and general procedures
2. Synthesis
3. General procedure for catalysis
4. Dye uptake experiments
5. **Table S1.** Crystal data and structure refinement for **1** and **2**
6. **Table S2.** Selected bond lengths [Å] and angles [°] for **1**
7. **Table S3.** Selected bond lengths [Å] and angles [°] for **2**
8. **Figures S1-S2.** Additional X-ray Crystallographic Structures
9. **Figure S3.** Solid-state CD spectra
10. **Figure S4.** TGA curves
11. **Figure S5.** PXRD patterns
12. **Figure S6.** The CO₂ adsorption isotherms
13. **Figure S7.** Proposed catalytic mechanism of CO₂ fixation
14. **Table S4.** Results of recycle experiments
15. **Figure S8.** NMR spectra
16. **Figure S9.** ESI-MS spectra
17. References

1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C and H were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in a nitrogen atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu $K\alpha$ radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single-crystal reflection data. ^1H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 400 MHz. ESI-MS spectrum was recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. The CO_2 adsorption isotherms were recorded at 195 K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurement, the samples were activated at 80 $^{\circ}\text{C}$ under vacuum ($< 10^{-3}$ torr) for 4 h.

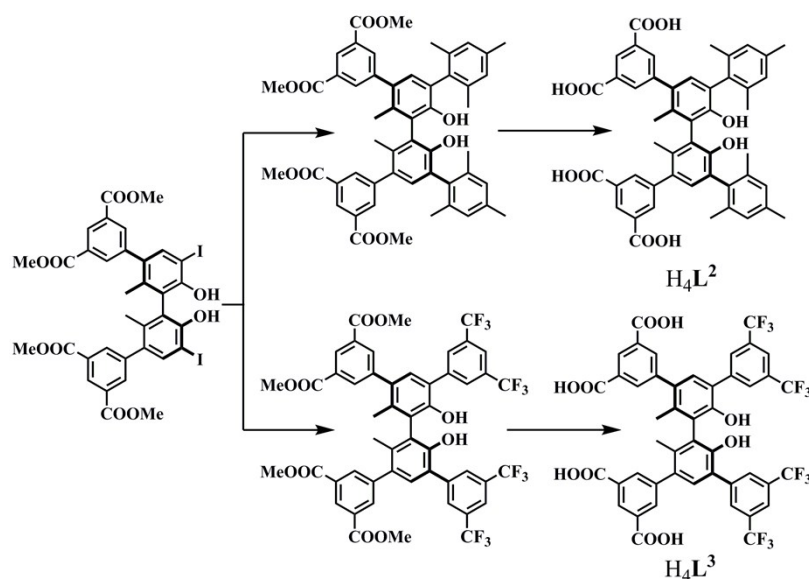
X-ray Crystallography. Single-crystal XRD data for the compound **1** and **2** were collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 123 and 173K, respectively. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996).

All structures were solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL-2015, program for crystal structure refinement, University of Göttingen, Germany, 1997). In all crystals, the guest molecules and H-atoms were refined isotropically, while the other atoms were refined anisotropically. Crystal data and details of the data collection are given in Tables S1, while the selected bond distances and angles are presented in Tables S2 and S3.

2. Synthesis

H_4L^1 was synthesized according to the published procedure.¹

2.1 Synthesis of H_4L^2



(*R*)-6,6'-dimethyl-3,3'-diiodo-5,5'-di(3,5-bis(methoxycarbonyl))phenyl-1,1'-biphenyl-2,2'-diol (**S1**) was synthesized according to the published procedure.²

Synthesis of Me₄L². A 250 ml flame-dried round-bottom flask was charged with (*R*)-6,6'-dimethyl-3,3'- diiodo-5,5'-di(3,5-bis(methoxycarbonyl))phenyl-1,1'-biphenyl-2,2'-diol (**S1**, 5.6 g, 6.58 mmol), 2,4,5-trimethylphenylboronic acid (4.32 g, 26.32 mmol, 4 equiv), K₃PO₄ (8.4g, 39.9 mmol, 6 equiv.), Pd₂(dba)₃ (940 mg, 1.03 mmol, 0.15 equiv) and S-Phos (810.4 mg, 1.97 mmol, 0.3 equiv.). Degassed anhydrous toluene (100 mL) was then added. The suspension was heated at 100 °C for 24 h. After cooling down to the room temperature, the mixture was extracted by EtOAc. The combined organic extracts were dried over Na₂SO₄ and then concentrated. The crude product was purified by column chromatography on silica gel (EtOAc/PE, 1:10, v/v) to afford (*R*)-6,6'-dimethyl-3,3'-di(2,4,5-trimethyl)phenyl-5,5'-di(3,5-bis (methoxycarbonyl))phenyl-1,1'-biphenyl-2,2'-diol as a white solid (Me₄L², 3.9 g, 4.67 mmol, 71%). ¹H NMR (CDCl₃, 400 MHz) δ: 8.64 (t, J = 4 Hz, 2H), 8.25 (d, J = 4 Hz, 4H), 7.04 (s, 2H), 6.98 (s, 4H), 4.80 (br, 2H), 3.96 (s, 12H), 2.33 (d, J = 4Hz, 6H), 2.12 (s, 6H), 2.10(s, 6H), 2.06(s, 6H). ¹³C NMR (DMSO-d₆) δ:166.60, 150.33, 142.92, 139.75, 138.01, 137.57, 137.43, 135.17, 135.01, 133.43, 132.38, 131.76, 130.72, 129.11, 128.86, 128.75, 127.39, 125.21, 123.30, 52.66, 22.25, 21.33, 20.75, 20.61, 17.84.

Synthesis of H₄L². A solution of (*R*)-6,6'-dimethyl-3,3'-di(2,4,5-trimethyl)phenyl-5,5'-di (3,5-bis(methoxycarbonyl))phenyl-1,1'-biphenyl-2,2'-diol (Me₄L², 3.9 g, 4.67 mmol), and LiOH·H₂O (1.96 g, 46.7 mmol, 10 equiv.) in THF (15 mL), MeOH (45 mL) and H₂O (45 mL) was heated at 75 °C for 8 h. The solution was cooled to room temperature, acidified to pH= 1~2 with 6M HCl and extracted with EtOAc. The organic phase was dried over Na₂SO₄ and then the solvent was evaporated under reduced pressure to give a white solid (H₄L², 3.31 g, 4.25 mmol, 91%), ¹H NMR (DMSO-d₆, 400 MHz) δ:8.41 (s, 2H), 8.11 (s, 4H), 7.61 (s, 2H), 6.88 (s, 4H), 6.81 (s, 2H), 2.23 (s, 6H), 2.05 (d, J = 14.7 Hz, 12H), 1.93 (s, 6H). ¹³C NMR (DMSO-d₆) δ:167.38 , 152.16 (s), 143.29 , 137.02, 136.36 (s), 135.31,134.74, 134.34 (s), 132.16, 132.02, 131.44, 129.61, 128.40 , 126.16, 125.08, 21.36, 21.24, 18.09. ESI-MS: m/z 801.2687 (Calcd m/z 801.2676 for [H₆L²+Na])

2.2 Synthesis of H₄L³

(*R*)-6,6'-dimethyl-3,3'-di(3,5-bis(trifluoromethyl))phenyl-5,5'-di(3,5-bis(methoxycarbonyl))phenyl-1,1'-biphenyl-2,2'-diol (Me₄L³) was synthesized according to the published procedure.²

A solution of Me₄L³ (1.02 g, 1 mmol) and LiOH·H₂O (1.68 g, 10 mmol, 10 equiv.) in THF (15 mL), MeOH (45 mL) and H₂O (45 mL) was heated at 75 °C for 8 h. The solution was cooled to room temperature, acidified to pH = 1~2 with 6M HCl and extracted with EtOAc. The organic phase was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure to give a white solid (H₄L³, 830 mg, 0.86 mmol, 86%), ¹H NMR (DMSO-d₆, 500 MHz) δ: 12.97 (br, 6H), 8.57 (s, 2H), 8.48 (s, 2H), 8.34 (s, 4H), 8.20 (s, 4H), 7.47 (s, 2H), 1.90 (s, 6H). ¹³C NMR (DMSO-d₆) δ:172.45, 167.10, 151.93, 142.69, 141.43, 136.87, 134.72, 133.26, 131.74, 131.56, 130.87, 130.61, 130.36, 130.10, 128.74, 127.23, 125.99, 125.07, 124.37, 122.90, 120.73, 120.47, 65.34, 60.17, 21.45, 21.13, 18.25, 15.55, 14.47. ¹⁹F NMR (471 MHz, DMSO-d₆) δ -61.25 (s, 1H). ESI-MS: m/z 965.1256 (Calcd m/z 965.1268 for [H₄L³-H]).

2.3 Synthesis of 1

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (47.6 mg, 0.16 mmol), H_4L^1 (40 mg, 0.07 mmol), DMF (3 mL), THF (0.5 mL), H_2O (0.1 mL) was sealed in a 80 mL vial with a screw cap and heated at 85 °C for 24 h. Colorless cubic crystals were obtained, washed with MeOH, and dried at room temperature in air. Yield: 85%.

Calcd for $\text{Zn}_{28}\text{C}_{444}\text{H}_{492}\text{O}_{208}\text{N}_{28}$: C, 46.88; H, 4.36; N, 3.44; Found: C, 46.80; H, 4.21; N, 3.30.

FTIR (KBr cm^{-1}): 3394(s), 2981(w), 1857(w), 1704(w), 1689(w), 1614(s), 1565(s), 1447(m), 1415(m), 1365(s), 1304(m), 1258(w), 1243(w), 1180(m), 1128(m), 1085(m), 1039(s), 969(w), 925(m), 900(w), 888(w), 828(w), 781(s), 726(s), 696(m), 634(w), 567(m), 477(m), 465(m).

2.4 Synthesis of 2

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.08 mmol), H_4L^2 (30 mg, 0.04 mmol), DMF (2.5 mL), THF (0.5 mL), H_2O (0.1 mL) was sealed in a 80 mL vial with a screw cap and heated at 85 °C for 12 h. Colorless cubic crystals were obtained, washed with MeOH, and dried at room temperature in air. Yield: 89%.

Calcd for $\text{Zn}_{28}\text{C}_{681}\text{H}_{769}\text{O}_{213}\text{N}_{43}$: C, 55.28; H, 5.24; N, 4.07. Found: C, 55.23; H, 5.30; N, 3.96.

FTIR (KBr cm^{-1}): 3517(m), 3426(m), 3066(w), 3030(w), 2974(m), 2921(m), 2864(w), 2737(w), 1616(s), 1569(s), 1447(s), 1408(s), 1361(s), 1301(m), 1237(s), 1173(m), 1160(w), 1139(m), 1105(m), 1058(m), 1030(m), 1004(m), 919(m), 898(m), 852(m), 783(s), 748(w), 726(s), 701(s), 679(w), 640(m), 605(m), 828(w), 586(w), 539(w), 525(w), 495(w), 475(m), 467(w).

2.5 Synthesis of 3

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.08 mmol), H_4L^3 (40 mg, 0.04 mmol), DMF (2.5 mL), THF (0.8 mL), H_2O (0.1 mL) was sealed in a 80 mL vial with a screw cap and heated at 85 °C for 12 h. Colorless cubic crystals were obtained, washed with MeOH, and dried at room temperature in air. Yield: 85%.

Calcd for $\text{Zn}_{28}\text{C}_{609}\text{H}_{497}\text{O}_{213}\text{N}_{27}\text{F}_{144}$: C, 45.24; H, 3.10; N, 2.34 Found: C, 45.26; H, 3.21; N, 2.20.

FTIR (KBr cm^{-1}): 3531(m), 3039(w), 2936(m), 2553(w), 1712(s), 1605(s), 1457(m), 1388(m), 1287(s), 1251(w), 1186(s), 1143(s), 1073(m), 1039(m), 1017(m), 1003(w), 925(w), 896(s), 847(m), 828(w), 813(m), 764(m), 727(w), 705(s), 683(s), 607(w), 580(w), 512(w), 410(w).

3. General procedure for catalysis

In a typical reaction, MOF (0.02 mmol, 0.2 mol% based on Zn paddlewheel) catalyzed reaction was conducted in an autoclave reactor with 10.0 mmol epoxide and CO_2 purged at 1 MPa under solvent free environment at room temperature for 24 hours. The catalysts were separated by centrifugation and the reaction mixture was analyzed by ^1H NMR to calculate the yields of the products.

Recycle experiments of CO_2 cycloaddition of epoxides were operated under the same condition. After reaction, the catalysts were collected by centrifugation after each cycle, dried in vacuum and then reused for next runs. The yields were calculated by ^1H NMR.

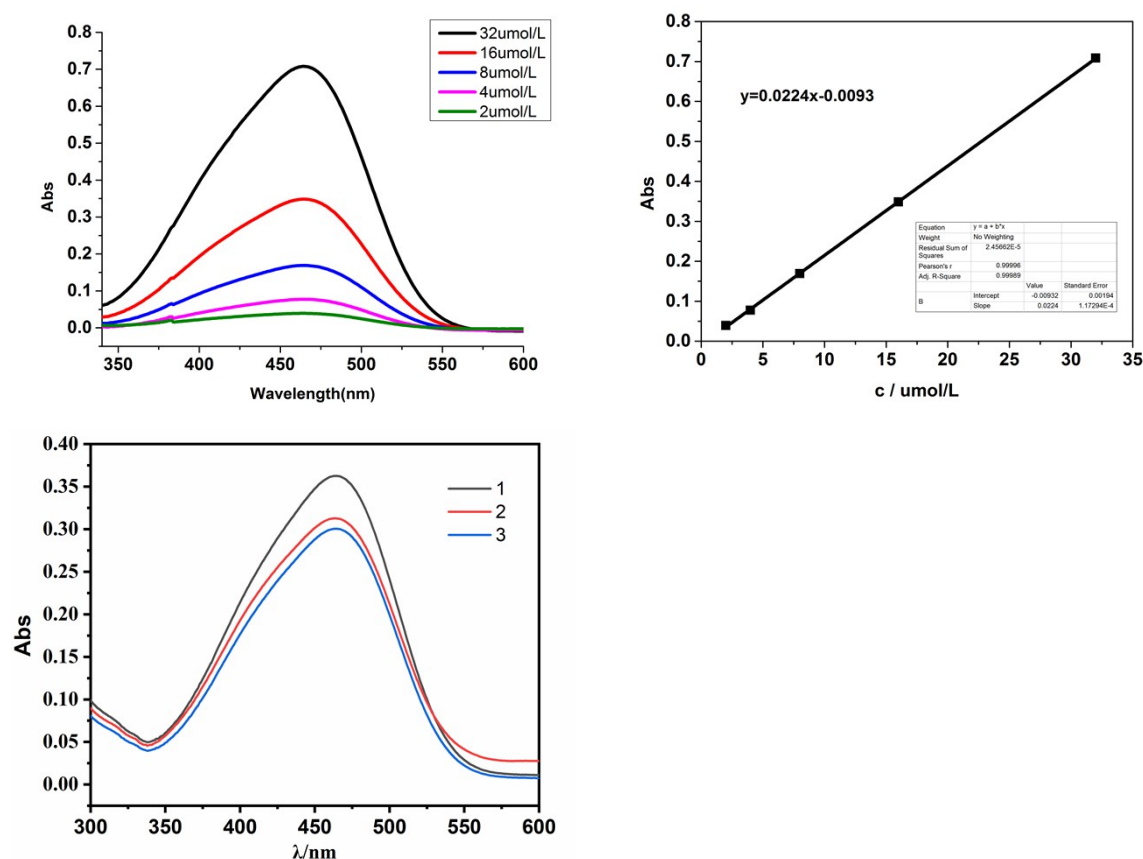
4. Dye uptake experiments

The activated MOFs (5 mg) were soaked in a solution of MO (60 mmol) in methanol for 24 h. To remove the dye adsorbed on the surface of crystals, the resulting red crystals were washed with methanol until the solution became colorless. Then the samples were sonicated with methanol and the resulting solution was diluted to 100 mL. Absorption experiments were performed on Lambda

20 UV/Vis Spectrometer. The amounts of dyes were determined by comparing the UV absorptions with the standard curves.

Creation of a standard curve: (1) MO (3.27mg) was dissolved in MeOH and diluted to 100 mL. The solution of MO (100 $\mu\text{mol/L}$) is stock solution, and 1, 2, 4, 8 and 16 mL stock solution were diluted to 100mL, respectively. (2) The absorbance of different concentrations of MO was determined by UV/Vis Spectrometer. Data for known concentrations of MO were used to make the standard curve, plotting concentration on the X axis, and the assay measurement of absorbance on the Y axis. According to the Lambert–Beer law, the standard curve can be calculated by linear fitting of the data.

Calculation of the MO number: The samples solution were diluted to 100 mL to meet the needs of linear range of concentration. The absorbance of the sample solutions were determined by the UV/Vis Spectrometer (**Figure S1**). The concentrations of MO can be calculated by comparing the UV-Vis absorbance with a standard curve.



MOF	1	2	3
Methyl orange	10.88 wt%	9.42 wt%	9.04 wt%

5. Table S1. Crystal data and structure refinements for 1 and 2

Empirical formula	C ₉₃ H ₆₆ O ₄₁ Zn ₂₈	C ₁₄₄ H ₁₁₄ O ₃₇ Zn ₇
Formula weight	2297.00	2893.94
Temperature (K)	123	173
Wavelength (Å)	1.54178	1.54178
Crystal system	Cubic	Cubic
Space group	<i>P</i> 432	<i>P</i> 432
Unit cell dimensions	$a = 30.3978(2) \text{ \AA}$ $\alpha = 90^\circ$ $b = 30.3978(2) \text{ \AA}$ $\beta = 90^\circ$ $c = 30.3978(2) \text{ \AA}$ $\gamma = 90^\circ$	$a = 30.3776(7) \text{ \AA}$ $\alpha = 90^\circ$ $b = 30.3776(7) \text{ \AA}$ $\beta = 90^\circ$ $c = 30.3776(7) \text{ \AA}$ $\gamma = 90^\circ$
Volume (Å ³), <i>Z</i>	28088.4(6), 12	28032.4(19), 4
Density (calculated) (mg/m ³)	0.621	0.701
Absorption coefficient (mm ⁻¹)	0.972	0.992
<i>F</i> (000)	5368	6064
θ range for data collection (°)	1.453 to 49.983	1.454 to 51.006
Limiting indices	-21 ≤ <i>h</i> ≤ 30, -26 ≤ <i>k</i> ≤ 26, - 26 ≤ <i>l</i> ≤ 21	-28 ≤ <i>h</i> ≤ 29, -13 ≤ <i>k</i> ≤ 30, - 30 ≤ <i>l</i> ≤ 20
Reflections collected / unique	30967 / 5360	35931 / 5003
<i>R</i> _{int}	0.0597	0.1141
Completeness to theta	26.000, 98.8 %	26.000, 98.7%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	4535 / 224 / 238	4994 / 284 / 263
Goodness-of-fit on F ²	0.902	0.846
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0950, <i>wR</i> 2 = 0.2778	<i>R</i> 1 = 0.0879, <i>wR</i> 2 = 0.2253
Absolute structure parameter	0.01(3)	0.02(4)
Largest diff. peak and hole (e.Å ⁻³)	0.548 and -0.273	0.49 and -0.33

6. Table S2. Selected bond lengths [Å] and angles [°] for 1

Zn(1)-O(2)	2.008(9)
Zn(1)-O(2W)	1.870(19)
Zn(2)-O(1)	2.012(10)
Zn(2)-O(1W)	2.173(18)
Zn(4)-O(3)	1.961(9)

Zn(4)-O(4W)	1.970(18)
Zn(3)-O(4)	2.150(12)
Zn(3)-O(3W)	2.226(13)
O(2)-Zn(1)-Zn(2)	81.5(3)
O(2W)-Zn(1)-Zn(2)	180.0
O(2W)-Zn(1)-O(2)	98.5(3)
O(1)-Zn(2)-Zn(1)	78.9(3)
O(1)-Zn(2)-O(1W)	101.1(3)
O(1W)-Zn(2)-Zn(1)	180.0
O(3)-Zn(4)-O(4W)	101.9(3)
O(4)-Zn(3)-O(3W)	82.4(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z #2 y,-x+1,z #3 -y+1,x,z
 #4 -y+1,-z+1,x #5 z,-x+1,-y+1 #6 -y+1,-x+1,-z+2

7. Table S3. Selected bond lengths [Å] and angles [°] for 2

Zn(1)-O(1)	2.000(10)
Zn(1)-O(1W)	1.982(18)
Zn(2)-O(2)	2.002(9)
Zn(2)-O(2W)	2.015(16)
Zn(3)-O(3)	1.896(10)
Zn(3)-O(3W)	2.148(15)
Zn(4)-O(4W)	2.051(16)
Zn(4)-O(4)	1.984(11)
O(1)-Zn(1)-Zn(2)	80.2(3)
O(1W)-Zn(1)-Zn(2)	180.0
O(1W)-Zn(1)-O(1)	99.8(3)
O(2)-Zn(2)-Zn(1)	77.9(3)
O(2)-Zn(2)-O(2W)	102.1(3)
O(2W)-Zn(2)-Zn(1)	180.0
O(3)-Zn(3)-O(3W)	108.0(3)
O(4)-Zn(4)-O(4W)	118.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-z-1,y #2 x,z,-y-1 #3 x,-y-1,-z-1
 #4 -z-1,x,-y-1 #5 y,-z-1,-x-1 #6 -x,-z-1,-y-1

8. Additional X-ray Crystallographic Structures

Figure S1. Coordination environments of H_4L^1 (a) and H_4L^2 (b)

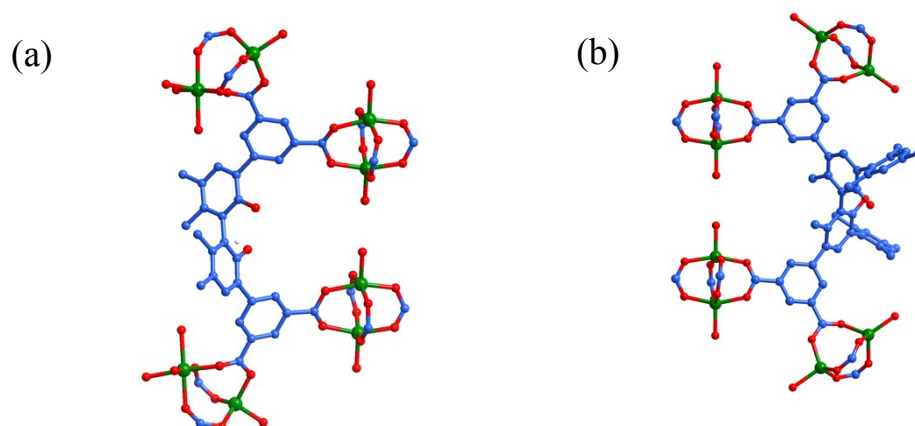
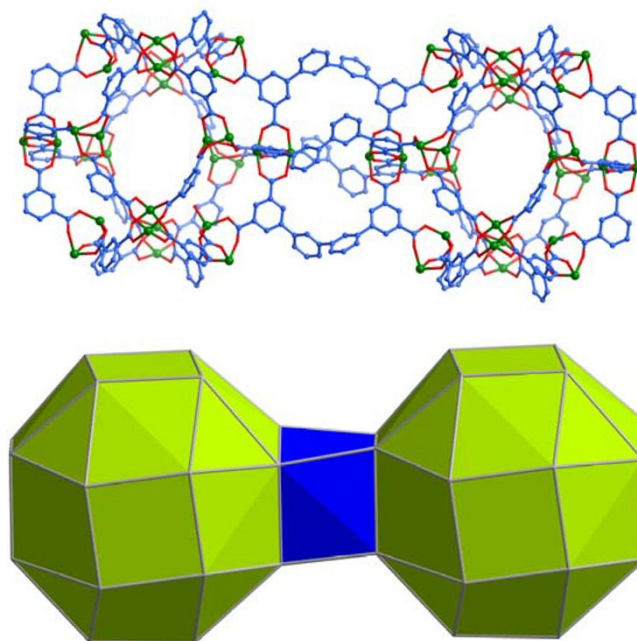
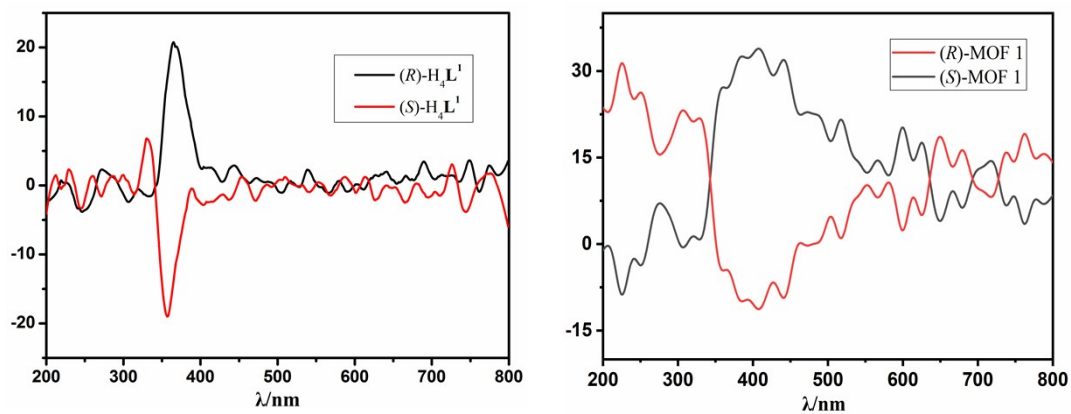
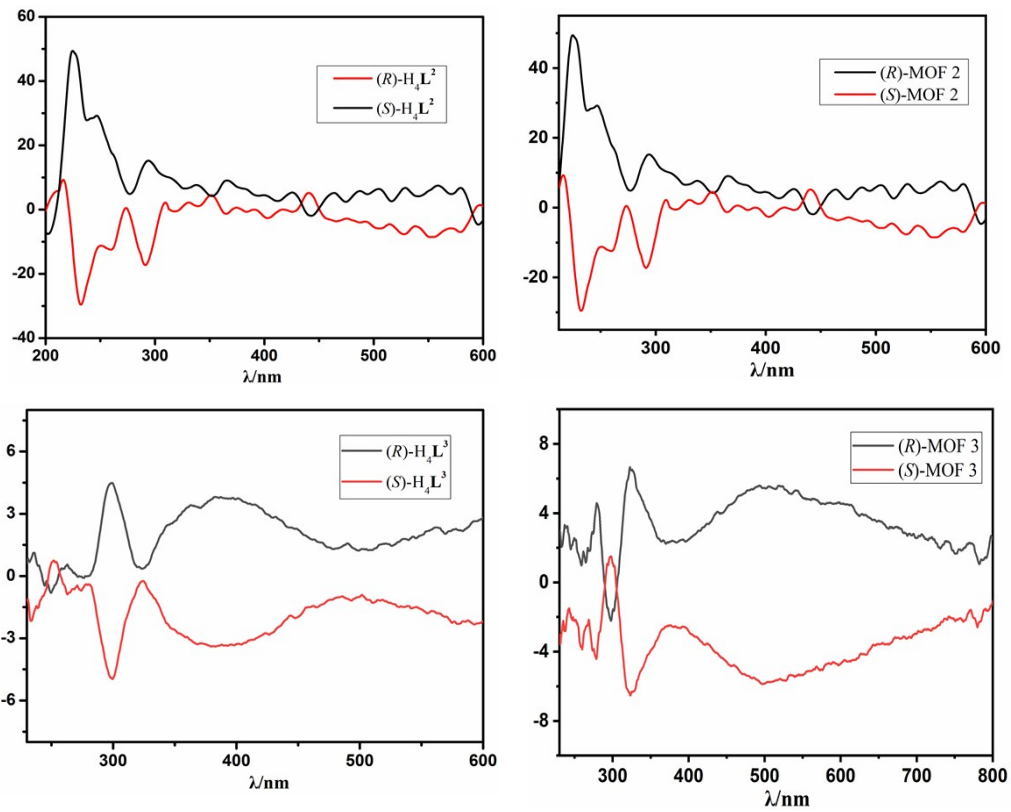


Figure S2. Schematic illustration of the connection of two neighbour small cubicuboctahedra.

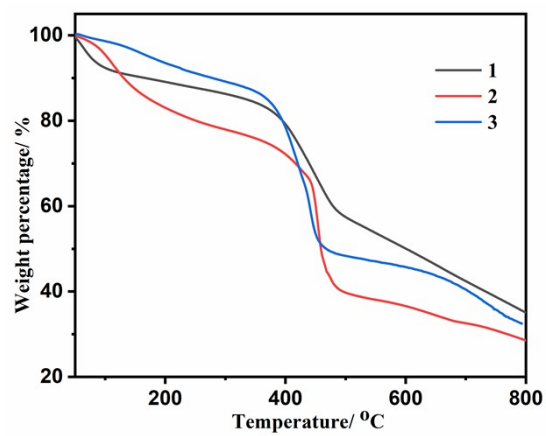


9. Figure S3. Solid-state CD spectra

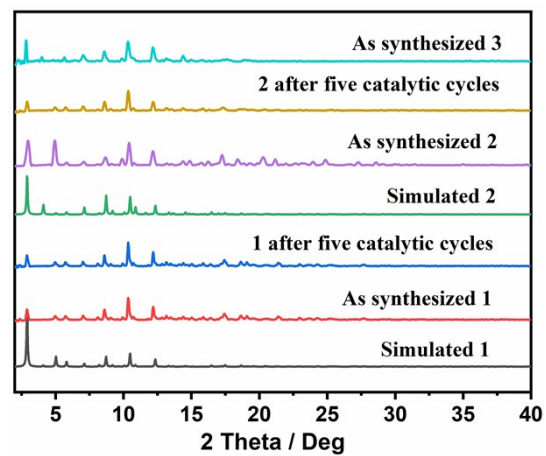




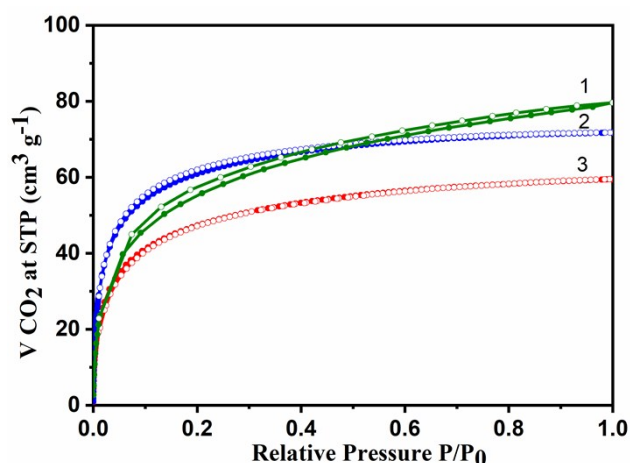
10. Figure S4. TGA curves



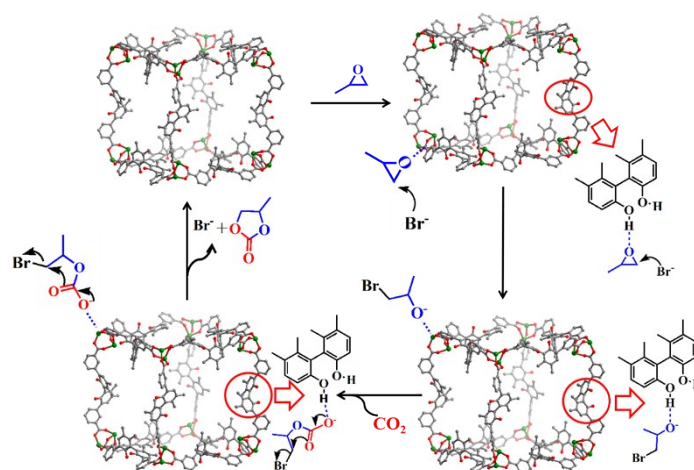
11. Figure S5. PXRD patterns



12. Figure S6. The CO₂ adsorption isotherms

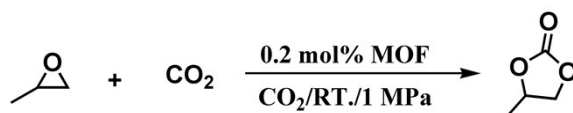


13. Figure S7. Proposed catalytic mechanism of CO₂ fixation reaction catalyzed by **1**



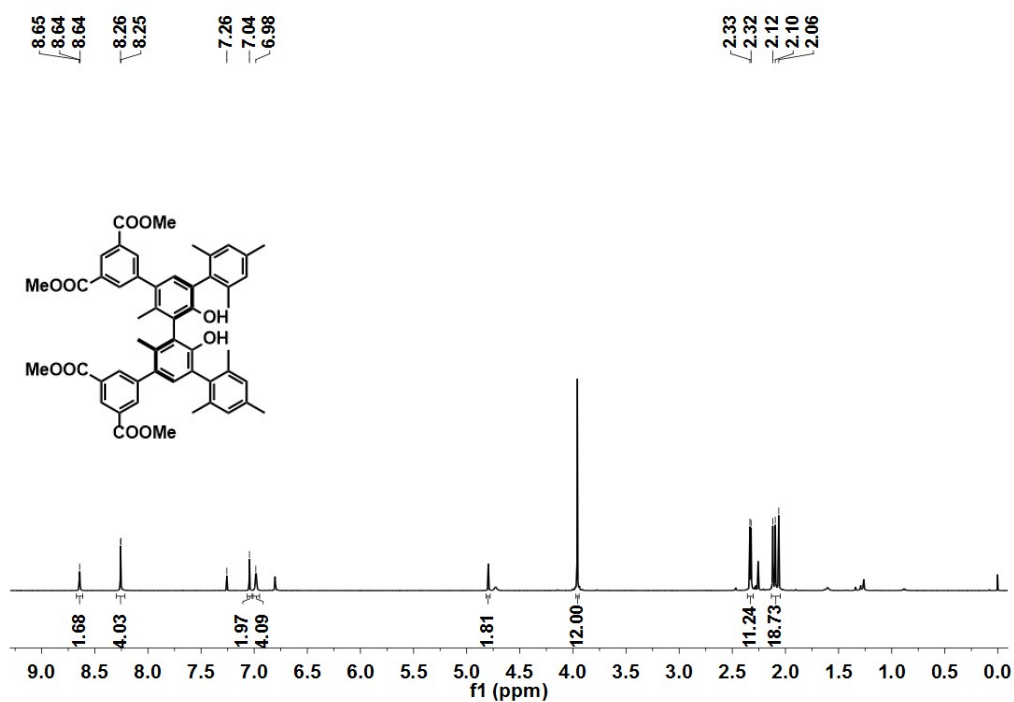
Based on the crystal structure, a possible mechanism was proposed for the CO₂ fixation reaction by **1** (Figure S8). Firstly, the epoxide ring is activated by coordinating with open Zn^{II} Lewis sites and also forming hydrogen bonds with the -OH functional groups at the ligands. Subsequently, the Br⁻ from co-catalyst TBAB attack the less-hindered carbon atoms of both the coordinated and hydrogen-bonded epoxides. This process can be confirmed by the enantioselective fashion when using (+)-(*S*)-styrene epoxide as reactant. Then the resulting oxygen anions rapidly react with the surrounding CO₂ molecules within the framework to generate alkylcarbonate anions. Cyclization of alkylcarbonate anions is achieved to form the corresponding cyclic carbonates.

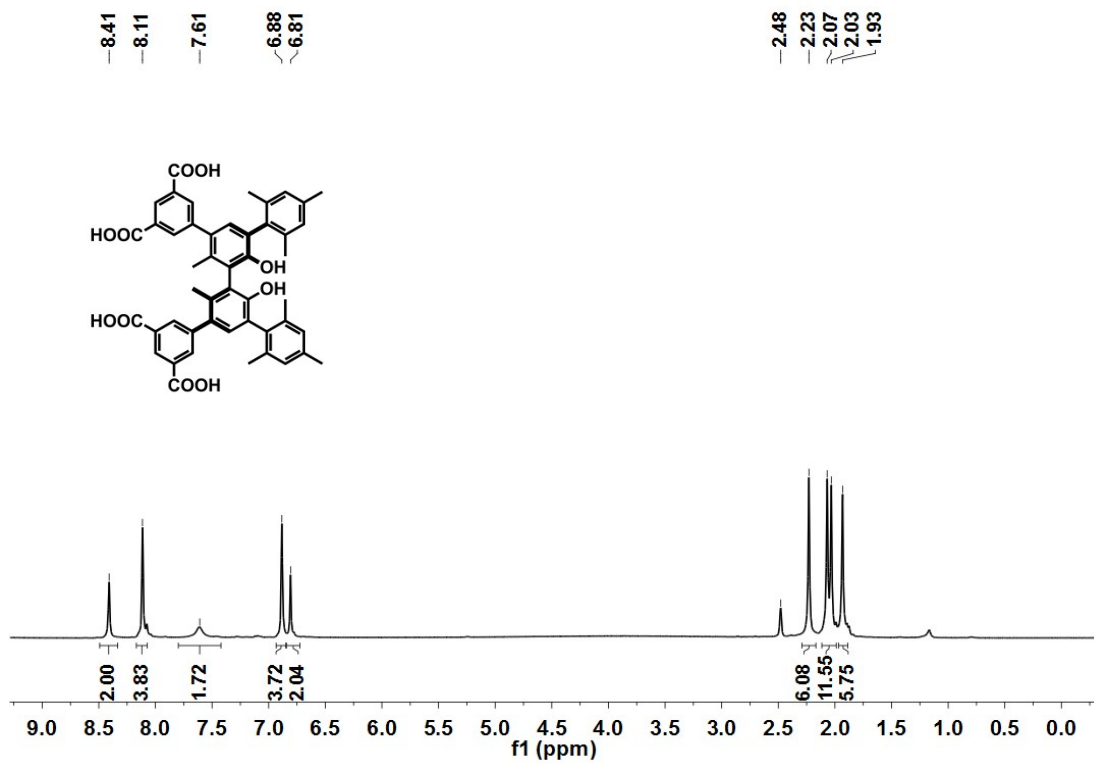
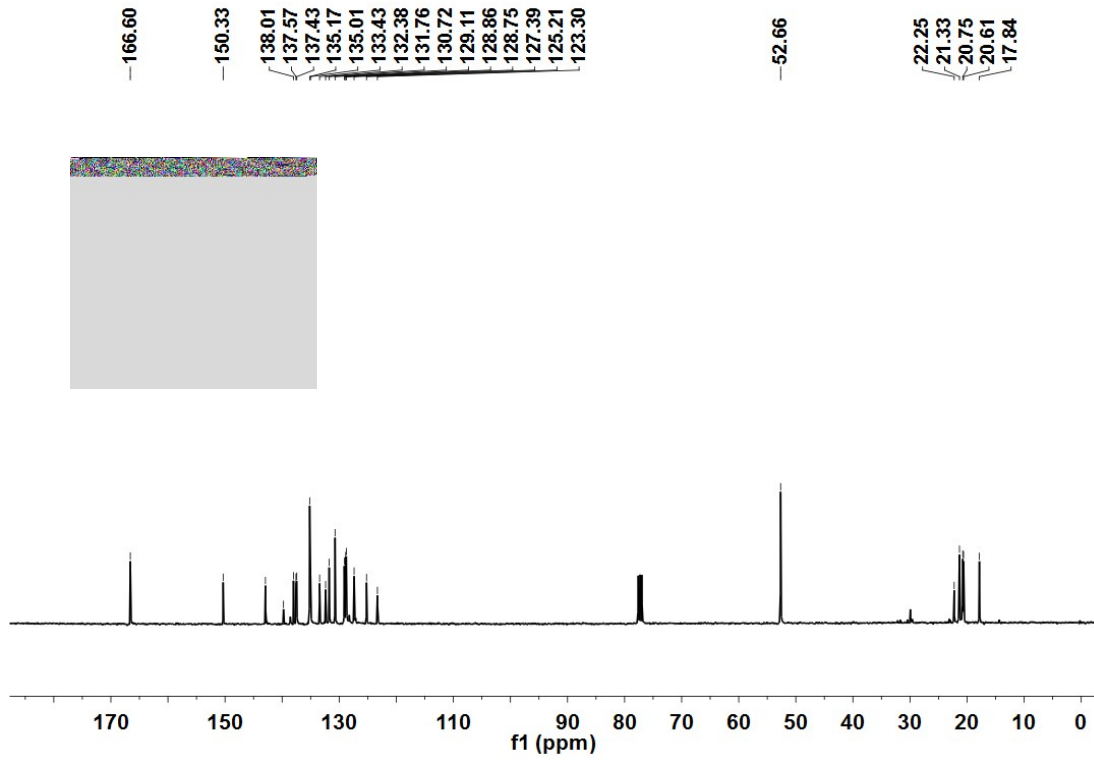
14. Table S4. Results of recycle experiments

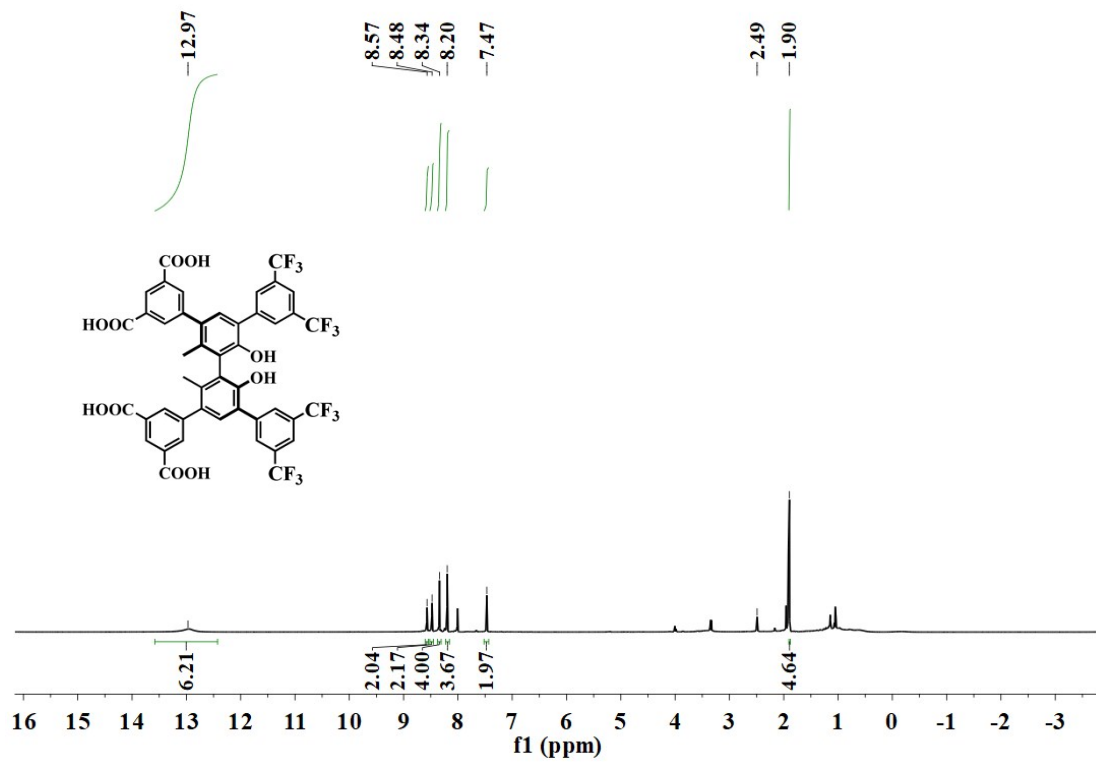
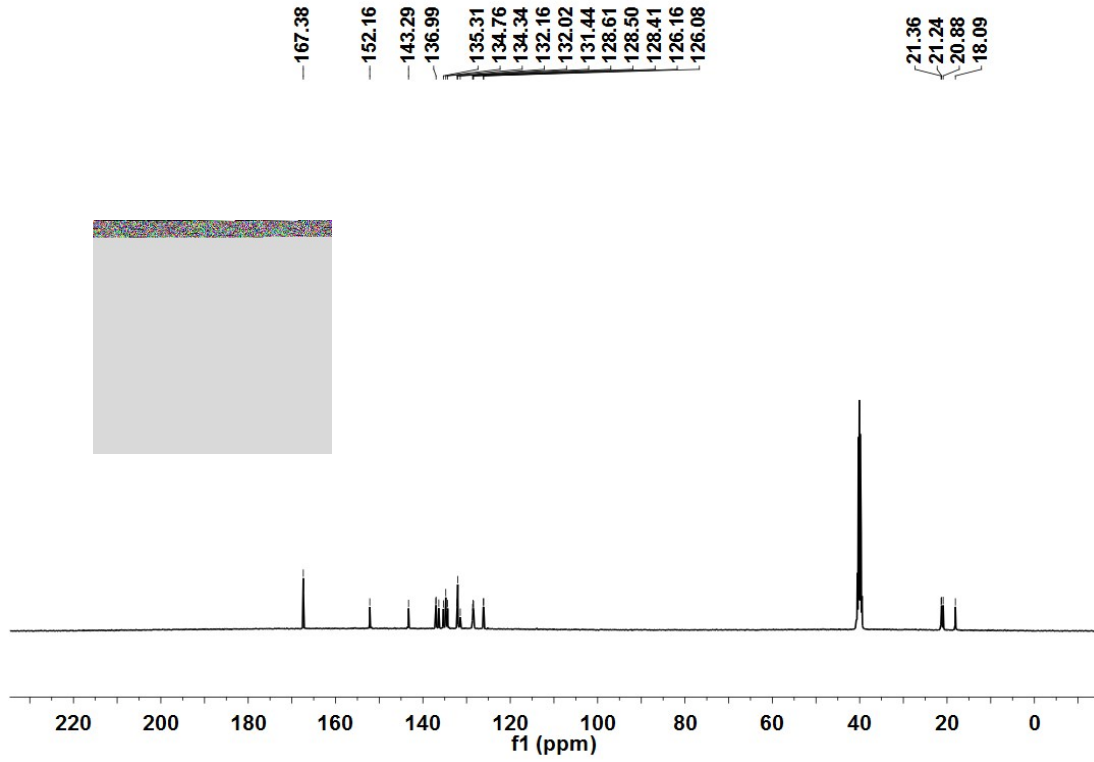


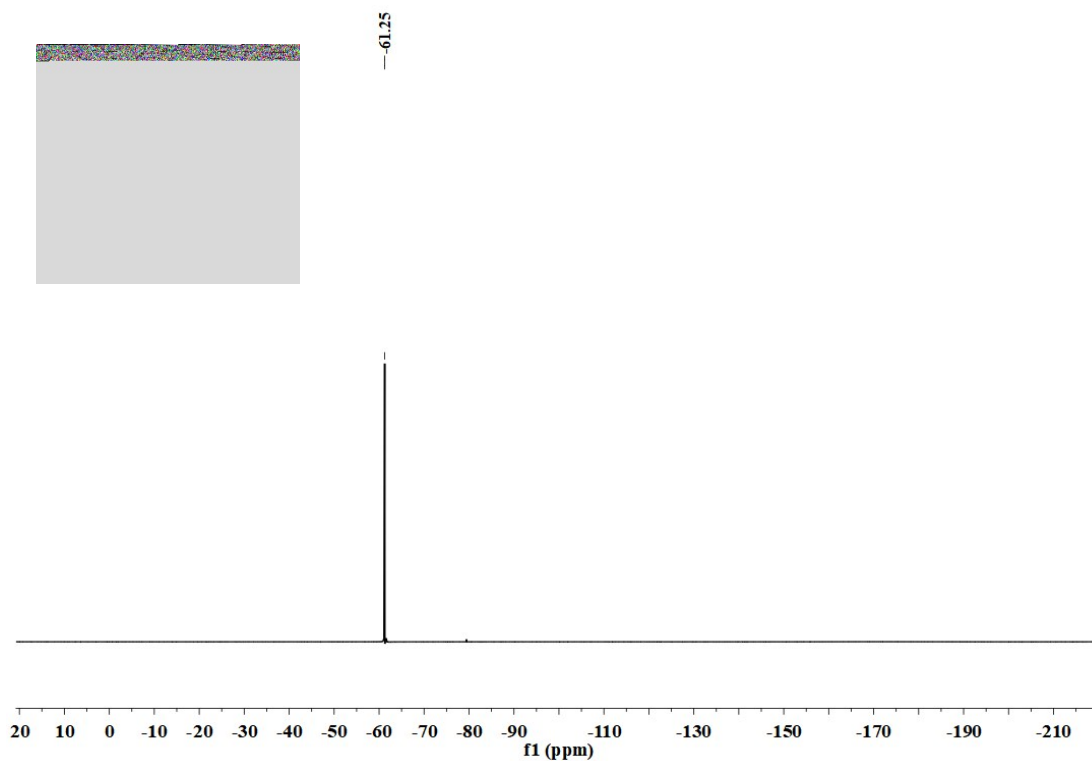
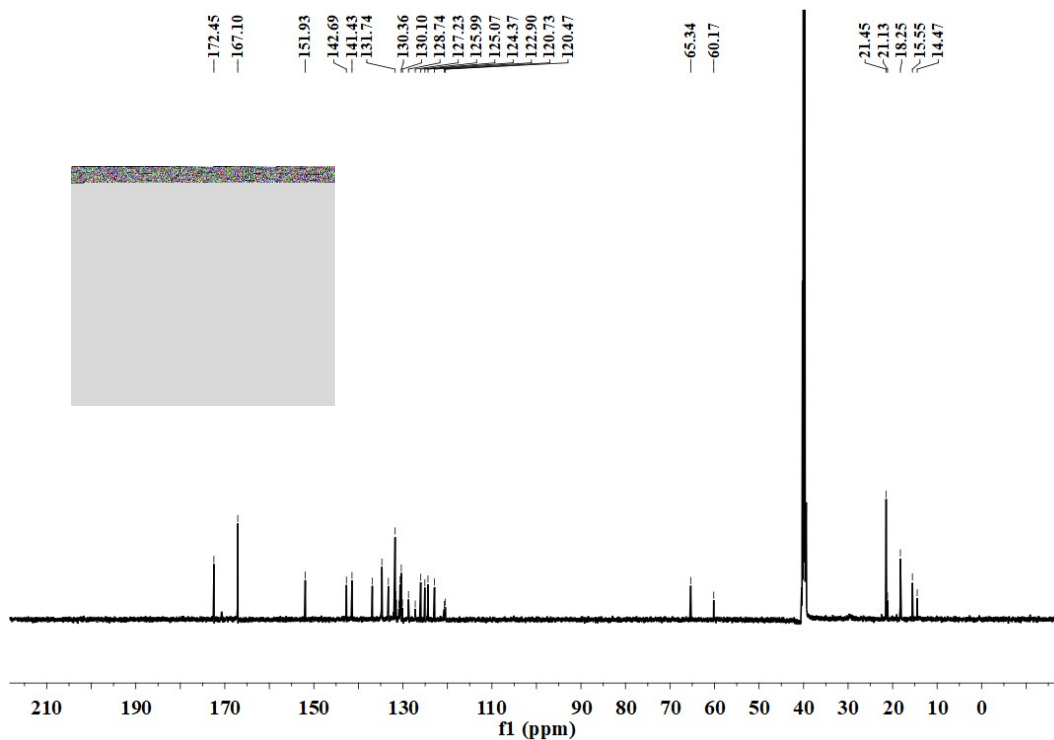
Entry	Catalyst	Yield/%
1	1 (run 1)	96
2	1 (run 2)	96
3	1 (run 3)	95
4	1 (run 4)	94
5	1 (run 5)	92
6	2 (run 1)	94
7	2 (run 2)	93
8	2 (run 3)	94
9	2 (run 4)	92
10	2 (run 5)	90

15. Figure S8. NMR spectra

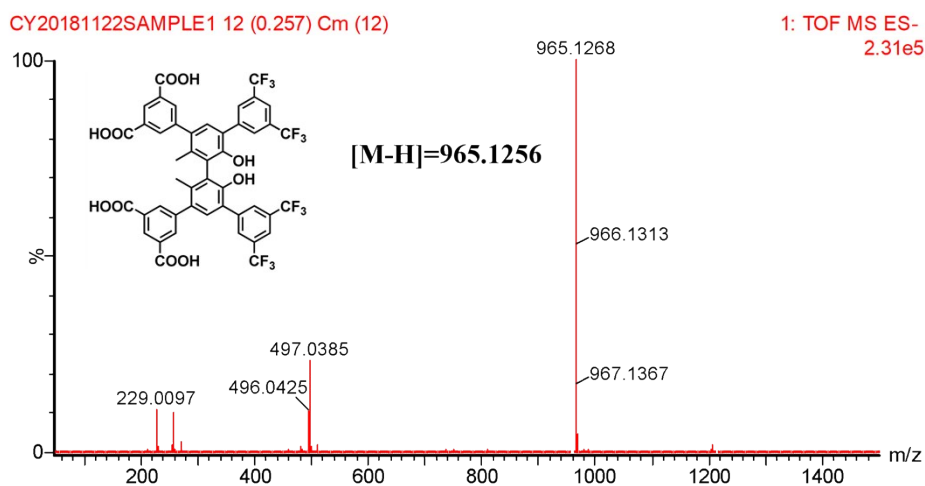
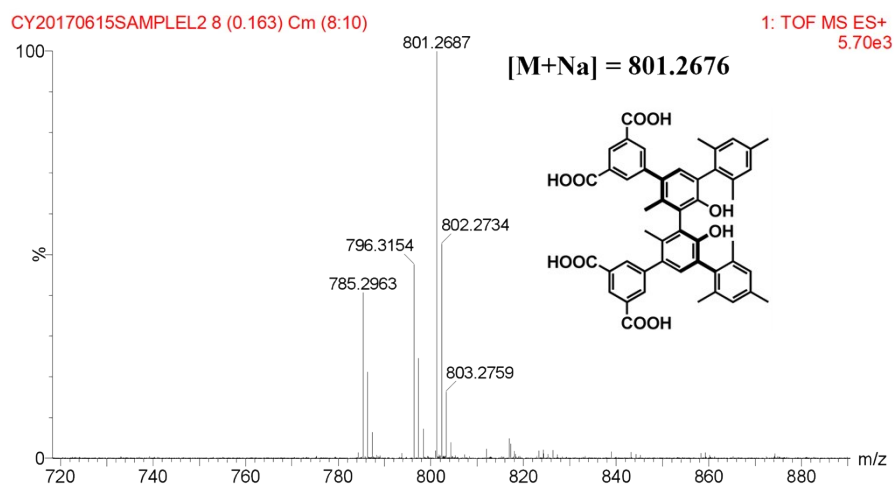








16. Figure S9. ESI-MS spectra



17. References

- (1) K. Mo, Y. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746-1749.
- (2) X. Chen, H. Jiang, B. Hou, W. Gong, Y. Liu and Y. Cui, *J. Am. Chem. Soc.*, 2017, **139**, 13476-13482.