Supporting Information

Chiral emissive porous organic cages

Yu-Ling Sun, [a] Zhen Wang, [a, b] Hui Ma, [a] Qing-Pu Zhang, [a] Bin-Bin Yang, [a] Xianggao Meng, [c] * Yaohua Zhang, [d] * and Chun Zhang[a] *

a. College of Life Science and Technology, National Engineering Research Center for Nanomedicine, Huazhong University of Science and Technology, Wuhan, 430074, China.

b. Technology Institute, National Engineering Laboratory for Advanced Yarn and Fabric Formation and Clean Production, Wuhan Textile University, Wuhan, Hubei 430200, China.

c. College of Chemistry, Central China Normal University, Wuhan 430079, China.

d. Technology R&D Center, Hubei Tobacco (Group) Co., Ltd., Wuhan, 430070, China.

*Corresponding Author(s): Chun Zhang: chunzhang@hust.edu.cn ; Xianggao Meng: mengxianggao@ccnu.edu.cn; Yaohua Zhang: zhangyh@hbtobacco.cn

Table of Contents

General information, Experimental details 1
FT-IR , NMR and TG analyse 3
X-ray crystallographic data 10
UV-vis, and Fluorescence spectra 12
Pore size distribution calculated of 3P-1 and 3M-1 14
Chiral resolution of mandelic acid 15
Chiral resolution of 1-naphthaleneethanol 16
Chiral resolution of 1,1'-Bi-2-naphthol 17

1. General information.

4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)-tetrabenzaldehyde (ETTBA), (*R, R*)- or (*S, S*)-diaminocyclohexane (CHDA) and reagents were of AR grade quality, which were purchased from commercial sources and used without further purification unless otherwise noted. ^{1}H NMR spectra were recorded on a DMX600 NMR.^{1}H chemical shifts were determined using residual signals of the deuterated solvents or using TMS as the internal standard, and were reported in parts per million (ppm). All spectra used for characterization were obtained using deuterated chloroform as the solvent. The terms s., d., t., q., and m. indicate singlet, doublet, triplet, quartet, and multiplet, respectively; dd is doublet of doublets; dt is doublet of triplets. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker model VERTEX 70 infrared spectrometer. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. UV spectra were recorded on SHIMADZU UV-2041PC spectrometer at 20 °C in a 1 cm quartz cell. Emission spectra were obtained on HITACHI F-4500 spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectrometer at 20 °C in a 1 cm quartz cell. circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-300 spectrometer.

2. Experimental details

Synthesis of 3*P*- 1 or 3*M*- 1.

To a stirred solution of 4, 4', 4'', 4'''-(ethene-1,1,2,2-tetrayl)-tetrabenzaldehyde (ETTBA) (300 mg, 0.67 mmol, 1 eq.) and (*R, R*)- or (*S, S*)-cyclohexane-1,2-diamine (CHDA) (153 mg, 1.34 mmol, 2 eq.) in

chloroform (100 mL), 2μL TFA were added[1]. The reaction was stirred at RT for 3d. The mixture was concentrated in vacuo to ~2 mL, methanol (~100 mL) was added with stirring and the resulting precipitate was collected by filtration, affording yellow solid (334.0 mg, 83% for the **3*P*- 1**, 366.2 mg, 91% for the **3*M*- 1**).

3*P*- 1: ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.85 (s, 6H), 7.78 (s, 6H), 7.35 (d, J = 7.1 Hz, 12H), 7.02 (d, J = 6.18 Hz, 12H), 7.00 (d, J = 7.38 Hz, 12H), 6.94 (d, J = 7.8 Hz, 12H), 3.31 (s, 6H), 3.16 (s, 6H), 2.29 – 1.62 (m, 48H). HRMS: m/z calcd. for $C_{126}H_{120}N_{12}$ $[M+H]^+$ 1801.9792, found 1801.9821.

3*M*- 1: ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.85 (s, 6H), 7.78 (s, 6H), 7.35 (d, J = 5.82 Hz, 12H), 7.02 (d, J = 7.68 Hz, 12H), 7.00 (d, J = 7.80 Hz, 12H), 6.94 (d, J = 7.7 Hz, 12H), 3.31 (s, 6H), 3.16 (s, 6H), 2.25 – 1.64 (m, 48H). HRMS: m/z calcd. for $C_{126}H_{120}N_{12}$ $[M+H]^+$ 1801.9792, found 1801.9819.

3. FT-IR, NMR and TG analyses

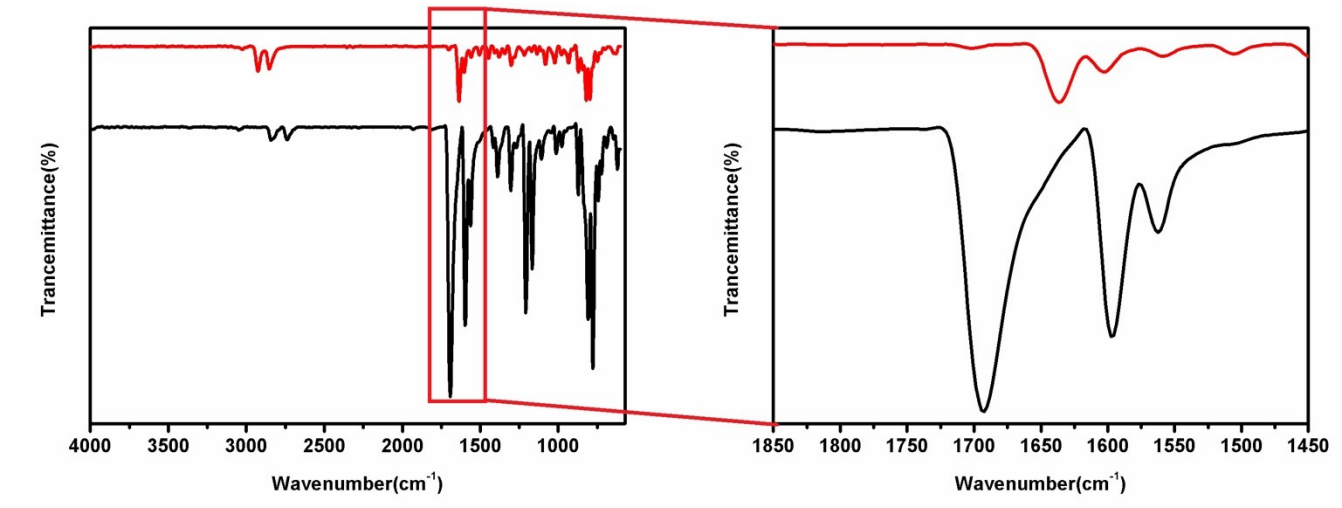


Figure S1. FT-IR deta for **3*P*-1** and **ETTBA**. (red for **3*P*-1**, black for **ETTBA**)

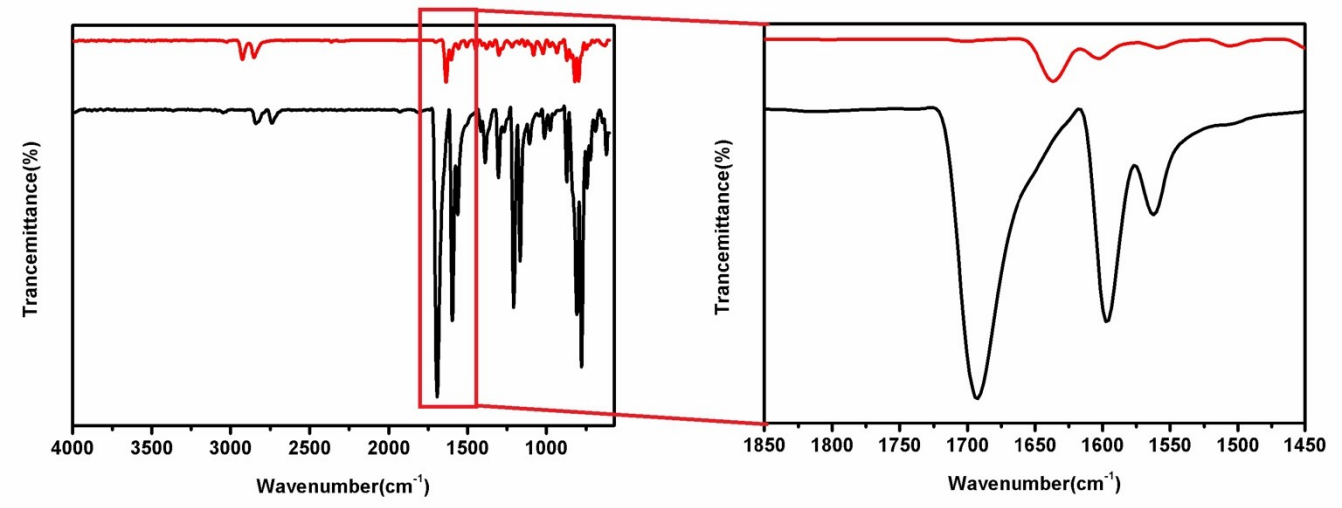


Figure S2. FT-IR deta for **3*M*-1** and **ETTBA**. (red for **3*M*-1**, black for **ETTBA**)

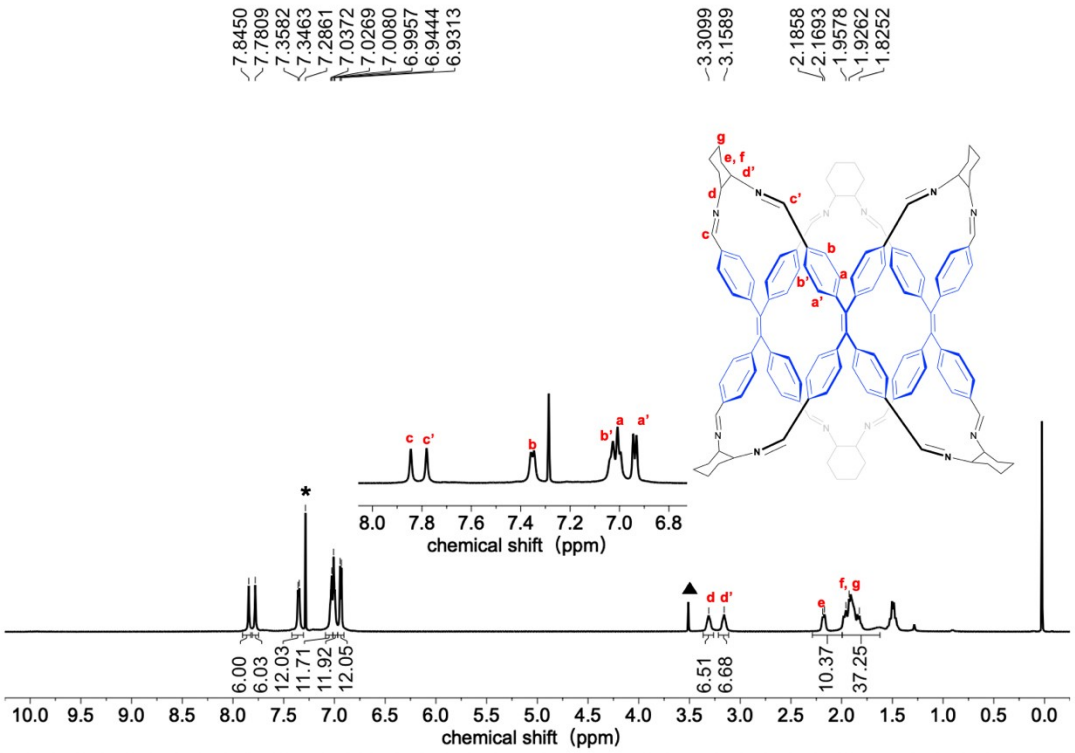


Figure S3. ^{1}H NMR ($CDCl_3$) spectrum of ***3P*- 1**. (* chloroform; ▲ methanol)

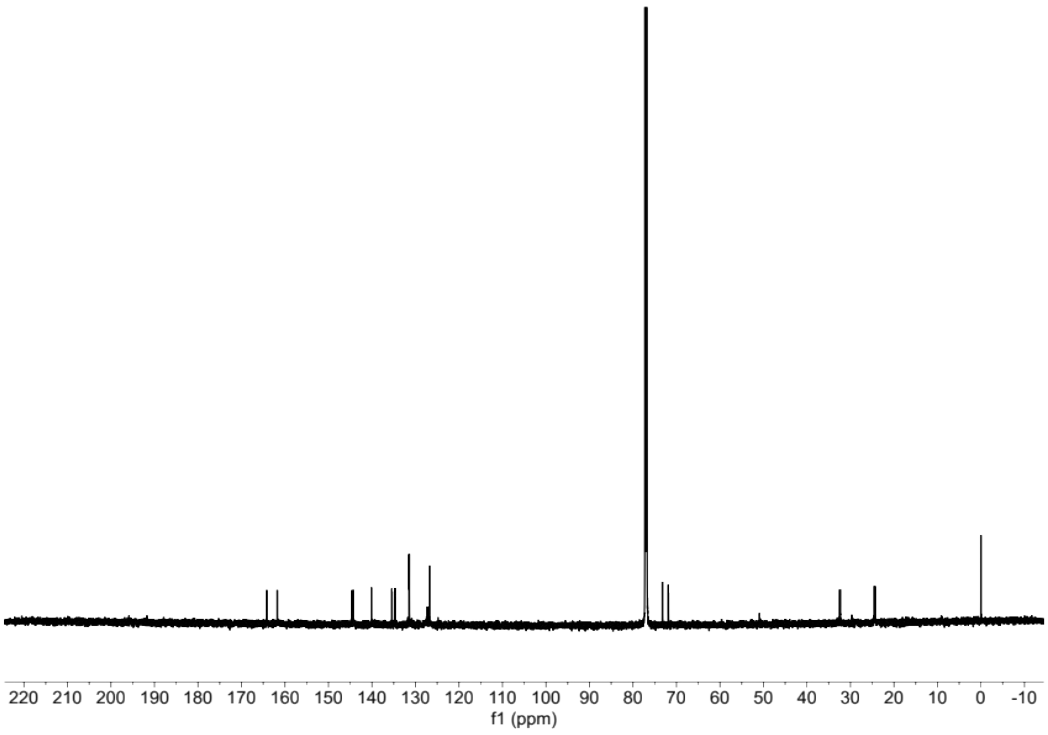


Figure S4. ^{13}C NMR ($CDCl_3$) spectrum of ***3P*- 1**.

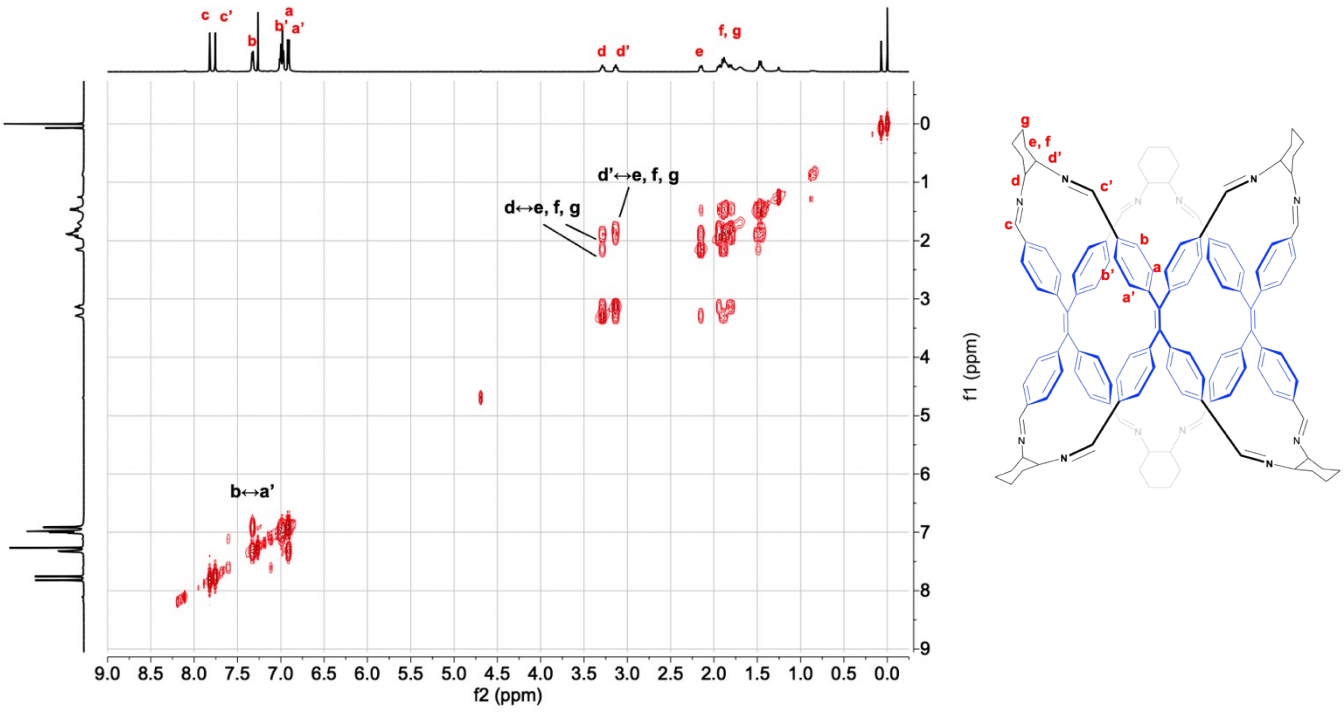


Figure S5. ^{1}H-^{1}H COSY NMR ($CDCl_3$) spectrum of ***3P-* 1**.

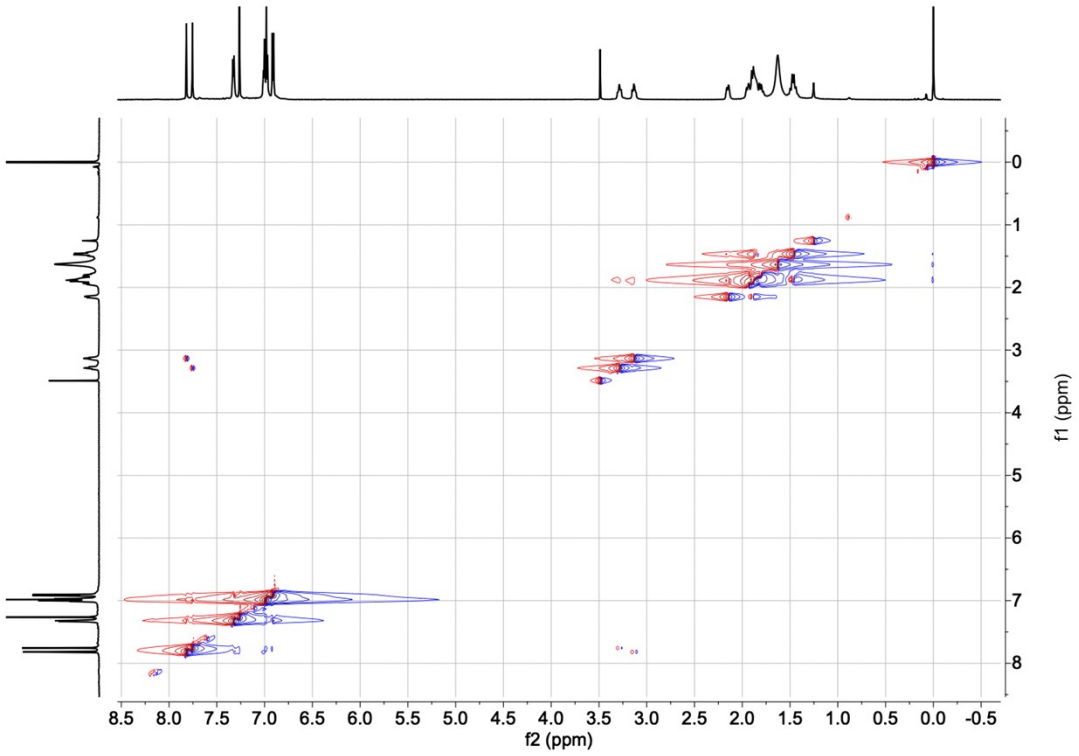


Figure S6. ^{1}H-^{1}H NOESY NMR ($CDCl_3$) spectrum of ***3P-* 1**.

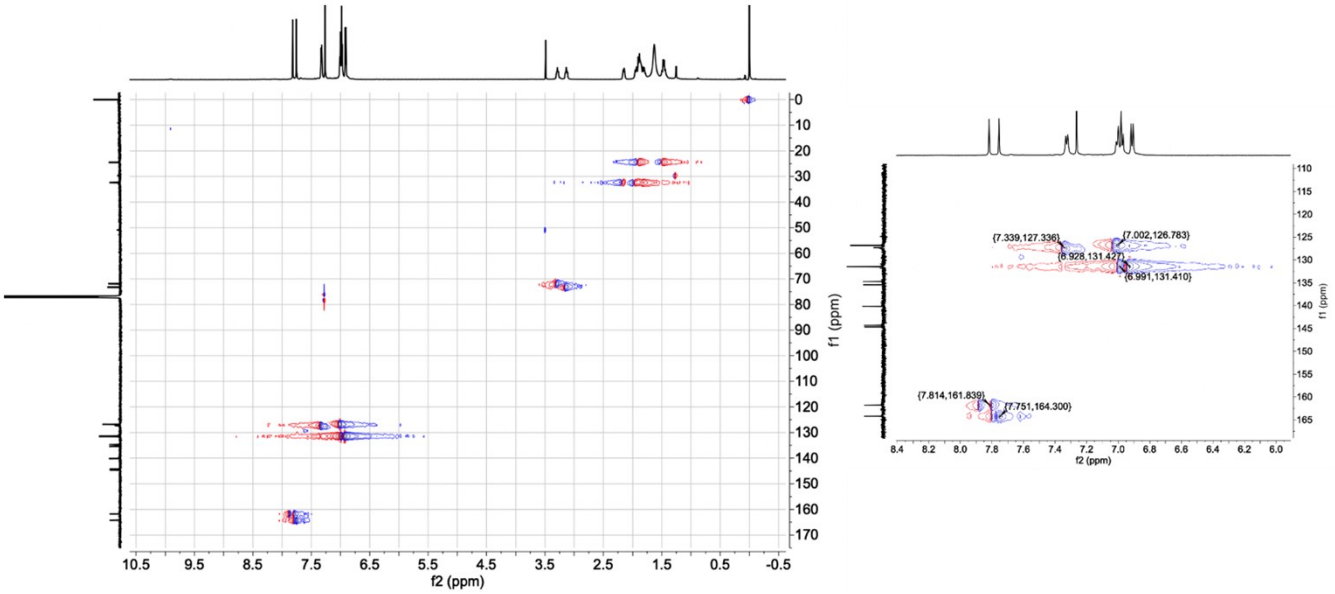


Figure S7. ^{13}C-^{1}H HSQC NMR ($CDCl_3$) spectrum of **3*P*- 1**.

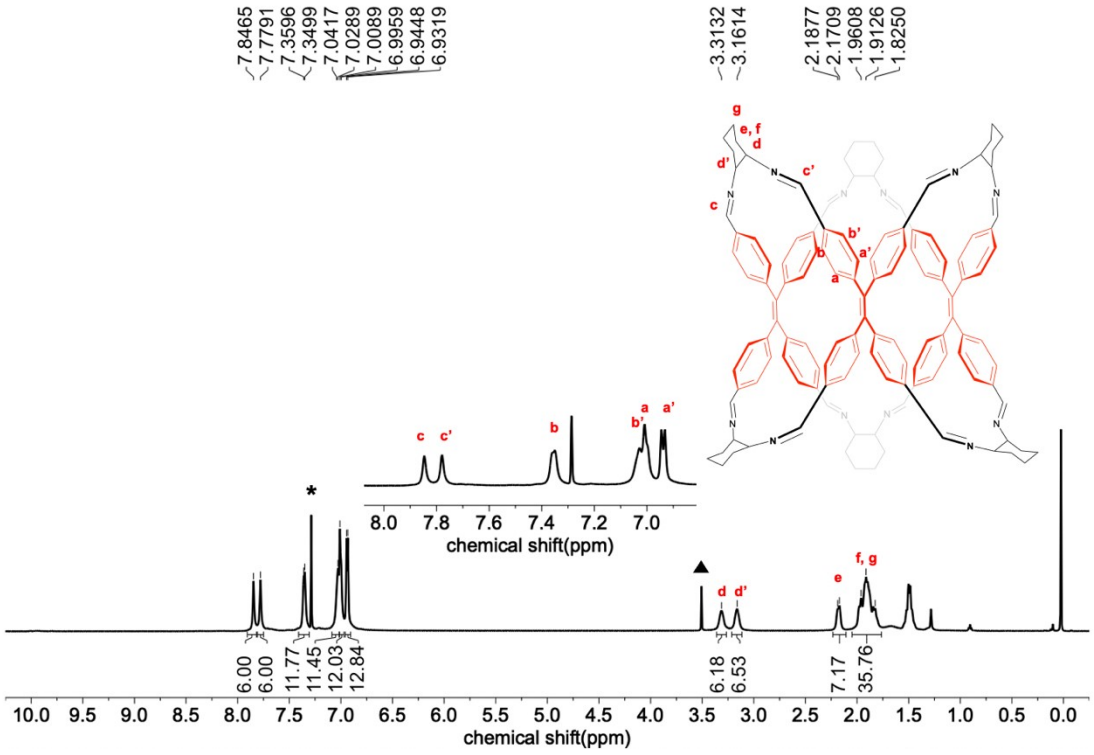


Figure S8. ^{1}H NMR ($CDCl_3$) spectrum of **3*M*- 1**. (* chloroform; ▲ methanol)

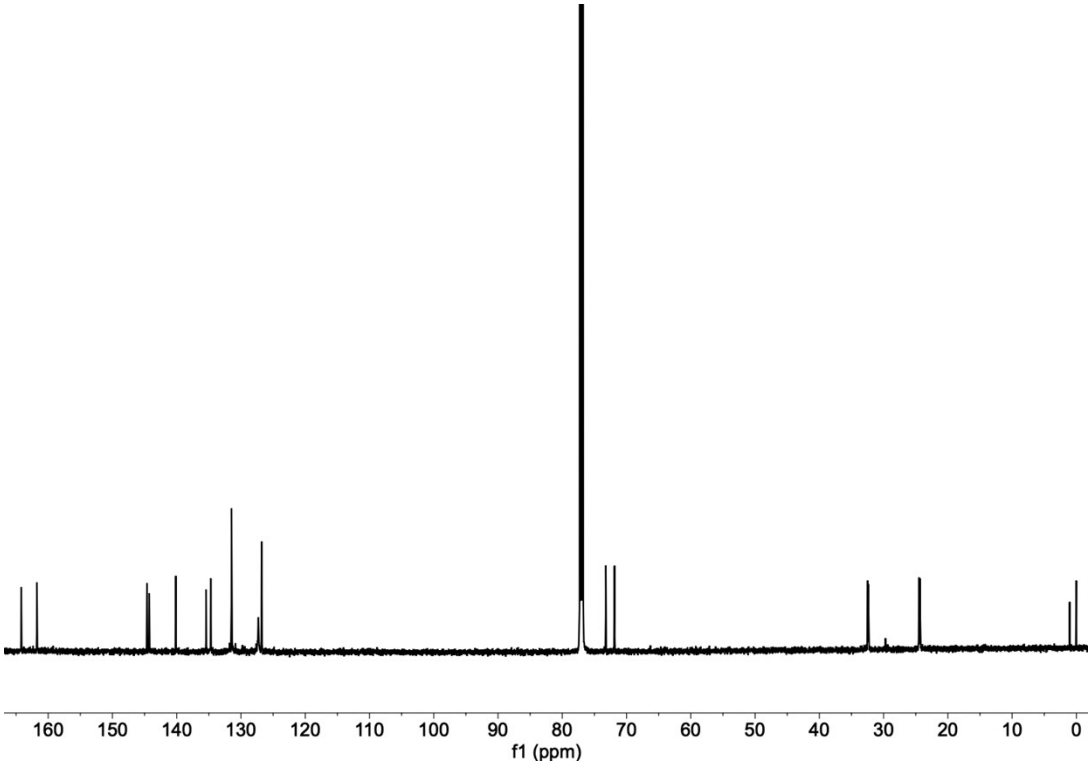


Figure S9. ^{13}C NMR ($CDCl_3$) spectrum of **3*M*- 1**.

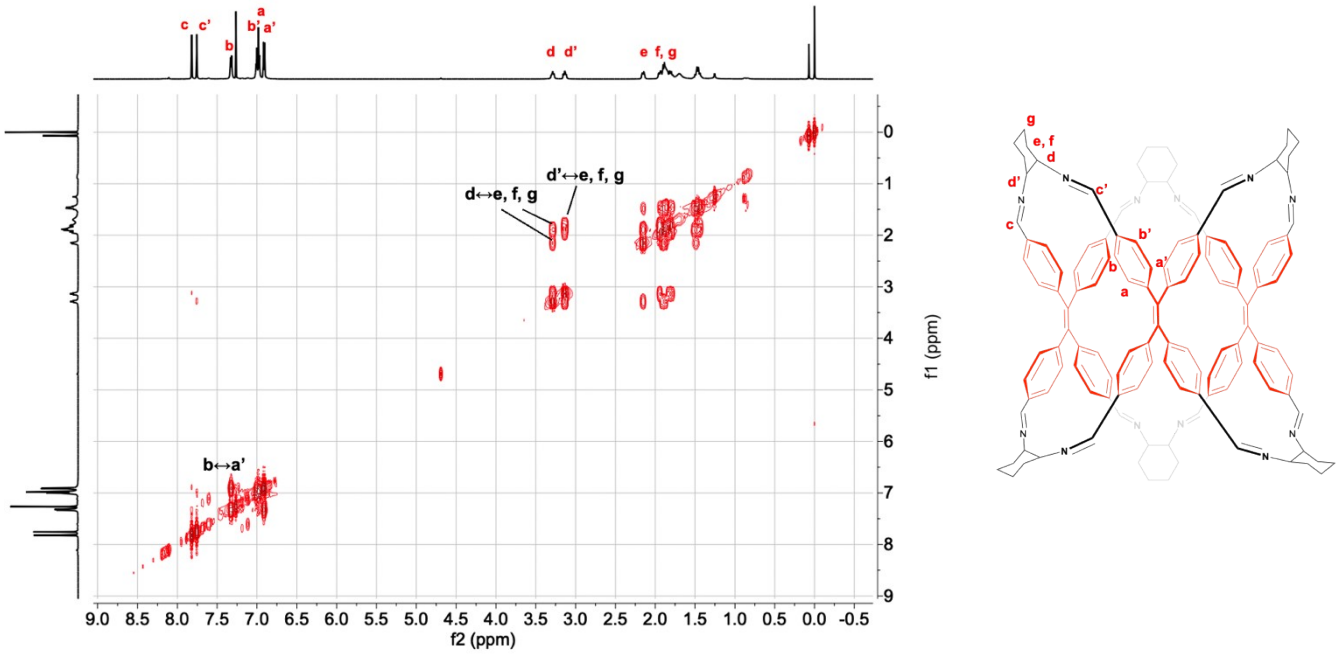


Figure S10. ^{1}H-^{1}H COSY NMR ($CDCl_3$) spectrum of **3*M*- 1**.

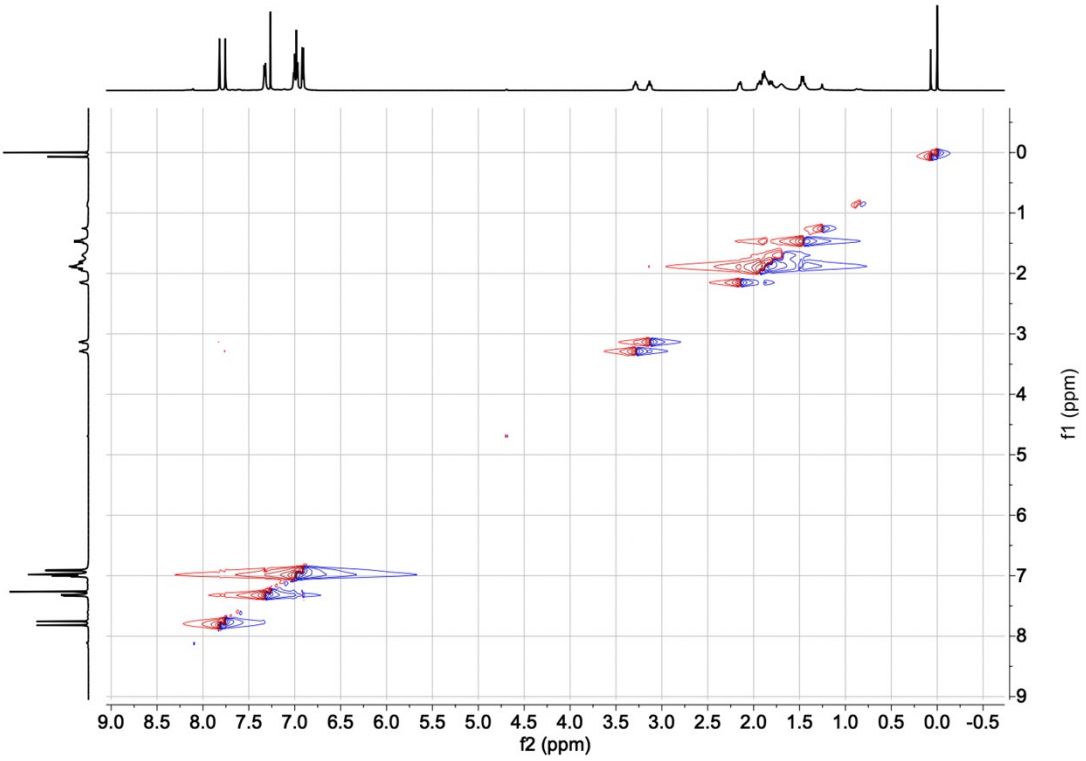


Figure S11. ^{1}H-^{1}H NOESY NMR ($CDCl_3$) spectrum of **3*M*- 1**.

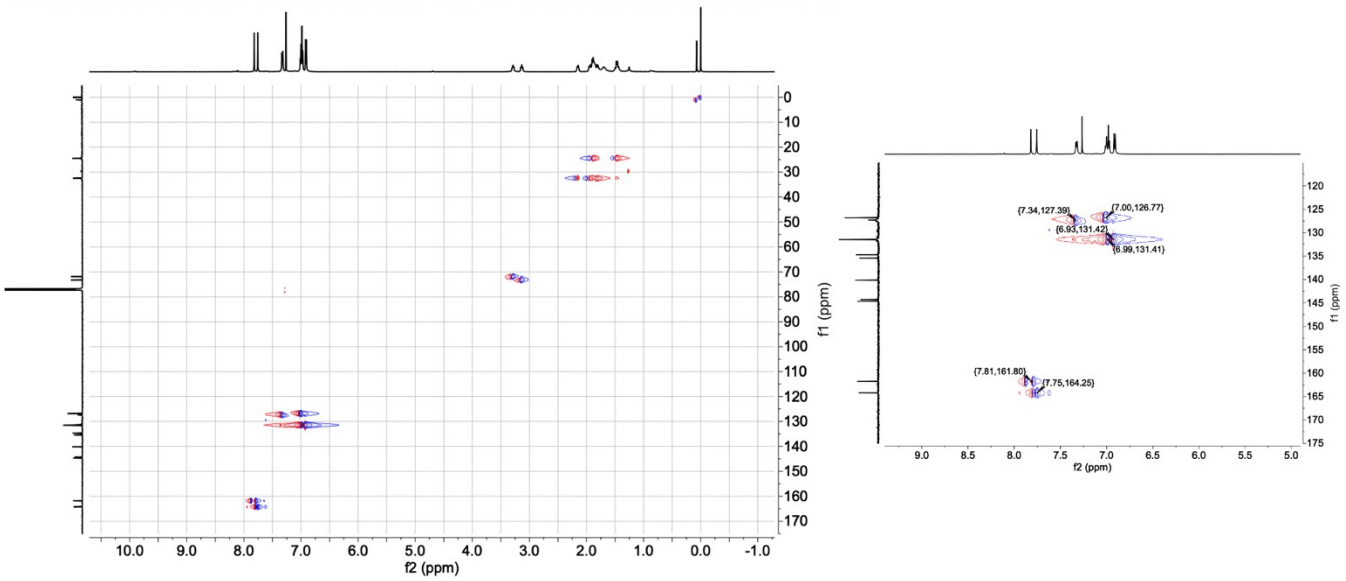


Figure S12. ^{13}C-^{1}H HSQC NMR ($CDCl_3$) spectrum of **3*M*- 1**.

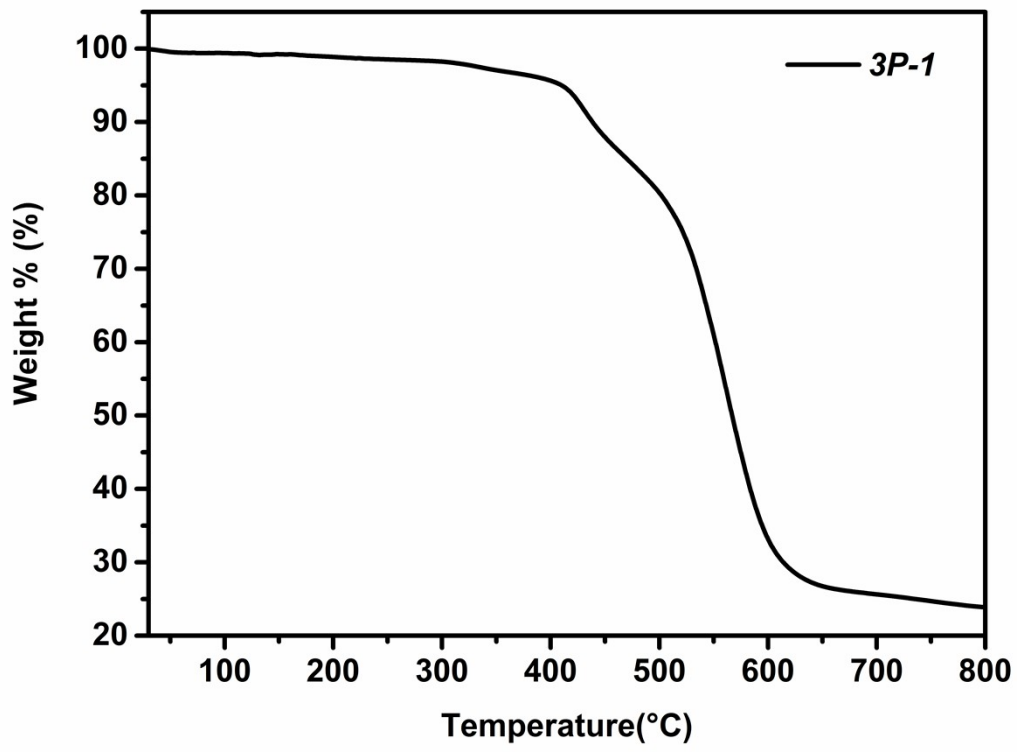


Figure S13. Thermal gravimetric analysis(TGA) of 3P-1.

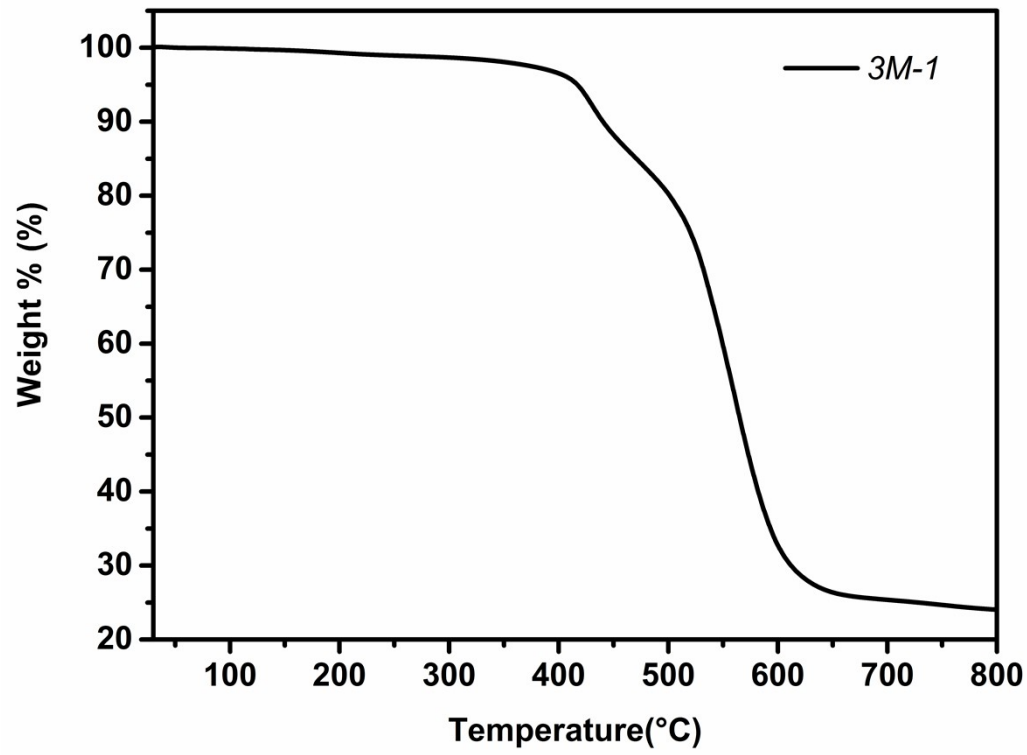


Figure S14. Thermal gravimetric analysis(TGA) of 3M-1.

4. X-ray crystallographic data

The X-ray intensity data for **3*P*-1** and **3*M*-1** were collected on a standard Bruker SMART-1000 CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator. The structures were solved by using direct methods and were refined by employing full-matrix least-squares cycles on F2 (Bruker, SHELXTL-97).

Crystallographic data for **3*P*-1**: *Mr* = 1286.48, Cubic, Space group *P23*, a = 24.8853(2) Å, b = 24.8853(2) Å, c = 24.8853(2) Å, α = 90°, β = 90°, γ = 90°, V = 15410.9(4) Å^3, Z = 6, $\rho_{calcd.}$ = 0.832 g/cm^3, μ = 0.839 mm^{-1}, reflections collected 83118, data/restraints/parameters 10373/10/439, GOF on F^2 1.011, final R_1 = 0.0617, wR_2 = 0.1790, R indices (all data): R_1 = 0.0817, wR_2 = 0.1997, largest diff. peak and hole: 0.40/-0.45 e/Å^{-3}, CCDC - 2077306.

Crystallographic data for **3*M*-1**: *Mr* = 1286.48, Cubic, Space group *P23*, a = 24.96801(9) Å, b = 24.96801(9) Å, c = 24.96801(9) Å, α = 90°, β = 90°, γ = 90°, V = 15565.10(17) Å^3, Z = 6, $\rho_{calcd.}$ = 0.823 g/cm^3, μ = 0.831 mm^{-1}, reflections collected 106403, data/restraints/parameters 10506/295/438, GOF on F^2 1.068, final R_1 = 0.0475, wR_2 = 0.1561, R indices (all data): R_1 = 0.0510, wR_2 = 0.1608, largest diff. peak and hole: 0.20/-0.43 e/Å^{-3}, CCDC - 2077307.

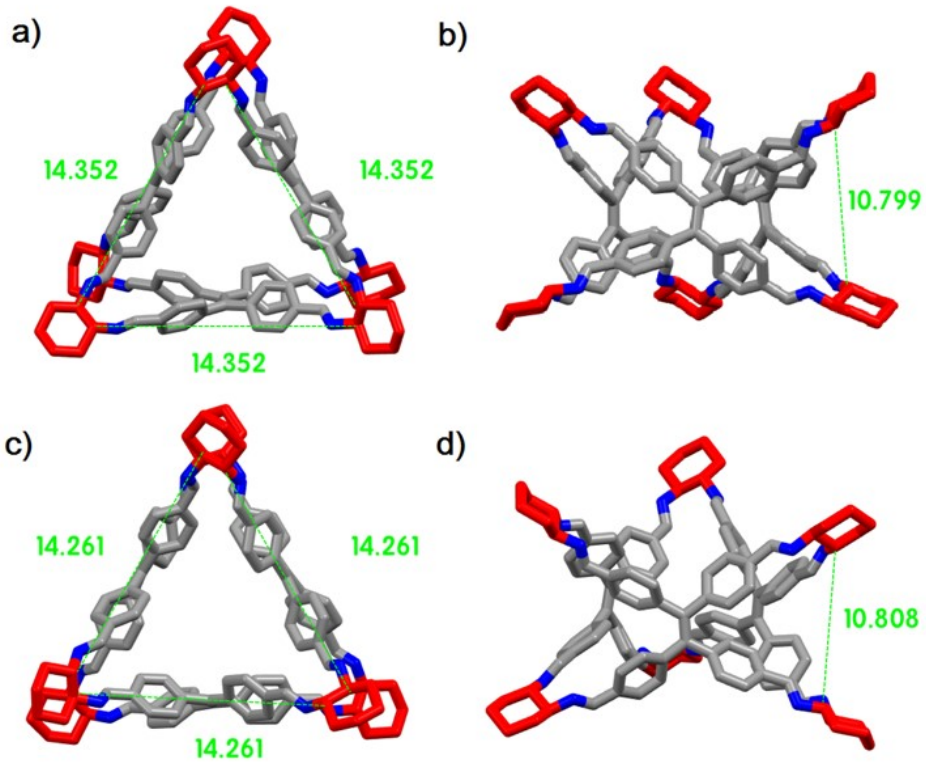


Figure S15. a) Top view and b) side view of the X-ray crystal structure of **3*P*-1**. c) Top view and d) side view of the X-ray crystal structure of **3*M*-1**. Hydrogen atoms and solvent molecule were omitted for clarity.

5. UV-vis, and Fluorescence spectra

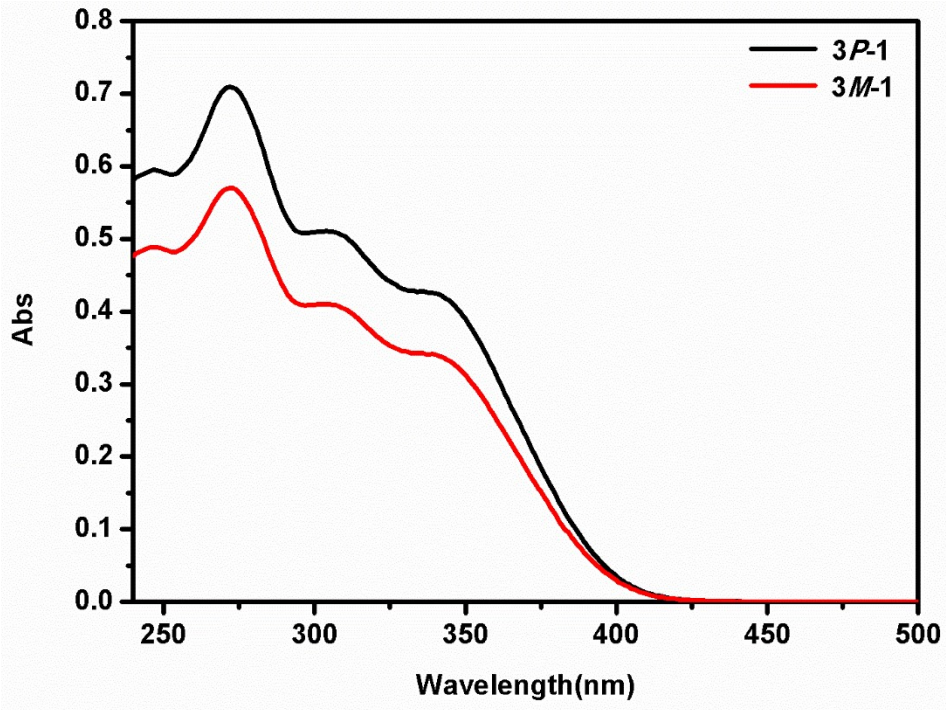


Figure S16. UV-vis spectra of **3*M*-1** and **3*P*-1** (solvent: CH_2Cl_2, c = 1×10^{-6} mol·L^{-1}).

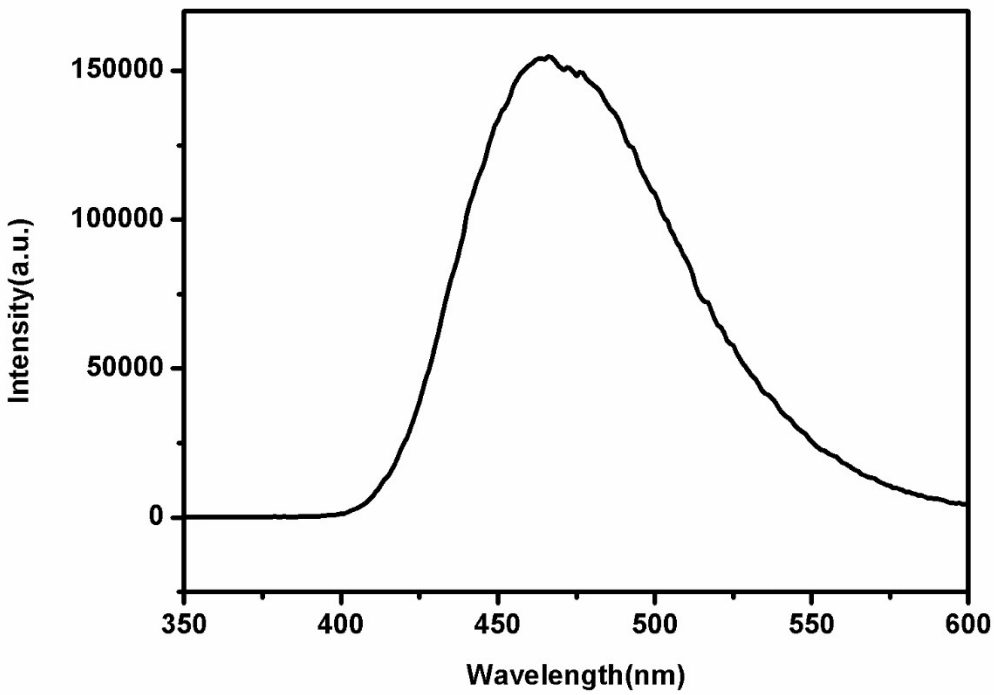


Figure S17. Fluorescence spectrum of ***3M*-1** in CH_2Cl_2, excited at 340 nm.

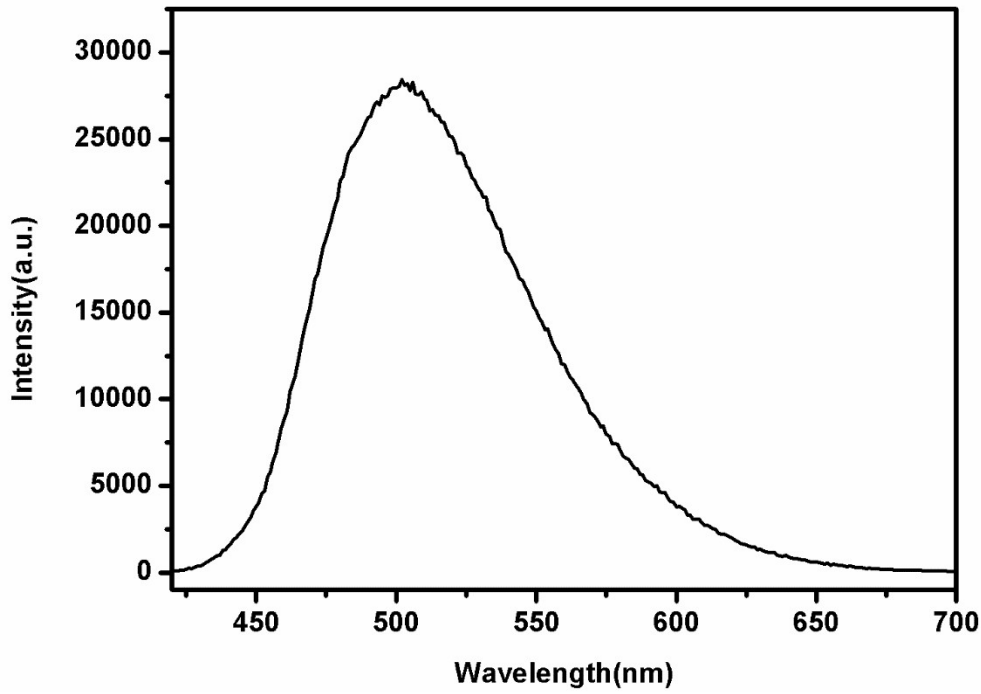


Figure S18. Fluorescence spectrum of ***3M*-1** in the solid state, excited at 398 nm.

6. Pore size distribution calculated of 3*P*-1 and 3*M*-1

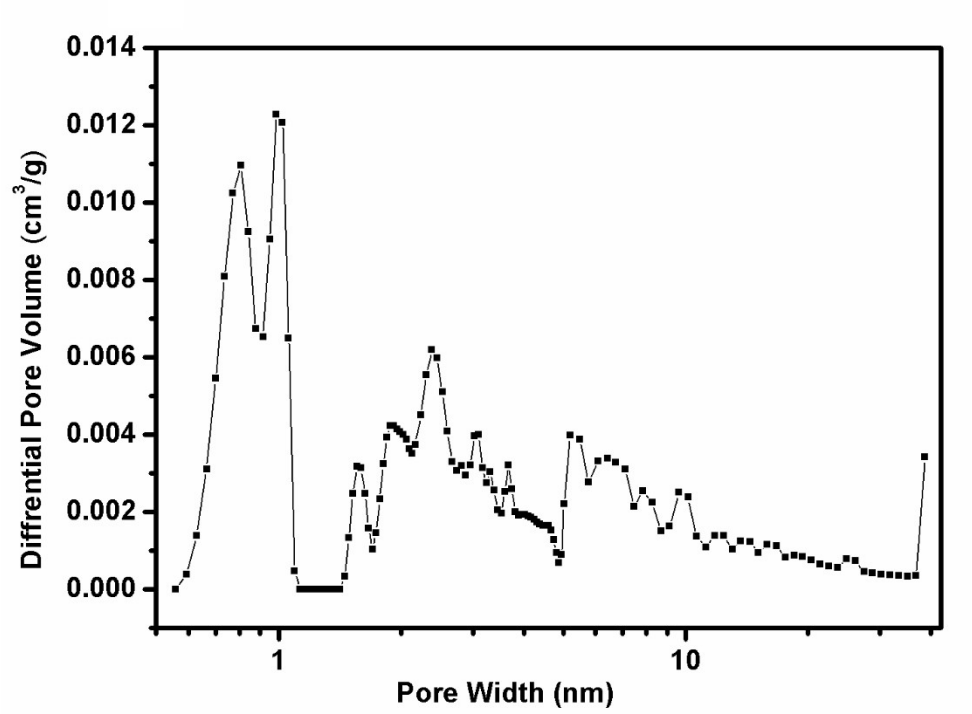


Figure S19. Pore size distributions of **3*P*-1** calculated using the NLDFT method.

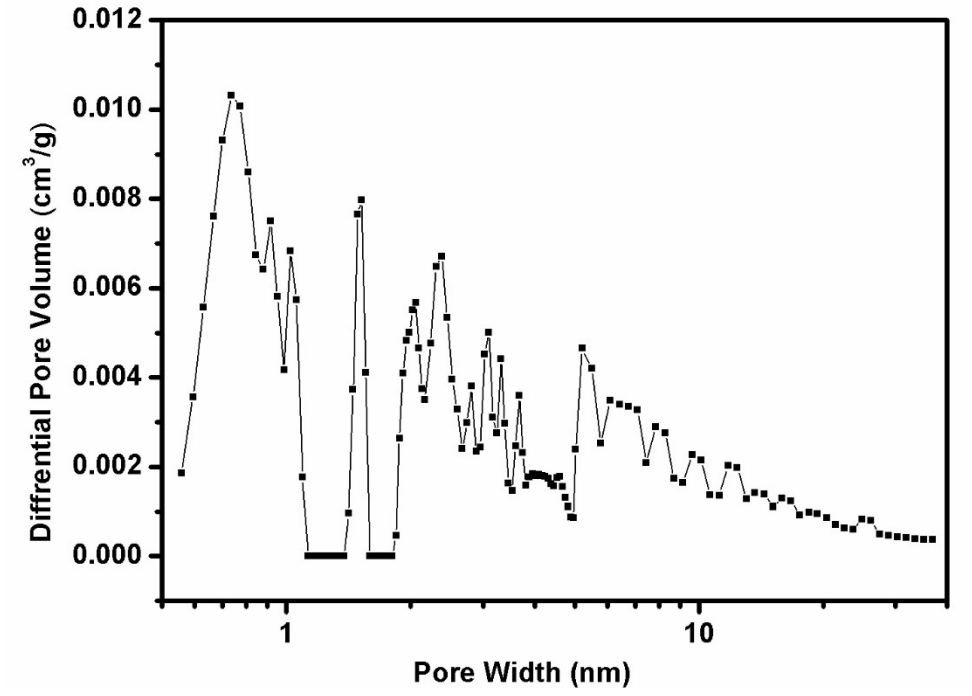


Figure S20. Pore size distributions of **3*M*-1** calculated using the NLDFT method.

7. Chiral resolution by 3*P*-1 and 3*M*-1

Chiral resolution of mandelic acid 3

18 mg of cage compound **3*P*-1** (0.01 mmol) was added into a solution of racemic mandelic acid **3** (4.56 mg, 0.03 mmol, in 3 mL of isopropanol). The mixture was sonicated for one minute and kept at room temperature for 24 hours with stirring. The suspension was filtered and washed with isopropanol, and then the solid was extracted with methanol (3 mL × 2) to get the encapsulated guest molecules out. The solution was centrifuged(1 × 10^4 r/min, 10 min, 2 times) and concentrated to ~1ml, followed by the determination of *ee* value by chiral HPLC using a Daicel CHIRALCEL. AD-H column with specified conditions (Table S1). Resolution of mandelic acid **3** by cage compound **3*M*-1** was done following the same procedure as that of cage compound **3*P*-1**.[2]

Table S1. Chiral HPLC condition for the resolution of **3**

Column	CHIRALPAK®ADHOCE-RK014
Column size	0.46 cm I.D. ×25 cm L ×5 μm
Injection	30μl
Mobile phase	n-Hexane/ IPA/Trifluoroacetic acid= 95/5/ 0.1(v/v/v)
Flow rate	1.0ml/min
Wave length	UV 220 nm
Temperature	35℃

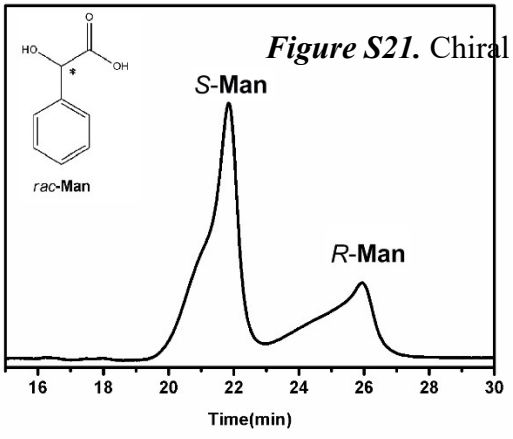


Figure S21. Chiral HPLC data for the resolution of **3** by **3*P*-1**.

Peak No.	Time	Area	Area %
1	21.387	1533568	57.2063
2	24.984	1147198	42.7937

Peak No.	Time	Area	Area %
1	20.071	650580	36.981

2	23.451	1108670	63.019

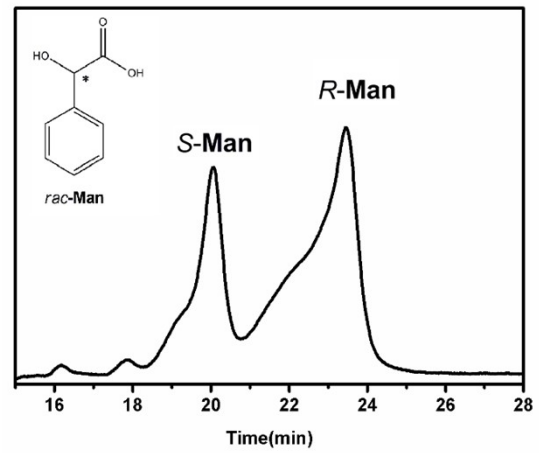


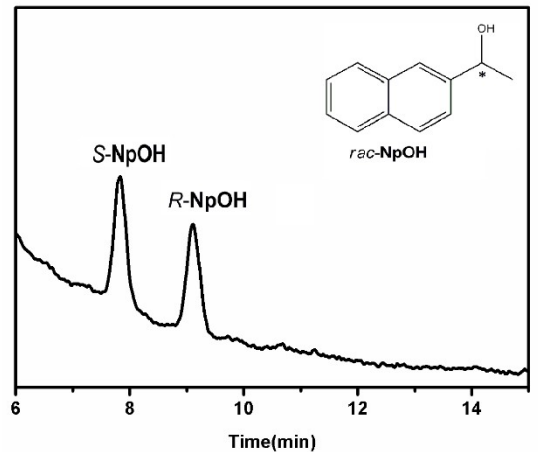
Figure S22. Chiral HPLC data for the resolution of **3** by **3*M*-1**.

Chiral resolution of 1-naphthaleneethanol 4

18 mg of cage compound **3*P*-1** (0.01 mmol) was added into a solution of racemic 1-naphthaleneethanol **4** (5.17 mg, 0.03 mmol, in 3 mL of isopropanol). The mixture was sonicated for one minute and kept at room temperature for 24 hours with stirring. The suspension was filtered and washed with isopropanol, and then the solid was extracted with methanol (3 mL × 2) to get the encapsulated guest molecules out. The solution was centrifuged(1×10^4 r/min, 10 min, 2 times) and concentrated to ~1ml, followed by the determination of *ee* value by chiral HPLC using a Daicel CHIRALCEL. OJ-H column with specified conditions (Table S2). Resolution of 1-naphthaleneethanol **4** by cage compound **3*M*-1** was done following the same procedure as that of cage compound **3*P*-1**.[2]

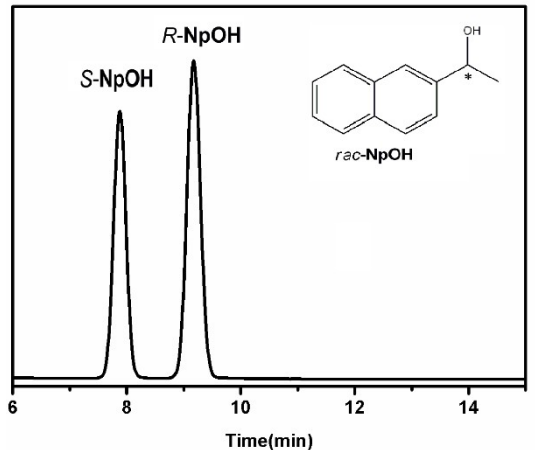
Table S2. Chiral HPLC condition for the resolution of **4**.

Column	CHIRALCEL®OJH0CE-NJ031
Column size	0.46 cm I.D. ×25 cm L ×5μm
Injection	50μl
Mobile phase	n-Hexane/Ethanol/Diethylamine=80/20/0.1(v/v/v)
Flow rate	1.0ml/min
Wave length	UV 274nm
Temperature	35℃



Peak No.	Time	Area	Area %
1	7.824	29576	63.6438
2	9.103	16895	36.3562

Figure S23. Chiral HPLC data for the resolution of **4** by **3*P*-1**.



Peak No.	Time	Area	Area %
1	7.875	1219727	43.4164
2	9.171	1589643	56.5836

Figure S24. Chiral HPLC data for the resolution of **4** by **3*M*-1**.

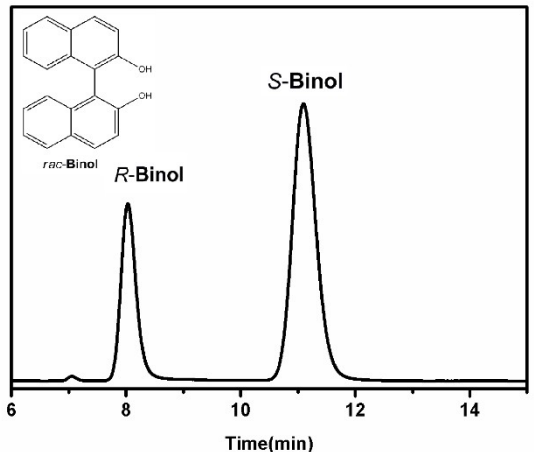
Chiral resolution of 1,1'-Bi-2-naphthol 5

18 mg of cage compound **3*P*-1** (0.01 mmol) was added into a solution of racemic 1,1'-Bi-2-naphthol **5** (8.49 mg, 0.03 mmol, in 3 mL of isopropanol). The mixture was sonicated for one minute and kept at room temperature for 24 hours with stirring. The suspension was filtered and washed with isopropanol, and then the solid was extracted with methanol (3 mL × 2) to get the encapsulated guest molecules out. The solution was centrifuged(1×10^4 r/min, 10 min, 2 times) and concentrated to ~1ml, followed by the determination of *ee* value by chiral HPLC using a Daicel CHIRALCEL. OJ-H column with specified

conditions (Table S3). As for the recyclability of cage's separation capabilities, we repeated the above steps for three consecutive times and measured the separation ability of ***3P-1*** to **5**. Resolution of 1,1'-Bi-2-naphthol **5** by cage compound **3*M*-1** was done following the same procedure as that of cage compound **3*P*-1**.[2]

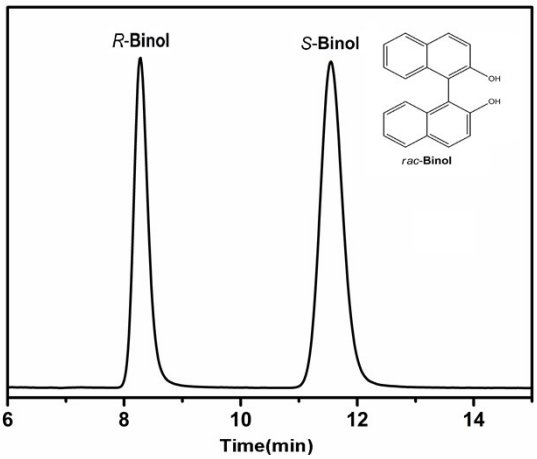
Table S3. Chiral HPLC condition for the resolution of **5**.

Column	CHIRALCEL®OJH0CE-UF035
Column size	0.46 cm I.D. ×25 cm L ×5 μm
Injection	20μl
Mobile phase	n-Hexane/Isopropanol=70/30(v/v)
Flow rate	1.0ml/min
Wave length	UV 220nm
Temperature	35℃



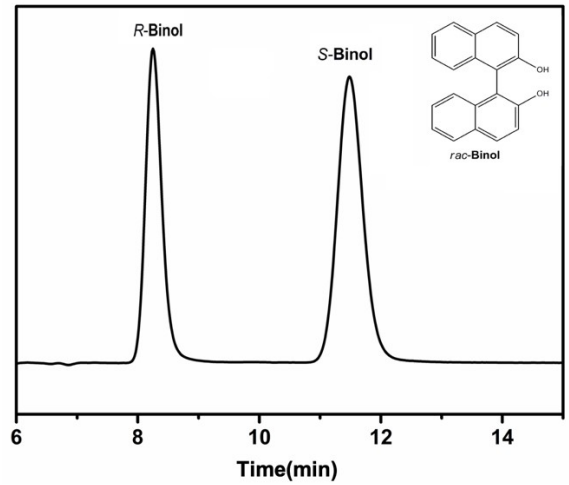
Peak No.	Time	Area	Area %
1	8.031	3153899	29.280
2	11.095	7617604	70.720

Figure S25. Chiral HPLC data for the resolution of **5** by **3*P*-1**(the first time).



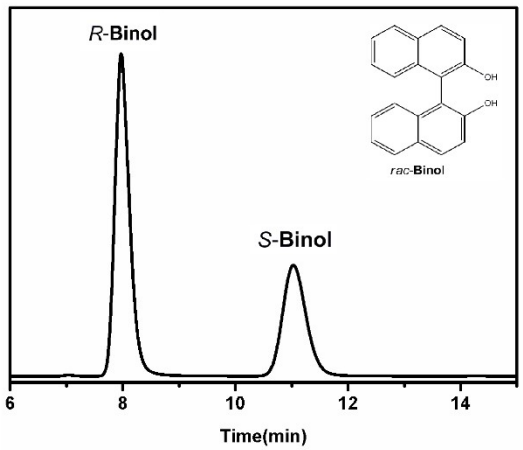
Peak No.	Time	Area	Area %
1	8.269	1805810	38.841
2	11.538	2853378	61.159

Figure S26. Chiral HPLC data for the resolution of **5** by **3*P*-1**(the second time).



Peak No.	Time	Area	Area %
1	8.242	2291811	40.9428
2	11.475	3305781	59.0572

Figure S27. Chiral HPLC data for the resolution of **5** by **3*P*-1**(the third time).



Peak No.	Time	Area	Area %
1	7.970	47747750	64.256
2	11.029	26560510	35.744

Figure S28. Chiral HPLC data for the resolution of **5** by **3*M*-1**.

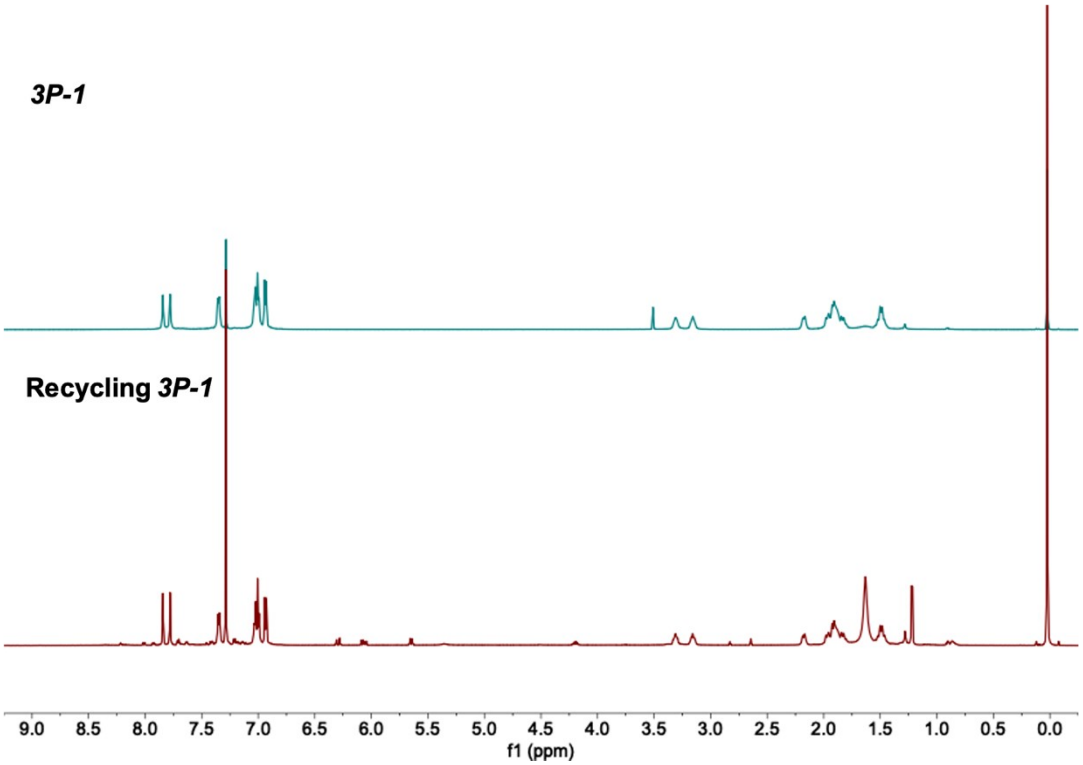


Figure S29.^{1}H NMR ($CDCl_3$) spectrum of ***3P-* 1** and recycling ***3P-1***

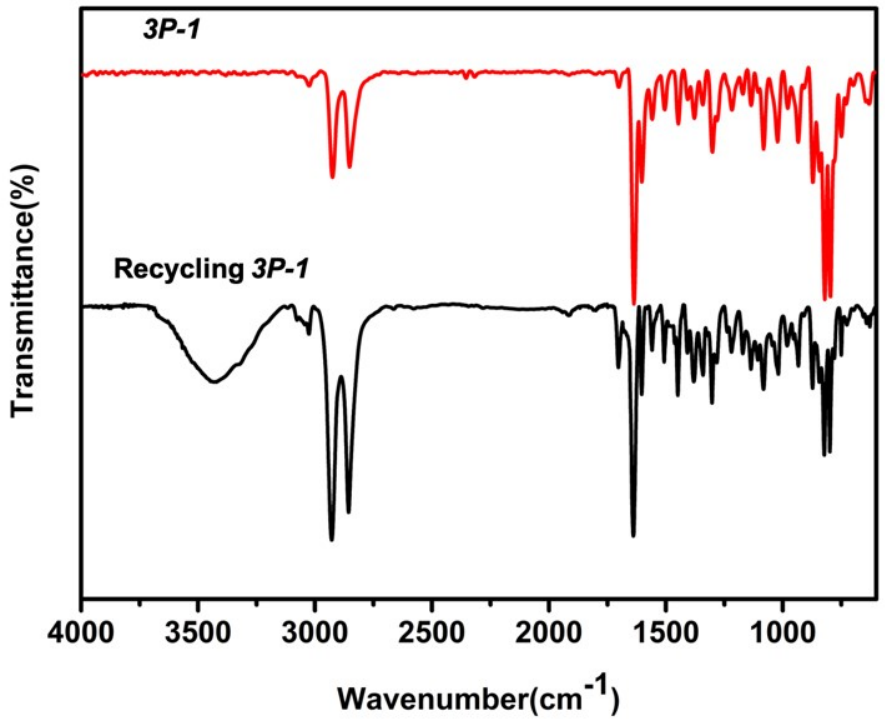


Figure S30.FT-IR spectrum of ***3P-* 1** and recycling ***3P-1***

References

1. Qu, H.; Wang, Y.; Li, Z.; Wang, X.; Fang, H.; Tian, Z.; Cao, X. Molecular Face-Rotating Cube with Emergent Chiral and Fluorescence Properties. *J. Am. Chem. Soc.* **2017**, *139,* 18142–18145.

2. Malik, A U.; Gan, F.; Shen, C.; Yu, N.; Wang, R.; Crassous, J.; Shu, M.; Qiu, H. Chiral Organic Cages with a Triple-Stranded Helical Structure Derived from Helicene. *J. Am. Chem. Soc.* **2018**, *140*, 2769−2772.