Supporting information

Construction of pillar[5]arene-based supramolecular chiral polymer linked to aminophosphine salt for chiral recognition of enantiomers of mandelic acid

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Contents

S1 Experimental Section

1.1 General

The infrared spectra (KBr particle method) were recorded on the Nicolet is 50 FT-IR spectrometer (Thermo Scientific Co., Ltd., Madison, WI, USA). ^{1}H NMR, ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on Bruker avance III HD 600 MHz spectrometer (Bruker Ltd., Zurich, Switzerland). The chemical shifts were expressed in ppm (δ) relative to TMS as internal standard. Other reagents were purchased from commercial suppliers and used as received. The mass spectra were recorded on a TSQ Quantum Access MAX HPLC-MS instrument (Thermo Scientific Co., Ltd., Waltham, MA, USA). Melting points were determined on a MP420 automatic melting point apparatus (Hanon Instruments Co., Ltd., Jinan, China), and were not corrected. SEM was recorded on scanning electron microscope (TESCAN MIRA LMS, Czech) . Other reagents were purchased from commercial suppliers and used as received.

1.2 Determination of association constants

UV titrations were done with solutions which had a constant concentration of host (0.01 mM) and varying concentrations of guest. By the linear curve-fitting methods, the association constants for S-MA and R-MA complexes in $CHCl_3$ were determined to be 6.5×10^4 M^{-1} and 4.51×10^5 M^{-1} (the complexation ratio of the host ***L*-TPP-P** (pillar[5]arene monomer as a reference) and the guest **MA** was 0.05，0.1，0.2，0.3，0.4，0.5，0.7，0.9，1.0，2.5，4，5，7.5，10，15，20，25).

$P=\Delta A/\Delta A_0$ is the abscissa and $P/[G_N]*10\text{^}5$ is the ordinate, and the slope is Ka where $[G_0]=[H_0]=0.01$mM, A_{H0} is the absorbance of $[H_0]$ and A_{G0} is the absorbance of $[G_0]$.

$\Delta A=A_{obs}-A_{H0}-A_{G0}*([G]/[H])$, $\Delta A_{0=}A_{HG0}-A_{H0}-A_{G0}$, $A_{HG0}= A_{obs}$, ([G]/[H]=25), UV absorbance at 295.5 nm.

1.3 The NMR titration method

Take 5 mg of ***L*-TPP-P** and different amounts of **R-MA** and **S-MA** each time to dissolve in $CDCl_3$, and performed ^{1}H NMR analysis with a 600 MHz NMR machine, and the number of tests and corresponding amounts were shown in Table 3-1.

Table 3-1 ^{1}H NMR (600 MHz, $CDCl_3$, 298K) test numble and quantity of ***L*-TPP-P** and **MA**

Entry	***L*-TPP-P**	**R-MA**	**S-MA**	ee%(R%-S%/R%+S%)
a	1equiv	0	0	0
b	0	0.5equiv	0.5equiv	0
c	1equiv	0.5equiv	0	100%
d	1equiv	0.5equiv	0.1equiv	66.67%
e	1equiv	0.5equiv	0.2equiv	42.86%
f	1equiv	0.5equiv	0.3equiv	25%
g	1equiv	0.5equiv	0.5equiv	0
h	1equiv	0	0.5equiv	-100%
i	1equiv	0.1equiv	0.5equiv	-66.67%
j	1equiv	0.2equiv	0.5equiv	-42.86%
k	1equiv	0.3equiv	0.5equiv	-25%

S2 The synthetic route of of *L*-TPP-P

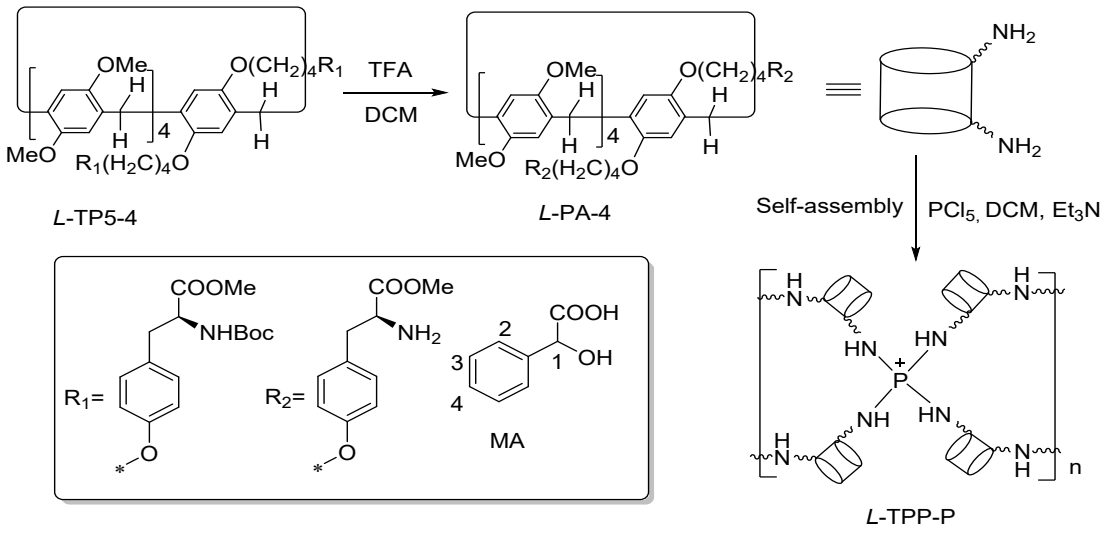
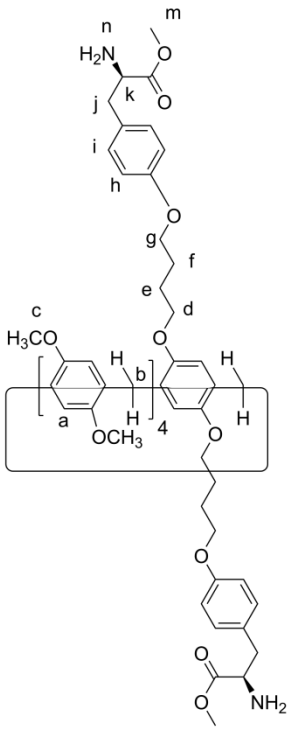


Figure S1. The synthetic route of ***L*-TPP-P**.

2.1 Synthesis of compound *L*-PA-4



L*-TP5-4** (L*-TP5-4** had previously synthesized by our team[1]. 100 mg, 0.071 mmol) was dissolved in 8 mL dichloromethane, trifluoroacetic acid (3 mL) was added , and the reaction time was 1h at 25°C, and TLC was used to follow the reaction. The reacted solution was placed in a dialysis bag with a MWCO of 1000 and water was changed at half hour, four hours and six hours and the reaction was followed by TLC. After drying, ***L*- PA-4** was obtained as a white solid in 76% yield. ***L*-PA-4** melting point: 134.4-141.6°C; $[\alpha]_{L\text{-}PA\text{-}4}$= 36.8400; IR (KBr) cm^{-1}: 3424.05 (N-H), 2937.58, 2851.77 (C–H), 1501.34 (Ar–C=C), 1212.06, 1046.69 (Ar–O, C–O); ^1H NMR (600 MHz, Chloroform-d) δ 9.55 (s, 4H, H-n), 7.09 (d, 4H, H-i), 6.87 – 6.81 (d, 4H, H-h), 6.79 – 6.74 (m, 10H, H-a), 4.00 (t, J = 5.9 Hz, 4H, H-d), 3.92 – 3.87 (t, 6H, H-g, k), 3.77 (s, J = 7.1, 5.9 Hz, 6H, H-m), 3.73 (s, 10H, H-b), 3.64 (s, J = 17.9, 6.0 Hz, 24H, H-c), 3.04 (dd, J = 13.7, 5.2 Hz, 2H, H-j), 2.83 (dd, J = 13.7, 7.7 Hz, 2H, H-j), 1.85 (m, 8H, H-e, f); ^{13}C NMR (151 MHz, Chloroform-*d*) δ168.50, 151.44, 150.27, 140.88, 140.82, 130.24, 128.98, 127.59, 121.07, 119.18, 114.55, 113.62, 67.43, 56.15, 55.57, 51.95, 47.48, 44.24, 43.94, 42.48, 40.68, 40.16, 29.85, 29.81, 29.74, 29.71, 29.67, 29.63, 26.29, 26.08; HRMS (ESI) m/z: Calcd for $[C_{71}H_{84}N_2O_{16}+H]^+$, 1221.5894; Found: 1221.58923.

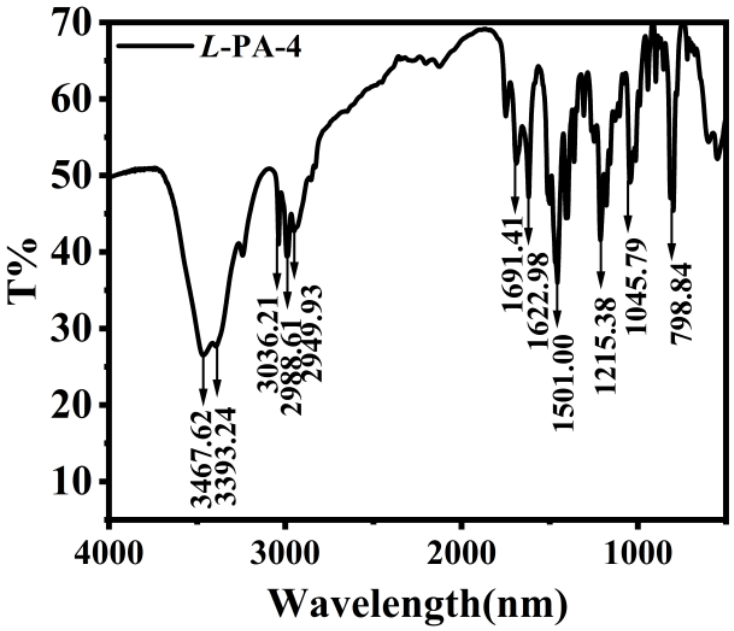


Figure S2. FT-IR spectrum of ***L*-PA-4**.

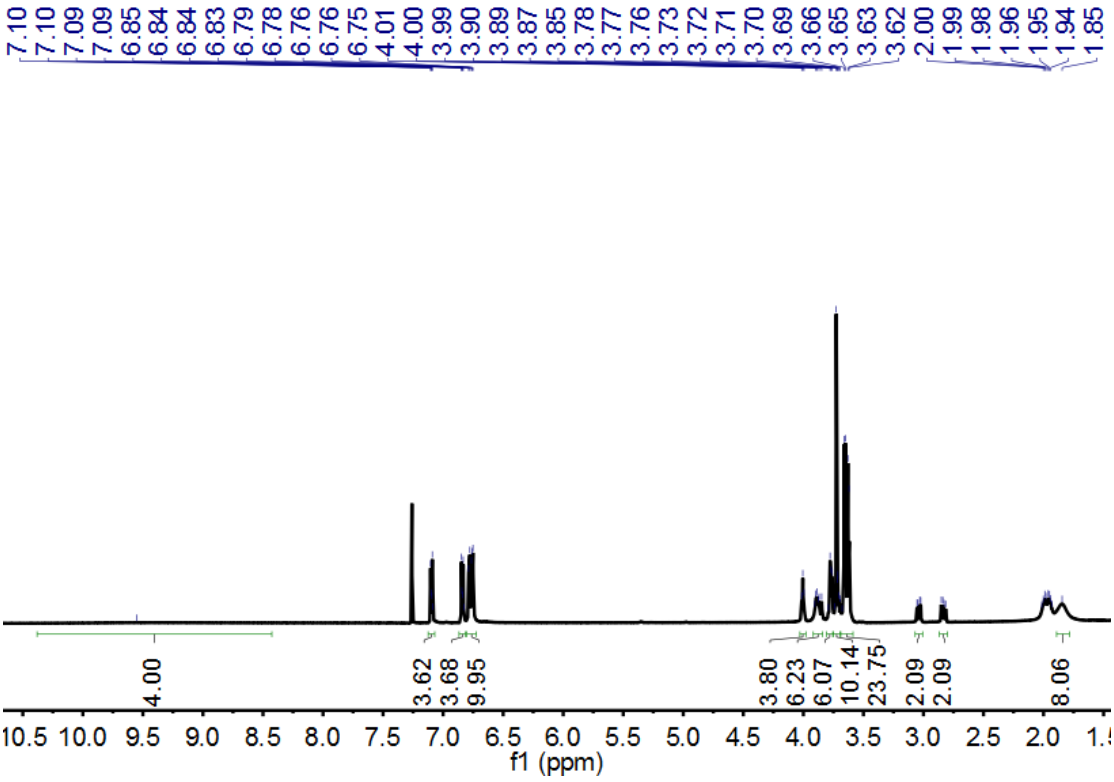


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-PA-4**.

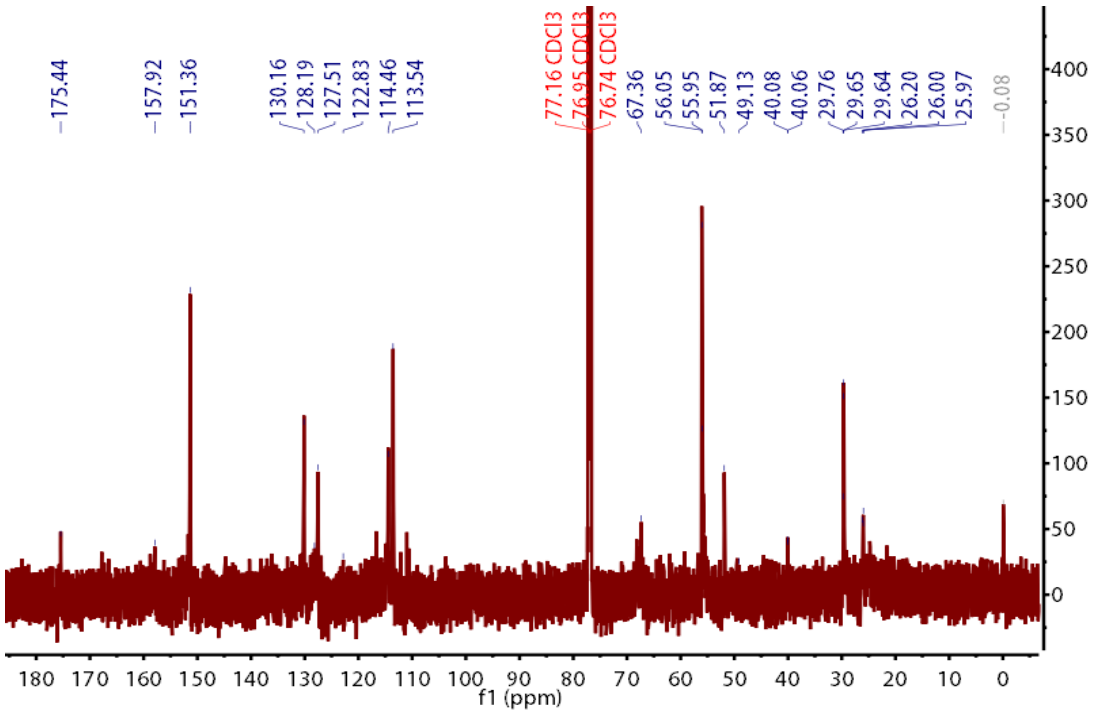


Figure S4. ^{13}C NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-PA-4**.

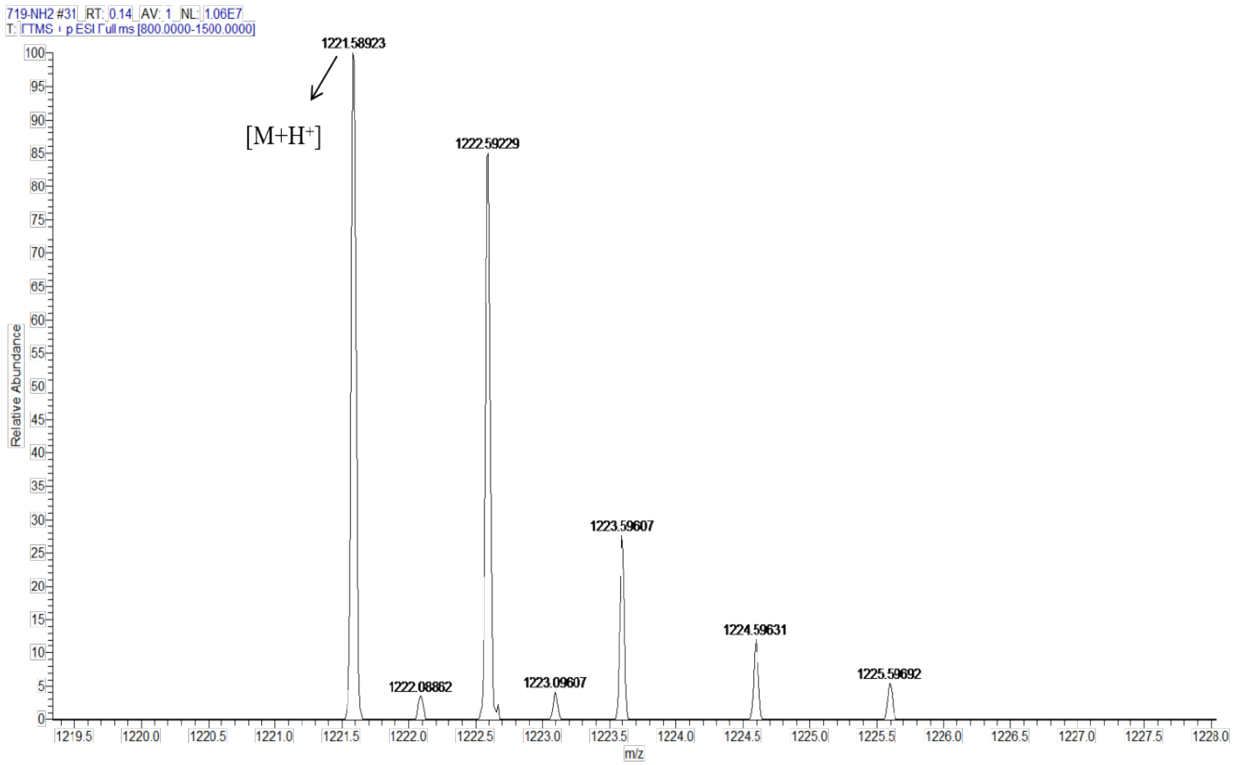
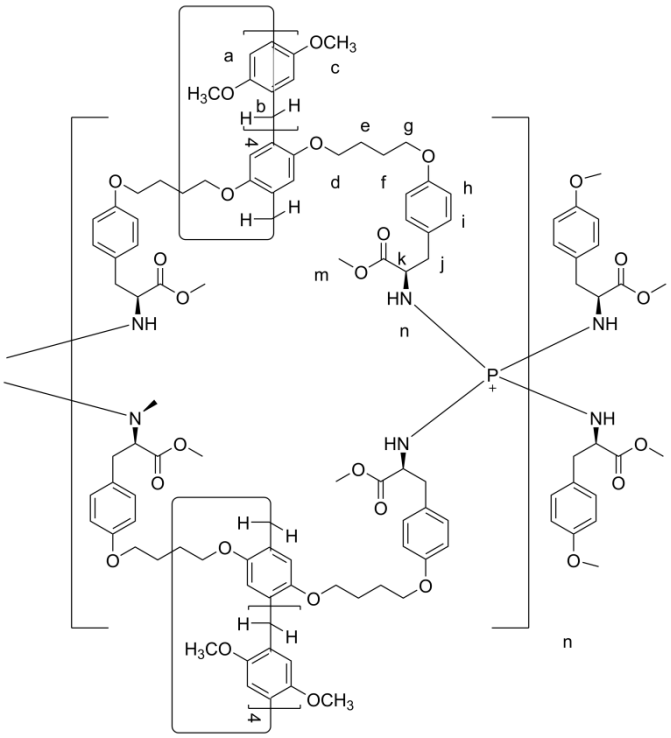


Figure S5. ESI-MS spectrum of ***L*-PA-4**.

2.2 Synthesis of compound *L*-TPP-P



***L*-PA-4** (15 mg, 0.0124 mmol, 2 equiv) and triethylamine (0.5 mL) were added to dichloromethane (3 mL) and stirred for 12 hours at 25°C. Then phosphorus pentachloride (1.2 mg, 0.0062 mmol, 1 equiv) was dissolved in 2 mL dichloromethane and added to the mixed solution and reacted at room temperature for 24 h. The solution obtained from the reaction was evaporated to dryness and purified by washing with deionized water (0.5 mL) and ether (0.5 mL) to obtain ***L*-TPP-P** as a white solid in 86% yield. IR (KBr) cm^{-1}: 3475.69, 3398.14 (N-H), 3039.19 (Ar-H), 2934.87, 2851.75 (C-H), 1740.99 (C=O), 1502.21, 1468.27 (Ar-C=C), 1214.45, 1045.79 (Ar-O, C-O); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.51 (s, 2H, H-n), 7.11 – 7.05 (d, 4H, H-i), 6.87 – 6.80 (d, 4H, H-h), 6.80 – 6.71 (m, 10H, H-a), 4.00 (t, *J* = 5.9 Hz, 4H, H-d), 3.88 (t, 6H, H-g, k), 3.78 – 3.74 (s, 6H, H-m), 3.74 – 3.68 (s, 10H, H-b), 3.67 – 3.59 (s, 24H, H-c), 3.03 (dd, *J* = 13.7, 5.2 Hz, 2H, H-j), 2.82 (dd, *J* = 13.7, 7.8 Hz, 2H, H-j), 1.87 (m, 8H, H-e, f). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 123.91, 123.41, 123.41, 115.88, 56.07, 56.06, 52.86, 52.62, 45.52, 34.67, 34.67, 34.19, 34.19, 31.86, 31.86, 31.56, 29.63, 29.59, 29.30, 29.30, 22.63, 22.63, 14.05, 7.96, 7.55. ^{31}P NMR (600 MHz, Chloroform-d) δ -17.57 (s, 1P).

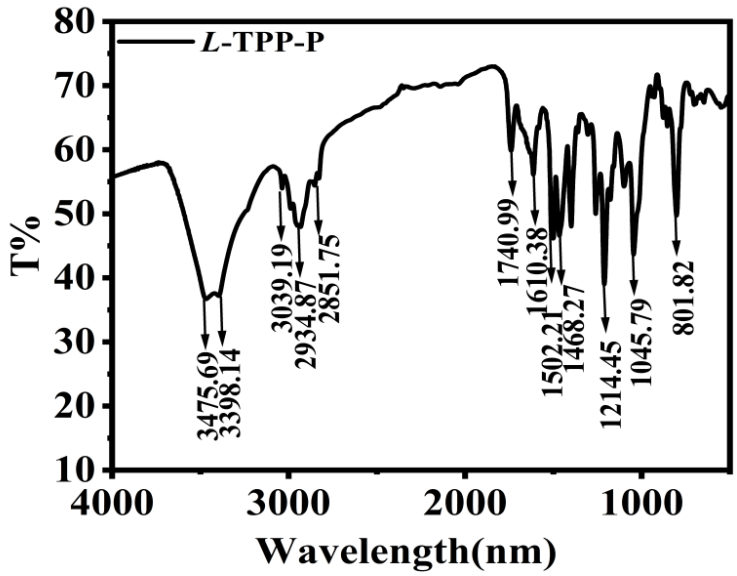


Figure S6. FT-IR spectrum of ***L*-TPP-P**.

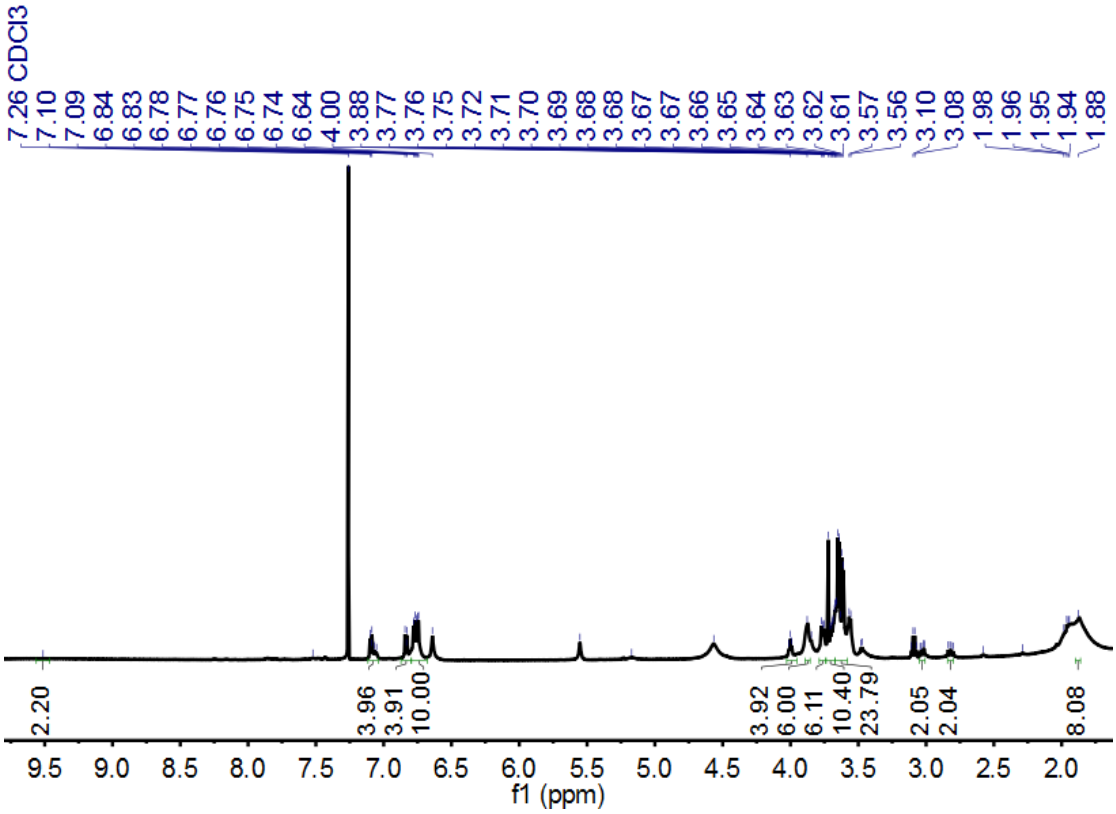


Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-TPP-P**.

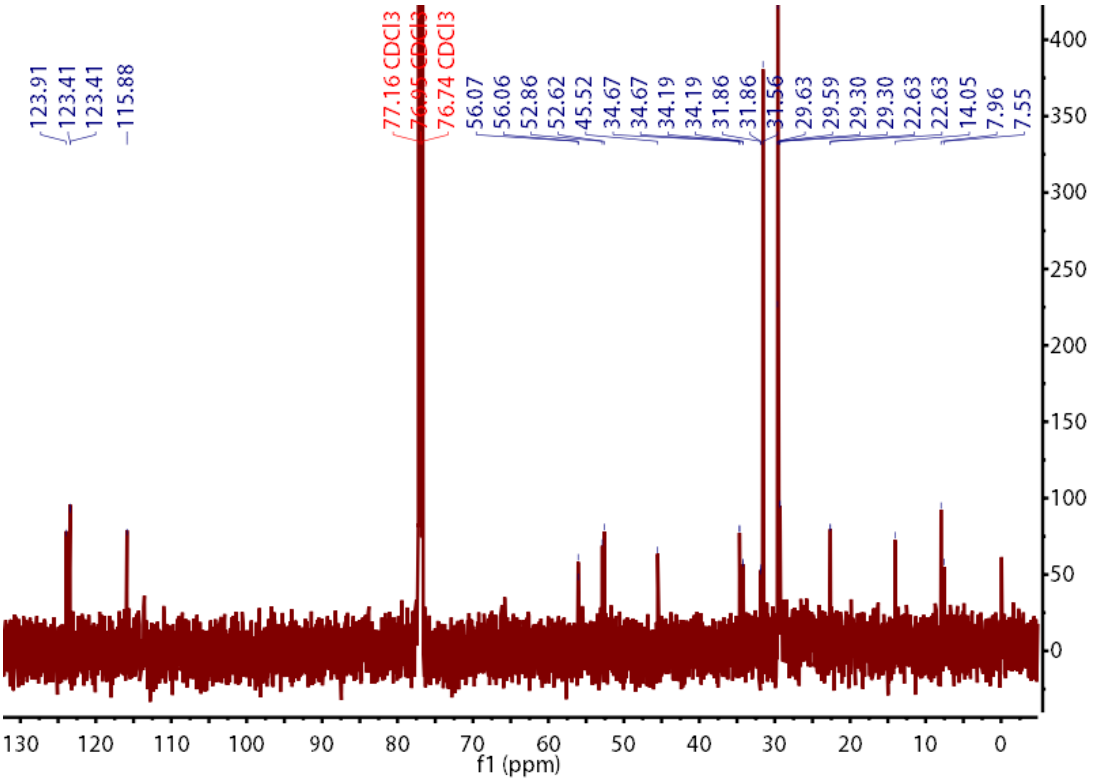


Figure S8. ^{13}C NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-TPP-P**.

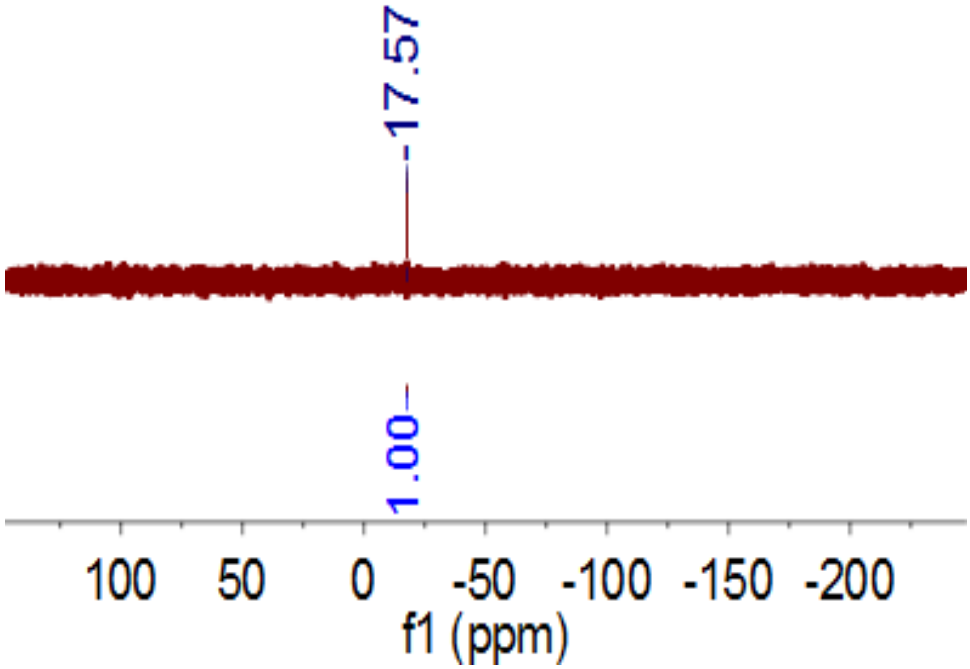


Figure S9. ^{31}P NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-TPP-P**.

S3 Host-guest binding behavior of *L*-PA-4, *L*-TPP-P with (±)MA

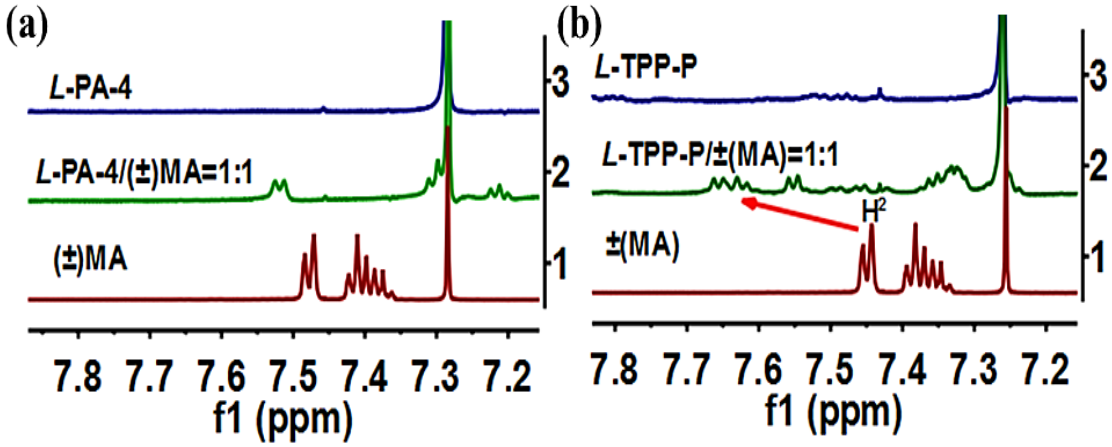


Figure S10. (a) ^{1}H NMR spectrum (600 MHz) of ***L*-PA-4**, ***L*-PA-4**/ (±) **MA**=1:1, (±) **MA** in $CDCl_3$; (b) ^{1}H NMR spectrum (600 MHz) of ***L*-TPP-P**, ***L*-TPP-P**/ (±) **MA**=1:1, (±) **MA** in $CDCl_3$.

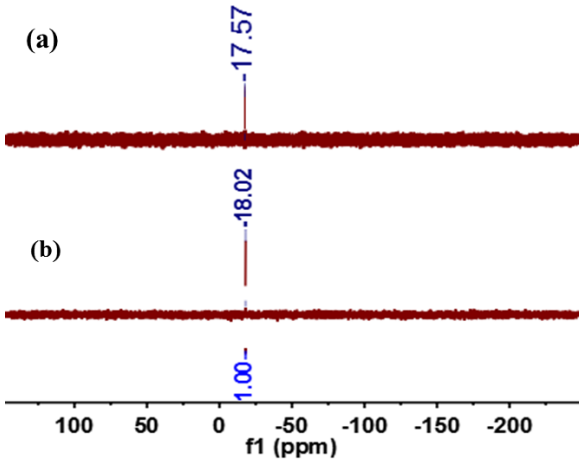


Figure S11. (a) ^{31}P NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-TPP-P**; (b) ^{31}P NMR spectrum (600 MHz, $CDCl_3$, 298K) of ***L*-TPP-P**/ (±)**MA**=1:1.

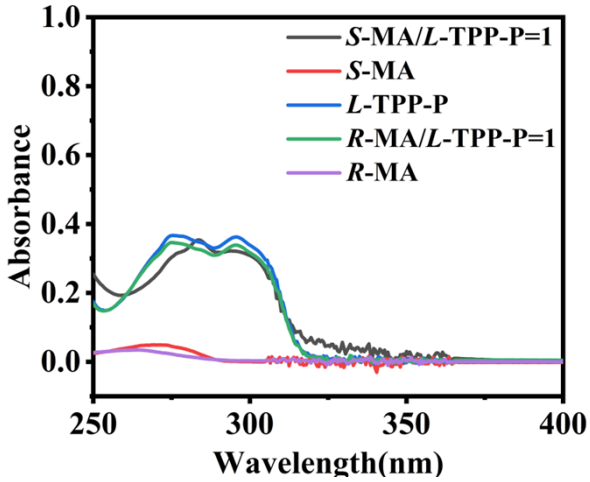


Figure S12. UV spectrum of ***L*-TPP-P**, **MA**, **L-TPP-P** with **R-/S-MA** in $CHCl_3$ (molar ratio=1:1).

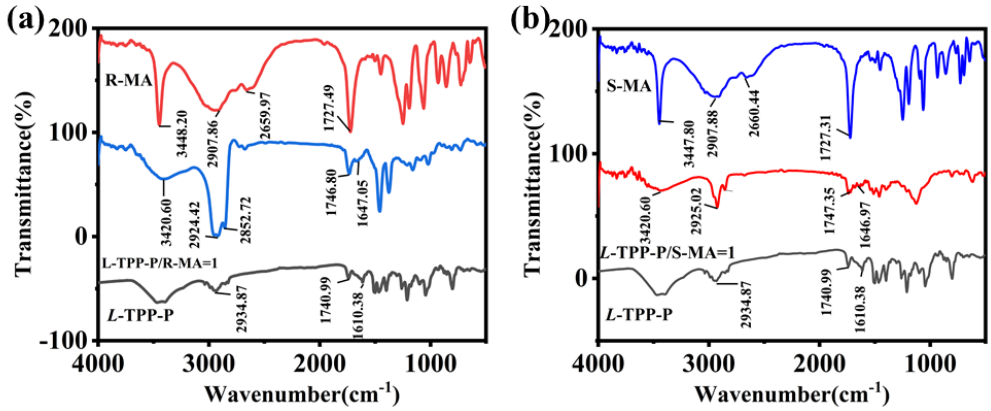


Figure S13. FT-IR spectrum of ***L*-TPP-P**, **MA**, **L-TPP-P** with **MA** (molar ratio=1:1).

S4 References

1 L. Z. Liu, C. G. Ma, Q. He, Y. Huang and W. G. Duan, Effective enantiomeric identification of aromatic amines by tyrosine-modified pillar[5]arenes as chiral NMR solvating agents, *Organic Chemistry Frontiers*, 2021, **8**, 4144-4152.