# Supporting Information

## Enantioselective Recognition of Chiral Acids by Supramolecular Interactions with Chiral AIEgens

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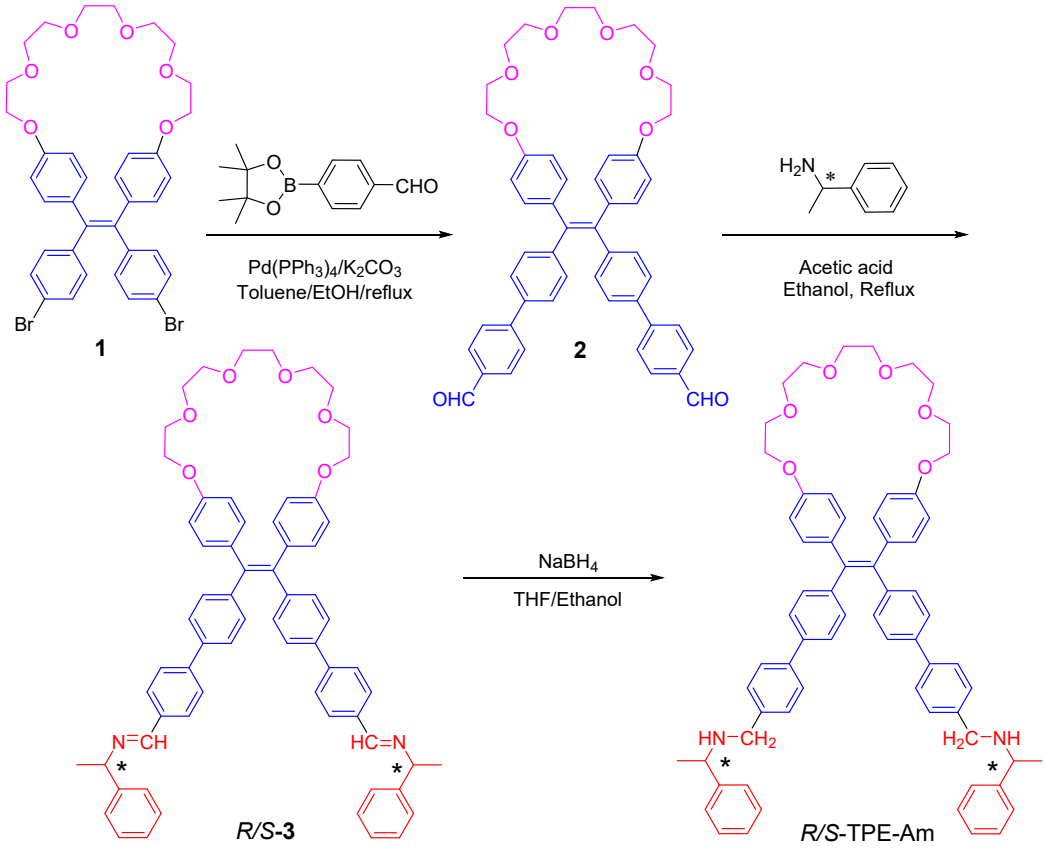
## 1. General information

**Materials:** All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise indicated.

**Measurements:** $^{1}H$ NMR and $^{13}C$ NMR spectra were obtained by an Agilent NMR Systems 400MHz NMR Spectrometer at 298 K in $CDCl_3$. The compound was purified by LaboACE LC-5060 high performance liquid chromatography (HPLC). Absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer. High-resolution mass spectra (HRMS) were measured by an AB SCIEX 4600 mass spectrometer. Fluorescence spectra were collected on a HORIBA FLOUROMAX-4 fluorophotometer at 298 K. The surface morphologies of the samples were analyzed using field emission scanning electron microscopy (FE-SEM, SU8010, Hitachi).

## 2. Synthesis




**Scheme S1** Synthetic procedure of chiral AIEgens *R*-TPE-Am and *S*-TPE-Am.

**Synthesis of 2:** Compound **1** are known molecules and were synthesized according to previous publication.[1] To a flask was added Compound **1** (2.0 g, 2.7606 mmol), 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (1.602 g, 6.9015 mmol), $Pd(PPh_3)_4$ (159.5 mg, 0.138 mmol), and $K_2CO_3$ (3.815 g, 27.606 mmol). The flask was

vacuumed and filled with nitrogen for three times before toluene (120 mL) and ethanol (60 mL) were added. The mixture was refluxed for about 12 h under nitrogen in heating mantle until Compound **1** was consumed (monitored by TLC). Dichloromethane and water was added. The separated organic phase was wished with water, dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The residue was separated by column chromatography (petroleum ether /ethyl acetate 2:1) to give compound **2** as a yellow solid (1.2 g, 56%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 10.02 (s, 2H), 7.89 (d, *J* = 8.4 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 4H), 6.70 (d, *J* = 8.8 Hz, 4H), 4.12 – 4.10 (m, 4H), 3.81 – 3.79 (m, 4H), 3.70 – 3.64 (m, 12H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 191.89, 157.60, 146.75, 144.21, 140.24, 137.60, 136.63, 135.30, 132.71, 132.23, 130.35, 127.48, 126.79, 114.39, 71.27, 70.86, 70.68, 69.68, 67.92.

**Synthesis of *R*-3:** To a one-neck 50 mL flask, compound **2** (100 mg, 0.1342 mmol) and (*R*)-(+)-1-Phenylethylamine (48.4 mg, 0.4026 mmol) were dissolved in ethanol (15 mL). Then 5 drops of acetic acid were added in the solvent and refluxed for 15 h. After reaction completion monitored by TLC, the solvent was removed under vacuum and obtained a yellow powder in 89% yield. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.376 (s, 2H), 7.80 (d, *J* = 8.4 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.35 – 7.32 (m, 4H), 7.25 – 7.21 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.8 Hz, 4H), 6.69 (d, *J* = 8.8 Hz, 4H), 4.55 (q, *J* = 6.4 Hz, 2H), 4.12 – 4.10 (m, 4H), 3.81 – 3.79 (m, 4H), 3.69 – 3.66 (m, 12H), 1.60 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 159.26, 157.40, 145.35, 143.38, 142.90, 140.07, 138.27, 136.94, 135.38, 132.74, 132.05, 128.81, 128.56, 127.05, 126.95, 126.79, 126.47, 114.27, 71.22, 70.83, 70.66, 69.91, 69.66, 67.84, 24.96.

**Synthesis of *S*-3:** The procedure was similar to that of *R*-**3**. *S*-**3** prepared from (S)-(-)-1-Phenylethylamine was obtained as a yellow solid (yield, 85%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 2H), 7.80 (d, *J* = 8.4 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.35 – 7.39 (m, 4H), 7.25 – 7.21 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.8 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 4H), 4.55 (q, *J* = 6.8 Hz, 2H), 4.12 – 4.10 (m, 4H), 3.81 – 3.79 (m, 4H), 3.69 – 3.65 (m, 12H), 1.60 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ = 159.25, 157.41, 145.37, 143.39, 142.90, 140.08, 138.27, 136.94, 135.40, 132.74, 132.06, 128.81, 128.56, 127.06, 126.95, 126.80, 126.48, 114.28, 71.24, 70.84, 70.67, 69.91, 69.67, 67.86, 24.97.

**Synthesis of *R*-TPE-Am:** To a one-neck 50 mL flask, compound *R*-**3** (110 mg, 0.1123 mmol) was dissolved in the mixed solvent of ethanol and tetrahydrofuran (1:1, 16 mL). Then sodium borohydride (127.4 mg, 3.369 mmol) was added under the ice bath, the

reaction was carried out at room temperature for 20 hours. After reaction completion monitored by TLC, the solvent was removed under vacuum. Ethyl acetate and water was added. The separated organic phase was wished with water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was separated by LaboACE LC-5060 high performance liquid chromatography (HPLC) to give *R*-TPE-Am as a yellow-green solid (76 mg, 68.7%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.4 Hz, 4H), 7.39 – 7.32 (m, 12H), 7.30 (d, *J* = 8.4 Hz, 4H), 7.27 – 7.22 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.8 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 4H), 4.11 (t, *J* = 4.4 Hz, 4H), 3.83 (q, *J* = 6.4 Hz, 2H), 3.80 (t, *J* = 3.6 Hz, 4H), 3.67 – 3.59 (m, 12H), 1.79 (s, 2H), 1.37 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 157.32, 145.59, 142.81, 140.00, 139.63, 139.45, 138.74, 137.07, 132.75, 131.95, 128.65, 128.62, 127.10, 126.95, 126.87, 126.27, 114.23, 71.22, 70.83, 70.65, 69.66, 67.84, 57.56, 51.39, 24.54. ESI$^+$ HRMS m/z calcd. for $C_{66}H_{68}N_2O_6$ 985.5156 [M+H], found 985.5167 [M+H].

**Synthesis of *S*-TPE-Am:** The procedure was similar to that of ***R*-TPE-Am**. ***S*-TPE-Am** prepared from ***S*-3** was obtained as a yellow-green solid (yield, 64%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.44 – 7.32 (m, 12H), 7.30 (d, *J* = 8.4 Hz, 4H), 7.27 – 7.23 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.69 (d, *J* = 8.8 Hz, 4H), 4.11 (t, *J* = 4.4 Hz, 4H), 3.82 (q, *J* = 6.8 Hz, 2H), 3.80 (t, *J* = 2.0 Hz, 4H), 3.70 – 3.59 (m, 12H), 1.72 (s, 2H), 1.37 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 157.32, 145.68, 142.80, 139.99, 139.72, 139.41, 138.75, 137.07, 132.75, 131.95, 128.62, 128.61, 127.07, 126.94, 126.85, 126.26, 114.23, 71.22, 70.82, 70.65, 69.65, 67.84, 57.57, 51.42, 24.58. ESI$^+$ HRMS m/z calcd. for $C_{66}H_{68}N_2O_6$ 985.5156 [M+H], found 985.5204 [M+H].

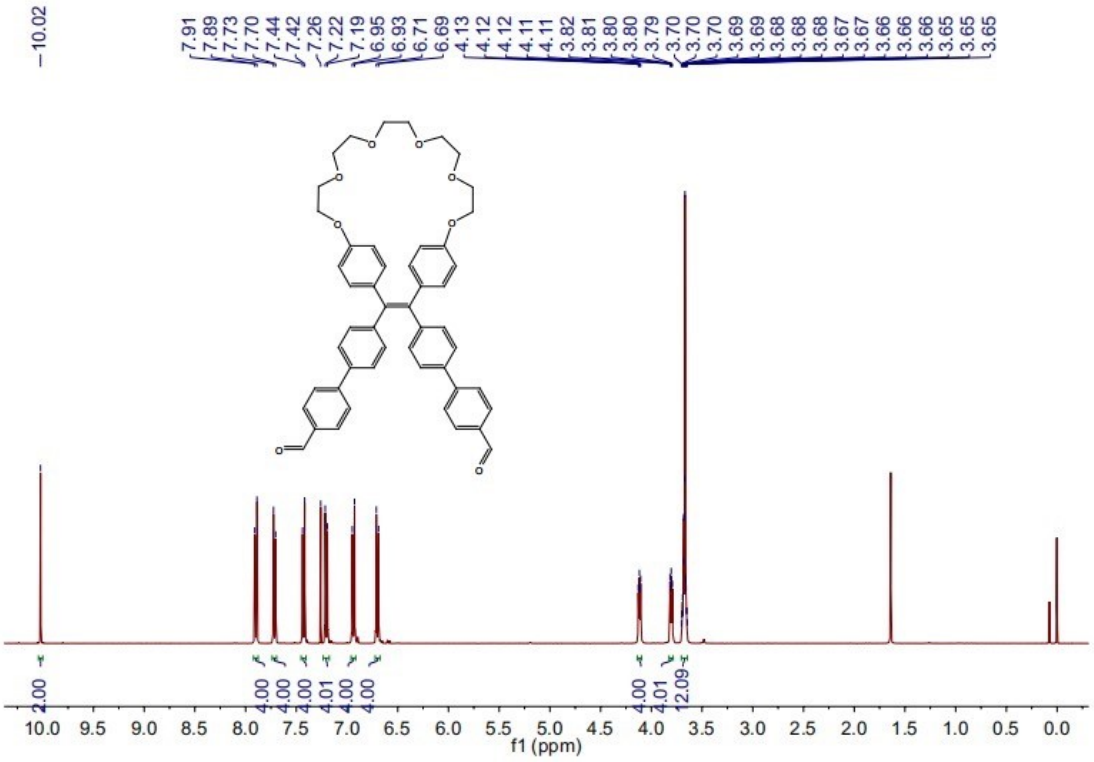



**Fig. S1.** $^{1}H$ NMR spectrum of compound **2** in $CDCl_3$.

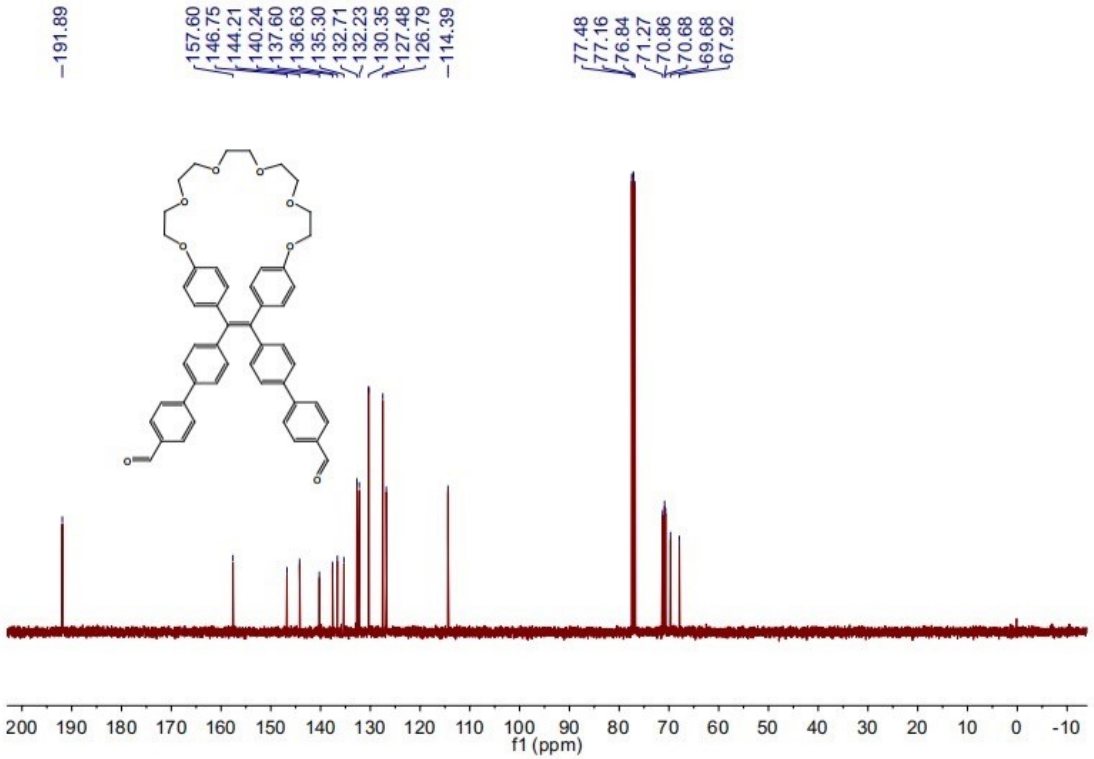



**Fig. S2.** $^{13}C$ NMR spectrum of compound **2** in $CDCl_3$.

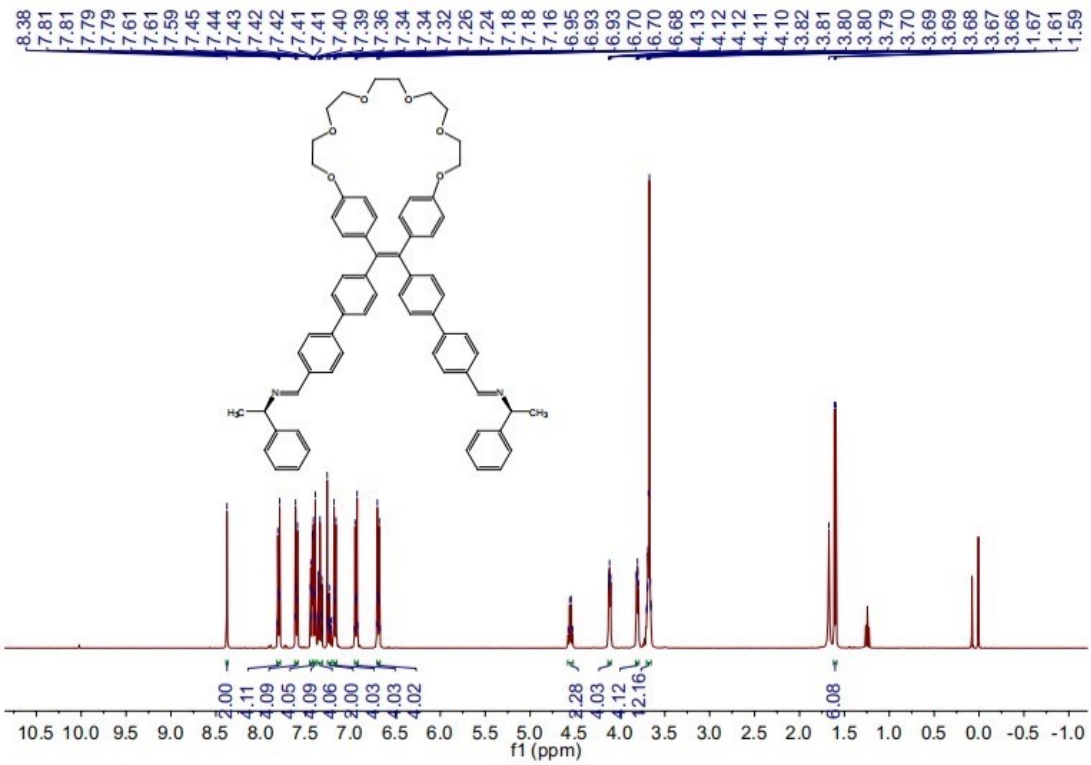



**Fig. S3.** $^{1}$H NMR spectrum of compound *R*-**3** in $CDCl_3$.

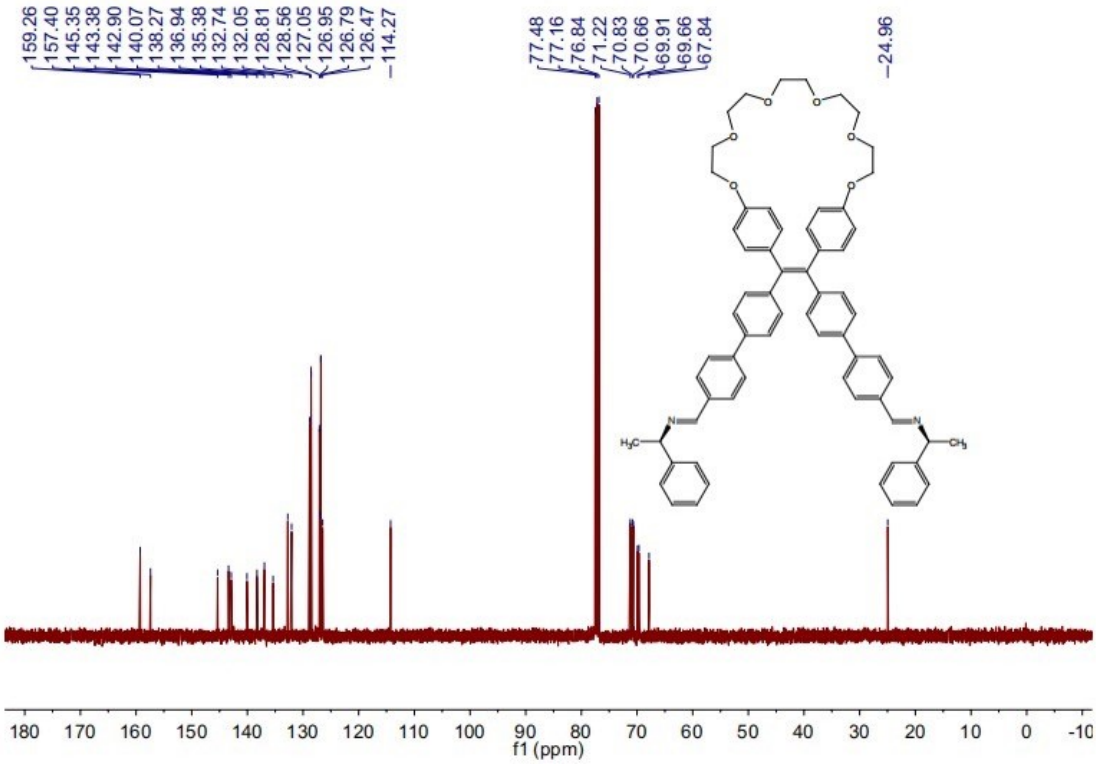



**Fig. S4.** $^{13}$C NMR spectrum of compound *R*-**3** in $CDCl_3$.

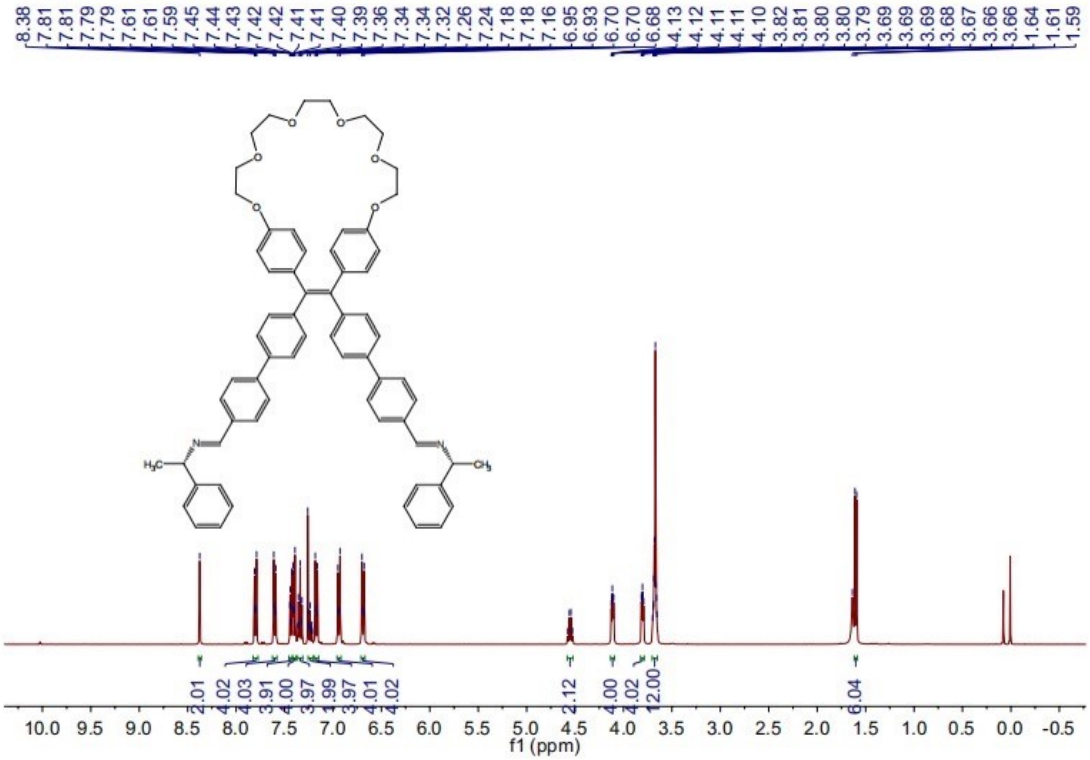



**Fig. S5.** $^{1}$H NMR spectrum of compound *S*-**3** in $CDCl_3$.

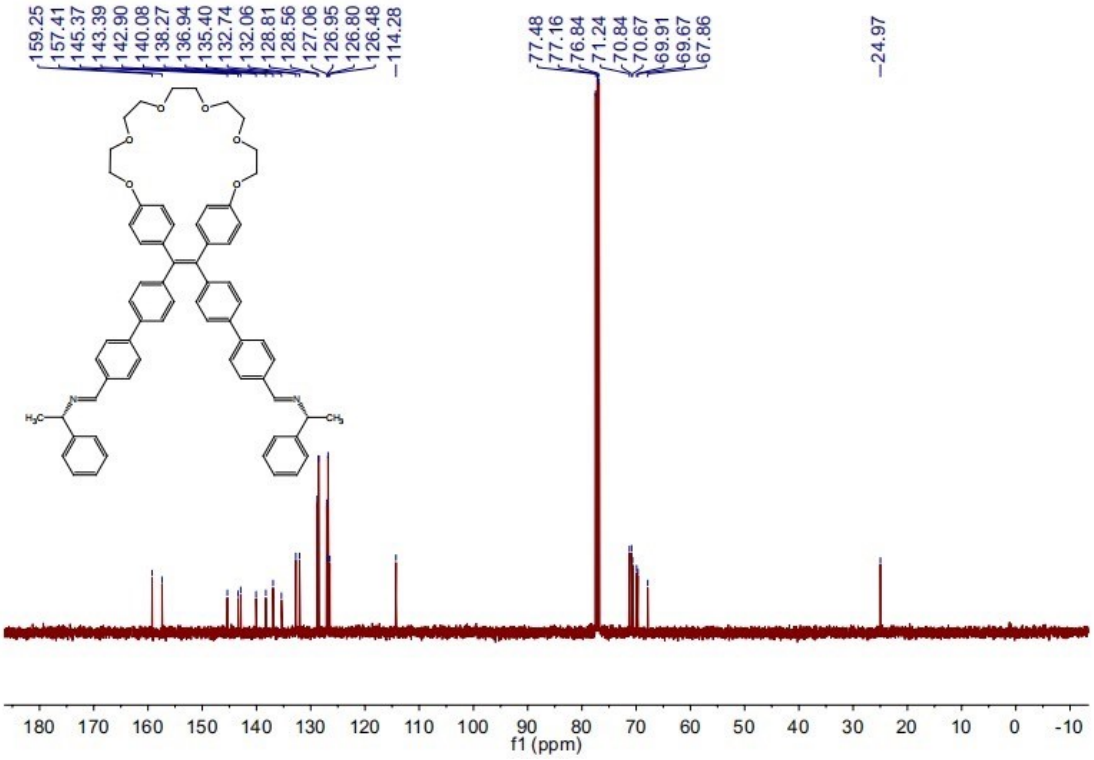



**Fig. S6.** $^{13}$C NMR spectrum of compound *S*-**3** in $CDCl_3$.

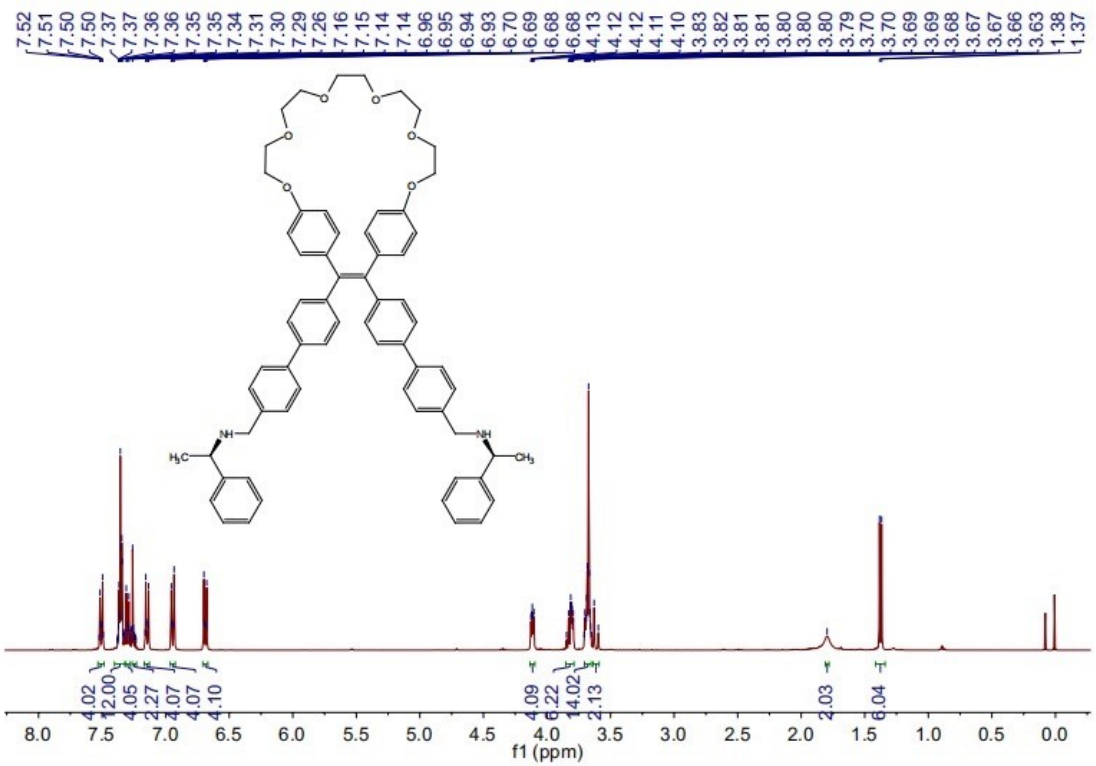



**Fig. S7.** $^{1}$H NMR spectrum of compound *R*-TPE-Am in $CDCl_3$.

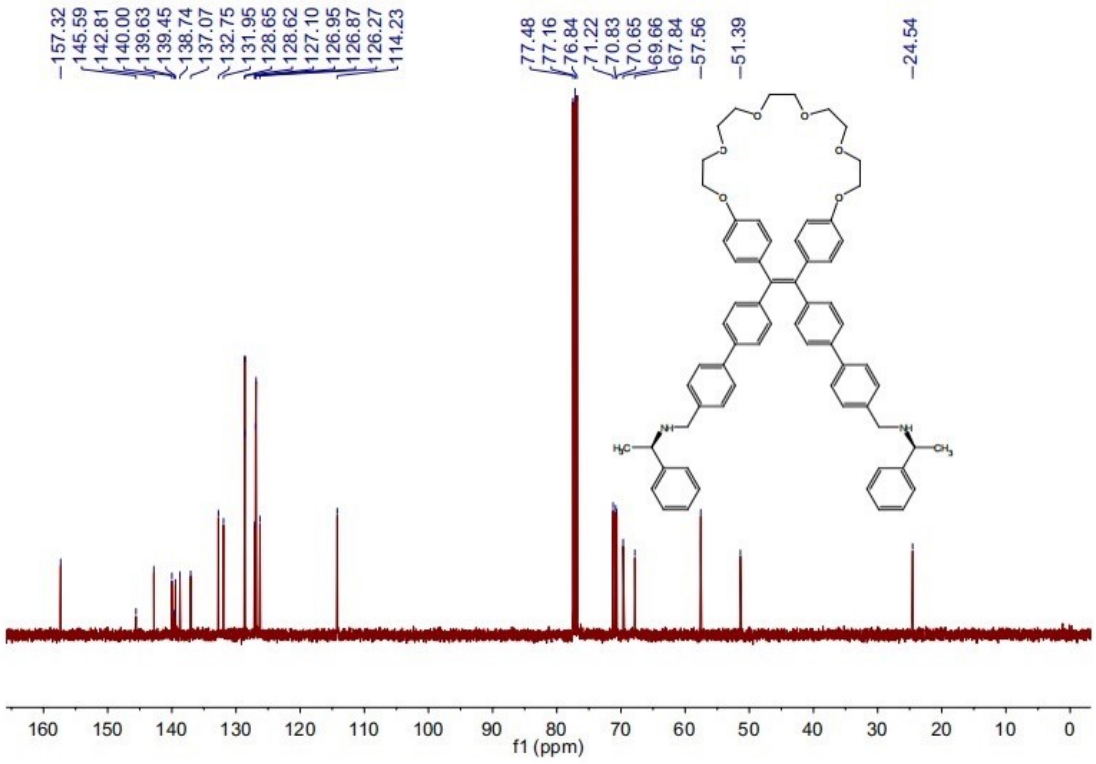



**Fig. S8.** $^{13}$C NMR spectrum of compound *R*-TPE-Am in $CDCl_3$.

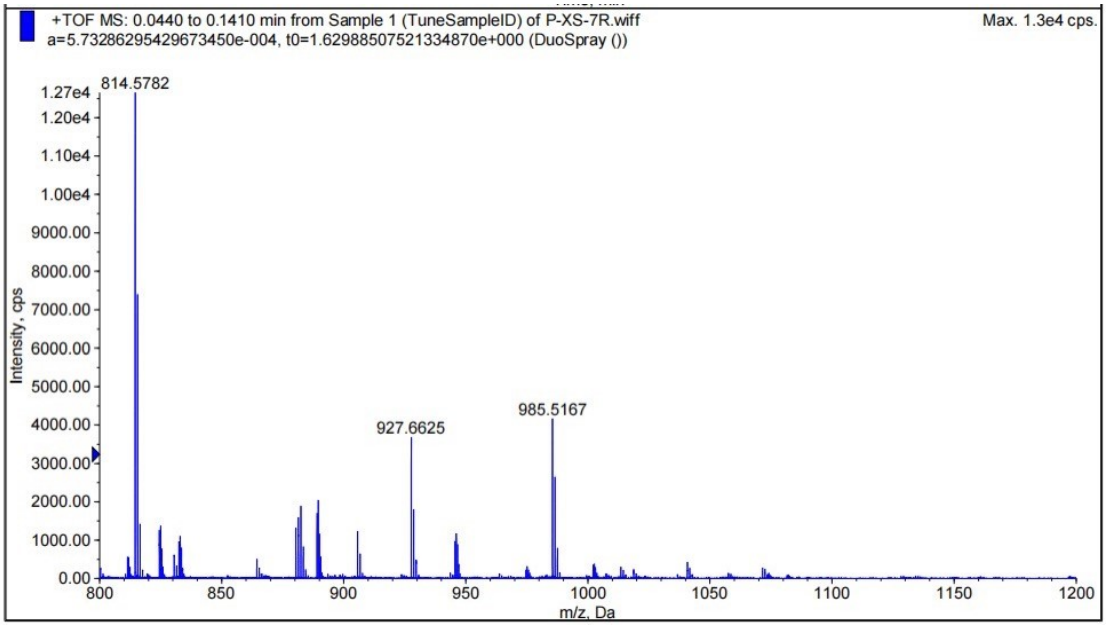



**Fig. S9.** HRMS spectrum of *R*-TPE-Am.

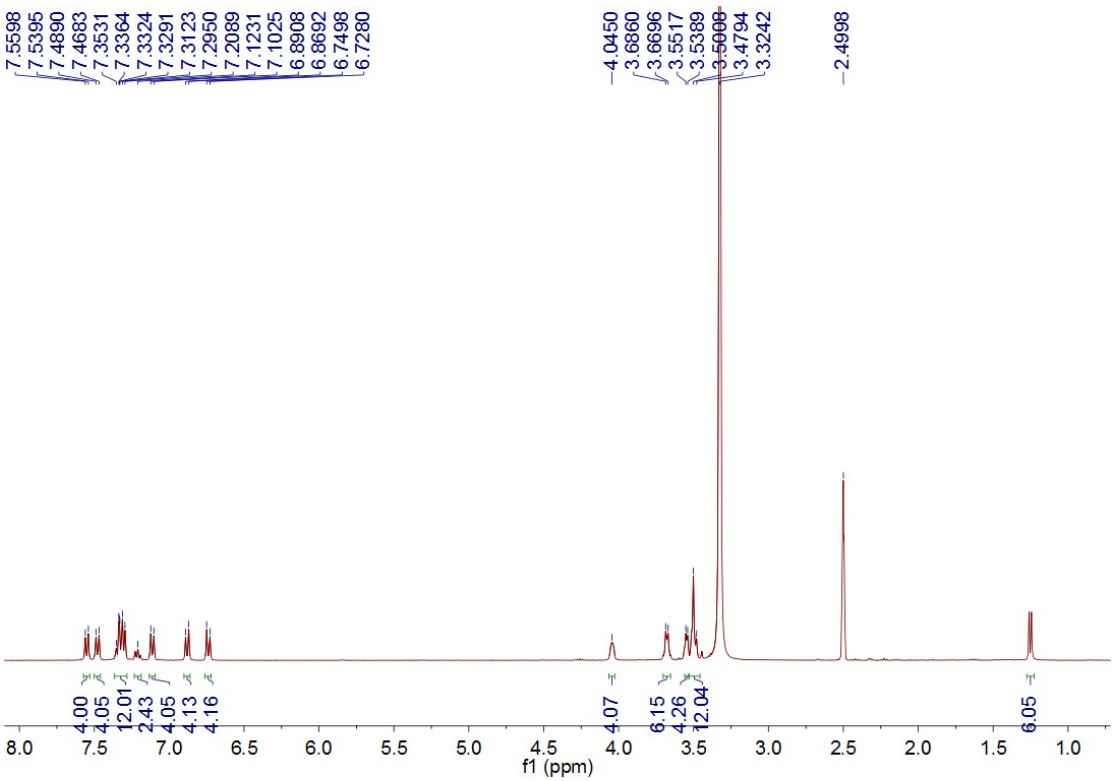



**Fig. S10.** $^{1}$H NMR spectrum of compound *S*-TPE-Am in $d_6$-DMSO.

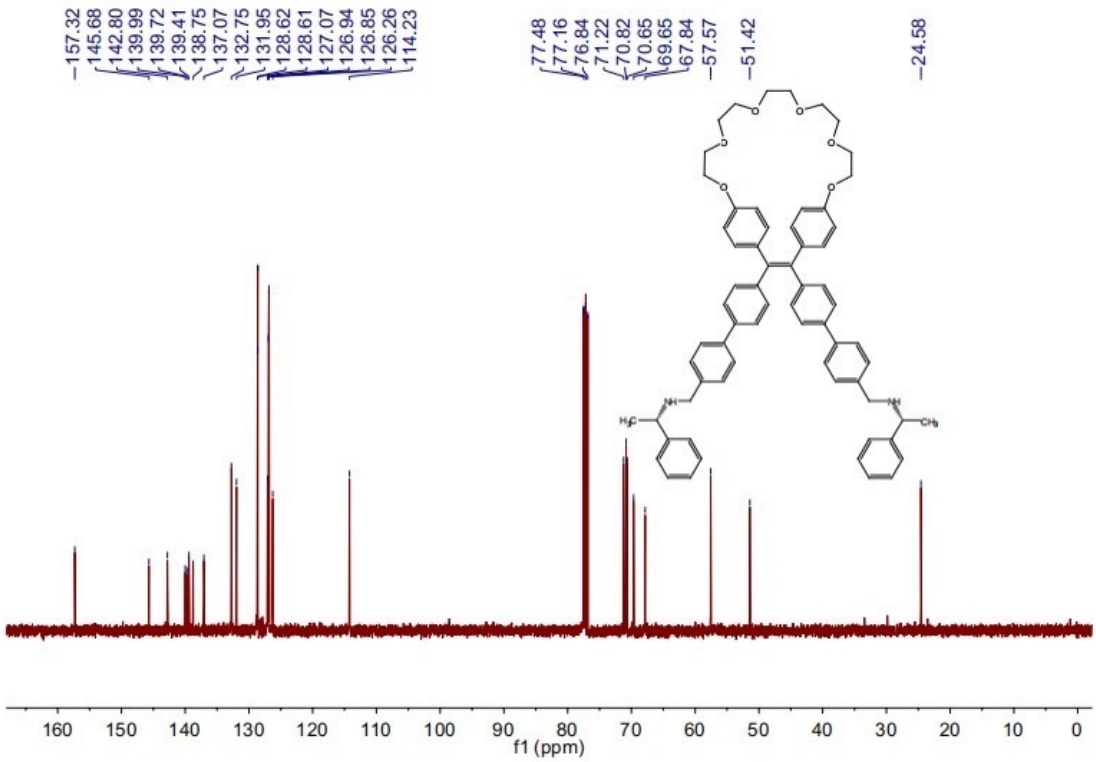



**Fig. S11.** $^{13}C$ NMR spectrum of compound *S*-TPE-Am in $CDCl_3$.

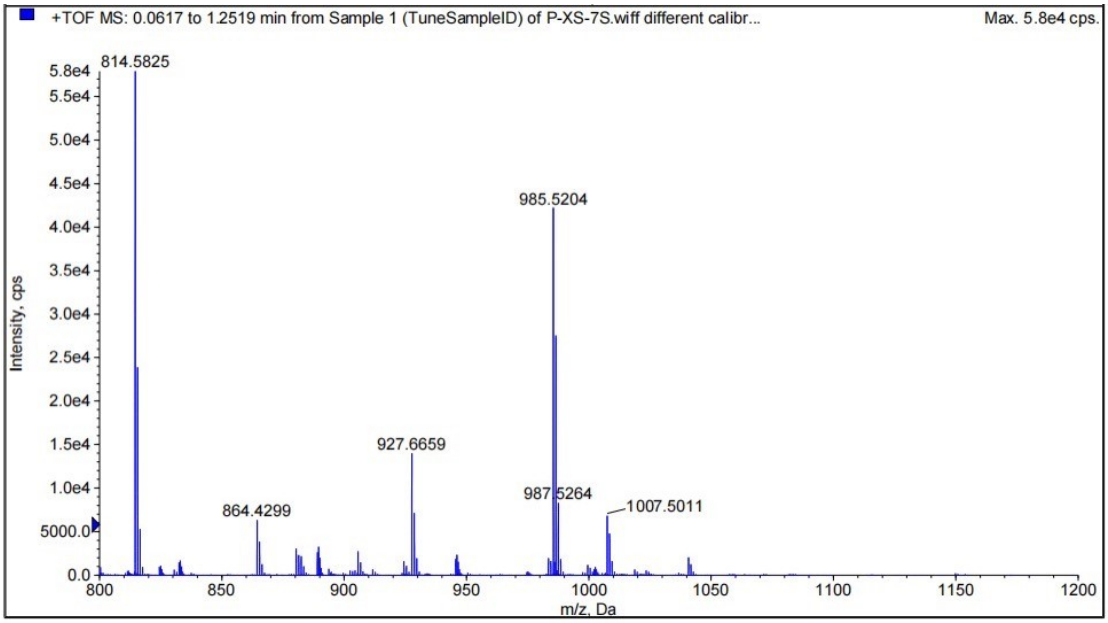



**Fig. S12.** HRMS spectrum of *S*-TPE-Am.

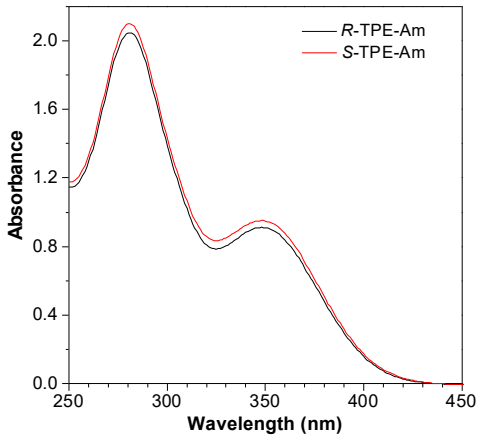



**Fig. S13.** (**A**) UV-vis spectra of *R*-TPE-Am and *S*-TPE-Am in THF, c = 5.0×10$^{-5}$ M.

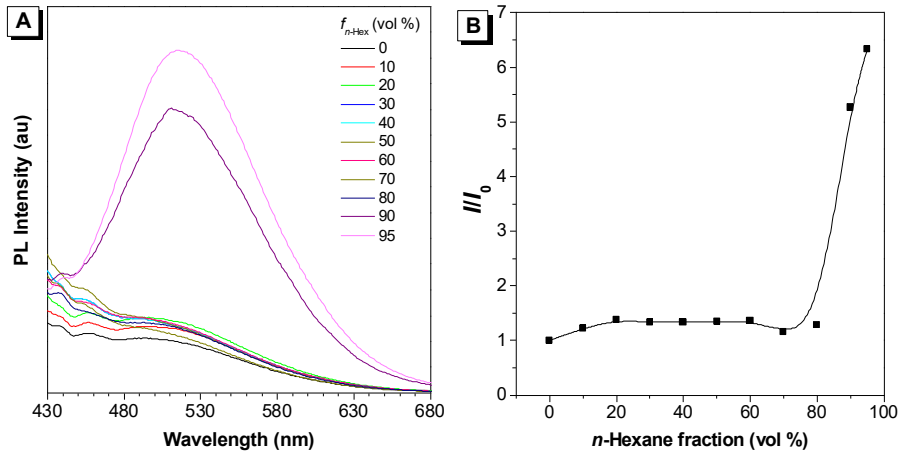



**Fig. S14.** (A) PL spectra of *S*-TPE-Am in THF and THF/*n*-hexane mixture with different *n*-hexane fraction. Excitation wavelength: 360 nm, [*S*-TPE-Am] = 1.0 ×10$^{-5}$ M. (B) PL intensity ratio of $I/I_0$ in different THF/*n*-hexane mixture.

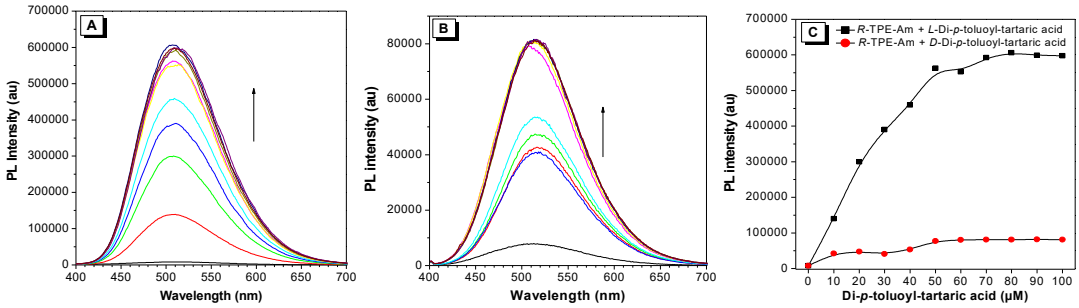



**Fig. S15.** (A) PL titration of *R*-TPE-Am in the presence of 0 to 100 μM of *L*-Di-p-toluoyl-tartaric acid in n-hexane/THF(70/30); (B) PL titration of *R*-TPE-Am in the presence of 0 to 100 μM of *D*-Di-p-toluoyl-tartaric acid in n-hexane/THF(70/30); (C) Curve of PL intensity versus concentration of D/*L*-Di-p-toluoyl-tartaric acid. [*R*-TPE-Am] = 50 μM.

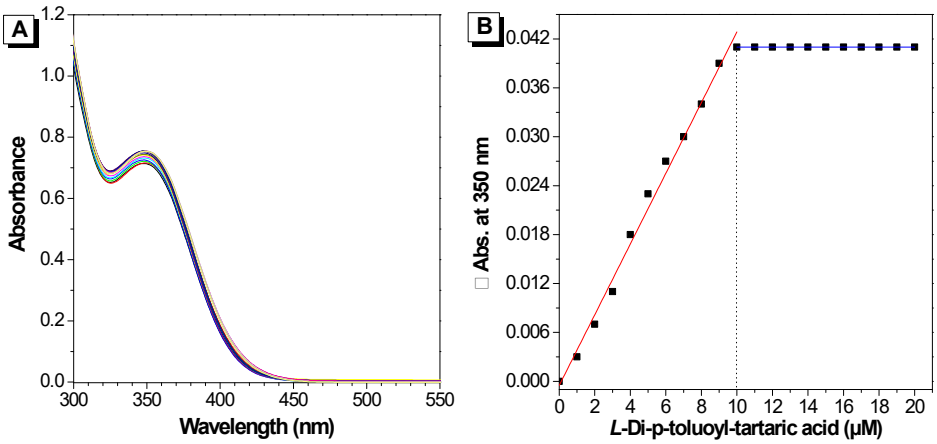



**Fig. S16.** (A) UV-vis titration of *R*-TPE-Am in the presence of 0 to 20 μM of *L*-Di-p-toluoyl-tartaric acid in THF. (B) Curve of absorbance versus concentration of *L*-Di-p-toluoyl-tartaric acid. [*R*-TPE-Am] = 10 μM.

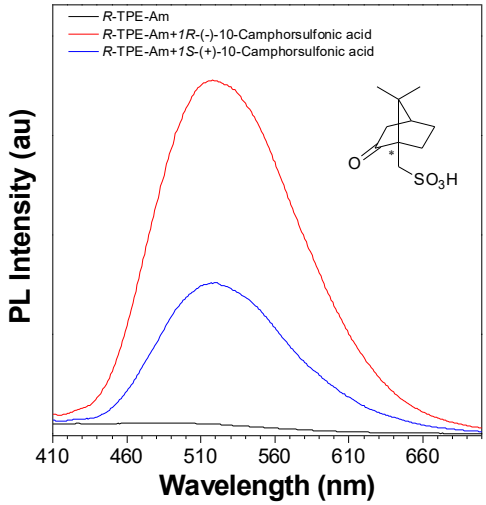



**Fig. S17.** PL spectra of a mixture of *R*-TPE-Am and enantiomers of *1R*/*1S*-10-Camphorsulfonic acid in THF/*n*-hexane (10/90), [*R*-TPE-Am] = $8.3\times10^{-6}$ M.

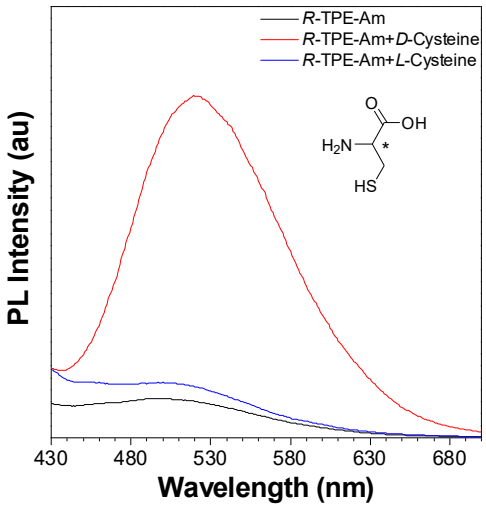



**Fig. S18.** PL spectra of a mixture of *R*-TPE-Am and enantiomers of *D*/*L*-Cysteine in THF/*n*-hexane (10/90), [*R*-TPE-Am] = $8.3\times10^{-6}$ M.

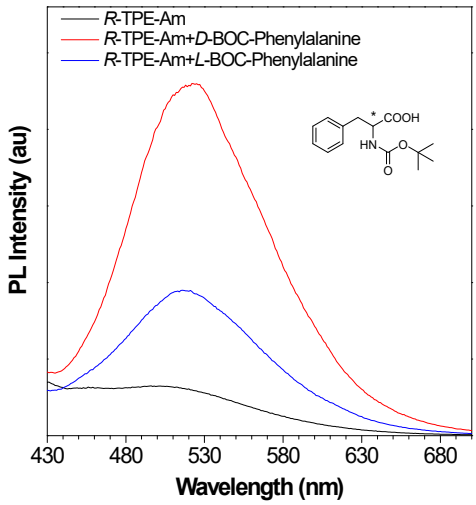



**Fig. S19.** PL spectra of a mixture of *R*-TPE-Am and enantiomers of *D/L*-BOC-Phenylalanine in THF/*n*-hexane (10/90), [*R*-TPE-Am] = $1.67\times10^{-5}$ M.

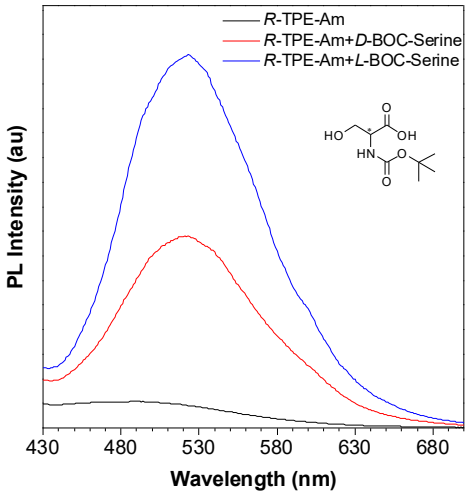



**Fig. S20.** PL spectra of a mixture of *R*-TPE-Am and enantiomers of *D/L*-BOC-Serine in THF/*n*-hexane (10/90), [*R*-TPE-Am] = $8.3\times10^{-6}$ M.

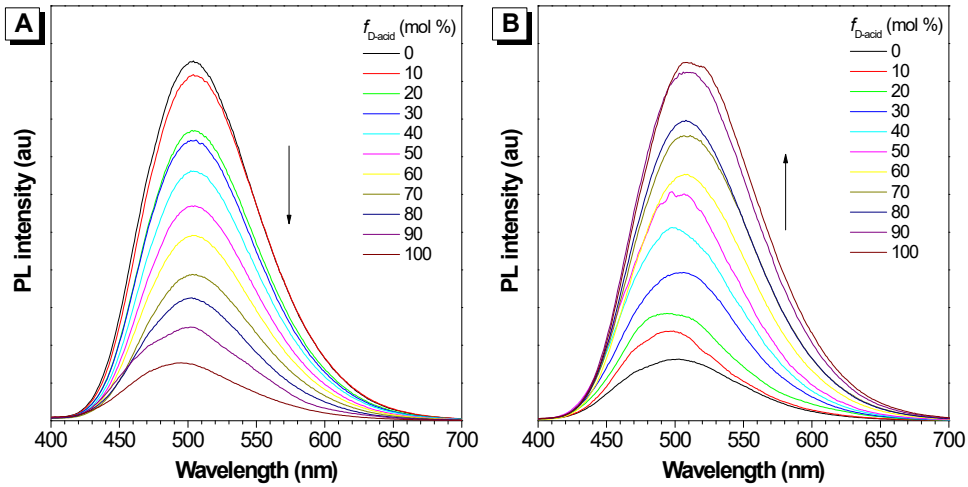



**Fig. S21.** (A) PL spectra of a mixture of *R*-TPE-Am and Di-p-toluoyl-tartaric acid with various enantiomer content in *n*-hexane/THF (v/v, 70/30). (B) PL spectra of a mixture of *S*-TPE-Am and Di-p-toluoyl-tartaric acid with various enantiomer content in *n*-hexane/THF (v/v, 70/30). [*R*-TPE-

Am] = [*S*-TPE-Am] = [*D*-Di-p-toluoyl-tartaric acid] + [*L*-Di-p-toluoyl-tartaric acid] = $5.0 \times 10^{-5}$ M.

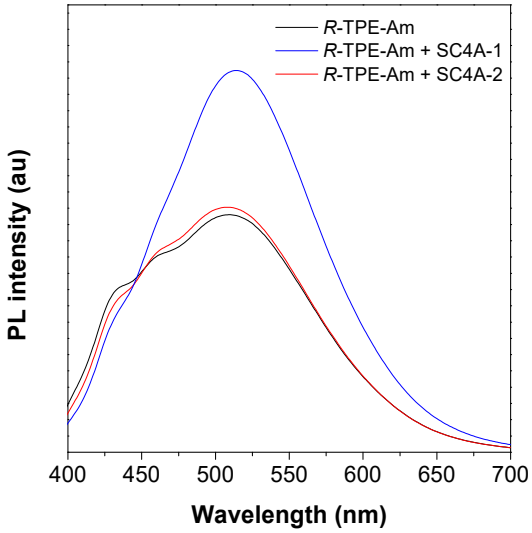



**Fig. S22.** (A) PL spectra of a mixture of *R*-TPE-Am and SC4A-**1**, SC4A-**2** in THF. (B) PL spectra of a mixture of *R*-TPE-Am and SC4A-**1**, SC4A-**2** in THF. [*R*-TPE-Am] = 1/2[SC4A-**1**] = 1/2[SC4A-**2**] = $1.0 \times 10^{-5}$ M.

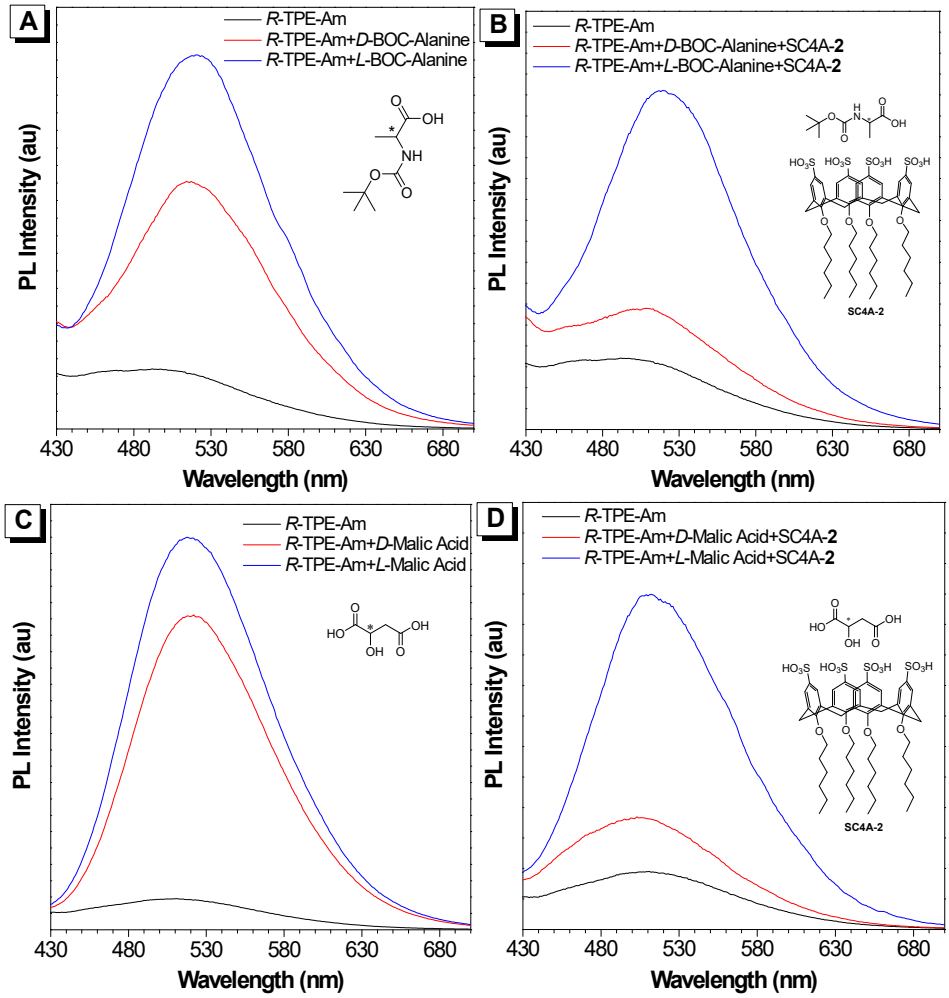



**Fig. S23.** PL spectra of a mixture of *R*-TPE-Am and enantiomers of *D*/*L*-BOC-Alanine (A), and their mixtures and SC4A-**2** (B) in THF/*n*-hexane (5/95), [*R*-TPE-Am] = $8.3 \times 10^{-6}$ M. PL spectra of

a mixture of *R*-TPE-Am and enantiomers of *D/L*-Malic acid (C), and their mixtures and SC4A-**2** (D) in THF/*n*-hexane (20/80), [*R*-TPE-Am] = $3.3 \times 10^{-5}$ M.

**Table S1**. Changes of chemical shift of *R*-TPE-Am and *L*-Di-*p*-toluoyl-tartaric acid during $^1$H NMR titration.

| Chemical shift | Ha | Hb | Hd | He | Hf | Hi | Hj | Hm | Hn | Ho | Hp |
|---|---|---|---|---|---|---|---|---|---|---|---|
| From | 7.172 | 7.067 | 3.652 | 1.226 | 3.518 | 7.539 | 7.468 | 2.372 | 7.358 | 7.855 | 5.788 |
| To | 7.310 | 7.088 | 4.013 | 1.408 | 3.637 | 7.540 | 7.448 | 2.286 | 7.202 | 7.730 | 5.547 |
| △δ/ppm | 0.138 | 0.021 | 0.361 | 0.182 | 0.119 | -0.001 | -0.020 | -0.086 | -0.156 | -0.125 | -0.241 |

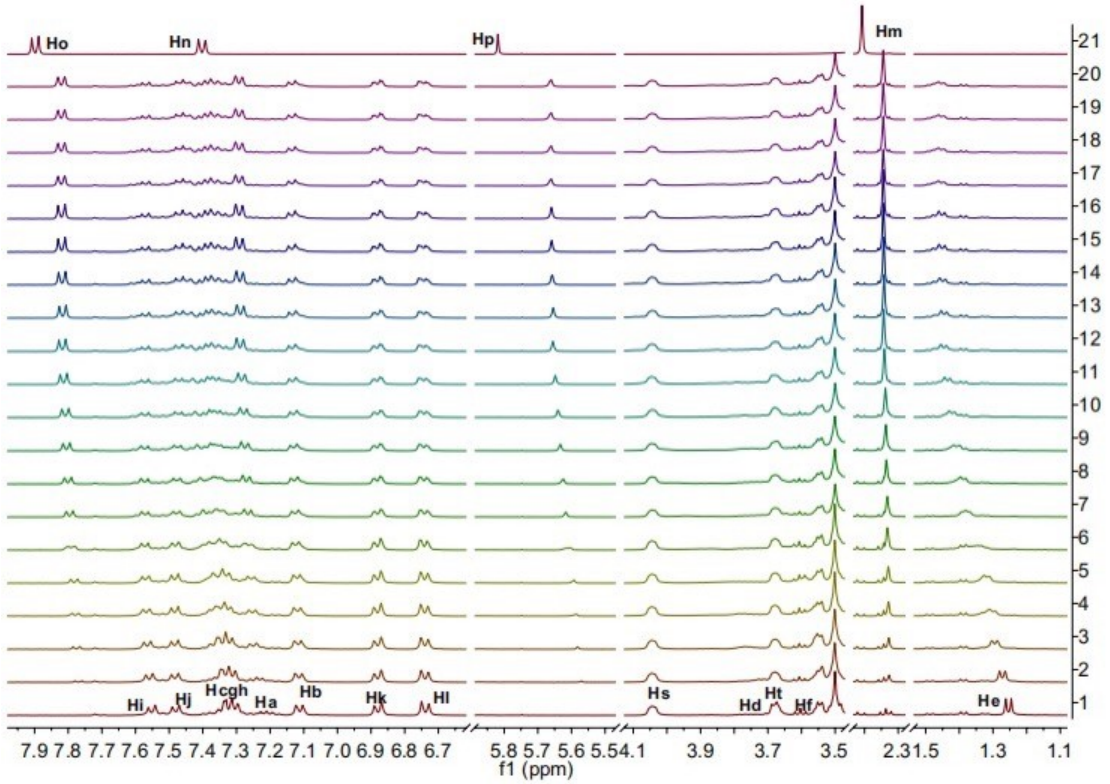



**Fig. S24.** $^1$H NMR titration of *R*-TPE-Am with *L*-Di-p-toluoyl-tartaric acid in $d_6$-DMSO at 298 K. (1) Resonance signals for free *S*-TPE-Am (4.0 mM). (2−20) Changes in resonance signals of *R*-TPE-Am in the presence of 0.1 to 2.0 equivalents of *L*-Di-p-toluoyl-tartaric acid. (21) Resonance signals for the free *L*-Di-p-toluoyl-tartaric acid.

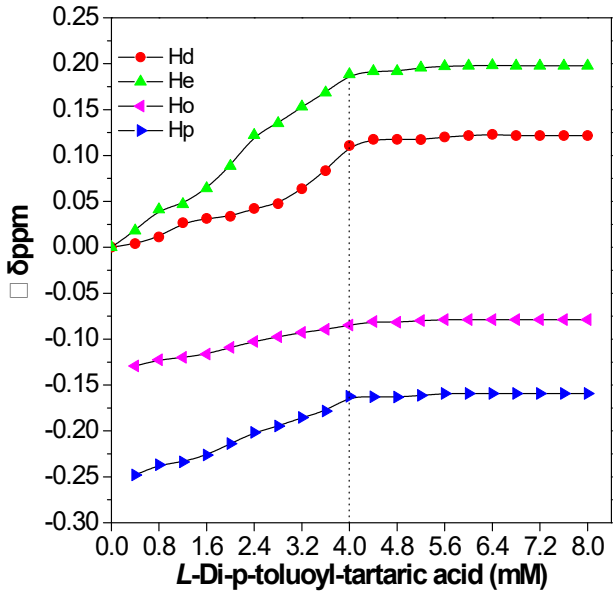



**Fig. S25.** Plot obtained by recording the $^1$H NMR expriments for the solution of *R*-TPE-Am (4.0 mM) and *L*-Di-p-toluoyl-tartaric acid in $d_6$-DMSO at RT, confirming the 1:1 stoichiometry of their complex (0-2 equiv.)

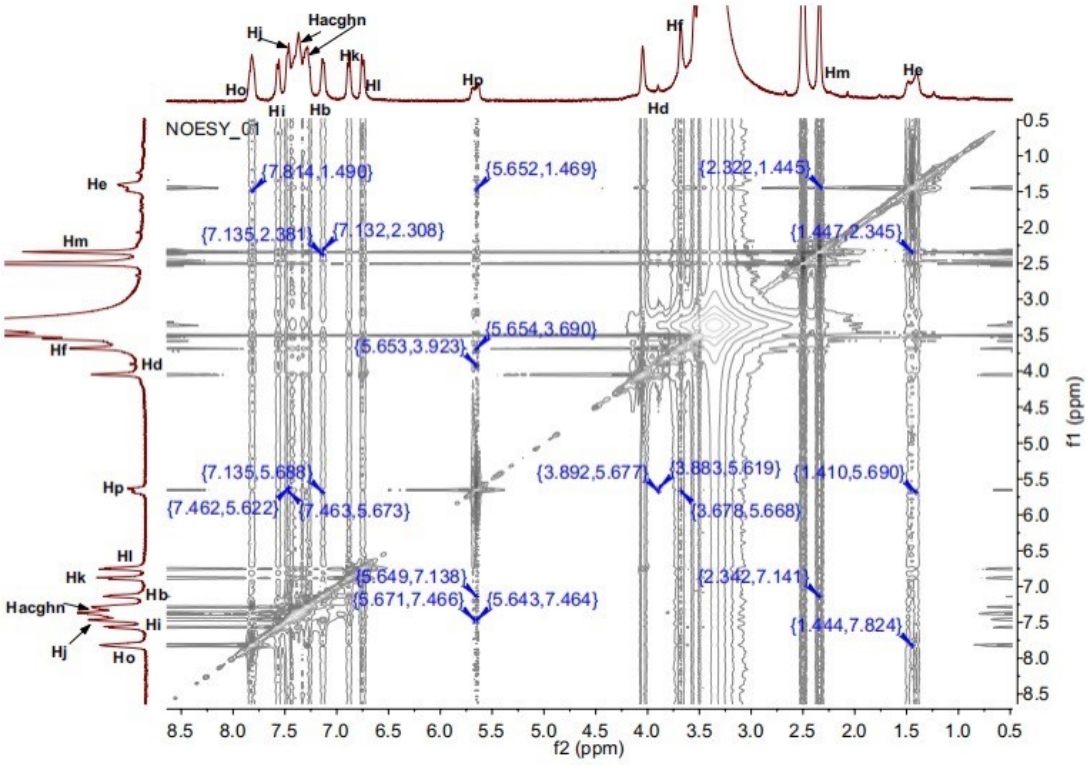



**Fig. S26.** 2D NOESY spectrum of a 1:1 mixture of mixture of *R*-TPE-Am and *L*-Di-p-toluoyl-tartaric acid (measured by a 400 MHz instrument over 9 h, 5 mM in DMSO-$d_6$ at 298 K).

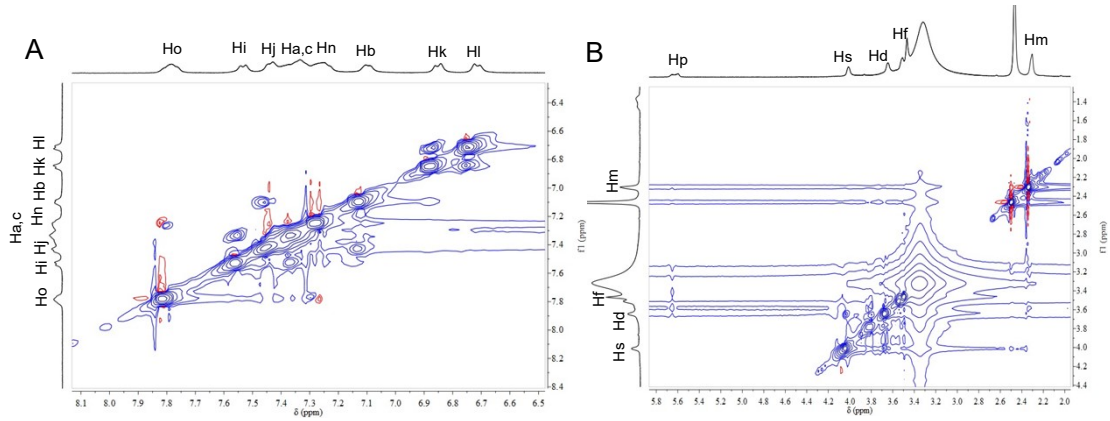



**Fig. S27.** Partial 2D NOESY spectra of *R*-TPE-Am and *L*-Di-p-toluoyl-tartaric acid.

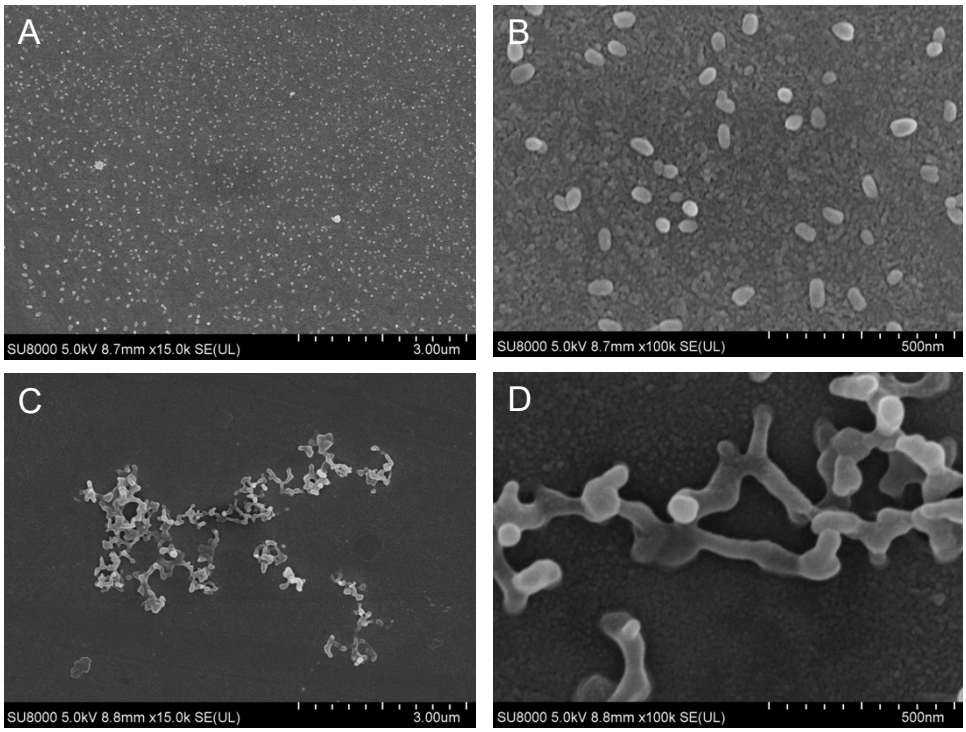



**Fig. S28.** SEM images of the mixture of *R*-TPE-Am and *L*-Di-*p*-toluoyl-tartaric acid (A and B), mixture of *R*-TPE-Am and *D*-Di-*p*-toluoyl-tartaric acid (C and D) in *n*-hexane/THF (v/v, 70/30).