Supplementary information

The Largest CPL Enhancement by Further Assembling of Self-Assembled Superhelices Based on Helical TPE Macrocycle

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Materials and Methods

Materials: All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and most of them were bought from China National Pharmaceutical Group Corporation, Aladdin (Shanghai) Bio-Chem Technology Co Ltd, and Meryer (Shanghai) Chemical Technology Co Ltd et al. These reagents and solvents were used as received unless otherwise indicated.

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in $CDCl_3$ or DMSO-d_6. Infrared spectra were recorded on Bruker EQUINAX55 spectrometer. Mass spectrum was measured on an Ion Spec 4.7 Tesla FTMS instrument. Absorption spectra were recorded on a Hewlett Packard 8453 UV–Vis spectrophotometer. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectrometer. Circular polarized luminescence (CPL) spectra were measured on a JASCO CPL8200 spectrometer. The relative fluorescence quantum yield was measured using quinine sulfate (Φ_f = 0.546) in 1N H_2SO_4 as standard. Absolute fluorescence quantum yields were recorded on Absolute PL Quantum Yield Spectrometer C11347 with a calibrated integrating sphere system. Field emission scanning electron microscope (FE-SEM) images were taken on an electron microscope operating at 5 kV or 10 kV. Atomic Force Microscope (AFM) images were got on a VEECO Nano Scope IV instrument using tapping mode. The solution was dropped on a freshly broken mica (19 × 19 mm) and dried in air. Transmission Electron Microscope (TEM) images were recorded on a FEI Technai G2 20 electron microscopy at 200 kV. The solution was dropped onto a copper grid covered with a thin carbon film on a filter paper and air dried.

The theoretical calculation of the energy of M-1 trimers: The single point energy of the trimer aggregation was calculated by Gussian 16 package with PM6-D3 method, which could directly calculate the formation enthalpy of the trimmers. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A.

Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

The preparation of M-1/P-1 samples for CD and CPL measurements: By dissolving 3.46 mg of M-**1** and P-**1**, respectively, in 4 mL of 1,2-dichloroethane (DCE), 1.0 mM solution of M-**1** and P-**1** in DCE was prepared. The M-**1** and P-**1** films were formed by dropping the solution on the quartz glass sheet and air dried. In the same way, 1.0 mM solution of M-**1**/P-**1** in THF or in H_2O/THF 90:10 was prepared. CD and CPL spectra were directly measured once the solution and films were prepared.

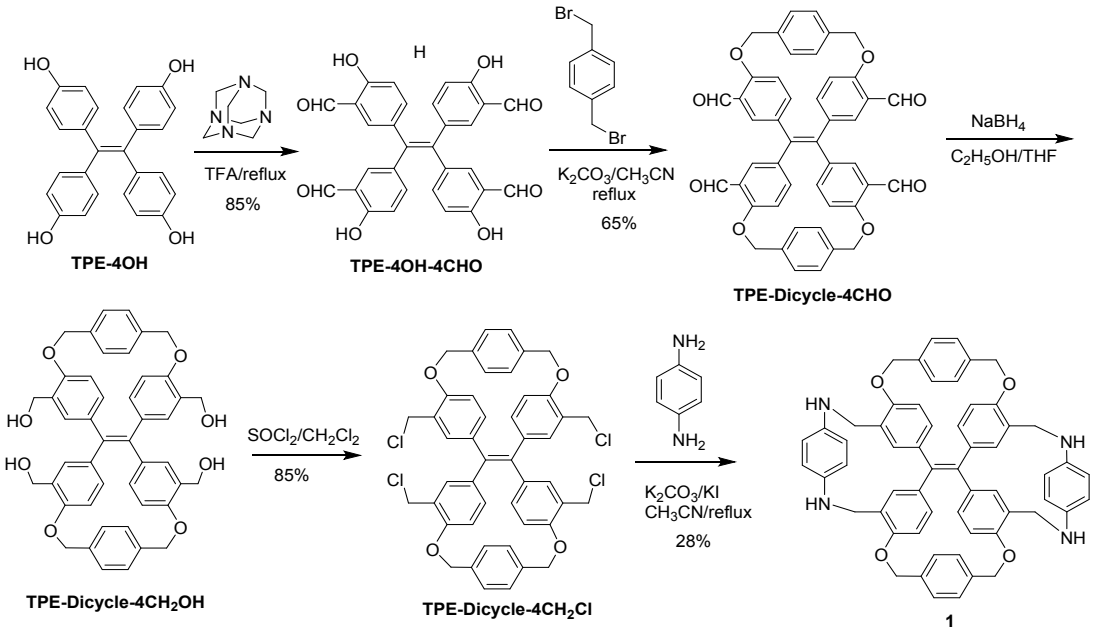
The preparation of solution of M-1-DSA and P-1-DSA mixture for CD and CPL measurements: Firstly, 1.0 mM solution of M-**1** was prepared by dissolving 8.65 mg of M-**1** in 10 mL of DCE. Secondly, 400 mM solution of *p*-dodecylbenzene sulfonic acid (DSA) was prepared by dissolving 130.6 mg of DSA in 1.0 mL of DCE. Then, 5.0 uL, 10 uL, 15 uL, 20 uL, and 25 uL of 400 mM DSA solution were mixed, respectively, with 2 mL of 1 mM M-**1** to offer a series of solutions of M-**1**-DSA mixture having M-**1:**DSA ratio of 1:1, 1:2, 1:3, 1:4, and 1:5. The M-**1**-DSA mixture solutions were left to stand for more than 10 h at room temperature before measurement of CD and CPL spectra. The P-**1**-DSA mixture solutions and other solutions with different concentration were prepared in the similar way.

The films of M-**1**-DSA and P-**1**-DSA mixture were prepared by dropping the solution of the mixture on the quartz glass sheet and air dried.

The preparation of solution of M-1-DSA-chiral acid and P-1-DSA-chiral acid mixture: After solutions of M-**1**-DSA and P-**1**-DSA mixture (1:2) in DCE were prepared and left to stand for 10 h at room temperature, the solution of enantiomer of chiral acid in DCE, DCE-acetone, or acetone was added. The resultant solutions of M-**1**-DSA-chiral acid and P-**1**-DSA-chiral acid mixture were left to stand for more than 4 h before measurement.

The films of M-**1**-DSA-chiral acid and P-**1**-DSA-chiral acid mixture were prepared by dropping the solution of the mixture on the quartz glass sheet and air dried.

Synthesis of helical TPE tetracycle tetramine M-1 and P-1



Synthesis of TPE-4OH-4CHO

To a 200 mL round-bottom flask was added TPE-4OH (2.0 g, 5.0 mmol), hexamethylenetetramine (2.42 g, 20 mmol) and trifluoroacetic acid (70 mL). After the solution was refluxed for 4 h, it was cooled to room temperature before a large amount of water was added. The mixture was stirred at room temperature overnight and filtered. The filter cake was the crude product, which was purified by column chromatography (silica gel, ethyl acetate: dichloromethane 1:40) to obtain **TPE-4OH-4CHO** as yellow powder (2.15 g, 85%). This compound and the following ones **TPE-Dicycle-4CHO**, **TPE-Dicycle-4CH_2OH**, and **TPE-Dicycle-4CH_2Cl** are known compounds, see *J. Am. Chem. Soc.* 2016, 138, 11469.

Synthesis of TPE-Dicycle-4CHO: TPE-4OH-4CHO (500 mg, 0.98 mmol), 1,4-bis (bromomethyl) benzene (570 mg, 2.16 mmol), anhydrous potassium carbonate (480 mg, 3.48 mmol), and dry acetonitrile (150 mL) were added into a 250 mL round bottom flask. After the mixture was refluxed for about 6 h under nitrogen protection, and the solvent of acetonitrile was removed by rotary evaporation under vacuum. Water and dichloromethane were added to obtain a two-phase solution. The organic phase was separated and the aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate, filtered under reduced pressure, and the filtrate was evaporated to dryness. The residue was separated by column chromatography (silica gel,

ethyl acetate / dichloromethane 1:50) to give **TPE-Dicycle-4CHO** as yellow solid (455 mg, 65%).

Synthesis of TPE-Dicycle-4CH_2OH: TPE-Dicycle-4CHO (250 mg, 0.35 mmol), THF/EtOH mixture (V / V = 2: 3, 50 mL) to a 100 mL round bottom flask, and then sodium borohydride NaBH4 (330 mg, 8.77 mmol) was added to the above mixed solution. The solution gradually became clear. The mixture was stirred at room temperature for 3 h. Then water was slowly added to quench the reaction and the solvent was dried. Water was added to the residue, filtered, and the residue was dried and used directly in the next step.

Synthesis of TPE-Dicycle-4CH_2Cl: TPE-Dicycle-4CH_2OH (200 mg, 0.28 mmol) and anhydrous dichloromethane (30 mL) were added to a 50 mL round bottom flask, and then freshly distilled dichlorosulfoxide (0.4 mL, 5.56 mmol) was added to the reaction system by dropwise. After the addition was completed, the mixture was stirred at room temperature for 3 h. The solvent was removed by a rotary evaporator. The residue was separated by column chromatography (silica gel, ethyl acetate / petroleum ether 1: 8) to give **TPE-Dicycle-4CH_2Cl** (214 mg, 85%) as a white solid.

Synthesis of rigid compound 1: To a 500 mL round bottom flask was added TPE-Dicycle-4CH_2Cl (0.5 g, 0.63 mmol), anhydrous K_2CO_3 (435 mg, 3.2 mmol), potassium iodide (532 mg, 3.2 mmol), 1,4-Benzenediamine (205 mg, 1.89 mmol), and dry acetonitrile (300 mL). Under nitrogen protection, the resultant mixture was refluxed for 5 h. After the reaction was completed, it was filtered. The solvent was removed by rotary evaporation under vacuum. The residue was separated by column chromatography (silica gel, methanol/ dichloromethane 1:40) to obtain **1** (135 mg, 28%) as a yellow solid. The obtained compound **1** was resolved into M-**1** and P-**1** enantiomers through a chiral high performance liquid chromatography column using CHIRALPAK IE column and 20:80:0.1 MeOH/DCM/DEA mobile phase. Racemic **1**: Mp > 300 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.167 (d, *J* = 8.7 Hz, 4H), 7.102 (d, *J* = 7.2 Hz, 4H), 6.645 (dd, *J* = 8.4, 2.6 Hz, 4H), 6.058 (dd, *J* = 8.4, 2.6 Hz, 4H), 5.933 (d, *J* = 7.9 Hz, 12H), 5.439 (d, *J* = 12.9 Hz, 4H), 5.080 (d, *J* = 12.9 Hz, 4H), 4.570 (d, *J* = 14.2 Hz, 4H), 3.685 (d, *J* = 14.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.910, 141.783, 140.778, 136.494, 135.055, 132.181, 132.135, 131.571, 127.048, 126.740, 122.329, 121.053, 115.392, 69.917, 49.234; IR (KBr) *v* 3403, 3262, 3022, 2929, 2880, 1668, 1602, 1497, 1308, 1265, 1215, 1171, 1120, 1000, 893, 812, 786, 698, 654, 552, 503, 473 cm-1; ESI$^+$ HRMS m/z calcd for $C_{58}H_{48}N_4O_4$ 865.3676 [M], found 865.3685 $[M+H]^+$

M-**1**: $[\alpha]^{25}_D$ = +636^o (5 mg/mL, $CHCl_3$); Mp > 300℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.188 (d, *J* = 8.7

Hz, 4H), 7.123 (d, *J* = 7.2 Hz, 4H), 6.662 (dd, *J* = 8.4, 2.6 Hz, 4H), 6.076 (dd, *J* = 8.4, 2.6 Hz, 4H), 5.952 (d, *J* = 7.9 Hz, 12H), 5.455 (d, *J* = 12.9 Hz, 4H), 5.098 (d, *J* = 12.9 Hz, 4H), 4.584 (d, *J* = 14.2 Hz, 4H), 3.702 (d, *J* = 14.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.874, 141.951, 140.785, 136.497, 135.059, 132.182, 132.111, 131.530, 127.045, 126.906, 122.349, 121.070, 115.374, 69.906, 49.277.

P-**1**: $[\alpha]^{25}_{D}$ =−688° (5 mg/mL, $CHCl_3$); Mp > 300℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.164 (d, *J* = 8.7 Hz, 4H), 7.101 (d, *J* = 7.2 Hz, 4H), 6.642 (dd, *J* = 8.4, 2.6 Hz, 4H), 6.056 (dd, *J* = 8.4, 2.6 Hz, 4H), 5.931 (d, *J* = 7.9 Hz, 12H), 5.435 (d, *J* = 12.9 Hz, 4H), 5.078 (d, *J* = 12.9 Hz, 4H), 4.565 (d, *J* = 14.2 Hz, 4H), 3.684 (d, *J* = 14.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.887, 141.917, 140.788, 136.504, 135.063, 132.182, 132.117, 131.540, 127.049, 126.876, 122.338, 121.059, 115.377, 69.912, 49.267.

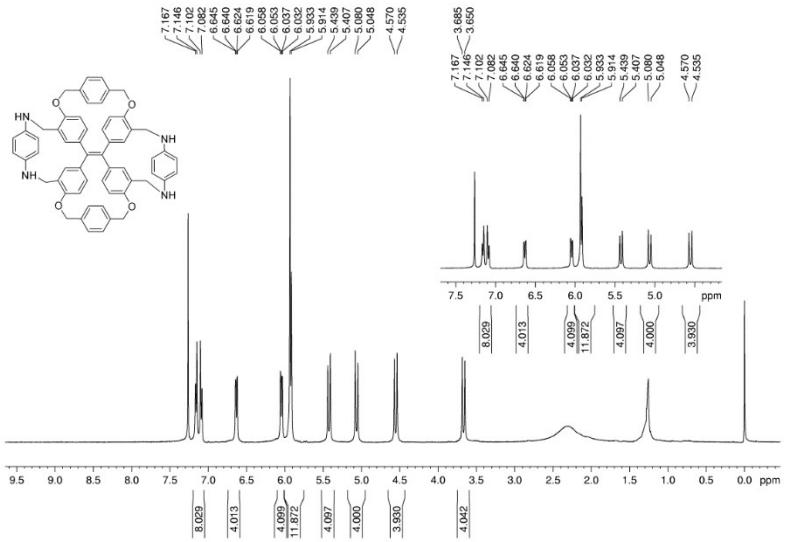


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

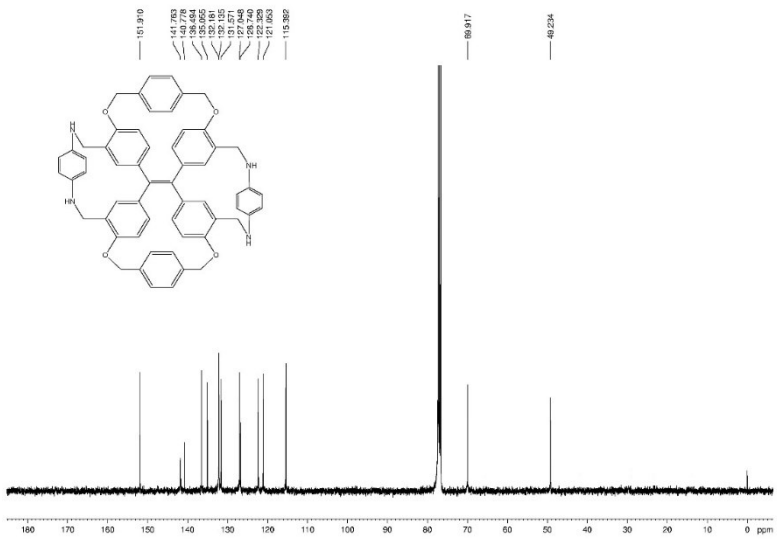


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

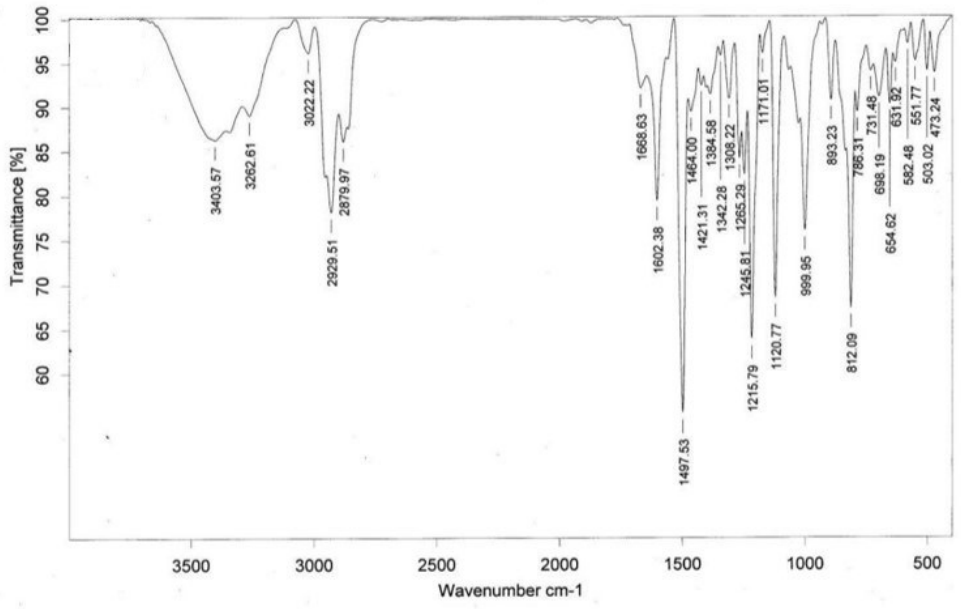
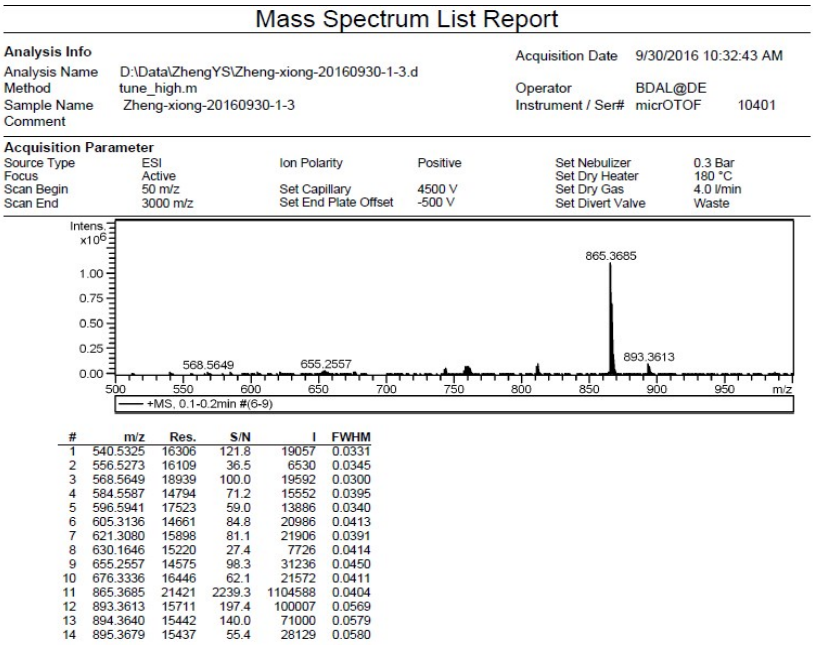


Figure S3. IR spectrum of compound **1** in KBr.



#	m/z	Res.	S/N	I	FWHM
1	540.5325	16306	121.8	19057	0.0331
2	556.5273	16109	36.5	6530	0.0345
3	568.5649	18939	100.0	19592	0.0300
4	584.5587	14794	71.2	15552	0.0395
5	596.5941	17523	59.0	13886	0.0340
6	605.3136	14661	84.8	20986	0.0413
7	621.3080	15898	81.1	21906	0.0391
8	630.1646	15220	27.4	7726	0.0414
9	655.2557	14575	98.3	31236	0.0450
10	676.3336	16446	62.1	21572	0.0411
11	865.3685	21421	2239.3	1104588	0.0404
12	893.3613	15711	197.4	100007	0.0569
13	894.3640	15442	140.0	71000	0.0579
14	895.3679	15437	55.4	28129	0.0580

Figure S4. HRMS spectrum of compound **1**.

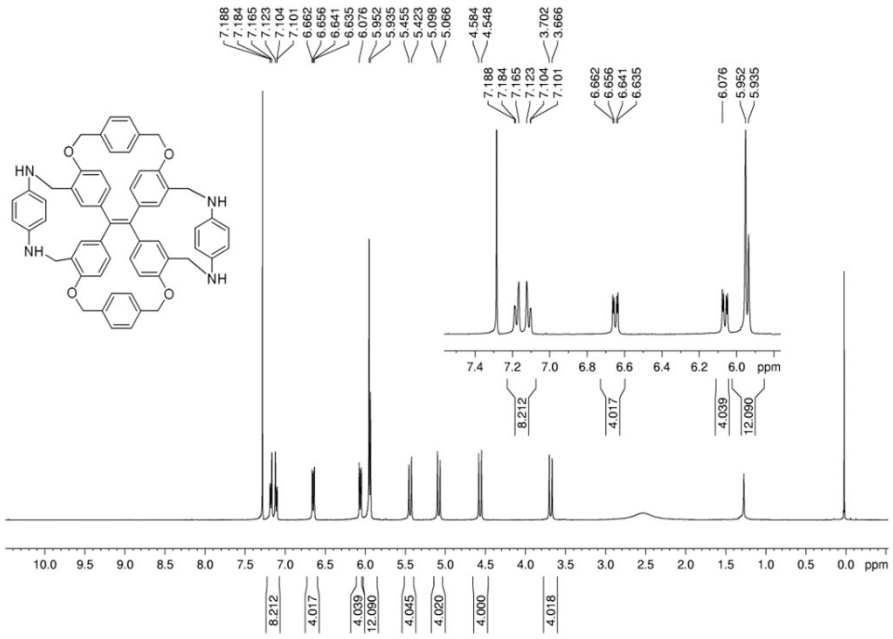


Figure S5. ^{1}H NMR spectrum of M-**1** in $CDCl_3$.

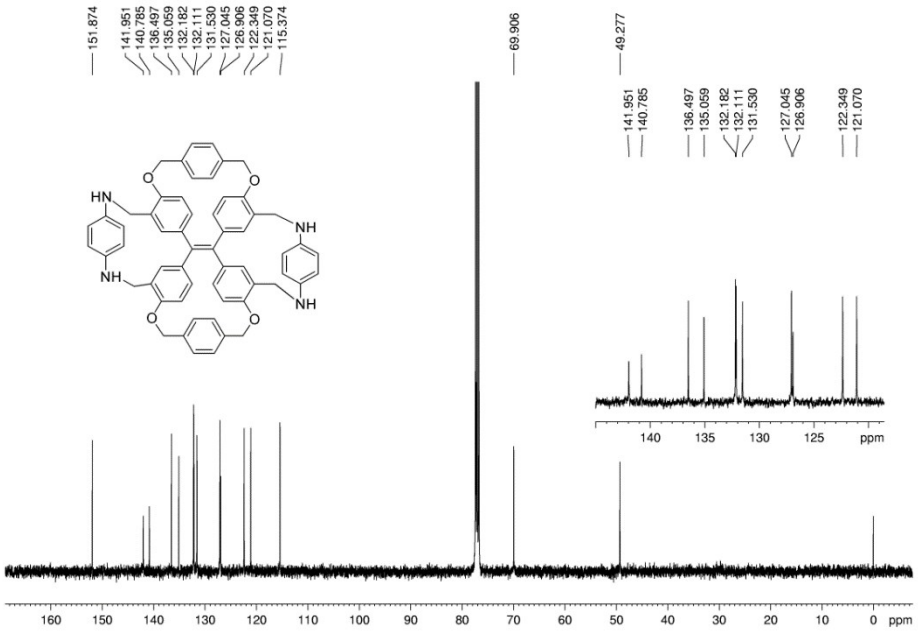


Figure S6. ^{13}C NMR spectrum of M-**1** in $CDCl_3$.

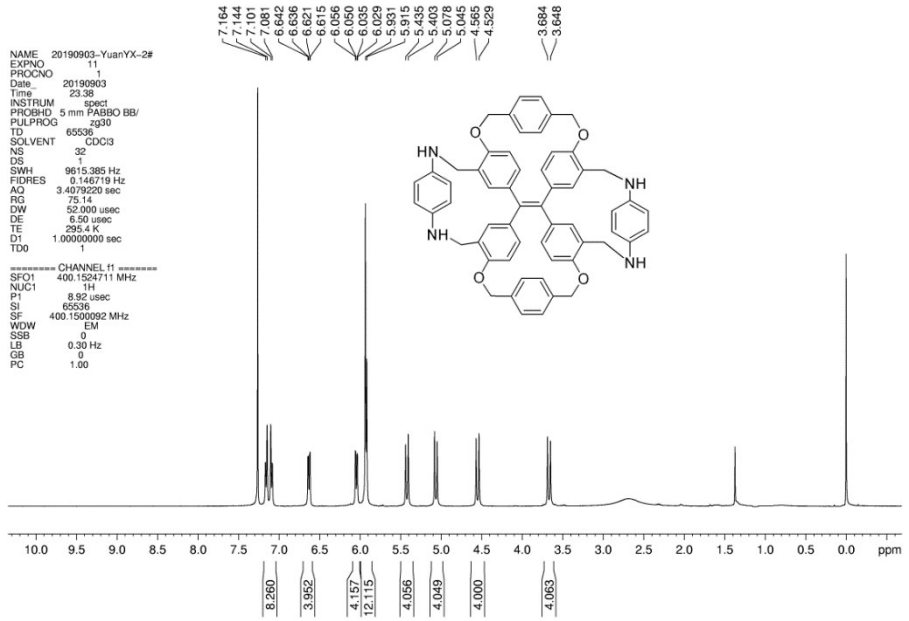


Figure S7. ^{1}H NMR spectrum of P-**1** in $CDCl_3$.

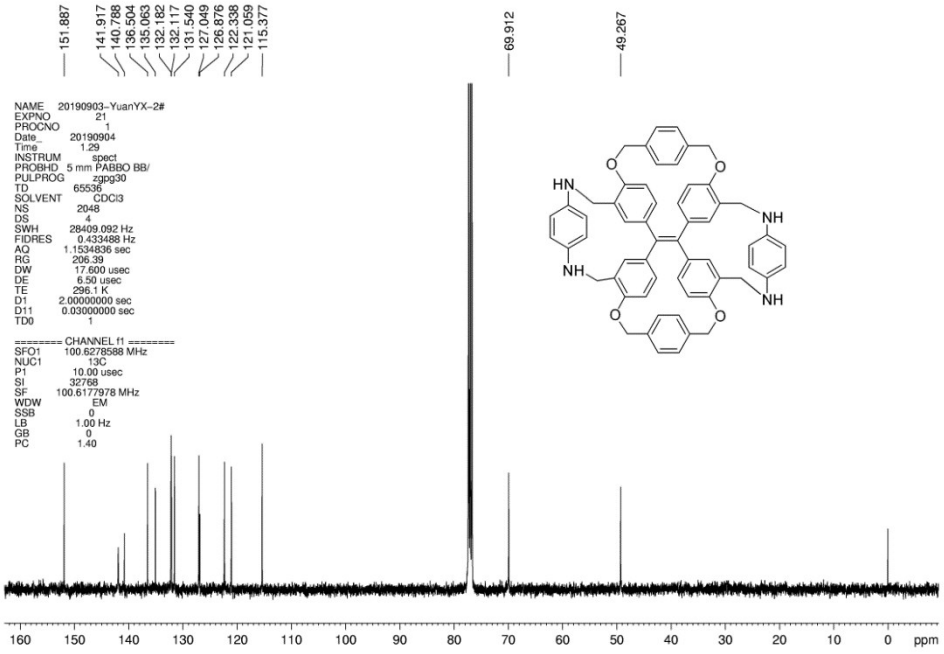


Figure S8 ^{13}C NMR spectrum of P-**1** in $CDCl_3$.

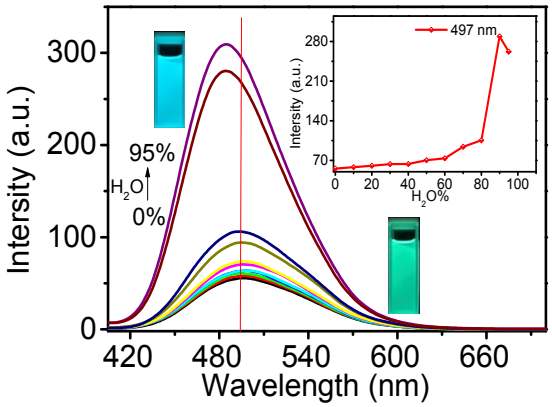


Figure S9. Change in the fluorescence spectra of **1** in H_2O/THF mixed solvent with water fraction. Inset, curve of maximum fluorescence intensity *vs* water fraction. [**1**] = 2.0×10^{-5} M, λ_{ex} = 370 nm, ex/em slit widths = 1.5/3 nm.

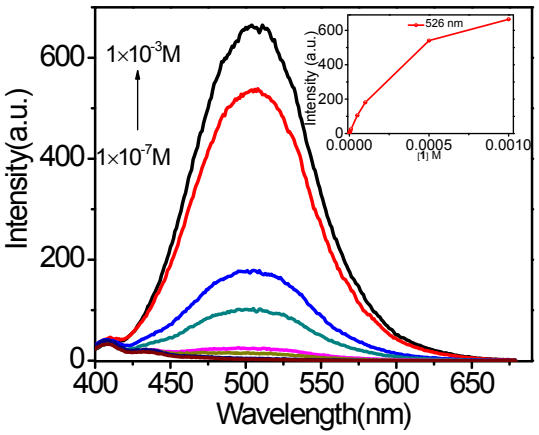


Figure S10. Change in the fluorescence spectra of **1** in THF with concentration. Inset, curve of fluorescence intensity at 526 nm vs concentration of **1** in THF. λ_{ex} = 370 nm, ex/em slit widths = 1.5/3 nm.

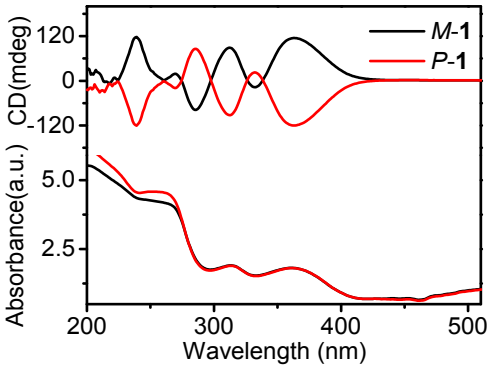


Figure S11. CD and absorption spectra of M-**1** and P-**1** in DCE (1.0×10^{-3} M).

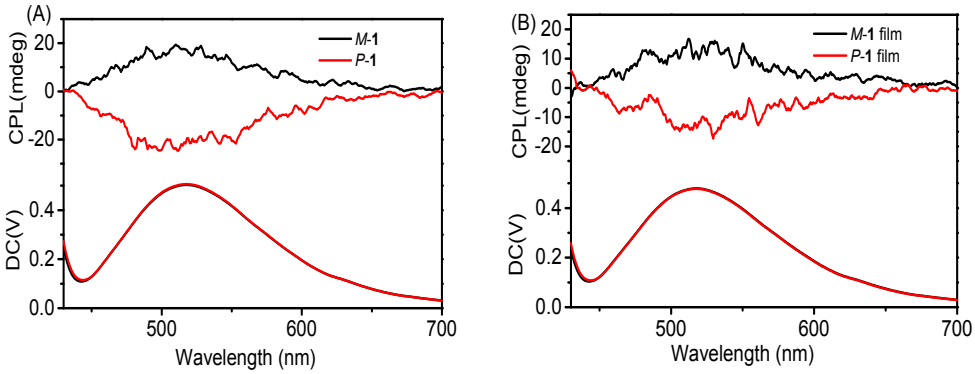


Figure S12. CPL spectra of the solution (A) and the films (B) of M-**1** and P-**1** in DCE (1.0×10^{-3} M). Excited at 370 nm. The CPL g_{lum} was 2.5×10^{-3} for M-**1** and -2.4×10^{-3} for P-**1** in solution, and 2.3×10^{-3} for M-**1** and -2.1×10^{-3} for P-**1** in film.

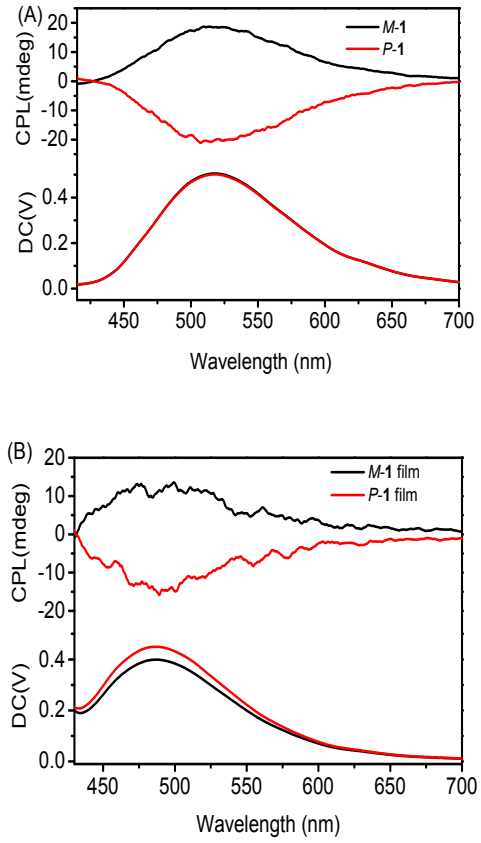


Figure S13. CPL spectra of the solution (A) and the films (B) of M-**1** and P-**1** in DCE (2.0×10^{-3} M). Excited at 370 nm. The CPL g_{lum} was 2.5×10^{-3} for M-**1** and -2.8×10^{-3} for P-**1** in solution, and 2.2×10^{-3} for M-**1** and -2.3×10^{-3} for P-**1** in film.

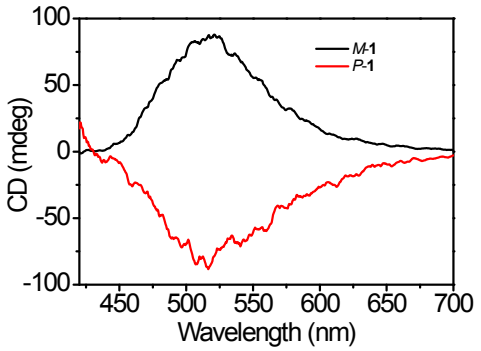


Figure S14. CPL spectra of the suspensions of M-**1** and P-**1** in 90:10 H_2O/THF (5.0×10^{-4} M). Excited at 370 nm. The CPL g_{lum} was 0.0121 for M-**1** and –0.0122 for P-**1** at 509 nm. The CPL g_{lum} was 0.0121 for M-**1** and –0.0122 for P-**1**.

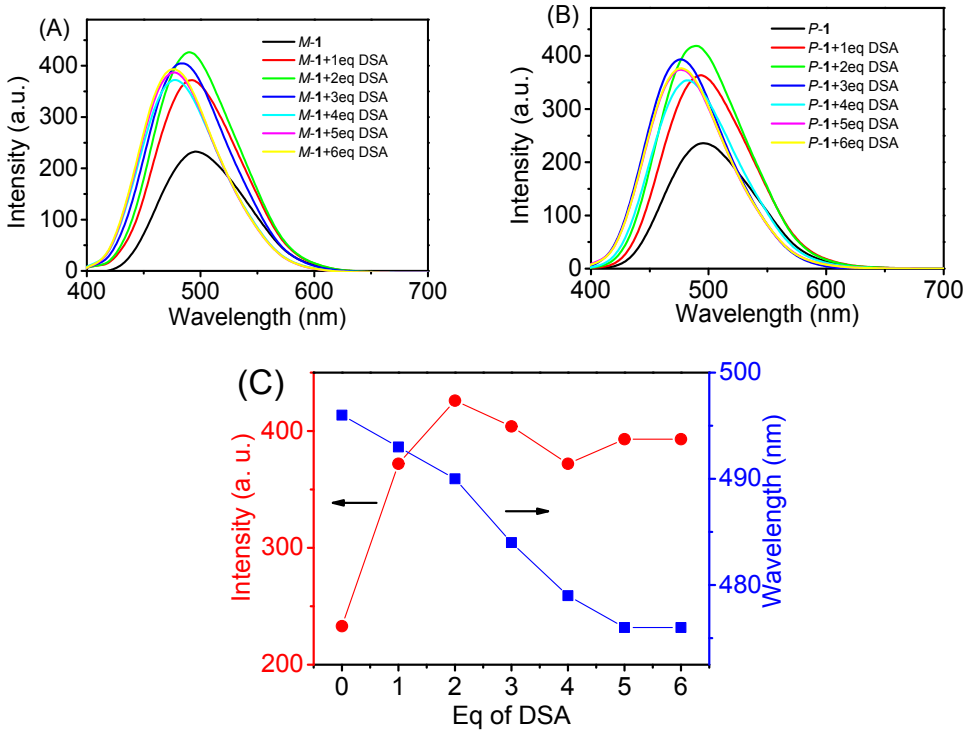


Figure S15. Change in the fluorescence spectra of M-**1** (A) and P-**1** (B) in DCE with DSA ratios. (C) Change in emission intensity and wavelength of M-**1** with molar equivalents of DSA. [**1**] = 1.0 × 10^{-5} M, λ_{ex} = 370 nm, ex/em slit widths = 3/3 nm.

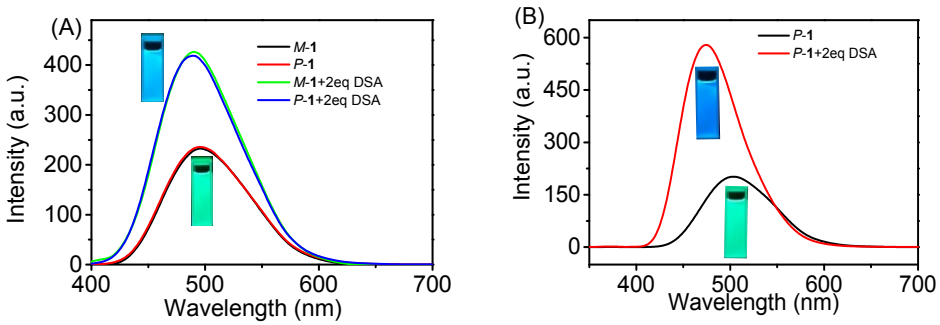


Figure S16. Fluorescence spectra of M-**1** (A) and P-**1** (B) in DCE with 2eq DSA. λ_{ex} = 370 nm, ex/em slit widths = 3/3 nm. Inset, photo of the solution under 365 nm light. [**1**] = 2.0 × 10^{-5} M.

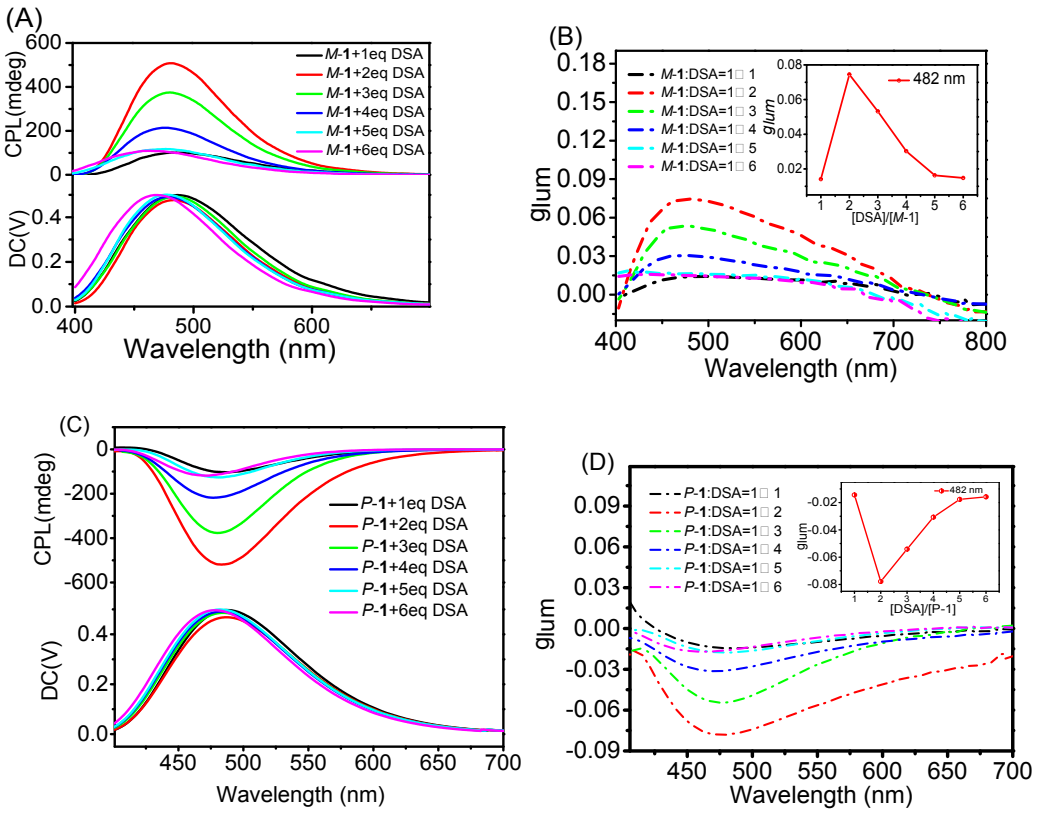


Figure S17. Change of the CPL spectra and g_{lum} value of M-**1**-DSA mixture (A, B) and P-**1**-DSA mixture (C, D) in DCE with **1**/DSA ratios. Inset, curve of CPL g_{lum} at 482 nm *vs* DSA/**1** ratios. [**1**] = 1.0×10^{-3} M, excited at 360 nm.

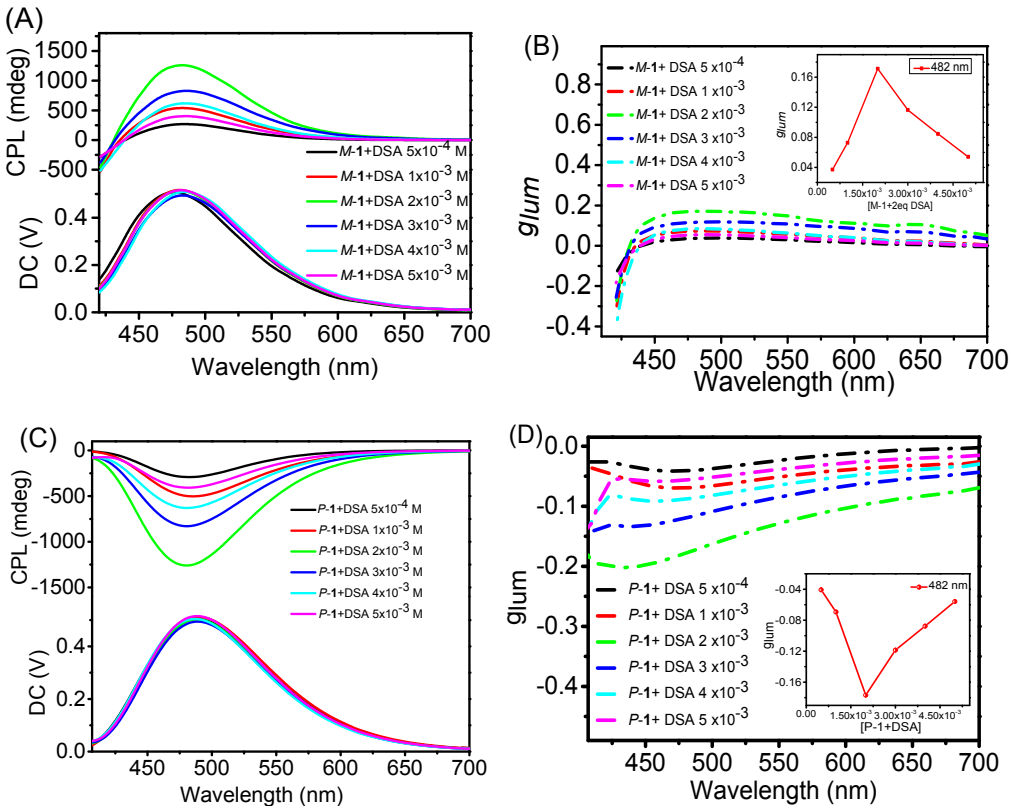


Figure S18. Change of the CPL spectra and g_{lum} values of M-**1**-2eq DSA mixture (A, B) and P-**1**-2eq DSA mixture (C, D) in DCE with concentration. Inset, curve of CPL g_{lum} at 482 nm *vs* concentration of **1**-2eq DSA mixture in DCE. Excited at 360 nm.

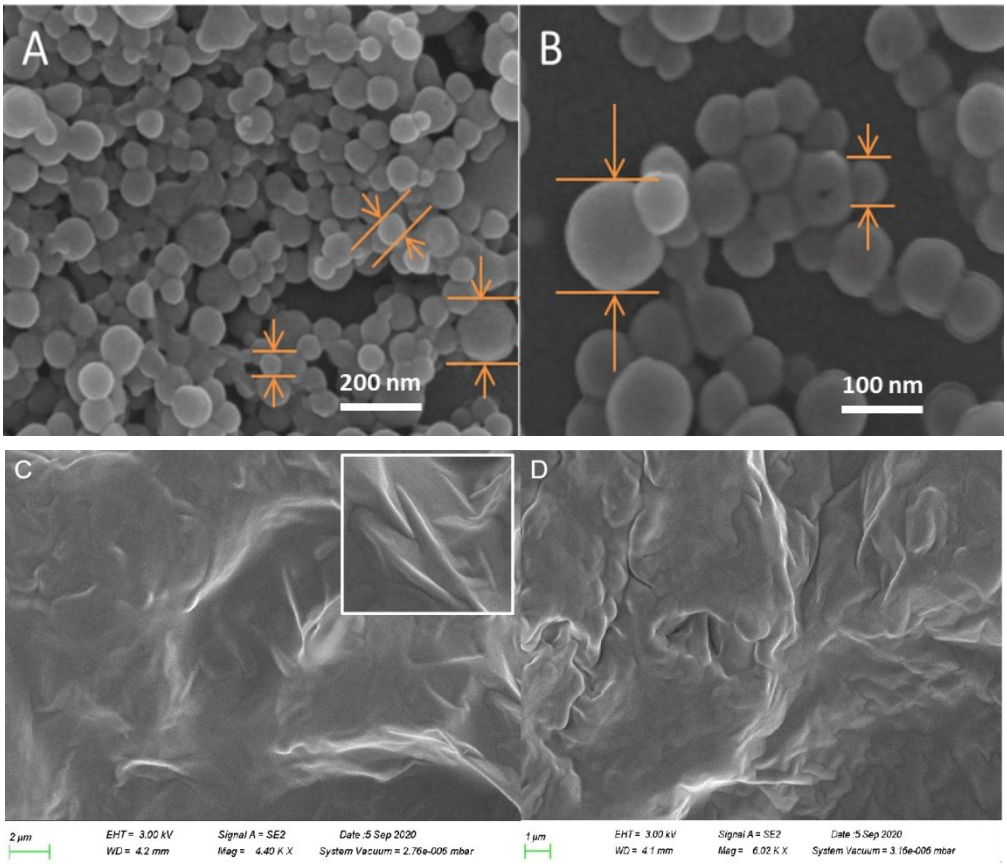


Figure S19. FE-SEM images of M-**1** (A) and P-**1** (B) in H_2O/THF 90:10, and FE-SEM images of M-**1** (C) and P-**1** (D) in DCE, inset: magnified images of M-**1**.

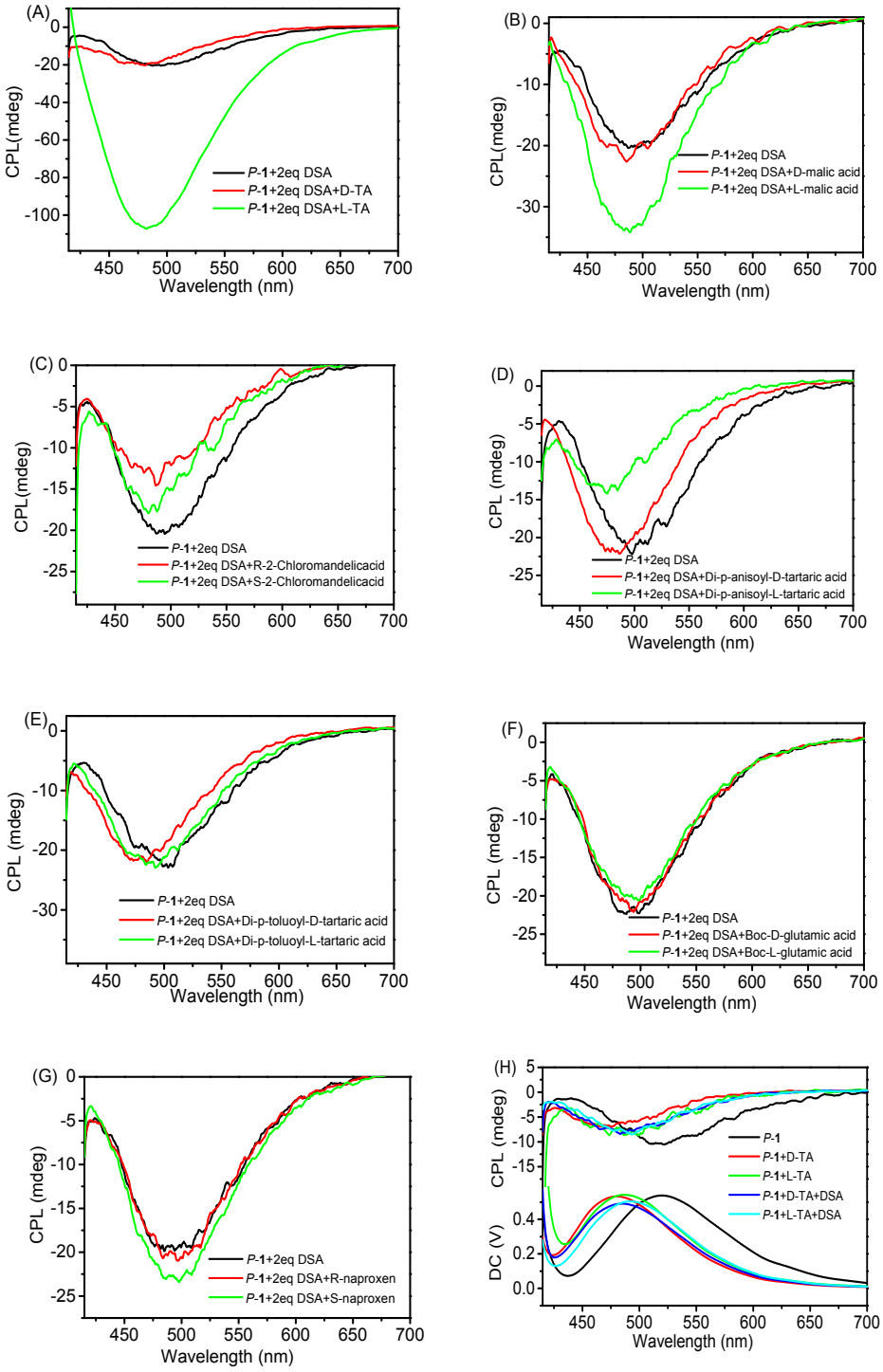


Figure S20. Change in the CPL spectra of a mixture of P-**1** with chiral acid in DCE. (A) D/L-tartaric acid; (B) D/L-malic acid; (C) *R*/*S*-2-chloro-Mandelic acid; (D) D/L-dimethoxybenzoyltartaric acid; (E) D/L-dimethylbenzoyltartaric acid; (F) Boc-D/L-glutamic acid; (G) *R*/*S*-naproxen; and (H) CPL spectra of P-**1** which was mixed first with D/L-tartaric acid before addition of DSA in DCE. ([P-**1**] = 1.0×10^{-4} M, [DSA] = 2.0×10^{-4} M), [chiral acid] = 4.0×10^{-4} M. The mixture is allowed to stand at room temperature for 10 h before measurement. Excited at 360 nm.

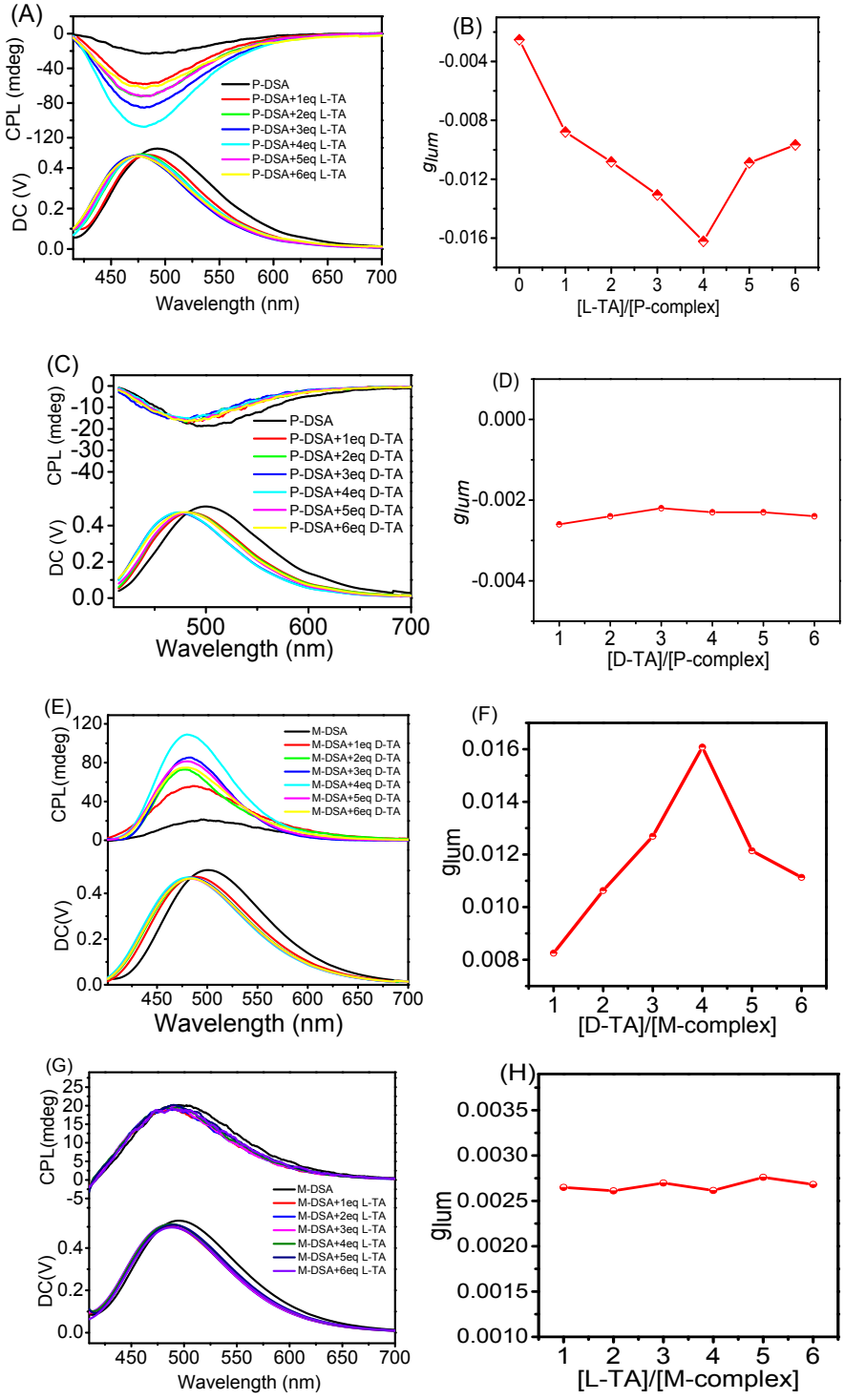


Figure S21. Change in the CPL spectra of a mixture of P-**1** and TA with ratios of L-TA (A) or D-TA (C) vs P-**1** in DCE, and CPL g_{lum} change with ratios of L-TA (B) or D-TA (D) vs P-**1**. Change in the CPL spectra of a mixture of M-**1** and TA with ratios of D-TA (E) or L-TA (G) vs M-**1** in DCE, and CPL g_{lum} change with ratios of D-TA (F) or L-TA (H) vs M-**1**. [P-**1**] = [M-**1**] = 1.0×10^{-4} M. The mixture of M/P-**1** and DSA was left to stand for 10 h at room temperature before addition of TA and measurement.

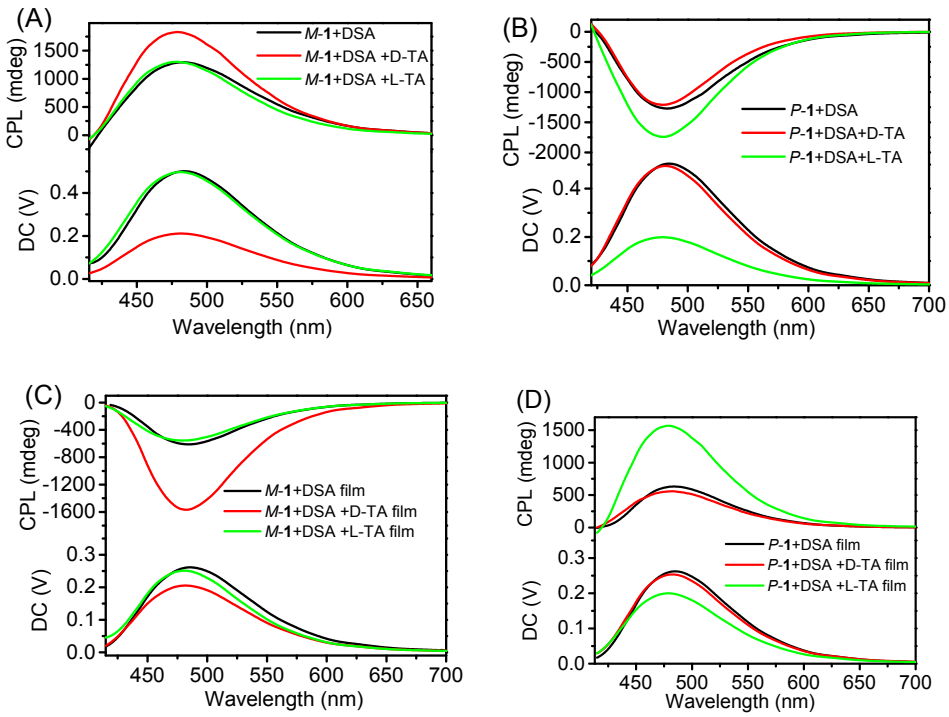


Figure S22. Change in the CPL spectra of M-**1**-DSA-TA and P-**1**-DSA-TA mixture in DCE solution (A, B) and in film (C, D). [**1**] = 1/2[DSA] = 1/4[TA] = 2.0×10^{-3} M. The M-**1**-DSA and P-**1**-DSA mixture was left to stand for 10 h at room temperature before addition of TA and measurement.

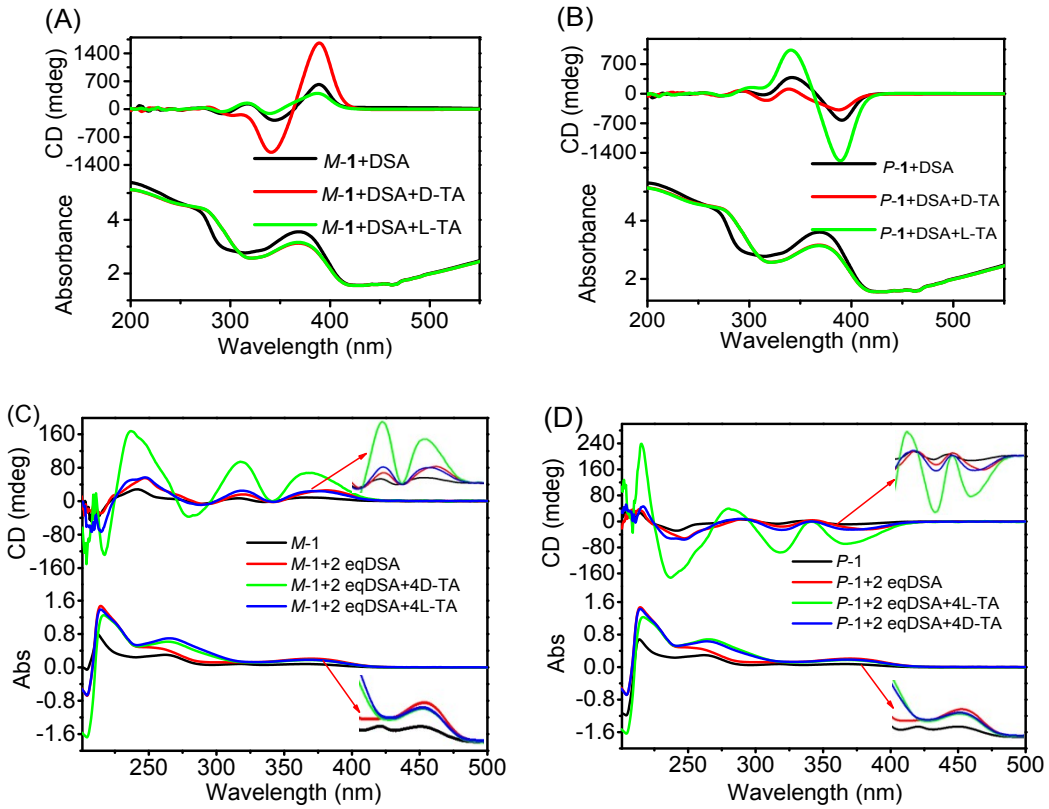


Figure S23. CD spectra of M-**1**-DSA-TA and P-**1**-DSA-TA mixture in DCE at [**1**] = 1/2[DSA] = 1/4[TA] = 2.0×10^{-3} M (A, B) and at [**1**] = 1/2[DSA] = 1/4[TA] = 1.0×10^{-4} M (C, D). The M-**1**-DSA *and* P-**1**-DSA mixture was left to stand for 10 h at room temperature before addition of TA and measurement.

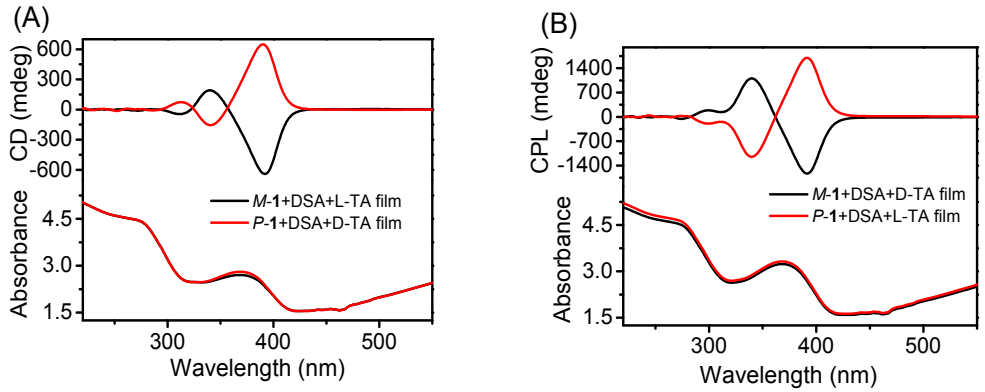


Figure S24. CD spectra of M-**1**-DSA-TA and P-**1**-DSA-TA mixture in film. [**1**] = 1/2[DSA] = 1/4[TA] = 2.0×10^{-3} M. The M-**1**-DSA *and* P-**1**-DSA mixture was left to stand for 10 h at room temperature before addition of TA and measurement.

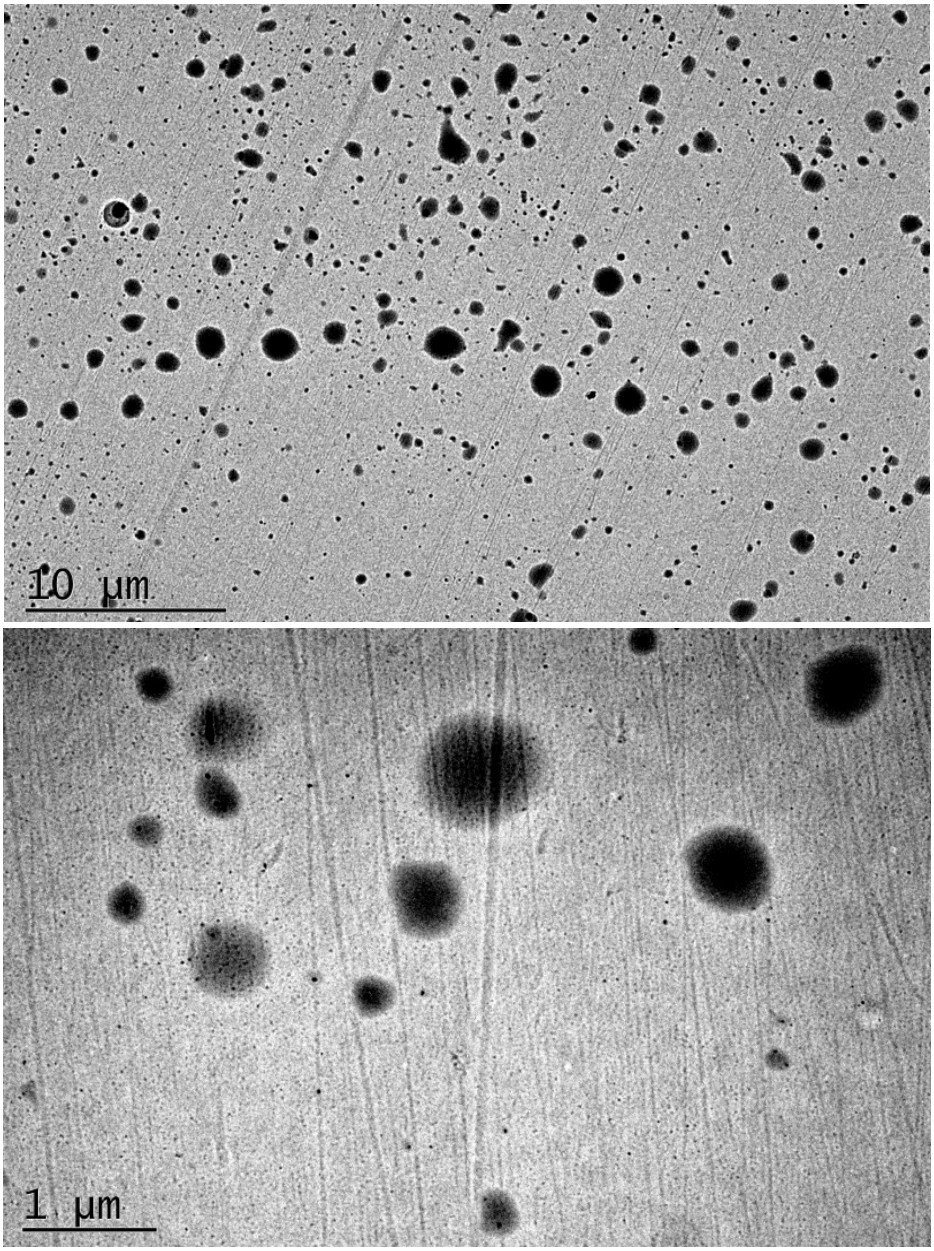


Figure S25. TEM images of M-**1**-DSA-D-TA mixture in DCE. [M-**1**] = 1/2[DSA] = 1/4[D-TA] = 2.0 × 10^{-4} M. One drop of the solution was put on a copper grid covered with a thin carbon film on a filter paper and air dried before measurement. The particles in the images should be the aggregates resulted from excess of TA.

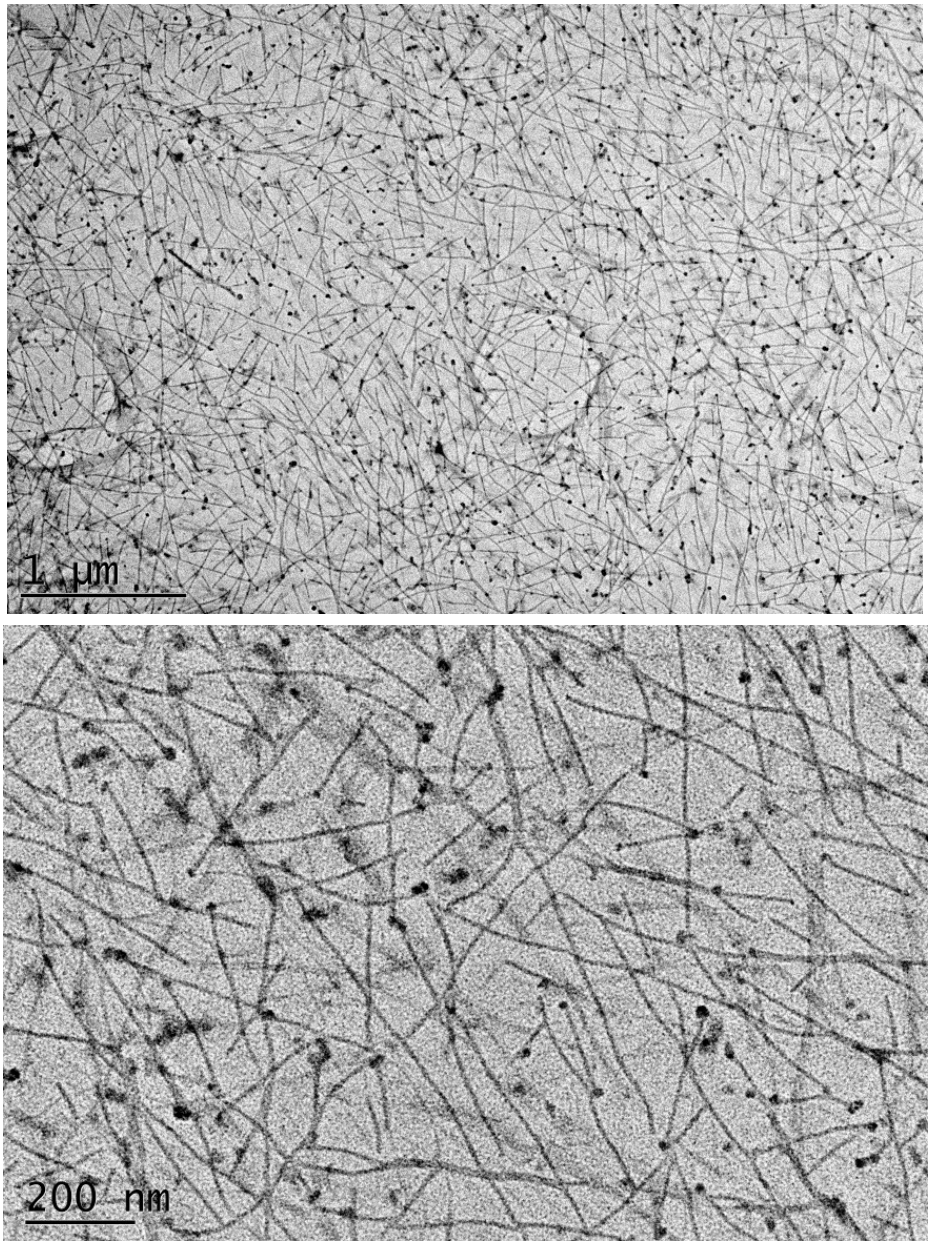


Figure S26. TEM images of M-**1**-DSA-L-TA mixture in DCE. [M-**1**] = 1/2[DSA] = 1/4[L-TA] = 2.0×10^{-4} M. One drop of the solution was put on a copper grid covered with a thin carbon film on a filter paper and air dried before measurement. The particles in the images should be the aggregates resulted from excess of TA.

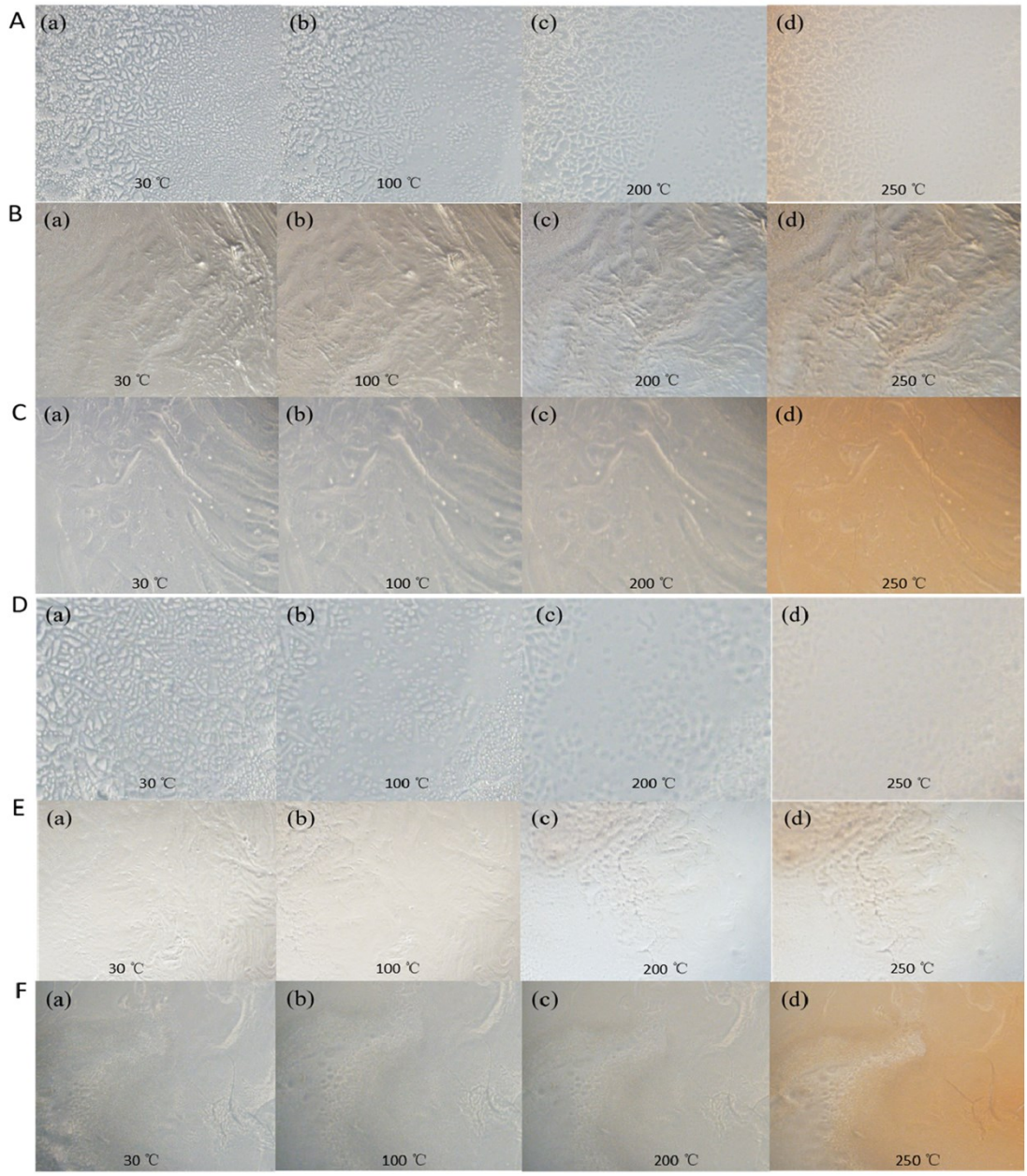


Figure S27. Polarized optical microscopy (POM) of the films of a mixture of M-**1**/P-**1**-2DSA with and without TA from DCE at different temperatures. The POM images of M-**1**-2DSA films (A), M-**1**-2DSA-L-TA films (B), M-**1**-2DSA-D-TA films (C), P-**1**-2DSA films (D), P-**1**-2DSA-D-TA films (E), and P-**1**-2DSA-L-TA films (F).