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Strong Circularly Polarized Luminescence Induced from Chiral Supramolecular Assembly Helical Nanorods

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1. Instrumentation and Materials.

NMR spectra were obtained by using a 400 MHz Bruker spectrometer with 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR and the chemical shifts are reported as parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. Fluorescence spectra were obtained by using HORIBA Scientific Fluoromax-4 Spectrofluorometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were recorded with a JASCO CPL-300 spectrofluoropolarimeter. Scanning electron microscope (SEM) images were taken in Hitachi S-4800 field emission scanning electron microscopy. All solvents and reagents were commercially available A.R. grade.

2. Synthesis procedures of the compound BPP.

Synthesis of compound 2 (1-ethynylpyrene)

1-bromopyrene (3.00 g, 10.67 mmol), $Pd(PPh_3)_2Cl_2$ (374 mg, 0.53 mmol), CuI (102 mg, 0.53 mmol), trimethylsilylacetylene (3.02 mL, 21.34 mmol) were dissolved in 50 mL degassed THF and Et_3N. The reaction mixture was stirred at 80 ºC under N_2 atmosphere for 12 h. After the reaction was finished, the solution was filtered through a short silica gel column and the solvent was evaporated under reduced pressure. The residues was dissolved in 60 mL CH_2Cl_2 and 30 mL CH_3OH. K_2CO_3 (3.00 g, 21.74 mmol) was added, and then the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered to remove K_2CO_3. The solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: petroleum ether) to give **compound 2** as grey solid.

Compound 2 (1.37 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 9.1 Hz, 1H), 8.25 – 8.15 (m, 4H), 8.10 (d, J = 8.6 Hz, 2H), 8.06 – 8.00 (m, 2H), 3.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.51, 131.61, 131.18, 130.99, 130.17, 128.57, 128.42, 127.20, 126.30, 125.76, 125.70, 125.32, 124.39, 124.35, 124.21, 116.51, 82.77, 82.63.

Synthesis of compound 3

1-ethynylpyrene (630 mg, 2.79 mmol), 2,6-dibromopyridine (300 mg, 1.27 mmol), $Pd(PPh_3)_2Cl_2$ (44 mg, 0.063 mmol), CuI (12 mg, 0.063 mmol), were dissolved in 20 mL THF and 10 mL Et_3N. The reaction mixture was stirred at 80 ºC under N_2 atmosphere for 24 h. After the reaction was finished, the solution was filtered, and the solids were collected. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2) to give **compound 3** as brown-yellow solid.

Compound 3 (473 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.8 Hz, 2H), 8.35 (d, J = 7.8 Hz, 2H), 8.25 (dd, J = 13.6, 5.7 Hz, 6H), 8.20 – 8.12 (m, 4H), 8.07 (dd, J = 15.0, 8.1 Hz, 4H), 7.87 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.09, 136.74, 132.54, 131.97, 131.21, 131.06, 130.27, 128.72, 128.69, 127.24, 126.60, 126.35, 125.95, 125.83, 125.66, 124.56, 124.42, 124.24, 116.41, 93.75, 89.59. MS (ESI, m/z): 528.15 (M^++1).

Synthesis of BPP

Compound 3 (200 mg, 0.38 mmol) was dissolved in 20 mL CH_2Cl_2. After adding 10 mL CH_3I, the solution was refluxed for 24 h. The reaction mixture was filtered, and the solids were washed with 20 mL CH_2Cl_2. The solids were dried in vacuum to give **BPP** as red solid.

BPP (218 mg, 86%). ^{1}H NMR (400 MHz, DMSO) δ 8.82 – 8.66 (m, 5H), 8.53 (ddd, J = 29.0, 24.8, 7.7 Hz, 11H), 8.35 (d, J = 7.9 Hz, 2H), 8.24 (t, J = 6.2 Hz, 2H), 4.91 (s, 3H). MS (ESI, m/z): 542.15 (M^+). ^{13}C NMR spetra can't be obtained because of the poor solubility.

3. FTIR spectra of S-BNS, BPP and S-BNS-BPP assemblies.

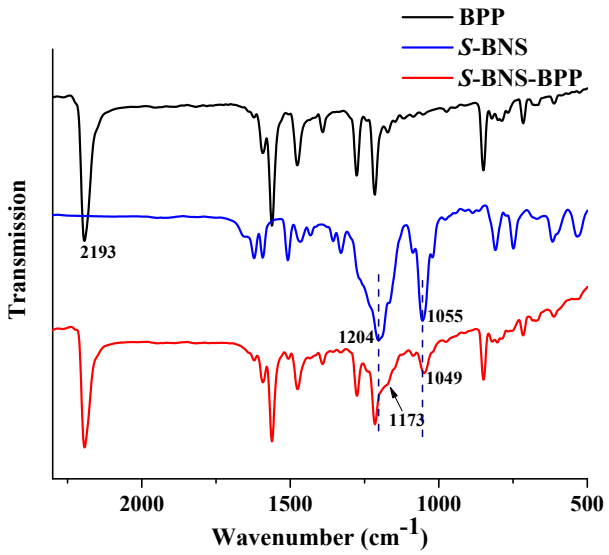

Fig. S1 FTIR spectra of *S*-BNS, BPP and *S*-BNS-BPP assemblies.

4. The Job's plot of the absorption at 576 nm of BNS-BPP.

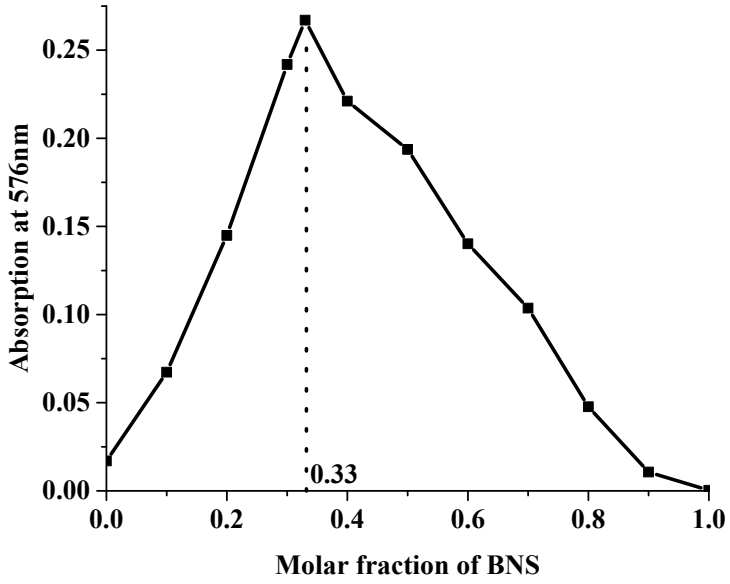

Fig. S2 The Job's plot of the absorption at 576 nm of BNS-BPP in methanol-water (50:50 v/v). The total concentration of BPP and BNS is fixed at 2×10^{-5} mol/L. The optimum mixing ratio of BNS: BPP is found to be 1.0 : 2.0.

5. CD spectra of BNS and BNS-BPP.

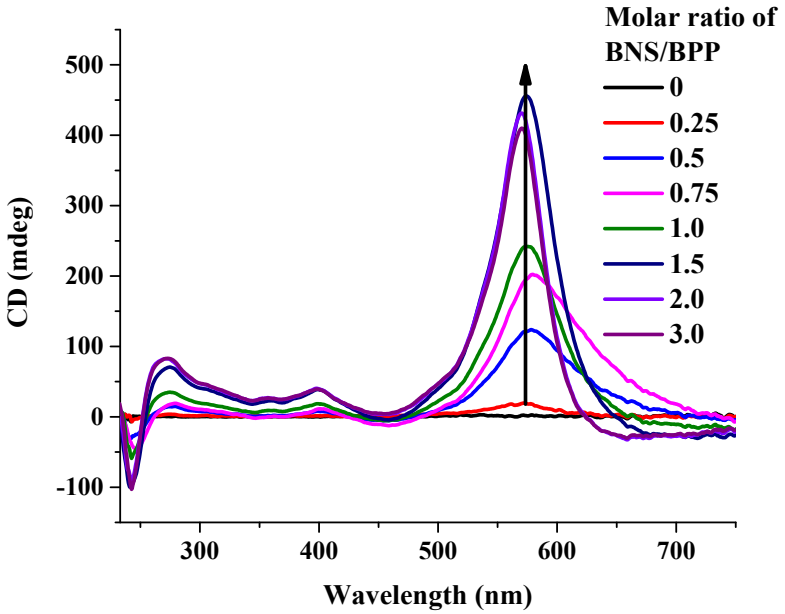

Fig. S3 CD spectra of *R*-BNS-BPP in methanol-water (50:50 v/v). Concentration: 1 × 10^{-5} mol/L for BPP.

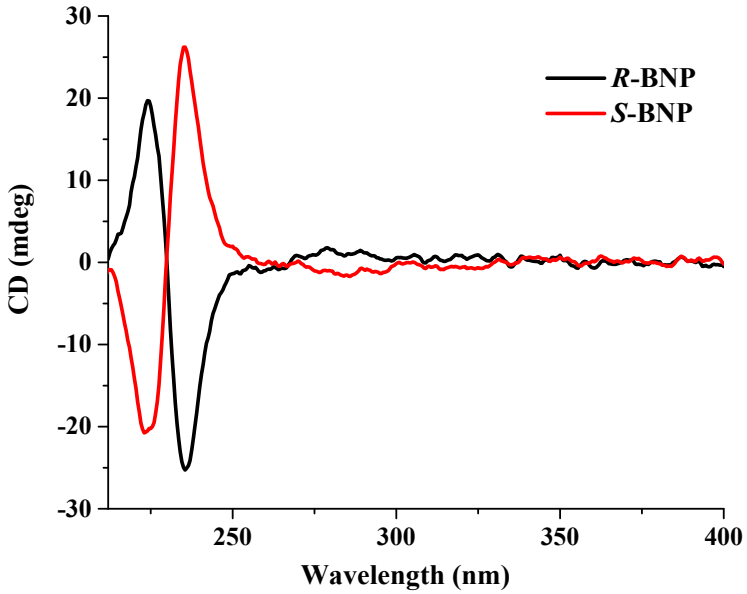

Fig. S4 CD spectra of *R*/*S*-BNS in methanol-water (50:50 v/v). Concentration: 0.5 × 10^{-5} mol/L for BNS.

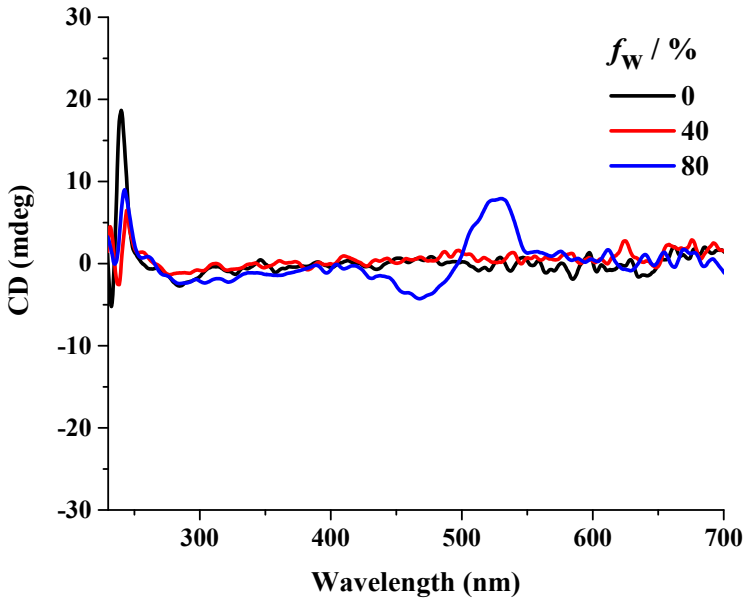

Fig. S5 CD spectra of *S*-BNS-BPP in methanol-water. Concentration: 1×10^{-5} mol/L for BPP, 0.5×10^{-5} mol/L for BNS.

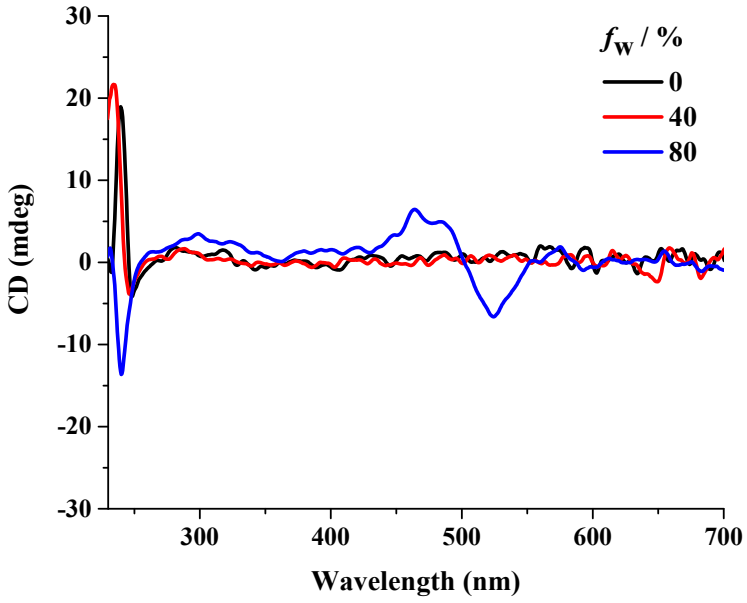

Fig. S6 CD spectra of *R*-BNS-BPP in methanol-water. Concentration: 1×10^{-5} mol/L for BPP, 0.5×10^{-5} mol/L for BNS.

6. Fluorescent spectra of *R*-BNS-BPP.

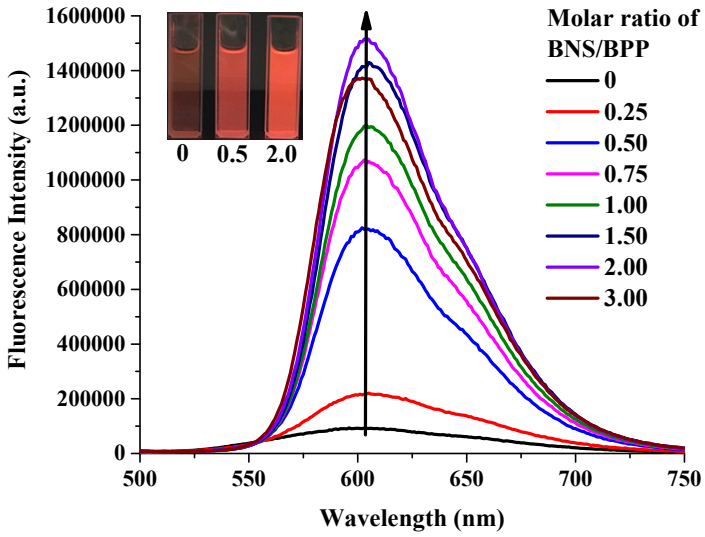

Fig. S7 Fluorescent spectra of *R*-BNS-BPP in MeOH-H_2O (50:50 v/v) solution (excitation: 467 nm). The concertration of BPP is fixed at 1.0 × 10^{-5} mol/L. Insert: photographs taken under UV illumination (365 nm).

7. CPL spectra of BNS-BPP.

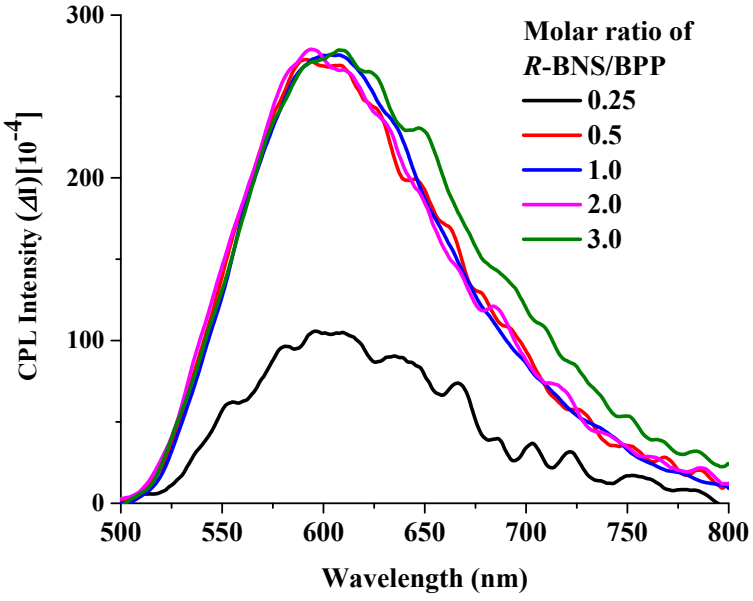

Fig. S8 CPL spectra of *R*-BNS-BPP in methanol-water. Concentration: 1 × 10^{-5} mol/L for BPP, DC (intensity of the unpolarized emission) is fixed at 0.5.

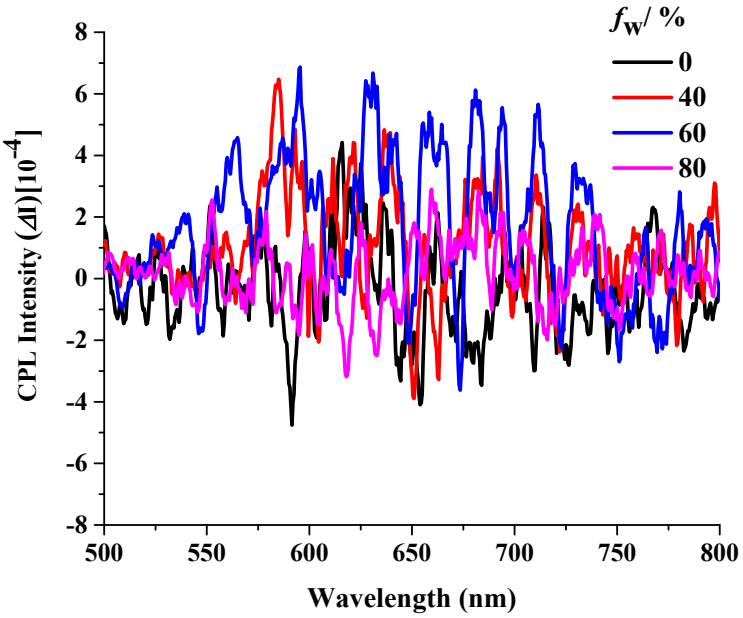

Fig. S9 CPL spectra of *R*-BNS-BPP in methanol-water. Concentration: 1 × 10^{-5} mol/L for BPP, 0.5 × 10^{-5} mol/L for BNS.

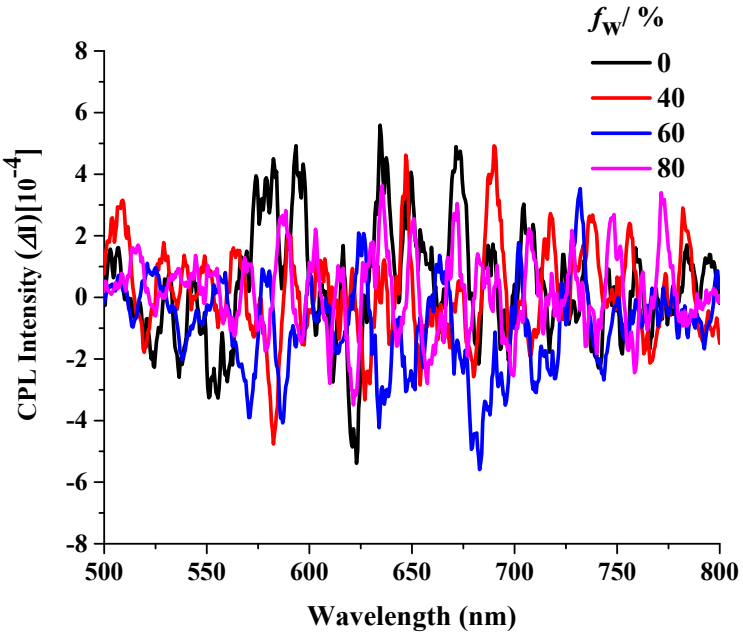

Fig. S10 CPL spectra of *S*-BNS-BPP in methanol-water. Concentration: 1 × 10^{-5} mol/L for BPP, 0.5 × 10^{-5} mol/L for BNS.

8. SEM images of BNS-BPP.

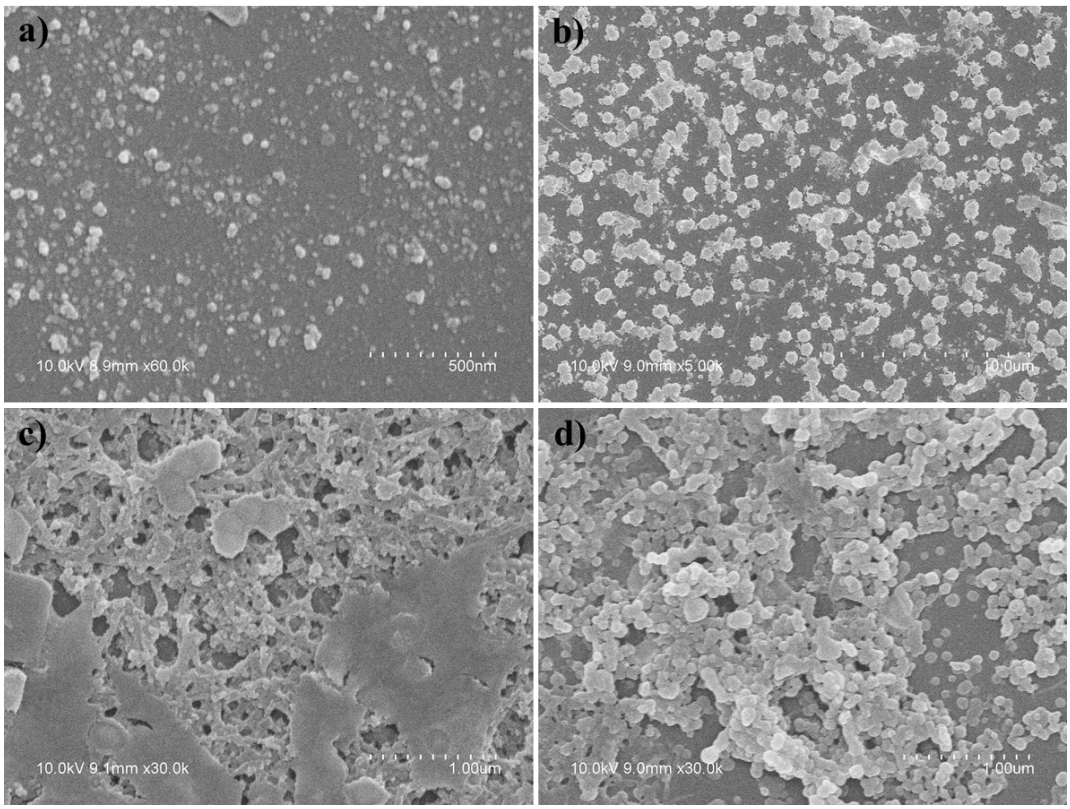

Fig. S11 SEM images of samples obtained from drying the solutions of BNS-BPP in methanol-water (a, b, c and d for f_w = 0, 40%, 60% and 80%). Concentration: 1 × 10^{-5} mol/L for BPP, 0.5 × 10^{-5} mol/L for BNS.

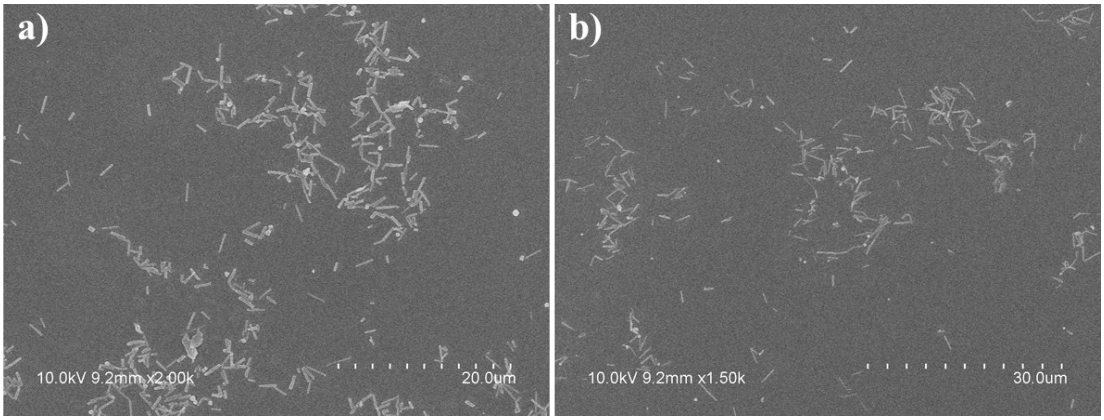

Fig. S12 SEM images of samples obtained from drying the solutions of (a) *R*-BNS-BPP and (b) *S*-BNS-BPP in methanol-water (50:50 v/v). Concentration: 1 × 10^{-5} mol/L for BPP, 0.5 × 10^{-5} mol/L for BNS.

9. NMR spectra of several compounds.

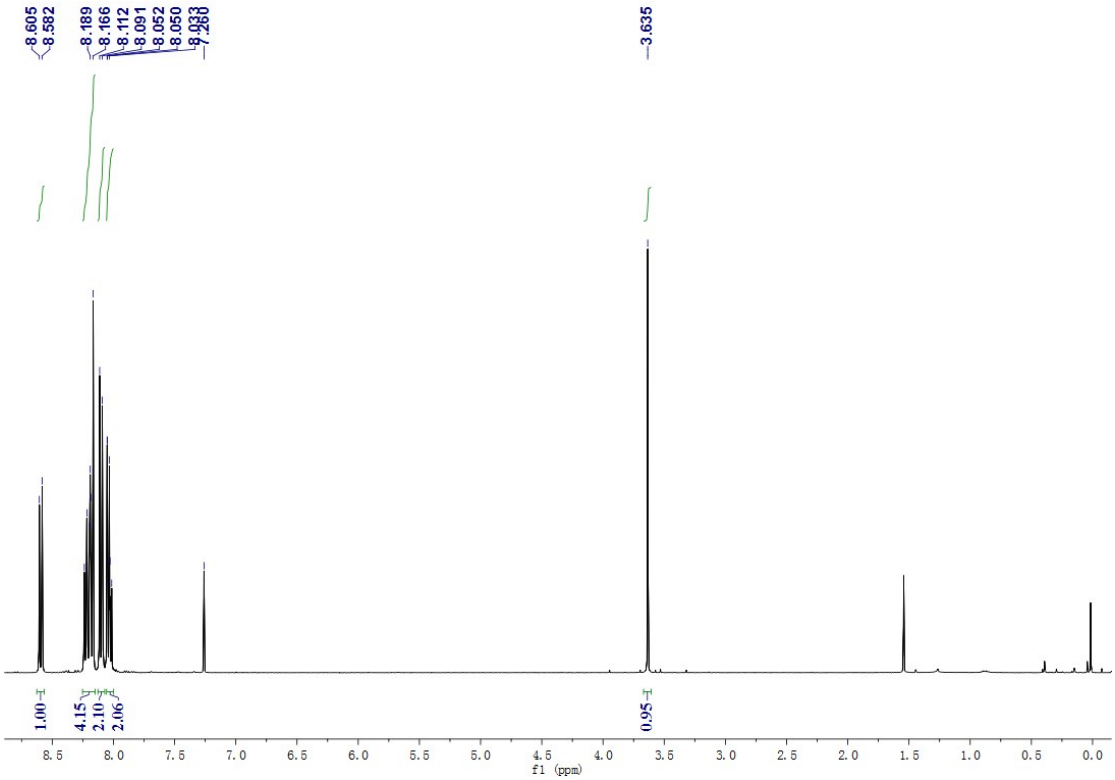

Fig. S13 ^{1}H NMR spectra of compound 2 (400 MHz, $CDCl_3$).

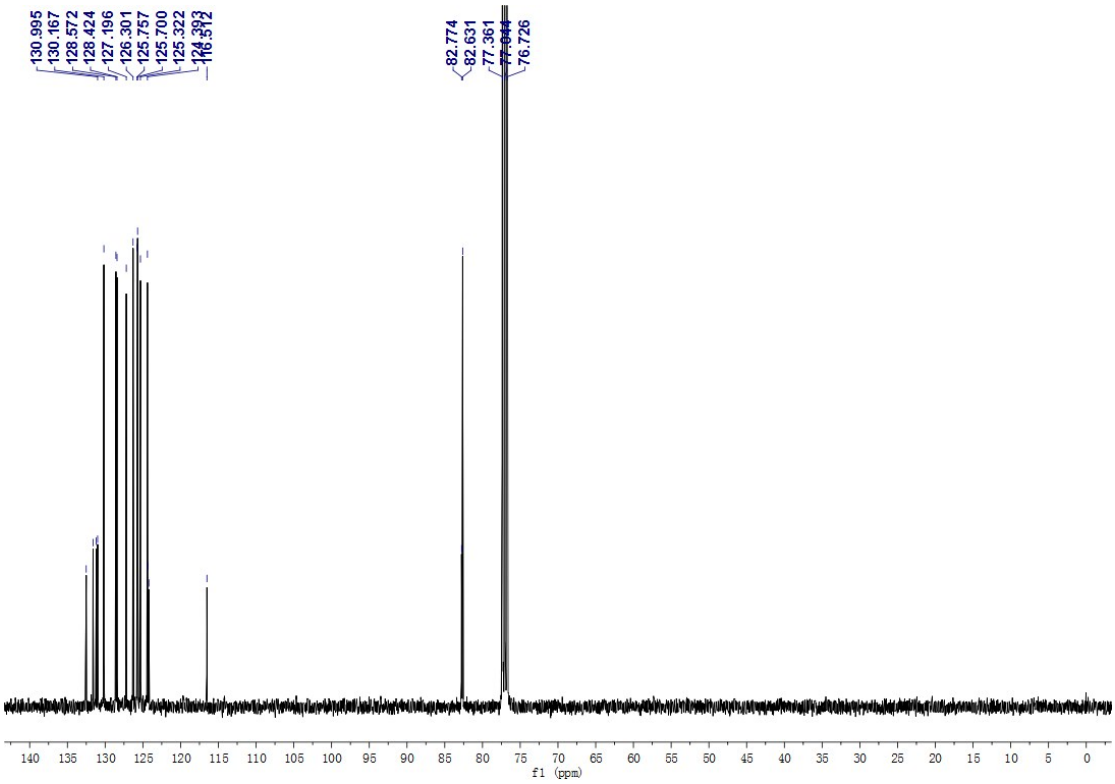

Fig. S14 ^{13}C NMR spectra of compound 2 (100 MHz, $CDCl_3$).

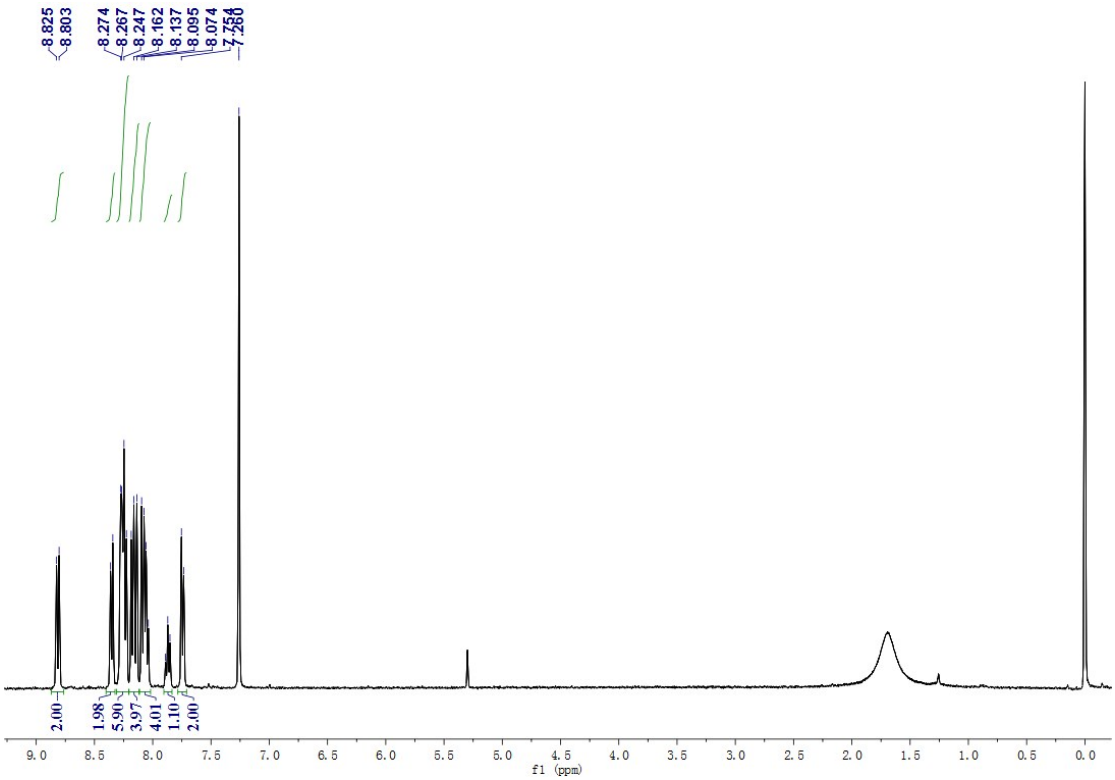

Fig. S15 ^{1}H NMR spectra of compound 3 (400 MHz, $CDCl_3$).

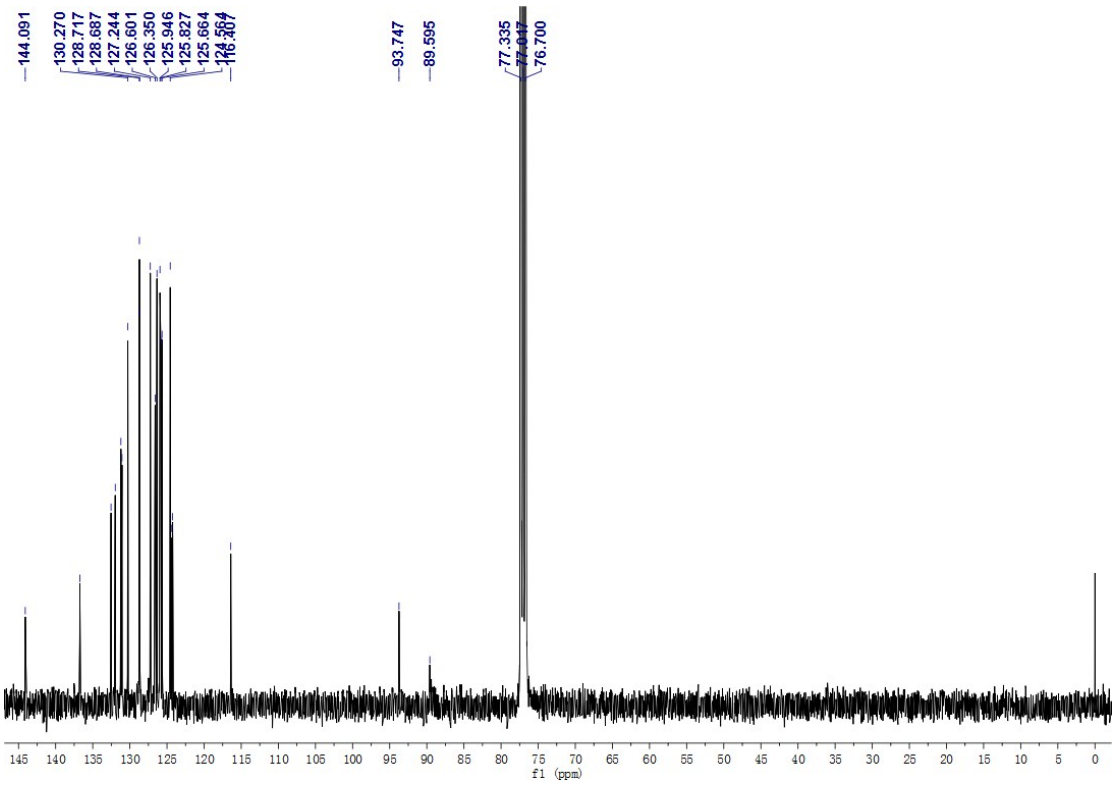

Fig. S16 ^{13}C NMR spectra of compound 3 (100 MHz, $CDCl_3$).

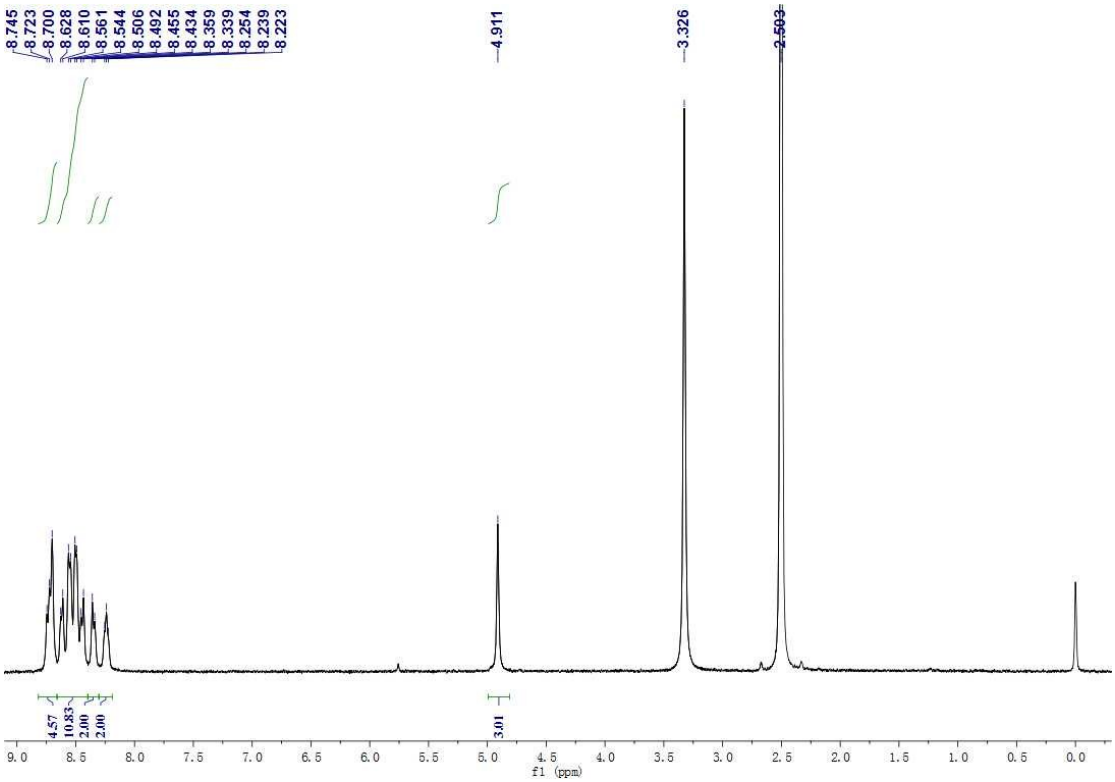

Fig. S17 ^{1}H NMR spectra of compound BPP (400 MHz, DMSO).

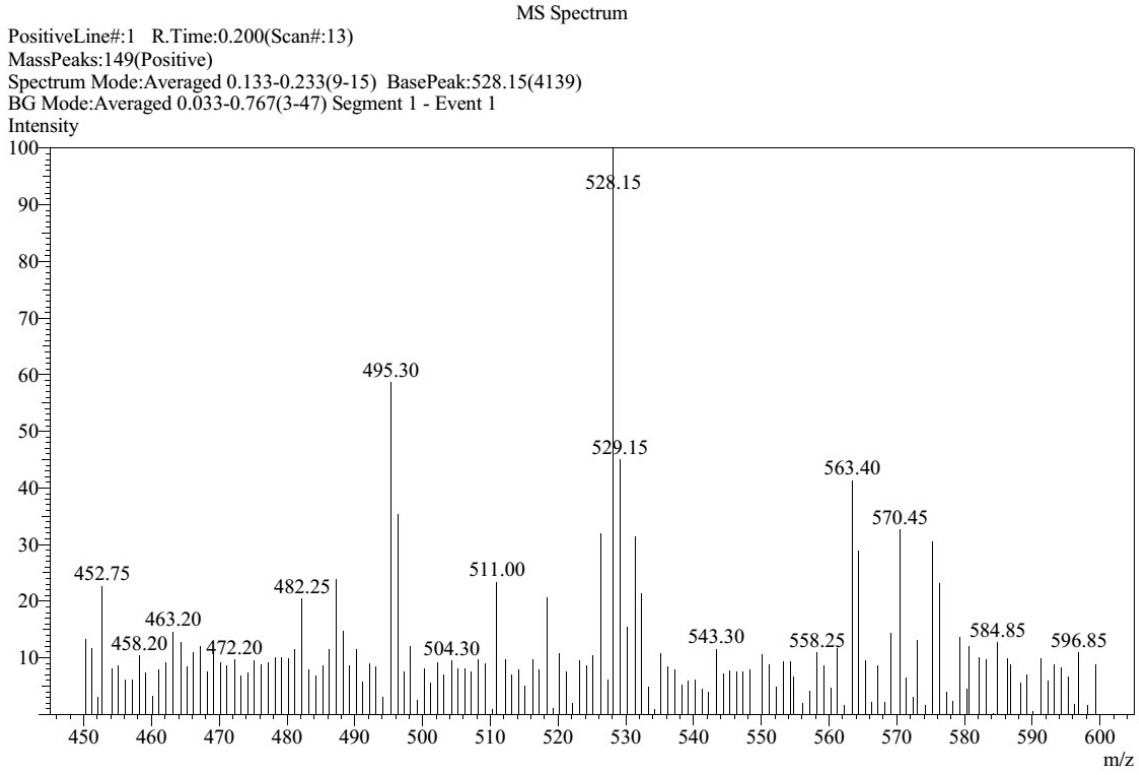

Fig. S18 MS spectra of compound 3.

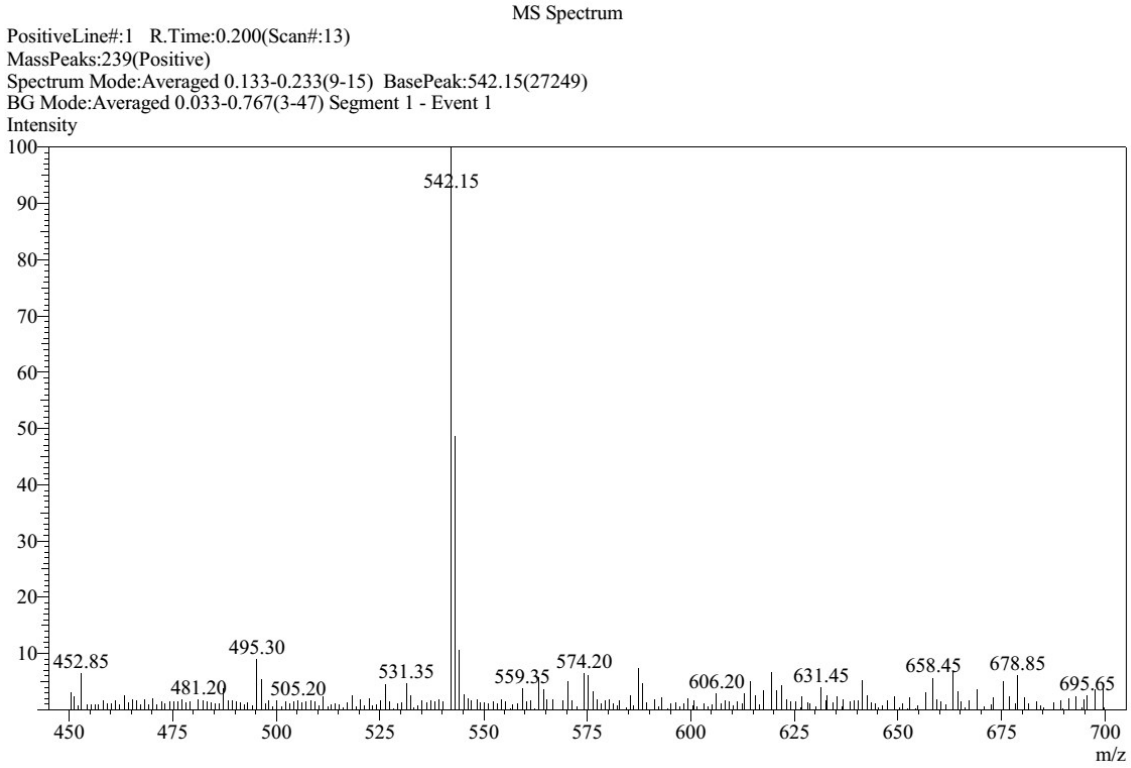

Fig. S19 MS spectra of BPP.