Electronic Supplementary Information (ESI)

Multi-stimuli-responsive metallosupramolecular gel based on pillararene hierarchical assembly

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1. Materials and methods

Materials: Reactions were performed in an N_2 atmosphere unless otherwise stated and were monitored by thin-layer chromatography. All reagents and chemicals were obtained from commercial sources at the highest purity available and used without further purification unless noted otherwise. All solvents were of AR quality. Twice-distilled water, purified by Experimental Water System (Lab-UV-20), was used in relevant experiments. Anions (including F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, OH^-) were prepared in DMSO solution from their tetra-*n*-butylammonium (TBA) salts, CN^-, SCN^- and N_3^- were used as their sodium salts, which were purchased from Sigma-Aldrich Chemical and stored in a vacuum desiccator.
Methods: NMR spectra were recorded at 298 K on Bruker 400 MHz Ultrashield spectrometer (400 MHz for ^1H NMR; 101 MHz for ^{13}C NMR). Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and referred to the residual peak of the solvent peak. Coupling constants (J) are given in Hz. Multiplicity is abbreviated as s: singlet; d: doublet; t: triplet; q: quartet; dd: doublet of doublets; and m: multiplet. ROESY and DOSY NMR were recorded with a Bruker Avance DMX 600 spectrophotometer at room temperature. Fourier transform infrared (FT-IR) spectra were recorded on a Vertex 80 V spectrometer. Low-resolution electrospray ionization (LR-ESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion (Billerica, MA, USA). Hydrodynamic diameters of dynamic light scattering (DLS) were measured on a Zetasizer Nano ZS instrument. Ultraviolet-visible (UV-vis) absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer in a 2-mm quartz cuvette. Fluorescence spectra were collected on a Shimadzu RF-5301PC spectrofluorometer. Powder X-ray diffraction (PXRD) analysis was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated Cu*Ka* radiation (λ = 1.54073 Å). Rheological Properties Test were performed on a Rheolaser Lab Diffusing Wave Spectroscopy instrument (Rheolaser LAB 6 master, Formulaction, France). Density functional theory (DFT) calculations were performed with the Gaussian 09 program. Geometry optimizations were calculated by means of density functional theory B3LYP level with the basis set of 6-31G* (B3LYP, 6-31G*).[S1] The orbital representations were generated with Gaussview 6.0 (scaling radii of 75%, isovalue = 0.02). HOMO-LUMO energy gap: $\Delta E = E_{LUMO} - E_{HOMO}$. Electrostatic surface potential (ESP) was simulated by Multiwfn 3.6 program and visualized using VMD software.[S2] Electrochemical measurements were conducted on a CHI 760E electrochemical workstation at a scan rate of 100 mV/s. The electrochemical cell was a standard three-compartment cell composed of a glass carbon working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. All tests were performed using potassium chloride (0.2 M in water) as the supporting electrolyte.

2. Experimental section

2.1 ^{1}H NMR titration experiments

First, two stock solutions were prepared in DMSO-d_6, one containing the DSPy⊂SHP5 only and the second containing an appropriate concentration of Zn^{2+} ions. Second, a stock solution of DSPy⊂SHP5 was mixed with a solution of Zn^{2+} with gradually increased concentration, whereas the total solvent volume in each NMR tube remained constant (0.5 mL). The resulting solutions were well-mixed, and then their ^{1}H NMR spectra were recorded.

2.2 ^{1}H NMR Job's plot experiments

In this method, the total concentration of model host DMP5 and guest DSPy was kept at 5 mM, and the molar ratio of DSPy (X_{DSPy} : X_{total} = [DSPy]/{[DMP5] + [DSPy]}) was changed from 0 to 1. Similarly, the total concentration of host SHP5 and Zn^{2+} was kept at 5 mM, and the molar ratio of host SHP5 (X_{SHP5} : X_{total} = [SHP5]/{[SHP5] + [Zn^{2+}]}) was also changed from 0 to 1. The resulting samples were shaken for 10 s. Subsequently, the ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of all samples were recorded.

2.3 Concentrations-Dependent ^{1}H NMR experiments

A series of DMSO-d_6 solutions of DSPy⊂SHP5@Zn^{2+} ([DSPy]: [SHP5]: Zn^{2+} = 1: 2: 2) with different concentrations (2.5 mM, 5.0 mM, 10.0 mM, 25.0 mM, 40.0 mM, and 60.0 mM) as well as DSPy⊂SHP5 ([DSPy]: [SHP5] = 1: 2) with different concentrations (3.0 mM, 15.0 mM, 30.0 mM, and 50.0 mM) were prepared and then recorded their ^{1}H NMR spectra, respectively.

2.4 General procedure for UV-vis absorption spectra experiments

The solution of metallosupramolecular polymer network DSPy⊂SHP5@Zn (2×10^{-3} M) in DMSO was prepared and stored in a dry atmosphere. The resulting solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anion (1×10^{-2} M) were prepared, respectively, via tetra-*n*-butylammonium (TBA) salts for F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, OH^- and sodium salts for CN^-, SCN^-, N_3^-. All the UV-vis experiments were carried out in DMSO-H_2O (7:3, v:v) binary solution on a Shimadzu UV-2550 spectrometer. Any changes in the UV–vis spectra of the DSPy⊂SHP5@Zn were recorded upon adding anions while keeping the concentration of DSPy⊂SHP5@Zn (2.0×10^{-4} M) in all experiments.

2.5 General procedure for fluorescence emission spectra experiments

The solution of metallosupramolecular polymer network DSPy⊂SHP5@Zn (2×10^{-3} M) in DMSO was prepared and stored in a dry atmosphere. The resulting solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anion (1×10^{-2} M) were prepared, respectively, via tetra-*n*-butylammonium (TBA) salts for F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, OH^- and the sodium salts for CN^-, SCN^-, N_3^-. All the fluorescence experiments were carried out in DMSO-H_2O (7:3, v:v) binary solution and the fluorescence spectra were obtained on a Shimadzu RF-5301PC spectrophotometer, the excitation wavelength was 375 nm and the excitation slit widths were 5 nm as well as the emission slit widths were 5 nm, respectively. Any changes in the fluorescence spectra of DSPy⊂SHP5@Zn were recorded upon adding anions while keeping the concentration of DSPy⊂SHP5@Zn (2.0×10^{-4} M) in all experiments.

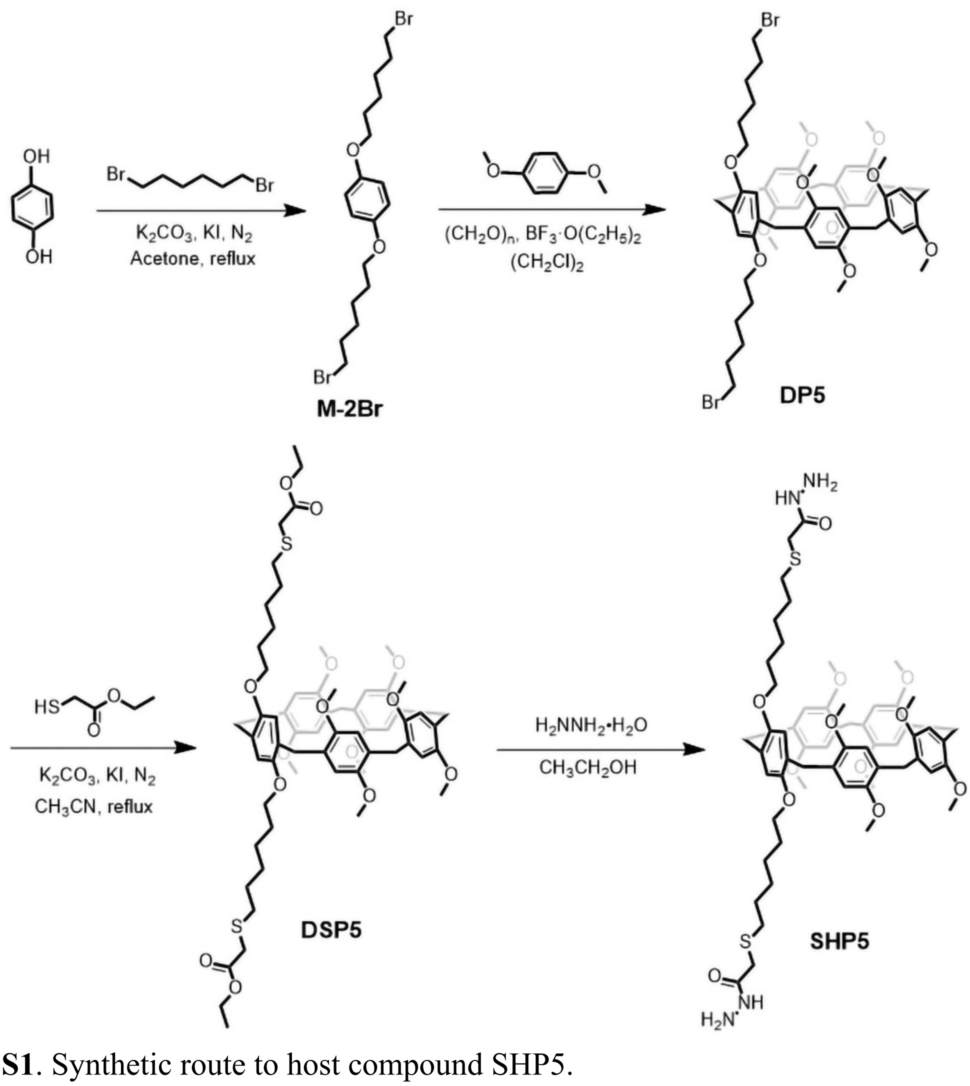
2.6 Preparation of metallosupramolecular gel

The mixture of SHP5 (33.0 mg, 50 mmol), Zn^{2+} (11.2 mg, 50 mmol), and DSPy (17.0 mg, 25 mmol) were weighed and added into DMSO-H_2O (7:3, v/v) mixed solvent (0.6 mL), the resulting mixture was heated until all the monomers were dissolved. Subsequently, the system was allowed to equilibrate at room temperature, obtaining stable metallosupramolecular gel.

2.7 SEM sample preparation

The solution of DSPy⊂SHP5 and DSPy⊂SHP5@Zn in DMSO-H_2O binary solution (c = 200 μM, DMSO:H_2O = 7:3, v:v) was dropped onto the silicon slice to get SEM samples, respectively. Meanwhile, the xerogel of DSPy⊂SHP5@Zn-G, DSPy⊂SHP5@Zn-G + adiponitrile, DSPy⊂SHP5@Zn-G + OH^-, and DSPy⊂SHP5@Zn-G upon the subsequent treatment with DTT and I_2 were prepared by freeze-drying and adhered to conductive tape to obtain corresponding SEM samples, respectively.

3. Synthetic procedures and characterizations



Scheme S1. Synthetic route to host compound SHP5.

Compounds M-2Br and DP5 were synthesized according to reported procedure.[S3]

Synthesis of M-2Br: Following a previously reported procedure, K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,6-dibromohexane (34.6 g, 160 mmol), PEG-400 (1 mL) as a phase transfer catalyst and acetone (400.0 mL) were added in a 500 mL round–bottom flask at room temperature, and the mixture was stirred for 30 min under N_2 atmosphere. Then hydroquinone (2.3 g, 20.0 mmol) was added into the above mixture and was heated at reflux under a nitrogen atmosphere for 72 h. After the solid was filtered off, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10:1) as an eluent to give the product a white solid (6.5 g, yield: 71.6%). The ^{1}H NMR spectrum of compound M-2Br is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.81 (s, 4H), 3.90 (t, J = 6.4 Hz, 4H), 3.42 (t, J = 6.8 Hz, 4H), 1.89 (p, J = 6.8 Hz, 4H), 1.77 (p, J = 6.5 Hz, 4H), 1.56 – 1.41 (m, 8H). The ^{13}C NMR spectrum of compound M-2Br is shown in Figure S2. ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm): 153.14, 115.39, 68.35, 33.79, 32.68, 29.19, 27.92, 25.29. LRESIMS is shown in Figure S3: m/z calcd for $[M + H]^+$ $C_{18}H_{29}Br_2O_2$, 437.05; found 437.01.

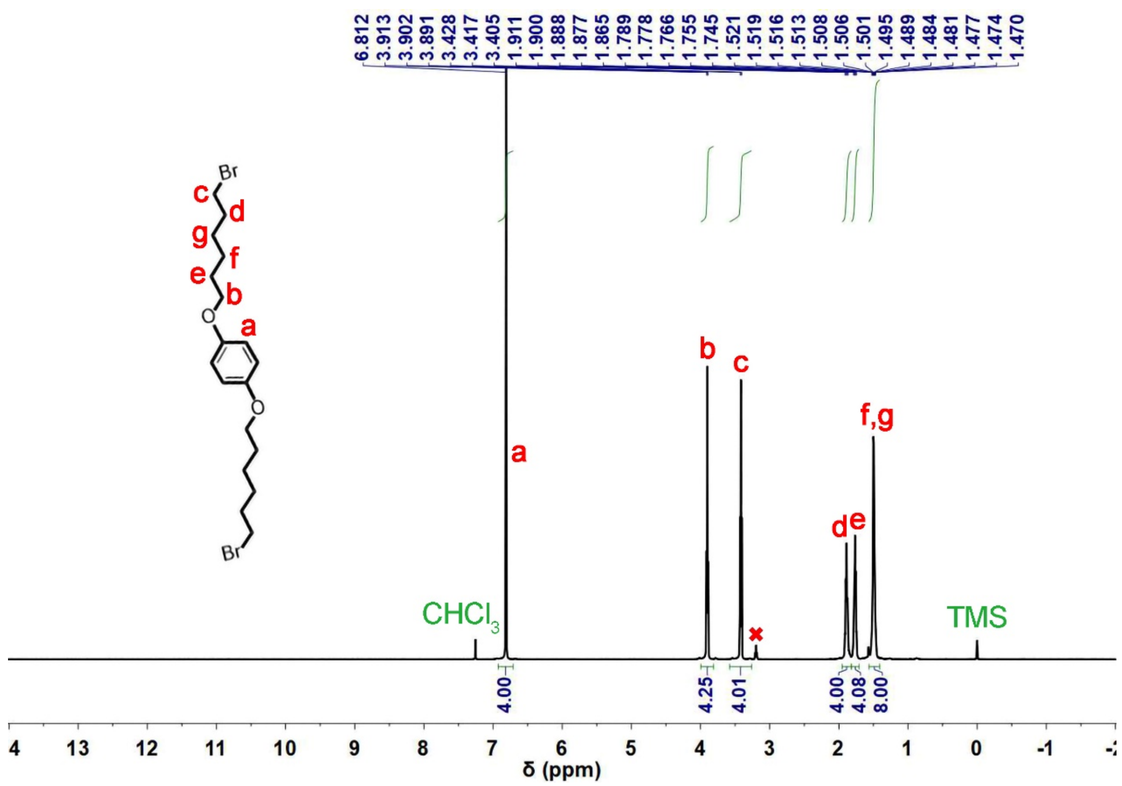


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of M-2Br.

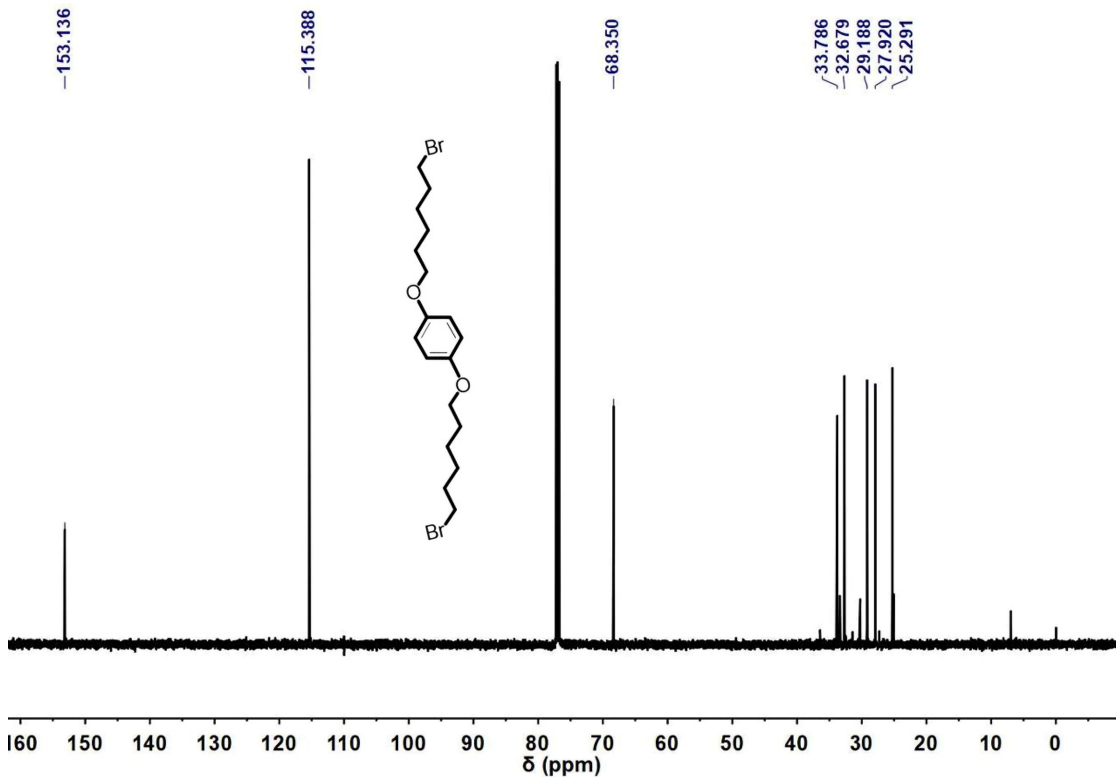


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of M-2Br.

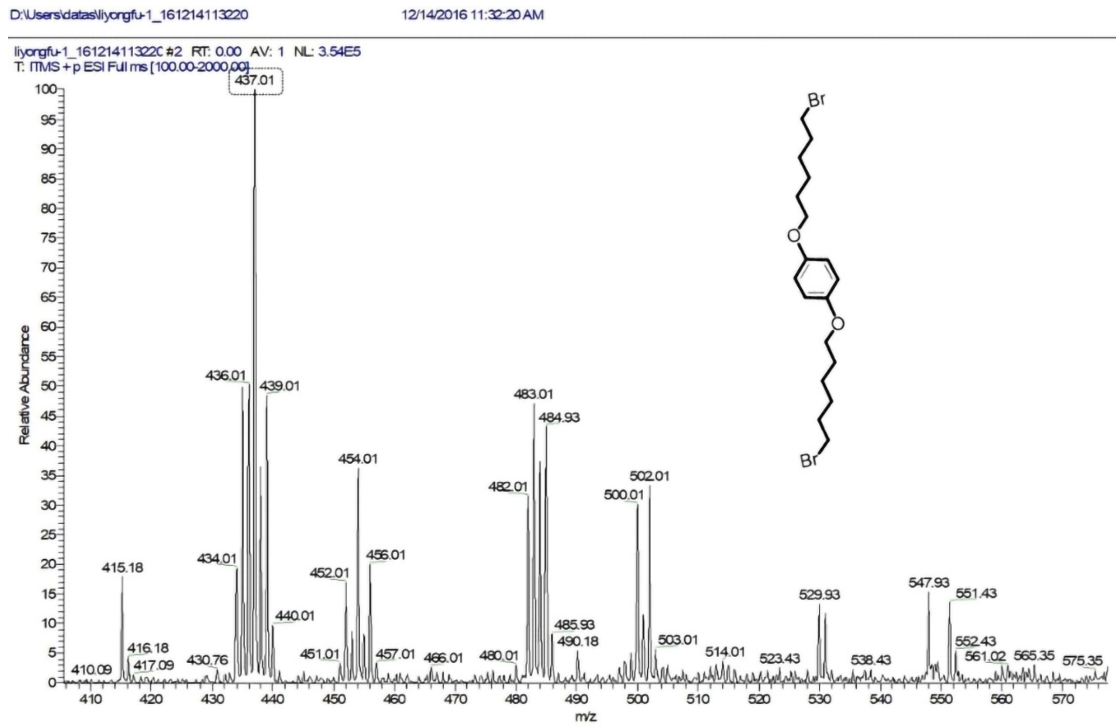


Figure S3. ESI-MS of M-2Br.

Synthesis of DP5: To a solution of M-2Br (2.18 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (100 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at 30°C. After reacting for ca. 25 min, water (300 mL) was poured into the reaction mixture to quench the reaction. The aqueous layer was extracted with dichloromethane and the organic layer was dried with anhydrous Na_2SO_4. After that, the combined organic phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether: dichloromethane: ethyl acetate = 100:50:1) to give the product as a white solid (1.6 g, yield: 30.4%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.98-6.86 (m, 10H), 4.21-3.48 (m, 42H), 1.93-1.43 (m, 8H), 1.26 (d, J = 4.4 Hz, 4H), 0.90- 0.83 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm): 150.42, 150.19, 150.15, 149.61, 128.07, 128.02, 127.93, 127.87, 127.80, 114.01, 113.03, 112.87, 68.15, 55.57, 55.28, 55.21, 33.63, 33.52, 31.94, 29.68, 29.38, 29.26, 29.08, 28.10, 28.02, 27.82, 26.94, 25.46, 22.71. HRESIMS is shown in Figure S6: m/z calcd for $[M + NH_4]^+$ $C_{55}H_{72}Br_2NO_{10}$, 1066.3497; found 1066.3496, error 0.4 ppm.

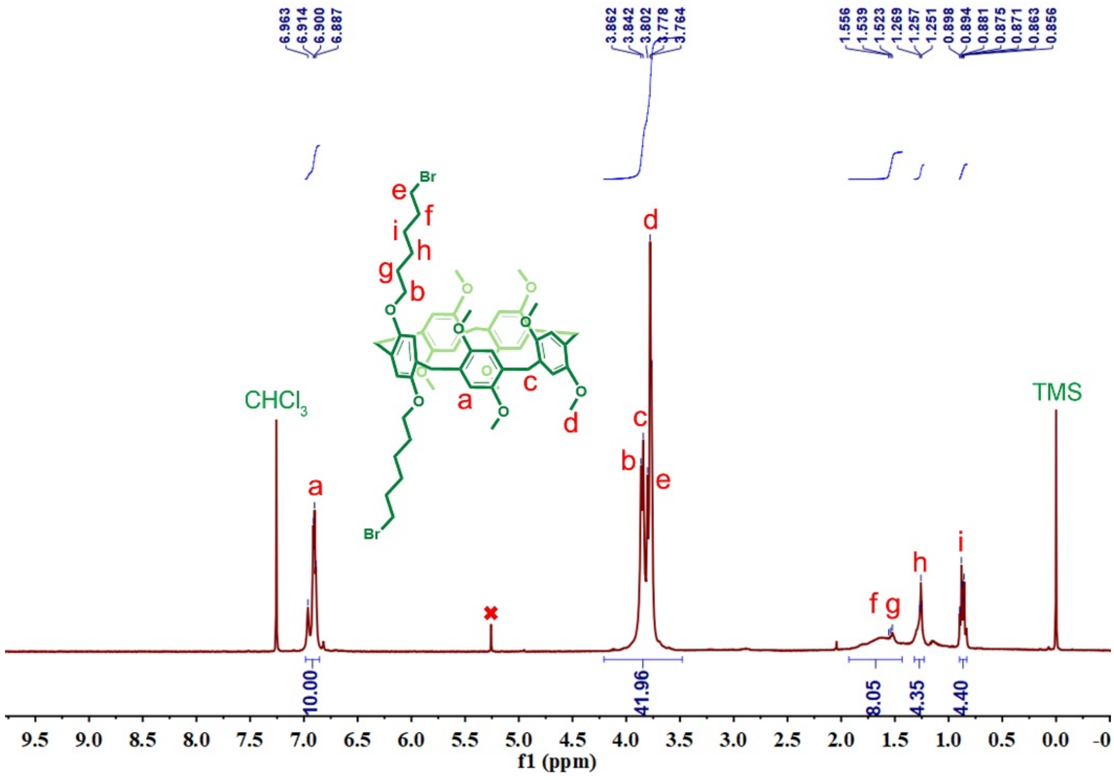


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of DP5.

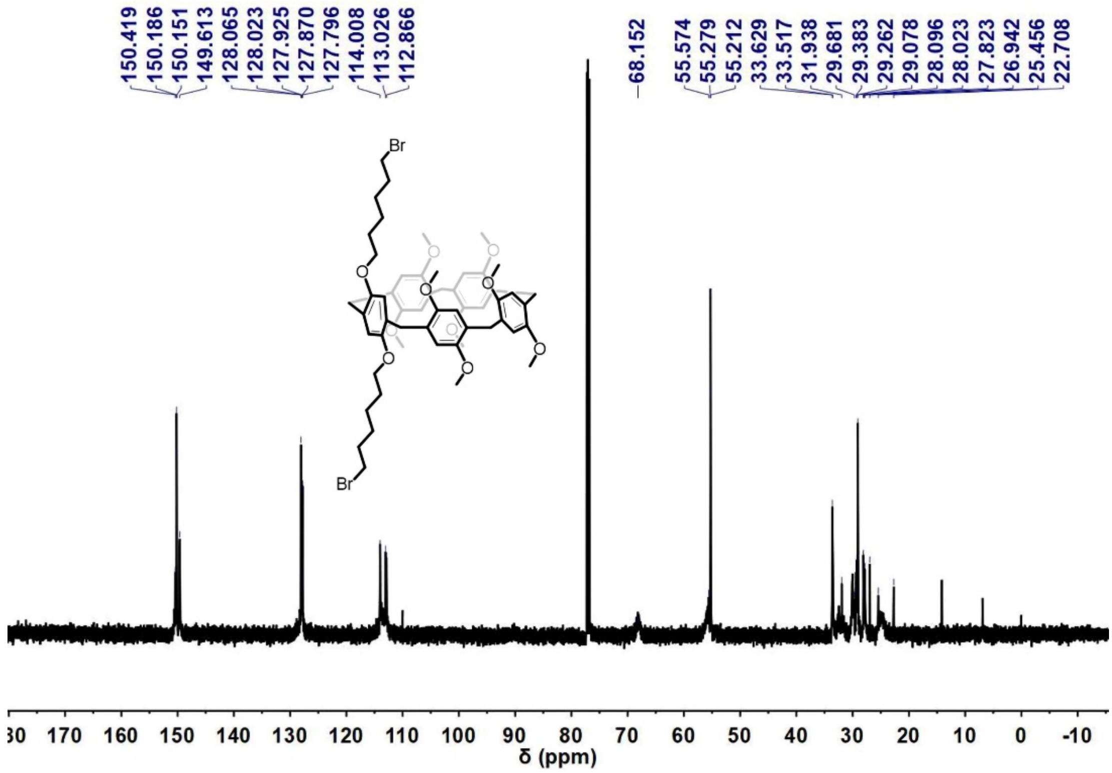


Figure S5. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of DP5.

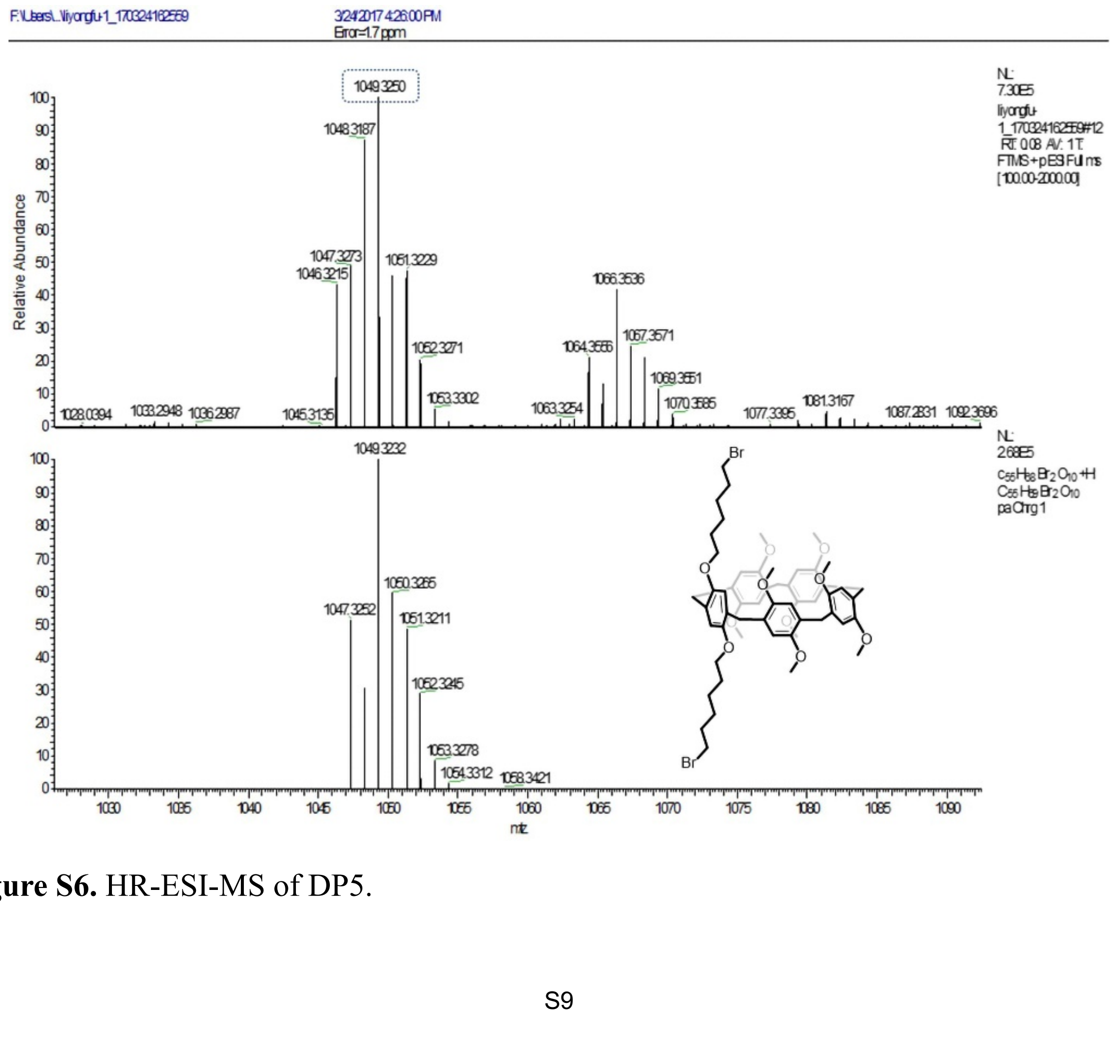


Figure S6. HR-ESI-MS of DP5.

DSP5: Compound DP5 (2.09 g, 2 mmol) was dissolved in CH_3CN, then K_2CO_3 (2.76 g, 20 mmol) and KI (3.98 g, 24 mmol) were also added into the mixture, and the resulting reaction mixture was stirred for 30 min under nitrogen atmosphere. Then, ethyl thioglycolate (4.5 mL, 40 mmol) was added into the reaction. The reaction mixture was heated at 95 °C for 72 h under nitrogen protection. Then, the mixture was filtered and the solvent was dried and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) to get the product as a white solid (1.06 g, yield: 48.6%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.85-6.69 (m, 10H), 4.15 (q, J = 7.1 Hz, 4H), 3.82 (t, J = 6.5 Hz, 4H), 3.79-3.72 (m, 10H), 3.71-3.58 (m, 24H), 3.20 (s, 4H), 2.58 (s, 4H), 1.76 (q, J = 6.7 Hz, 4H), 1.64-1.34 (m, 12H), 1.24 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 170.55, 150.84, 150.81, 150.75, 150.70, 150.01, 128.36, 128.31, 128.28, 128.14, 128.08, 115.00, 114.23, 114.20, 114.09, 113.95, 68.36, 61.28, 55.86, 55.81, 55.80, 55.75, 33.77, 32.59, 29.72, 29.55, 28.88, 28.58, 25.87, 14.13. HRESIMS is shown in Figure S9: m/z calcd for $[M + H]^+$ $C_{63}H_{83}O_{14}S_2$, 1127.52187; found 1127.52182, error -0.04848 ppm.

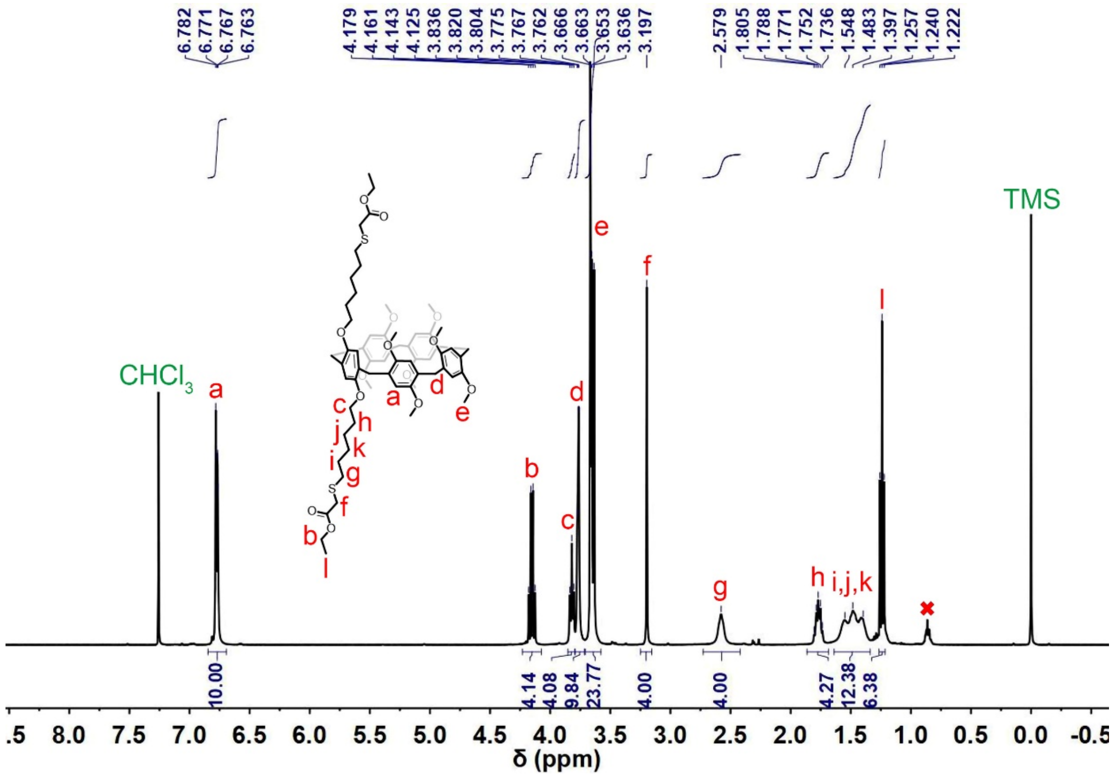


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of DSP5.

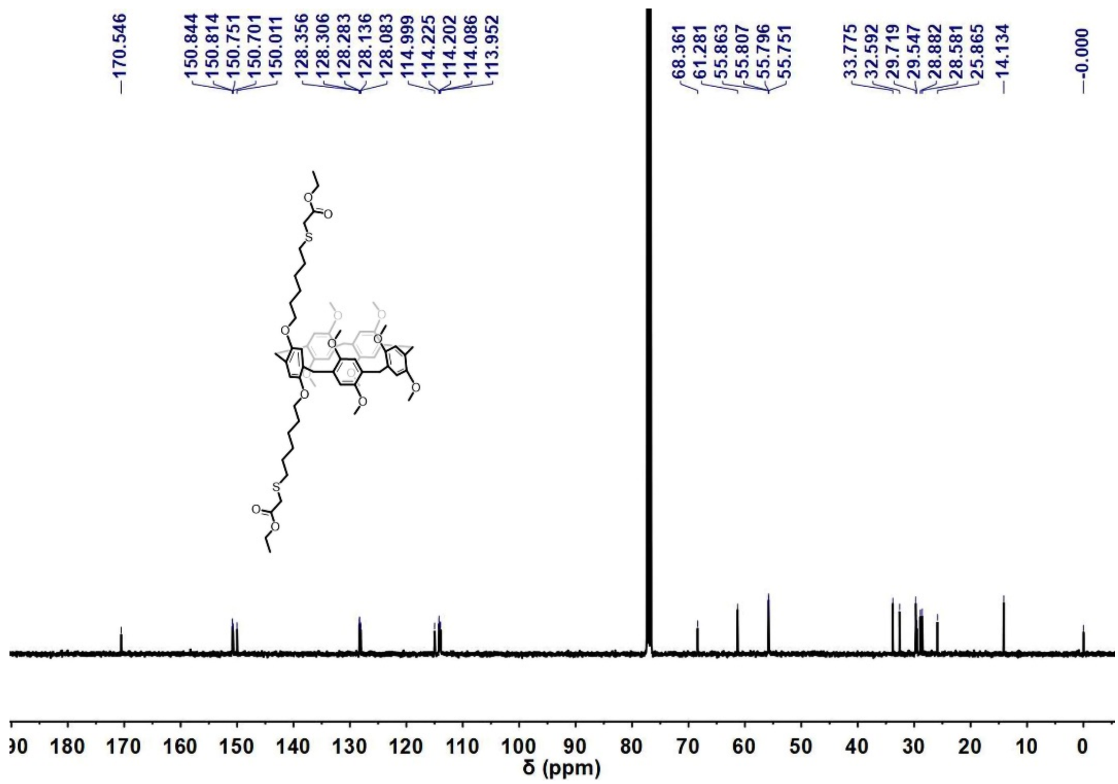


Figure S8. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of DSP5.

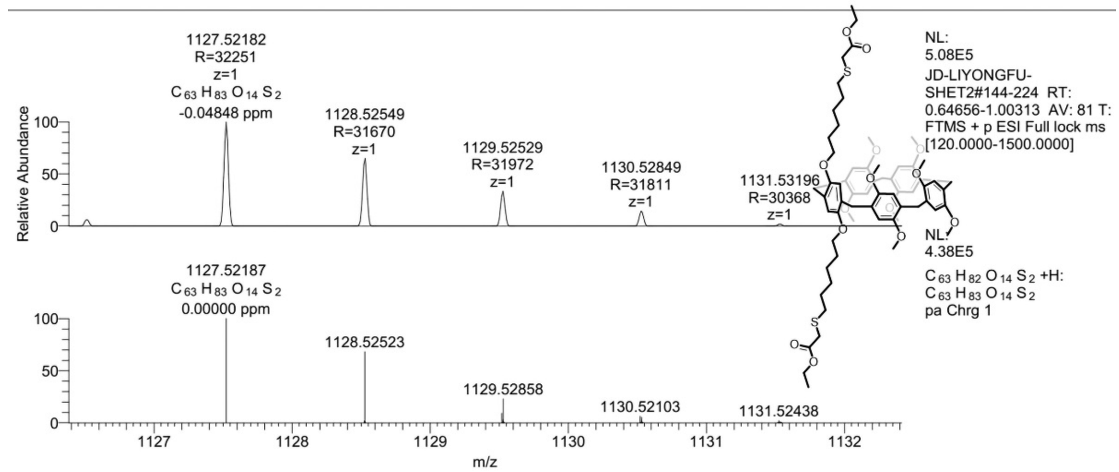


Figure S9. HR-ESI-MS of DSP5.

SHP5: Hydrazine hydrate (0.1591 g, 3 mmol, 80%) was added to a solution of the DSP5 (0.5355 g, 0.5 mmol) in alcohol (30 mL). The mixture was heated in a round-bottomed flask at 80°C for 24 h. Then, the mixture was concentrated under reduced pressure, and after washing with EtOH for 3 times, the crude product was crystallized by slow diffusion of petroleum ether into dichloromethane (CH_2Cl_2). The pure SHP5 was obtained after filtrating and drying in vacuum (0.4915 g, 96.75%). The ^1H NMR spectrum of compound SHP5 is shown in Figure S10. ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ 9.11 (s, 2H), 6.79 (d, J = 2.3 Hz, 10H), 4.27 (s, 4H), 3.82 (t, J = 6.5 Hz, 4H), 3.74 – 3.59 (m, 34H), 3.05 (s, 4H), 2.59 (t, J = 7.3 Hz, 4H), 1.75 (dd, J = 9.1, 5.4 Hz, 4H), 1.62 – 1.36 (m, 12H). The ^{13}C NMR spectrum of compound SHP5 is shown in Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 169.71, 150.76, 150.74, 150.70, 150.63, 149.91, 128.49, 128.44, 128.27, 115.03, 114.30, 114.27, 114.13, 113.97, 68.58, 56.07, 56.06, 55.92, 55.89, 34.45, 32.76, 29.72, 29.55, 29.42, 28.66, 28.50, 25.57. HRESIMS is shown in Figure S12: m/z calcd for $[M + H]^+$ $C_{59}H_{79}N_4O_{12}S_2$, 1099.5130; found 1099.5131, error 0.05034 ppm.

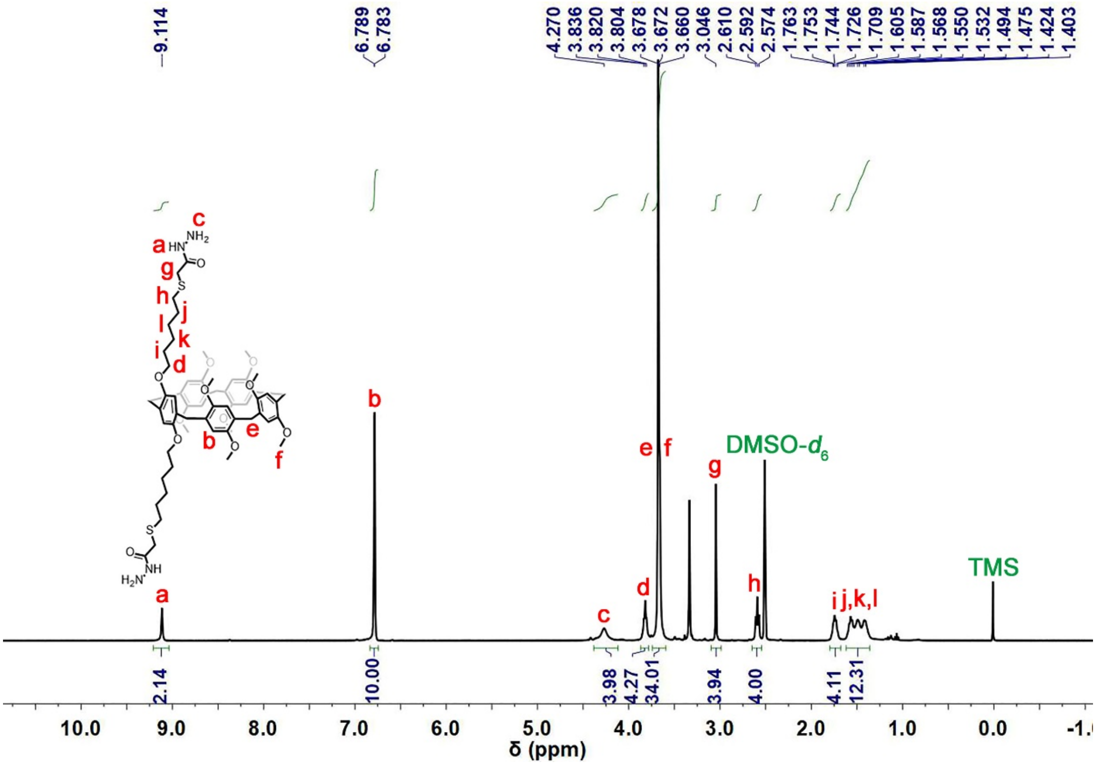


Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of SHP5.

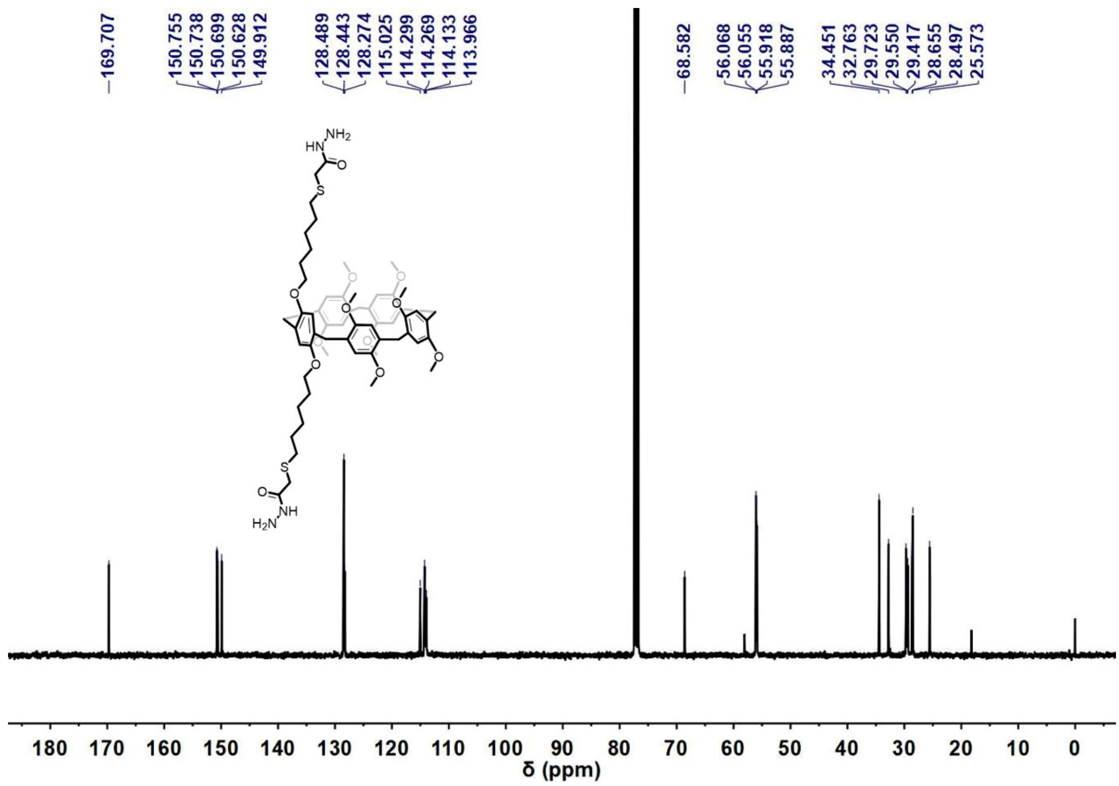


Figure S11. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of SHP5.

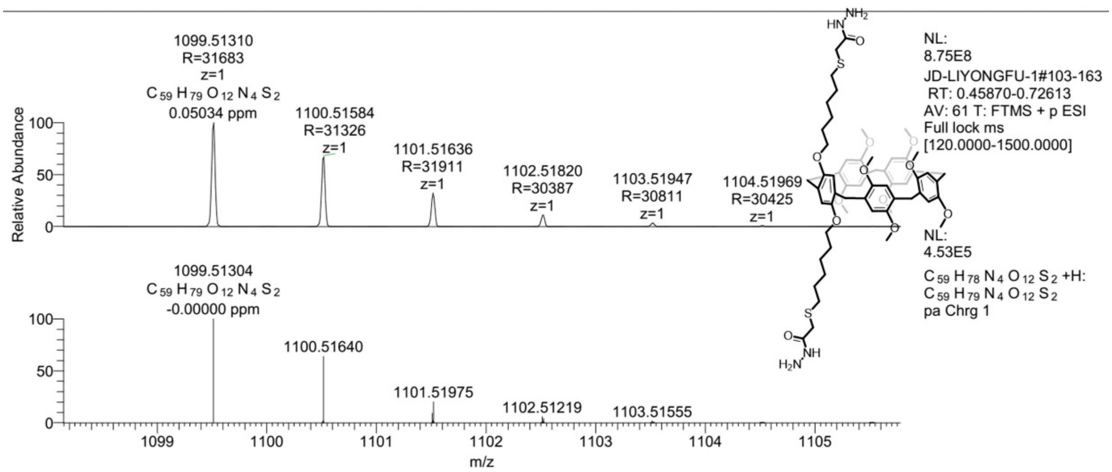
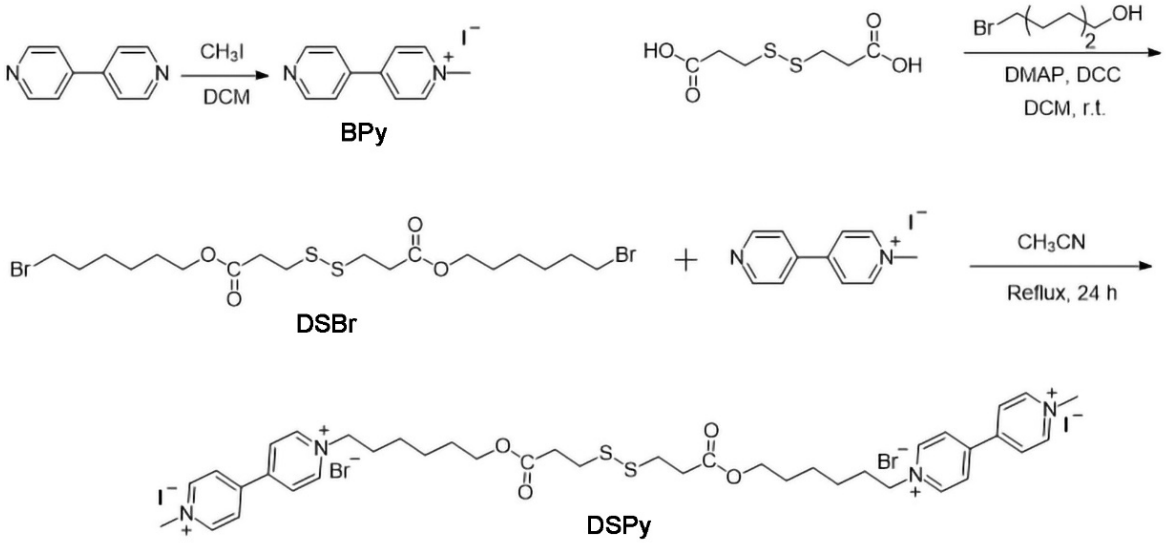


Figure S12. HR-ESI-MS of SHP5.



Scheme S2. Synthetic routes of guest DSPy.

Synthesis of compound BPy: Compound BPy was synthesized according to previously reported literature.[S4] The ^{1}H NMR spectrum of BPy is shown in Figure S13. ^{1}H NMR (400 MHz, D_2O, 298 K) δ (ppm): 8.88-8.76 (m, 2H), 8.71-8.58 (m, 2H), 8.35-8.21 (m, 2H), 7.79 (dt, J = 4.6, 1.0 Hz, 2H), 4.36 (s, 3H).

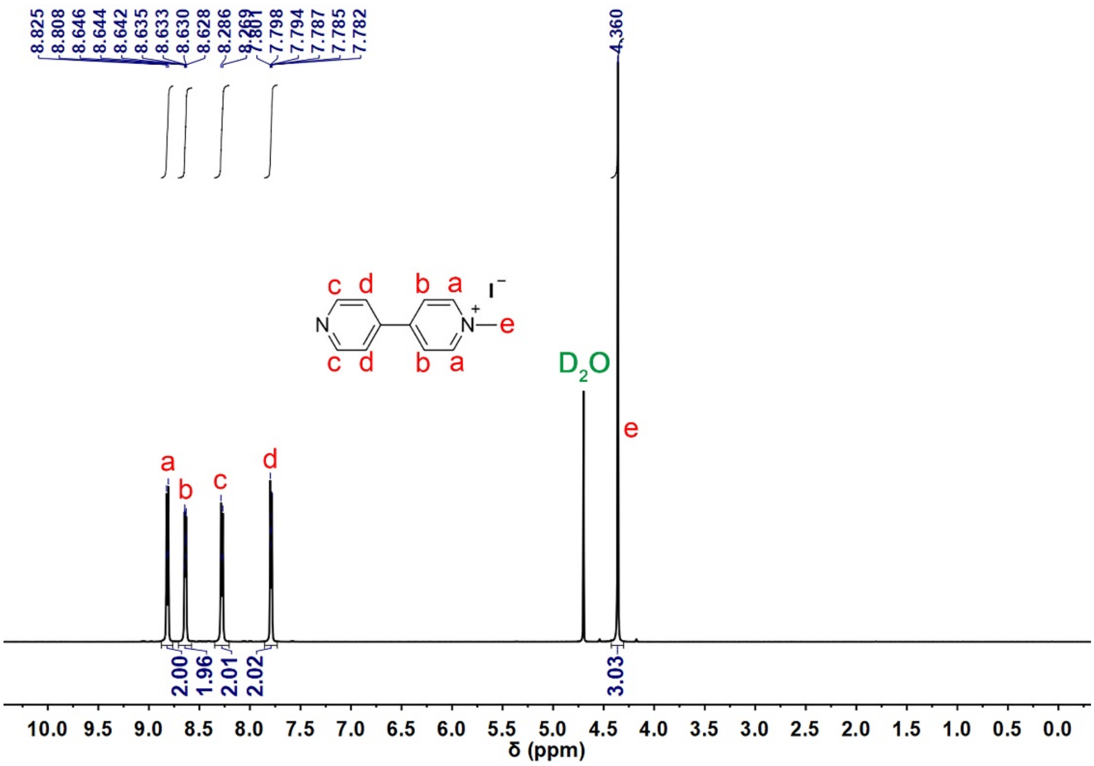


Figure S13. ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of BPy.

Synthesis of DSBr: In a 100 mL round-bottom flask, 3,3'-disulfanediyldipropionic acid (0.42 g, 2.0 mmol), 6-bromo-1-hexanol (1.07 g, 5.9 mmol) and DMAP (24.4 mg, 0.2 mmol) were dissolved in 10 mL dry dichloromethane. Subsequently, DCC (4.13 g, 20 mmol) in dry dichloromethane (15 mL) was added dropwise into the above reaction flask in an ice bath. The mixture was reacted at room temperature for one day. After that, the reaction mixture was filtered off and the filtrate was evaporated; the crude product was purified by column chromatography on silica gel using dichloromethane as eluent to afford product DSBr as a pale yellow oil (0.54 g, yield: 50%). The ^{1}H NMR spectrum of DSBr is shown in Figure S14. ^{1}H NMR (400 MHz, Chloroform-*d*, 298 K) δ (ppm): 4.10 (t, J = 6.7 Hz, 4H), 3.41 (t, J = 6.7 Hz, 4H), 3.01 – 2.83 (m, 4H), 2.73 (t, J = 8.3 Hz, 4H), 1.86 (q, J = 7.0 Hz, 4H), 1.65 (q, J = 7.0 Hz, 4H), 1.53 – 1.32 (m, 8H). The ^{13}C NMR spectrum of DSBr is shown in Figure S15. ^{13}C NMR (101 MHz, Chloroform-*d*, 298 K) δ (ppm): 171.70, 64.69, 34.13, 33.70, 33.22, 32.59, 28.42, 27.76, 25.14. HRESIMS is shown in Figure S16: *m/z* calcd for $[M + H]^{+}$ $C_{18}H_{33}Br_{2}O_{4}S_{2}$, 537.0161; found 537.0161.

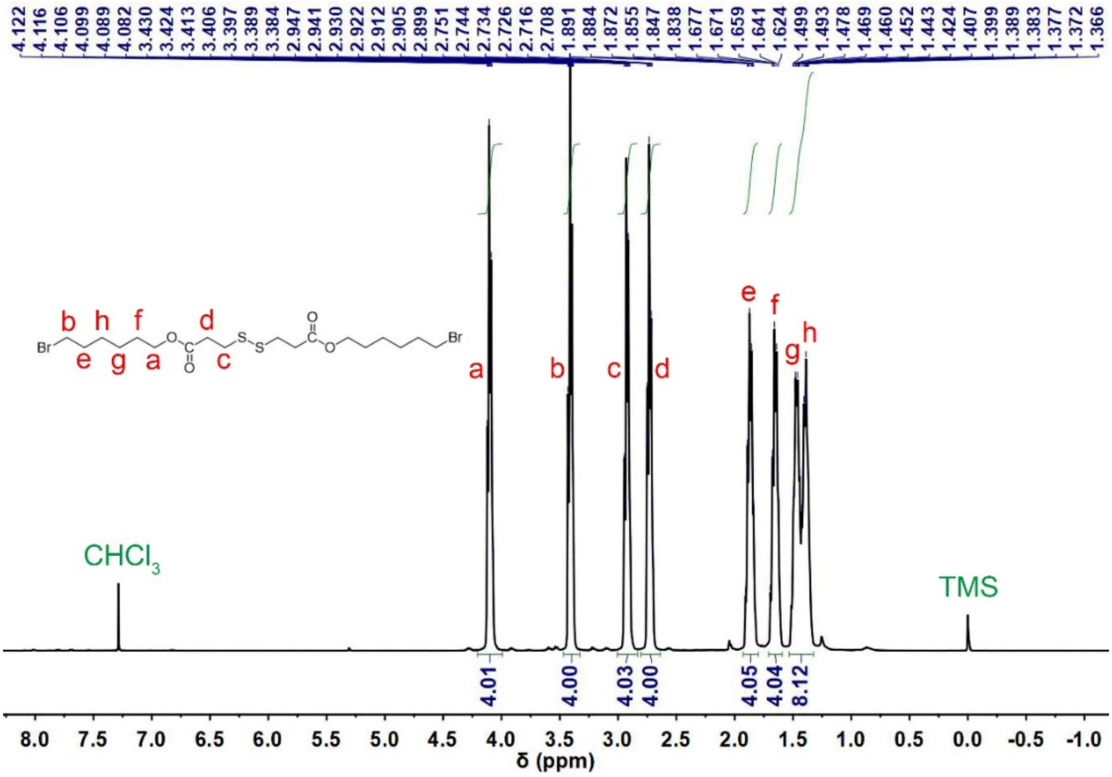


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of DSBr.

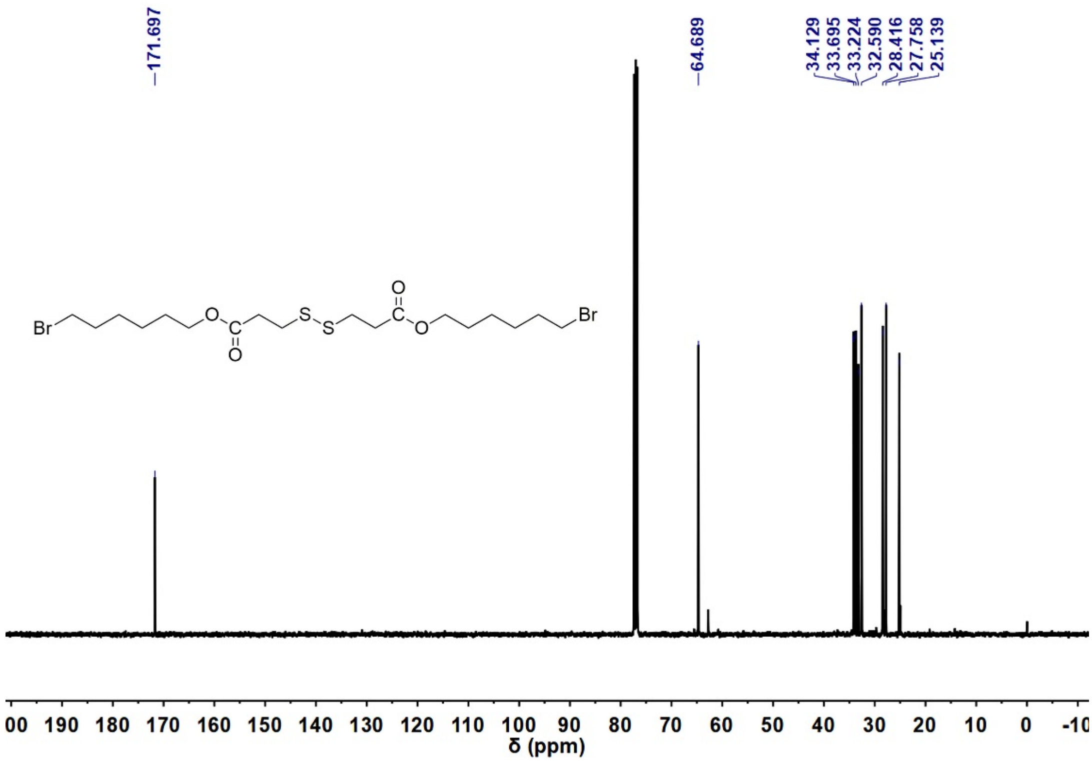


Figure S15. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of DSBr.

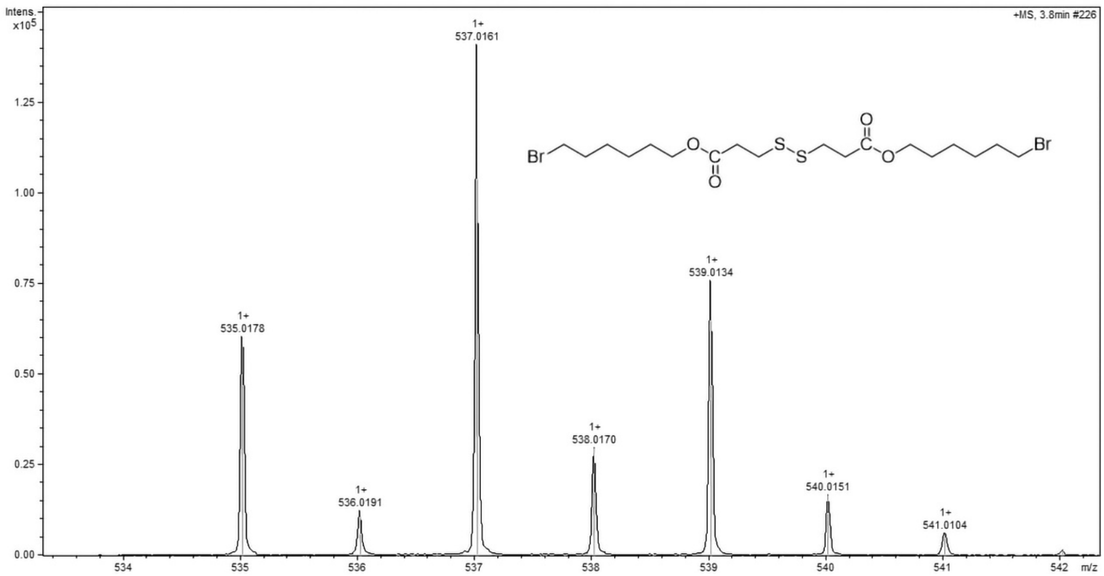


Figure S16. ESI-MS of DSBr.

Synthesis of guest compound DSPy: Compound DSBr (1.07 g, 2 mmol) and 1-methyl-[4,4'-bipyridin]-1-ium iodide (1.80 g, 6 mmol) were added into a flask. Then acetonitrile (50 mL) was added at room temperature. Then the mixture was heated at reflux for 72 h. After cooling to room temperature, the precipitate was filtered and washed with MeCN and DCM to produce a dark red product (1.36 g, yield: 60%). The ^{1}H NMR spectrum of DSPy is shown in Figure S17. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 9.38 (dd, J = 45.1, 6.3 Hz, 8H), 8.81 (dd,

J = 12.3, 6.2 Hz, 8H), 4.72 (t, J = 7.4 Hz, 4H), 4.46 (s, 6H), 4.04 (t, J = 6.5 Hz, 4H), 2.91 (t, J = 6.8 Hz, 4H), 2.70 (t, J = 6.8 Hz, 4H), 1.99 (t, J = 7.3 Hz, 4H), 1.58 (q, J = 7.0 Hz, 4H), 1.43-1.29 (m, 8H). The ^{13}C NMR spectrum of DSPy is shown in Figure S18. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 171.05, 148.35, 147.96, 146.49, 145.64, 126.41, 125.95, 63.86, 60.59, 47.91, 33.25, 32.52, 30.46, 27.68, 24.87, 24.60. ESIMS is shown in Figure S19: m/z calcd for $[M]^+$ $C_{40}H_{54}Br_2I_2N_4O_4S_2$, 1132.6329; found 1132.6404.

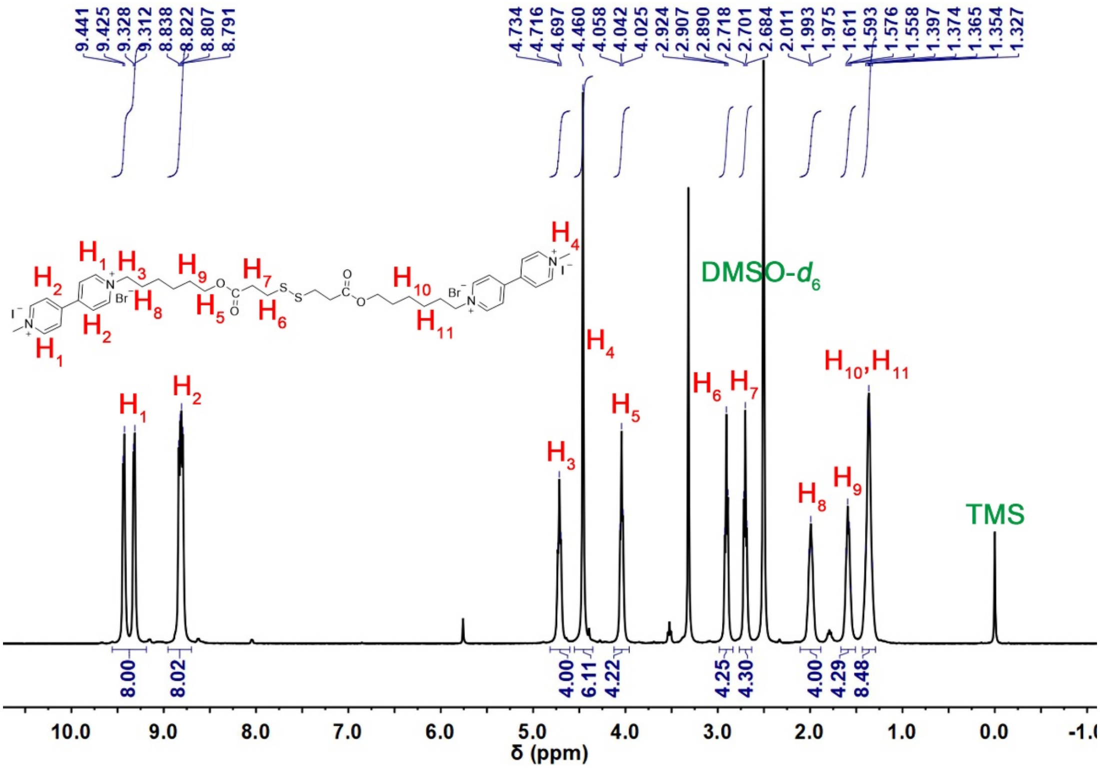


Figure S17. ^1H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of DSPy.

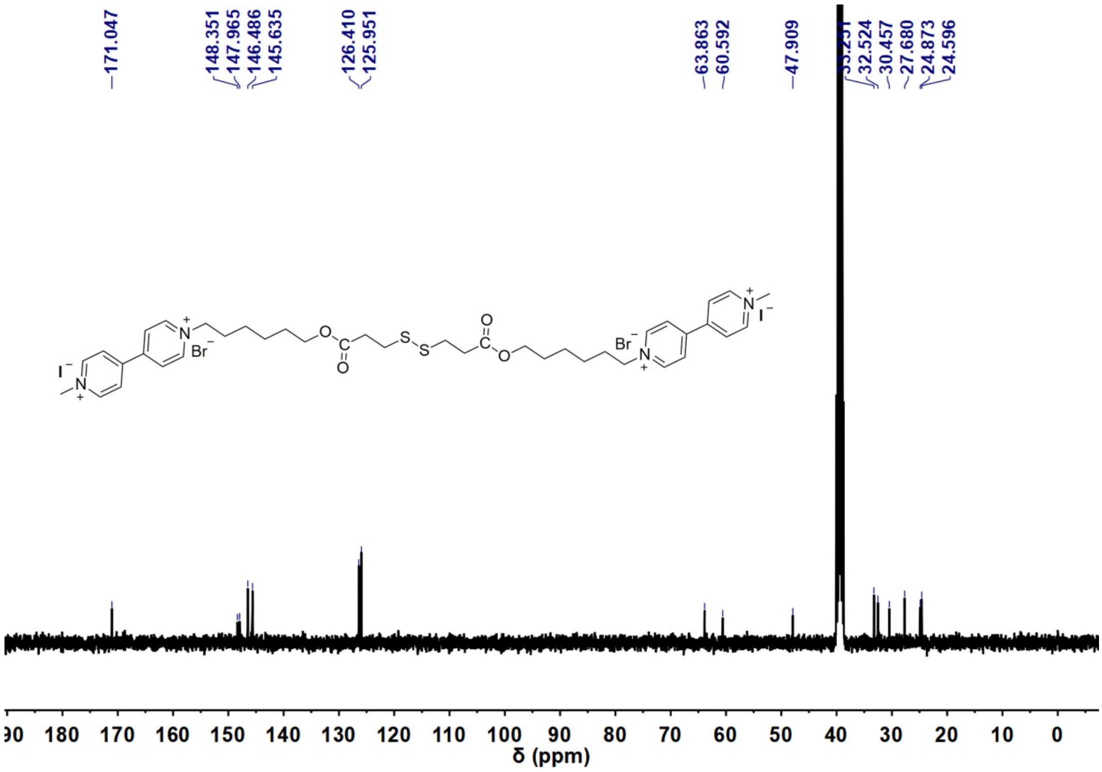


Figure S18. ^{13}C NMR spectrum (101 MHz, DMSO-d_6, 298 K) of DSPy.

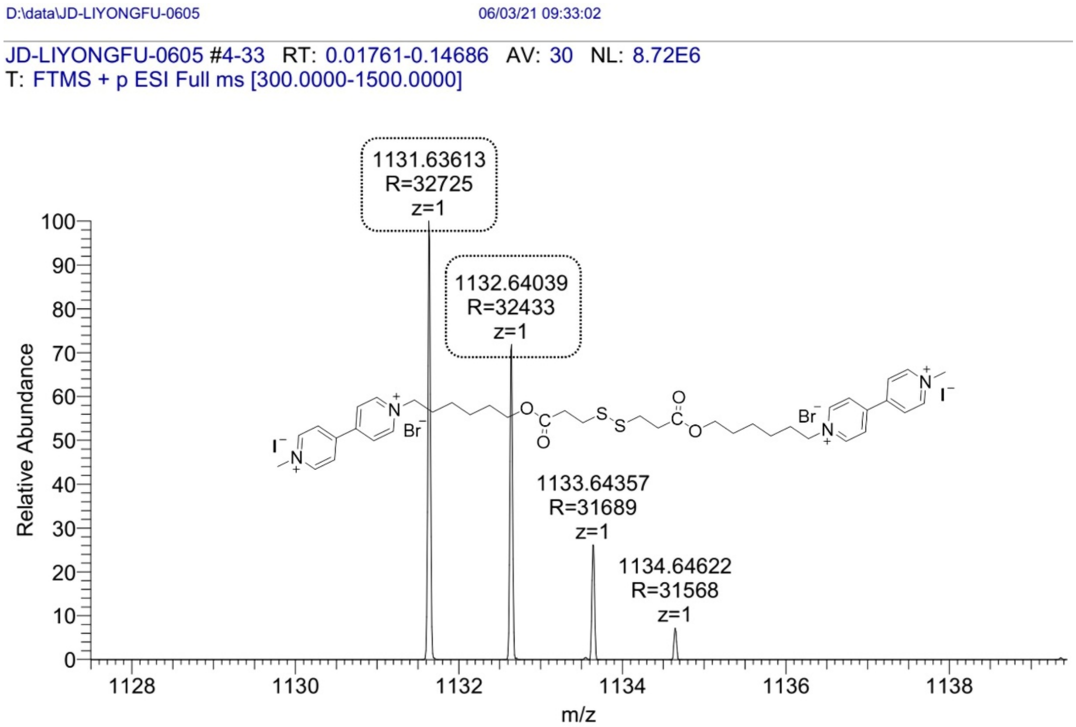


Figure S19. ESI-MS of DSPy.

4. 2D ROESY spectra of host SHP5

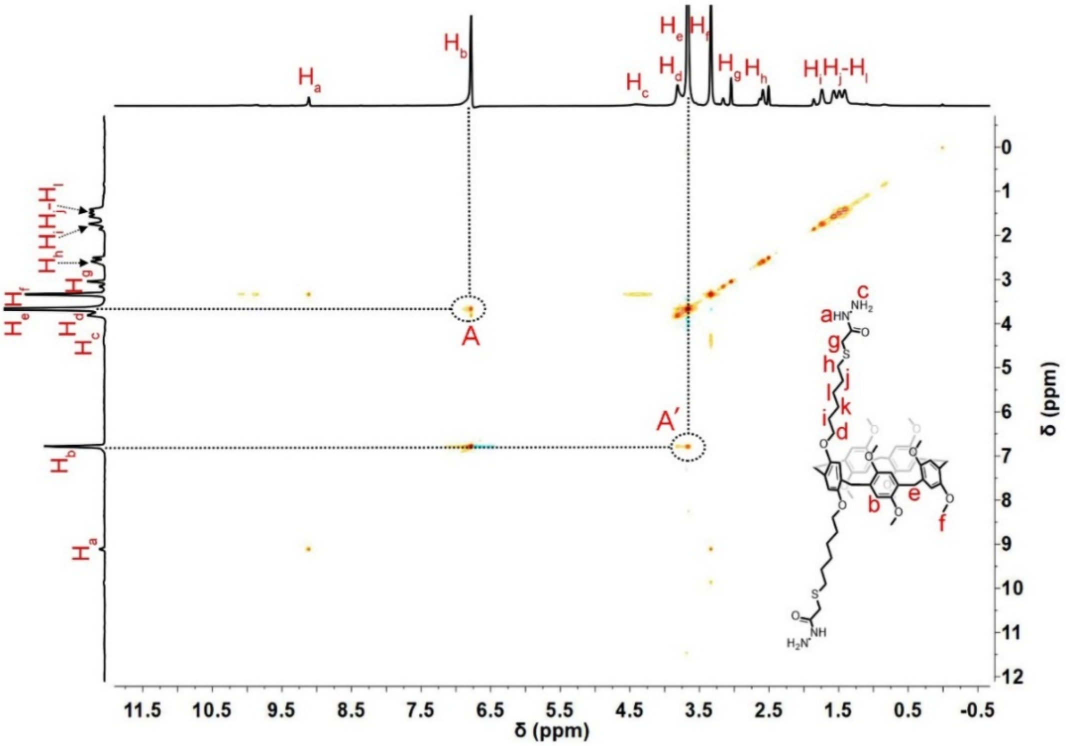


Figure S20. Partial 2D ROESY spectrum (600 MHz, DMSO-d_6, 298 K) of SHP5 (20 mM) with a mixing time of 200 ms.

5. Stoichiometry determination between DMP5 and DSPy

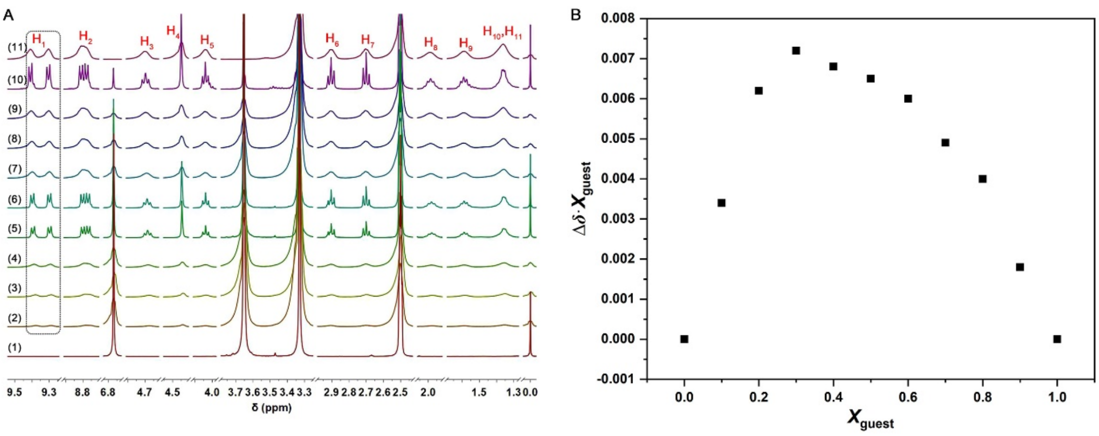


Figure S21. (A) Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of DMP5 and DSPy at different molar ratios, [DMP5]+[DSPy] = 5 mM. (1) [DMP5]/[DSPy] = 10:0, (2) [DMP5]/[DSPy]=9:1, (3) [DMP5]/[DSPy]= 8:2, (4) [DMP5]/[DSPy] = 7:3, (5) [DMP5]/[DSPy] = 6:4, (6) [DMP5]/[DSPy] = 5:5, (7) [DMP5]/[DSPy] = 4:6, (8) [DMP5]/[DSPy] = 3:7, (9) [DMP5]/[DSPy] = 2:8, (10) [DMP5]/[DSPy] = 1:9, (11) [DMP5]/[DSPy] = 0:10. (B) Job Plot showing the 2:1 stoichiometry of the complexation between DMP5 and DSPy in DMSO-d_6 by plotting the $\Delta\delta$ in chemical shift of the proton H_1 observed by ^{1}H NMR spectroscopy against the mole fraction of DSPy ([DMP5] + [DSPy] = 5 mM).

6. FT-IR characterization of the host-guest assembly DSPy⊂SHP5

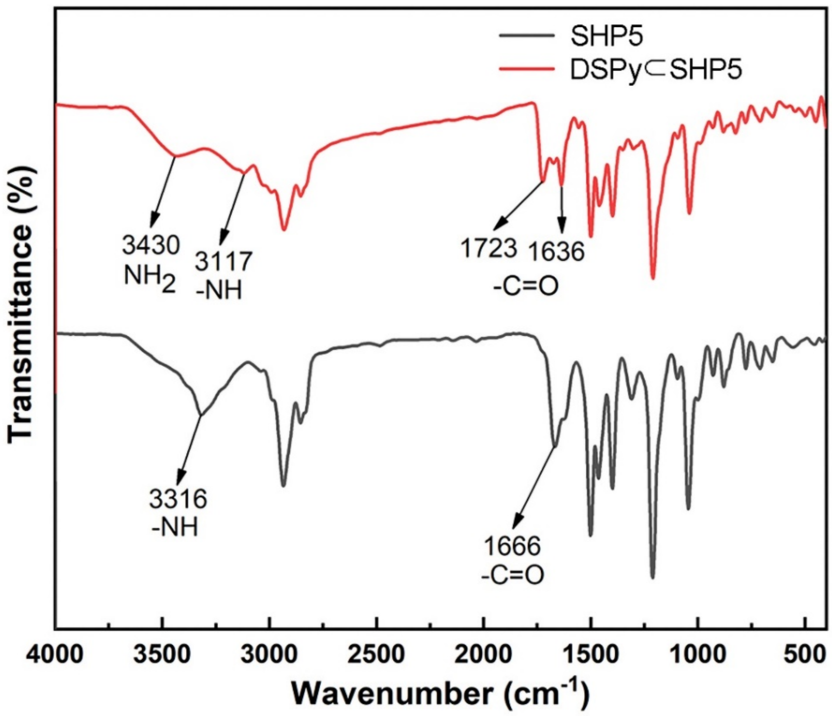


Figure S22. FT-IR spectra of SHP5 (black), and DSPy⊂SHP5 (red).

7. DLS characterization of the host-guest complexation of SHP5 and DSPy

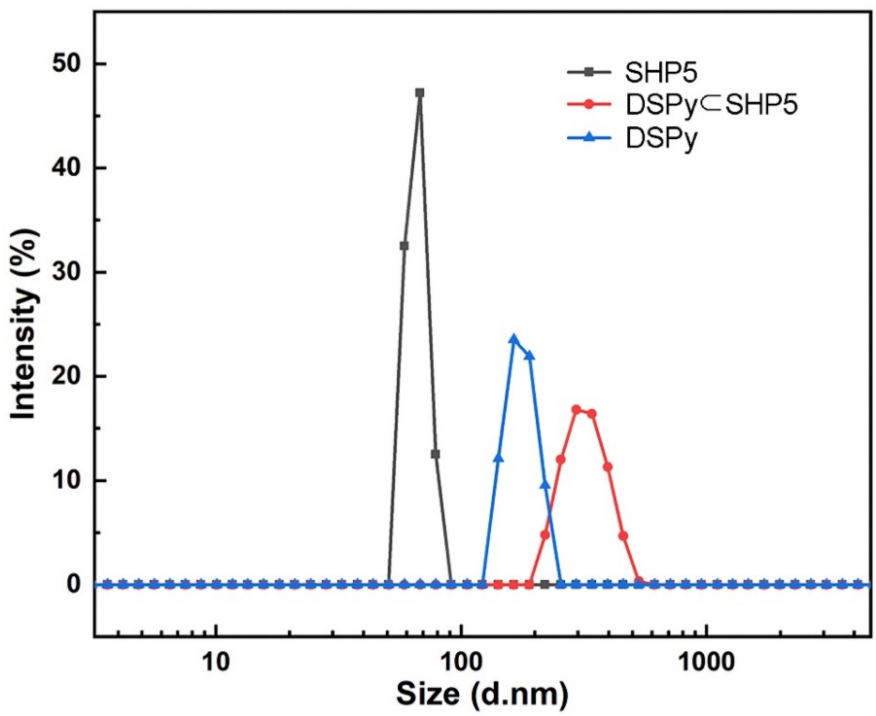


Figure S23. Selected DLS profiles of SHP5 (0.02 mmol/L), DSPy (0.02 mmol/L) and DSPy⊂SHP5 (0.02 mmol/L) in DMSO solution at 298 K.

8. SEM images of DSPy⊂SHP5 and DSPy⊂SHP5@Zn in solution state

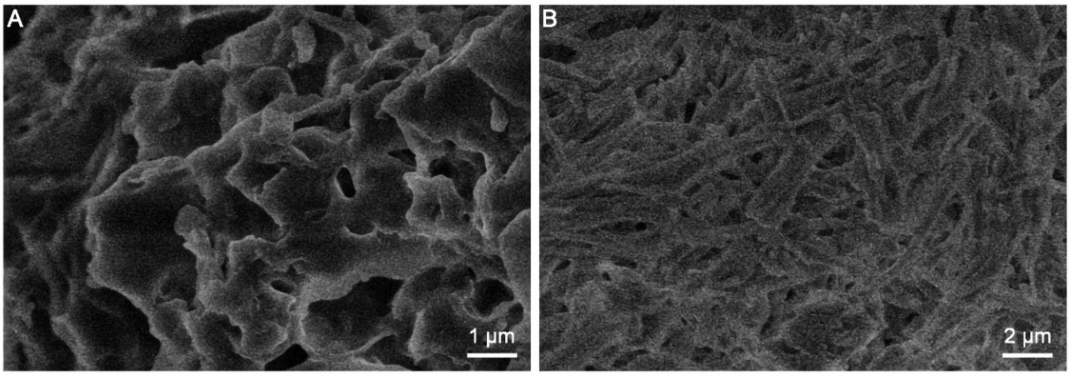


Figure S24. Representative SEM images showing the morphology of (A) DSPy⊂SHP5; and (B) DSPy⊂SHP5@Zn in DMSO-H_2O binary solution (c = 200 μM, DMSO:H_2O = 7:3, v:v).

9. The data of theoretical calculations and statistical analysis

Table S1. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of SHP5

atom	X	Y	Z	atom	X	Y	Z
C	3.6913	-2.5341	-0.062	H	0.2877	3.5034	5.4332
C	4.9945	-2.6415	0.7206	H	-2.5204	0.0367	5.5282
C	6.213	-2.86	-0.1848	H	-3.4865	-1.014	4.4555
C	7.5276	-2.9716	0.599	H	-2.9929	0.612	3.9036
C	8.7506	-3.1924	-0.3028	H	4.34	0.8896	2.2423
C	10.0489	-3.3085	0.5005	H	4.6554	0.3536	3.9183
S	11.4829	-3.5464	-0.627	H	5.2321	1.9517	3.3686
C	12.8396	-3.6522	0.6145	H	-1.7807	-2.3299	1.7072
C	14.1719	-4.1861	0.0598	H	1.7805	-2.3303	-1.7069
N	14.0295	-5.1967	-0.8564	H	1.6027	-2.7872	3.0451
O	15.2303	-3.7523	0.4711	H	-0.122	-2.8079	3.4256
N	15.1502	-5.8001	-1.4389	H	-2.8267	-0.6849	-2.934
C	-0.7708	5.4973	2.0526	H	1.132	1.691	-4.6721
C	-0.5468	4.6742	3.1596	H	0.1218	-2.8081	-3.4253
C	0.7558	4.2571	3.4783	H	-1.6029	-2.7874	-3.0447
C	1.807	4.7012	2.671	H	-5.232	1.9517	-3.3687

C	1.5826	5.5214	1.5619	H	-4.34	0.8896	-2.2424
C	0.2784	5.9248	1.2335	H	-4.6555	0.3536	-3.9183
O	2.5899	5.9771	0.7372	H	2.9929	0.6117	-3.9032
O	-1.5522	4.2275	3.991	H	2.5205	0.0362	-5.5278
C	0.0002	6.7703	-0.0002	H	3.4865	-1.0144	-4.455
C	-2.8707	4.6767	3.7417	H	-2.806	4.3635	-2.9179
C	3.9252	5.6563	1.0782	H	1.7745	5.8049	-1.7846
C	-0.2651	1.1548	4.306	H	-0.2875	3.503	-5.4333
C	-0.3715	-0.1741	3.8862	H	-2.0122	3.525	-5.0531
C	0.7526	-0.8484	3.3828	H	-4.1911	6.033	-2.0755
C	1.968	-0.1594	3.3343	H	-4.5536	6.1456	-0.3308
C	2.0737	1.1699	3.7522	H	-4.1041	4.5728	-1.049
C	0.9454	1.8505	4.2378	H	3.2353	4.3463	-2.7594
O	3.2519	1.8862	3.7196	H	2.945	5.7709	-3.7983
O	-1.5466	-0.8944	3.9334	H	3.493	4.2342	-4.5237
C	1.0204	3.3149	4.6433	H	3.5233	-3.4425	-0.6601
C	-2.6888	-0.2681	4.4863	H	3.7256	-1.6811	-0.7565
C	4.423	1.222	3.2864	H	4.9043	-3.4682	1.4371
C	-1.0063	-2.3498	0.9499	H	5.1273	-1.7259	1.3126
C	-1.3364	-2.352	-0.4083	H	6.2903	-2.0332	-0.906
C	-0.3236	-2.3387	-1.3814	H	6.0686	-3.7729	-0.7805
C	1.0061	-2.35	-0.9496	H	7.4503	-3.7984	1.3196
C	1.3362	-2.3522	0.4087	H	7.674	-2.0589	1.1946
C	0.3234	-2.3386	1.3817	H	8.8369	-2.3618	-1.0158
O	2.6347	-2.3658	0.8739	H	8.6084	-4.1035	-0.8992
O	-2.6349	-2.3655	-0.8736	H	9.9985	-4.1573	1.193
C	0.6526	-2.2761	2.8659	H	10.2159	-2.3998	1.0903
C	-1.9681	-0.1595	-3.3342	H	12.516	-4.3144	1.4274
C	-2.0736	1.1698	-3.7522	H	13.0526	-2.668	1.0357
C	-0.9453	1.8502	-4.2378	H	13.0925	-5.4534	-1.1529
C	0.2652	1.1545	-4.3059	H	15.1366	-5.6481	-2.4452
C	0.3714	-0.1744	-3.8859	C	-3.6915	-2.5337	0.0623
C	-0.7527	-0.8486	-3.3826	C	-4.9946	-2.6411	-0.7203
O	1.5466	-0.8947	-3.9331	C	-6.2132	-2.8596	0.185

O	-3.2518	1.8861	-3.7197	C	-7.5277	-2.9712	-0.5988
C	-0.6527	-2.2762	-2.8656	C	-8.7508	-3.1921	0.3029
C	-4.423	1.222	-3.2865	C	-10.049	-3.3082	-0.5005
C	2.6888	-0.2686	-4.4859	S	-11.4831	-3.5461	0.627
C	-1.8068	4.7012	-2.6712	C	-12.8397	-3.652	-0.6146
C	-1.5823	5.5213	-1.5621	C	-14.172	-4.1861	-0.06
C	-0.2781	5.9247	-1.2338	N	-14.0296	-5.1967	0.8562
C	0.7711	5.4971	-2.0529	N	-15.1502	-5.8003	1.4386
C	0.547	4.674	-3.1598	O	-15.2305	-3.7525	-0.4715
C	-0.7555	4.2569	-3.4785	H	-3.5236	-3.442	0.6605
O	1.5524	4.2272	-3.9911	H	-3.7258	-1.6806	0.7567
O	-2.5896	5.9772	-0.7375	H	-4.9044	-3.4678	-1.4368
C	-1.0202	3.3146	-4.6434	H	-5.1275	-1.7255	-1.3123
C	-3.9249	5.6564	-1.0784	H	-6.2906	-2.0329	0.9063
C	2.871	4.6762	-3.7419	H	-6.0688	-3.7726	0.7807
H	-1.7742	5.8051	1.7843	H	-7.4505	-3.798	-1.3195
H	2.8062	4.3636	2.9177	H	-7.6742	-2.0585	-1.1944
H	0.8611	7.4153	-0.1966	H	-8.8371	-2.3615	1.016
H	-0.8608	7.4154	0.1962	H	-8.6086	-4.1032	0.8993
H	-2.9447	5.7713	3.798	H	-9.9986	-4.157	-1.193
H	-3.4928	4.2348	4.5236	H	-10.2161	-2.3994	-1.0902
H	-3.2351	4.3467	2.7592	H	-12.5159	-4.3142	-1.4275
H	4.1044	4.5727	1.0487	H	-13.0528	-2.6678	-1.0358
H	4.1914	6.033	2.0752	H	-13.0926	-5.4534	1.1527
H	4.5539	6.1454	0.3305	H	-15.1367	-5.6483	2.4449
H	-1.1319	1.6914	4.6722	H	-15.1294	-6.8013	1.2576
H	2.8266	-0.6849	2.9341	H	15.1295	-6.8012	-1.2579
H	2.0124	3.5252	5.0529				

Table S2. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of DSPy

atom	**X**	**Y**	**Z**	**atom**	**X**	**Y**	**Z**
C	-4.0544	-4.0513	0.3256	C	7.3953	-3.2673	0.4854
C	-3.2883	-5.2703	-0.1602	C	8.436	-2.309	-0.1091

C	-1.8908	-5.3338	0.4539	C	9.6232	-2.0566	0.8304
S	-1.0087	-6.8029	-0.2379	C	10.6431	-1.0683	0.2481
O	-5.3214	-4.0666	-0.1387	C	11.8097	-0.8258	1.2123
O	-3.6026	-3.1728	1.028	N	12.8012	0.1366	0.6923
C	-6.1462	-2.943	0.243	C	13.6916	-0.3014	-0.2516
C	-7.5284	-3.16	-0.3546	C	14.6314	0.6148	-0.776
C	-8.4896	-2.0154	-0.0057	C	14.766	1.8791	-0.2395
C	-9.8928	-2.2135	-0.5947	C	13.9044	2.2471	0.8397
C	-10.8526	-1.0689	-0.2402	C	12.9647	1.3598	1.2808
C	-12.2421	-1.2861	-0.8486	C	15.7629	2.8328	-0.7648
N	-13.1856	-0.1917	-0.5396	C	17.0565	2.437	-1.0585
C	-14.2778	-0.4088	0.2548	C	17.9955	3.3667	-1.5418
C	-15.1951	0.5751	0.4945	N	17.5728	4.6138	-1.9121
C	-15.033	1.8509	-0.1258	C	16.3329	5.0497	-1.5406
C	-13.9535	2.0327	-0.9695	C	15.424	4.2039	-0.9683
C	-13.058	0.9782	-1.2317	C	18.5771	5.5541	-2.4178
C	-16.0158	2.9256	0.1042	H	-3.2382	-5.2235	-1.2559
C	-16.5679	3.1466	1.3553	H	-3.8723	-6.1675	0.0773
C	-17.5367	4.1423	1.5461	H	-1.9454	-5.4312	1.5404
N	-17.8591	4.9746	0.5149	H	-1.3308	-4.4256	0.2198
C	-17.3784	4.7316	-0.7425	H	-5.6821	-2.0214	-0.1254
C	-16.4588	3.7466	-0.9744	H	-6.1784	-2.8817	1.3362
C	-18.9361	5.9466	0.7344	H	-7.9306	-4.1133	0.0122
C	4.1028	-4.5476	-0.4292	H	-7.437	-3.2547	-1.4443
C	3.2129	-5.4929	0.3601	H	-8.0751	-1.0644	-0.3701
C	1.8255	-5.6126	-0.2687	H	-8.5646	-1.9188	1.0871
S	0.8111	-6.7589	0.7667	H	-10.3082	-3.1651	-0.2332
O	5.2787	-4.3572	0.2054	H	-9.8218	-2.3037	-1.6874
O	3.8118	-4.0276	-1.4847	H	-10.4352	-0.1198	-0.6018
C	6.2131	-3.4712	-0.4506	H	-10.9428	-0.9778	0.8507
H	-12.6849	-2.2119	-0.4712	H	8.8066	-2.7122	-1.0624
H	-12.2048	-1.3503	-1.943	H	10.1236	-3.0086	1.0545
H	-14.3631	-1.402	0.6787	H	9.2496	-1.6718	1.7903
H	-16.0597	0.3631	1.1128	H	10.1516	-0.1117	0.0243

H	-13.7841	2.9727	-1.4808	H	11.025	-1.4569	-0.7053
H	-12.1122	1.1471	-1.7188	H	12.3647	-1.7479	1.4237
H	-16.2882	2.5454	2.2122	H	11.4416	-0.4297	2.1628
H	-17.8696	4.4421	2.527	H	13.4037	-1.1806	-0.8038
H	-17.7655	5.3678	-1.5289	H	15.2579	0.2793	-1.5938
H	-16.1075	3.5709	-1.9846	H	14.0103	3.2035	1.3376
H	-18.6866	6.5868	1.5844	H	12.297	1.5782	2.1055
H	-19.8549	5.3871	0.9525	H	17.3965	1.4294	-0.8476
H	-19.06	6.5606	-0.158	H	18.9606	3.0592	-1.9129
H	3.1557	-5.1316	1.3939	H	16.1122	6.0882	-1.7553
H	3.711	-6.47	0.4085	H	14.4353	4.5758	-0.7262
H	1.8901	-6.0073	-1.2846	H	18.091	6.487	-2.7051
H	1.3395	-4.6348	-0.3117	H	19.0786	5.1233	-3.288
H	5.7063	-2.5275	-0.6782	H	19.3089	5.7264	-1.6175
H	6.5176	-3.92	-1.4029	Br	15.2164	-2.0845	0.9392
H	7.8571	-4.2389	0.7027	I	19.6436	3.9293	0.8133
H	7.026	-2.8729	1.4411	Br	-13.6739	0.4239	-3.7879
H	7.9542	-1.3497	-0.3485	I	-19.926	2.4269	1.9954

Table S3. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of DSPy⊂SHP5.

atom	X	Y	Z	atom	X	Y	Z
C	-4.1209	-6.1667	0.6701	C	4.0238	-6.1085	-0.6042
C	-3.3153	-7.2716	0.0069	C	3.2386	-7.2044	0.0975
C	-1.8805	-7.3102	0.5303	C	1.8062	-7.2911	-0.4267
S	-0.9614	-8.6332	-0.3753	S	0.9125	-8.599	0.5248
O	-5.4092	-6.2118	0.2732	O	5.3104	-6.1099	-0.1991
O	-3.6792	-5.3459	1.445	O	3.5692	-5.3284	-1.4129
C	-6.2717	-5.1842	0.8121	C	6.1542	-5.0858	-0.7732
C	-7.674	-5.4276	0.275	C	7.5574	-5.277	-0.2178
C	-8.6698	-4.3735	0.7778	C	8.5345	-4.2225	-0.7555
C	-10.0904	-4.599	0.2442	C	9.9553	-4.397	-0.2036
C	-11.0727	-3.5163	0.7119	C	10.9189	-3.3131	-0.7061
C	-12.4698	-3.7678	0.1389	C	12.3162	-3.515	-0.1141

N	-13.4218	-2.6696	0.4597	N	13.2493	-2.4108	-0.4687
C	-14.4016	-2.8378	1.3811	C	14.2387	-2.594	-1.3768
C	-15.2935	-1.8277	1.6687	C	15.1142	-1.5787	-1.6943
C	-15.1983	-0.5878	1.0015	C	14.9915	-0.3177	-1.0727
C	-14.1762	-0.4467	0.0524	C	13.959	-0.1608	-0.1376
C	-13.3018	-1.4916	-0.2021	C	13.1021	-1.2121	0.1487
C	-16.1495	0.5005	1.308	C	15.9272	0.7749	-1.4106
C	-17.4568	0.2019	1.7133	C	17.2447	0.4834	-1.7867
C	-18.3136	1.2108	2.0923	C	18.0886	1.4912	-2.1965
N	-17.9156	2.5018	2.0858	N	17.6678	2.774	-2.2482
C	-16.6801	2.8316	1.64	C	16.4207	3.0995	-1.8319
C	-15.7874	1.8535	1.2383	C	15.5403	2.1227	-1.4007
C	-18.7971	3.5466	2.6344	C	18.5377	3.8108	-2.8301
H	-3.3372	-7.1004	-1.0773	H	3.2546	-6.9936	1.1748
H	-3.8292	-8.2261	0.1722	H	3.772	-8.1537	-0.0323
H	-1.86	-7.5314	1.5998	H	1.7927	-7.5509	-1.4875
H	-1.3913	-6.347	0.3705	H	1.2971	-6.3329	-0.3023
H	-5.8846	-4.2046	0.5111	H	5.7438	-4.1037	-0.5139
H	-6.2374	-5.231	1.9062	H	6.1287	-5.1767	-1.8647
H	-8.0027	-6.4313	0.575	H	7.9097	-6.2846	-0.4756
H	-7.6454	-5.418	-0.8216	H	7.5205	-5.2248	0.8773
H	-8.3279	-3.3749	0.4717	H	8.1694	-3.2202	-0.4912
H	-8.6829	-4.3737	1.8782	H	8.5559	-4.2658	-1.8548
H	-10.4473	-5.5906	0.5601	H	10.335	-5.3925	-0.4779
H	-10.0756	-4.5936	-0.8529	H	9.9319	-4.349	0.8923
H	-10.72	-2.5436	0.349	H	10.5443	-2.3348	-0.3828
H	-11.1138	-3.4716	1.8098	H	10.9674	-3.3095	-1.8046
H	-12.9078	-4.692	0.5264	H	12.7753	-4.444	-0.4636
H	-12.4063	-3.8064	-0.958	H	12.2445	-3.5139	0.9828
H	-14.4377	-3.8031	1.8713	H	14.2963	-3.5755	-1.8316
H	-16.0519	-2.0064	2.4203	H	15.8815	-1.7695	-2.4339
H	-14.0646	0.4514	-0.5411	H	13.8259	0.7562	0.4217
H	-12.5383	-1.4662	-0.9867	H	12.3319	-1.1726	0.9262
H	-17.8215	-0.8121	1.7431	H	17.627	-0.5244	-1.7698

H	-19.3184	1.0128	2.4365	H	19.1011	1.2975	-2.5199
H	-16.432	3.884	1.6439	H	16.1545	4.1463	-1.8827
H	-14.8001	2.1623	0.9255	H	14.5436	2.4256	-1.1128
H	-18.7766	4.4605	2.0224	H	18.4868	4.7515	-2.2622
H	-18.4471	3.7965	3.638	H	18.2001	4.0067	-3.8499
H	-19.8168	3.1631	2.6739	H	19.5654	3.4473	-2.8348
C	-15.6251	-2.1837	-3.5494	C	15.3739	-1.7089	3.5788
C	-15.6932	-3.6908	-3.7563	C	15.4453	-3.2071	3.8409
C	-14.6653	-4.1738	-4.7892	C	14.4436	-3.6462	4.9185
C	-14.6511	-5.6997	-4.9494	C	14.4105	-5.1669	5.1188
C	-13.6086	-6.1773	-5.9728	C	13.4268	-5.599	6.2178
C	-13.6302	-7.6986	-6.1424	C	13.396	-7.1199	6.3903
S	-12.3572	-8.4199	-7.2604	S	12.2087	-7.782	7.6323
C	-12.8282	-7.6751	-8.8701	C	12.9347	-7.1464	9.1941
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N	-11.1661	-5.8802	-8.6321	N	11.3942	-5.2345	9.2866
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C	-19.0872	-0.194	4.9152	C	18.9191	-0.0229	-4.9458
C	-18.7172	-1.5036	4.5602	C	18.568	-1.3239	-4.5431
C	-17.3881	-1.8841	4.7892	C	17.2498	-1.7385	-4.7757
C	-16.4386	-0.9907	5.3022	C	16.2918	-0.8846	-5.3377
C	-16.7963	0.3375	5.6022	C	16.6292	0.4371	-5.6857
O	-15.1278	-1.341	5.537	O	14.9913	-1.269	-5.5761
O	-20.4007	0.1596	4.6918	O	20.2224	0.3643	-4.7184
C	-15.7802	1.3382	6.1425	C	15.6025	1.3962	-6.2788
C	-20.9283	1.2693	5.4133	C	20.7412	1.4512	-5.48
C	-14.8069	-2.7184	5.6313	C	14.6971	-2.6549	-5.6181
C	-20.567	-1.3537	1.7827	C	20.3734	-1.0312	-1.7449
C	-20.4809	-1.0411	0.4211	C	20.2603	-0.6671	-0.3982
C	-19.5201	-1.6732	-0.3946	C	19.2952	-1.2808	0.4263
C	-18.7427	-2.682	0.1825	C	18.542	-2.323	-0.1229
C	-18.8384	-3.005	1.544	C	18.6652	-2.698	-1.469

C	-19.7219	-2.3003	2.3803	C	19.5522	-2.0133	-2.3181
O	-18.0357	-3.9598	2.142	O	17.887	-3.6882	-2.041
O	-21.2707	-0.1003	-0.1879	O	21.027	0.308	0.1861
C	-19.7015	-2.4662	3.8972	C	19.5596	-2.24	-3.8272
C	-22.3689	0.4366	0.5334	C	22.1318	0.8296	-0.5363
C	-17.579	-5.0306	1.3245	C	17.4374	-4.7352	-1.1893
C	-18.586	1.1906	-1.8843	C	18.2972	1.6245	1.7768
C	-17.6581	2.2102	-2.1317	C	17.3532	2.641	1.9685
C	-16.3518	1.8911	-2.5596	C	16.0476	2.3236	2.4
C	-16.0296	0.5402	-2.7226	C	15.7428	0.9774	2.6225
C	-16.9559	-0.4837	-2.4663	C	16.6847	-0.0445	2.4206
C	-18.2606	-0.1636	-2.0493	C	17.9886	0.2746	2.0006
O	-16.6517	-1.8169	-2.6089	O	16.3951	-1.3737	2.6201
O	-17.9451	3.5436	-1.9996	O	17.6223	3.971	1.776
C	-19.3132	-1.2533	-1.844	C	19.0581	-0.8082	1.8547
C	-15.0038	4.5566	-0.8964	C	14.672	4.8941	0.608
C	-14.3709	4.9334	0.2956	C	14.0456	5.206	-0.606
C	-13.2618	4.2056	0.7687	C	12.9585	4.4344	-1.0602
C	-12.7473	3.1911	-0.0479	C	12.4556	3.4446	-0.2068
C	-13.3689	2.8306	-1.2512	C	13.0697	3.1499	1.018
C	-14.5507	3.4761	-1.6618	C	14.2324	3.8378	1.4138
O	-12.9302	1.7884	-2.0382	O	12.6435	2.1335	1.8447
O	-14.8195	5.9519	1.095	O	14.4819	6.1994	-1.4428
C	-15.3349	2.9885	-2.8742	C	15.0122	3.4191	2.6545
C	-15.6166	6.9819	0.4959	C	15.2443	7.274	-0.8777
C	-11.5505	1.4229	-1.9743	C	11.2732	1.7345	1.7805
C	-14.6101	4.2011	3.8541	C	14.3474	4.3263	-4.1246
C	-15.379	3.4629	4.7675	C	15.1429	3.5667	-4.9968
C	-15.0131	2.1442	5.0955	C	14.8068	2.2286	-5.2749
C	-13.8782	1.6055	4.4749	C	13.6746	1.6932	-4.6464
C	-13.1243	2.3371	3.5506	C	12.8946	2.4469	-3.7623
C	-13.4851	3.6584	3.2231	C	13.2249	3.7877	-3.4858
O	-12.0114	1.8356	2.9141	O	11.7836	1.9497	-3.1192
O	-16.5084	3.9638	5.3728	O	16.2703	4.0645	-5.6079

C	-12.7126	4.4509	2.169	C	12.4223	4.6076	-2.4761
C	-16.7084	5.382	5.3737	C	16.4427	5.4855	-5.6651
C	-11.5217	0.57	3.315	C	11.3237	0.6594	-3.474
H	-18.4199	1.7155	5.679	H	18.2283	1.8414	-5.7953
H	-17.1075	-2.9038	4.5479	H	16.9845	-2.7531	-4.4978
H	-15.0546	0.7935	6.7543	H	14.8952	0.8139	-6.8776
H	-16.3028	2.0392	6.7985	H	16.121	2.08	-6.9558
H	-20.7177	1.18	6.4857	H	20.5487	1.3114	-6.5504
H	-22.0074	1.2494	5.2492	H	21.8178	1.4583	-5.2995
H	-20.53	2.2244	5.0483	H	20.3205	2.4138	-5.1631
H	-14.8511	-3.2202	4.654	H	14.7376	-3.1155	-4.6205
H	-15.4757	-3.24	6.3274	H	15.3846	-3.1917	-6.2838
H	-13.7823	-2.7657	6.0059	H	13.6786	-2.7368	-6.0033
H	-21.2682	-0.8314	2.4226	H	21.0778	-0.5238	-2.3935
H	-18.0162	-3.1818	-0.4501	H	17.8129	-2.8087	0.5173
H	-19.4216	-3.4929	4.1479	H	19.3028	-3.2811	-4.0407
H	-20.7052	-2.2844	4.292	H	20.5658	-2.0547	-4.2135
H	-23.0367	-0.3557	0.8946	H	22.8147	0.0318	-0.8547
H	-22.9063	1.0747	-0.17	H	22.6493	1.5008	0.1509
H	-22.0401	1.0444	1.3876	H	21.8115	1.3999	-1.4192
H	-16.7828	-4.715	0.637	H	16.6267	-4.4079	-0.5248
H	-18.4	-5.4613	0.739	H	18.2576	-5.129	-0.5771
H	-17.1834	-5.7866	2.0073	H	17.064	-5.5234	-1.8479
H	-19.5956	1.4375	-1.5761	H	19.3063	1.8711	1.4667
H	-15.0305	0.2908	-3.0637	H	14.7441	0.73	2.9659
H	-19.0137	-2.1298	-2.4239	H	18.7594	-1.6658	2.4628
H	-20.2666	-0.8974	-2.2446	H	20.0001	-0.4251	2.2573
H	-15.8995	5.0735	-1.2203	H	15.5525	5.4438	0.9193
H	-11.8739	2.651	0.2988	H	11.5982	2.8713	-0.5399
H	-14.6333	2.6076	-3.6214	H	14.3093	3.0627	3.4126
H	-15.8657	3.8386	-3.3124	H	15.5261	4.2967	3.0572
H	-15.6759	7.7802	1.2359	H	15.2972	8.0401	-1.6515
H	-16.6361	6.6428	0.2912	H	16.268	6.9692	-0.6424
H	-15.1402	7.3492	-0.4211	H	14.744	7.6693	0.0147

H	-11.2857	1.0042	-0.9946	H	11.0305	1.2675	0.817
H	-10.9109	2.2906	-2.177	H	10.6121	2.5955	1.9373
H	-11.4072	0.6457	-2.7267	H	11.1373	0.9879	2.5646
H	-14.8975	5.2136	3.5951	H	14.6114	5.3543	-3.9045
H	-13.5948	0.5933	4.7388	H	13.4145	0.6655	-4.8717
H	-11.6581	4.1637	2.2019	H	11.3746	4.2965	-2.5095
H	-12.7816	5.5163	2.4043	H	12.472	5.6631	-2.7562
H	-15.8063	5.9024	5.7165	H	15.5357	5.9728	-6.0418
H	-17.5243	5.5645	6.0753	H	17.2649	5.6549	-6.3626
H	-17.0037	5.7606	4.3874	H	16.7165	5.9106	-4.6916
H	-12.2421	-0.2322	3.099	H	12.0568	-0.1188	-3.2172
H	-11.2791	0.5496	4.3857	H	11.0949	0.591	-4.5457
H	-10.6116	0.4009	2.7355	H	10.4099	0.4958	-2.8987
H	-15.7957	-1.6487	-4.4937	H	15.5486	-1.1388	4.5016
H	-14.6329	-1.9026	-3.1748	H	14.379	-1.4454	3.1988
H	-16.7111	-3.9652	-4.0655	H	16.47	-3.4725	4.1351
H	-15.5112	-4.1859	-2.7914	H	15.2366	-3.7385	2.9012
H	-13.6667	-3.8258	-4.4949	H	13.441	-3.2925	4.6449
H	-14.8853	-3.7117	-5.7626	H	14.7024	-3.1618	5.8713
H	-15.6497	-6.0521	-5.2494	H	15.4187	-5.5333	5.365
H	-14.4406	-6.1655	-3.9749	H	14.1296	-5.65	4.1709
H	-12.6087	-5.8546	-5.6585	H	12.4206	-5.236	5.9751
H	-13.8077	-5.6936	-6.9377	H	13.7172	-5.124	7.1637
H	-14.6135	-8.0376	-6.491	H	14.3916	-7.5054	6.6426
H	-13.442	-8.1937	-5.1822	H	13.092	-7.6045	5.4549
H	-13.9151	-7.687	-8.9877	H	14.0214	-7.2647	9.1802
H	-12.4152	-8.3433	-9.6348	H	12.5458	-7.8007	9.9831
H	-10.6902	-6.4684	-7.9622	H	10.8163	-5.726	8.6179
H	-11.1706	-3.9091	-8.481	H	11.7471	-3.2931	9.2258
C	-19.3127	3.9574	-1.9041	C	18.9846	4.4	1.6733
C	-19.3571	5.4746	-2.0148	C	19.0051	5.9214	1.7083
C	-20.7863	6.0275	-1.9377	C	20.4259	6.4927	1.6137
C	-20.8187	7.5607	-1.9804	C	20.4337	8.0265	1.5852
C	-22.2445	8.1276	-1.9232	C	21.8504	8.6134	1.5057

C	-22.2486	9.658	-1.896	C	21.8295	10.1407	1.4055
S	-23.9768	10.2983	-1.8784	S	23.5473	10.8074	1.3627
C	-23.6559	12.1054	-1.8587	C	23.1976	12.6061	1.2553
C	-23.1584	12.7953	-3.1442	C	22.6859	13.3493	2.5052
N	-23.4043	12.0975	-4.2953	N	22.9372	12.7105	3.6889
N	-23.0706	12.6286	-5.547	N	22.5913	13.2957	4.9129
O	-22.6327	13.8915	-3.0777	O	22.1451	14.4335	2.3849
H	-19.8947	3.4814	-2.7066	H	19.565	3.9734	2.5042
H	-19.7369	3.6322	-0.9424	H	19.4239	4.0334	0.7334
H	-18.8843	5.7715	-2.9603	H	18.5204	6.2575	2.6345
H	-18.7662	5.9063	-1.198	H	18.4137	6.3028	0.8671
H	-21.251	5.6963	-0.9993	H	20.9018	6.1256	0.6943
H	-21.3921	5.6158	-2.7598	H	21.0331	6.1294	2.4572
H	-20.3208	7.9143	-2.8959	H	19.9269	8.4139	2.4818
H	-20.2408	7.9413	-1.1286	H	19.8529	8.3578	0.7149
H	-22.7507	7.7504	-1.0256	H	22.3661	8.2025	0.6285
H	-22.8231	7.7722	-2.7879	H	22.4314	8.309	2.388
H	-21.7331	10.0637	-2.7742	H	21.3041	10.5793	2.2616
H	-21.7368	10.0226	-0.999	H	21.3155	10.4533	0.4904
H	-22.9416	12.3495	-1.0678	H	22.4815	12.8002	0.4523
H	-24.6081	12.5719	-1.5815	H	24.1429	13.0739	0.9577
H	-23.8613	11.1935	-4.2123	H	23.4072	11.8102	3.6504
H	-23.9148	12.7484	-6.1032	H	23.4314	13.4529	5.4658
H	-22.4495	11.9857	-6.0332	H	21.9766	12.6683	5.4267
H	-10.6296	-4.4851	-9.8997	H	11.0111	-3.8023	10.5788
Br	-11.4848	-2.4185	-2.9736	Br	11.2737	-2.0684	2.9335
I	-11.5329	-2.4571	4.1042	I	14.7821	-6.6077	-2.8448

10. The concentration-dependent ^{1}H NMR spectra of DSPy⊂SHP5

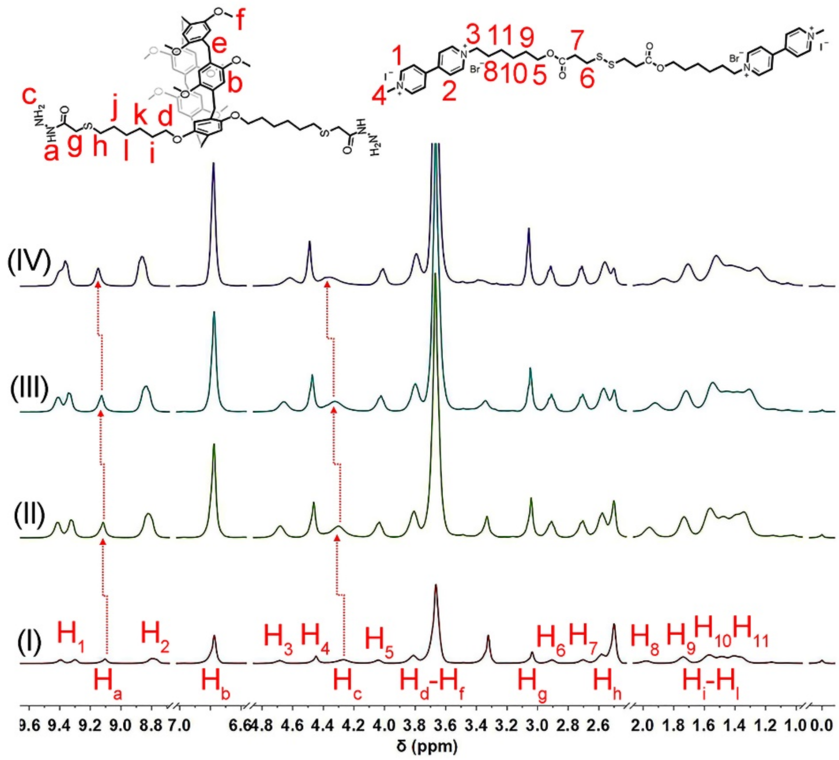

Figure S25. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of DSPy⊂SHP5 at various concentrations: (I) 3.0 mmol/L, (II) 15.0 mmol/L, (III) 30.0 mmol/L, and (IV) 50.0 mmol/L.

11. Metal-ligand coordination between SHP5 and Zn^{2+}

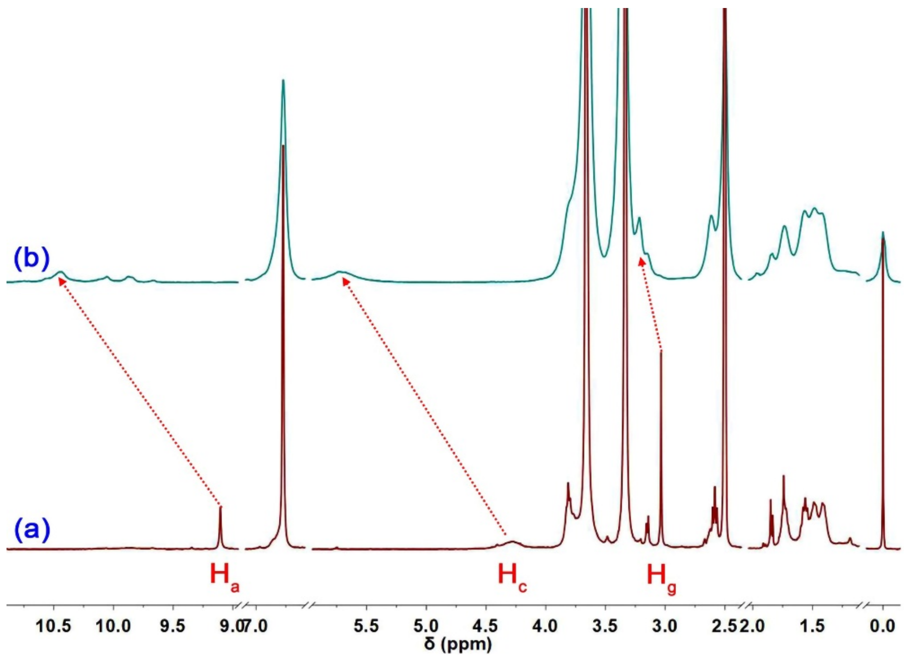

Figure S26. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of (a) 5 mM SHP5; (b) 5 mM SHP5 and 10 mM Zn^{2+}.

12. ^{1}H NMR spectra of Job's Plot Experiments between SHP5 and Zn^{2+}

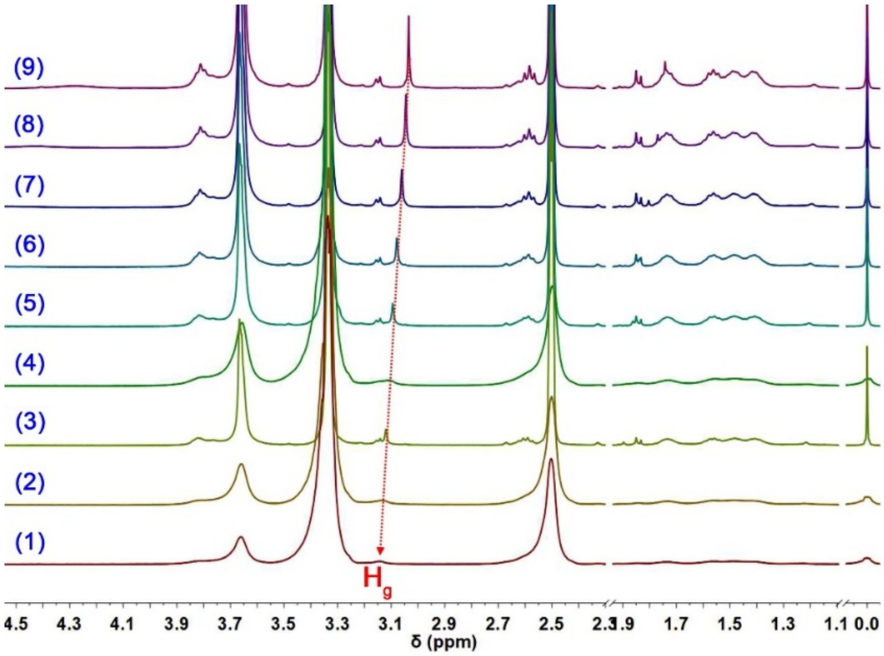

Figure S27. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of SHP5 and Zn^{2+} at different molar ratios while [SHP5] + [Zn^{2+}] = 5 mM. (1) [SHP5]/[Zn^{2+}] = 2:8, (2) [SHP5]/[Zn^{2+}] = 3:7, (3) [SHP5]/[Zn^{2+}] = 4:6, (4) [SHP5]/[Zn^{2+}] = 5:5, (5) [SHP5]/[Zn^{2+}] = 6:4, (6) [SHP5]/[Zn^{2+}] = 7:3, (7) [SHP5]/[Zn^{2+}] = 8:2, (8) [SHP5]/[Zn^{2+}] = 9:1, (9) free SHP5.

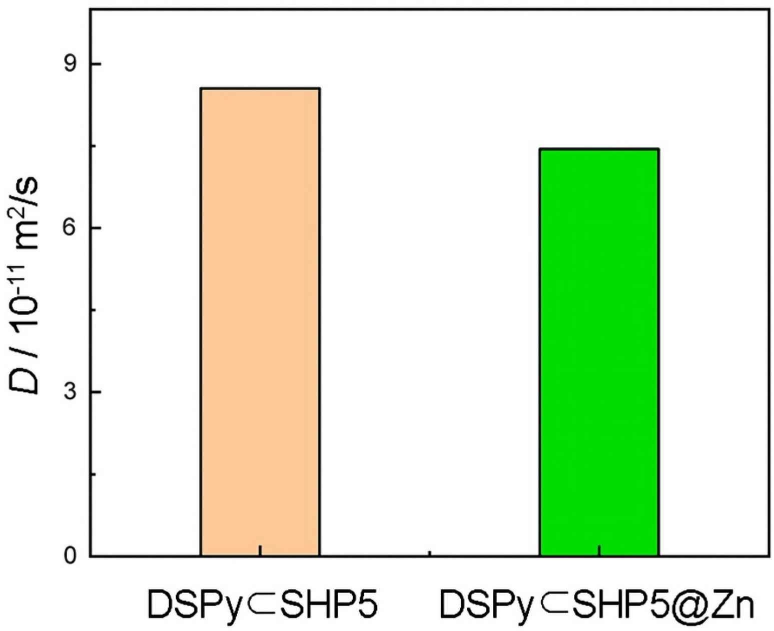

Figure S28. 2D DOSY values (600 MHz, DMSO-d_6, 298 K) for DSPy⊂SHP5 and DSPy⊂SHP5@Zn at 10 mmol/L.

13. PXRD patterns of DSPy⊂SHP5@Zn

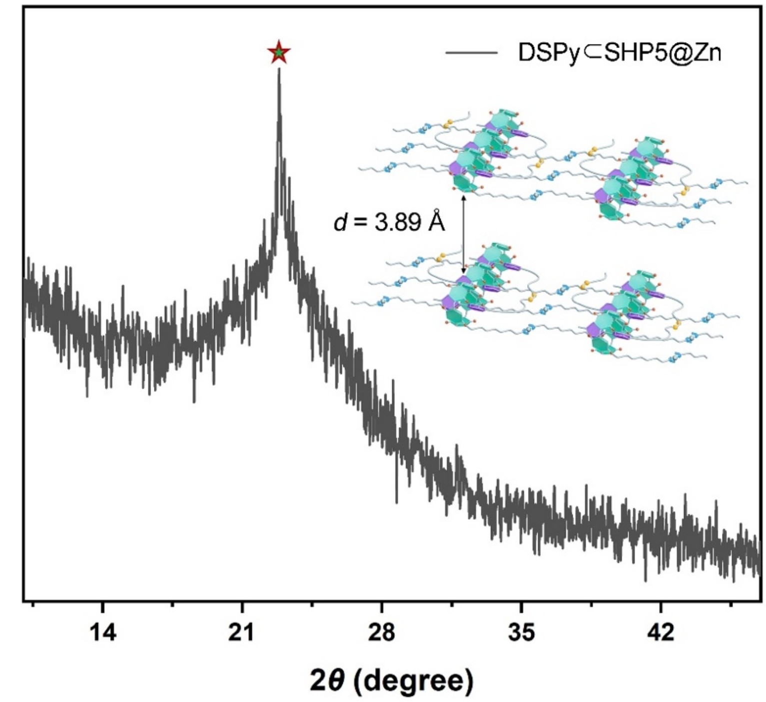

Figure S29. PXRD patterns of xerogel powder formed by the DSPy⊂SHP5@Zn.

14. Photoluminescence of DSPy⊂SHP5@Zn

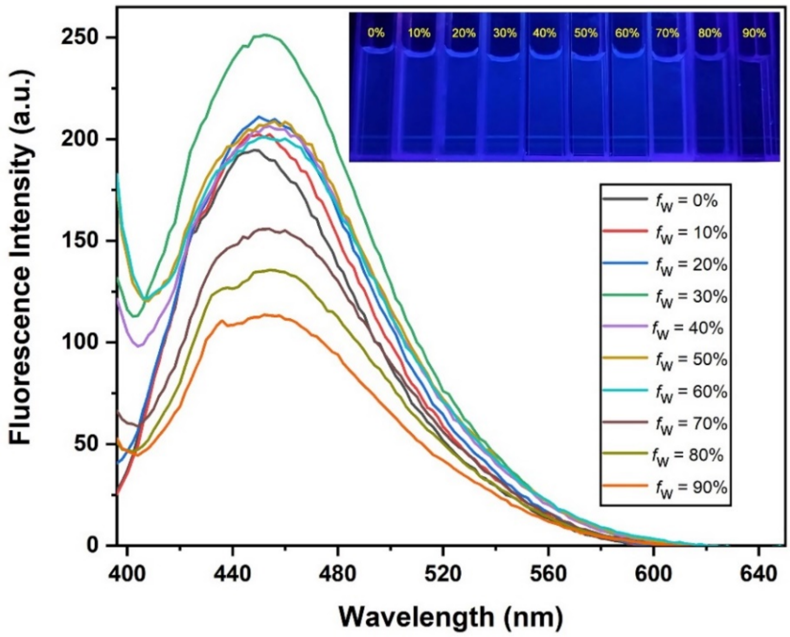

Figure S30. Fluorescence spectra of the DSPy⊂SHP5@Zn (200 μM) in DMSO-H_2O binary solutions with different volumetric fractions of water (vol %). (Experimental conditions: λ_{ex} = 375 nm; λ_{em} = 452 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 ℃) Inset: Fluorescence photographs of the DSPy⊂SHP5@Zn (200 μM) in DMSO/water binary solutions with different volumetric fractions of water (vol %).

15. Photos of different concentrations of DSPy⊂SHP5@Zn

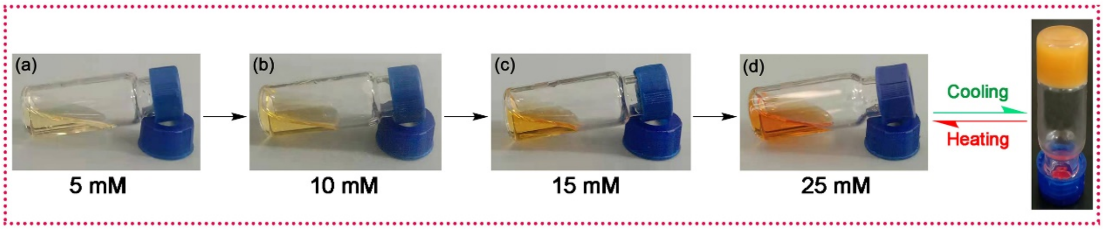

Figure S31. Vial inversion test to estimate the critical gelation concentration (CGC) of DSPy⊂SHP5@Zn in DMSO-H_2O (7: 3, v/v) mixed solvent at room temperature, suggesting a CGC of ca. 25 mM. The samples were aged overnight.

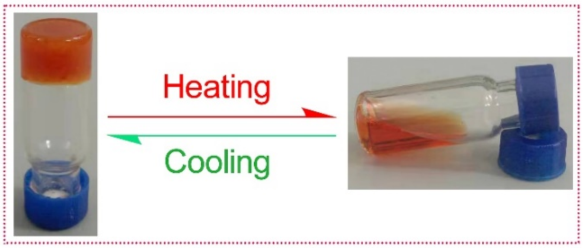

Figure S32. The gel–sol transitions of the supramolecular gel DSPy⊂SHP5-G triggered by temperature change.

16. Rheology measurements for DSPy⊂SHP5@Zn-G and DSPy⊂SHP5-G

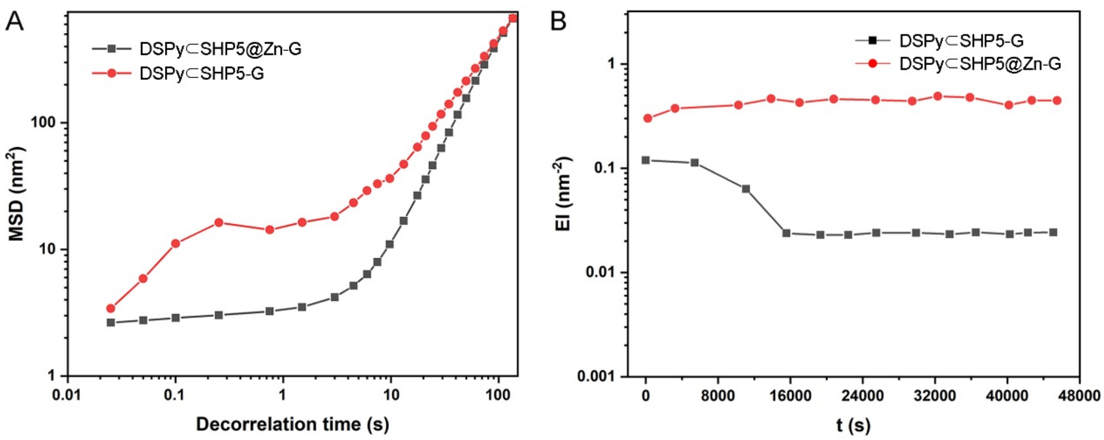

Figure S33. (A) Graph of mean squared displacement (MSD) of metallosupramolecular gel DSPy⊂SHP5@Zn-G and supramolecular gel DSPy⊂SHP5-G against decorrelation time curves; (B) EI of DSPy⊂SHP5@Zn-G and DSPy⊂SHP5-G versus time.

17. Characterization research of DSPy⊂SHP5@Zn toward various stimuli

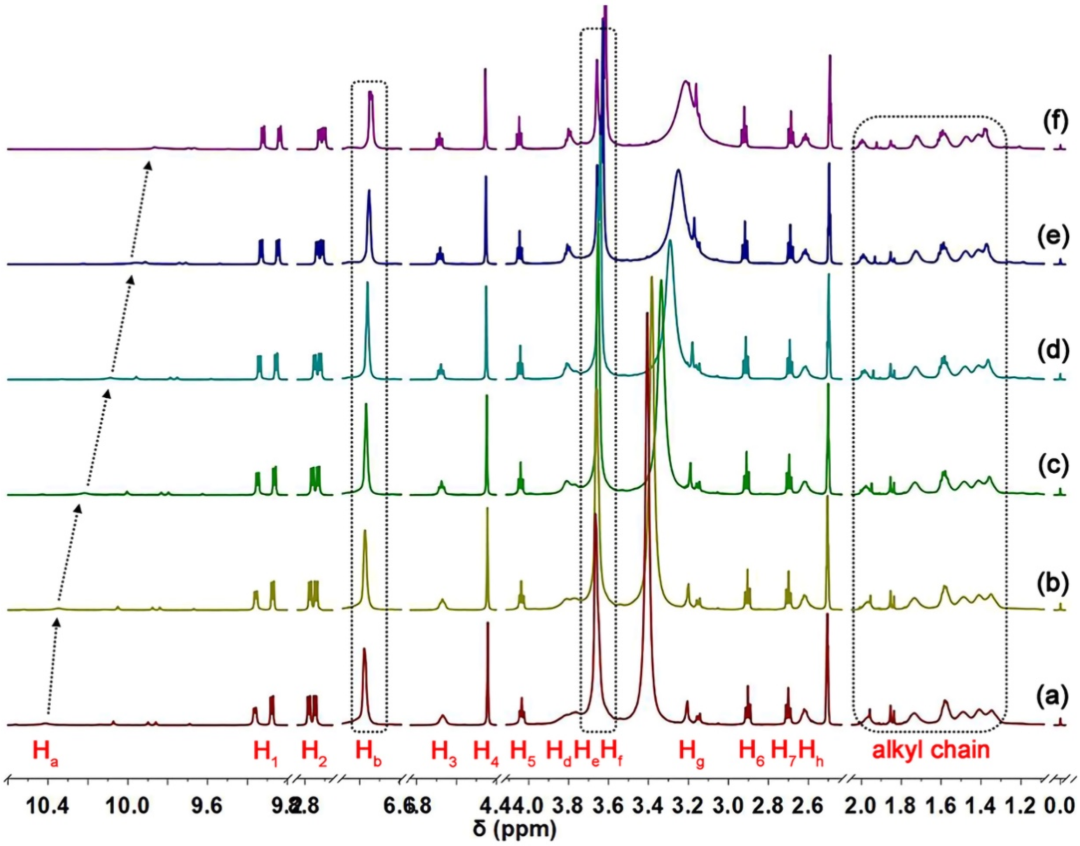

Figure S34. Variable temperature partial ^{1}H NMR spectra of DSPy⊂SHP5@Zn (40 mM, $CDCl_3$, 600 MHz): (a) 298 K; (b) 303 K; (c) 308 K; (d) 313 K; (e) 318 K and (f) 323 K.

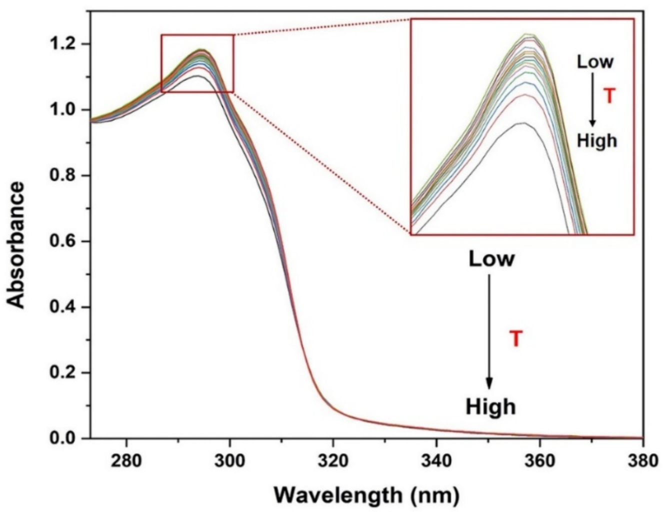

Figure S35. Absorbance spectra of DSPy⊂SHP5@Zn (20 μM) at different temperatures in DMSO-H_2O (v/v = 7/3) binary solution.

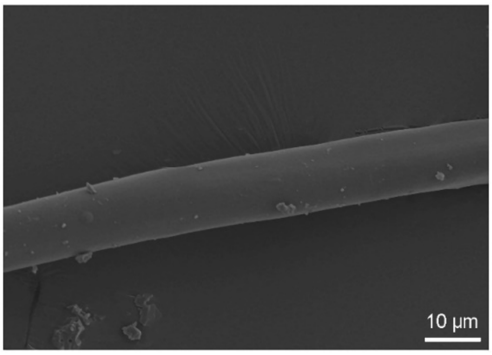

Figure S36. Representative SEM images showing the morphology of xerogels of DSPy⊂SHP5@Zn + adiponitrile.

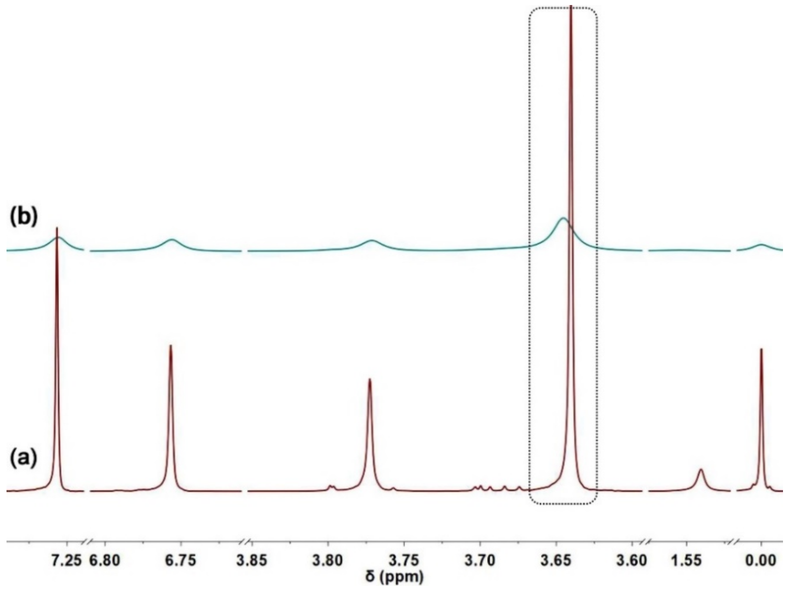

Figure S37. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of (a) DMP5 and (b) DMP5 with excess I_2.

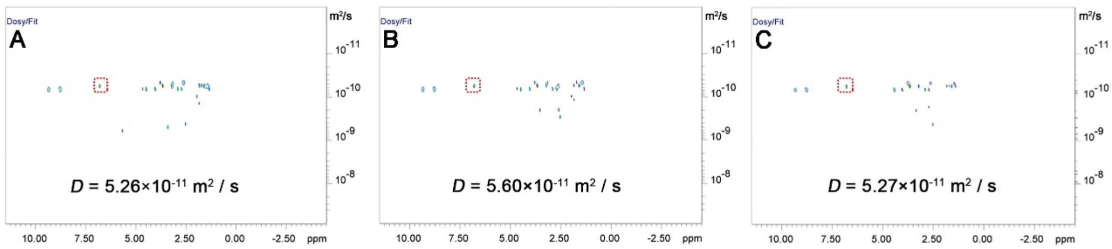

Figure S38. 2D DOSY spectra (600 MHz, DMSO-d_6, 298 K) of (A) DSPy⊂SHP5@Zn (25 mM), (B) DSPy⊂SHP5@Zn + DTT, (C) DSPy⊂SHP5@Zn-DTT + I_2.

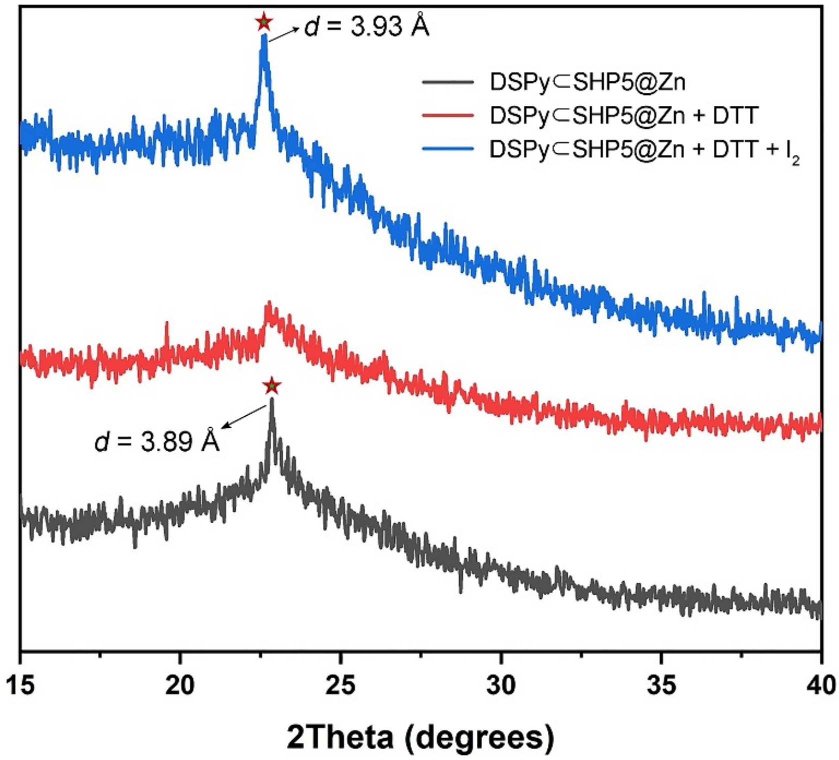

Figure S39. PXRD patterns of xerogels of DSPy⊂SHP5@Zn, DSPy⊂SHP5@Zn + DTT, and DSPy⊂SHP5@Zn-DTT treated with iodine.

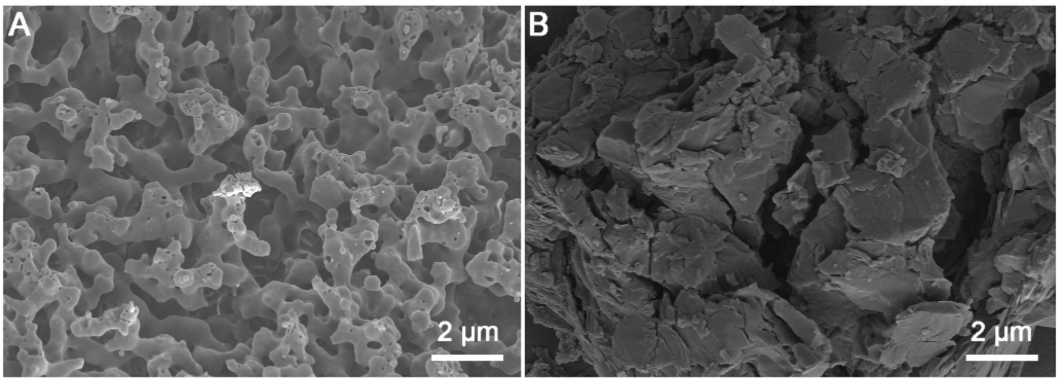

Figure S40. Representative SEM images showing the morphology of xerogels of (A) DSPy⊂SHP5@Zn + DTT, (B) DSPy⊂SHP5@Zn-DTT + I_2.

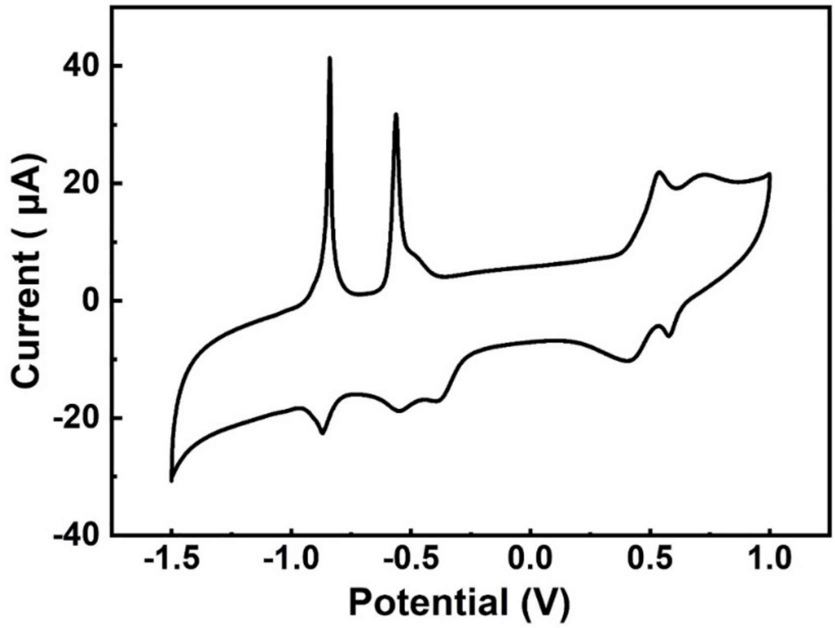

Figure S41. Cyclic voltammetry curves (298 K, scan rate 100 mV/s) of 0.1 mM DSPy in the solution of potassium chloride (0.2 M in water).

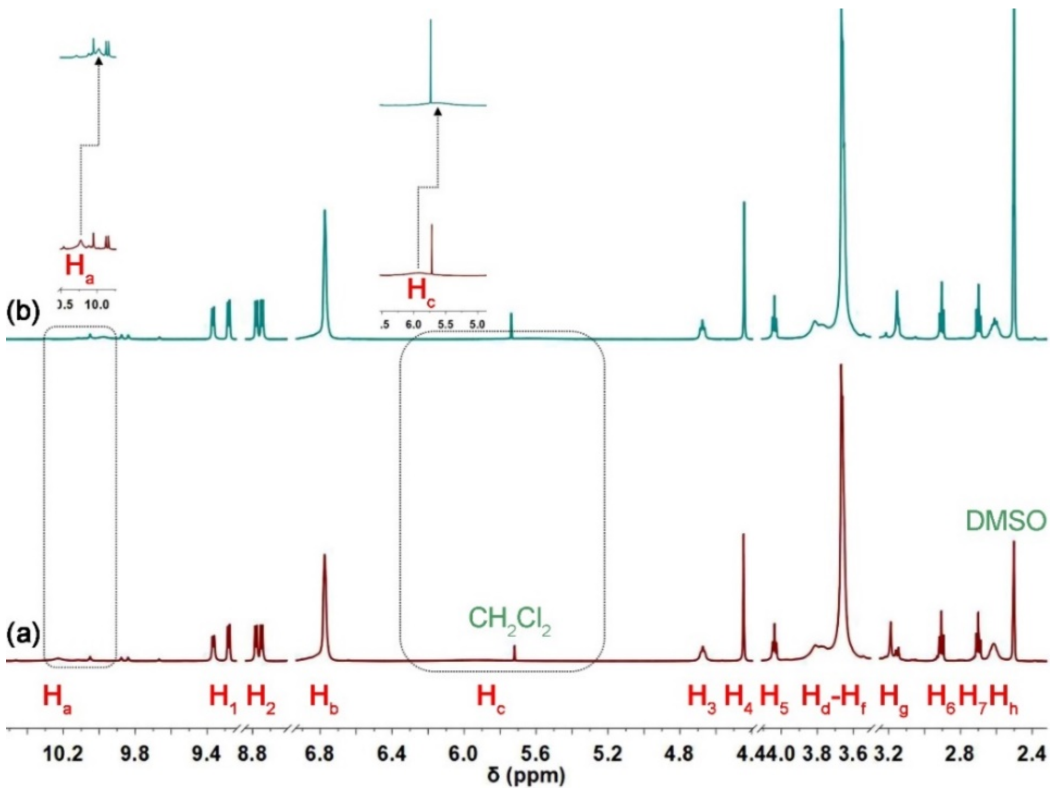

Figure S42. Partial [1]H NMR spectra (400 MHz, DMSO-d_6, 298 K) of (a) 20 mM DSPy⊂SHP5@Zn; (b) 20 mM DSPy⊂SHP5@Zn + CH_3COOH.

18. Dual-channel sensing of OH^- by DSPy⊂SHP5@Zn in solution

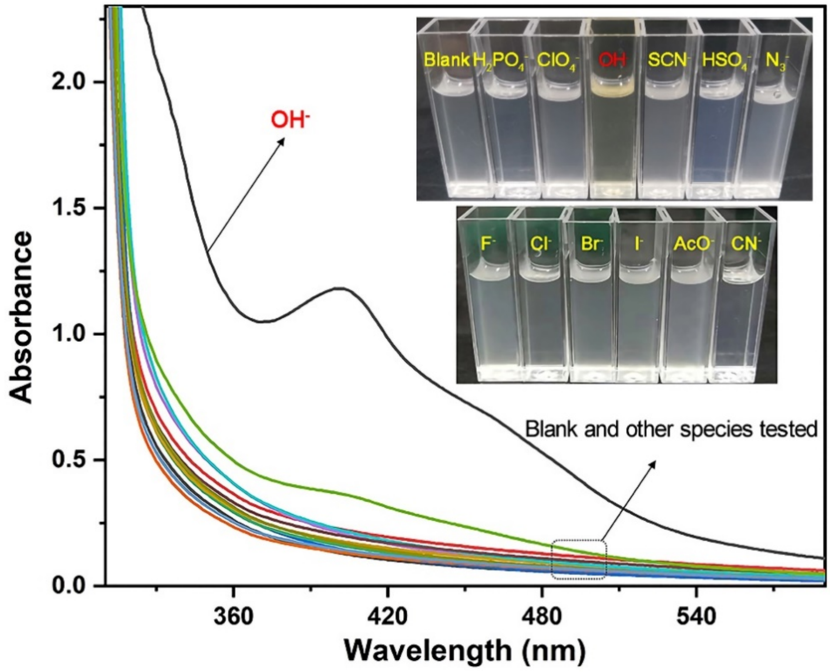

Figure S43. UV-vis spectra of DSPy⊂SHP5@Zn upon the addition of 5.0 equivalents of various anions: F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, OH^-, SCN^-, CN^-, and N_3^-. Inset: Photographs showing the color change of the solution of DSPy⊂SHP5@Zn alone and after the addition of 5.0 equivalents of various anions at room temperature (Experimental conditions: DMSO-H_2O (7: 3, v/v) binary solution as solvent; 298 K; [DSPy⊂SHP5@Zn] = 2.0×10^{-4} mol/L).

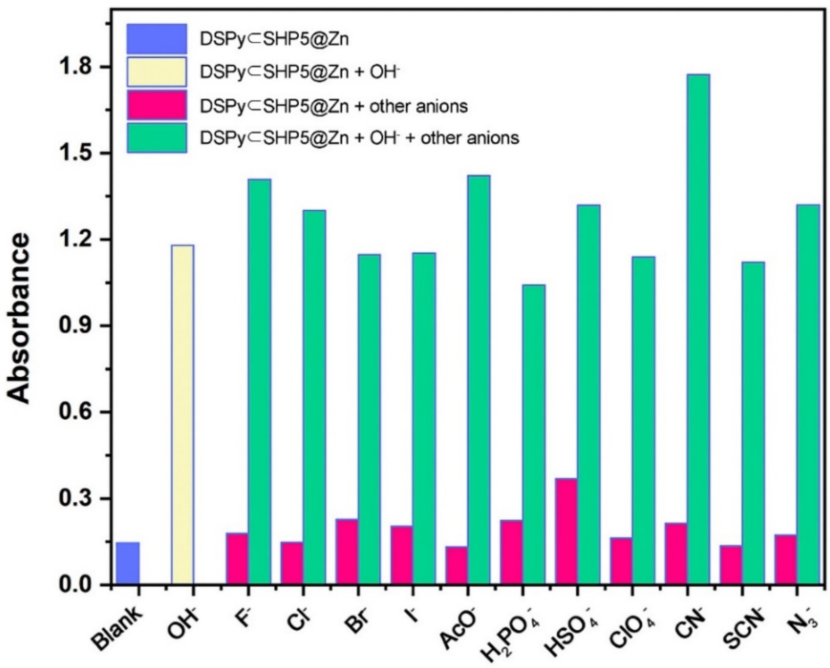

Figure S44. Absorbance data of DSPy⊂SHP5@Zn at 401 nm in the presence of 5 equivalents of various anions and equal equiv. of OH^-.

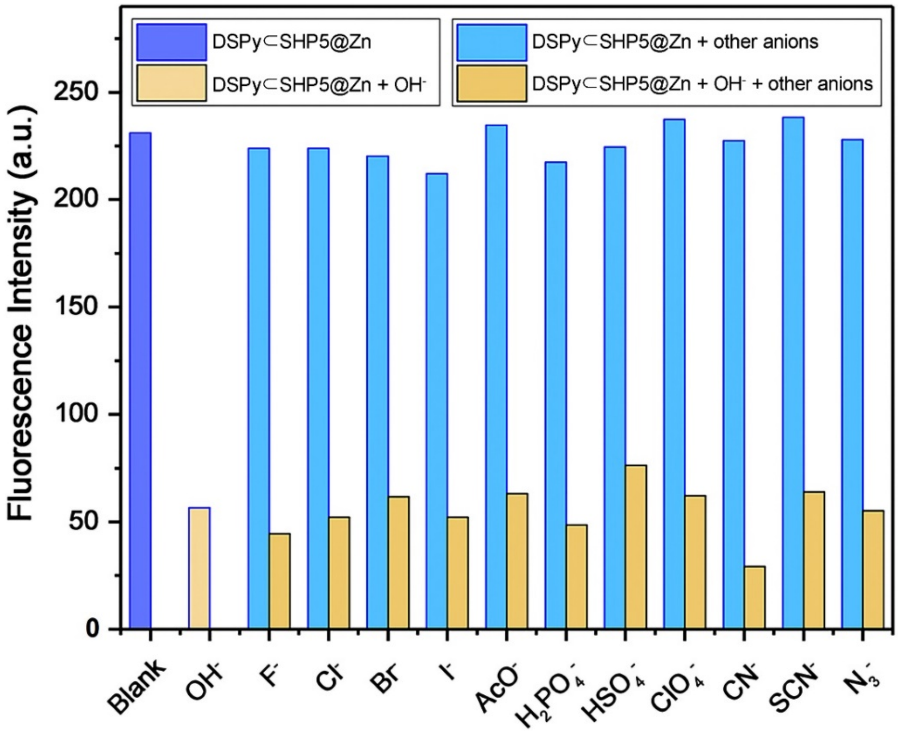

Figure S45. Fluorescence response of DSPy⊂SHP5@Zn in the presence of 5 equivalents of various anions and 5 equivalents of OH^-.

19. Determination of the UV-vis detection limit for OH^-

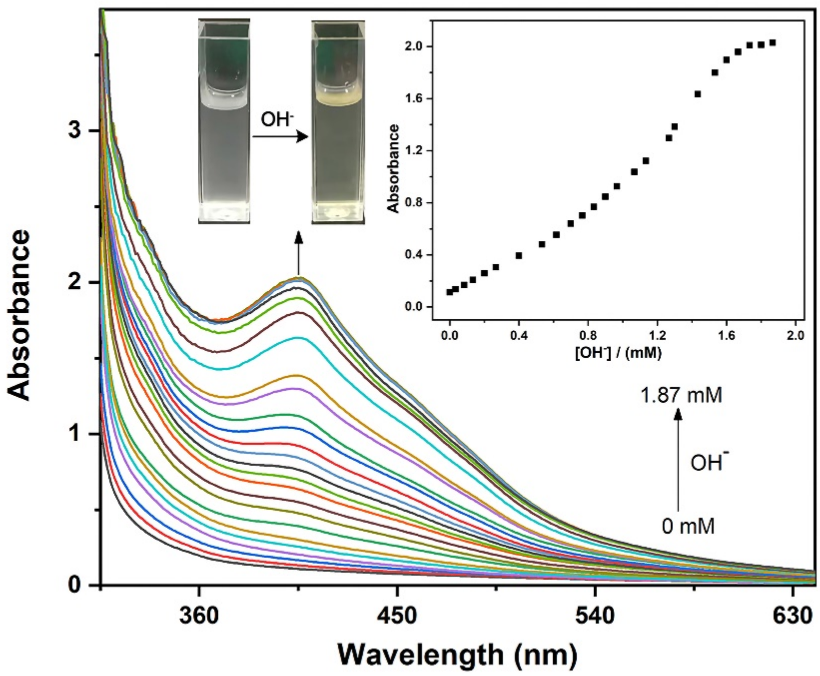

Figure S46. UV-vis spectra of DSPy⊂SHP5@Zn (2.0×10^{-4} M) in the presence of increasing amounts of OH^- (from 0 to 1.87 mM) in DMSO-H_2O (7:3, v/v) mixed solvent. Inset: A plot of absorption at 401 nm versus number of equivalents of OH^-.

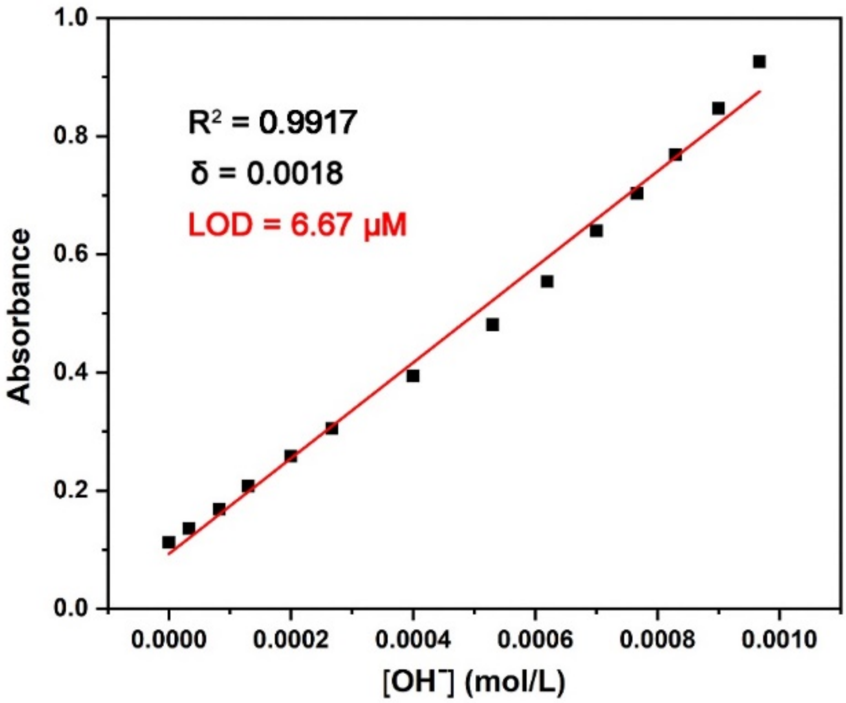

Figure S47. The linear fitting between the absorbance intensity of DSPy⊂SHP5@Zn at 401 nm and the concentration of OH^- in DMSO-H_2O (7: 3, v/v) mixed solvent.

The lowest limit of detection (LOD) was determined from the equation LOD = K × δ/S, where K = 3, A_i is the absorbance of DSPy⊂SHP5@Zn at 401 nm; A_a is the average of the F_i. δ is the standard deviation of blank measurements of DSPy⊂SHP5@Zn, and S is the slope of the linear fitting.

The result of the analysis is as follows:

Linear Equation: Y = 0.093+809.38*x

$R^2 = 0.9917$

$S = 8.094 \times 10^2$

$$\delta = \sqrt{\frac{\sum(A_i - A_a)^2}{n-1}} = 0.0018\ (n = 20)$$

K = 3

LOD = K × δ/S = 6.67 μM

20. Determination of the fluorescent detection limit for OH^-

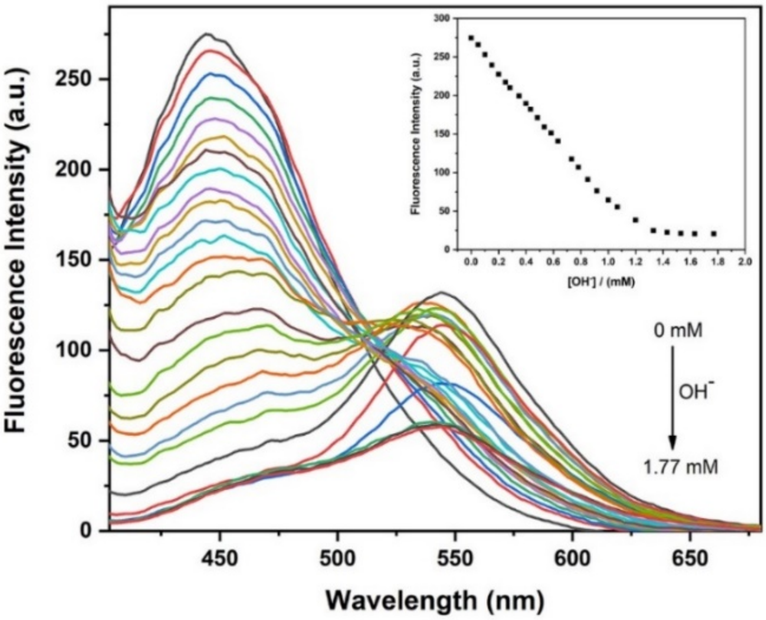

Figure S48. Fluorescence spectra of DSPy⊂SHP5@Zn (2.0×10^{-4} M) with increasing concentration of OH^- (from 0 to 1.77 mM). Inset: A plot of emission at 446 nm versus the number of equivalents of OH^-. Conditions: DMSO-H_2O (v/v = 7:3) as solvent; λ_{ex} = 375 nm; slit width: Ex. 5 nm, Em. 5 nm; 298 K.

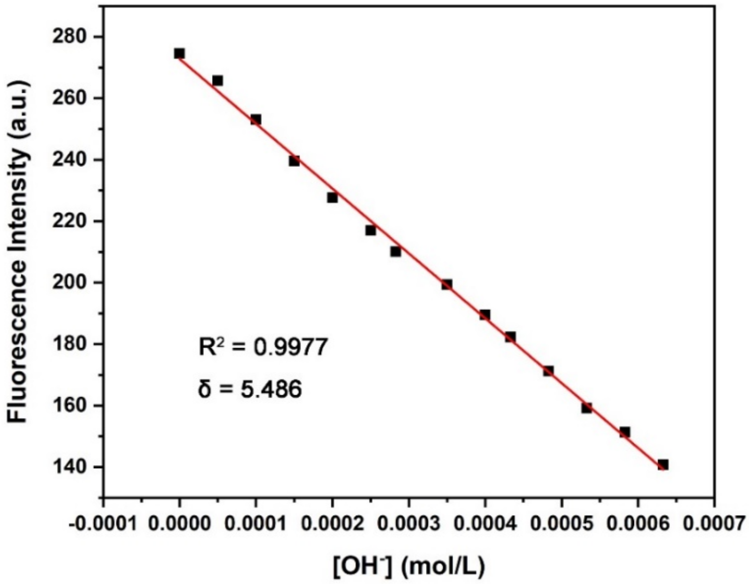

Figure S49. The linear fitting between the emission intensity of DSPy⊂SHP5@Zn and the concentration of OH^- in DMSO-H_2O (7: 3, v/v) binary solution.

The lowest limit of detection (LOD) was determined from the equation LOD = K × δ/S, where K = 3, F_i is the fluorescence intensity of DSPy⊂SHP5@Zn; F_a is the average of the F_i. δ is the standard deviation of blank measurements of DSPy⊂SHP5@Zn, and S is the slope of the linear fitting.

The result of the analysis is as follows:

Linear Equation: Y = 272.8422-210982*x

$R^2 = 0.9977$

$S = 2.11 \times 10^5$

$$\delta = \sqrt{\frac{\Sigma(F_i - F_a)^2}{n-1}} = 5.486\ (n = 20)$$

K = 3

LOD = K × δ/S = 78 μM

21. Sensing mechanism research of DSPy⊂SHP5@Zn toward OH^-

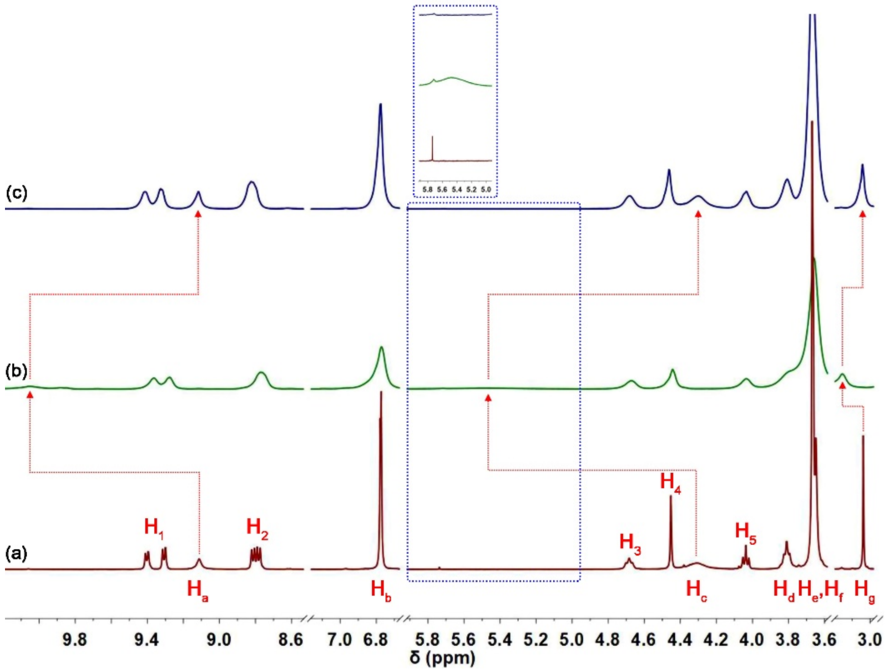

Figure S50. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) showing the assembly and disassembly of metallosupramolecular polymer network: (a) host-guest complex DSPy⊂SHP5, (b) after the addition of 2 equiv. Zn^{2+} to DSPy⊂SHP5, (c) further adding a slight excess of OH^- into DSPy⊂SHP5@Zn.

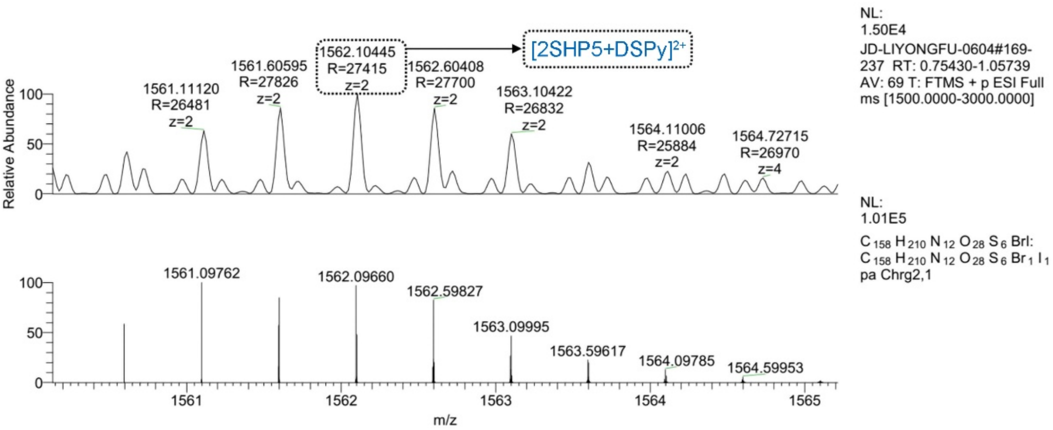

Figure S51. High-resolution mass data of DSPy⊂SHP5@Zn after being treated with OH^- (top: experimental, bottom: simulated).

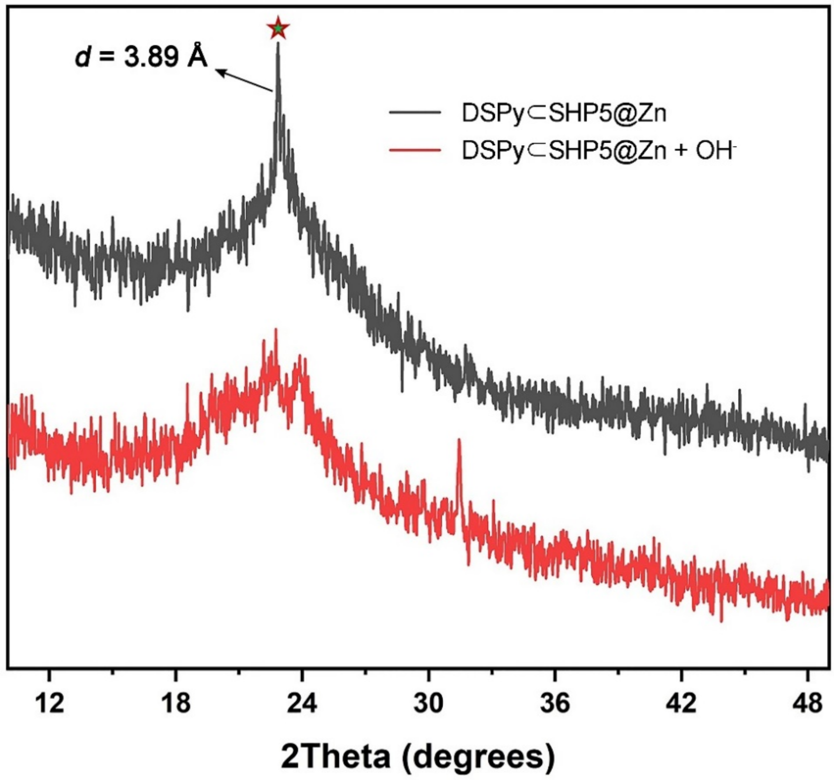

Figure S52. PXRD diagrams of xerogel powder formed by the gelator of DSPy⊂SHP5@Zn in DMSO-H_2O (7/3, v/v) binary solution and xerogel of DSPy⊂SHP5@Zn treated with OH^-.

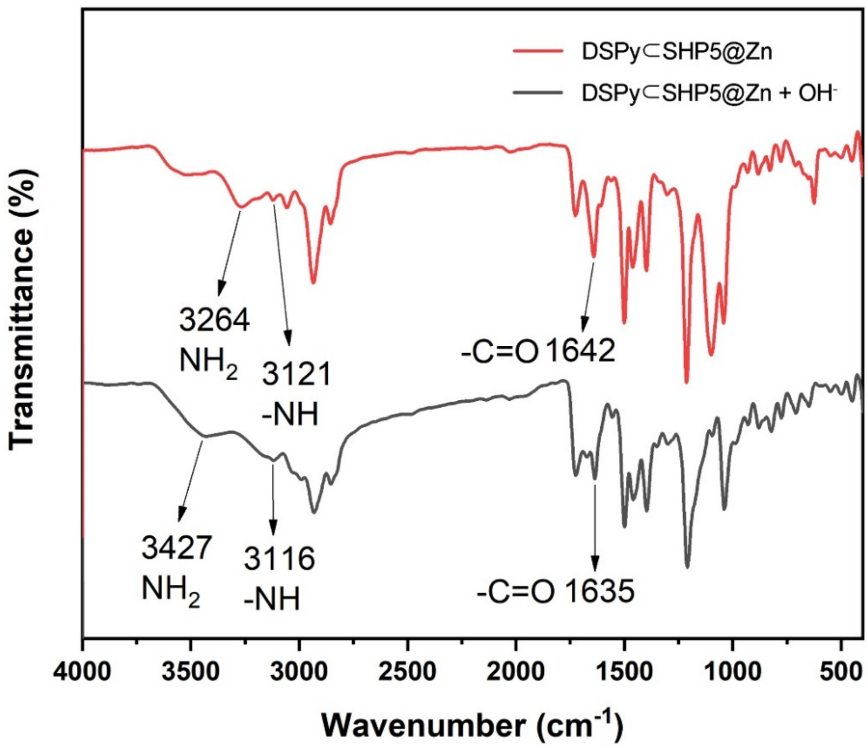

Figure S53. FT-IR spectra of DSPy⊂SHP5@Zn and DSPy⊂SHP5@Zn after the addition of OH^-.

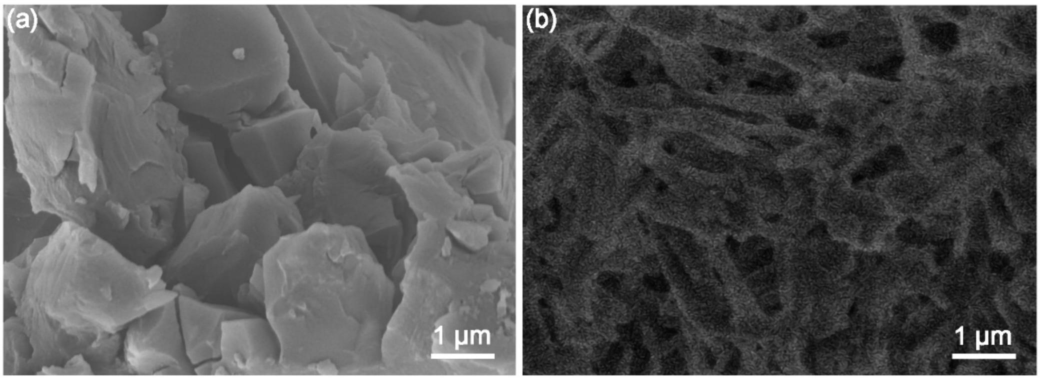

Figure S54. Representative SEM images showing the morphology of xerogels of (a) DSPy⊂SHP5@Zn, and (b) DSPy⊂SHP5@Zn + OH^-.

22. The practical applications of DSPy⊂SHP5@Zn

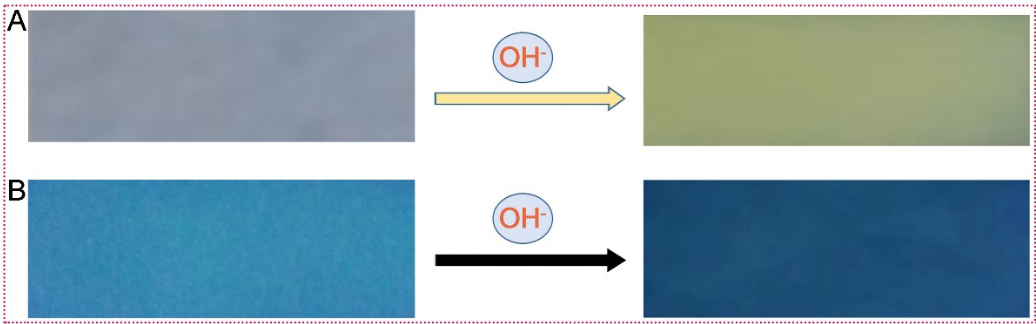

Figure S55. Photographs of test strips of DSPy⊂SHP5@Zn and DSPy⊂SHP5@Zn + OH^- under nature light (A), under irradiation at 365 nm using a UV lamp (B).

19. References

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[S3] Q. Lin, Y.-Q. Fan, P.-P. Mao, L. Liu, J. Liu, Y.-M. Zhang, H. Yao and T.-B. Wei, *Chem. Eur. J.*, 2018, **24**, 777-783.

[S4] H. Zhang, F. Liang and Y.-W. Yang, *Chem. Eur. J.*, 2020, **26**, 198-205.