Electronic supplementary information

The construction of single-layer two-dimensional supramolecular organic frameworks in water through the self-assembly of rigid vertexes and flexible edges

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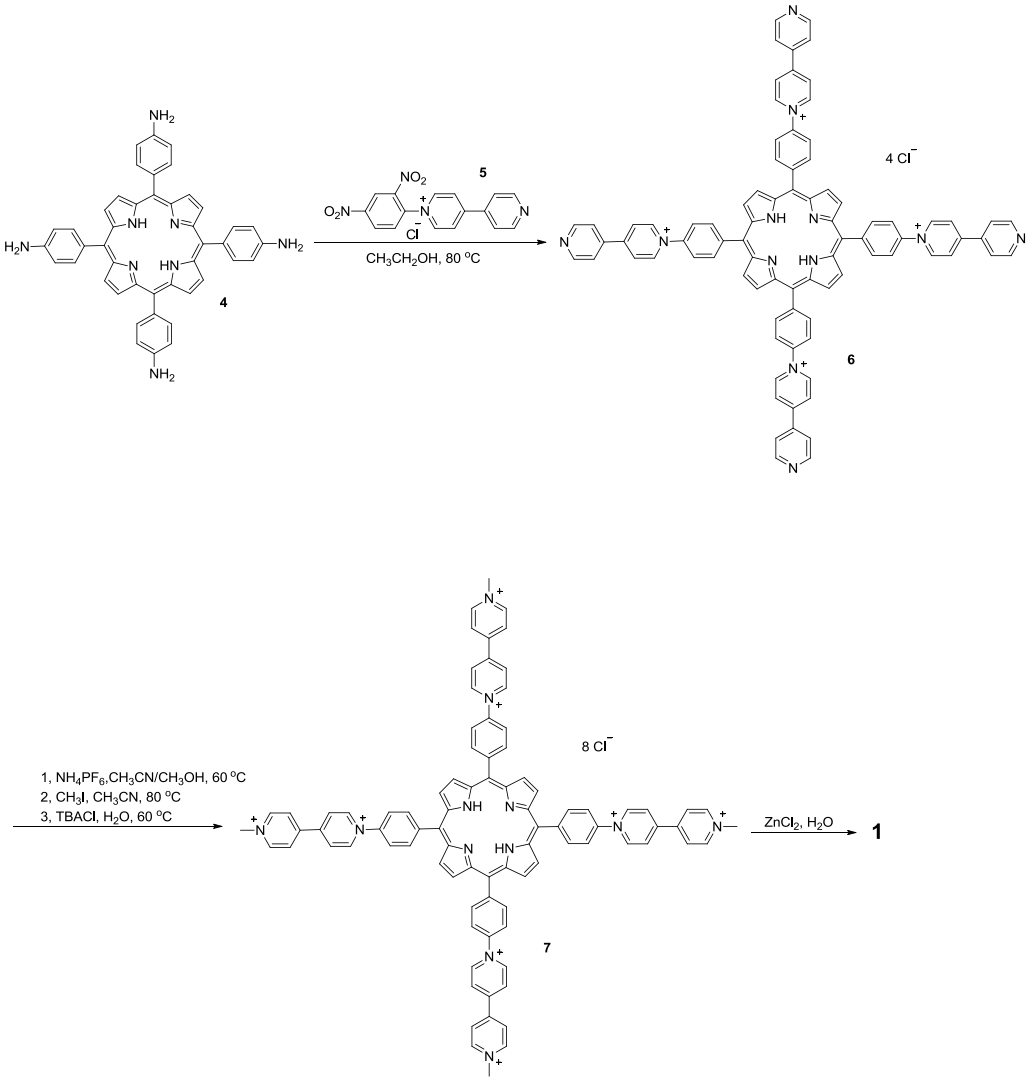
General methods. All solvents were dried following the standard procedures before use. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and used without further purification. UV-vis absorption spectra were recorded with a Unico 4802 UV-vis double beam spectrophotometer (Unico, USA). Fluorescence spectra were measured with a F-4600 FL Spectrophotometer (Hitachi, Japan). ^{1}H and ^{13}C NMR spectra were recorded on 400 or 500 MHz spectrometers in the indicated solvents. Chemical shifts were referenced to the residual solvent peaks. Mass spectra (ESI, MALDI) were obtained on Shimadzu LCMS-2010EV, IonSpec 4.7 Tesla FTMS and MICROTOF II spectrometers. DLS was performed on an Autosizer 4700 dynamic/static light scattering instrument. AFM was recorded on a Nano scope IIIa MultiMode microscope. Transmission electron microscopy was performed on a Philips CM 200/FEG transmission electron microscope. Scanning electron microscopy was carried out using a Philips XL30FEG Scanning electron microscope. The SAXS measurement was performed in SAXSess mc^2 system (Anton Paar, Austria) with Ni filtered Cu K_α radiation source. The power of X-ray source was operated at 30 mA and 50 kV. Synchrotron radiation SAXS experiments were performed on the BL16B beamline of Shanghai Synchrotron Radiation Facility, using a fixed wavelength of 0.124 nm, a sample to detector distance of 2.01 m and an exposure time of 3,600 s. The 2D scattering pattern was collected on a charge-coupled device camera, and the curve intensities versus q were obtained by integrating the data from the pattern. Compound **4** was synthesized according a procedure reported previously (M. Yuasa, K. Oyaizu, A. Yamaguchi and M. Kuwakado, *J. Am. Chem. Soc.*, 2004, **126**, 11128.).

Procedures for synthesis



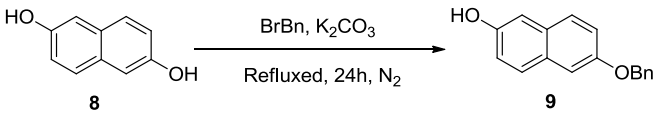
Synthesis of compound 6. A solution of compound **4** (67.5 mg, 0.1 mmol) and compound **5** (0.3 g, 0.8 mmol) in ethanol (10 mL) was stirred at 80 ^{o}C for 3 days. After being cooled to room temperature, the precipitate was collected by filtration and purified by flash column chromatography (CH_3OH/H_2O/saturated ammonium chloride solution, 6:3:1) to yield compound **6** as a red brown solid (57.8 mg, 42%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.88 (d, J = 5.7 Hz, 8H), 9.02 (d, J = 11.7 Hz, 24H), 8.67 (d, J = 7.8 Hz, 8H), 8.44 (d, J = 7.9 Hz, 8H), 8.28 (d, J = 4.6 Hz, 8H), -2.83 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 153.95, 151.68, 146.16, 144.29, 142.69,

141.03, 135.90, 125.93, 123.99, 122.58, 119.19, 109.99. MS (MALDI-TOF): *m/z* 1235.8 $[M-4Cl]^+$.

Synthesis of compound 7. Hexafluorophosphate (163 mg, 1.0 mmol) was added to a solution of compound **6** (37.6 mg, 0.027 mmol) in methanol and acetonitrile (20 mL, 1:3) and the resulting mixture was refluxed overnight. After being cooled to room temperature, the resulting dark brown solid was collected through filtration and washed with methanol. After dried under reduced pressure, iodomethane (1.87 mL, 0.3 mmol) and CH_3CN (5 mL) was added and the solution was refluxed overnight. After being cooled down to room temperature, dark brown solid was obtained through filtration and washed with ethanol. The solid was dissolved in H_2O (5 mL) after dried under reduced pressure, to which TBACl (55.6 mg, 0.2 mmol) was added and the solution was stirred at 60 ^oC overnight. The resulting black solid was collected by filtration and washed with ethanol and acetone to afford compound **7** as a black solid (93.9 mg, 48%). ^1H NMR (500 MHz, D_2O) δ: 9.80 (d, *J* = 6.8 Hz, 8H), 9.19 (d, *J* = 6.7 Hz, 8H), 8.94 (d, *J* = 6.9 Hz, 8H), 8.75 (dd, *J* = 7.4, 5.2 Hz, 16H), 8.38 (d, *J* = 8.5 Hz, 8H), 4.60 (s, 12H). ^{13}C NMR (100 MHz, D_2O) δ: 151.13, 149.53, 146.36, 145.64, 143.98, 142.56, 136.84, 127.17, 126.78, 123.07, 119.28, 48.35. MS (MALDI-TOF): *m/z* 1295.8 $[M-8Cl]^+$.

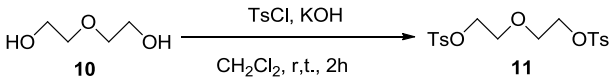
Synthesis of compound 1. To a solution of compound **7** (31.6 mg, 0.02 mmol) in H_2O (5 mL), $ZnCl_2$ (16.3 mg, 0.1 mmol) was added and the solution was refluxed overnight. After being cooled to room temperature, dark green solid was obtained after evaporation of solvent. The solid was washed with ethanol (20 mL) and dried under reduced pressure to give compound **1** as a black solid (28.5 mg, 87%). ^1H NMR (500 MHz, D_2O) δ: 9.80 (d, *J* = 6.8 Hz, 8H), 9.18 (s, 16H), 8.93 (d, *J* = 6.7 Hz, 8H), 8.74 (d, *J* = 6.7 Hz, 8H), 8.71 (d, *J* = 8.4 Hz, 8H), 8.33 (d, *J* = 8.5 Hz, 8H), 4.60 (s, 12H). ^{13}C NMR (100 MHz, D_2O) δ: 150.26, 149.65, 148.64, 145.92, 145.30, 141.84,

136.34, 132.58, 126.77, 126.20, 122.58, 118.94, 48.23. MS (MALDI-TOF): *m/z* 1358.9 $[M-8Cl]^+$.



8 **9**

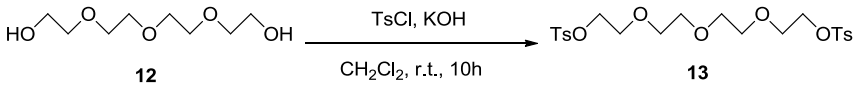
Synthesis of compound 9. To a solution of 2,6-dinaphthol (2 g, 12.5 mmol) and K_2CO_3 (2 g, 15 mmol) in acetone (40 mL), BnBr (1.6 mL, 13.7 mmol) was slowly added under a nitrogen atmosphere and the mixture was refluxed for 24 h. After being cooled to room temperature, ethyl acetate (100 mL) was added to the mixture and the organic phase was washed with H_2O and brine then dried over anhydrous sodium sulfate. The crude product was purified with flash column chromatography (acetone/PE, 1:4) to afford a yellow solid (1.0 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.59 (m, 2H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.43-7.38 (m, 2H), 7.34 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.23-7.17 (m, 2H), 7.13-7.05 (m, 2H), 5.16 (d, *J* = 2.3 Hz, 2H). MS (EI): *m/z* 250 $[M]^+$.



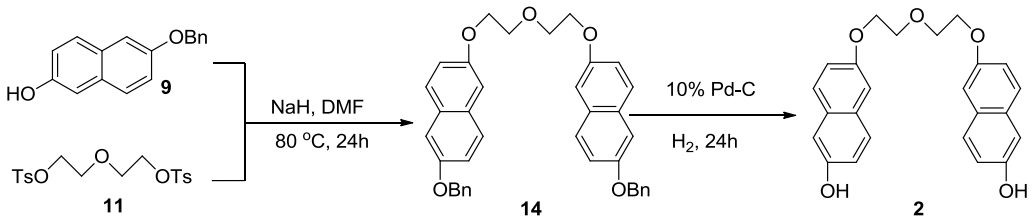
10 **11**

Synthesis of compound 11. Diethylene glycol (5.5 g, 0.05 mol) and TsCl (19 g, 0.10 mol) was dissolved in CH_2Cl_2 (100 mL) under ice bath, to which KOH (11.2 g, 0.20 mol) was slowly added and the solution was stirred for 2 h at room temperature, then the mixture was washed with H_2O and brine then dried over anhydrous sodium sulfate. The crude product was puridied by flash column chromatography (EA/PE, 1:4) to give a light yellow solid (9.3 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-7.65 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 4.16-4.02 (m, 4H), 3.66-3.55 (m, 4H), 2.45 (s, 6H). MS

(EI): *m/z* 414 $[M]^+$.



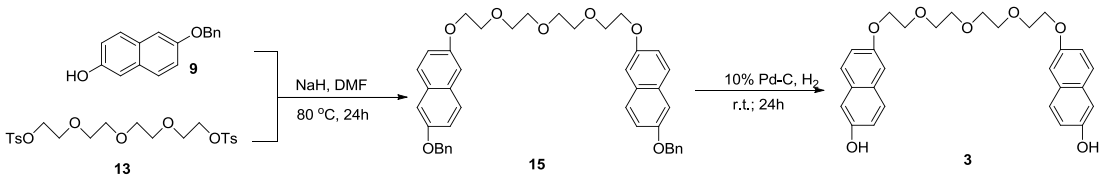
Synthesis of compound 13. Tetraethylene glycol (10 g, 0.05 mol) and TsCl (18 g, 0.10 mol) was dissolved in CH_2Cl_2 (100 mL) under ice bath, to which KOH (12 g, 0.20 mol) was slowly added and stirred for 10h at room temperature, then the mixture was washed with H_2O, brine and dried over anhydrous sodium sulfate, the resulting solution was evaporated under reduced pressure to give a light yellow oil (22.6 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: (ppm) 7.79 (d, J = 8.0 Hz, 4 H), 7.33 (d, J = 8.0 Hz, 4 H), 4.15 (t, J = 8.4 Hz, 4 H), 3.68 (t, J = 9.6 Hz, 4 H), 3.56 (s, 8 H), 2.44 (s, 6 H). MS (EI): *m/z* 525.1 $[M+Na]^+$.



Synthesis of compound 14. To a mixture of compound **9** (500 mg, 2.0 mmol) and NaH (96 mg, 4.0 mmol) in anhydrous DMF (15 mL), a solution of compound **11** (414 mg, 1.0 mmol) in anhydrous DMF (5 mL) was slowly injected through a microsyringe within 2 h under a N_2 atmosphere. The mixture was heated to 80 °C for 24 h and then cooled to room temperature. Ethyl acetate (100 mL) was added and the organic phase was washed with H_2O and brine and then dried over anhydrous sodium sulfate. The crude product was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:1.5) to give compound **14** as a light yellow solid (353.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 8.7, 3.4 Hz, 4H), 7.49 (d, *J* = 7.3 Hz, 4H), 7.40 (t,

J = 7.4 Hz, 4H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.17 (ddd, *J* = 19.5, 12.2, 6.4 Hz, 8H), 5.15 (s, 4H), 4.33 – 4.22 (m, 4H), 4.07 – 3.95 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.49, 155.46, 137.19, 129.95, 128.74, 128.39, 128.33, 128.11, 127.71, 119.44, 107.66, 107.39, 70.27, 70.17, 67.75. MS (MALDI-TOF): *m/z* 570.2 $[M]^+$.

Synthesis of compound 2. Compound **14** (100 mg, 0.18 mmol) and Pd/C (40 mg) was dissolved in CH_2Cl_2 and MeOH (5 mL, 1:1) and the solution was stirred at room temperature for 10 h under a H_2 atmosphere, after which the mixture was evaporated and purified by flash column chromatography (ethyl acetate/petroleum ether, 2:1) to give compound **2** as a white solid (38.2 mg, 56%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.44 (s, 2H), 7.60 (dd, *J* = 16.8, 8.9 Hz, 4H), 7.21 (d, *J* = 2.3 Hz, 2H), 7.14 – 6.98 (m, 6H), 4.28 – 4.16 (m, 4H), 3.92 – 3.82 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.15, 153.56, 129.83, 128.47, 128.06, 127.48, 118.80, 108.86, 107.04, 69.14, 67.16. MS (EI): *m/z* 390.



Synthesis of compound 15. To a mixture of compound **9** (600 mg, 2.4 mmol) and NaH (115 mg, 4.8 mmol) in anhydrous DMF (15 mL), a solution of compound **13** (498 mg, 1 mmol) in anhydrous DMF (5 mL) was slowly injected through a microsyringe within 2 h under a N_2 atmosphere. The mixture was heated to 80 °C for 24 h and then cooled to room temperature. Ethyl acetate (100 mL) was added and the organic phase was washed with H_2O and brine and then dried over anhydrous sodium sulfate. Compound **15** was obtained as a light yellow solid (262.3 mg, 40%) by purifying the crude product by flash column chromatography (ethyl acetate/petroleum ether, 1.5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (dd, *J* = 8.8, 5.8 Hz, 4H), 7.48 (d, *J*

= 7.1 Hz, 4H), 7.40 (dd, *J* = 8.1, 6.5 Hz, 4H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.22 – 7.12 (m, 6H), 7.08 (d, *J* = 2.4 Hz, 2H), 5.14 (s, 4H), 4.26 – 4.16 (m, 4H), 3.96 – 3.85 (m, 4H), 3.81 – 3.67 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.41, 155.39, 137.11, 129.88, 129.83, 128.65, 128.31, 128.26, 128.03, 127.64, 119.35, 107.57, 107.21, 70.91, 70.78, 70.14, 69.84, 67.54. MS (MALDI-TOF): *m/z* 681.3 $[M+Na]^+$.

Synthesis of compound 3. A solution of Compound **15** (100 mg, 0.15 mmol) and Pd/C(40 mg) in CH_2Cl_2 and MeOH (15 mL, 2:1) was stirred at room temperature for 10 h under a H_2 atmosphere, after which the mixture was evaporated and the crude product was purified by flash column chromatography (ethyl acetate/petroleum ether, 2:1) to give compound **3** as a white solid (55.1 mg, 76%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.43 (s, 2H), 7.59 (dd, *J* = 20.2, 8.9 Hz, 4H), 7.18 (d, *J* = 2.2 Hz, 2H), 7.04 (d, *J* = 6.5 Hz, 6H), 4.19 – 4.06 (m, 4H), 3.84 – 3.73 (m, 4H), 3.67 – 3.52 (m, 8H). ^{13}C NMR (100 MHz, CD_3OD) δ: 156.17, 154.72, 131.76, 130.60, 129.25, 128.65, 120.08, 119.49, 110.11, 108.10, 71.73, 71.63, 70.90, 68.57. MS (MALDI-TOF): *m/z* 501.2 $[M+Na]^+$.

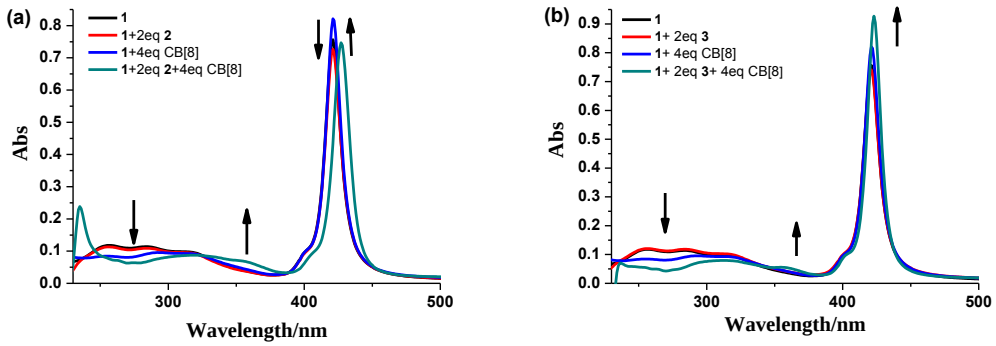


Fig. S1. (a) UV–vis spectra of **1** (2.5×10^{-6} M) and **1** in the presence of 2 equiv of **2**, 4 equiv of CB[8], and 2 equiv of **2** and 4 equiv of CB[8] in H_2O, respectively; (b) UV–vis spectra of **1** (2.5×10^{-6} M) and **1** in the presence of 2 equiv of **3**, 4 equiv of CB[8], and 2 equiv of **3** and 4 equiv of CB[8] in H_2O, respectively.

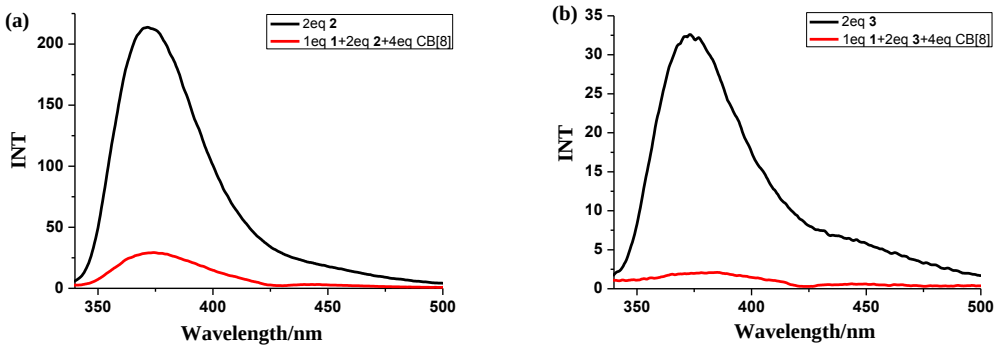
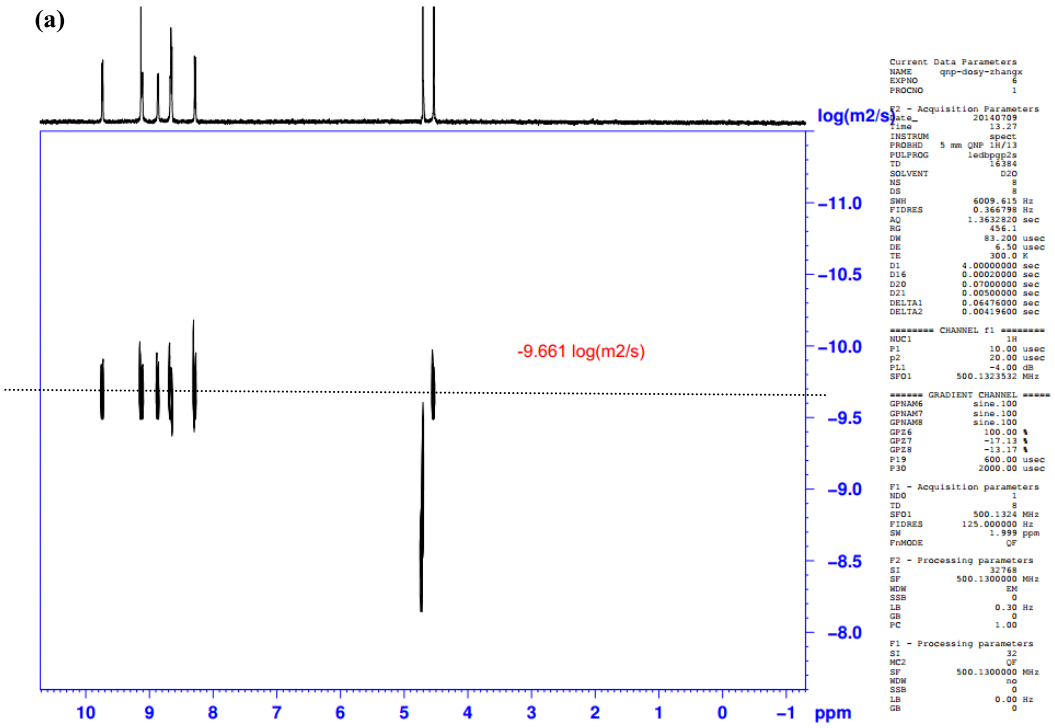


Fig. S2. (a) Fluorescence emission spectra (λ_{ex} = 267 nm) of **2** (5.0 × 10^{-6} M) and its mixture with CB[8] (1.0 × 10^{-5} M) and **1** (2.5 × 10^{-6} M) in H_2O, (b) Fluorescence emission spectra (λ_{ex} = 267 nm) of **3** (5.0 × 10^{-6} M) and its mixture with CB[8] (1.0 × 10^{-5} M) and **1** (2.5 × 10^{-6} M) in H_2O.



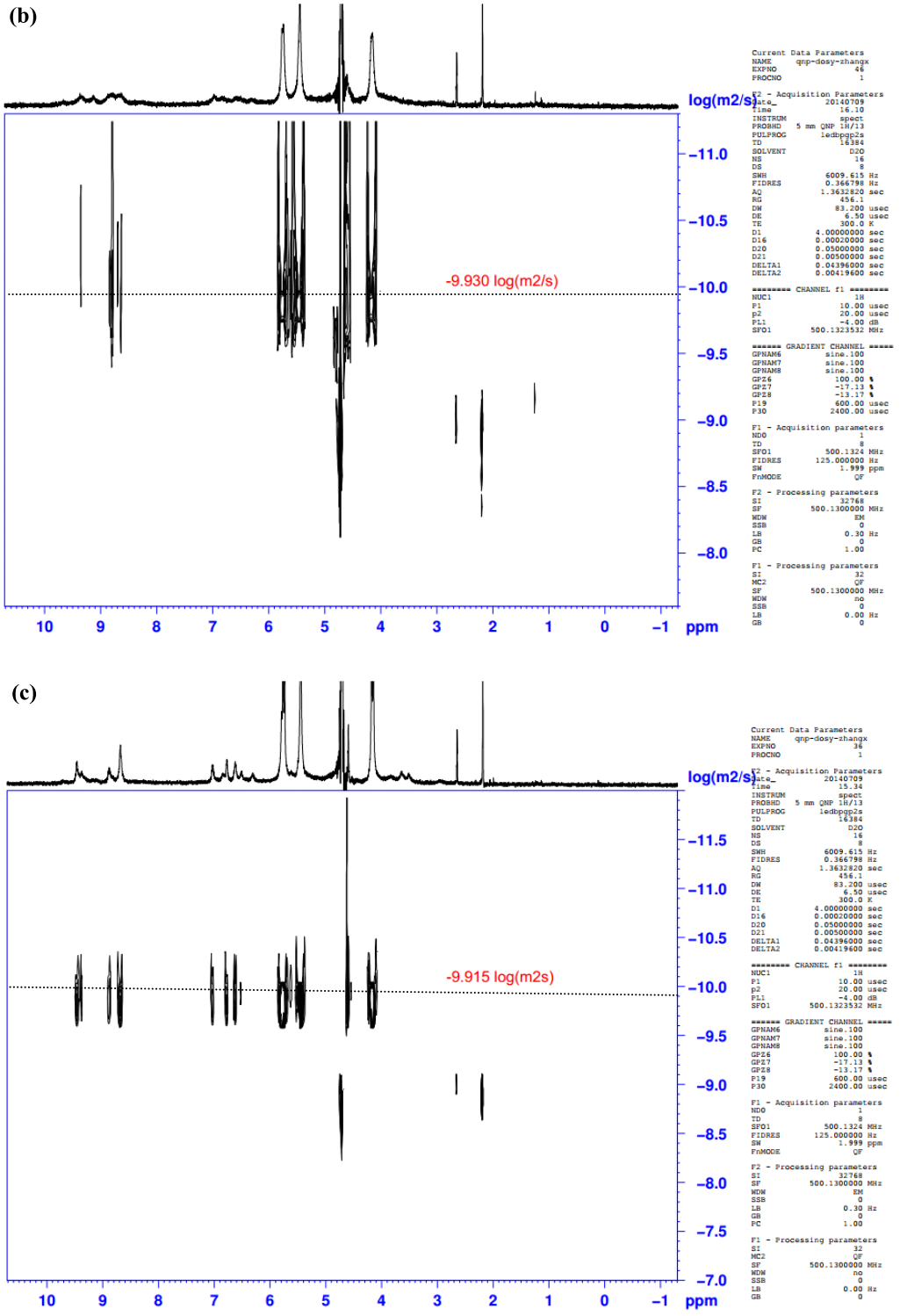


Fig. S3. Dosy-NMR spectra (400 MHz) of (a) **1**, (b) the mixture of **1**, **2** and CB[8] (1:2:4), and (c) the mixture of **1**, **3** and CB[8] (1:2:4) in D_2O at 25°C. The concentration of **1** was 0.80 mM.

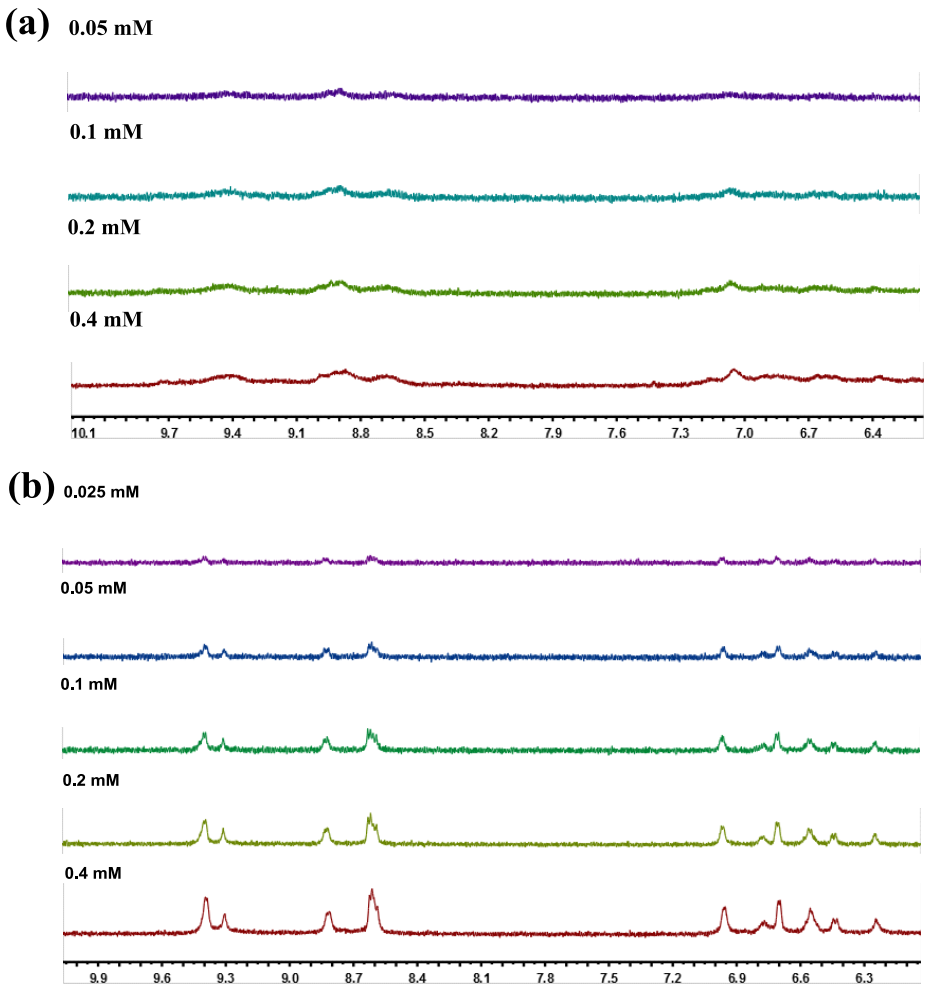


Fig. S4. Partial ^{1}H NMR spectra (500 MHz) of the mixtures of (a) **1**, **2** and CB[8] (1:2:4) and (b) **1**, **3** and CB[8] (1:2:4) in D_2O at different concentrations at 25^{o}C.

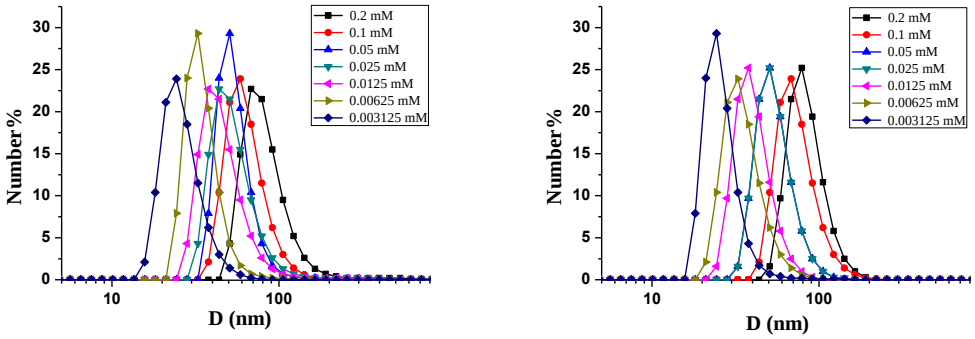


Fig. S5. DLS profiles of the mixtures of (a) **1**, **2,** and CB[8] (1:2:4) and (b) **1**, **3,** and CB[8] (1:2:4) at different concentrations in water at 25 ^{o}C.

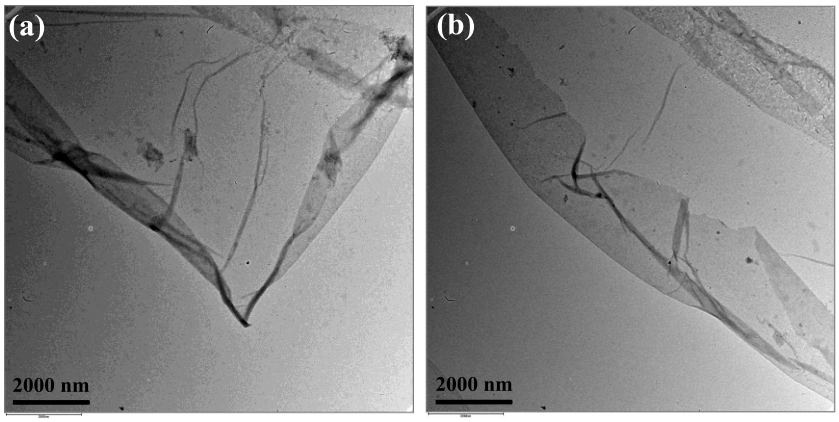


Fig. S6. TEM images of the aggregates fabricated from (a) **1**-**2**-CB[8] and (b)**1**-**3**-CB[8] in water. The concentration of **1** was 6.25 × 10^{-6} M and the molar ratio for **1**, **2** (or **3**), and CB[8] was 1:2:4.

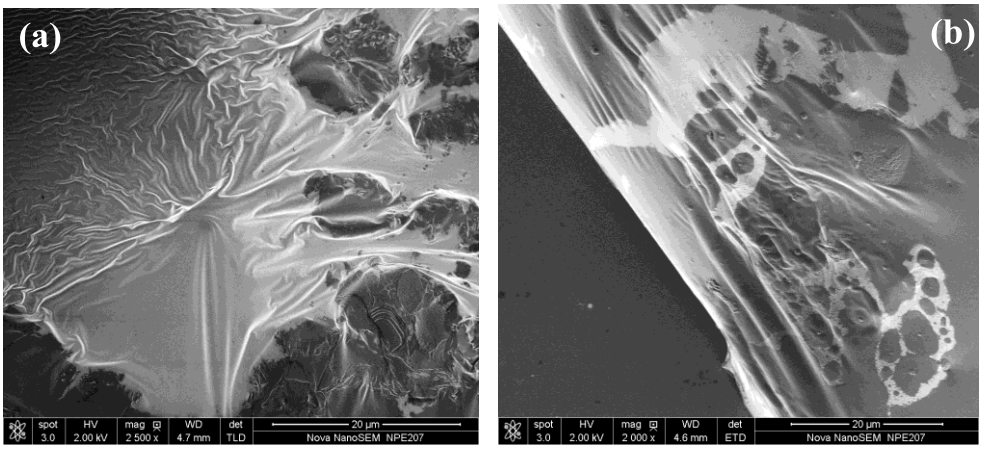


Fig. S7. SEM images of the aggregates fabricated from (a) **1**-**2**-CB[8] and (b)**1**-**3**-CB[8] in water. The concentration of **1** was 1.25 × 10^{-5} M and the molar ratio for **1**, **2** (or **3**), and CB[8] was 1:2:4.

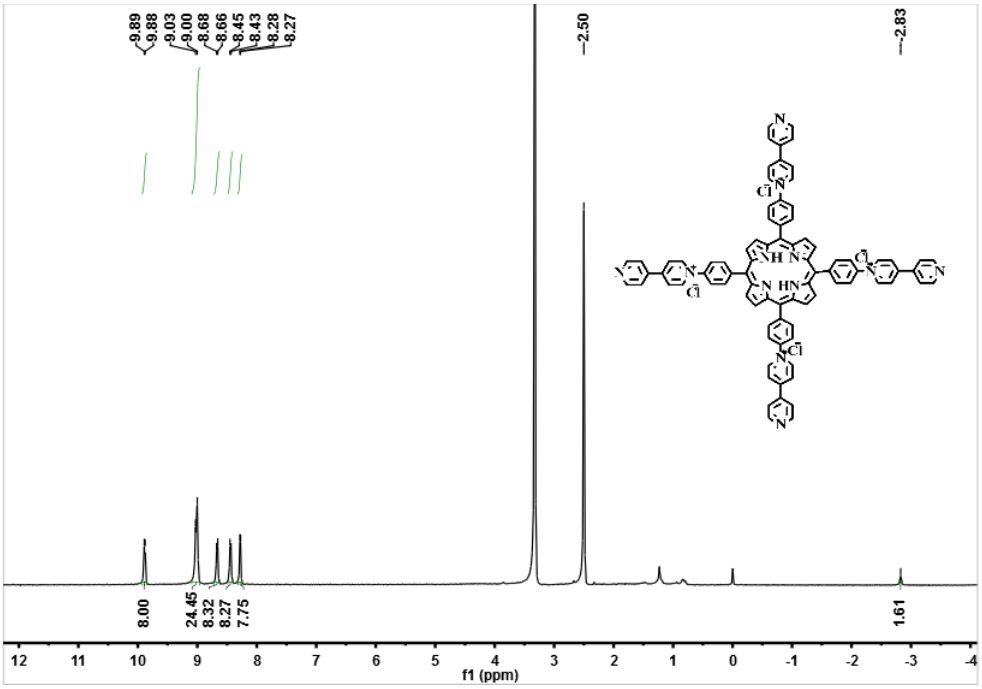


Fig. S8. ^{1}H NMR spectrum (400 MHz) of **6** in DMSO-d_6.

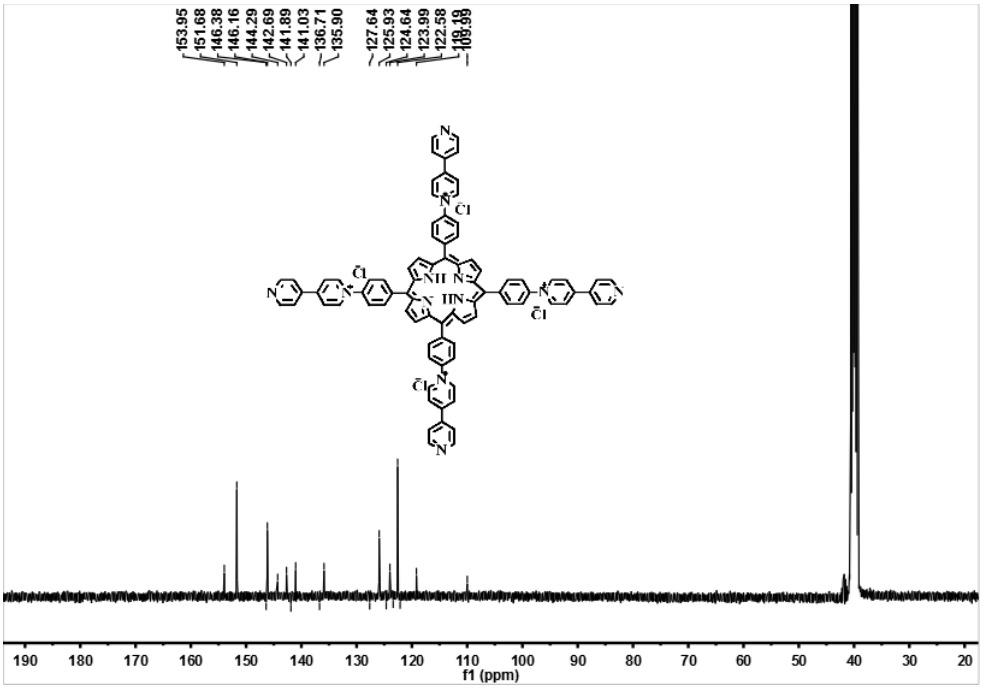


Fig. S9. ^{13}C NMR (100 MHz) spectrum of **6** in DMSO-d_6.

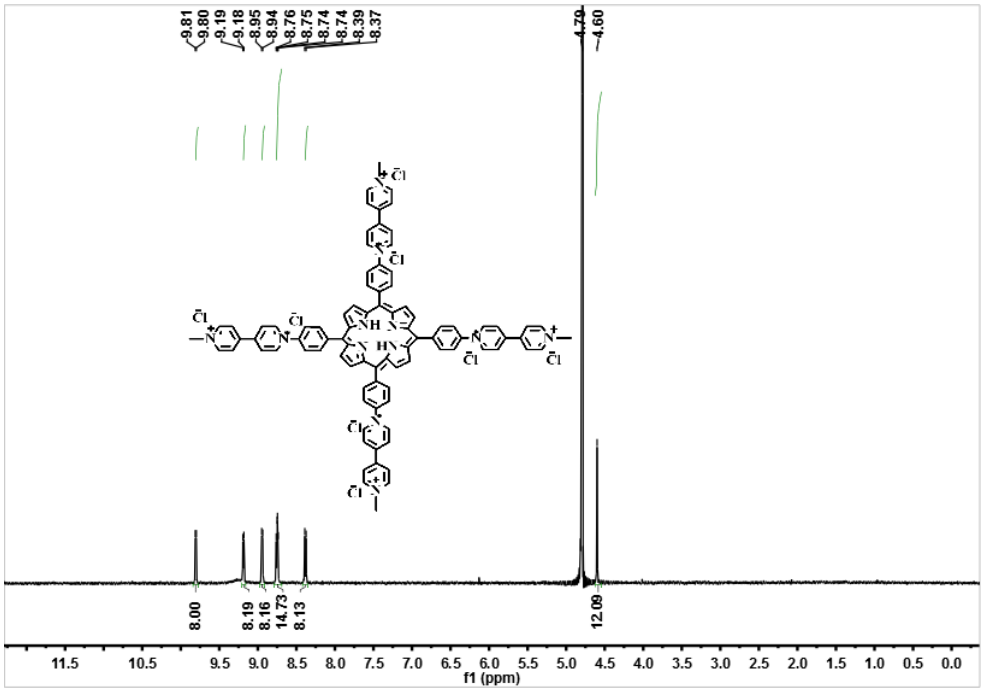


Fig. S10. ^{1}H NMR (500 MHz) spectrum of 7 in D_2O.

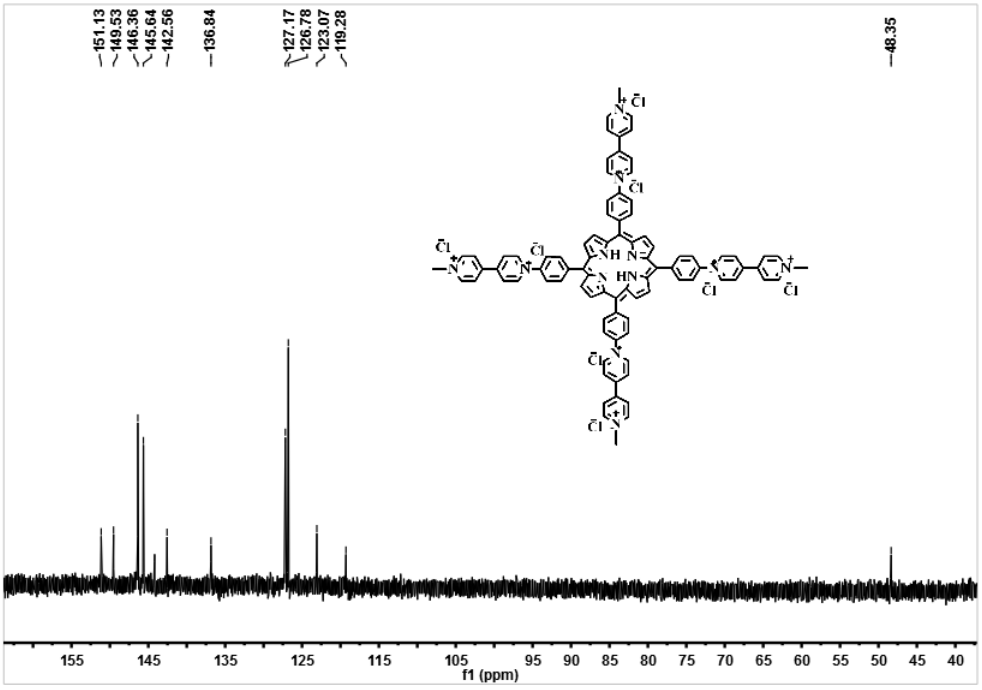


Fig. S11. ^{13}C NMR (100 MHz) spectrum of **7** in D_2O.

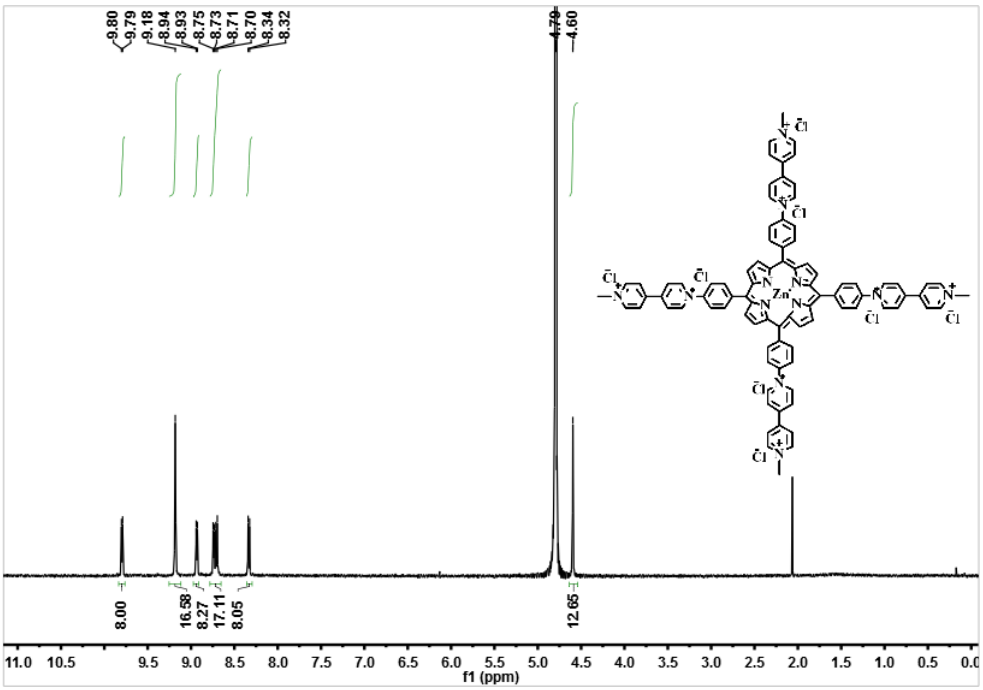


Fig. S12. ^{1}H NMR (500 MHz) spectrum of **1** in D_2O.

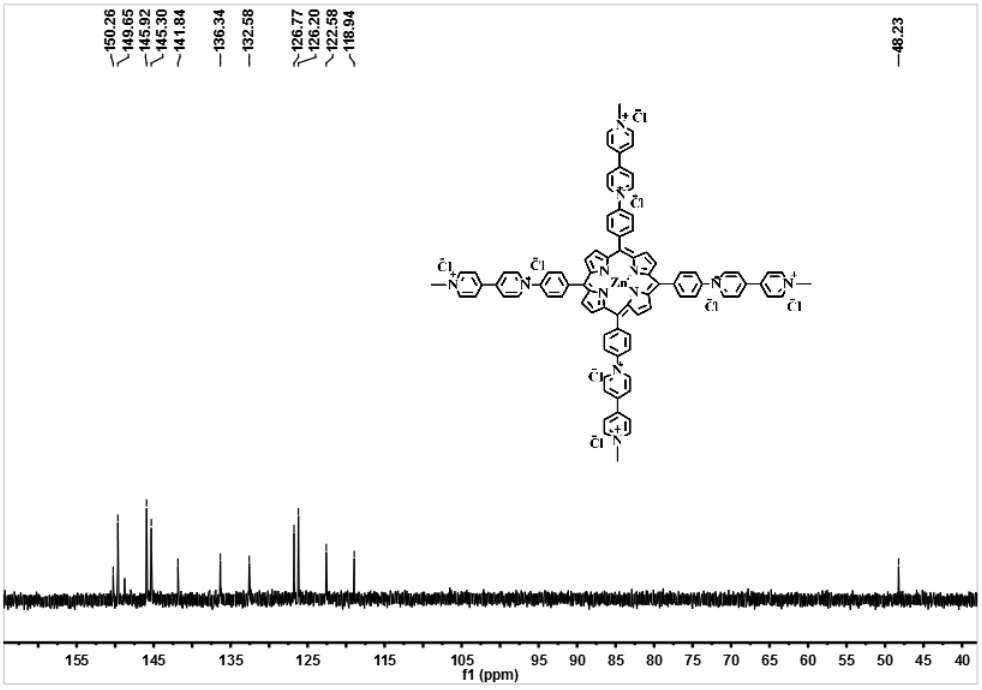


Fig. S13. ^{13}C-NMR (100 MHz) spectrum of **1** in D_2O.

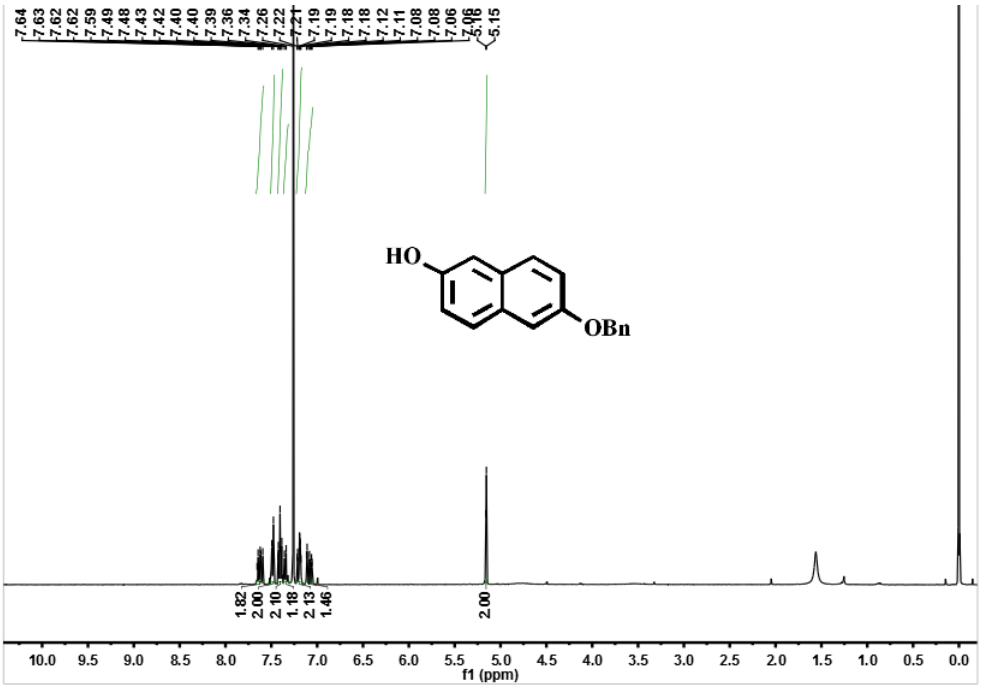


Fig. S14. ^{1}H-NMR (400 MHz) spectrum of **9** in $CDCl_3$.

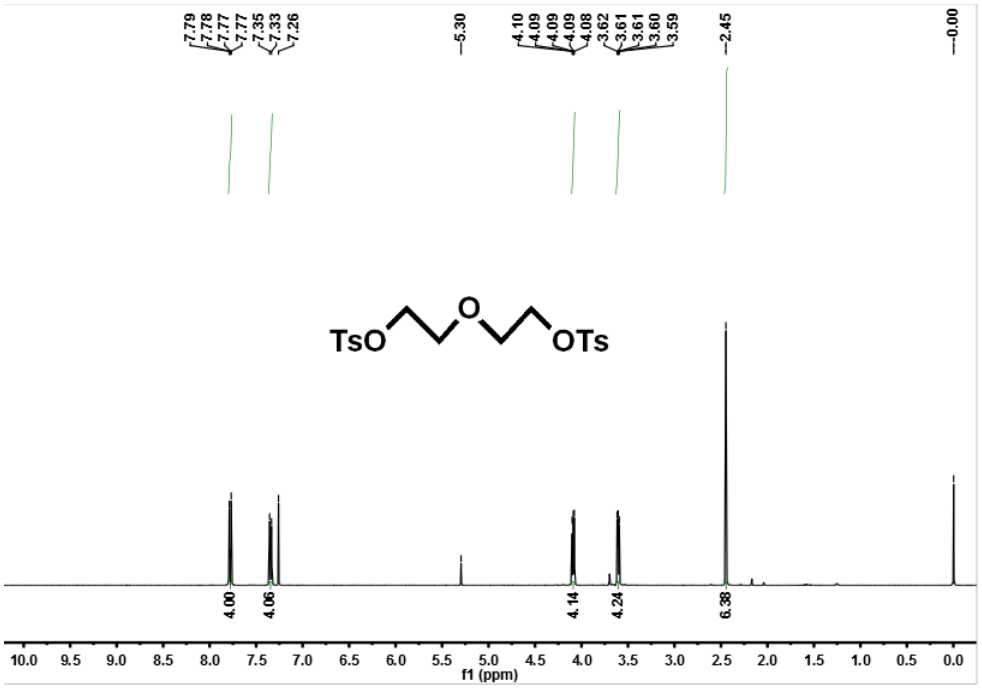


Fig. S15. ^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$.

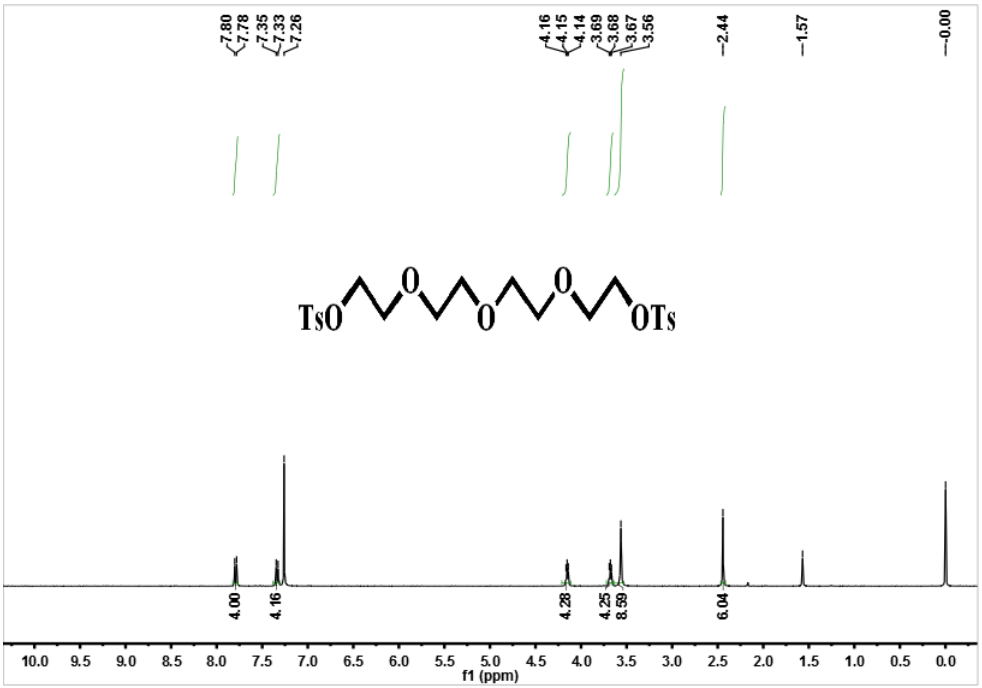


Fig. S16. ^{1}H NMR (400 MHz) spectrum of **13** in $CDCl_3$.

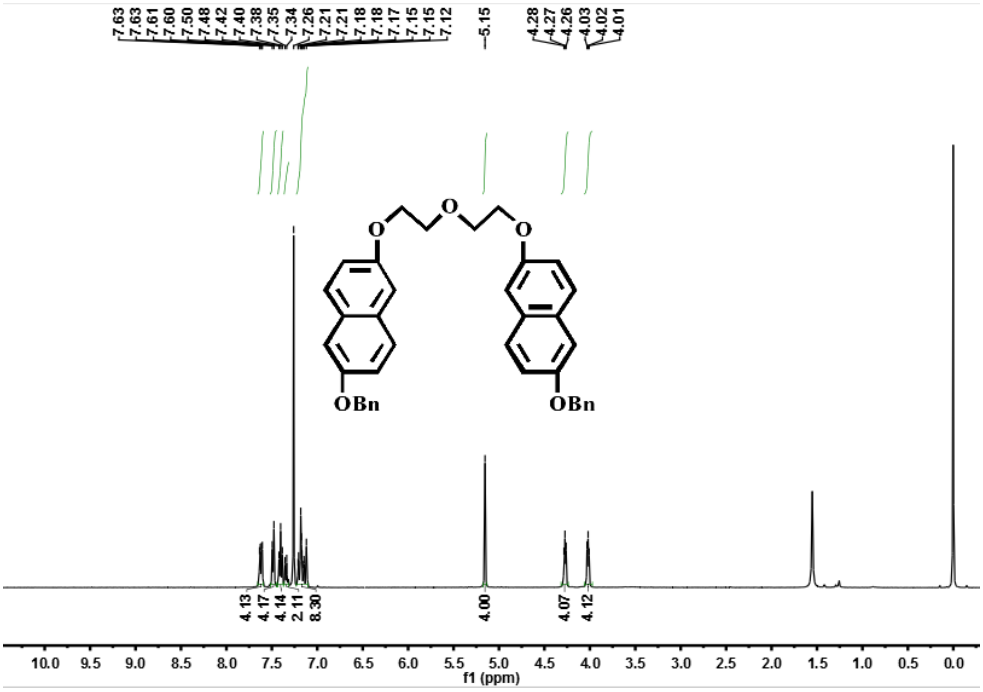


Fig. S17. ^{1}H NMR (400 MHz) spectrum of **14** in $CDCl_3$.

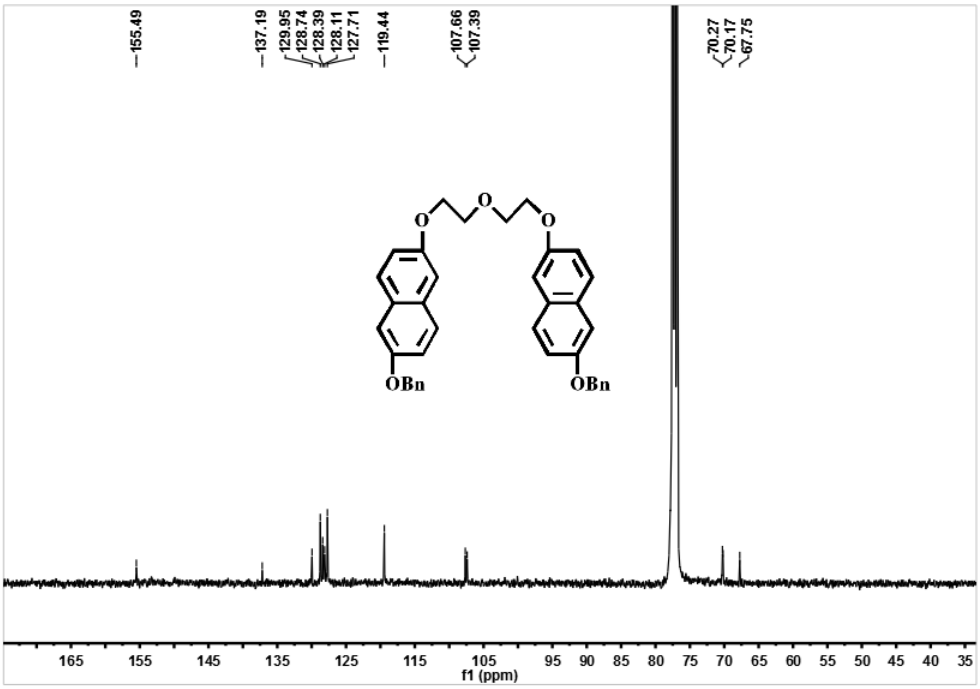


Fig. S18. ^{13}C NMR (100 MHz) spectrum of **14** in $CDCl_3$.

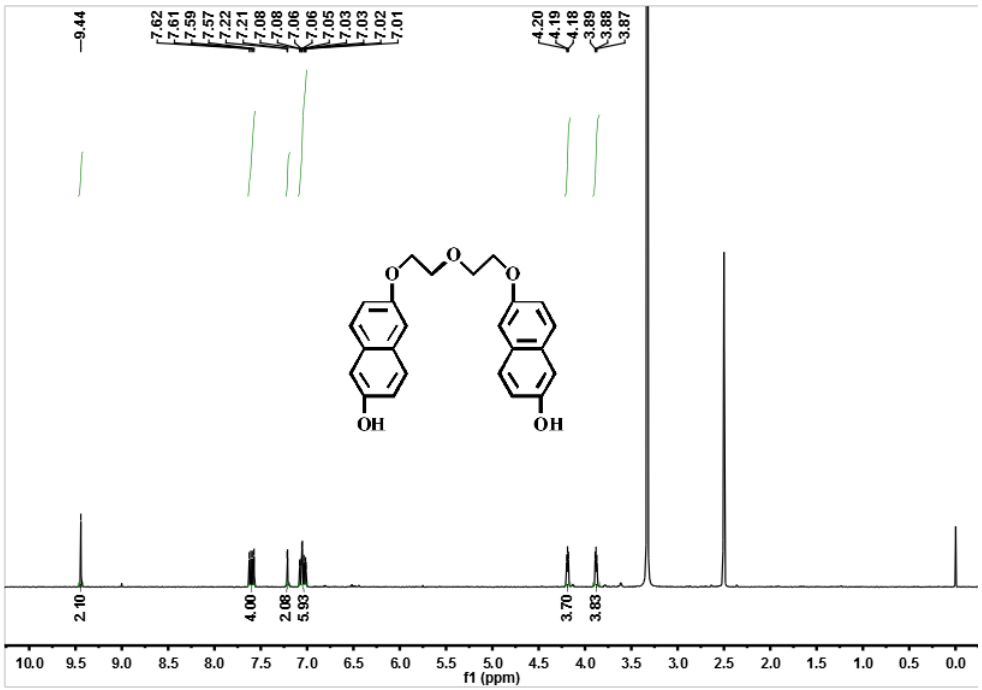


Fig. S19. ^{1}H NMR (500 MHz) spectrum of **2** in DMSO-d_6.

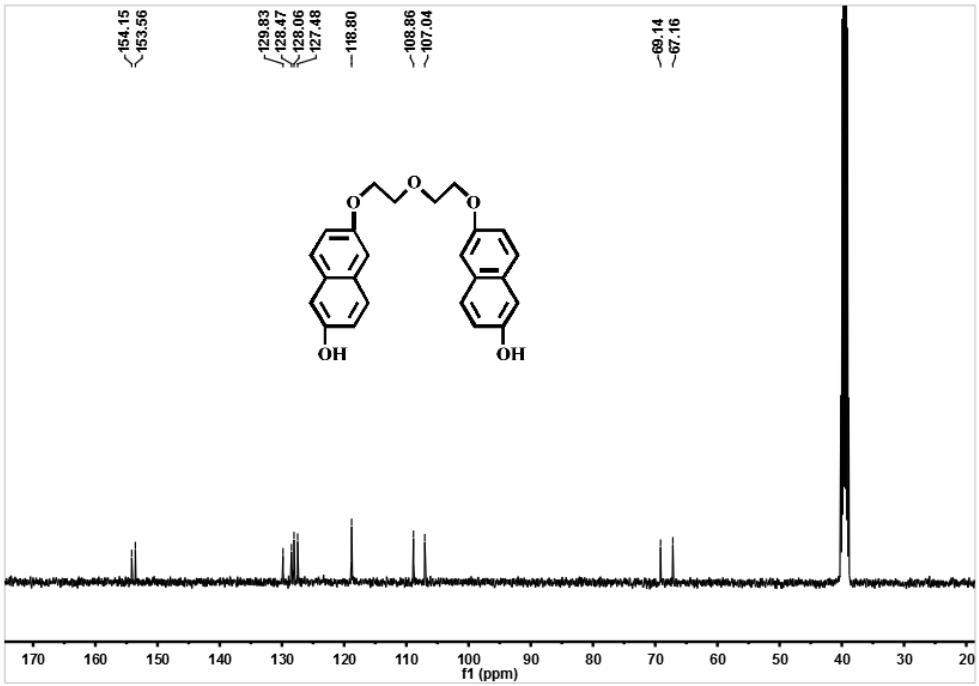


Fig. S20. ^{13}C NMR (100 MHz) spectrum of **2** in DMSO-d_6.

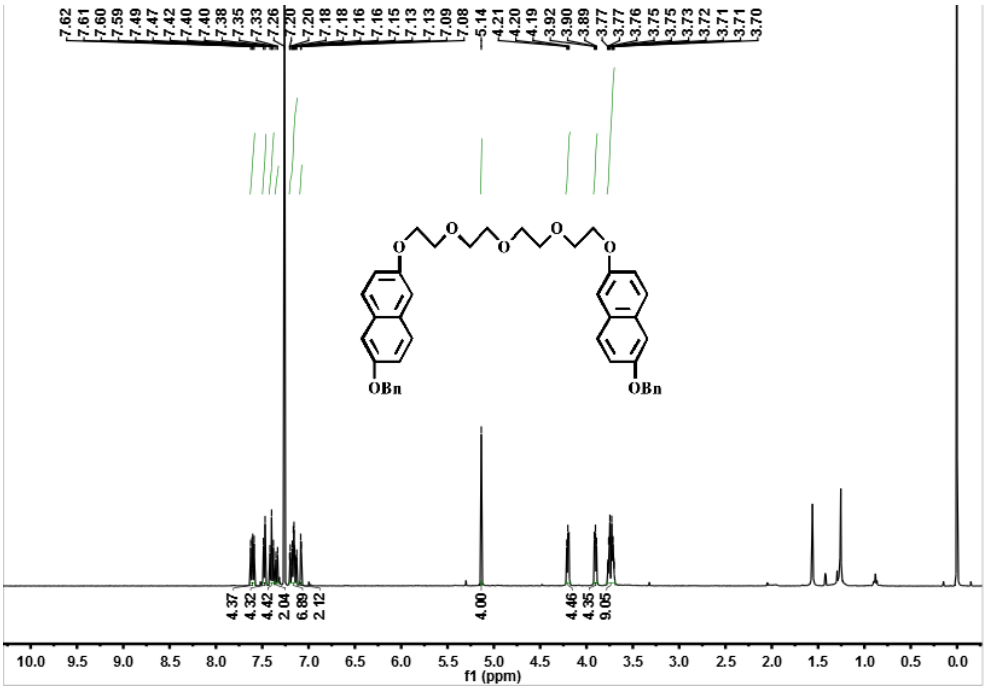


Fig. S21. ^{1}H NMR (400 MHz) spectrum of **15** in $CDCl_3$.

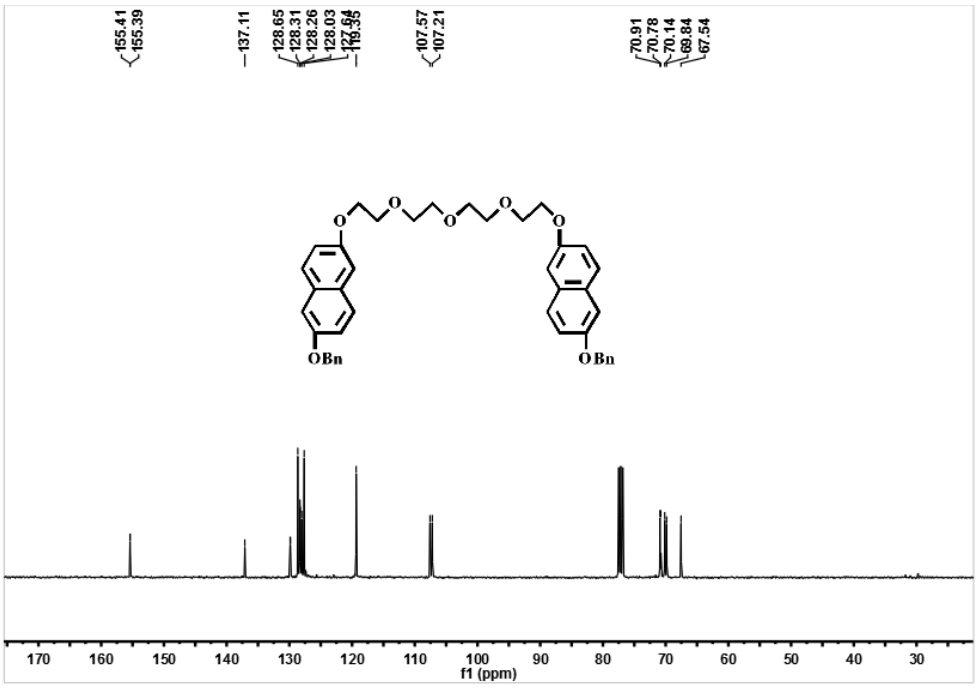


Fig. S22. ^{13}C NMR (100 MHz) spectrum of **15** in $CDCl_3$.

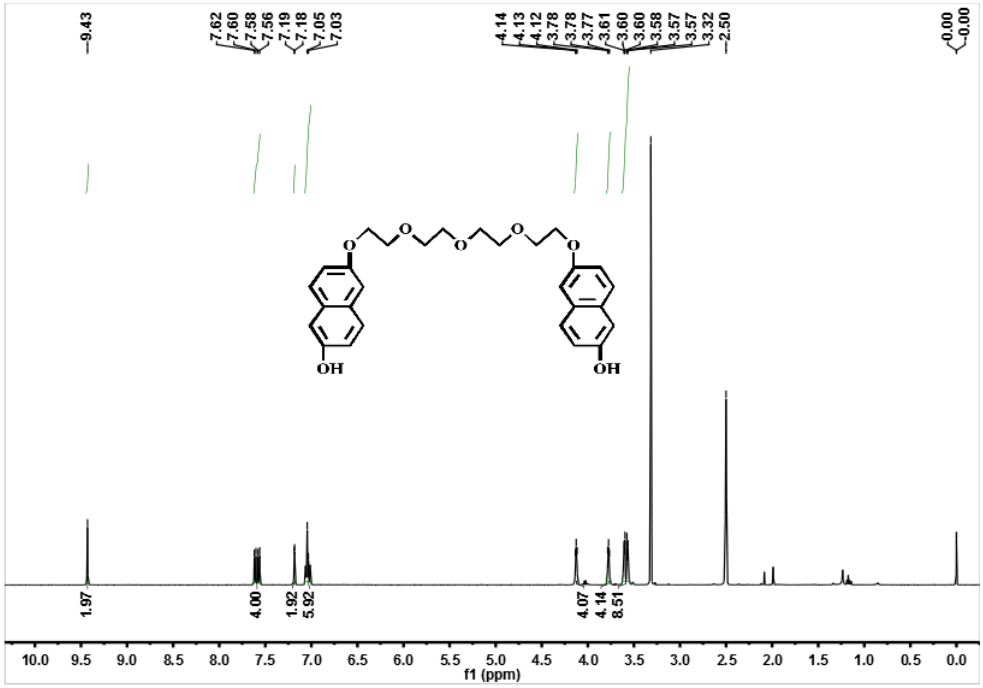


Fig. S23. ^{1}H NMR (500 MHz) spectrum of **3** in DMSO-d_6.

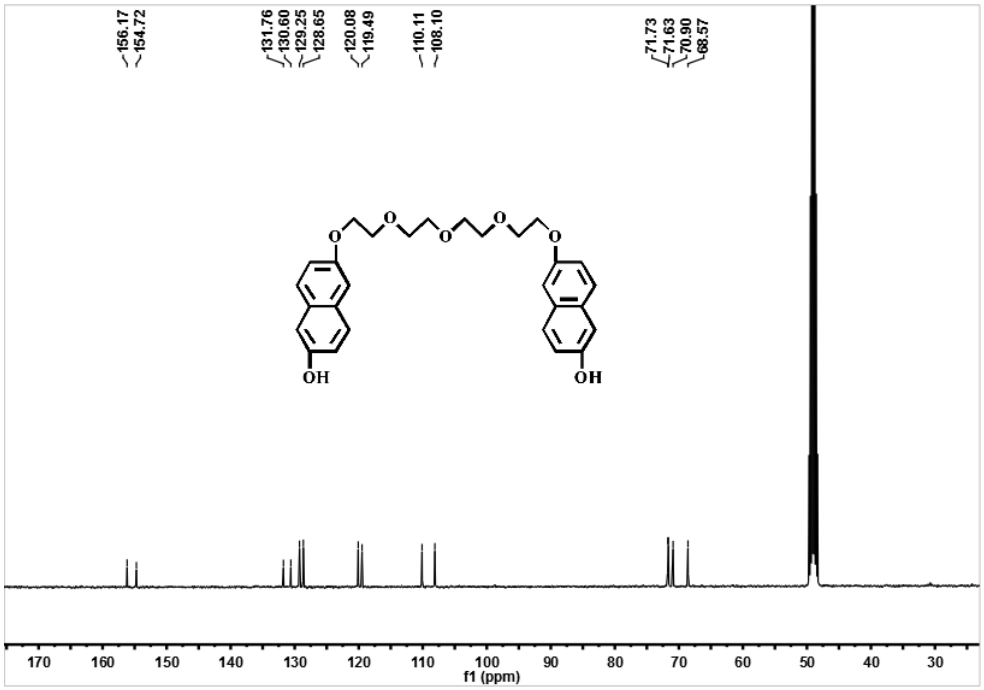


Fig. S24. ^{13}C NMR (100 MHz) spectrum of **3** in CD_3OD.