

Electronic Supporting Information

Self-Assembly of Two-Dimensional Structures in Water from Rigid and Curved Amphiphiles with a Low Molecular Weight

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Table of Contents

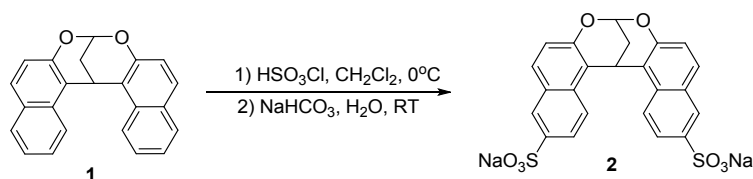
1. Experimental Section	S2
2. Characterization and Properties of Compound 2	S10
3. Characterization and Properties of Compound 4	S18
4. References	S21

1. Experimental Section

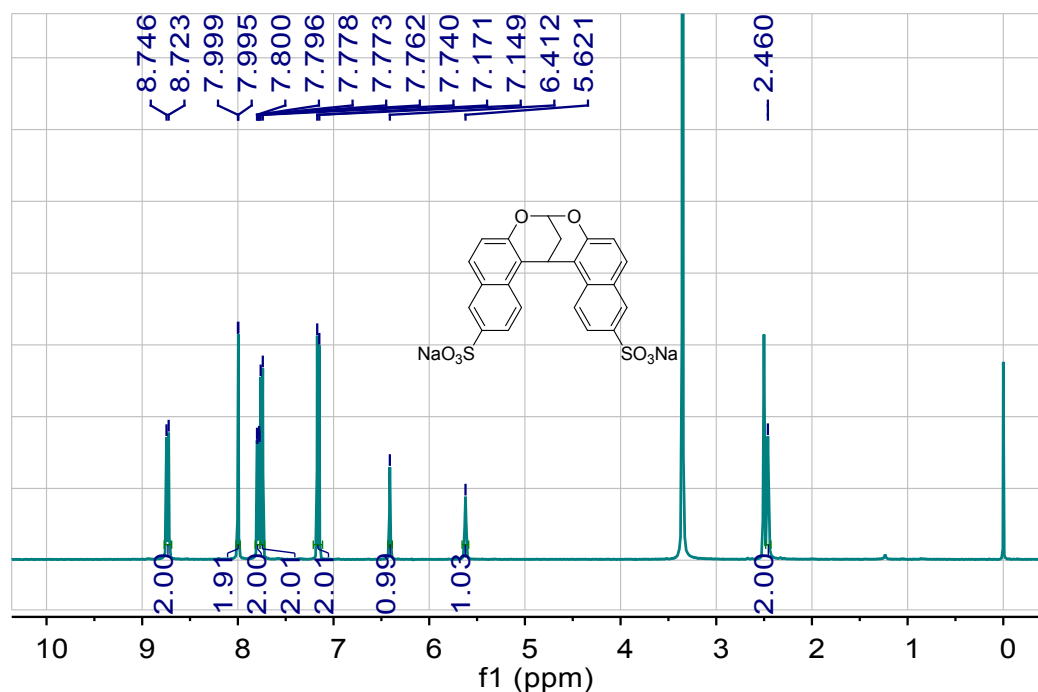
1.1 General. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. ^1H , ^{13}C NMR spectra were recorded on a Bruker Avance-400 or 500 NMR spectrometer. All chemical shifts are reported in *ppm* with residual solvents or TMS (tetramethylsilane) as the internal standards. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; dd, doublet of doublet; m, multiplet. Electrospray-ionization high-resolution mass spectrometry (ESI-HRMS) experiments were conducted on an applied Q EXACTIVE mass spectrometry system. UV-visible spectra were obtained on a Shimadzu UV-2600 spectrometer. Fluorescence spectra (FL) were obtained on a Shimadzu RF-5301pc spectrometer. Dynamic light scattering (DLS) data was obtained from a Brookhaven, BI-200SM instrument. Scanning electron microscope (SEM) images were obtained from the field emission SEM (FESEM, ZEISS Merlin). Atomic force microscope (AFM) data were obtained from a S II Nanonaviprobe station 300HV. Transmission electron microscopy (TEM) investigations were carried out on a HITACHI HT-7700 instrument.

1.2 Synthetic Procedures

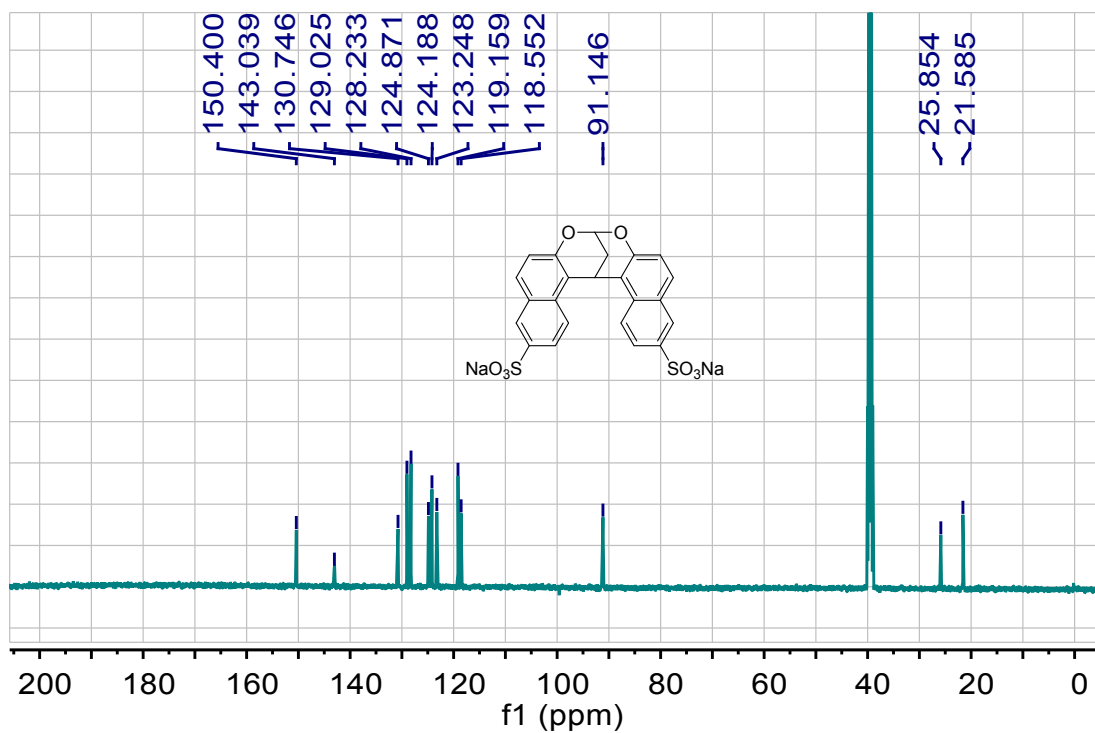
Compound 2



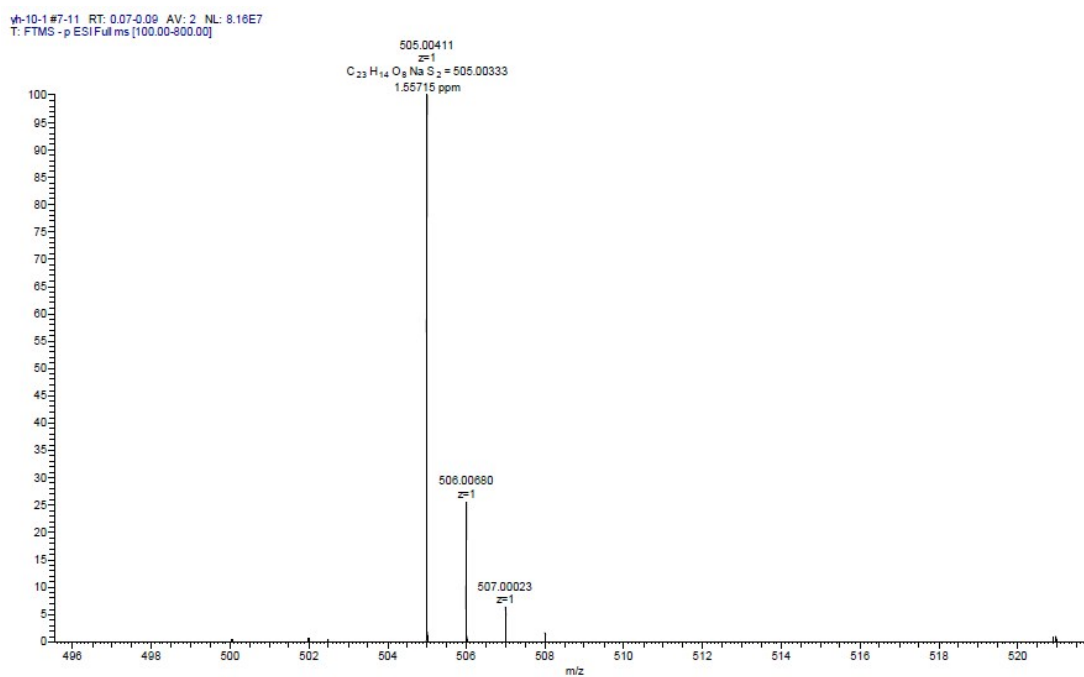
Compound **1** was synthesized by following the literature procedure.¹ The solution of chlorosulfonic acid (0.1 mL, 1.5 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of compound **1** (100 mg, 0.20 mmol) in dry CH_2Cl_2 (8 mL) at 0°C over 1 h. Then, the mixture was kept at 0°C for an additional 4 h to give a precipitate. The precipitate was collected by filtration and washed with CH_2Cl_2 . The residue was dissolved in H_2O , and a saturated sodium bicarbonate solution was added until the pH reached 7. The solvent was evaporated in vacuum to obtain the crude product. Then, dissolved crude product in MeOH (50 mL) and filtrated. The filtrate was evaporated in vacuum and recrystallized in H_2O to get compound **2**, a yellow solid, yield (290 mg, 60%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ [ppm]=8.73 (d, $J = 9.0$ Hz, 2H), 8.00 (d, $J = 1.6$ Hz, 2H), 7.79 (dd, $J = 8.9, 1.7$ Hz, 2H), 7.75 (d, $J = 8.9$ Hz, 2H), 7.16 (d, $J = 8.8$ Hz, 2H), 6.41 (s, 1H), 5.62 (s, 1H), 2.46 (s, 2H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ [ppm]=150.40, 143.08, 130.75, 129.03, 128.23, 124.87, 124.19, 123.25, 119.16, 118.55, 91.15, 25.85, 21.59. ESI-TOF-HRMS: m/z calcd for $[\text{M}-\text{Na}^+]$ $\text{C}_{23}\text{H}_{14}\text{O}_8\text{NaS}_2$, 505.0033; found 505.0041 (100%) (error = +1.6 ppm).



^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of compound **2**

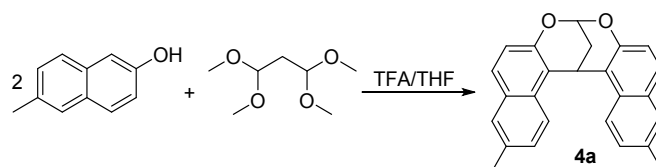


¹³C NMR spectrum ((126 MHz, DMSO-*d*₆) of compound 2

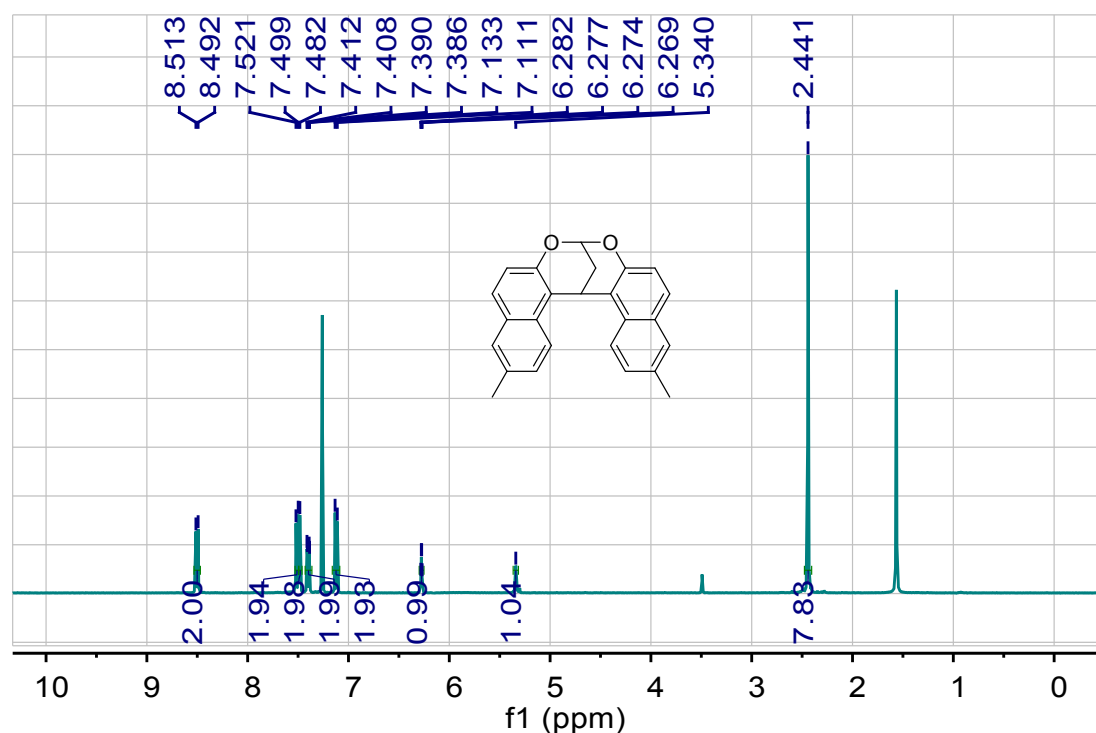


ESI-TOF mass spectrum of compound 2

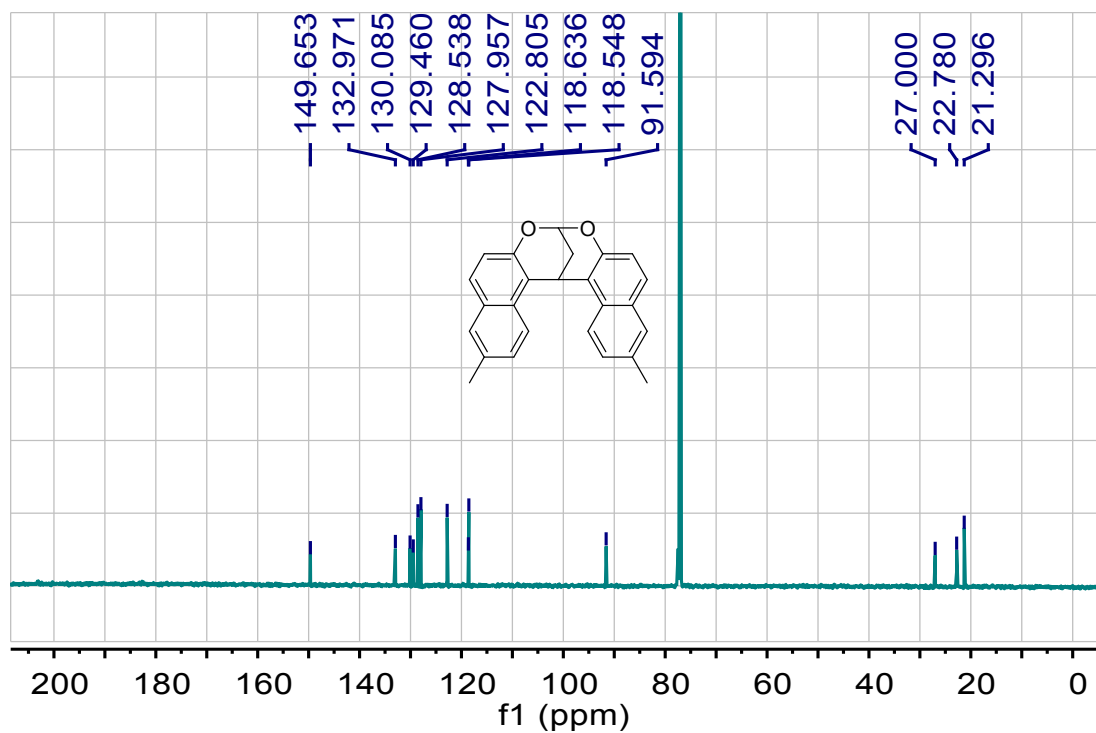
Compound 4a



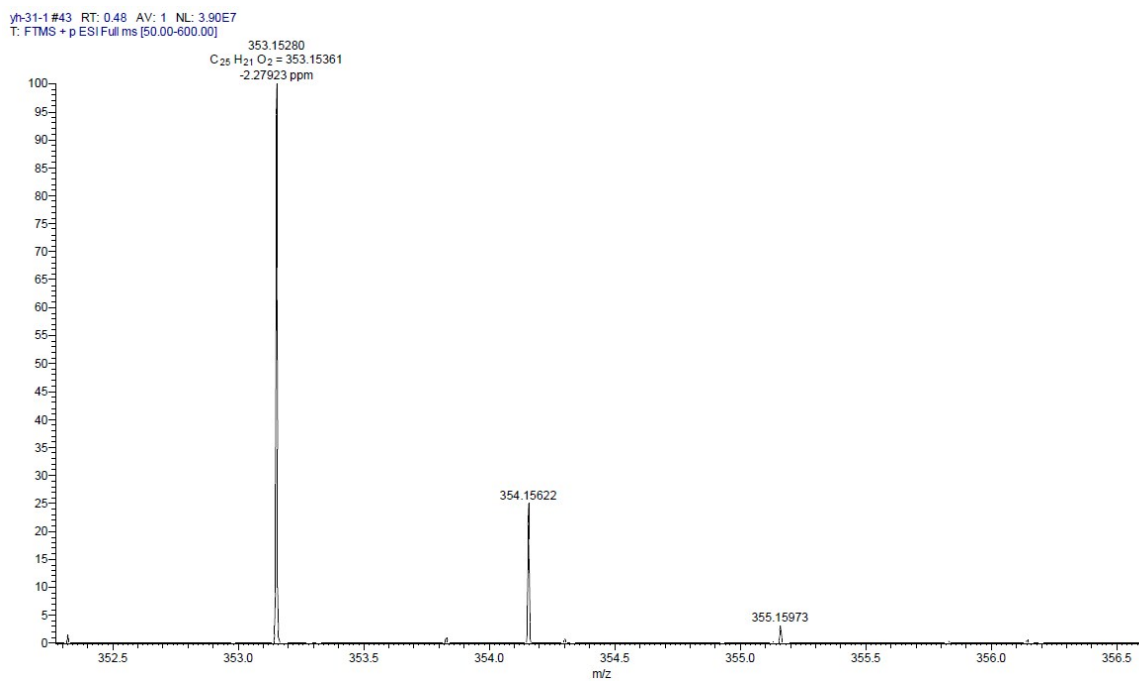
6-methylnaphthalen-2-ol (632 mg, 4.0 mmol) was dissolved in TFA (6 mL) and THF (3 mL). 1,1,3,3-Tetramethoxypropane (0.35 mL, 2.0 mmol) was diluted by THF (2 mL) and added via a separating funnel over 10 min while stirring. The resulting mixture was stirred at room temperature for another 3 h. Then, the reaction was quenched with excess saturated aqueous NaHCO_3 . The organic layer was extracted with CH_2Cl_2 , dried with Na_2SO_4 , and the solvent was evaporated in vacuum. The raw product was washed by MeOH until just one point remained on TLC (n-hexane: $\text{CH}_2\text{Cl}_2 = 3:1$). The pure product **4a** was obtained as a purple solid, yield (490 mg, 70%). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.50 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 7.48 (s, 2H), 7.40 (dd, $J = 8.7, 1.6$ Hz, 2H), 7.12 (d, $J = 8.8$ Hz, 2H), 6.28 (q, $J = 1.9$ Hz, 1H), 5.34 (s, 1H), 2.44 (s, 8H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 149.65, 132.97, 130.09, 129.46, 128.54, 127.96, 122.81, 118.64, 118.55, 91.59, 27.00, 22.78, 21.30. ESI-TOF-HRMS: m/z calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{25}\text{H}_{21}\text{O}_2$, 353.1536; found 353.1528 (100%) (error = -2.3 ppm).



^1H NMR spectrum (400 MHz, CDCl_3) of compound **4a**

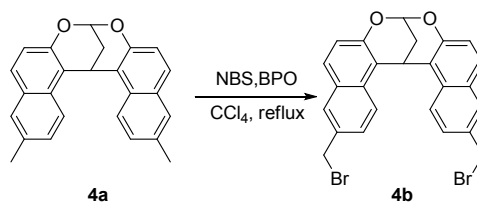


^{13}C NMR spectrum (126 MHz, CDCl_3) of compound **4a**

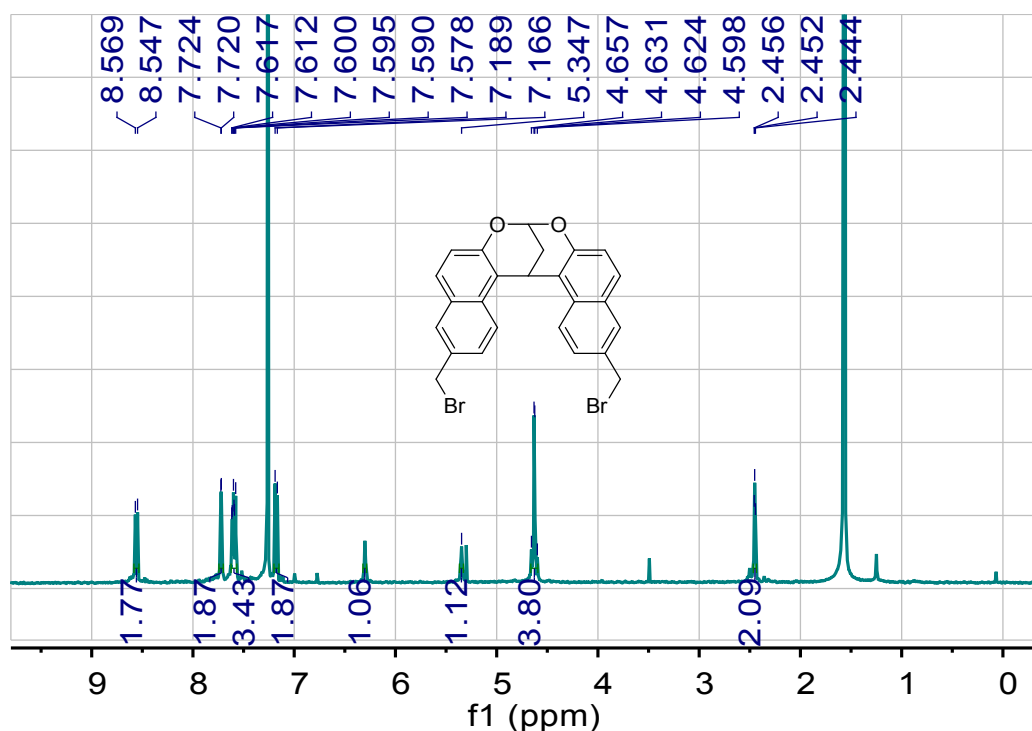


ESI-TOF mass spectrum of compound **4a**

Compound 4b

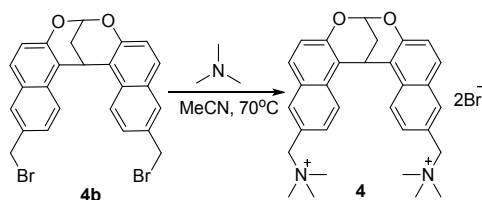


Compound **4a** (100 mg, 0.28 mmol) and NBS (109 mg, 0.62 mmol) was added into CCl_4 (20 mL) and heated to reflux. Then, BPO (8 mg, 0.033 mmol) was added as initiator with stirring. The resulting mixture was stirred for another 3 h. Then, the reaction was quenched with $\text{Na}_2\text{S}_2\text{O}_3$. The reaction mixture was filtered in vacuum and the filtrate was evaporated in vacuum to give a solid. Then, the solid was recrystallized by CH_2Cl_2 and MeOH to give compound **4b**, then used directly to the next step reaction without further purification, yellow solid, yield (91 mg, 64%). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.56 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 1.7$ Hz, 2H), 7.62 – 7.57 (m, 3H), 7.18 (d, $J = 8.8$ Hz, 2H), 6.321 – 6.284 (m, 1H), 5.35 (s, 1H), 4.66 – 4.59 (m, 4H), 2.47 – 2.43 (m, 2H).

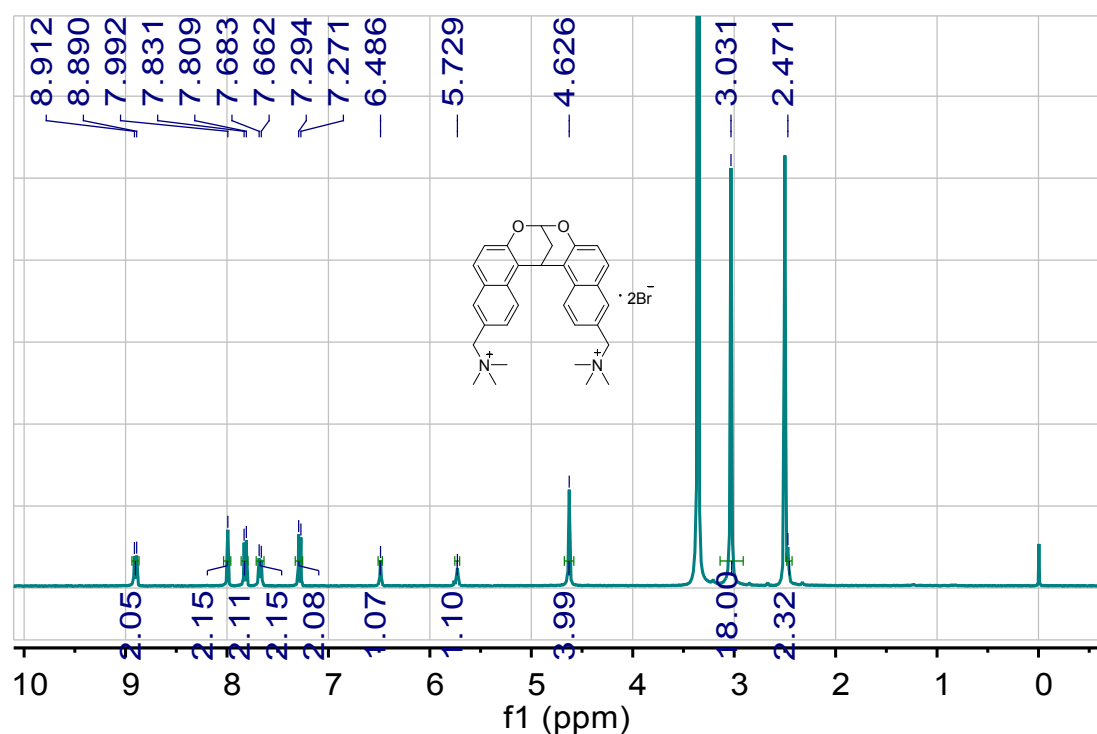


^1H NMR spectrum (400 MHz, CDCl_3) of compound **4b**

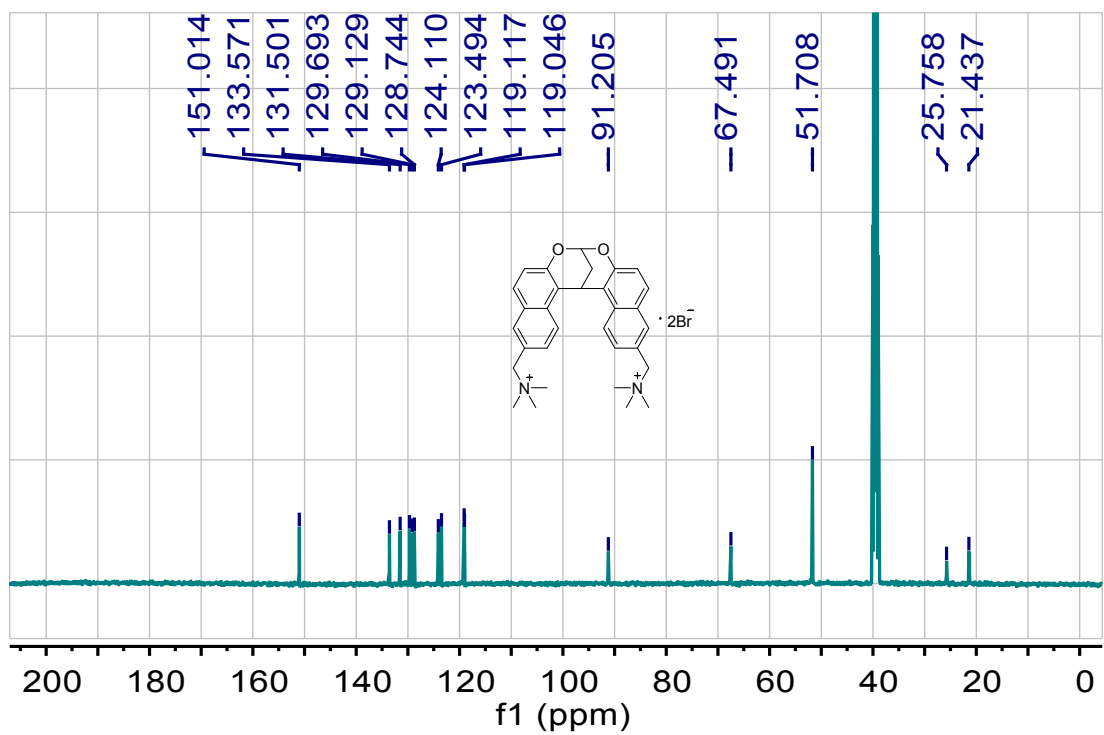
Compound 4



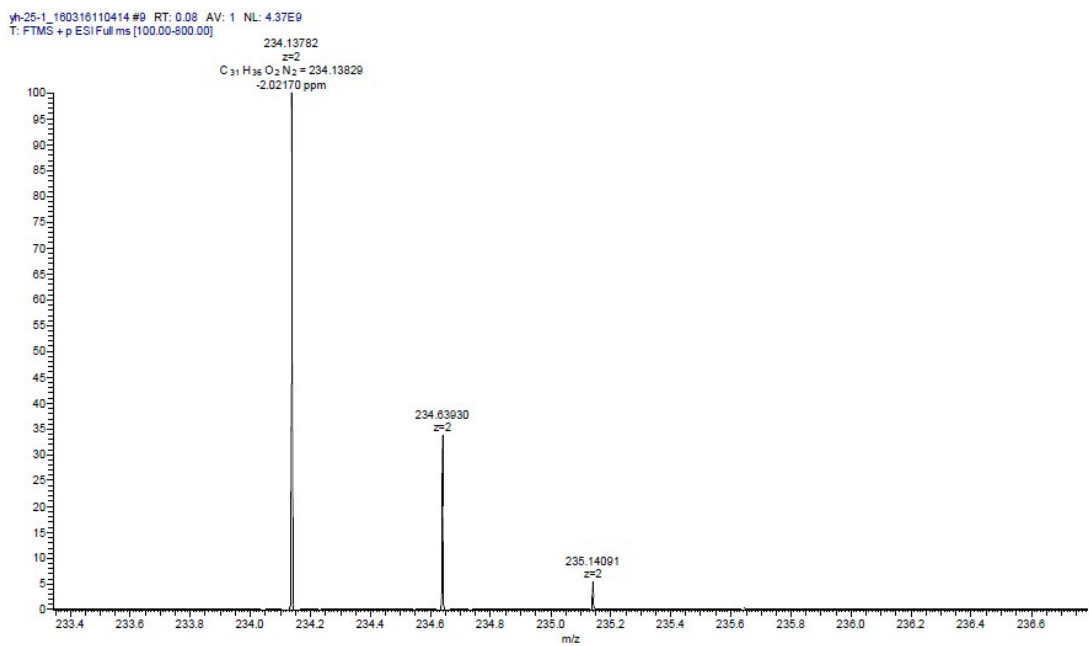
Compound **4b** (100 mg, 0.20 mmol) and TMA (1 mL, 25 wt. % in MeOH) was added into MeCN (10 mL) and heated to 70 °C. The resulting mixture was stirred for 4.5 h. Then stopped the reaction and cooling to room temperature. The reaction mixture was filtered in vacuum and washed by MeOH to give a white solid, yield (79 mg, 64%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ [ppm]=8.90 (d, $J = 8.8$ Hz, 1H), 7.99 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.28 (d, $J = 8.9$ Hz, 1H), 6.49 (s, 1H), 5.73 (s, 1H), 4.63 (s, 2H), 3.03 (s, 7H), 2.47 (s, 1H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$): δ [ppm]=151.01, 133.57, 131.50, 129.69, 129.13, 128.74, 124.11, 123.49, 119.12, 119.05, 91.21, 67.49, 51.71, 25.76, 21.44. ESI-TOF-HRMS: m/z calcd for $[\text{M}-2\text{Br}]^{2+}$ $\text{C}_{31}\text{H}_{36}\text{O}_2\text{N}_2$, 234.1383; found 234.1378 (100%) (error = -2.1 ppm).



^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of compound **4**



^{13}C NMR spectrum (126 MHz, $\text{DMSO-}d_6$) of compound 4



ESI-TOF mass spectrum of compound 4

2. Characterization and Properties of Compound 2.

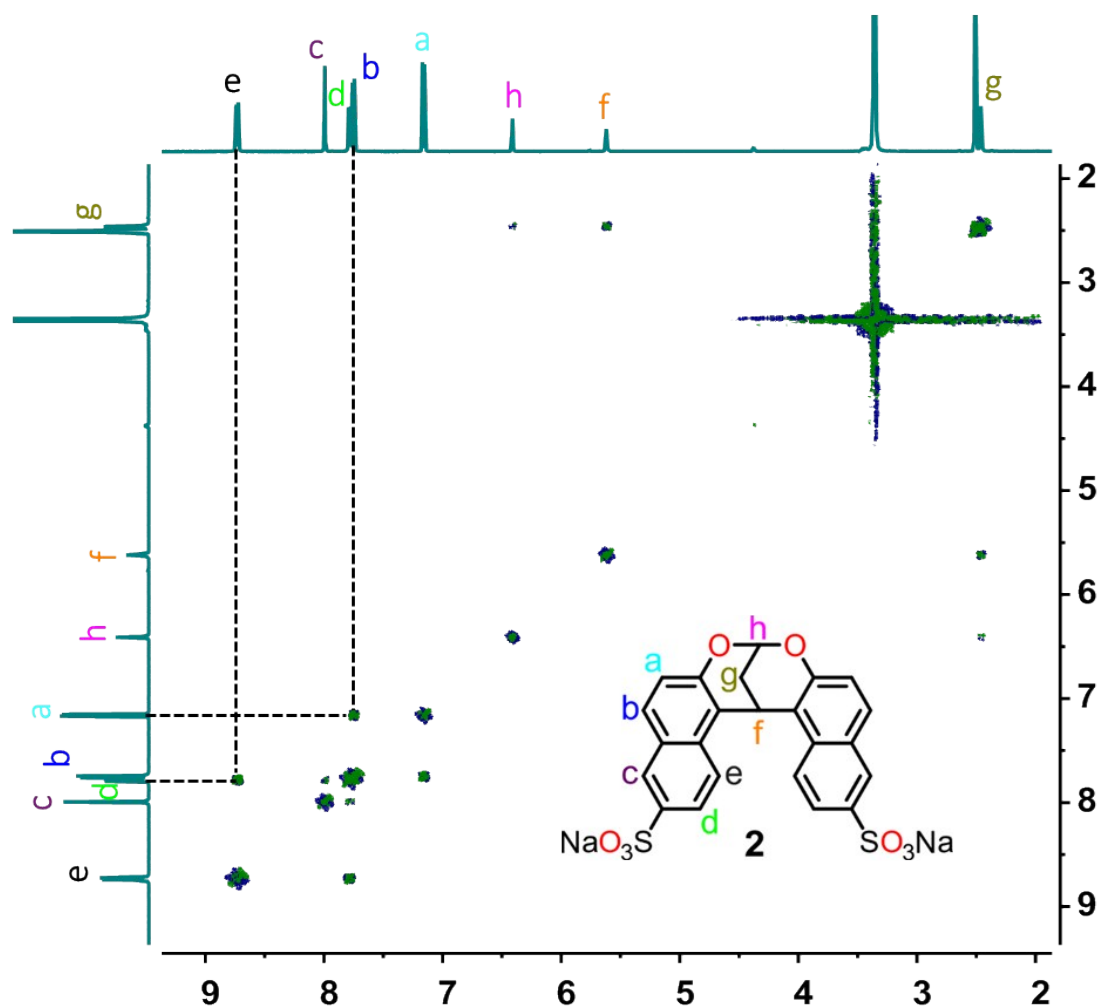


Fig. S1 ^1H , ^1H -COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$) of compound **2**

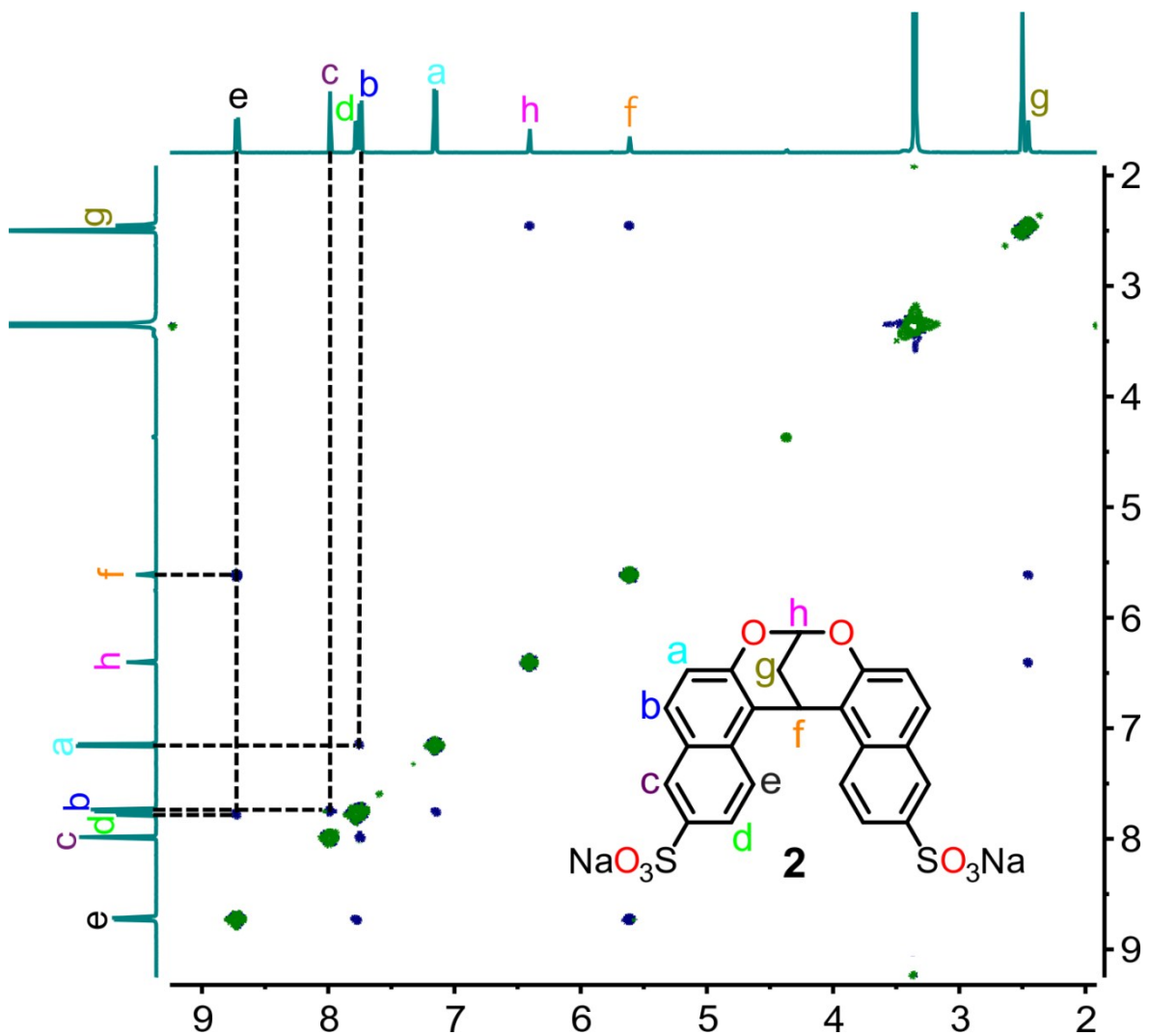


Fig. S2 ^1H , ^1H - ROESY NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 25 °C) of compound **2**. This 2D NMR spectrum is in support of the assignment of chemical structure **2**.

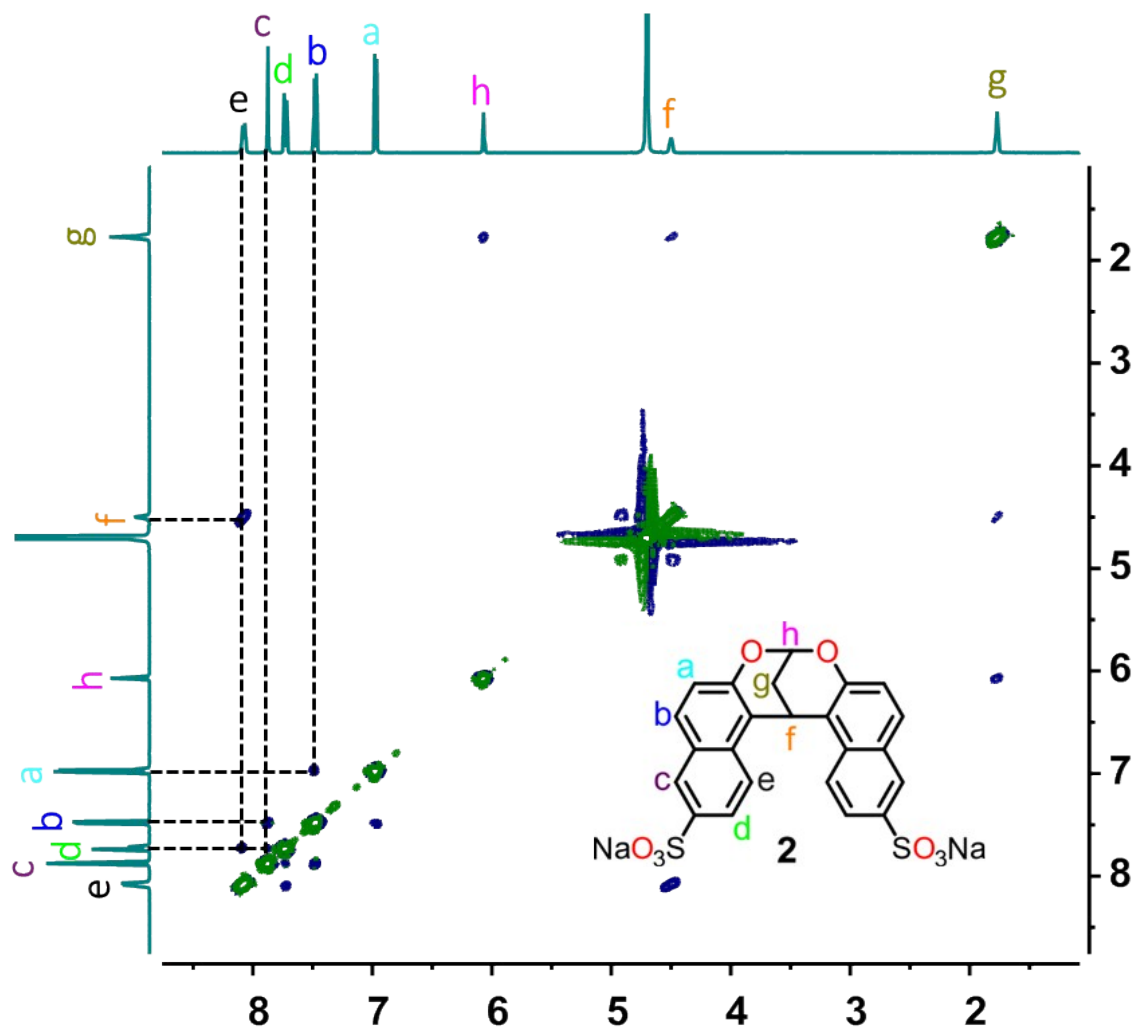


Fig. S3 ^1H , ^1H -ROESY NMR spectrum (500 MHz, D_2O , 25 $^\circ\text{C}$) of compound **2**. This 2D NMR spectrum is in support of the assignment of chemical structure **2**.

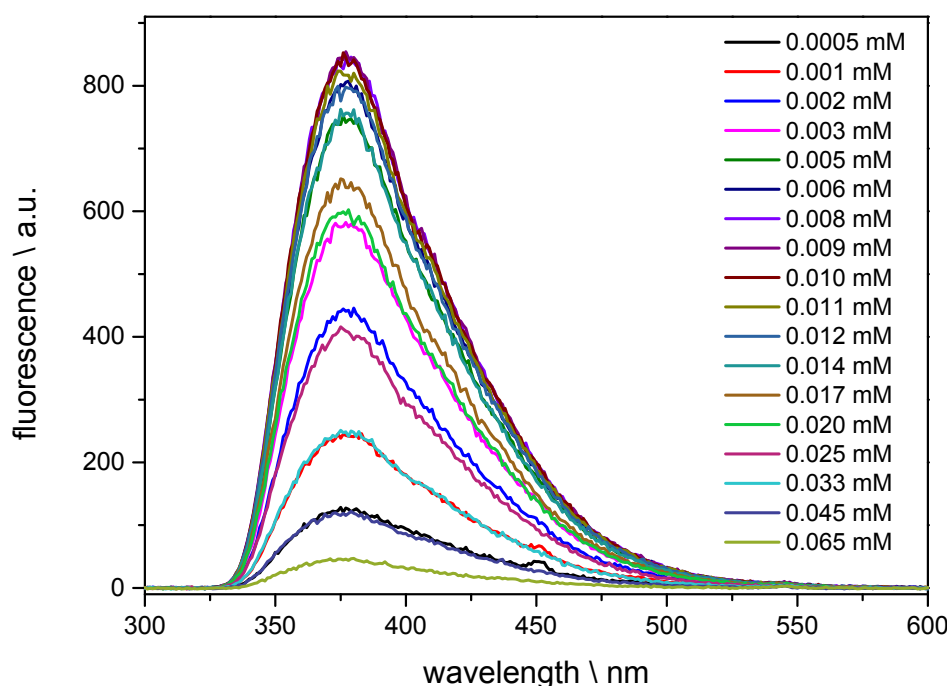


Fig. S4 Concentration-dependent fluorescence spectrum of compound **2** in water ($\lambda_{\text{ex}} = 227$ nm).

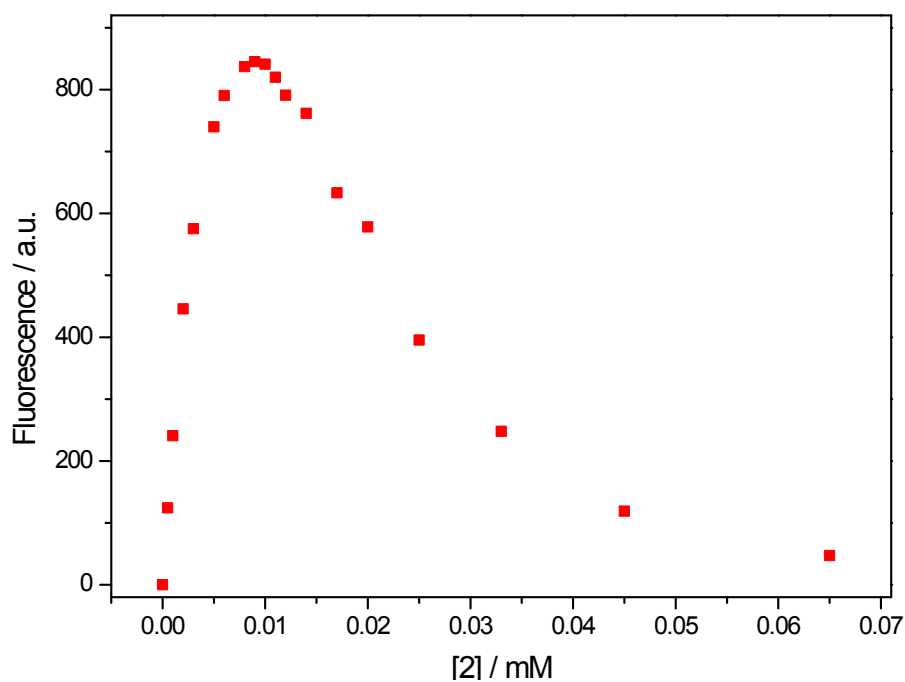


Fig. S5 Concentration-dependent fluorescence intensity at $\lambda_{\text{em}} = 380$ nm of compound **2** in water ($\lambda_{\text{ex}} = 227$ nm). This experiment revealed that the CAC of **2** in water is $9 \times 10^{-6} \text{ M}^{-1}$.

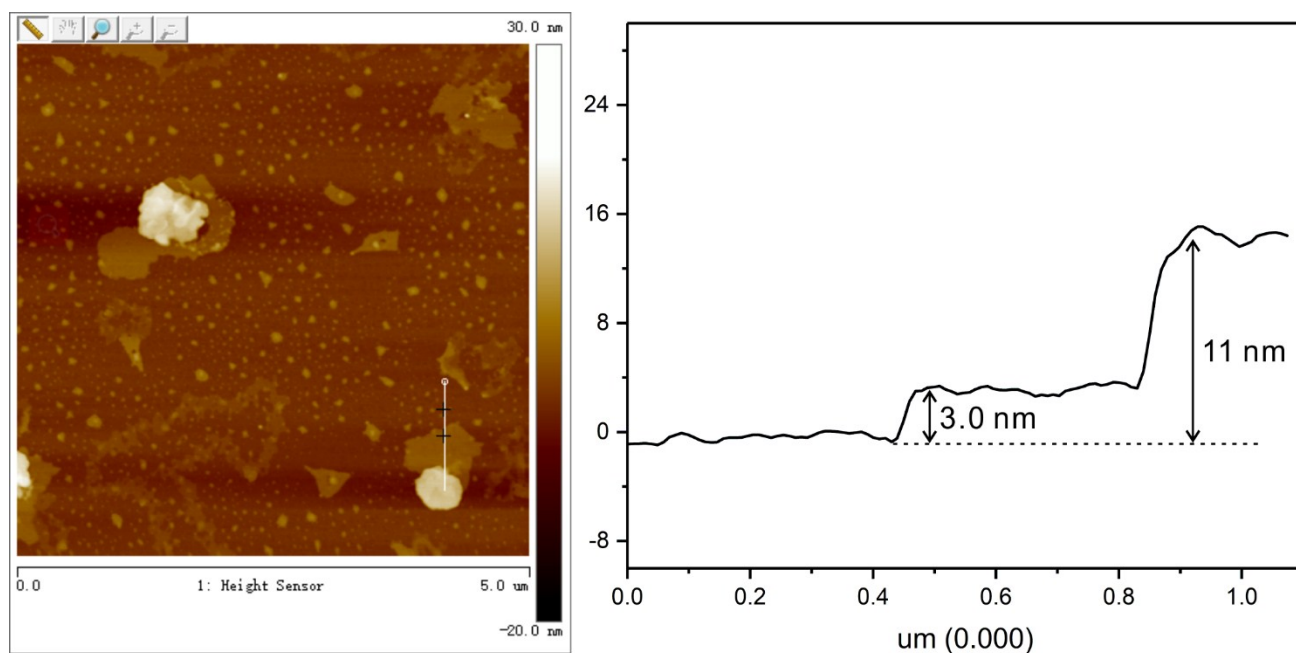


Fig. S6 AFM surface morphology of the 2D structure formed by **2**. The thickness of the 2D sheets was measured to be 3 – 11 nm. Therefore, 2D structures with two or multi layers are supported to be formed.

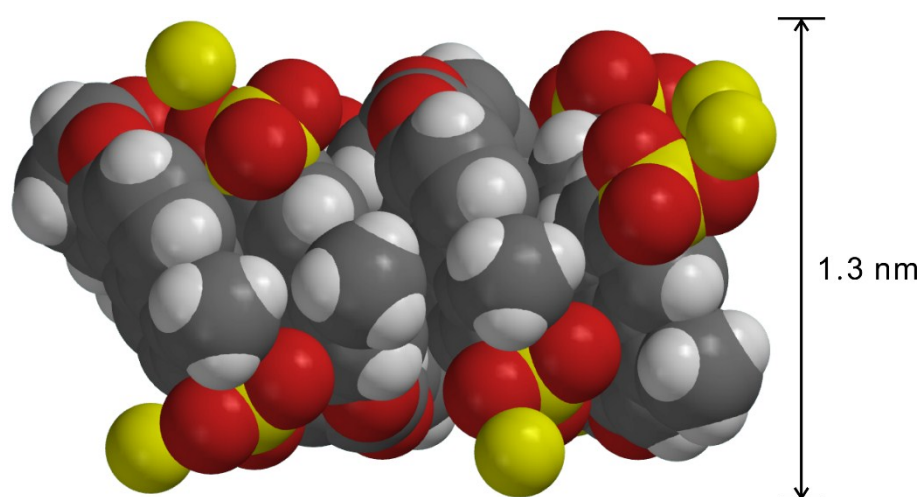


Fig. S7 Energy-minimized structure of the tetramer of **2** at the MMFF level of theory by using Spartan '14 (Wavefunction Inc.). This indicates single molecular layer has a thickness of ca. 1.3 nm.

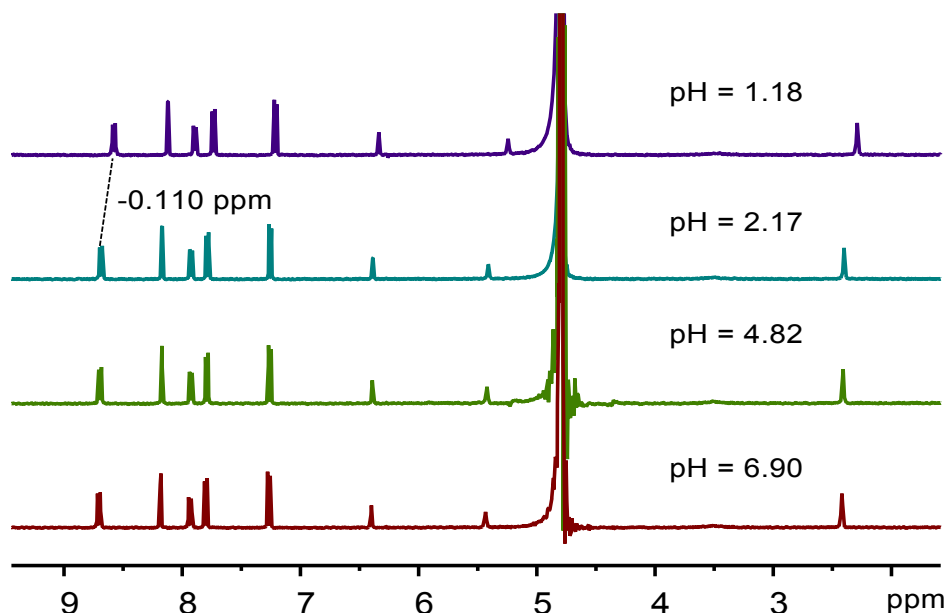


Fig. S8 ¹H NMR spectra of compound **2** (1 mM in D₂O) when changing the pH value from 6.90 to 1.18. The *pK_a* of sulfonate should be below 1. Therefore, the sulfonate groups of **2** remain in an anionic when the pH values were 6.90, 4.82, and 2.17. When the pH value of the solution was changed to 1.18, the proton peaks of **2** shift upfield. This indicated the sulfonate groups were neutralized, which promotes the further aggregation of **2**.

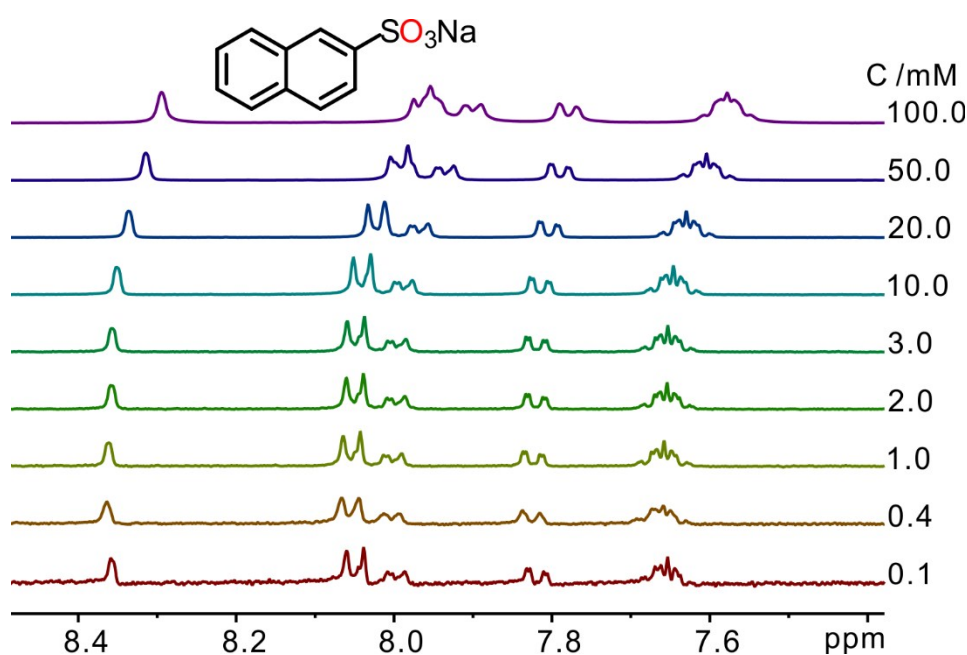


Fig. S9 ¹H NMR spectra of Sodium 2-naphthalenesulfonate in D₂O with increasing concentrations. No obvious aggregation was observed until 10 mM.

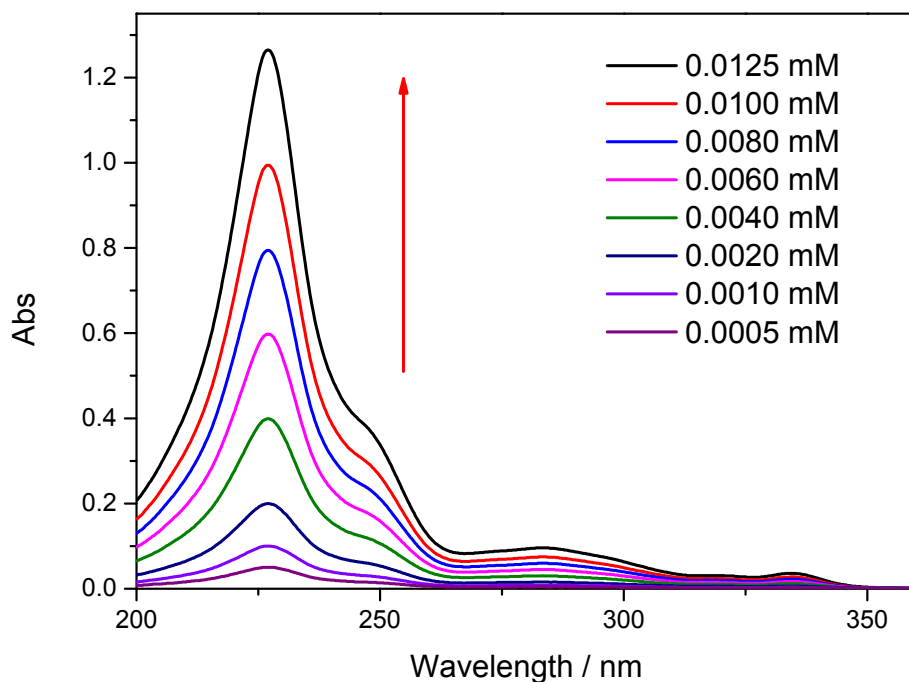


Fig. S10 Concentration-dependent UV-visible spectrum of compound **2** in water.

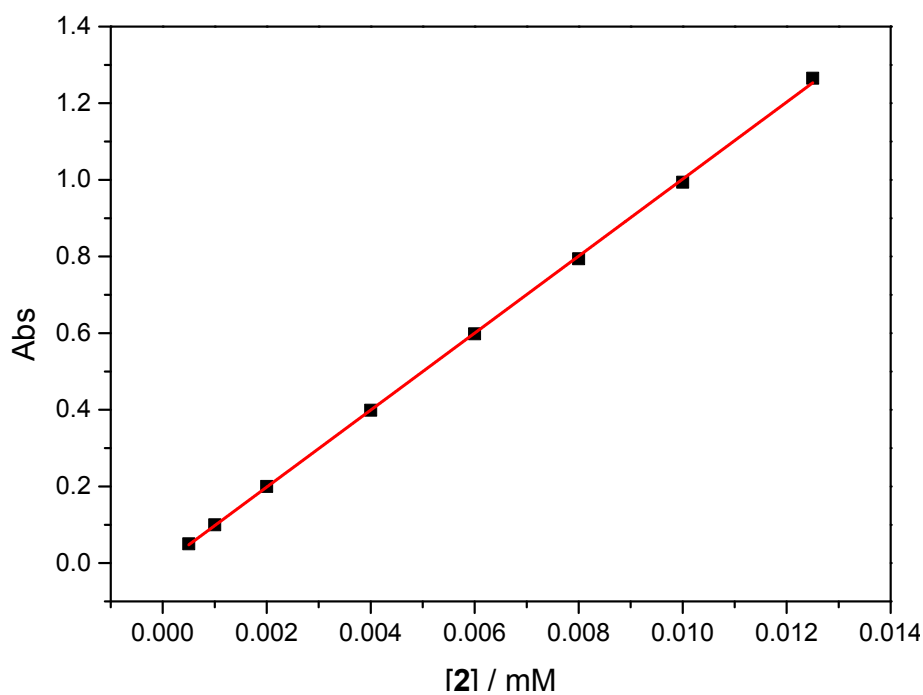


Fig. S11 Concentration-dependent UV-visible absorbance at $\lambda = 227$ nm of compound **2** in water. The concentration and absorbance have a strong linear relationship, suggesting no strong intermolecular interaction involving orbital overlapping exist in the assembly of **2**.

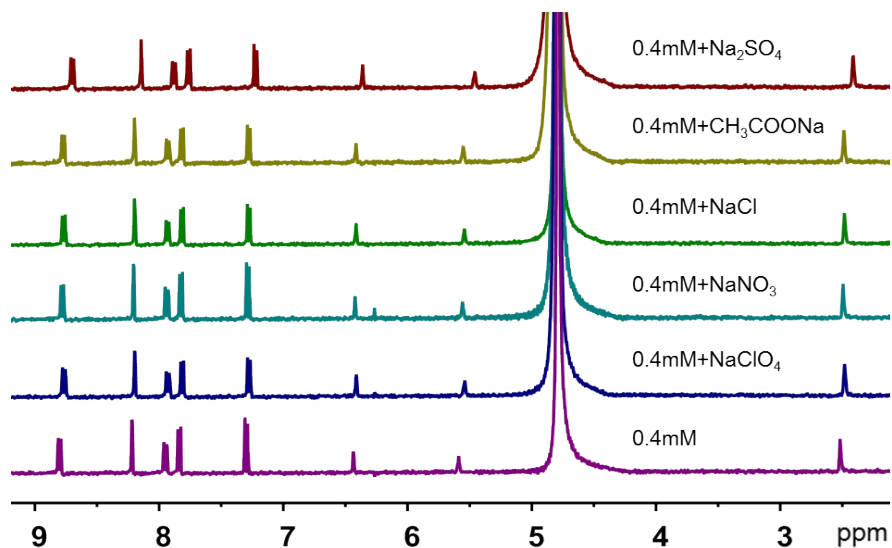


Fig. S12 Different kind of sodium salts (0.1 mM NaCl , 0.1 mM NaClO_4 , 0.1 mM NaNO_3 , 0.1 mM CH_3COONa , 0.1 mM Na_2SO_4) were added into D_2O solution of compound **2** (0.4 mM).

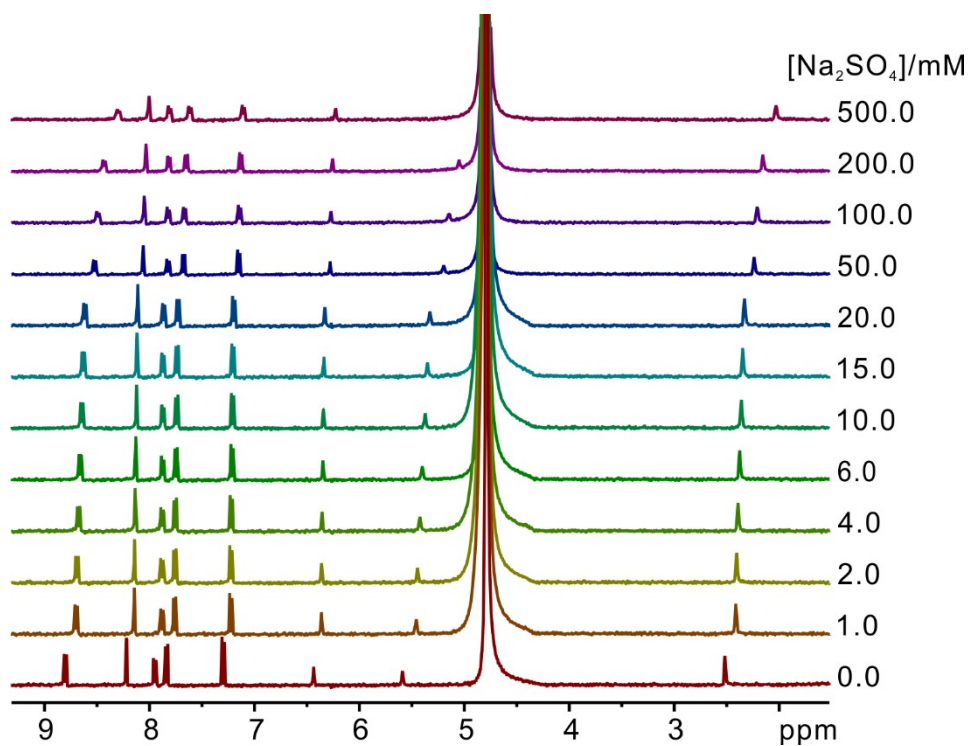


Fig. S13 ^1H NMR spectra of compound **2** (0.4 mM in D_2O) when increasing the concentration of Na_2SO_4 .

3. Characterization and Properties of Compound 4.

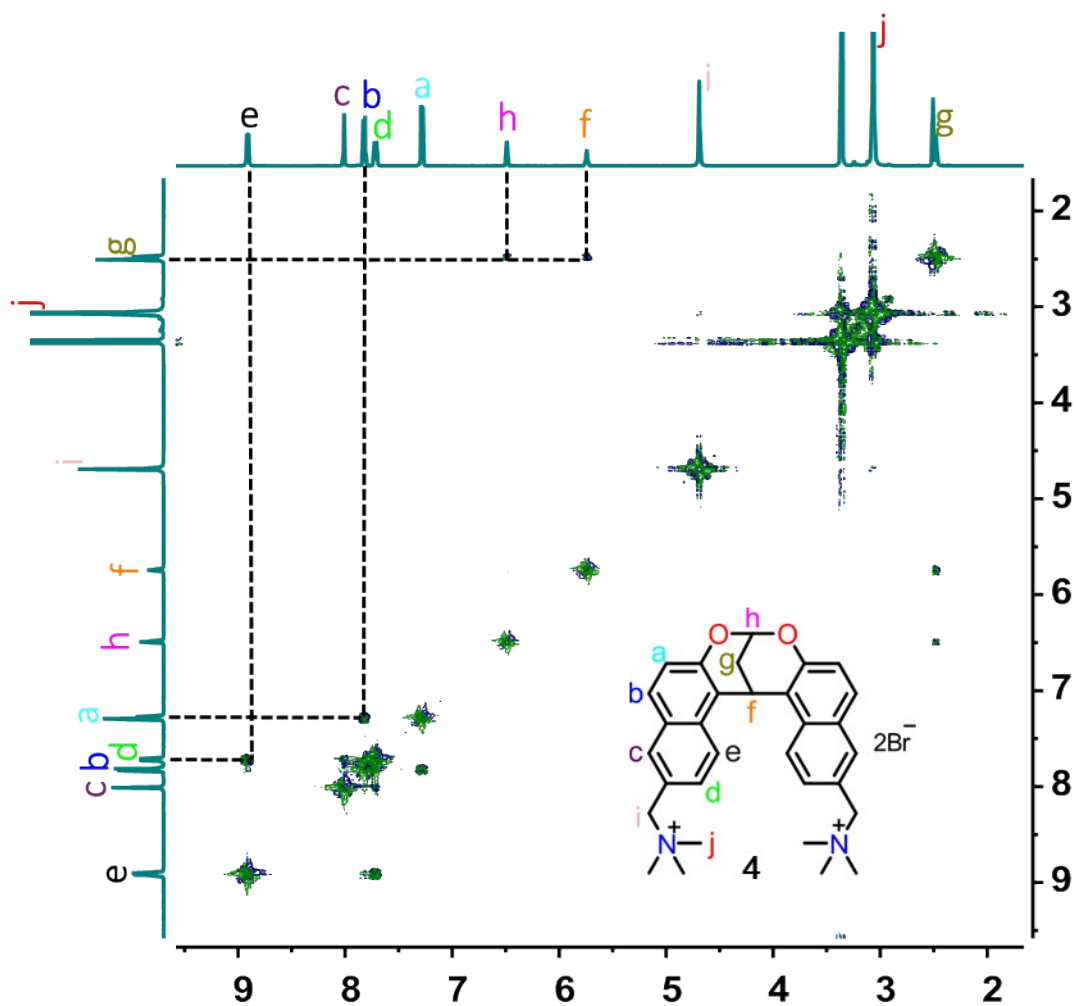


Fig. S14 ^1H , ^1H -COSY NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$) of compound 4

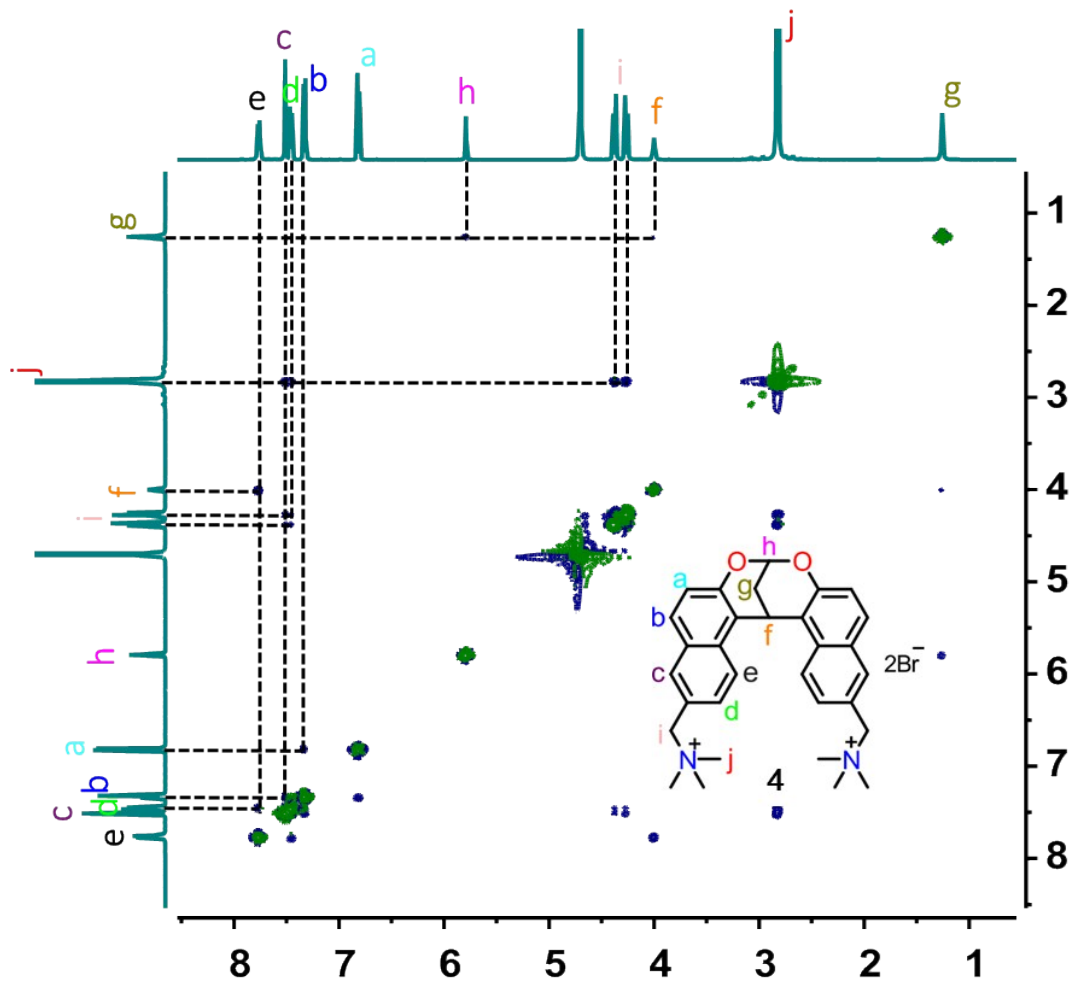


Fig. S15 ^1H , ^1H -ROESY NMR spectrum (500 MHz, D_2O , 25 $^\circ\text{C}$) of compound 4

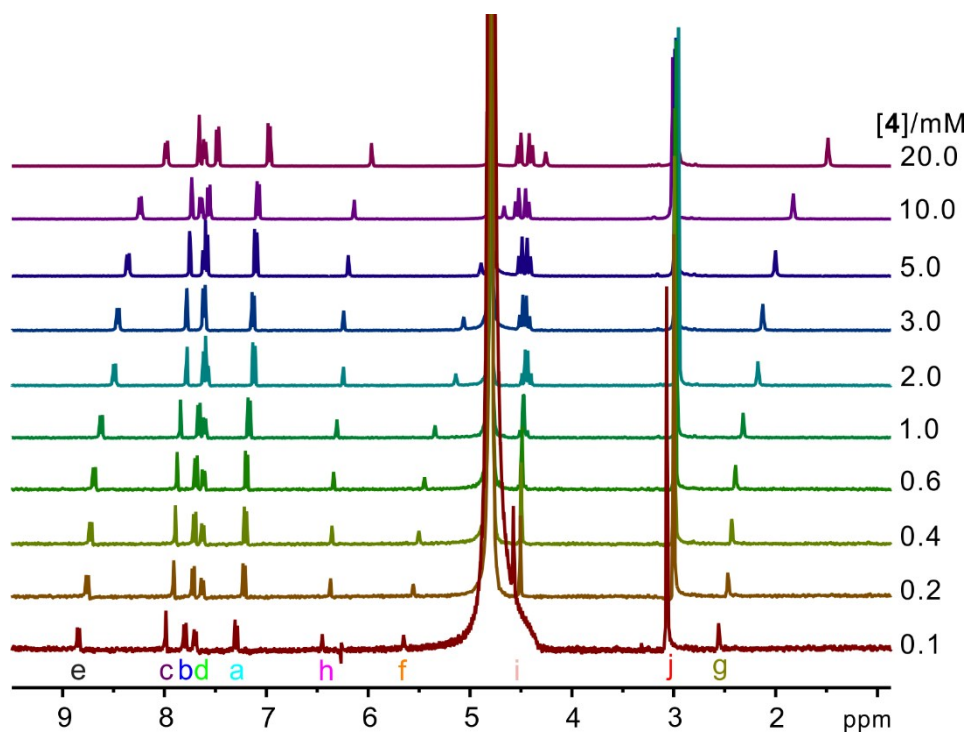


Fig. S16 ^1H NMR spectra of compound **4** in D_2O with increasing concentrations

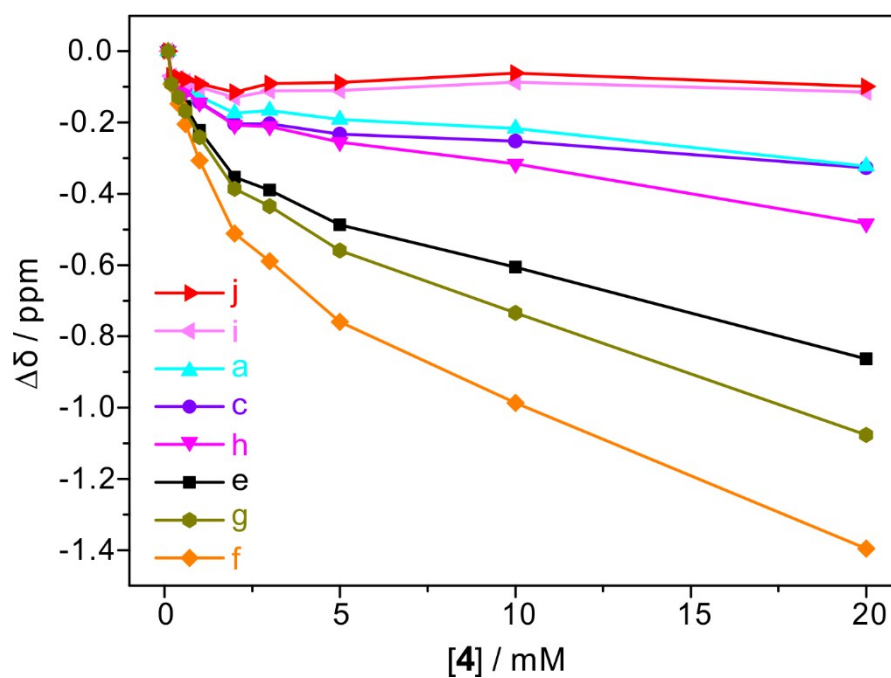


Fig. S17 Changes of $\Delta\delta$ values of the protons compound **4** relative to their chemical shifts at 0.1 mM when increasing its concentration in D_2O .

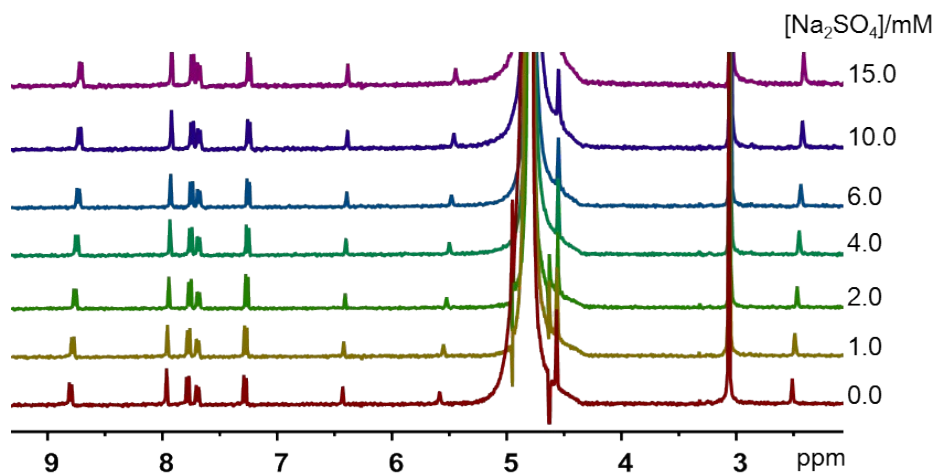


Fig. S18 ^1H NMR spectra of compound **4** (0.4 mM in D_2O) when increasing the concentration of Na_2SO_4 .

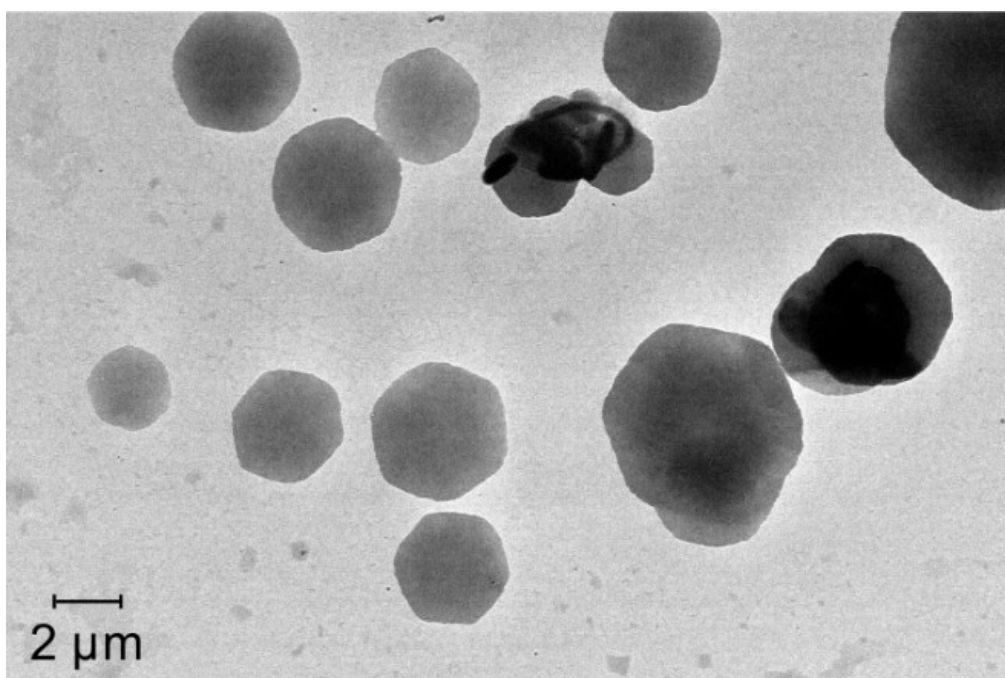


Fig. S19 TEM image of the sample prepared from the solution of compound **4** (1.0 mM). These 2D structures have a hexagonal shape typically observed in crystals, suggesting the self-assembly process may follow a nucleation and growth pathway.

4. References

1. Z. He, X. Yang and W. Jiang, *Org. Lett.*, 2015, **17**, 3880-3883.