Electronic Supplementary Information

Water-soluble two-dimensional supramolecular organic framework with aggregation-induced emission for DNA affinity and live-cell imaging

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Materials

Unless otherwise indicated, all reagents were purchased commercially from Shanghai Titan Scientific Co.,Ltd. and used without further purification. The brand is Admas-beta. All aqueous solutions were prepared with Milli-Q water. Hela cells were cultured in DMEM supplemented with 10% FBS (fetal bovine serum) and 1% P/S in an atmosphere of 5% CO_2 and 95% air at 37 °C. Grow Hela Cells in the exponential phase of growth on 35-mm glass-bottom culture dishes (Φ10mm) for 1-2 days to reach 70-90% confluency. These cells were used in co-localization experimentation. Wash cells twice with 2 mL PBS at room temperature, and then add 2 mL DMEM and observe under a Fluorescence microscope (Olympus DP80).

Instrumentation and methods

^{1}H and ^{13}C NMR, DOSY spectra were performed on 500 or 400 MHz spectrometers in the indicated solvents at room temperature. High temperature and 2D NOESY NMR were recorded on Agilent NMR Spectrometer (600-54-ASC) with D_2O as solvent.

MALDI-TOF mass spectrometry analysis was performed on a Bruker Microflex-LRF mass spectrometer in positive ion.

DLS and Zeta potential performed on a Malvern Zetasizer Nano ZS90.

SEM images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV.

TEM was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

The UV-vis absorbance was measured by UV spectrometer (HITACHI, 3900).

Fluorescence spectra were recorded on fluorescence spectrometer (HITACHI, F-2700).

The AFM images were recorded on Bruker Multimode 8 AFM with Nanoscope V controller.

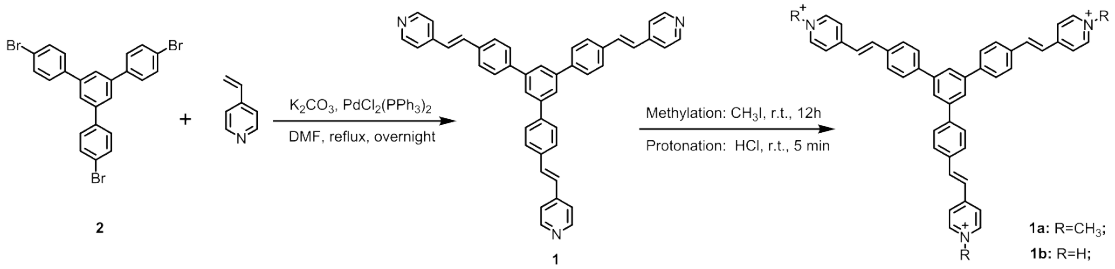
Unless otherwise indicated, column chromatography was carried out on silica gel (200-300 mesh). TLC analysis was performed on precoated silica gel plates (0.2 mm thick).

Isothermal Titration Calorimetry (ITC) experiments were carried out on a TAM III microcalorimetric system with a stainless-steel sample cell of 1 mL at 298.15 ± 0.01 K. All the sample solutions for titration were prepared with Milli-Q water. The reference cell was loaded with

765 μL buffer and the sample cell was initially loaded with 600 μL CB[8] or DNA solutions, and then the **1a** solutions (0.75 mM) were consecutively injected into the sample cell by 10 μL per injection via a 500 μL Hamilton syringe controlled by a 612 Thermometric Lund pump until the interaction progress was completed. The interval between two injections was long enough to reach the equilibrium. The solution in the sample cell was stirred at 90 rpm with a gold propeller.

Cryo-transmission electron microscopy (Cryo-TEM) experiments using a literature procedure.[1] Cryo-TEM experiments were conducted on a FEI T20 TEM operating at 200 kV, with a Gatan digital camera and analyzed using Gatan Digital Micrograph software. The vitrified specimens were prepared using a Vitrobot (FEI, Inc.). A 3 μL droplet of the water solution at a concentration of 1 mM was deposited on the surface of glow discharged grids with lacey carbon films. The droplet was blotted by filter paper for 1.5 s, followed by 1 s draining, and then plunged into liquid ethane to obtain a vitrified thin film. The Grids were then transferred to a Gatan cryo-stage at −190 °C for analysis.

Synthetic procedures



Scheme S1. Synthetic procedures of the guest molecules.

Compounds 1. To a stirred solution of compounds **2** (500 mg, 0.92 mmol) in DMF (12.5 mL) was added 4-vinylpyridine (384.6 mg, 3.66 mmol), $PdCl_2(PPh_3)_2$ (64.2 mg, 0.092 mmol), and Potassium carbonate (758.2 mg, 5.49 mmol). The reaction solution was refluxed overnight. The reaction solution was cooled down and poured over 100 mL ice water. The precipitate was collected by filtration, washed with H_2O for several times. Silica gel column chromatography of the residue (DCM/MeOH 25:1; Rf 0.36 with DCM/MeOH 25:1) gave pure **1** (345.5 mg, 62%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ:8.60 (d, J = 5.1 Hz, 6H), 7.84 (s, 3H), 7.75 (d, J = 8.2 Hz, 6H), 7.68 (d, J = 8.0 Hz, 6H), 7.43 – 7.32 (m, 9H), 7.10 (d, J = 16.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ:150.34, 144.61, 141.90, 141.24, 135.73, 132.64, 127.82, 126.39, 125.12, 120.96. MS (M^+), m/z=616.76.

Compounds 1a. A mixture of **1** (61.5 mg, 0.1 mmol), CH_3I (709.5 mg, 5 mmol), $CHCl_3$/MeOH (6 mL, 1/5 by vol.) was stirred at 40 ℃ for 24 h. The mixture was cooled down and the precipitate was collected by centrifugation, washed with DCM for several times to afford **1a** (98.9 mg, 95%) as orange solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ:8.89 (d, J = 6.6 Hz, 6H), 8.26 (d, J = 6.3 Hz, 6H), 8.15 - 8.06 (m, 12H), 7.92 (d, J = 8.2 Hz, 6H), 7.63 (d, J = 16.3 Hz, 3H), 4.28 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ:152.91, 145.63, 141.96, 141.30, 140.58, 135.20, 129.25, 128.40, 125.33, 123.93, 47.45.

Compounds 1b. To a stirred solution of compounds **1** (12.3 mg, 0.02 mmol) in CH_3OH (10 mL) was added 3M HCl (0.5 mL).The mixture was stirred for 0.5 h and the precipitate was collected by centrifugation, washed with CH_2Cl_2 for several times to afford **1b** (13.6 mg, 94%) as yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ:8.85 (d, J = 6.0 Hz, 6H), 8.19 (d, J = 6.0 Hz, 6H), 8.13 – 8.03 (m, 12H), 7.92 (d, J = 8.0 Hz, 6H), 7.64 (d, J = 16.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ:153.08, 143.18, 141.72, 141.37, 139.29, 135.40, 129.07, 128.34, 125.26, 124.75, 123.46.

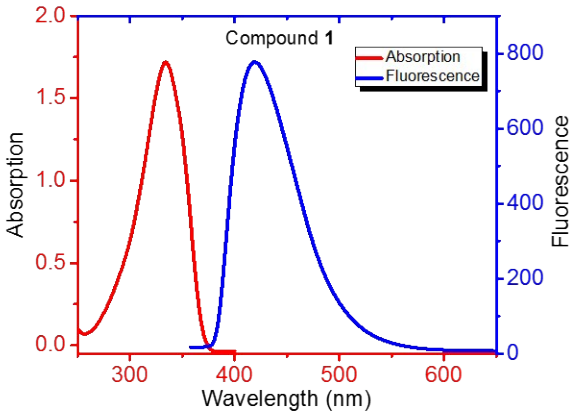


Figure S1. Uv-vis and Fluorescence spectra of **1**.

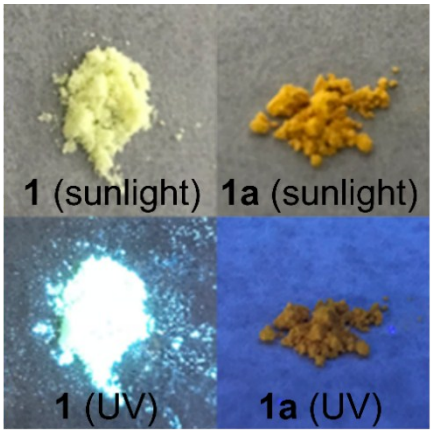


Figure S2. Photographs of sample **1**, **1a** under sunlight and 365 nm UV lamp.

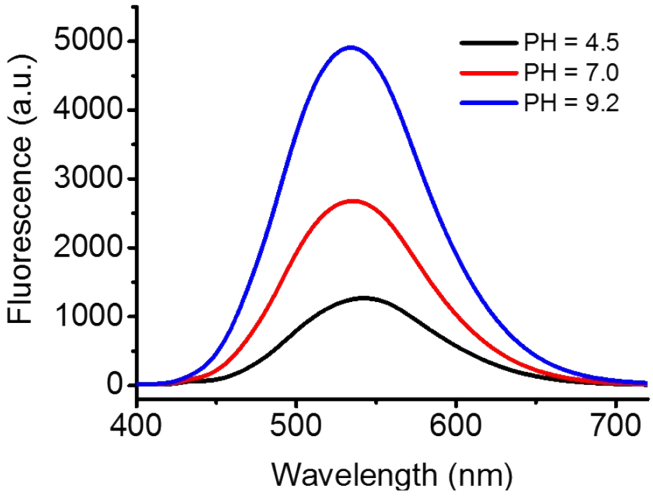


Figure S3. Fluorescence spectra of **1a** in different pH conditions.

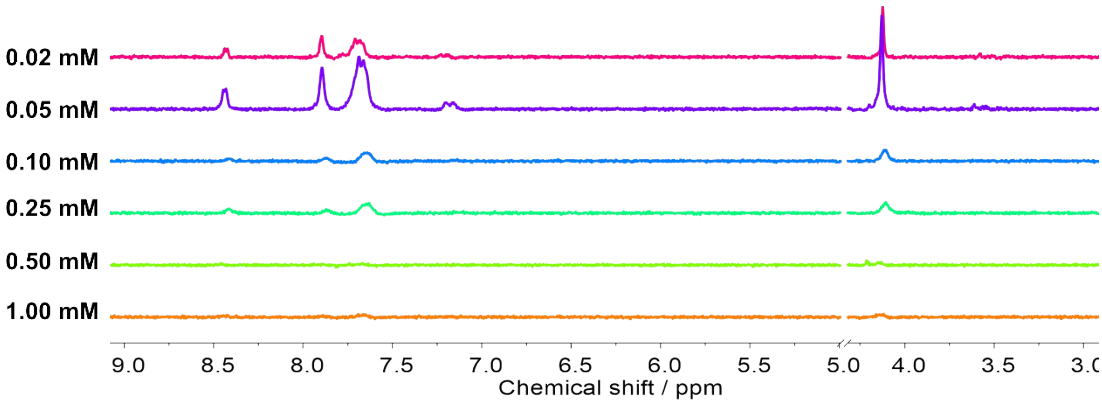


Figure S4. Concentration dependent study of **1a** in D_2O at room temperature.

Figure S5. 20 mM **1a** in H_2O at room temperature.

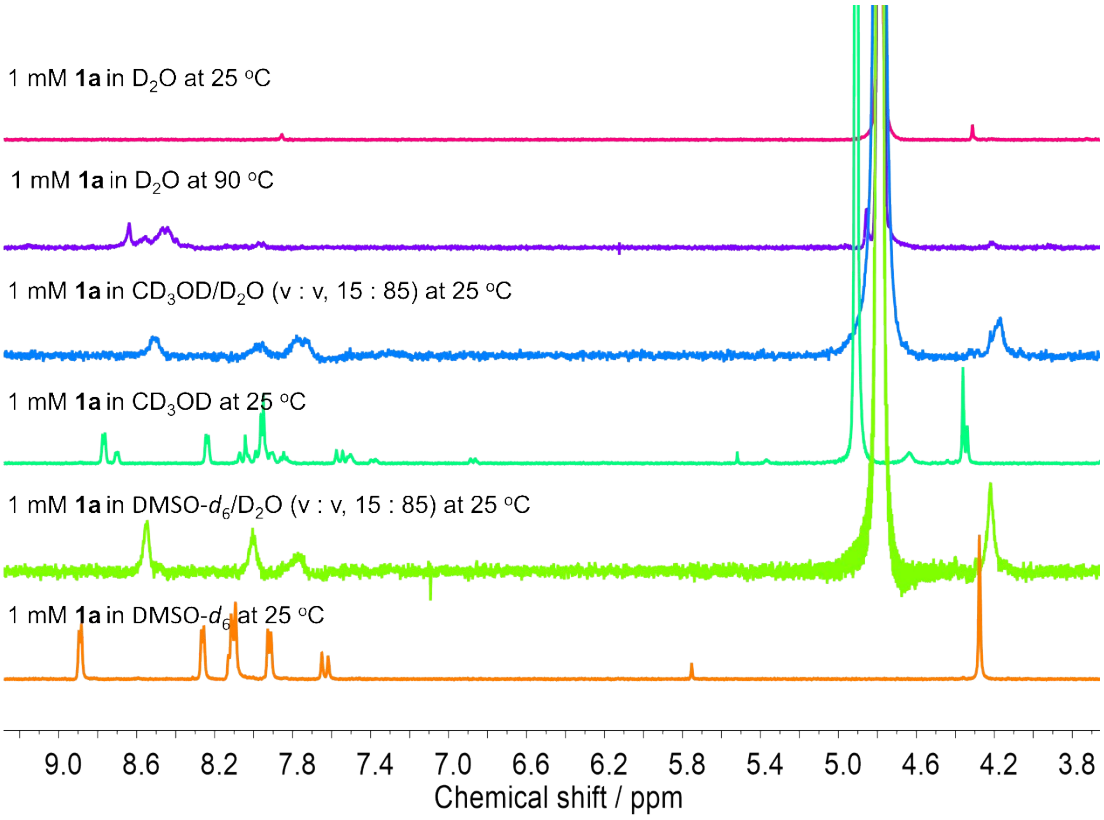


Figure S6. ^1H NMR of **1a** in different solvent.

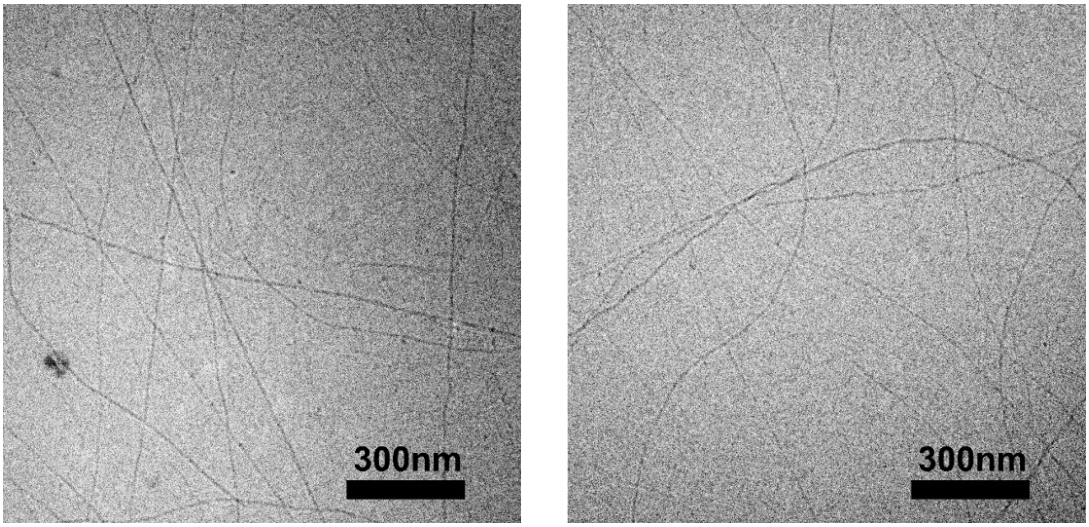


Figure S7. Cryo-TEM images of **1a** (1 mM).

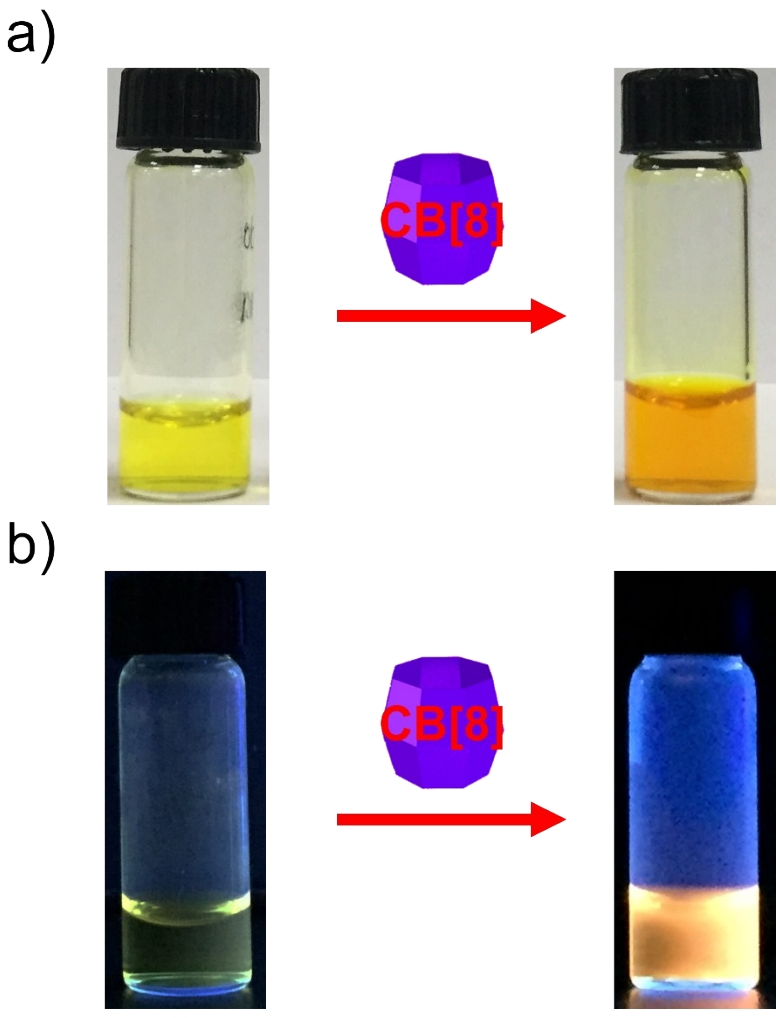


Figure S8. Photographs of an sample **1a**, **1a**_CB[8] (H_2O) (a) under sunlight and (b) 365 nm UV lamp.

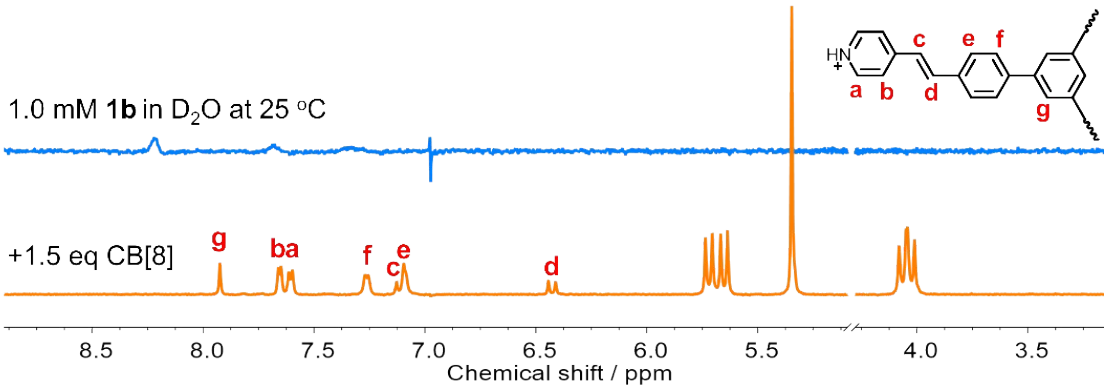


Figure S9. ^{1}H NMR spectra: **1b** (1.0 mM) in D_2O in the presence of 0, 1.5 equiv of CB[8].

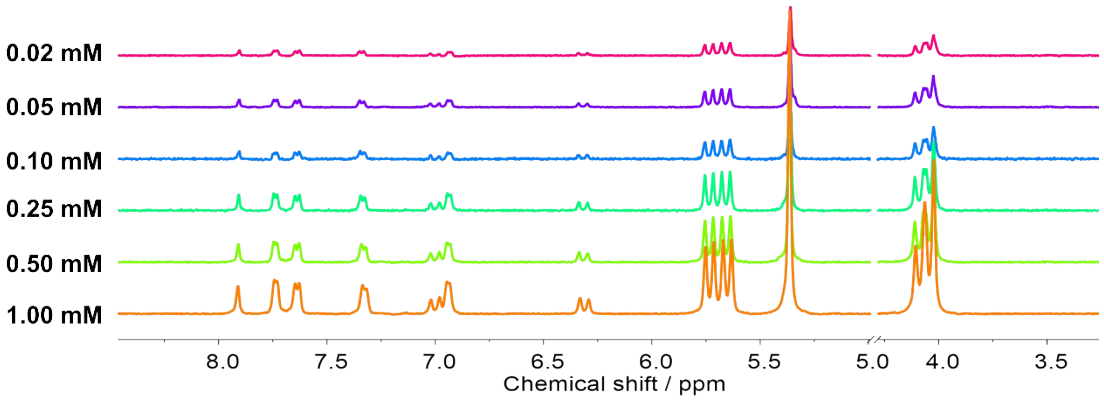


Figure S10. Concentration dependent study of **1a**_CB[8] in D_2O at room temperature.

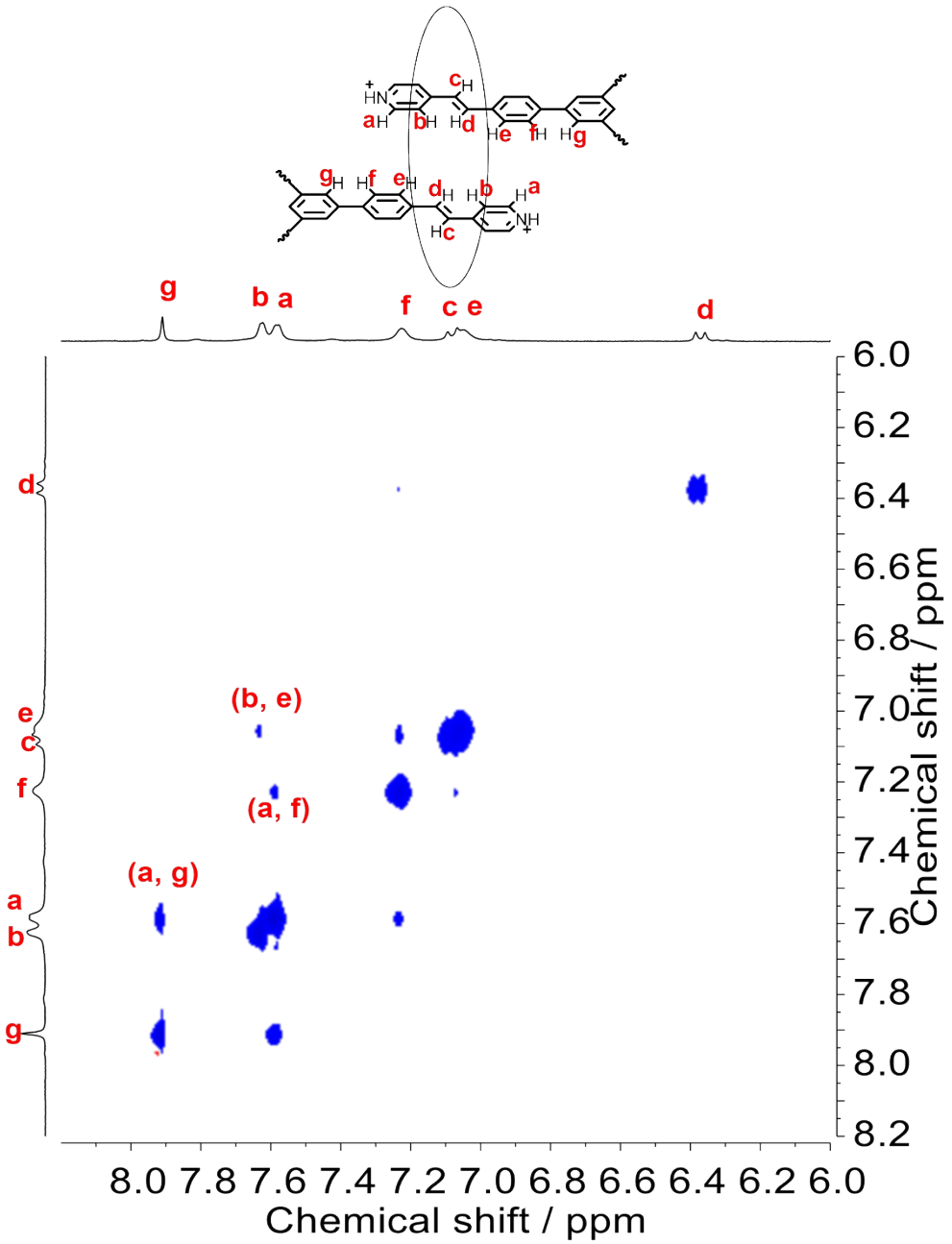


Figure S11. 2D ^{1}H NMR NOESY spectrum (600 MHz) of **1b**_CB[8] in D_2O at 25 °C (The ratio between guests and CB[8] is 2:3; the concentration of 1b is 1.0 mM).

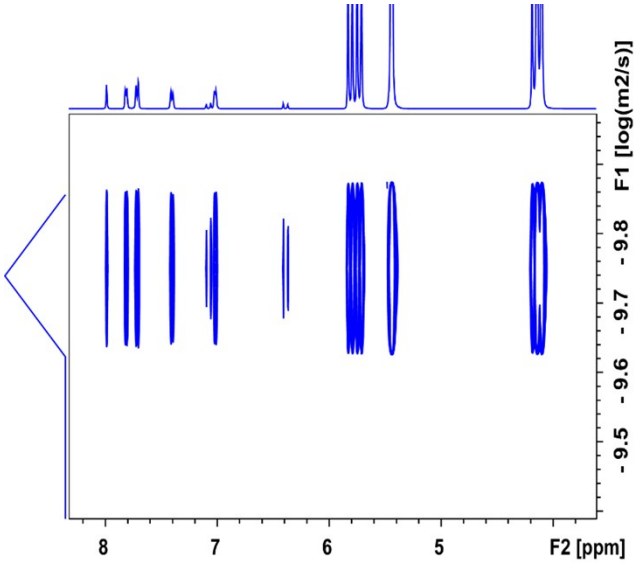


Figure S12. DOSY-NMR spectrum (400 MHz) of the solution of **1a**_CB[8] (2:3, 1.0 mM) in D_2O. The ordinate represents the log value of the diffusion constant.

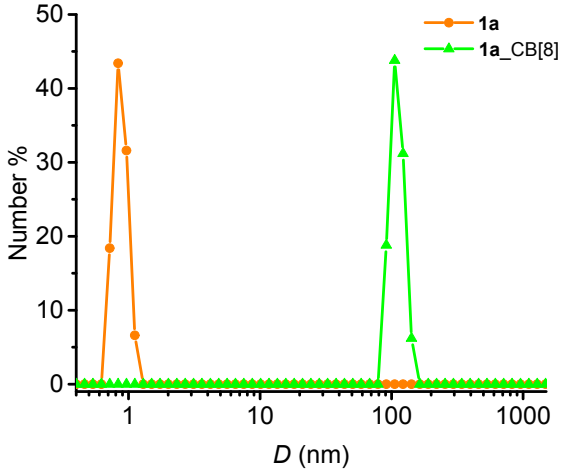


Figure S13. DLS profiles of **1a** solution (0.02 mM) and the mixture with CB[8] (the ratio is 2:3) in water.

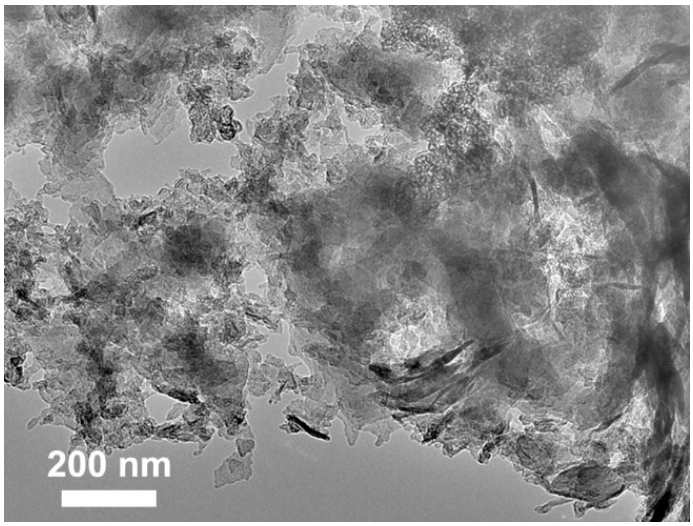


Figure **S14**. TEM images of **1a**_CB[8] (0.2 mM).

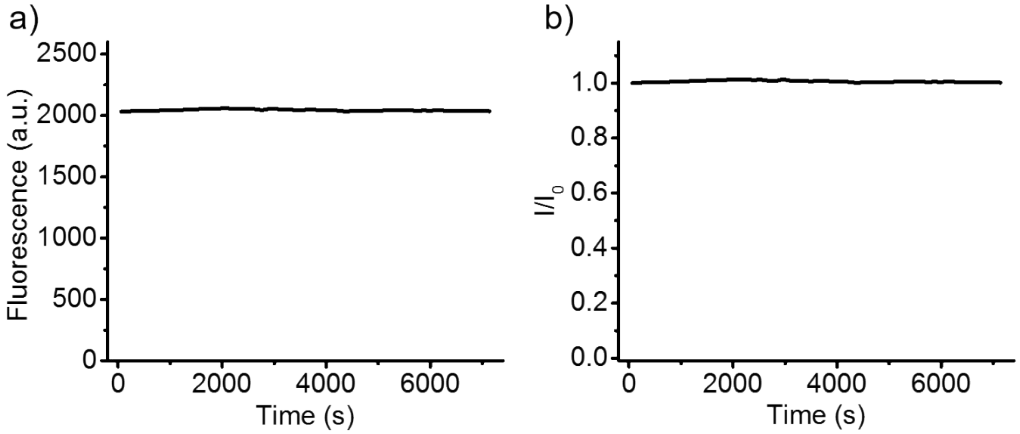


Figure S15. (a-b) Photofading behavior of **1a**_CB[8] (1 mM) in H_2O (λ_{ex} = 405 nm, λ_{em} = 608 nm)

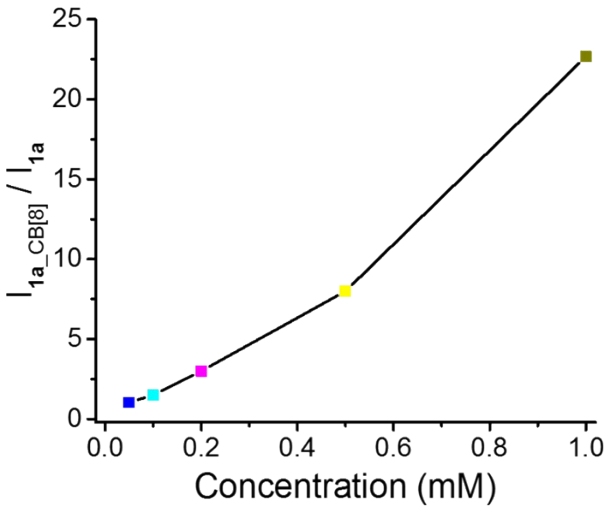


Figure S16. The fluorescence intensity ratio of **1a**_CB[8] (ratio of 2:3) and **1a** in aqueous solution at room temperature with different concentrations.

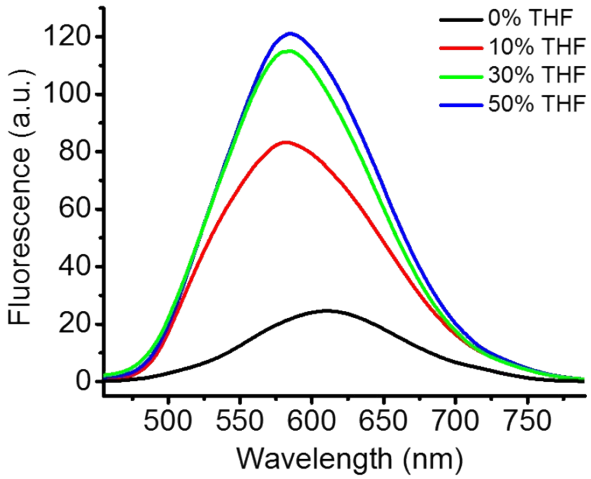


Figure S17. Fluorescence spectra of complex of **1a** and CB[8] (ratio of 2:3 and concentration of 0.01 mM) in water-THF at different water/THF ratios.

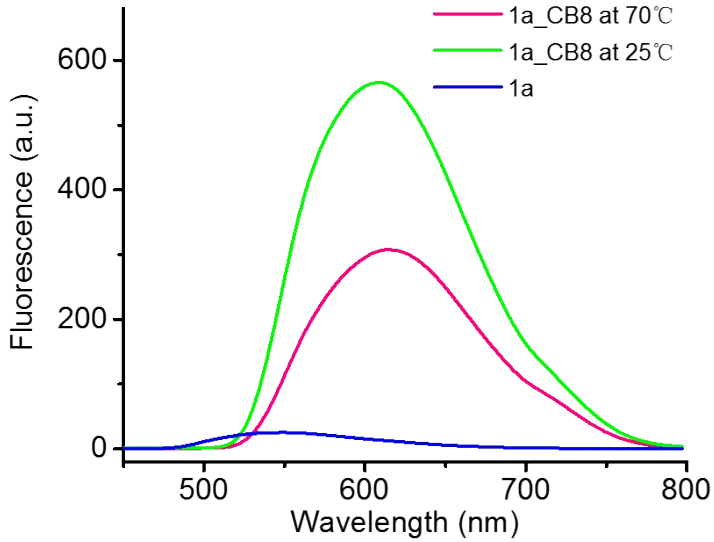


Figure S18. Fluorescence spectra of complex of **1a** and CB[8] (ratio of 2:3 and concentration of 1.0 mM) at 25 °C and 70 °C.

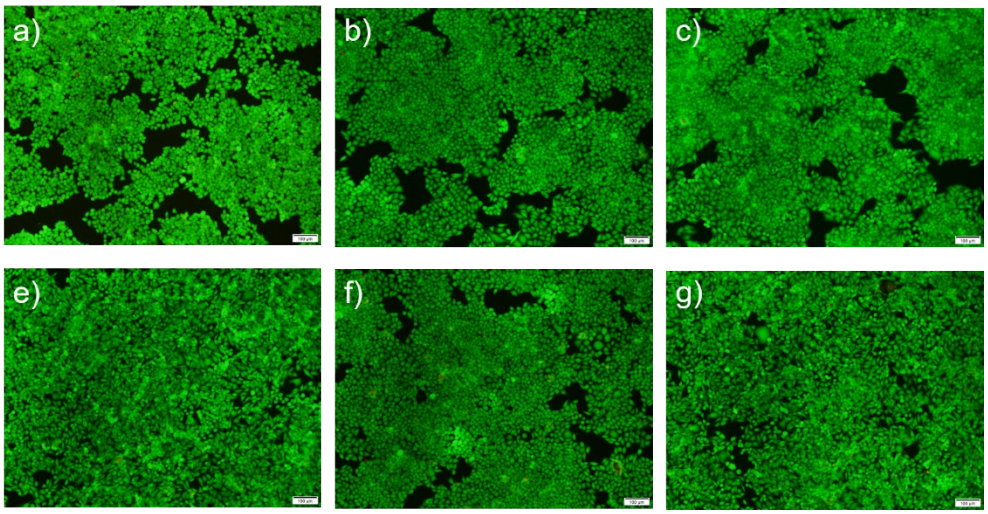


Figure S19. Cell viability of (a-c) **1a** (0.1 mM) and (e-g) **1a**_CB[8] (2:3, 0.1 mM) with Hela cells. The Hela cells were stained by Live/Dead staining after incubation for 24 h. Live cells are stained fluorescent green, and dead cells appear red. The images were captured at 3 different positions of the hybrid surface.

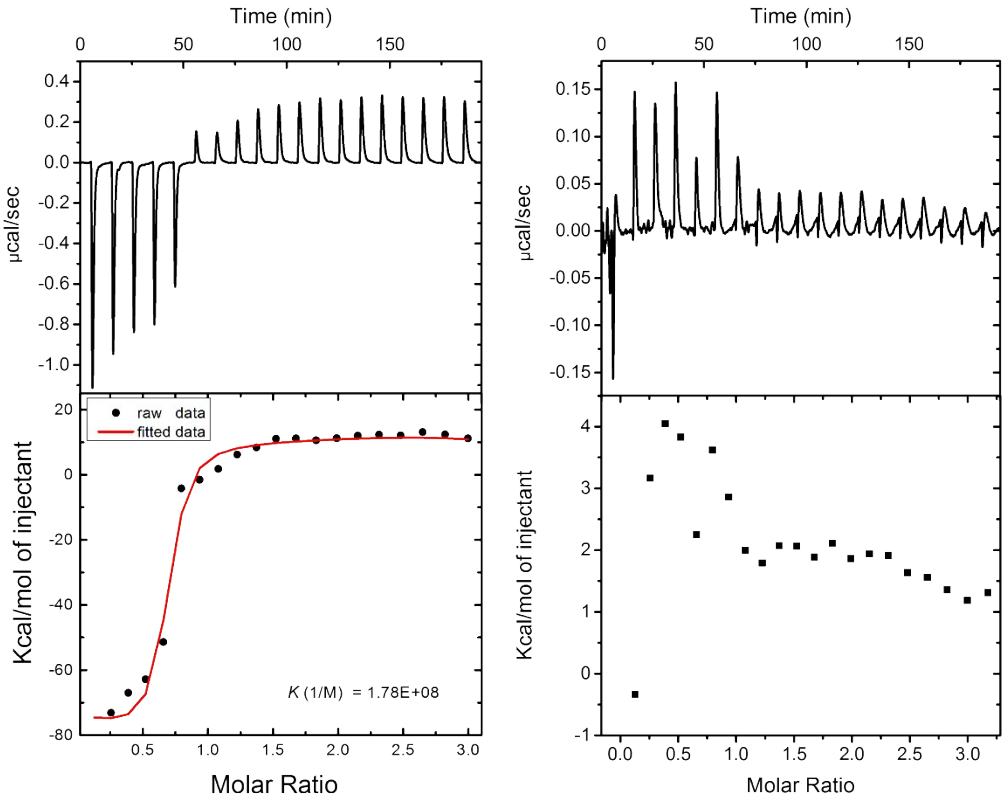


Figure S20. ITC titration data and fitting curves (Milli-Q water, 25.0 °C) of (a) **1a** (0.75 mM) titrated into CB[8] (0.05 mM) and (b) **1a** (0.75 mM) titrated into DNA (0.05 mM).

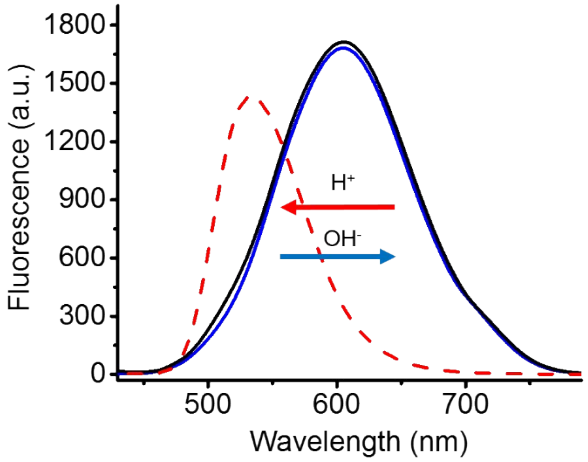


Figure S21. Fluorescence spectra of **1a**_CB[8] in different pH conditions (ratio of 2:3 and concentration of 0.05 mM). Aqueous solution with a pH of 7.0 (black solid line), adjust pH to 5.0 by adding an aqueous HCl solution (6M) (red dotted line), readjust pH to 7.0 by adding an aqueous NaOH solution (6M) (blue solid line)

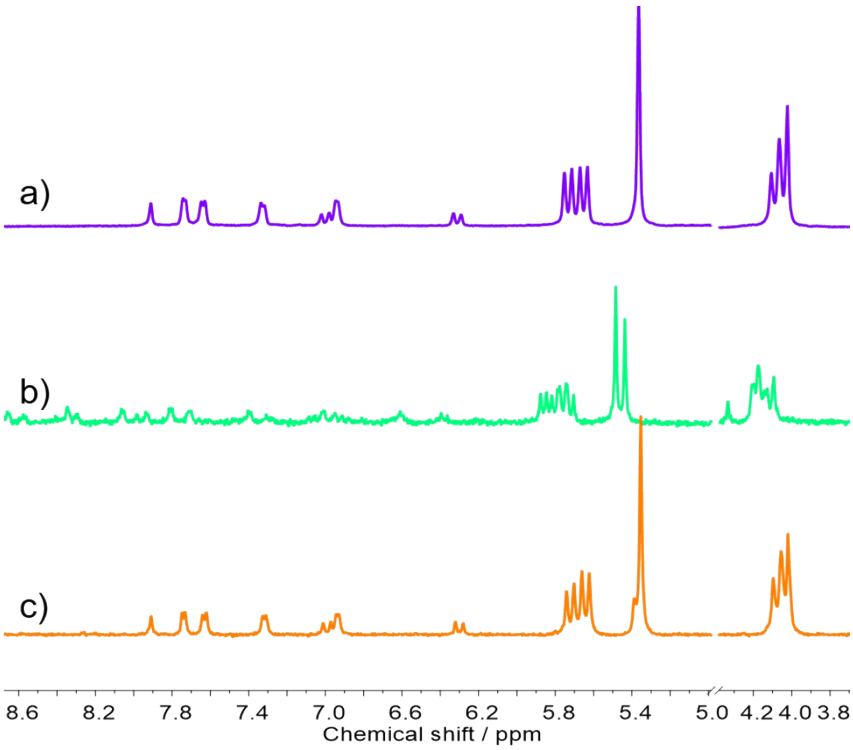
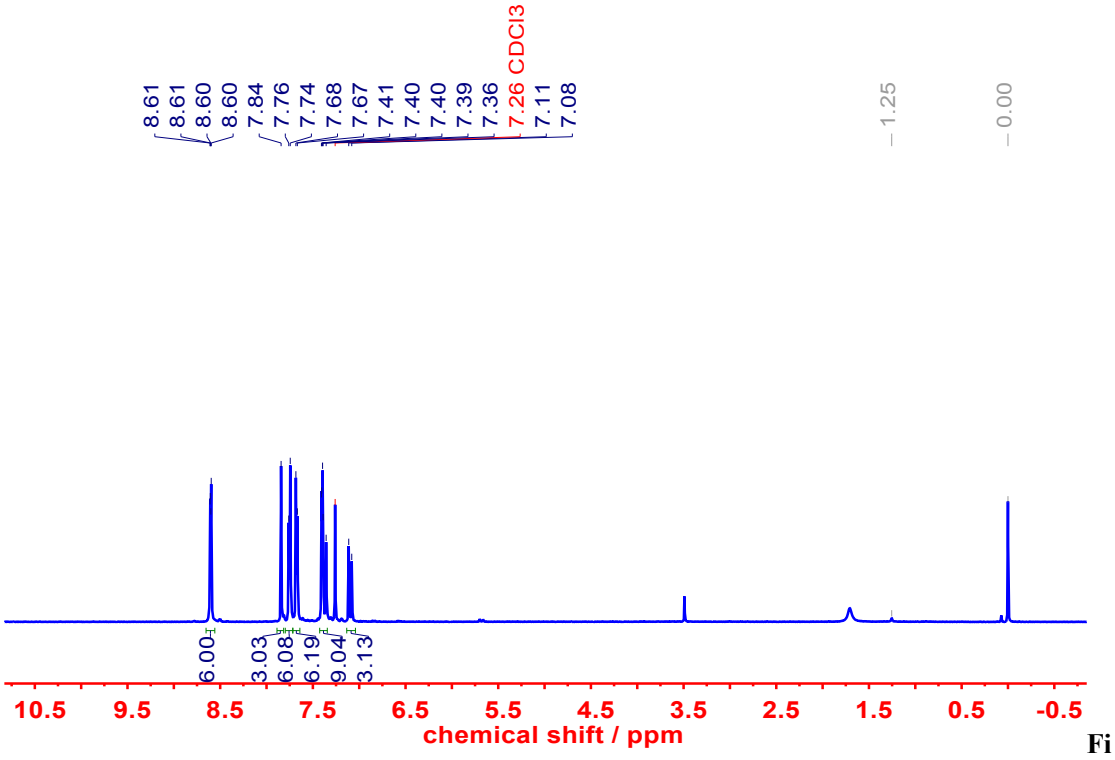


Figure S22. ^{1}H NMR spectra of **1a**_CB[8] in different pH conditions. (a) **1a**_CB[8] in D_2O (ratio of 2:3 and concentration of 0.05 mM); (b) adjust pH to 5.0 by adding an aqueous DCl solution (20%) to (a); (c) readjust pH to 7.0 by adding an aqueous NaOD solution (40%) to (b).



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gure S23. ^{1}H NMR (500 MHz) spectrum of compound **1** in $CDCl_3$.

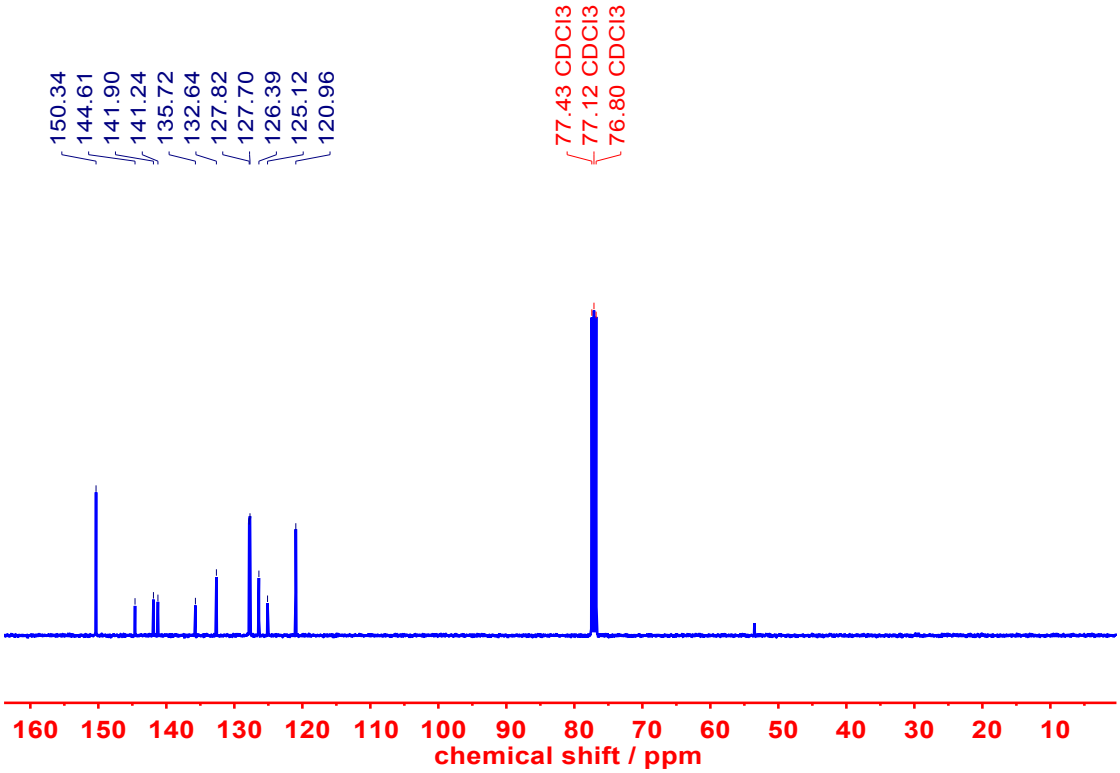
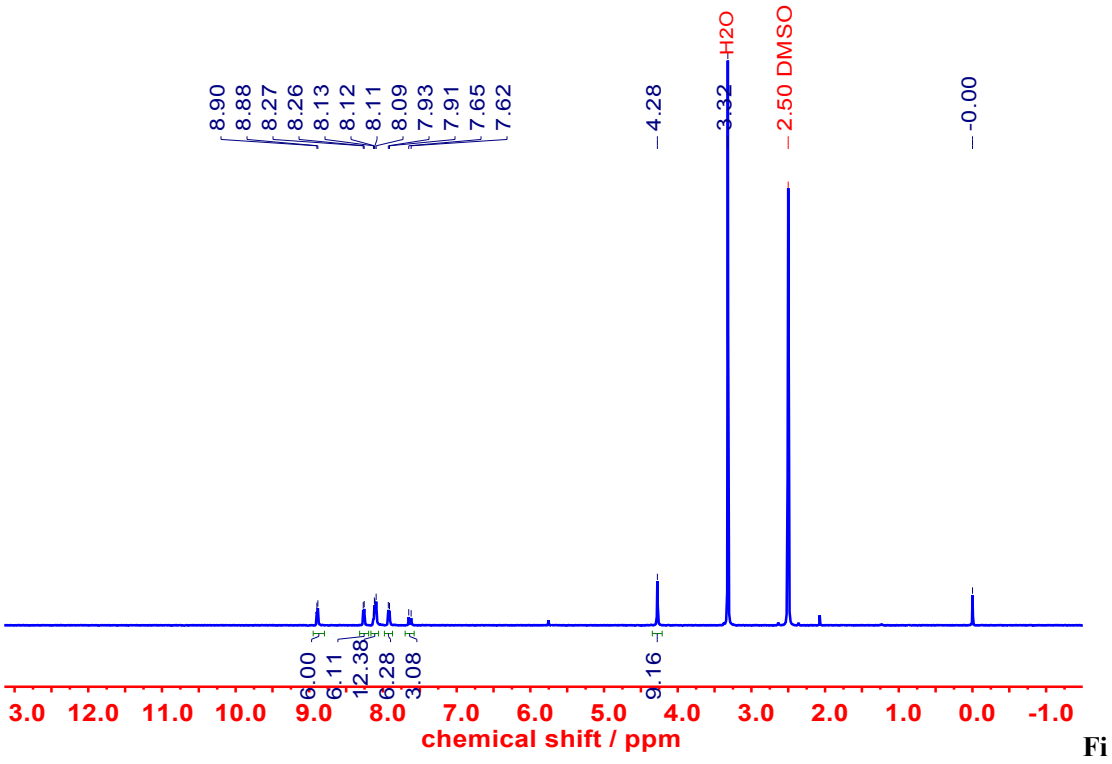


Figure S24. ^{13}C NMR (101 MHz) spectrum of compound **1** in $CDCl_3$.



gure S25. ^{1}H NMR (500 MHz) spectrum of compound **1a** in DMSO-d_6.

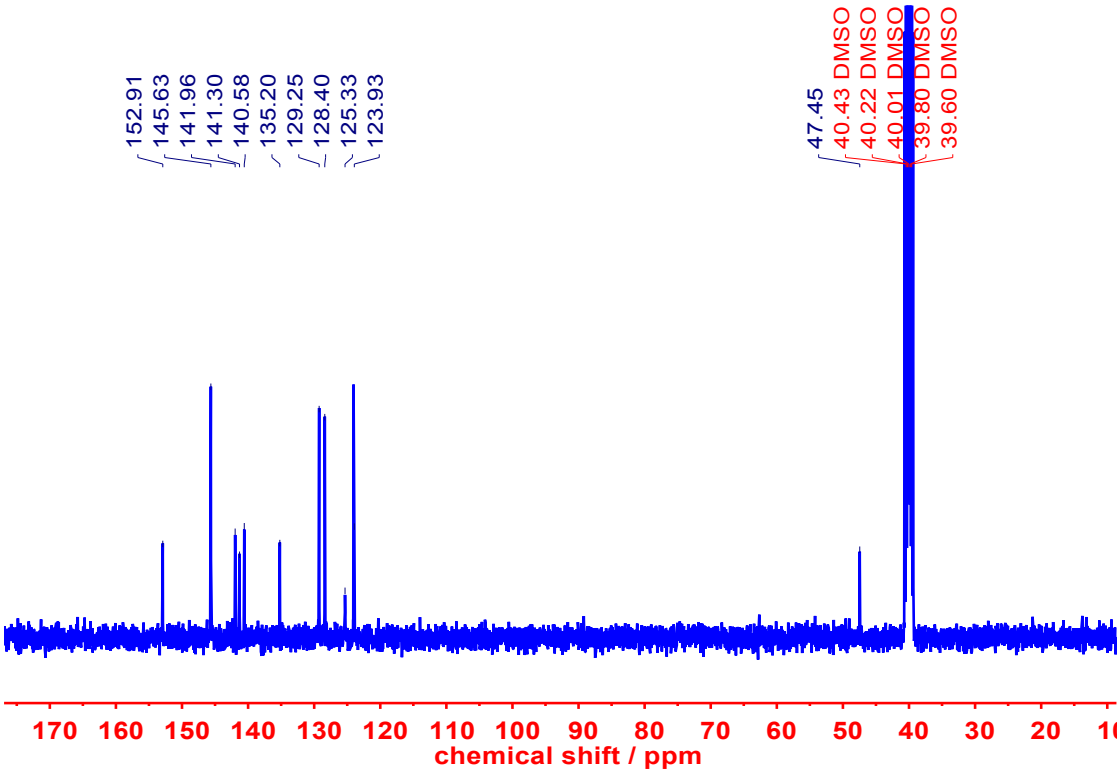


Figure S26. ^{13}C NMR (101 MHz) spectrum of compound **1a** in DMSO-d_6.

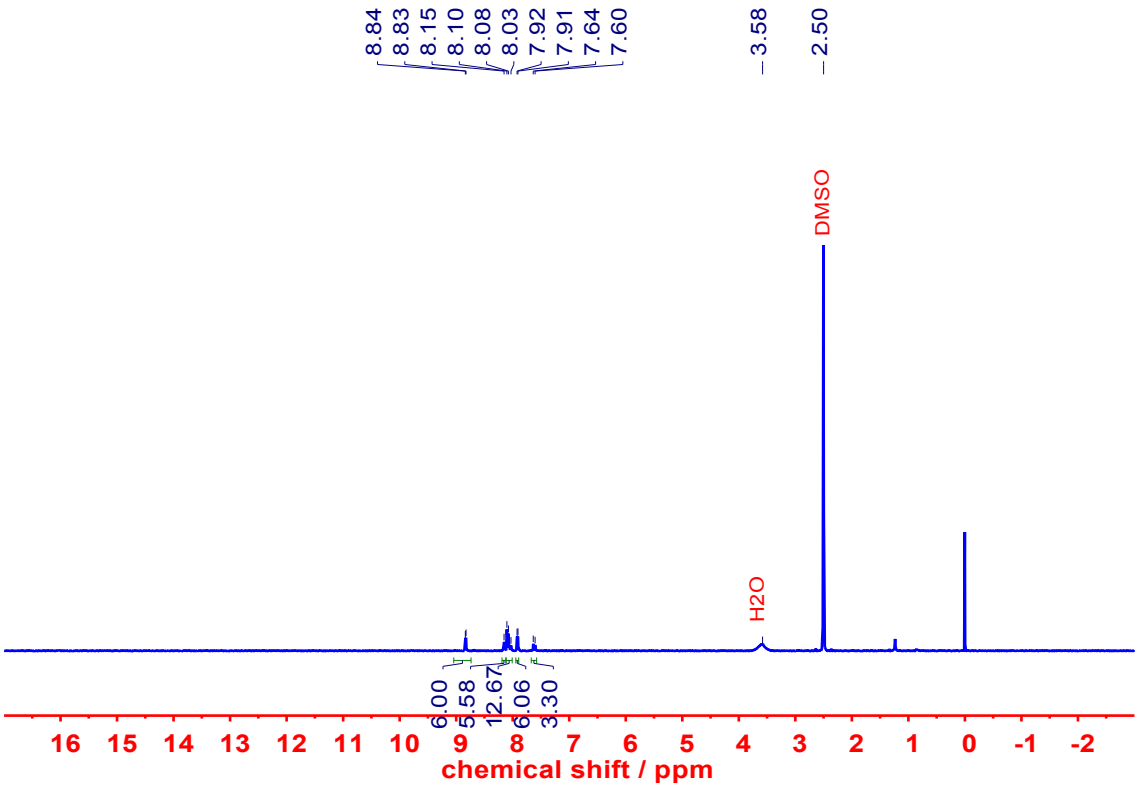


Figure S27. ^{1}H NMR (500 MHz) spectrum of compound **1b** in DMSO-d_6.

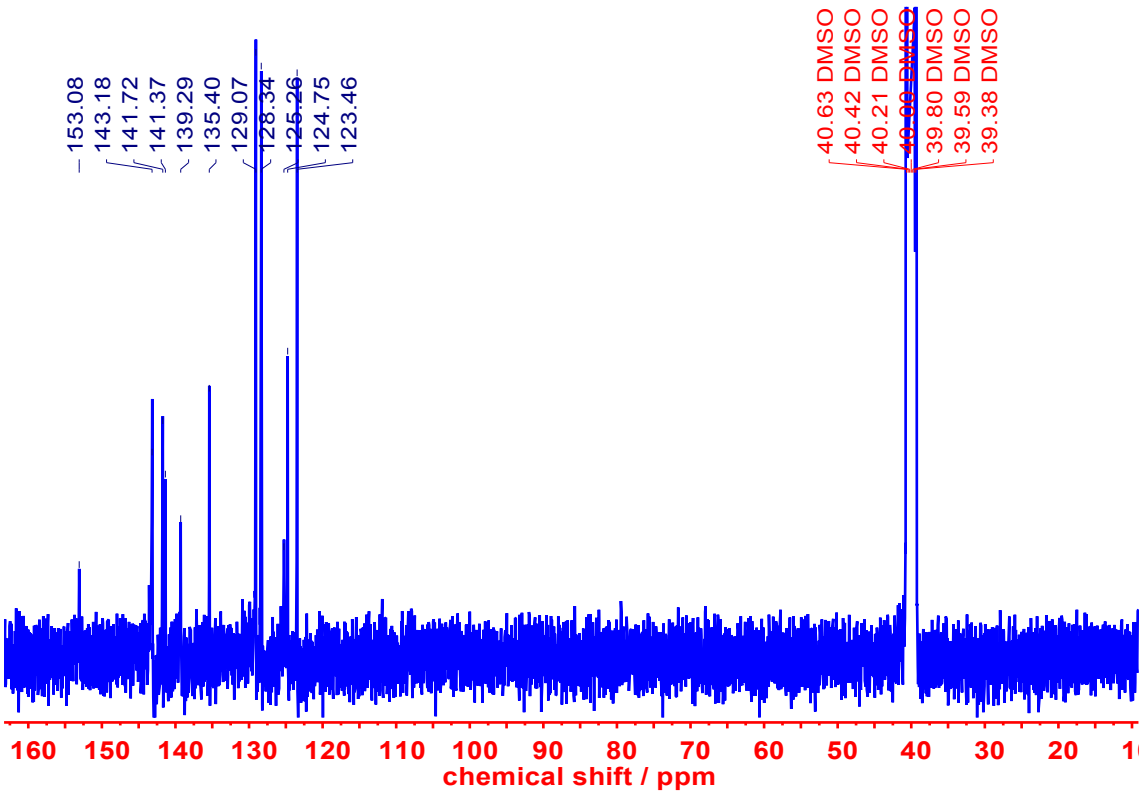


Figure S28. ^{13}C NMR (101 MHz) spectrum of compound **1b** in DMSO-d_6.

References

[1] Z. Shi, Y. Wei, C. Zhu, J. Sun, Z. Li, *Macromolecules* **2018,** *51,* 6344.