Electronic supplementary information

Highly thermally stable hydrogels derived from monolayered two-dimensional supramolecular polymers

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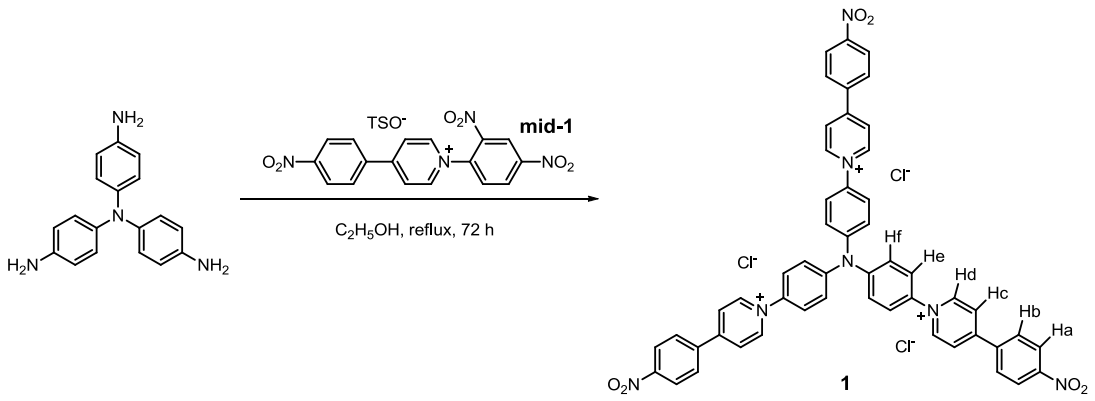
Instruments and Methods.

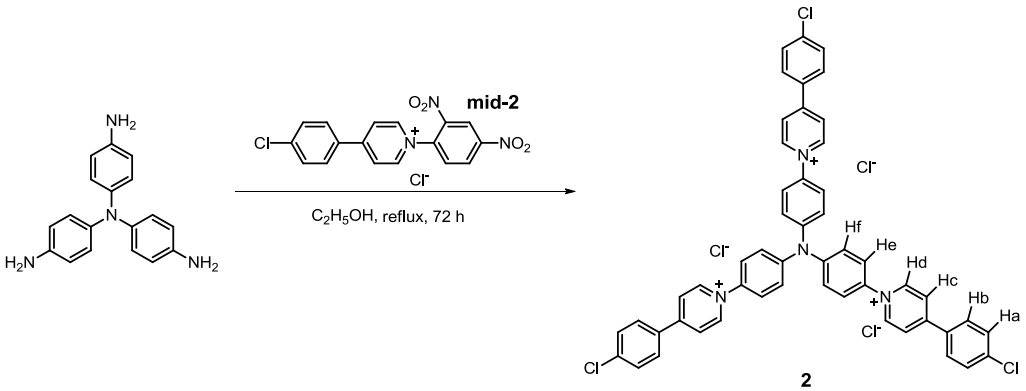
Atomic force microscopy was carried out with a Nano scope IIIa MultiMode microscope. The samples were prepared by slowly pipetting a drop of the corresponding solution on mica surface, dried under vacuum for 2 h, and then submitted to AFM characterization. Scanning electron microscopy was carried out using a Philips XL30FEG Scanning electron microscope (for field emission (FE)-SEM). The samples were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in an nitrogen atmosphere, sputtered for 200 s from a solid gold target at a current at 30 mA) before being submitted to SEM characterization. Transmission electron microscopy was performed on a Philips CM 200/FEG transmission electron microscope. The samples were prepared by carefully dropping the corresponding solution onto the carbon coated copper grid followed by removal of the solvent under vacuum. Small-angle X-ray scattering experiments were conducted on 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. The SAXS data was first corrected by subtracting a background scattering value and then desmeared. Rheological study was conducted on a Physica MCR302 (Anton Paar, Austria). UV-vis titration experiment was performed on a Perkin-Elmer 750s instrument.

Accelrys Material Studio 7.0 software package have been preformed to investigate the dynamics of hydrogels formed from **1** and CB[8]. The initial system was generated by Amorphous Cell. The Cartesian positions of the framework were fixed during the whole simulation. By using COMPASS II as the forcefield and Eward method to compute electrostatic interaction, an optimization of the geometry has been performed ahead in order to remove unphysical interactions. Subsequently, the molecular dynamics simulations were preformed under Forcite module within the NVT (Constant volume/constant temperature dynamics) ensemble at 298 K. The total simulation time was 0.25 ns with the time step of 1 fs. Moreover, 250 structures were recorded during the simulation and the last 50 structures were counted to give the density field of water.



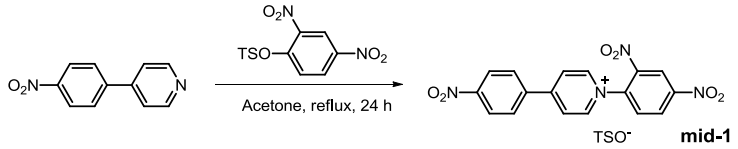
Scheme S1. The synthesis of compound **1**.

A solution of tris(4-aminophenyl)amine (100 mg, 0.34 mmol) and **mid-1** (860 mg, 2.07 mmol) in ethanol was refluxed for 72 h and then the solvent was evaporated under reduced pressure. The resulting residue was subjected to column chromatography (acetone, then acetone/EtOH 1:1, then MeOH: H_2O: saturated TsONa solution 6:3:1) to give an orange-colored solid. The solid was dissolved in a minimum amount of water. To the solution ammonium hexafluorophosphate was added until no more precipitate formed. The solid was filtrated and washed with water, and dried in vacuo and dissolved in acetone. To the solution tetrabutylammonium chloride was added and the resulting solid was filtrated, washed with acetone, and dried in vacuo to give compound **1** as a red solid (261 mg, 79.5%). mp>300 ℃ (decomp.). ^{1}H NMR (500 MHz, CD_3OD) δ 9.39 (d, J = 6.5 Hz, 6H), 8.70 (d, J = 6.5 Hz, 6H), 8.53 (d, J = 8.6 Hz, 6H), 8.35 (d, J = 8.7 Hz, 6H), 7.97 (d, J = 8.7 Hz, 6H), 7.62 (d, J = 8.7 Hz, 6H). ^{13}C NMR (125 MHz, CD_3OD) δ 154.95, 149.03, 144.58, 139.61, 138.43, 129.52, 125.90, 129.66, 125.80, 125.75, 124.34. MS(ESI): *m/z* 281.7 $[M]^{3+}$ HRMS (ESI): $[M - 3Cl^-]^{3+}$ Calcd for $C_{51}H_{36}N_7O_6^{3+}$: 280.7570. Found: 280.7573.



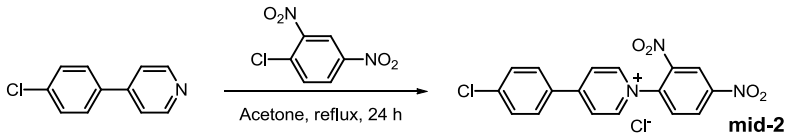
Scheme S2. The synthesis of compound **2**.

A solution of tris(4-aminophenyl)amine (100 mg, 0.34 mmol) and **mid-2** (607 mg, 1.55 mmol) in ethanol was refluxed for 72 h and then the solvent was evaporated under reduced pressure. The resulting residue was subjected to column chromatography (acetone, then acetone/EtOH 1:1, then MeOH: H_2O: saturated NH_4Cl solution 6:3:1) to give an orange-colored solid. The solid was dissolved in minimum amount of water. To the solution ammonium hexafluorophosphate was added until no more precipitate formed. The solid was filtrated and washed with water, and dried in vacuo and dissolved in acetone. To the solution tetrabutylammonium chloride was added and the resulting solid was filtrated, washed with acetone, and dried in vacuo to give compound **2** as a yellow solid (235 mg, 72.7%). mp>300 ℃ (decomp.). ^{1}H NMR (500 MHz, CD_3OD) δ 9.28 (d, J = 6.5 Hz, 6H), 8.61 (d, J = 6.5 Hz, 6H), 8.15 (d, J = 8.5 Hz, 6H), 7.95 (d, J = 8.6 Hz, 6H), 7.72 (d, J = 8.5 Hz, 6H), 7.60 (d, J = 8.6 Hz, 6H). ^{13}C NMR (126 MHz, CD_3OD) δ 155.81, 148.91, 144.20, 138.90, 138.37, 132.29, 129.84, 129.66, 125.80, 125.72, 124.70. MS(ESI): *m/z* 270.4 $[M]^{3+}$ HRMS (ESI): $[M - 3Cl^-]^{3+}$ Calcd for $C_{51}H_{36}Cl_3N_4^{3+}$: 269.7330. Found: 269.7329.



Scheme S3. The synthesis of compound **mid-1**.

A yellow solution of 4-(4-nitrophenyl) pyridine(1g, 5mmol) and 2,4-dinitrophenyl 4-methylbenzenesulfonate (2.03g, 6 mmol) in acetone(50 mL) was refluxed for 24 h to give light yellow precipitate. The precipitate was filtered and then washed by acetone to give compound **mid-1** (2.45 g, 92%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.39 (d, J = 7.1 Hz, 2H), 9.31 (d, J = 2.5 Hz, 1H), 8.95 (dd, J = 8.7, 2.5 Hz, 1H), 8.81 (d, J = 7.1 Hz, 2H), 8.61 – 8.52 (m, 2H), 8.44 – 8.38 (m, 2H), 8.34 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 157.07, 150.25, 149.68, 146.07, 143.17, 142.09, 140.25, 139.24, 138.49, 131.28, 129.79, 129.69, 128.38, 125.54, 125.44, 124.32, 121.73, 19.85. MS(ESI): *m/z* 367.2 $[M]^+$ HRMS (ESI): $[M - TSO^-]^+$ Calcd for $C_{17}H_{11}N_4O_6^+$: 367.0673. Found: 367.0677.



Scheme S4. The synthesis of compound **mid-2**

A yellow solution of 4-(4-chlorophenyl) pyridine (1g, 5.27 mmol) and 1-chloro-2, 4-dinitrobenzene (1.28g, 6.33 mmol) in acetone (50 mL) was refluxed for 24 h to give light yellow precipitate. The precipitate was filtered and then washed by acetone to give compound **2** (1.91 g, 92%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.31 (d, J = 2.5 Hz, 1H), 9.28 (d, J = 7.1 Hz, 2H), 8.95 (dd, J = 8.7, 2.5 Hz, 1H), 8.72 (d, J = 7.1 Hz, 2H), 8.34 (d, J = 8.7 Hz, 1H), 8.24 – 8.15 (m, 2H), 7.80 – 7.71 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 158.00, 149.69, 145.56, 143.31, 139.55, 138.53, 131.96, 131.28, 129.95, 129.93, 129.68, 124.36, 121.76. MS(ESI): *m/z* 356.2 $[M]^+$ HRMS (ESI): $[M- Cl^-]^+$ Calcd for $C_{17}H_{11}ClN_3O_4^+$: 356.0433. Found: 356.0439.

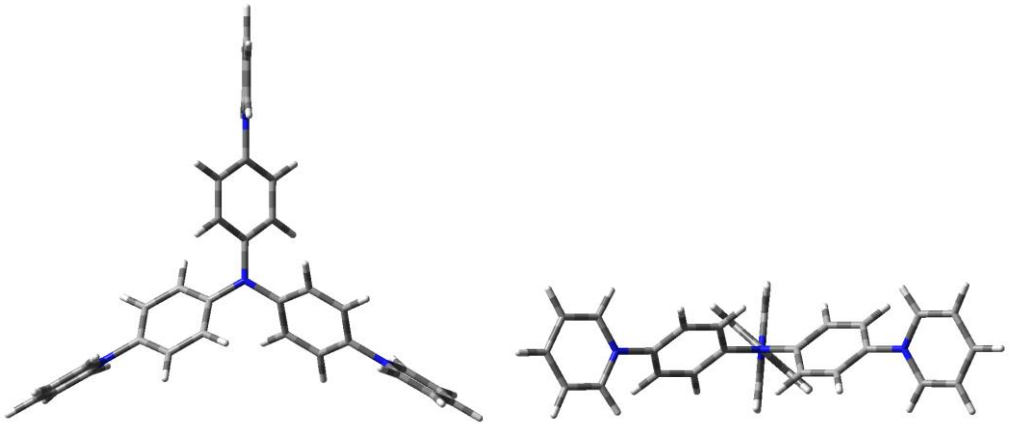


Fig. S1 The molecular optimization of the central part of **1** and **2** at B3LYP/6-31G level, indicating the coplanarity of the three N-Aryl bonds.

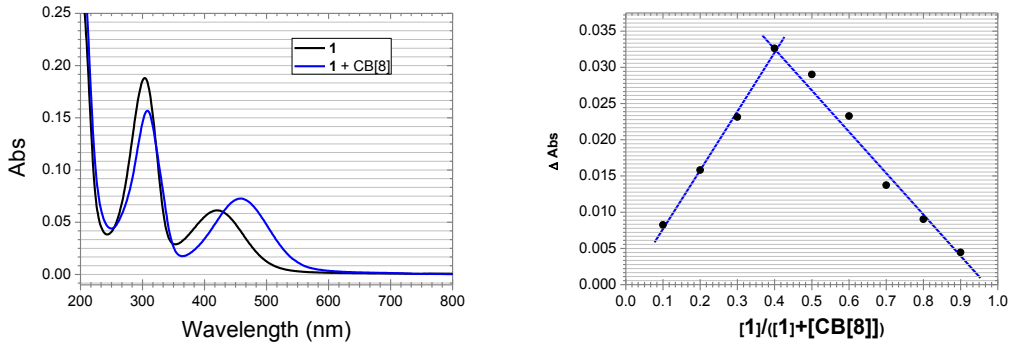


Fig. S2 UV-vis spectra of **1** (8.0 μM) without and with CB[8] (12 μM) in a sodium phosphate buffer (0.10 M， pH 7.0) at 25 ^{o}C (left), and Job's plot indicating a 2:3 stoichiometery for **1** and CB[8] (right). The total concentration used for generating the Job's plot was 20.0 μM.

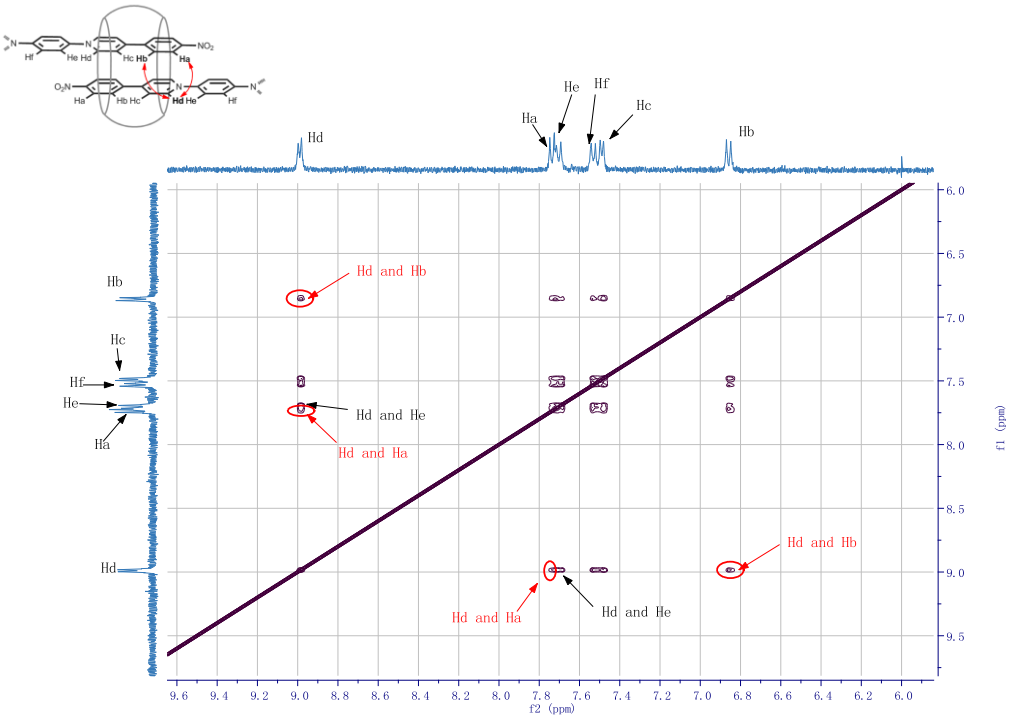


Fig. S3 2D ^{1}H NMR NOESY spectrum (400 MHz, 293 K) of a solution of **1** + CB[8] (2:3) in D_2O at 25 ^{o}C. The concentration for **1** was 0.50 mM.

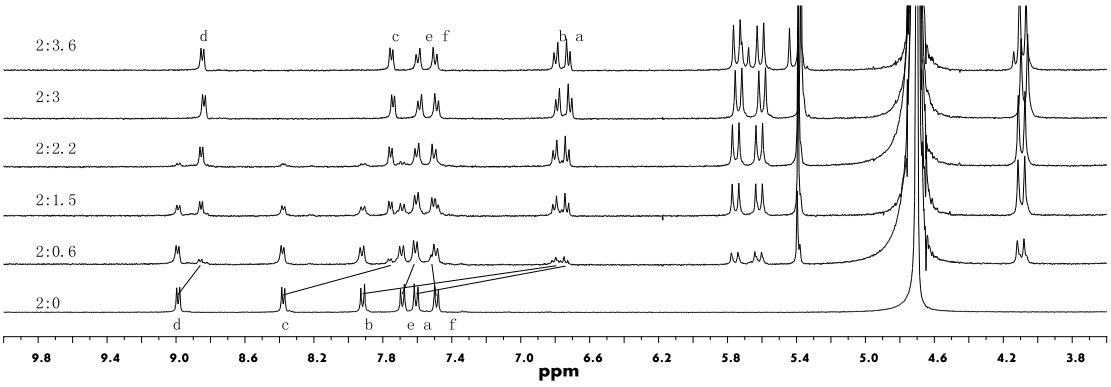


Fig. S4 ^{1}H NMR spectra (500 MHz) of mixtures of **2** and CB[8] at different ratios in D_2O at 25 ^{o}C.

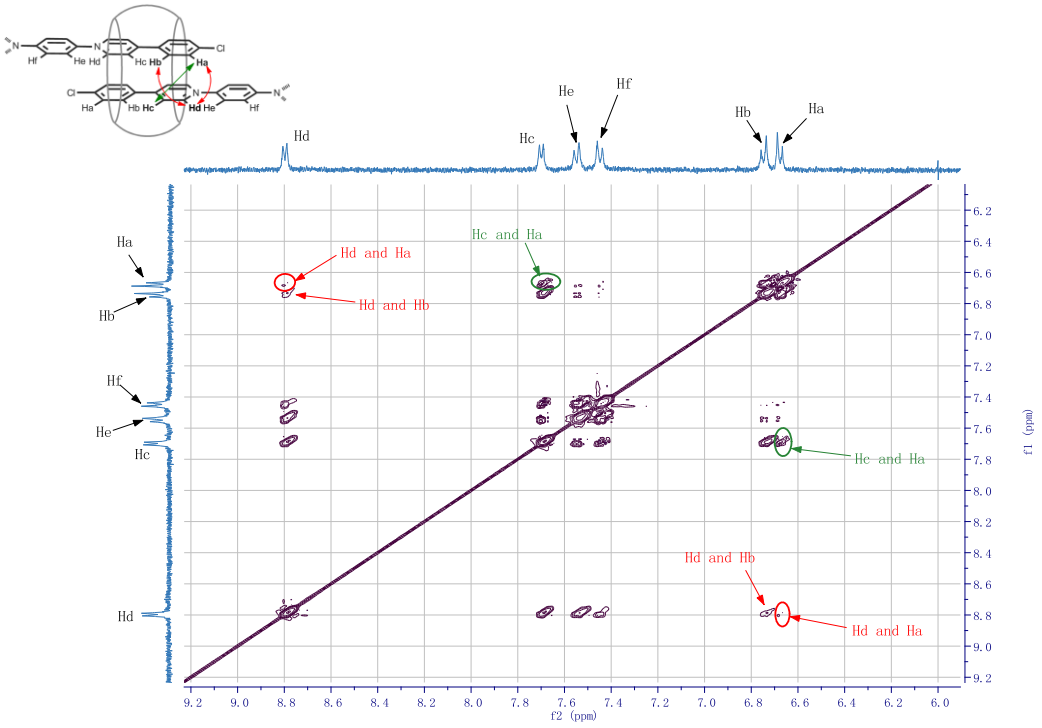


Fig. S5 2D ^{1}H NMR NOESY spectrum (400 MHz, 293 K) of a solution of **2** + CB[8] (2:3) in D_2O at 25 ^{o}C. The concentration for **2** was 0.50 mM.

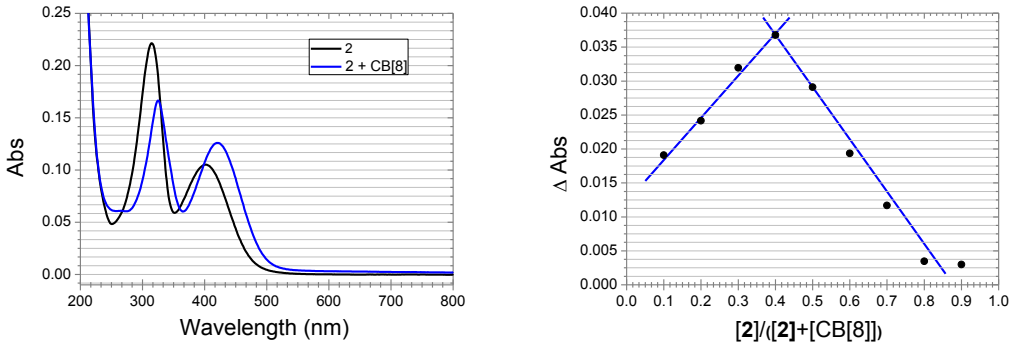


Fig. S6 UV-vis spectra of **2** (8.0 μM) without and with CB[8] (12.0 μM) in a sodium phosphate buffer (0.1 M， pH 7.0) at 25 ^{o}C (left), and Job's plot indicating a 2:3 stoichiometery for **2** and CB[8] (right). The total concentration used for generating the Job's plot was 20.0 μM.

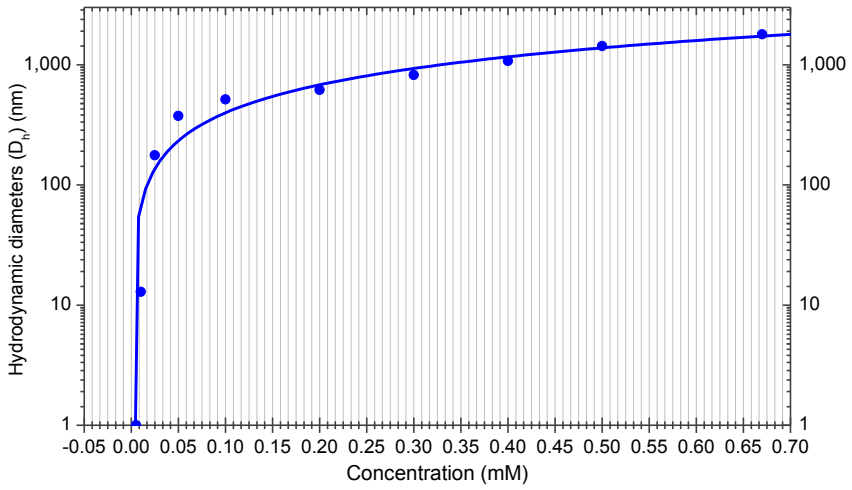


Fig. S7 DLS results of the mixture of **1** and CB[8] (2:3) in water at different concentrations 25 ° C. The concentration varies from 0.005 to 0.67 mM for **1**.

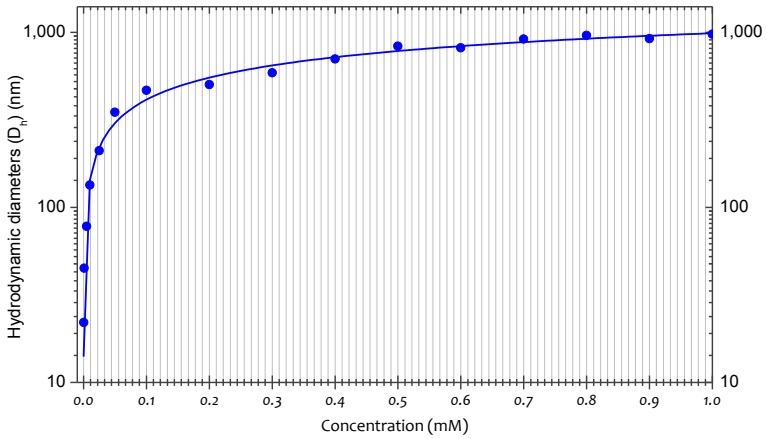


Fig. S8 DLS results of the mixture of **2** and CB[8] (2:3) in water at different concentrations 25 °C. The concentration varies from 0.0005 to 1.0 mM for **2**.

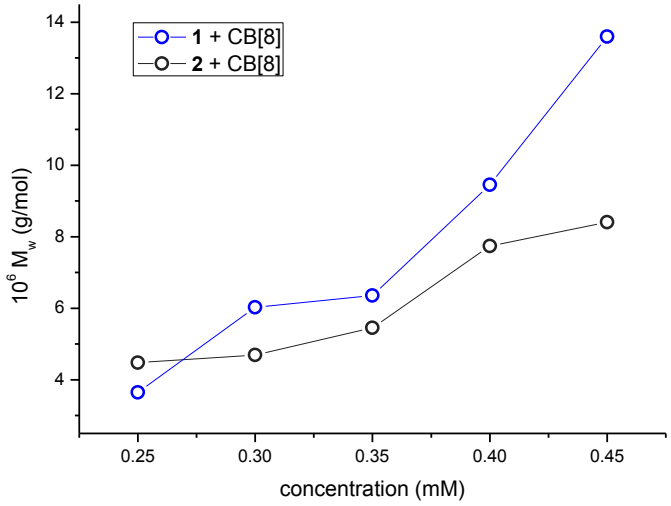


Fig. S9 SLS results of the apparent molecular weights of the supramolecular polymers prepared from (**1**+CB[8]) (blue) and (**2**+CB[8]) (black) at different concentrations in water at 25 ^{o}C.

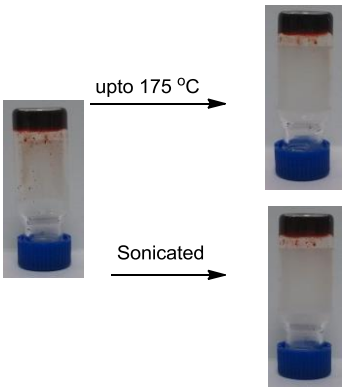


Fig. S10 Photographs of hydrogel formed by (**1**+ CB[8]).

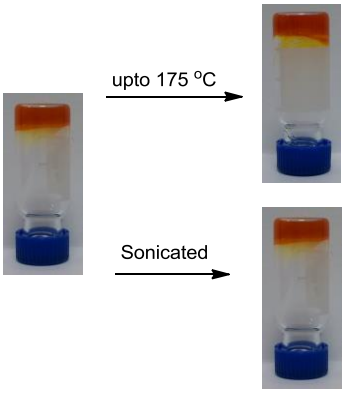


Fig. S11 Photographs of hydrogel formed by (**2** + CB[8]).

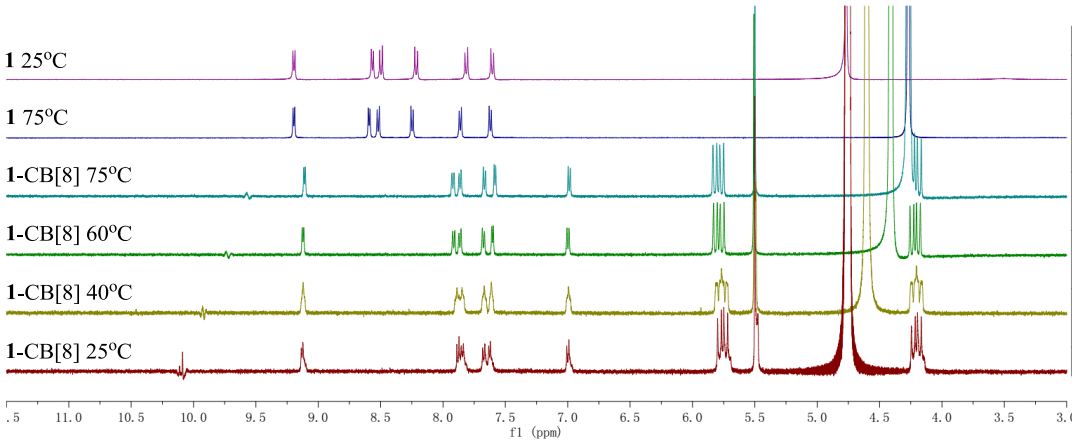


Fig. S12 ^{1}H NMR spectra (500 MHz) of **1**−CB[8] (2:3) and **1** in D_2O at different temperatures. The concentration for **1** was 0.50 mM. The spectra were calibrated by the temperature dependence of HDO chemical shifts reported by H. E. Gottlieb et al. *(J. Org. Chem.* **1997**, *61*, 7512-7515.).

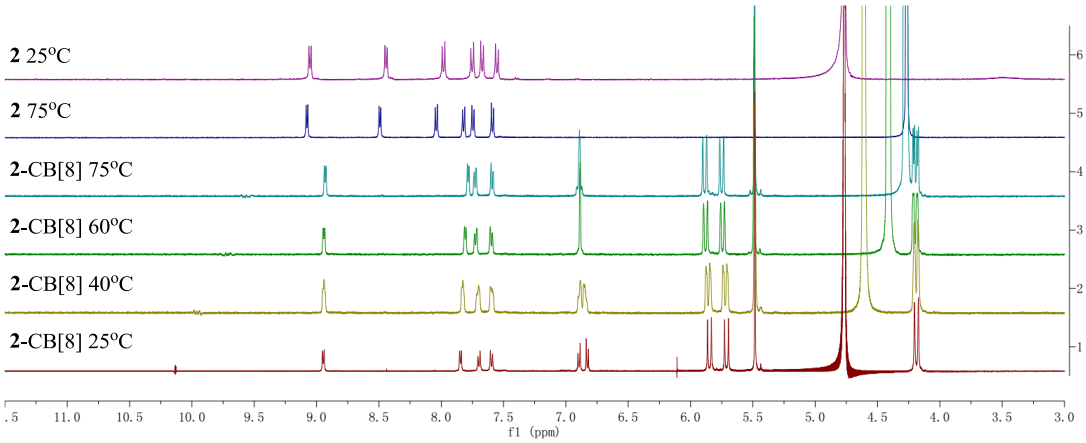


Fig. S13 ^{1}H NMR spectra (500 MHz) of **2**−CB[8] (2:3) and **2** in D_2O at different temperatures. The concentration for **2**was 0.50 mM. The spectra were calibrated by the temperature dependence of HDO chemical shifts reported by H. E. Gottlieb et al. *(J. Org. Chem.* **1997**, *61*, 7512-7515.).

The method of determining the apparent binding constants (K_a)

The apparent binding constants of the two SPs at different temperature were obtained by temperature variable UV spectra. A series of absorbance values of maximum absorption peak were recorded during the titration of CB[8] to **1** or **2** of constant concentration, giving a plot of concentration of CB[8] ($C_{CB[8]}$) to Absorbance. The K_a was obtained by fitting the curve by the following function:

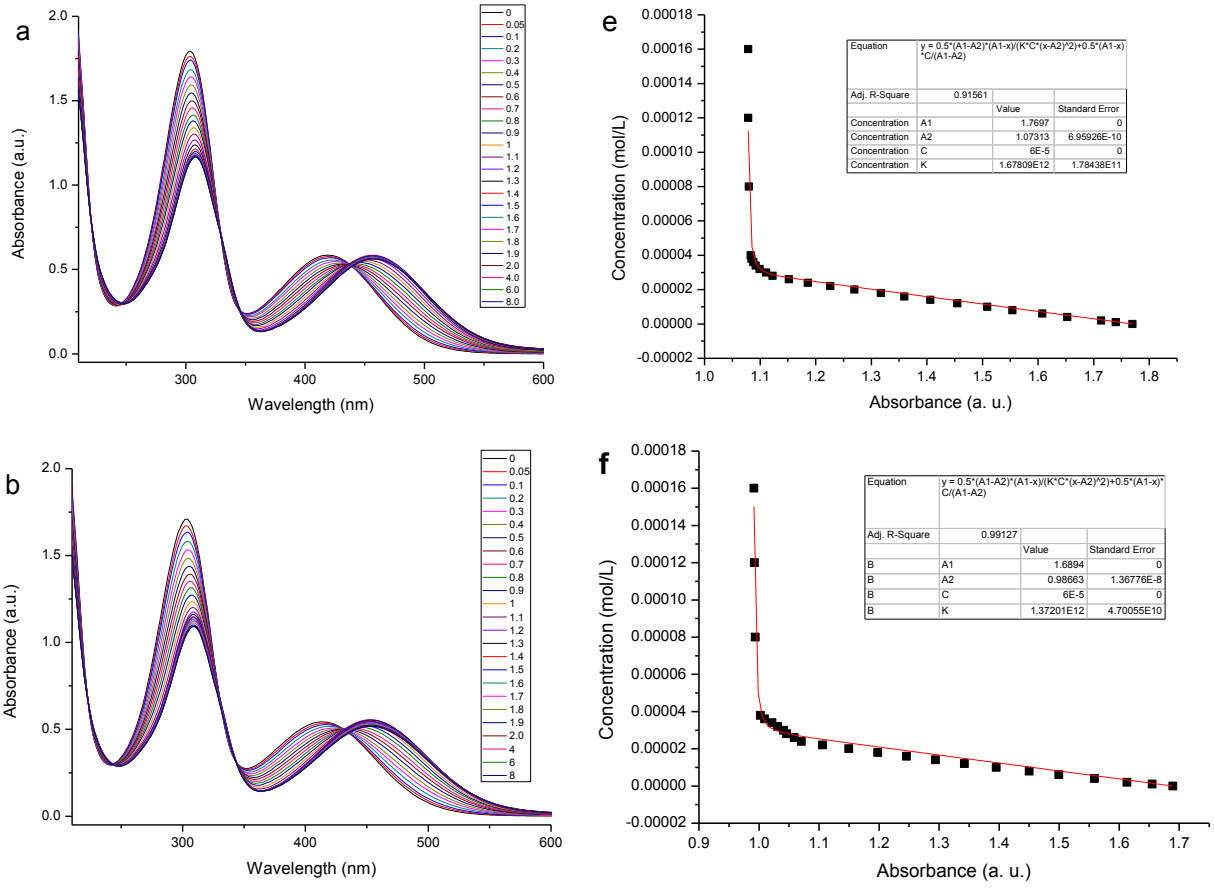
$$C_{CB[8]} = \frac{(A_1 - A_2)\cdot(A_1 - A)}{2K_a[G]_0(A - A_2)^2} + \frac{[G]_0(A_1 - A)}{2(A_1 - A_2)} \quad (1)$$

$[G]_0$ The constant concentration of **1** or **2**

A_1 The initial absorbance of **1** or **2** before CB[8] was added

A_2 The ultimate absorbance of **1** or **2** after excess of CB[8] was added

A The absorbance when CB[8] was being added



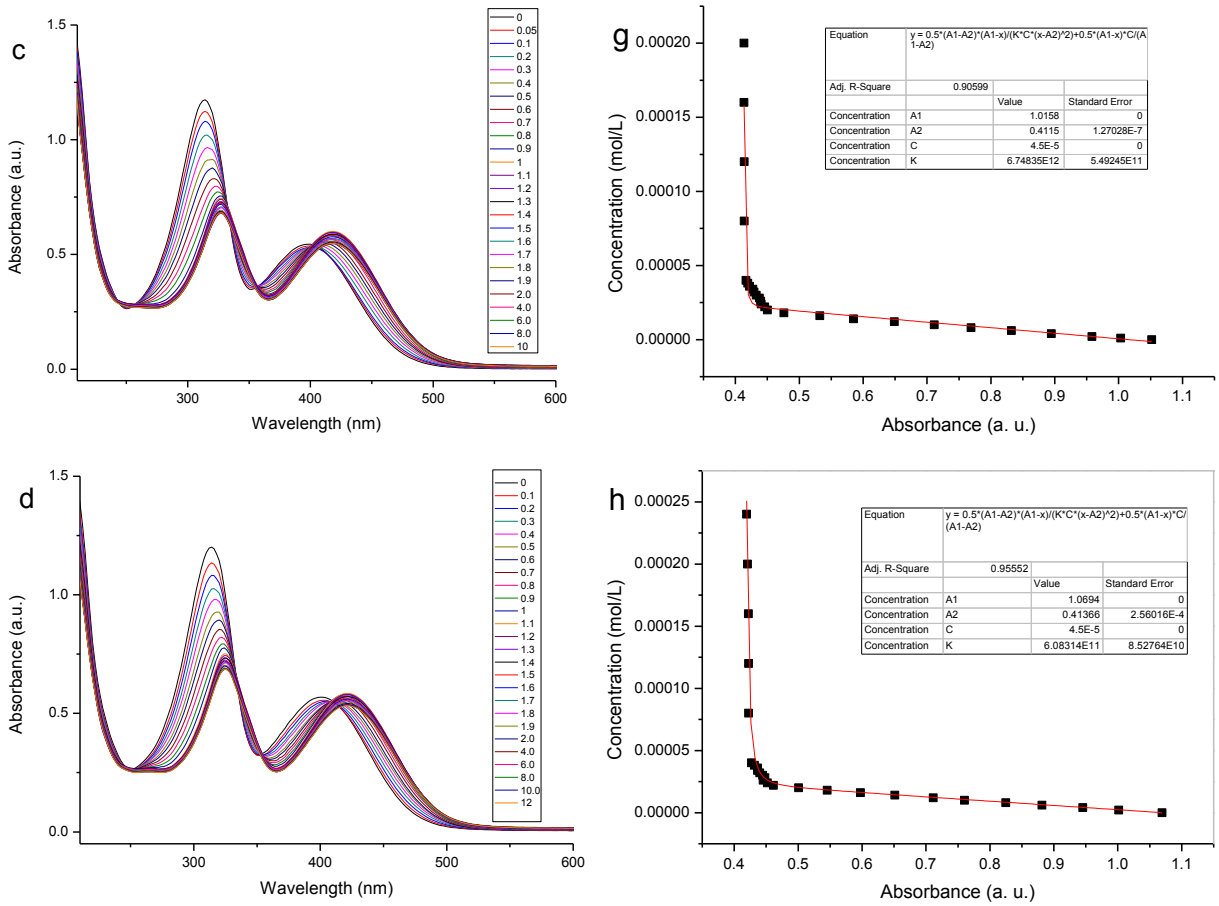


Fig. S14 The UV-vis spectra of (a) **1** upon the addition of CB[8] at 25 ^{o}C, (b) **1** upon the addition of CB[8] at 75 ^{o}C, (c) **2** upon the addition of CB[8] at 25 ^{o}C, and (d) **2** upon the addition of CB[8] at 75 ^{o}C. And Plots of absorbance changes and nonlinear fitting curves of (e) **1**-CB[8] at 25 ^{o}C, (f) **1**-CB[8] at 75 ^{o}C, (g) **2**-CB[8] at 25 ^{o}C, and (h) **2**-CB[8] at 75 ^{o}C. The absorbance at 300 and 304 nm was used for **1**-CB[8] and **2**-CB[8], respectively.

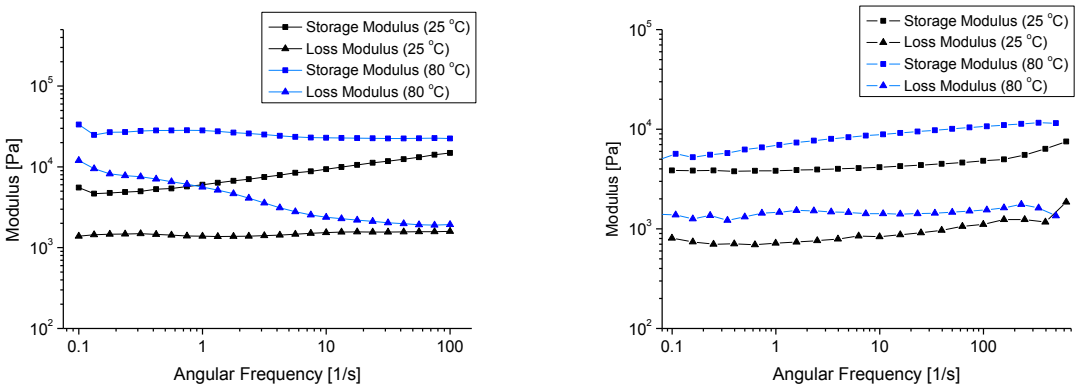


Fig. S15 Left: Storage modulus (G′) and loss modulus (G″) versus scanning frequency (ω) for the sample prepared from **1**−CB[8] (2:3) in water (T = 20 ℃ and T = 80 ℃). Right: Storage modulus (G′) and loss modulus (G″) versus scanning frequency (ω) for the sample made from **2**−CB[8] (2:3) in water (T = 20 ℃ and T = 80 ℃). The concentration for **1** and **2** was 5.0 mM.

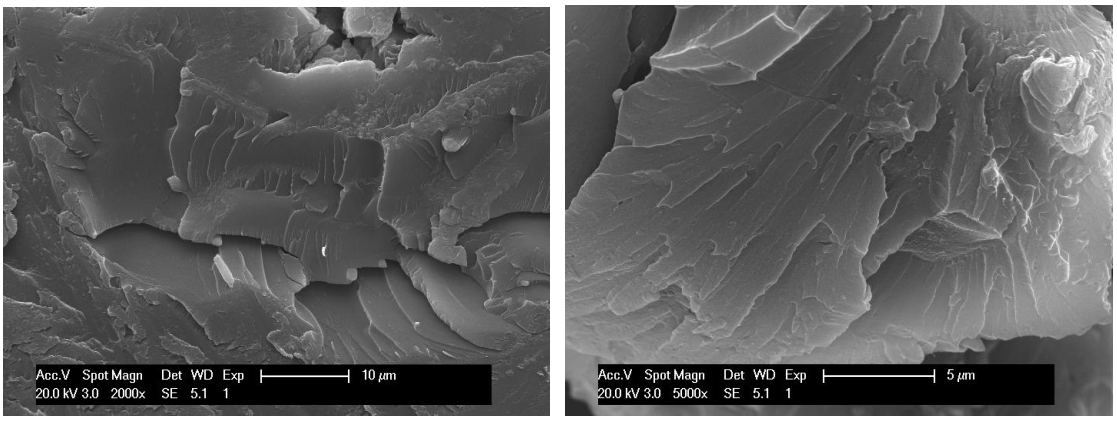


Fig. S16 Left: SEM image of the xerogel prepared from **1** and CB[8]; Right: SEM image of the xerogel prepared from **2** and CB[8].

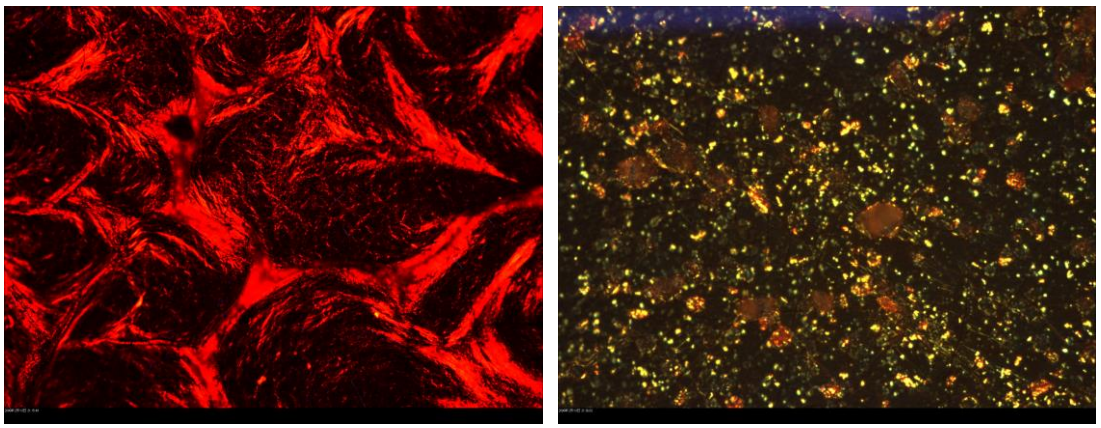


Fig. S17 Left: POM image of the xerogel prepared from **1** and CB[8]; Right: POM image of the xerogel prepared from **2** and CB[8].

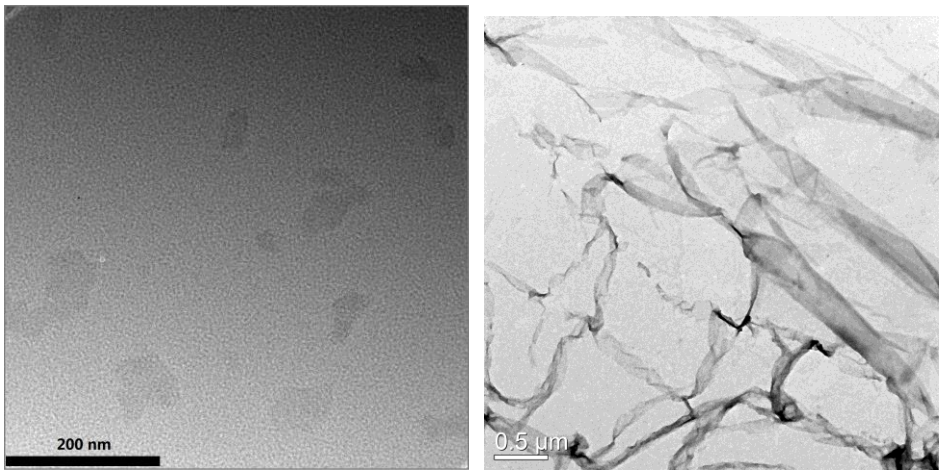


Fig. S18 Left: TEM image of the sample obtained by evaporating the solution of **2** (0.05 mM) and CB[8] (0.075 mM) in water under reduced pressure. Right: TEM image of the sample obtained by evaporating the solution of **2** (0.25 mM) and CB[8] (0.375 mM) in water under reduced pressure.

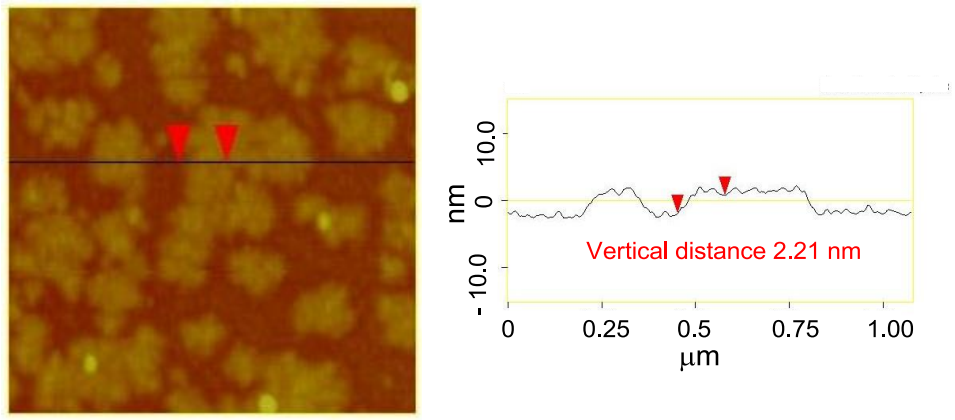


Fig. S19 Tapping-mode AFM image and cross-section analysis of the sample of [**2** + CB[8] (2:3)]. The concentration was 0.05 mM for **2**.

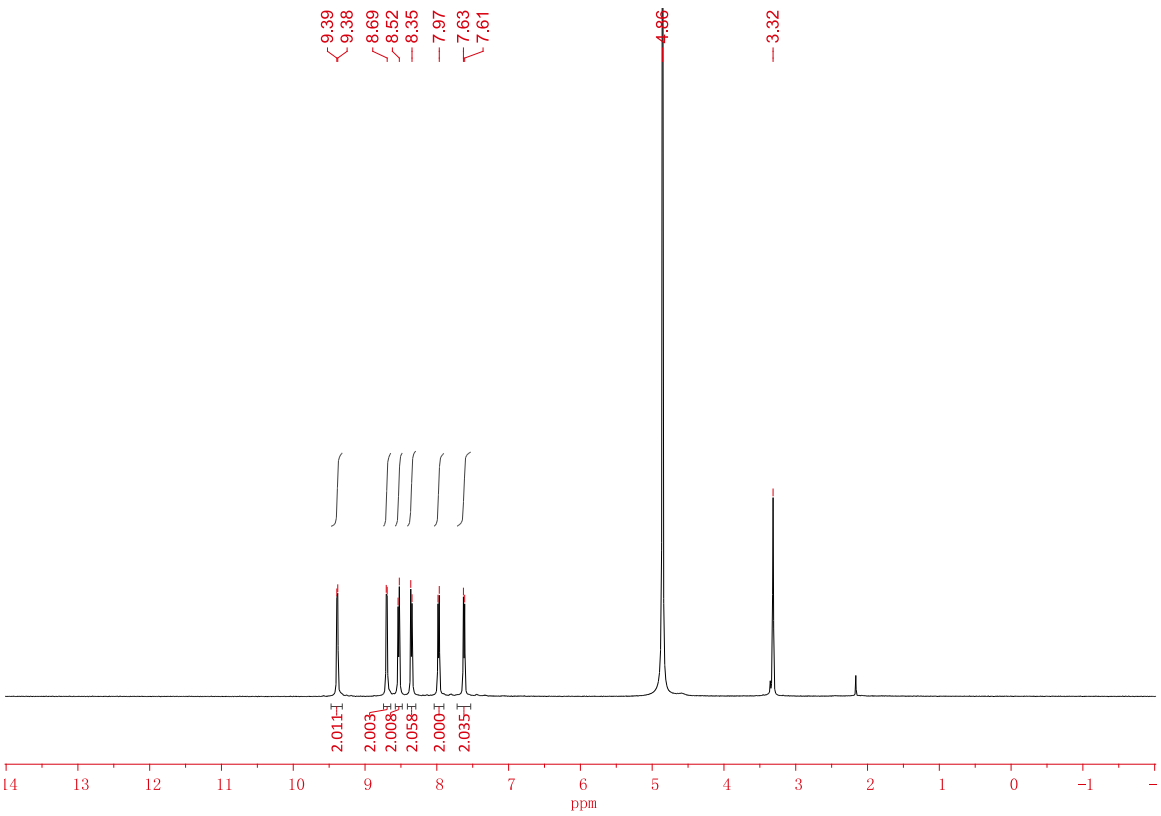


Fig. S20 ^{1}H NMR Spectrum (500 MHz, CD_3OD) of compound **1**.

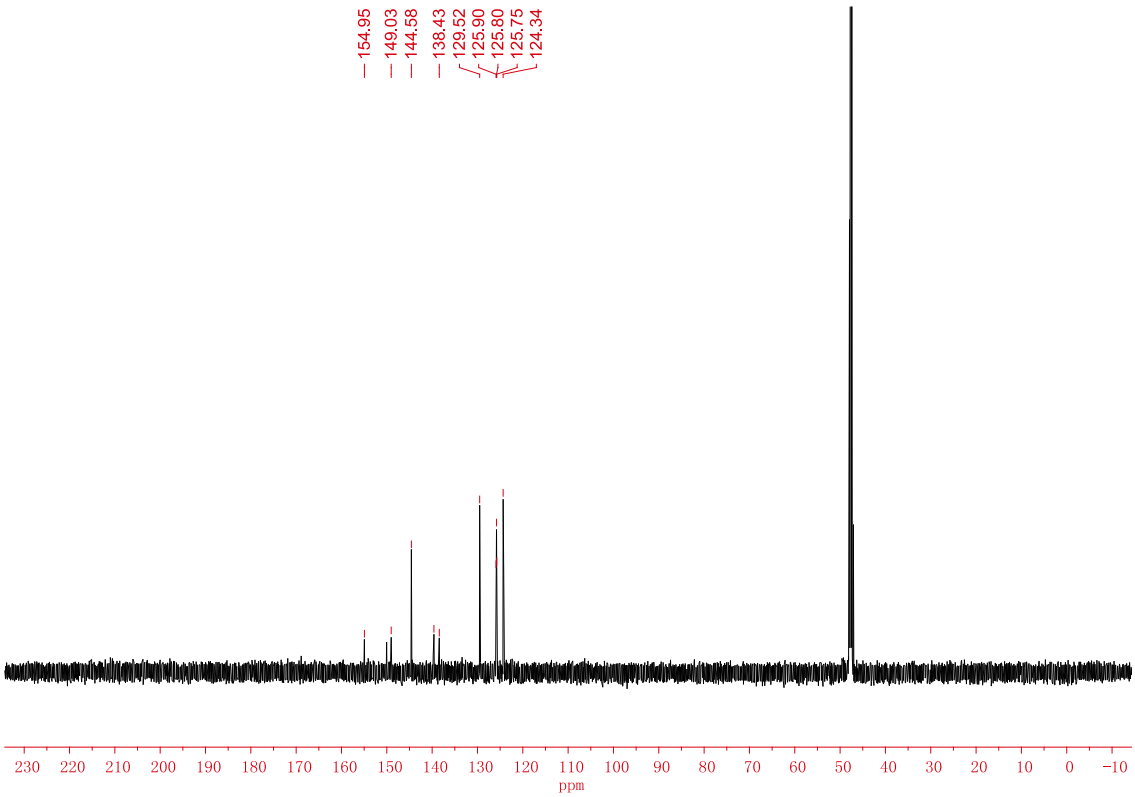


Fig. S21 ^{13}C NMR Spectrum (125 MHz, CD_3OD) of compound **1**.

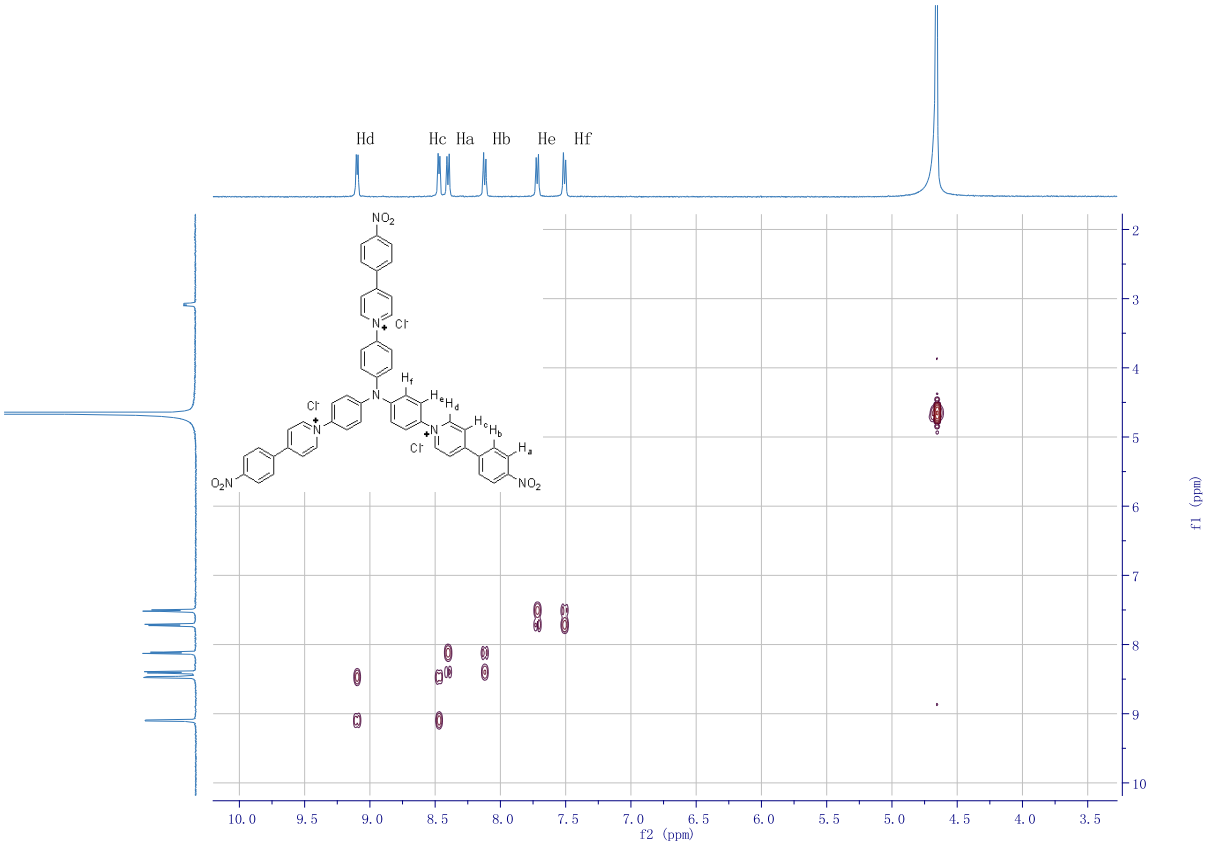


Fig. 22 2D ^{1}H NMR COSY spectrum (500 MHz, 293 K) of **1** (0.5 mM) in D_2O at 25 ^{o}C.

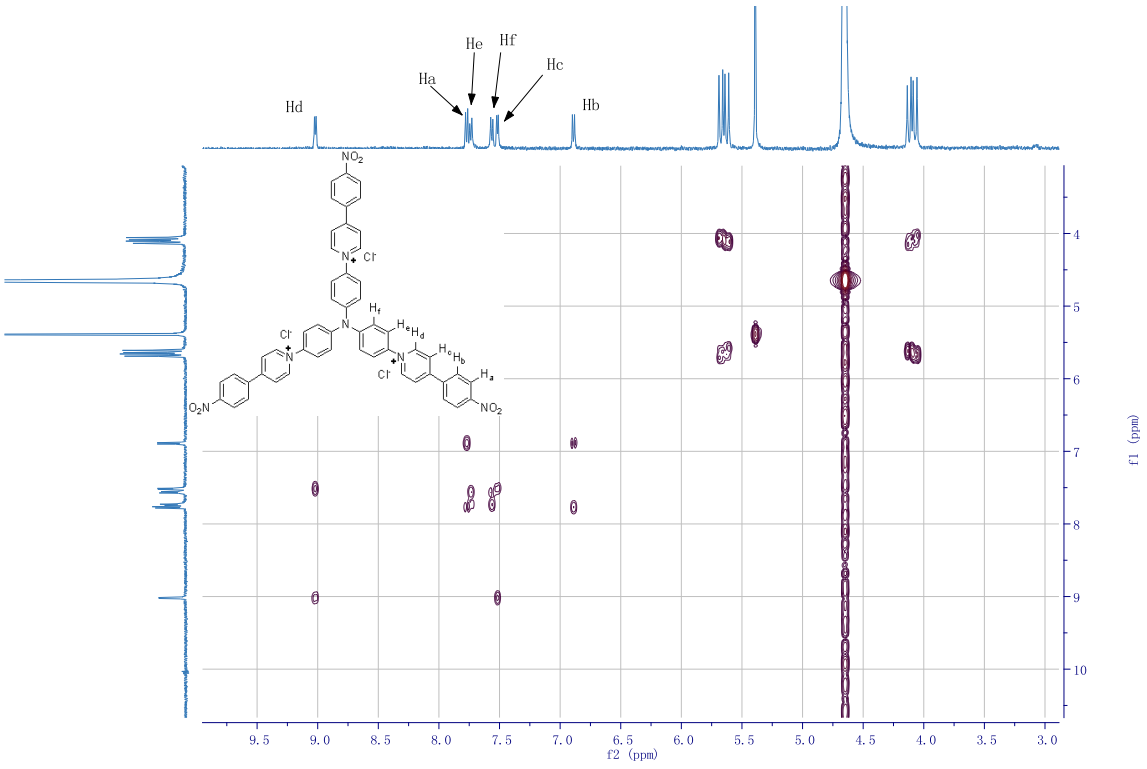


Fig. 23 2D ^{1}H NMR COSY spectrum (400 MHz, 293 K) of the 1:1.5 solution of **1** (0.5 mM) and CB[8] in D_2O at 25 ^{o}C.

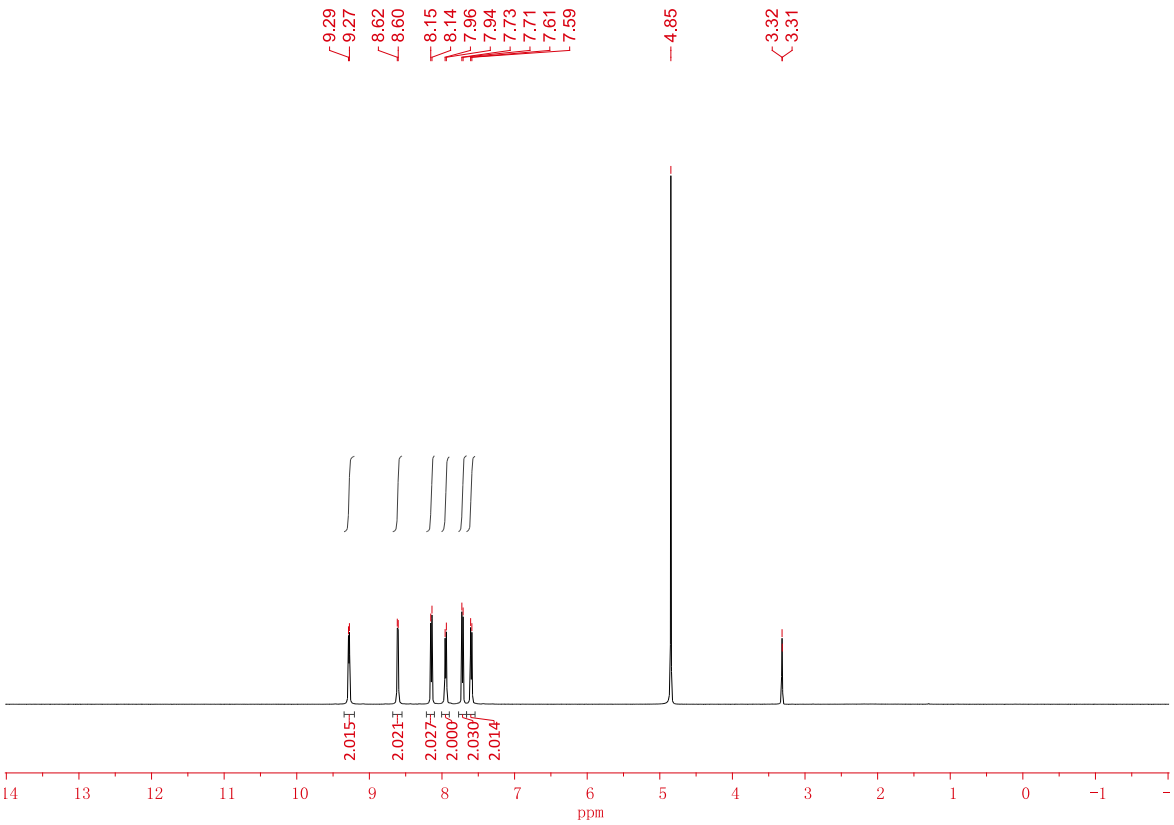


Fig. S24 ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **2**.

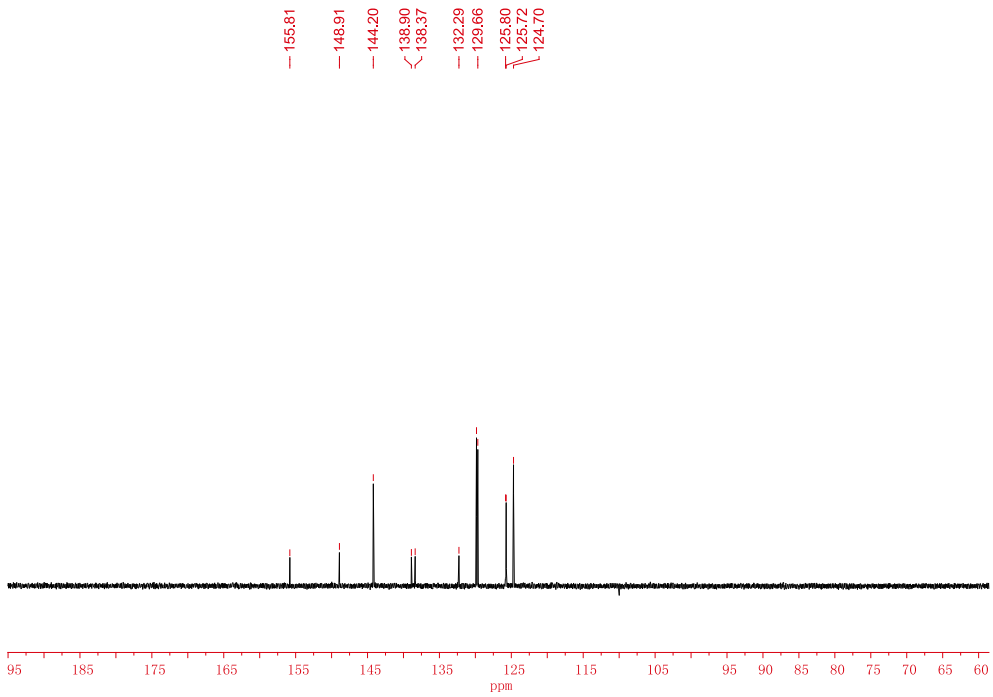


Fig. S25 ^{13}C NMR spectrum (125 MHz, CD_3OD) of compound **2**.

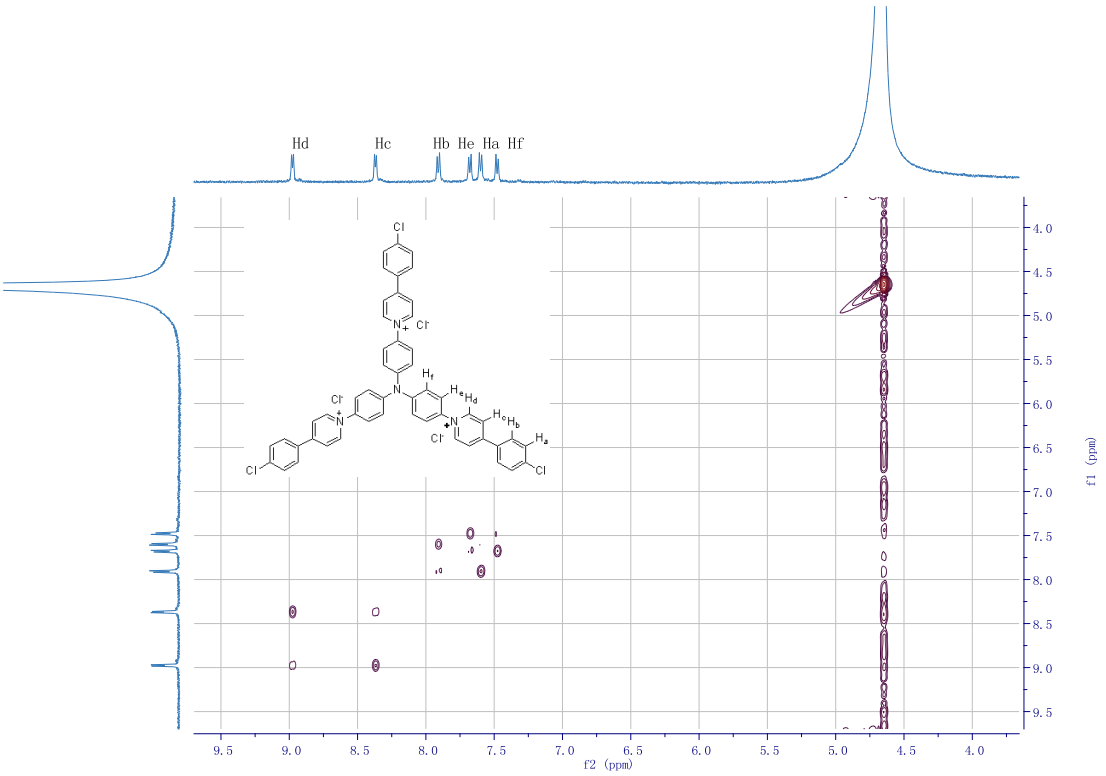


Fig. 26 2D ^{1}H NMR COSY spectrum (500 MHz, 293 K) of **2** (0.5 mM) in D_2O at 25 ^{o}C.

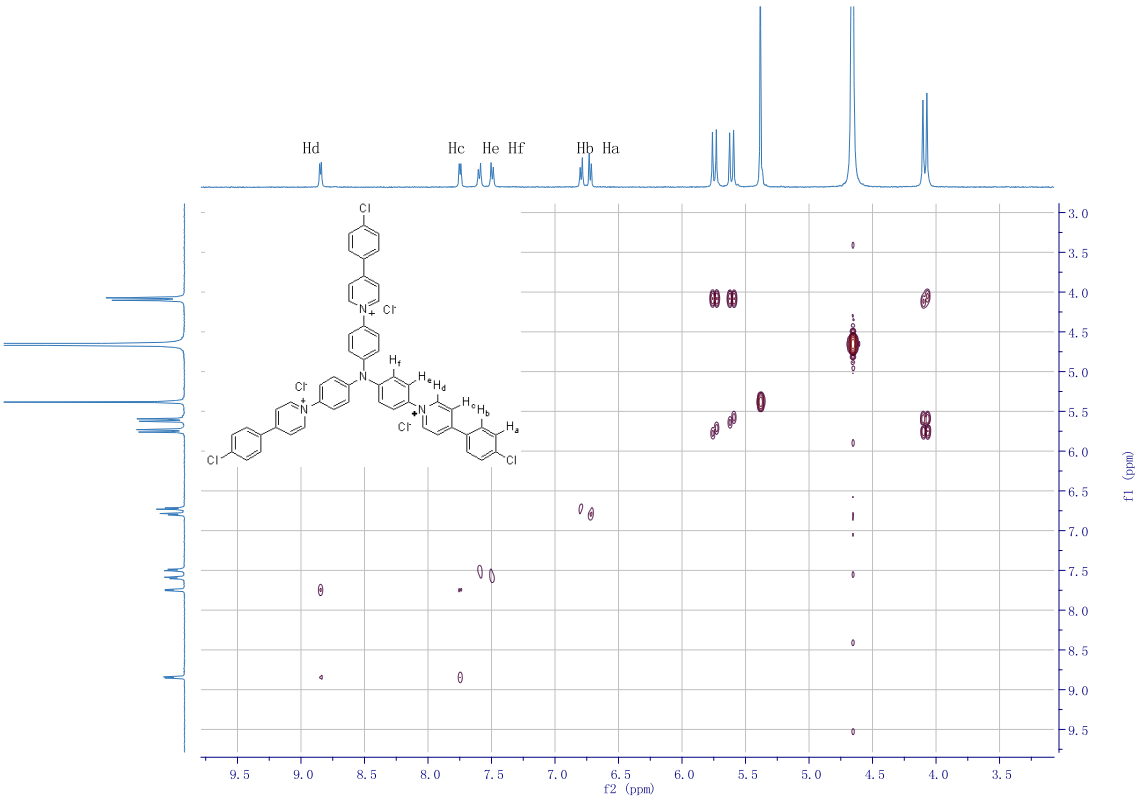


Fig. 27 2D ^{1}H NMR COSY spectrum (400 MHz, 293 K) of the 1:1.5 solution of **2** (0.5 mM) and CB[8] in D_2O at 25 ^{o}C.

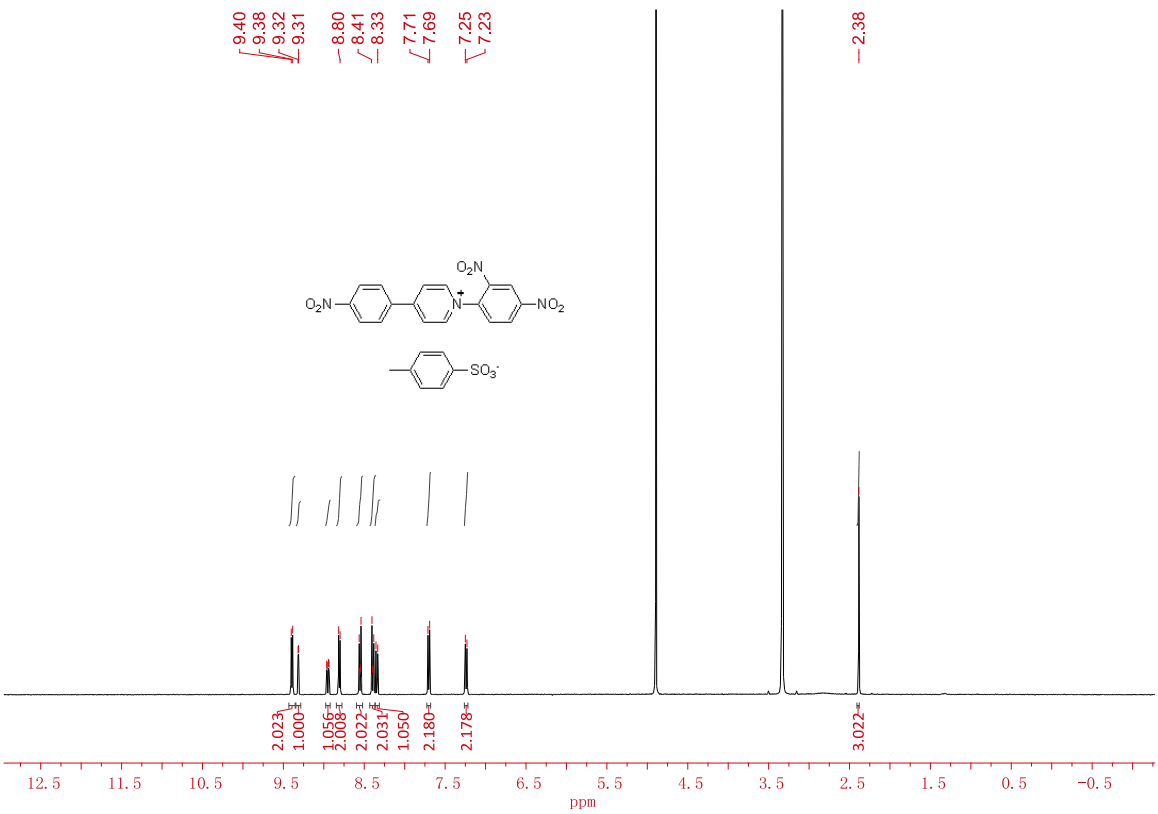


Fig. S28 ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **mid-1**.

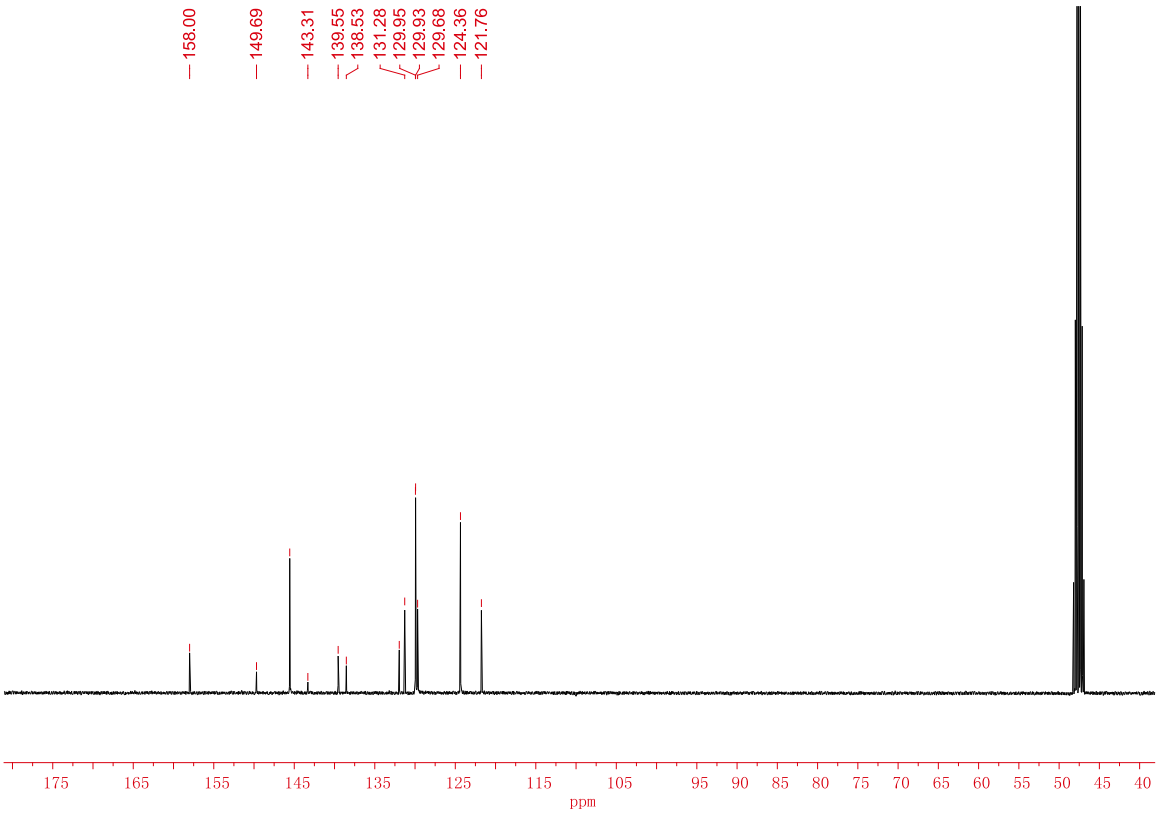


Fig. S29 ^{13}C NMR spectrum (100 MHz, CD_3OD) of compound **mid-1**.

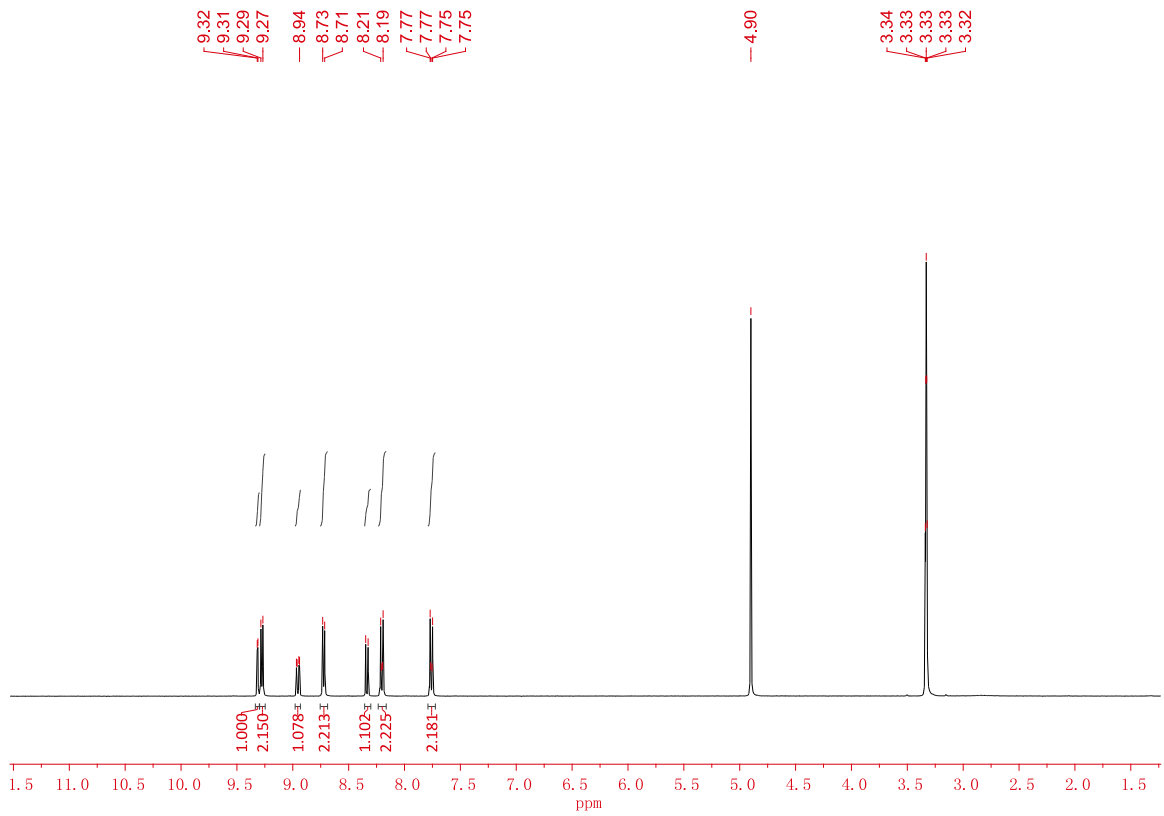


Fig. S30 ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **mid-2**.

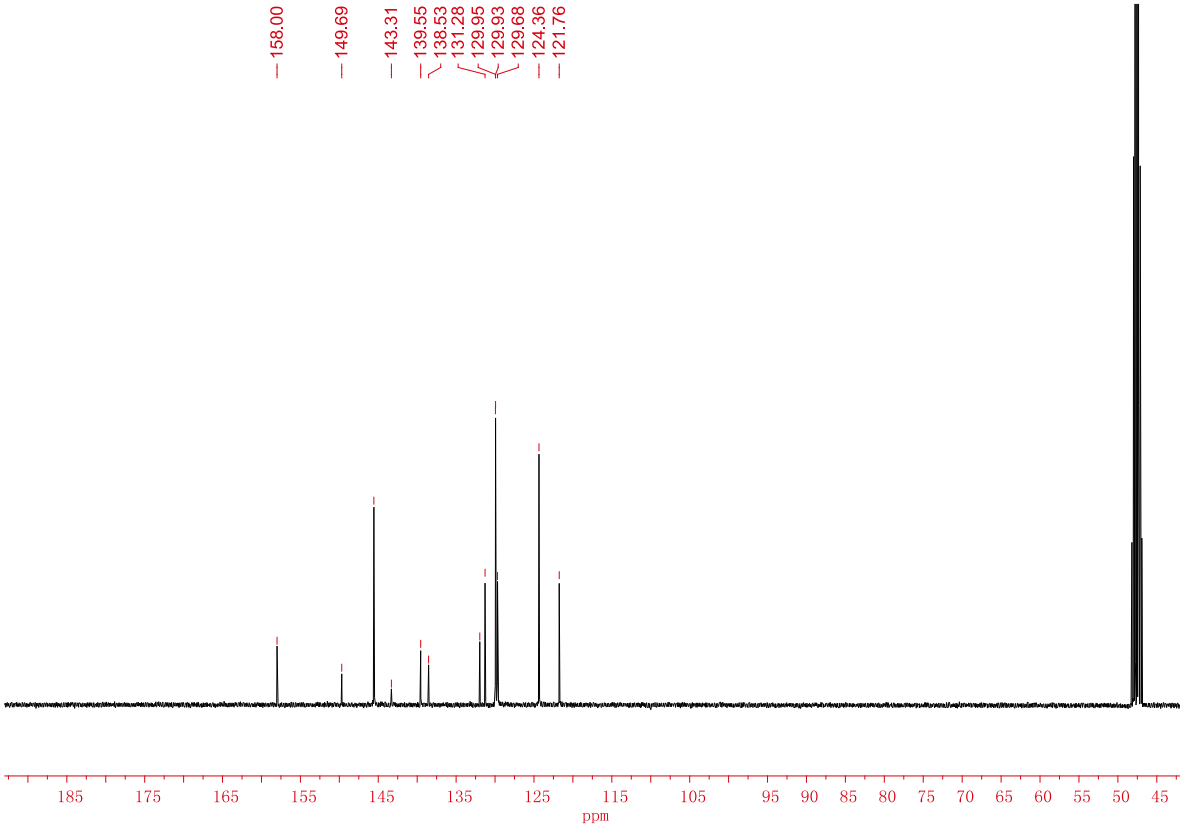


Fig. S31 ^{13}C NMR spectrum (100 MHz, CD_3OD) of compound **mid-2**.