Electronic Supplementary Information

Fluorescence enhancement through the formation of a single-layer two-dimensional supramolecular organic framework and its application in highly selective recognition of picric acid

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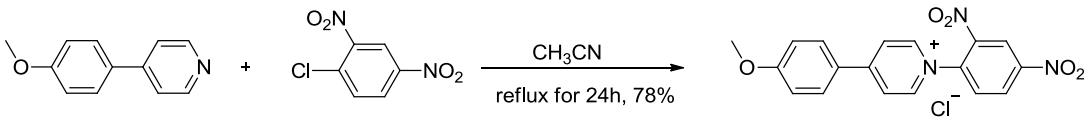
Section 1: Materials and General Methods

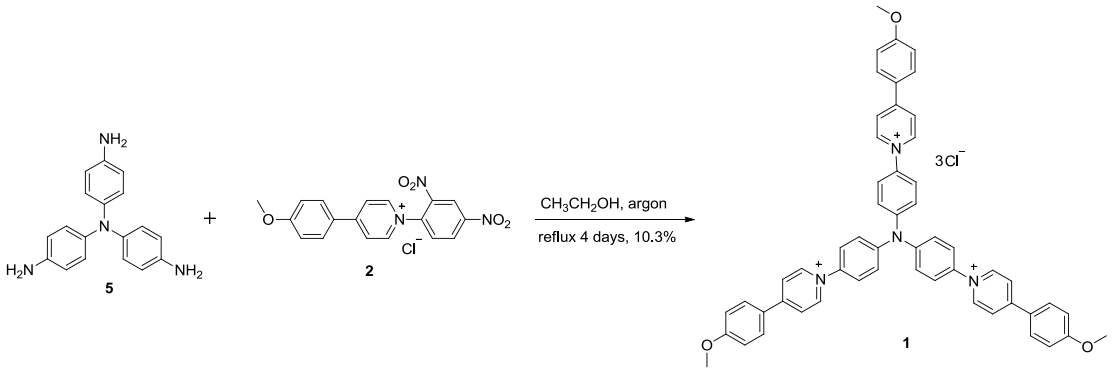
All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Compound **3** were synthesized according to the literature.[1] ^{1}H and ^{13}C NMR, NOESY, DOSY and COSY NMR spectra were recorded on a Bruker Avance DMX 400 or a 500 MHz Agilent spectrometer at 25^{o}C. UV-Vis absorption spectra were recorded with a Unico 4802 UV-vis double beam spectrophotometer at 25 ^{o}C. Fluorescence emission spectra were recorded with a F-4600 FL spectrophotometer at 25 ^{o}C. Dynamic light scattering (DLS) experiments were performed on a Zetasizer Nano ZS90 light-scattering instrument (Malvern, UK) at 25 ^{o}C. 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.

Section 2. Synthesis and Characterizations



3 4 2

Compound 2: Compounds **3** (6.1 g, 33 mmol) and **4** (10 g, 49.5 mmol) were dissolved in anhydrous CH_3CN (150 mL) and refluxed for 24 hours. The resulting mixture was cooled to room temperature and filtered. The filter cake was washed with acetone (100 ml × 3) and dried to give compound **2** as a yellow solid (10 g, 78%). ^{1}H NMR (500 MHz, CD_3OD): δ 9.27 (d, J = 2.5 Hz, 1 H), 9.09 (d, J = 7.3 Hz, 2 H), 8.91 (dd, J_1 = 8.7 Hz, J_2 = 2.5 Hz, 1 H), 8.61 (d, J = 7.2 Hz, 2 H), 8.32 (d, J = 8.6 Hz, 1 H), 8.22 (d, J = 9.0 Hz, 2 H), 7.25 (d, J = 8.9 Hz, 2 H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 164.70, 158.43, 149.59, 144.78, 143.48, 138.66, 131.32, 130.54, 129.64, 124.97, 122.71, 121.77, 115.34, 54.99. MS (ESI): *m/z* 352.2 $[M\text{-}Cl]^+$. HRMS (ESI) Calcd. for $C_{18}H_{14}N_3O_5$ $[M\text{-}Cl]^+$: 352.0928. Found: 352.0930.



Compound 1: Compounds **2** (0.8 g, 2.1 mmol) and **5** (0.1 g, 0.34 mmol) were dissolved in anhydrous ethanol (10 mL) and sealed in a schlenk tube under argon atmosphere. The mixture was refluxed for 4 days. After being cooled to room temperature, the solvent was evaporated and the resulting residue was purified by flash column chromatography (acetone, acetone/methanol = 1:1, then to methanol/H_2O/ NH_4Cl (saturated aq.) = 6:3:1 gradually). An orange solid was obtained and it was further dissolved in a small amount of water and then filtered (so as to remove excess NH_4Cl), The filter cake was dried to afford compound **1** as a red solid (32 mg, 10.3%). ^{1}H NMR (400 MHz, CD_3OD): δ 9.00 (d, *J* = 8.0 Hz, 6 H), 8.46 (d, *J* = 8.0 Hz, 6 H), 8.10 (d, *J* = 8.1 Hz, 6 H), 7.79 (d, *J* = 8.0 Hz, 6 H), 7.55 (d, *J* = 8.1 Hz, 6 H), 7.25 (d, *J* = 8.0 Hz, 6H), 3.95 (s, 9 H). ^{13}C NMR (125 MHz, CD_3OD): δ 164.15, 156.43, 148.76, 143.54, 138.35, 130.04, 125.67, 125.28, 124.39, 123.19, 115.21, 54.91. MS (ESI): *m/z* 266.1 $[M-3Cl]^{3+}$. HRMS (ESI) Calcd. for $C_{54}H_{45}N_4O_3$ $[M-3Cl]^{3+}$: 265.7825. Found: 265.7826.

Reference

1 Y. Zhang, T.-Y. Zhou, K.-D. Zhang, J.-L. Dai, Y.-Y. Zhu and X. Zhao, *Chem. Asian J.*, 2014, **9**, 1530.2

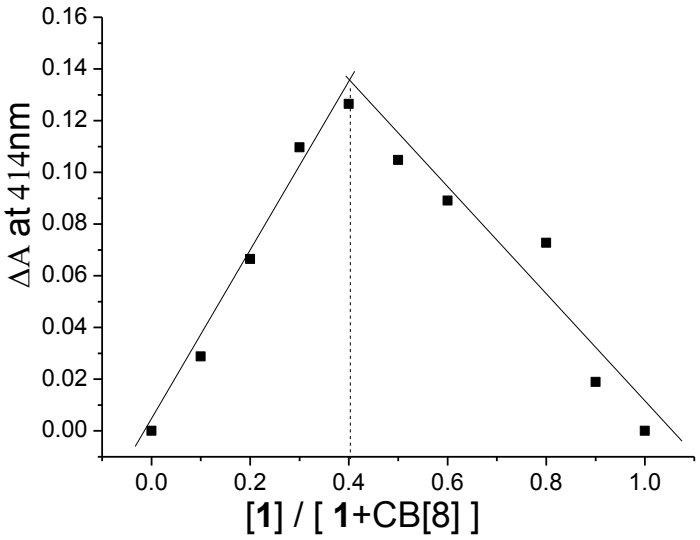


Figure S1 Job's plot obtained by recording the absorbance at 414 nm for the solution of **1** and CB[8] in a binary solvent of H_2O/CH_3OH(17:3) at 25 ^oC, ([**1**] + [CB[8]) = 2.0 × 10^{-5} M), confirming the 2:3 stoichiometry of their complex.

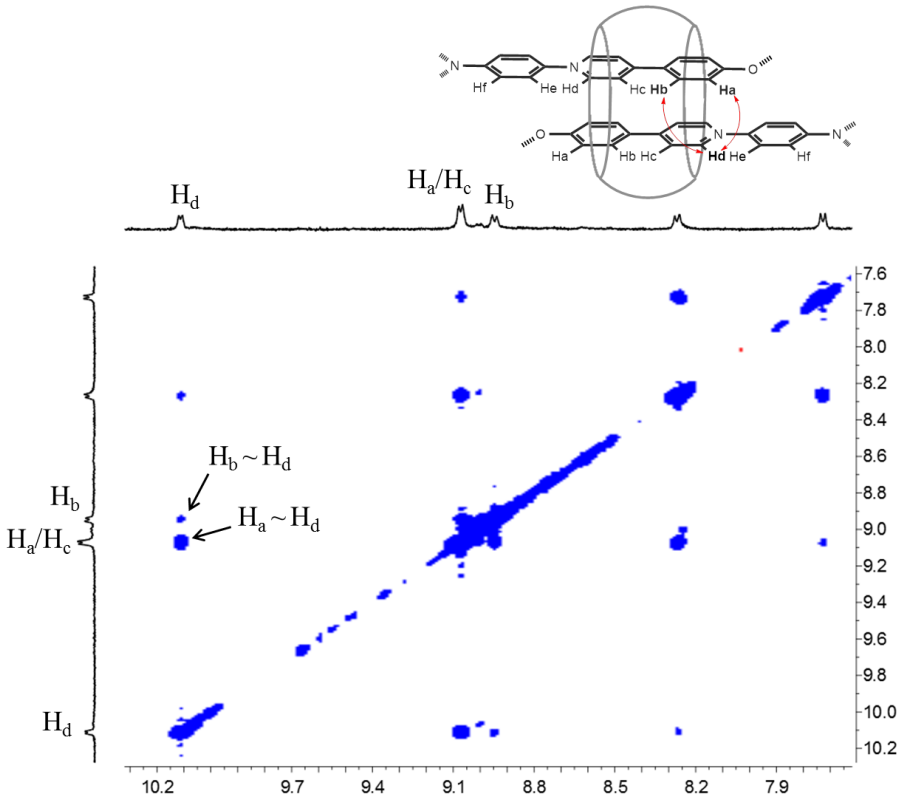


Figure S2 2D ^1H NMR NOESY spectrum (400 MHz) of (**1** + CB[8]) (2:3, [**1**] = 0.5 mM) in a binary solvent of D_2O/CD_3OD (17:3, v/v) at 25 ^oC.

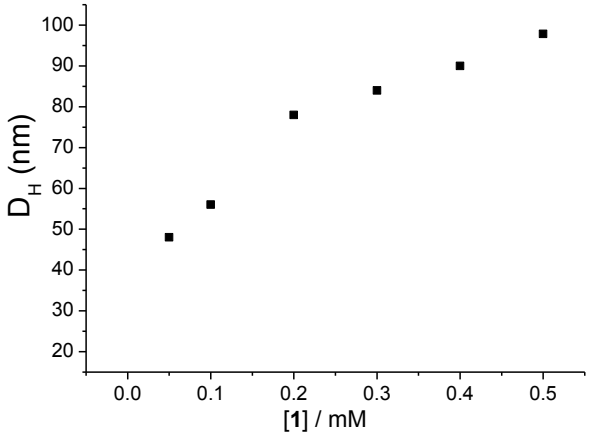


Figure S3 The plot of D_h vs. the concentration of (**1** + CB[8]) (2:3) in a binary solvent of H_2O/ CH_3OH (17:3, v/v) at 25 ^oC.

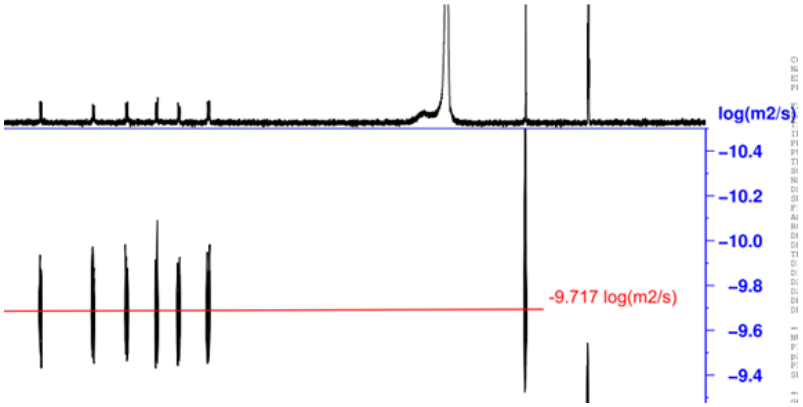


Figure S4 DOSY-NMR spectrum (500 MHz) of **1** (1.0 mM) in D_2O/CD_3OD (17:3, v/v). The ordinate represents the log value of the diffusion constant.

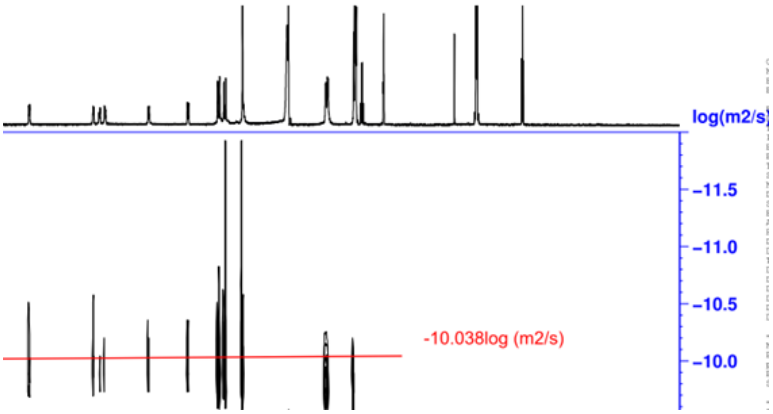


Figure S5 DOSY-NMR spectrum (500 MHz) of (**1** + CB[8]) (2:3, [**1**] =1.0 mM) in D_2O/CD_3OD (17:3, v/v). The ordinate represents the log value of the diffusion constant.

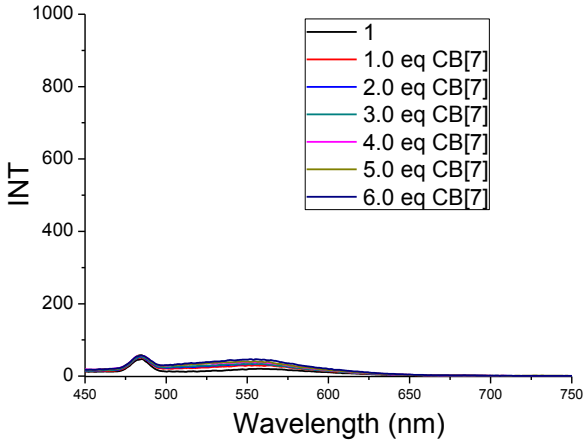


Figure S6 Fluorescence titration spectra of **1** (0.3 μM) with CB[7] in water at 25 ^{o}C. λ_{ex} = 414 nm.

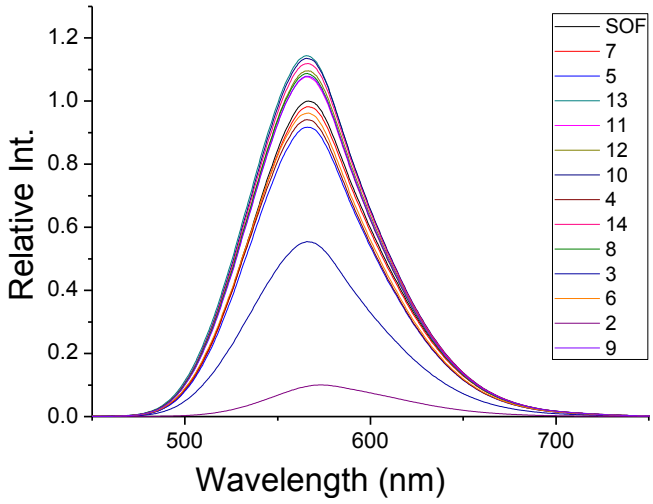


Figure S7 Fluorescence spectra of the 2D SOF in the presence of different nitroaromatics in water at 25 ^{o}C. λ_{ex} = 414 nm.

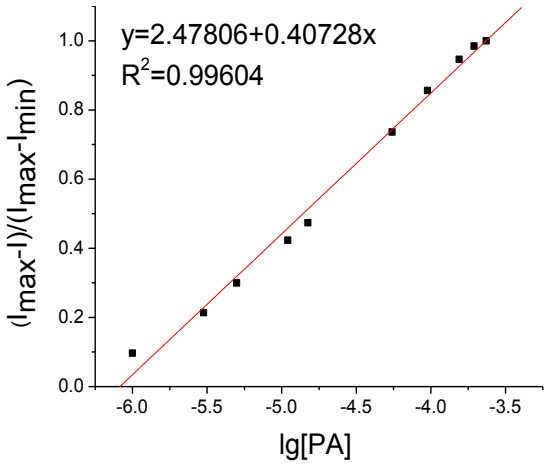


Figure S8 (I_{max} -I)/(I_{max} -I_{min}) vs lg[PA] plot for the fluorescence titration. The intercept at X-axis shows the lowest concentration of PA which can be detected.

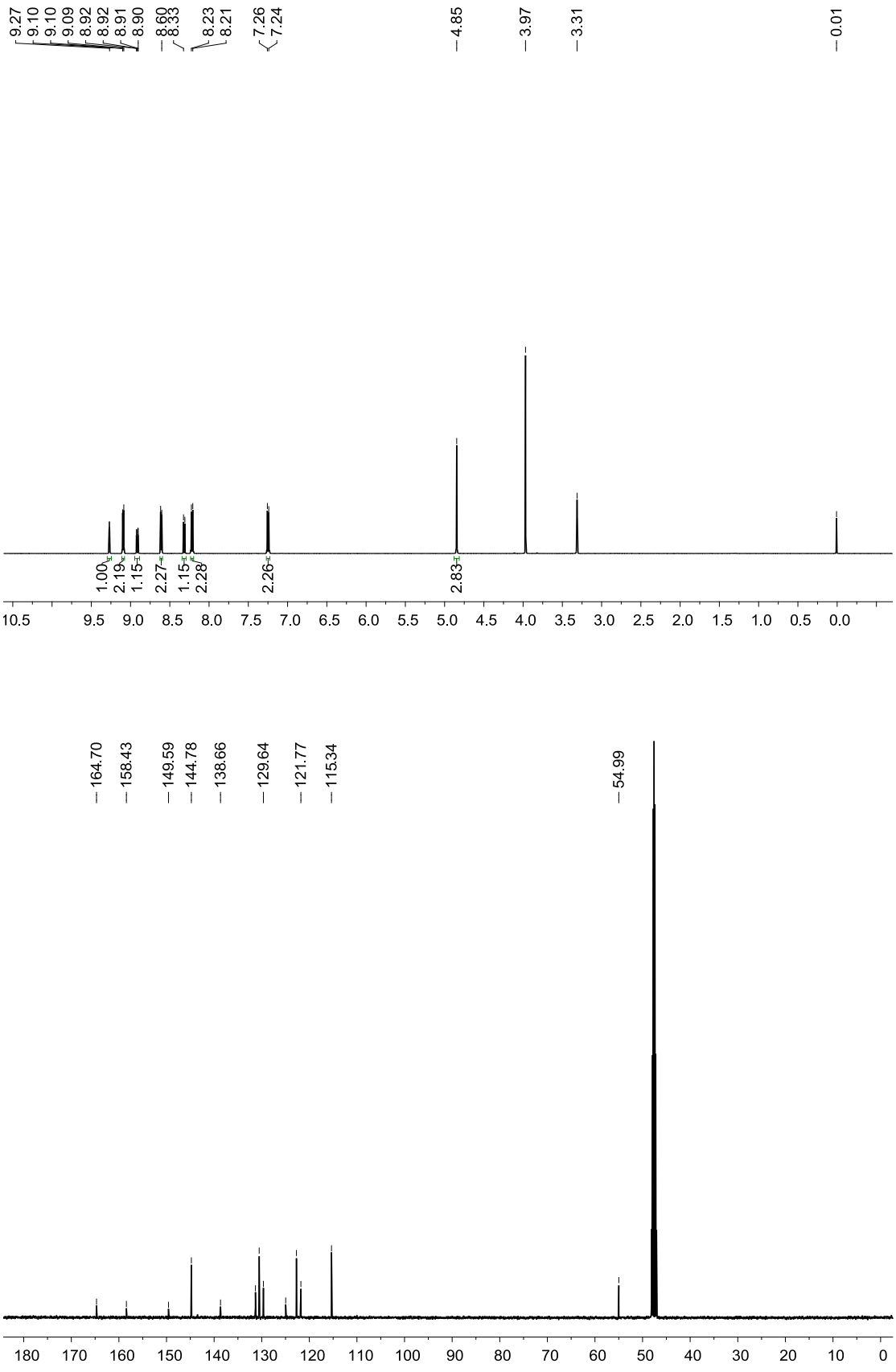


Figure S9 ^{1}H NMR (500MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra of compound **2**.

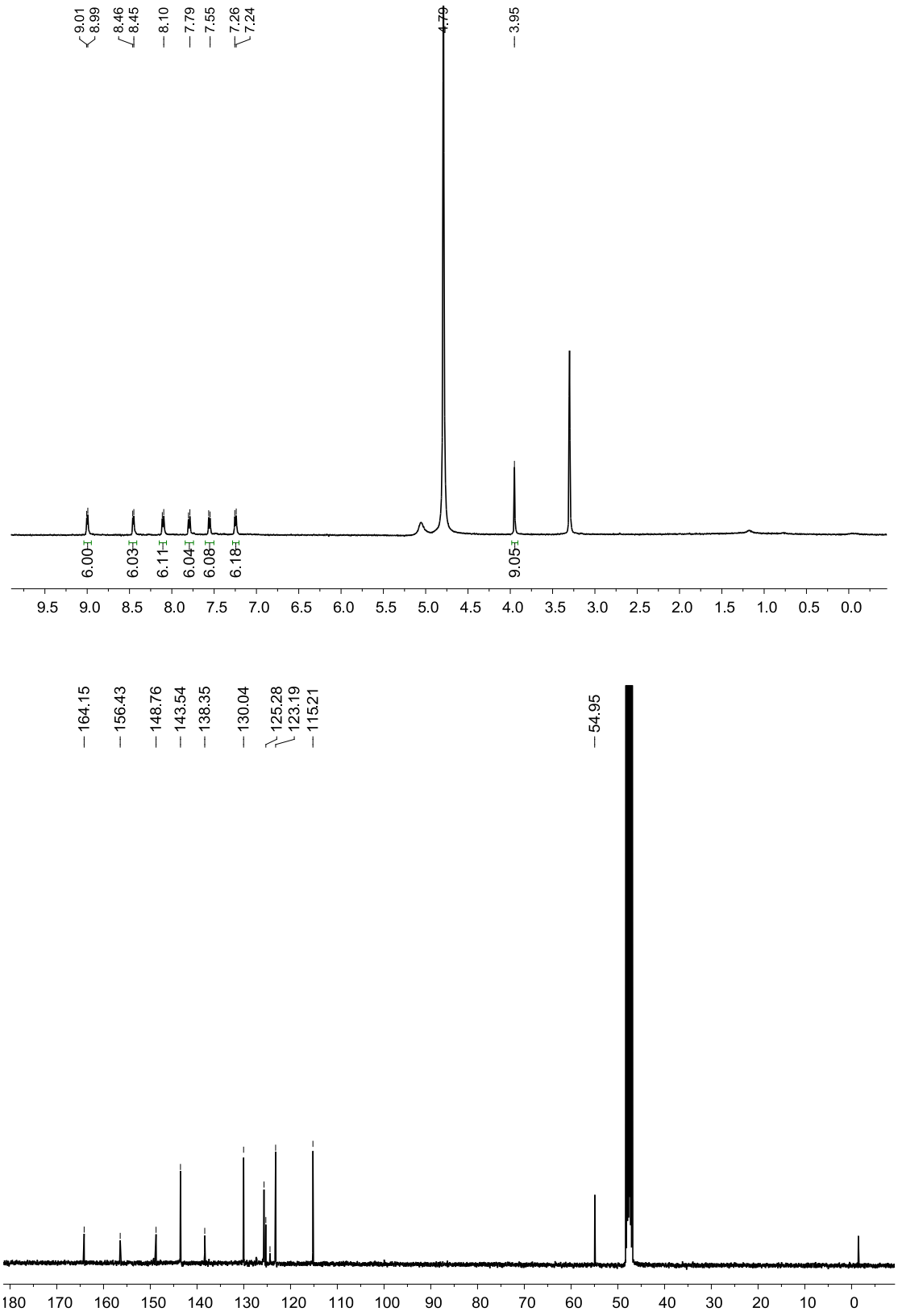


Figure S10 ^{1}H NMR (400MHz, CD_3OD) and ^{13}C NMR (125MHz, CD_3OD) spectra of compound **1**.

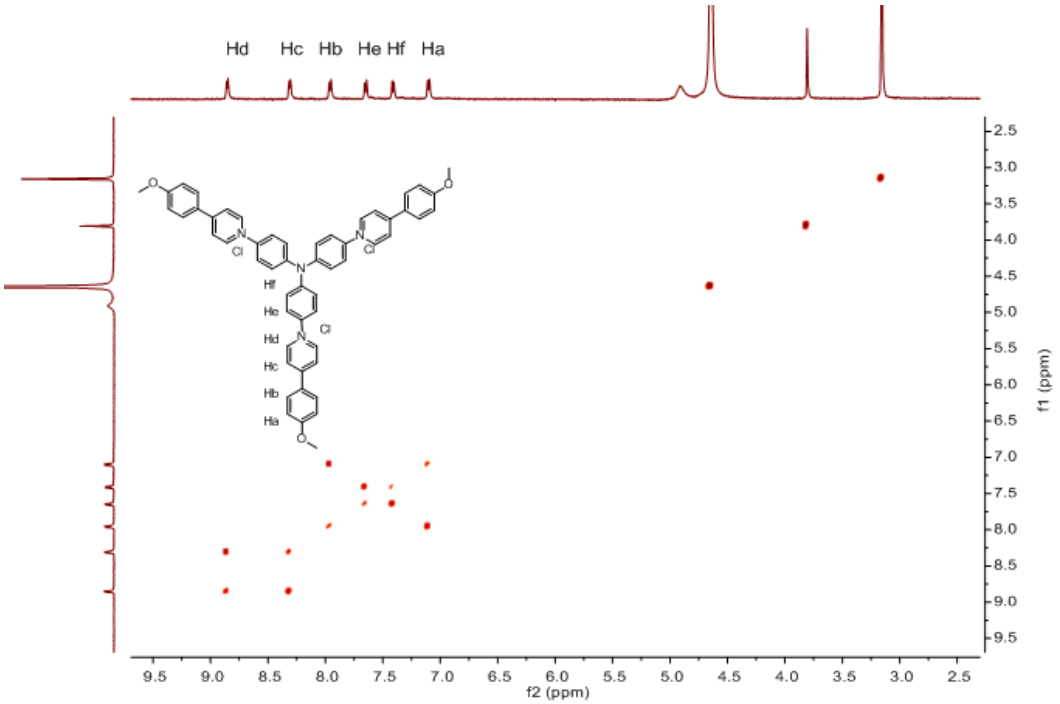


Figure S11 2D ^{1}H NMR COSY spectrum (500 MHz, CD_3OD) of **1** at 25 ^{o}C.