Electronic Supplementary Information

The construction of rigid supramolecular polymers in water through the self-assembly of rod-like monomers and cucurbit[8]uril

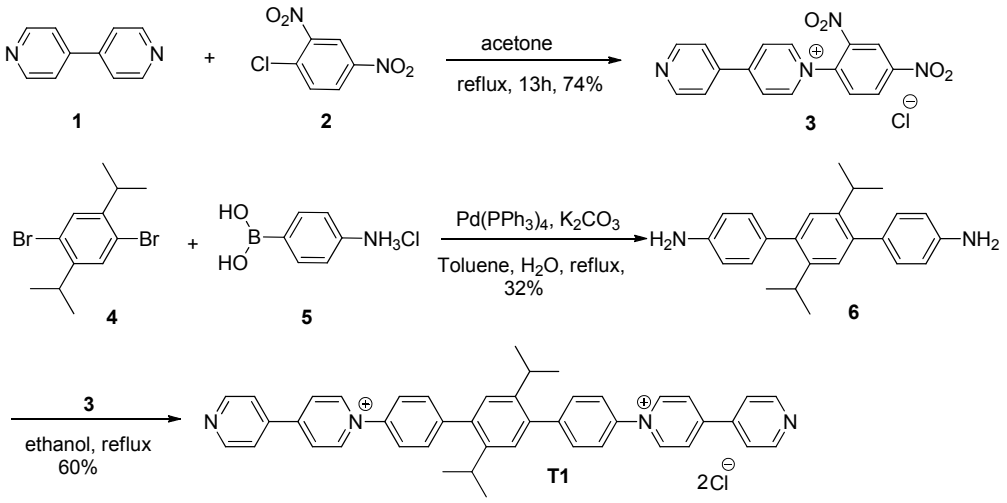
Feng Lin, Tian-Guang Zhan, Tian-You Zhou, Kang-Da Zhang, Guang-Yu Li, Jian Wu and Xin Zhao*

Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China.

E-mail: xzhao@mail.sioc.ac.cn

Table of Contents

The synthesis of T1



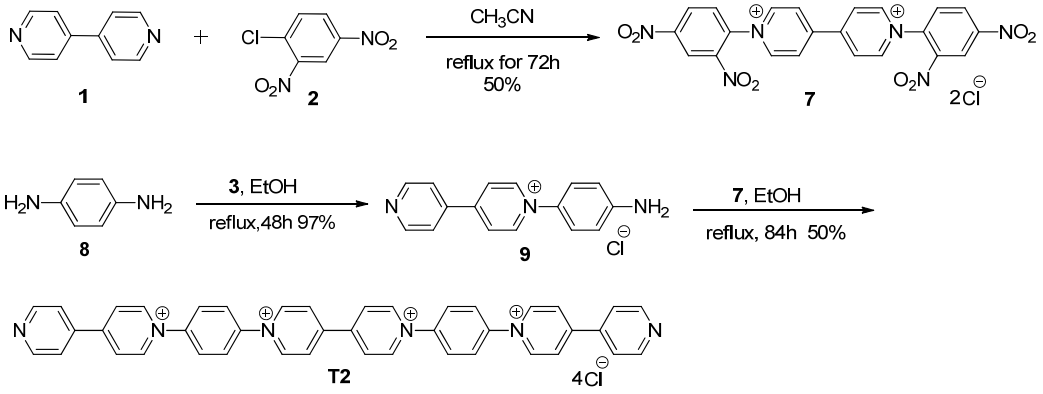
Compound 3. 4,4'-Bipyridine (3.5 g, 22.5 mmol) and 2,4-dinitrochlorobenzene (3.0 g, 15 mmol) were dissolved in acetone (25 mL). The solution was refluxed for 13 h, during which time a pale grey precipitate formed. The precipitate was collected by filtration and washed several times with dichloromethane. The product was dried *in vacuo* to yield compound **3** as a grey powder (3.57 g, 74%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.42 (d, J = 6.5 Hz, 2H), 9.31 (d, J = 2.2 Hz, 1H), 8.95 (dd, J_1 = 8.6 Hz, J_2 = 2.3 Hz, 1H), 8.91 (d, J = 5.8 Hz, 2H), 8.83 (d, J = 6.6 Hz, 2H), 8.33 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 5.9 Hz, 2H). MS(ESI): *m/z* 323.0 $[M\text{-}Cl]^+$.

Compond 6. To a stirred solution of 1,4-diiodo-2,5-diisopropylbenzene (3.0 g, 9.4 mmol) and 4-aminophenylboronic acid hydrochloride (4.85 g，28.1 mmol) in toluene (50 mL) was added an aqueous solution of potassium carbonate (3.9 M, 17 mL) and palladium tetra(triphenylphosphine) (109 mg, 0.094 mmol). The mixture was heated under reflux for 24 h and then concentrated. The slurry was triturated with ethyl acetate (30 mL) and the organic phased was washed with saturated solution of sodium hydroxide (30 mL, 3 M), water (3 × 30 mL), and brine(2 × 30 mL), and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the resulting residue was subjected to column chromatography (petroleum ether/CH_2Cl_2 4:1) to give compound **4** (1.04 g，32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 6H), 6.75 (d, J = 8.4 Hz, 4H), 3.71 (s, 4H), 3.11 (dt, J_1 = 13.7, J_2 = 6.9 Hz, 2H), 1.15 (d, J = 6.9

Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.16, 143.40, 140.04, 132.85, 130.49, 127.39, 114.81, 29.15, 24.54. MS (ESI): *m/z* 345.1$[M+H]^+$, 173.1$[M+2H]^{2+}$. HRMS (MALDI-TOF) Calcd for $C_{24}H_{28}N_2$: 344.2247. Found: 344.2252.

Compound T1. Compound **4** (300 mg，0.87 mmol) and compound **1** (1.18 g，3.29 mmol) was dissolved in ethanol (5 mL) under nitrogen atmosphere. The resulting solution was refluxed for 12 h and the formed precipitate was filtered and discarded. The filtrate was evaporated *in vacuo* and the crude product was refluxed with acetone (50 mL) for 2 h, filtered, and dried *in vacuo* to yield compound **T1** as a pale yellow powder (360 mg, 60%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.47 (d, J = 7.0 Hz, 4H), 8.90 (dd, J_1 = 4.6, J_2 = 1.7 Hz, 4H), 8.74 (d, J = 7.0 Hz, 4H), 8.12 (dd, J_1 = 4.6, J_2 = 1.7 Hz, 4H), 8.01 (d, J = 8.6 Hz, 4H), 7.76 (d, J = 8.6 Hz, 4H), 7.31 (s, 2H), 3.17 – 3.00 (m, 2H), 1.23 (d, J = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, CD_3OD) δ 156.05, 151.97, 147.01, 146.56, 144.93, 143.43, 140.79, 132.63, 128.26, 127.18, 125.43, 123.66, 30.62, 24.51. MS(ESI): *m/z* 312.1$[M-2Cl]^{2+}$. HRMS (MALDI-TOF): Calcd for $C_{44}H_{40}N_4^+$ [M-2Cl]: 624.3248. Found: 624.3249.

The synthesis of T2



Compound 7. A solution of 4,4'-bipyridine (3.6 g, 23 mmol) and 2,4-dinitrochlorobenzene (16.5 g, 81 mmol) in acetonitrile (70 mL) was heated under reflux for 72 h. The hot reaction mixture was filtered and the filtered cake refluxed with ethanol (300 mL). After the solid being dried under vacuum, compound **7** was collected as a white solid (6.0 g, 50%). ^{1}H NMR (400MHz, CD_3OD): 9.67 (d, J = 6.4 Hz, 2H), 9.34 (d, J = 2.4 Hz, 1H), 9.11(d, J = 6.4 Hz, 2H), 8.98 (dd, J_1 = 8.4 Hz, J_2 =

2.4 Hz, 2H), 8.41 (d, J = 8.8 Hz, 1H).

Compound 9. Compound **7** (3.64 g, 10 mmol) and benzene-1,4-diamine (3.26 g, 30 mmol) were dissolved in anhydrous ethanol (100 mL). The mixture was heated under reflux for 12 h. The hot mixture was filtered and the filtered cake was washed with acetone (300 mL). The resulting brownish red solid was redissolved in a minimum amount of methanol with heating and reprecipitated by the addition of THF. The precipitate was collected and then dried under vacuum to give compound **9** (2.75 g, 97%). ^{1}H NMR (400MHz, DMSO-d_6): 9.35 (d, J = 7.2 Hz, 2H), 8.88 (d, J = 6.4 Hz, 2H), 8.67 (d, J = 6.4 Hz, 2H), 8.12 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 6.01 (s, 2H). ^{13}C NMR (100MHz, CD_3CN): 154.22, 152.26, 152.14, 145.05, 142.02, 126.69, 126.07, 122.72, 118.26, 115.54. MS (ESI): *m/z* 248.0 $[M\text{-}Cl]^+$. HRMS (ESI) Calcd. for $C_{16}H_{14}N_3^+$ [M-Cl]: 248.1185. Found: 248.1182. Note: ^{13}C NMR was obtained from its hexafluorophosphate salt.

Compound T2. A suspension of compound **9** (0.45 g, 0.81mmol) and compound **7** (0.576 g, 2.0 mmol) in anhydrous ethanol (60 mL) were heated under reflux for 84 h. After being cooling down to room temperature, the resulting solid was filtrated and recrystallized from CH_3OH / THF. The gray solid was collected, washed with acetone and dried to offer compound **T2** (0.31 g, 50%). ^{1}H NMR (400 MHz, D_2O): 9.61 (d, J = 6.4 Hz, 4H), 9.42 (d, J = 6.8 Hz, 4H), 8.95 (d, J = 6.4 Hz, 4H), 8.89 (d, J = 5.2 Hz, 4H), 8.71 (d, J = 6.4 Hz, 4H), 8.29 (d, J=3.6 Hz, 8H), 8.12 (d, J = 5.6 Hz, 4H). ^{13}C NMR (100 MHz, D_2O): 164.69, 155.63, 151.36, 149.93, 145.86, 144.98, 144.52, 144.12, 144.11, 142.46, 127.52, 126.91, 126.31, 122.79. MS (ESI): *m/z* 206.5 $[M\text{-}4Cl]^{3+}$. HRMS(MALDI-TOF) was obtained from its hexafluorophosphate salt: Calcd. for $C_{42}H_{32}N_6^+$ $[M\text{-}4PF_6]$: 620.2689. Found: 620.2683.

Atomic force microscopy (AFM). AFM was carried out with a Nano scope IIIa MultiMode microscope. The samples were prepared by slowly pipetting aliquot of the corresponding solution on freshly cleaved mica surfaces, dried under vacuum for 2 h, and then submitted to AFM characterization.

Scanning electron microscopy (SEM). SEM was carried out using a JEOL

JSM-6390-LV microscope scanning electron microscope. Aliquot of the corresponding solution was dropped onto freshly cleaved mica surfaces followed by removal of the solvent under vacuum, coated with gold using a sputter coater (ambient temperature, 60 torr pressure in a nitrogen atmosphere, sputtered for 30 s from a solid gold target at a current at 30 mA), and then was submitted to SEM characterization.

Transmission electron microscopy (TEM). TEM 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.

Dynamic light sattering (DLS). DLS was performed using a Zetasizer NanoZS instrument. The samples were filtered on millipore filter (pore size 450 nm) before DLS characterization at 25 ℃.

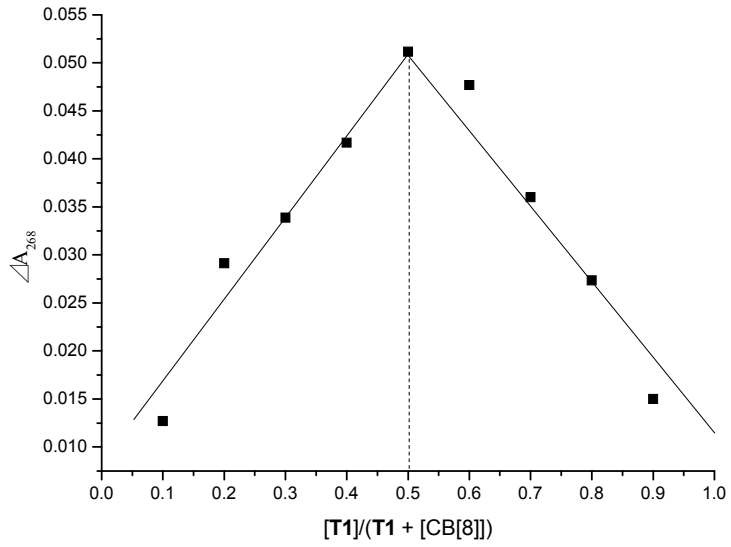


Figure S1. Job's plot for the binding of **T1** with CB[8] in water at 25°C. The total concentration was fixed at 1×10^{-5} M.

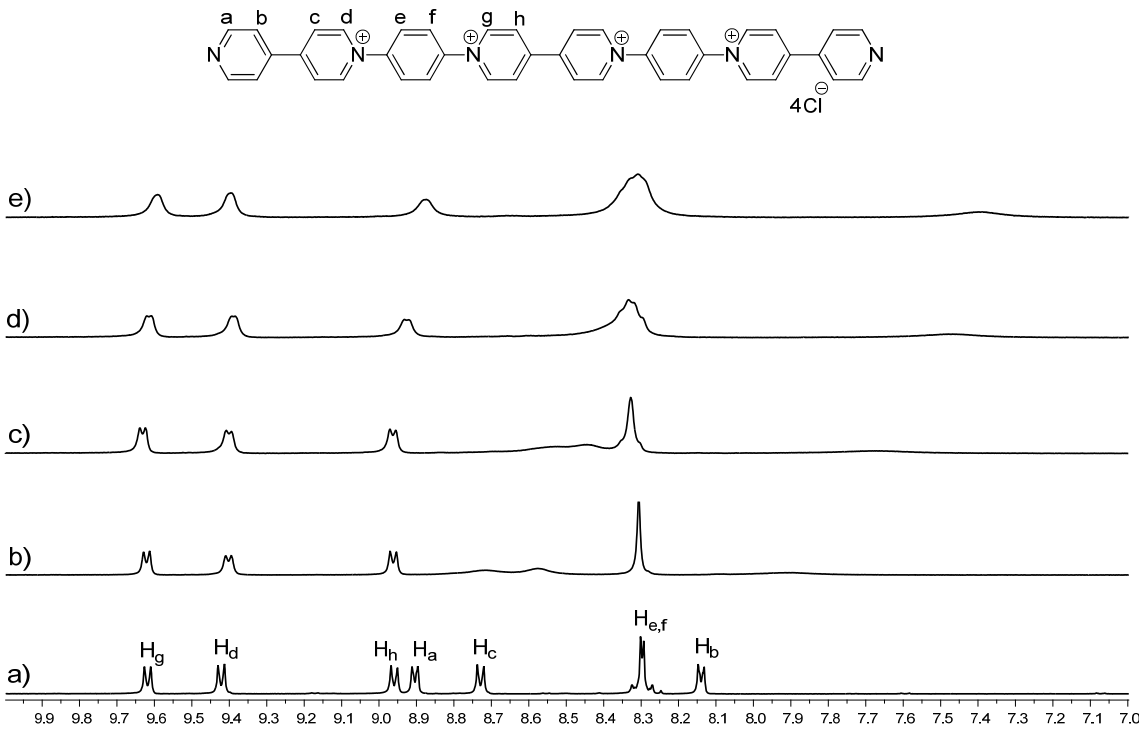


Figure S2 Partial ^{1}H NMR titration spectra of **T2** (5.0 mM) with different equiv of CB[8] (a) 0 eq, (b) 0.25 eq CB[8], (c) 0.5 eq CB[8], (d) 0.75 eq CB[8], and (e) 1.0 eq CB[8] in D_2O at 25^{o}C.

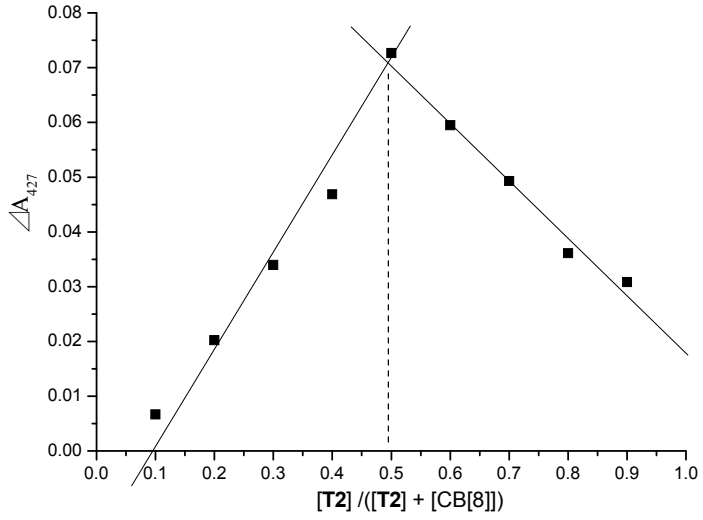


Figure S3. Job's plot for the binding of **T2** and CB[8] in water at 25^{o}C. The total concentration was fixed at 1 ×10^{-5} M.

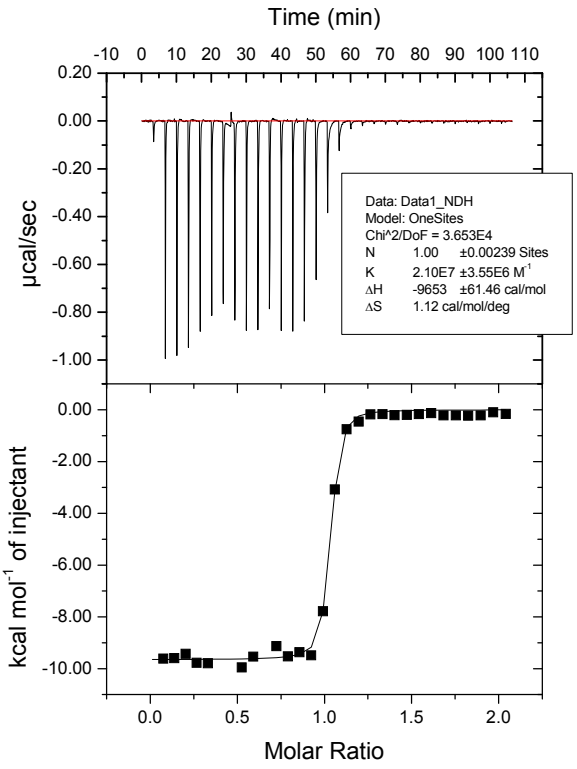


Figure S4. ITC data for the titration of CB[8] (0.1 mM) with **T1** (1.0 mM) in water at 25^{o}C.

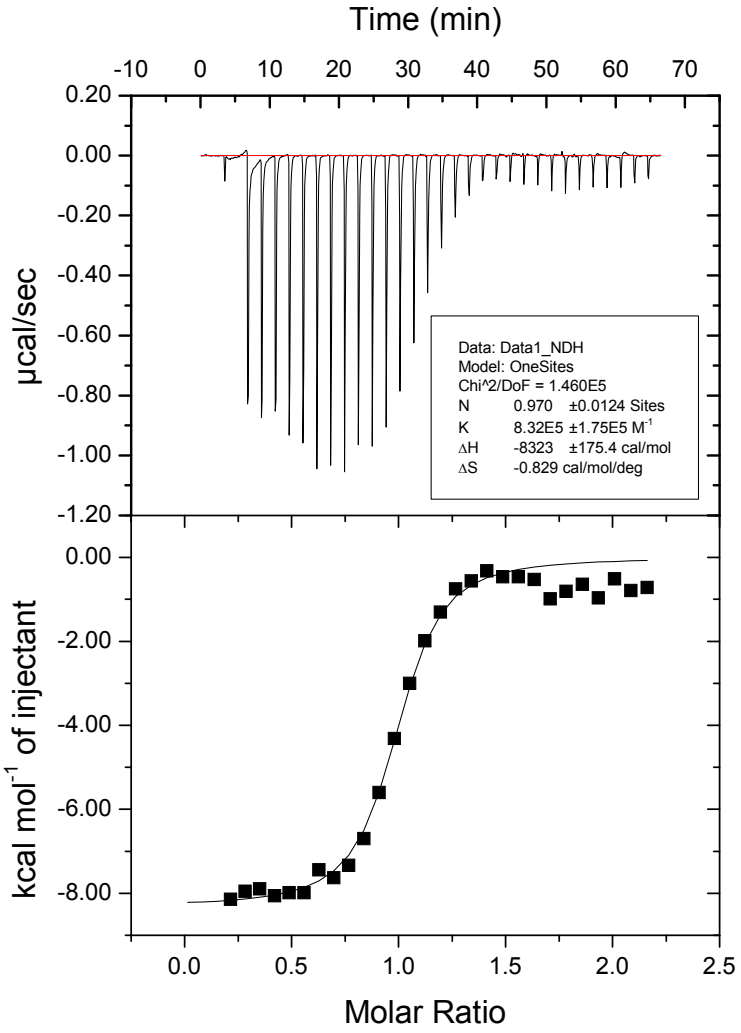


Figure S5. ITC data for the titration of CB[8] (0.1 mM) with **T2** (1.0 mM) in water at 25°C.

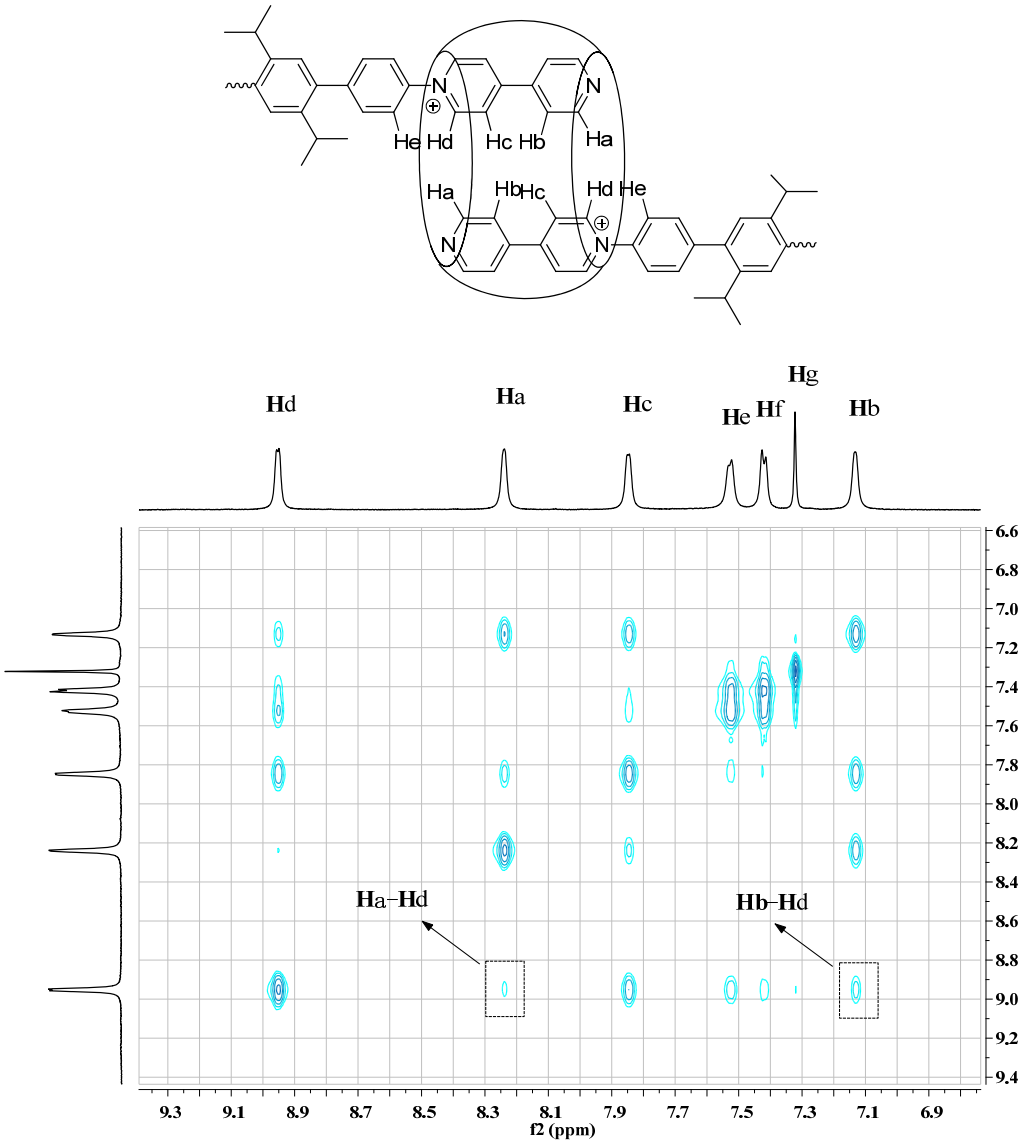


Figure S6. 2D ^{1}H NMR NOESY spectrum (600 MHz) of the mixture of **T1** and CB[8] (1:1) in D_2O at 25 ^{o}C. The concentration was 6.0 mM.

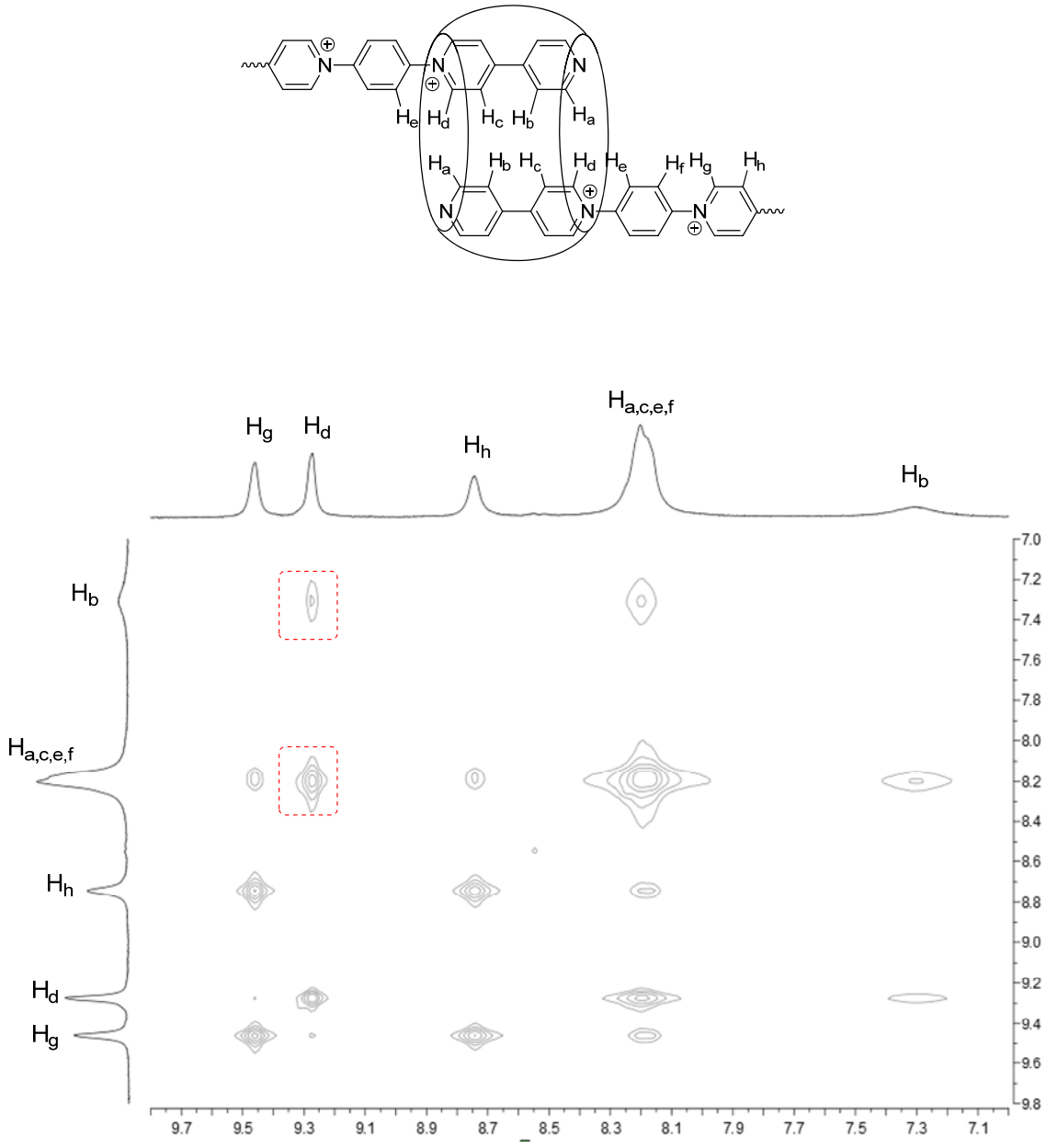


Figure S7. 2D ^{1}H NMR NOESY spectrum (400 MHz) of the mixture of **T2** and CB[8] (1:1) in D_2O at 25 ^{o}C. The concentration was 5.0 mM.

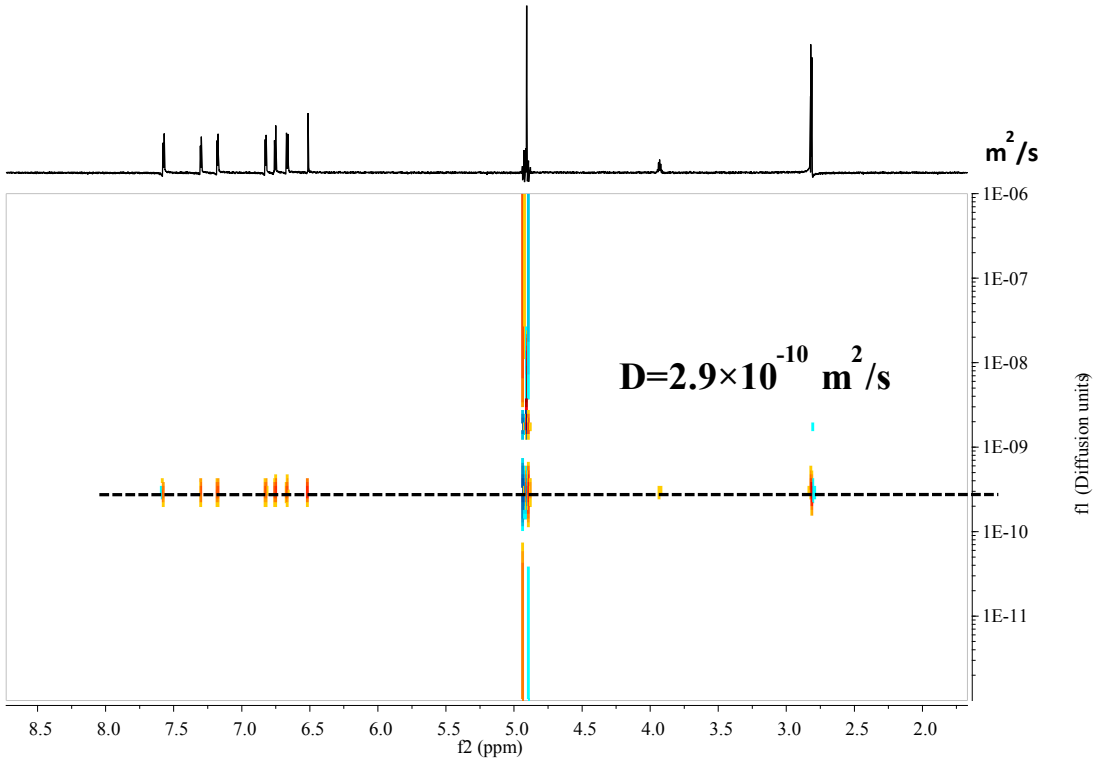


Figure S8. DOSY-NMR spectrum (500 MHz) of the solution of **T1** (1.0 mM) in D_2O at 25 ^oC.

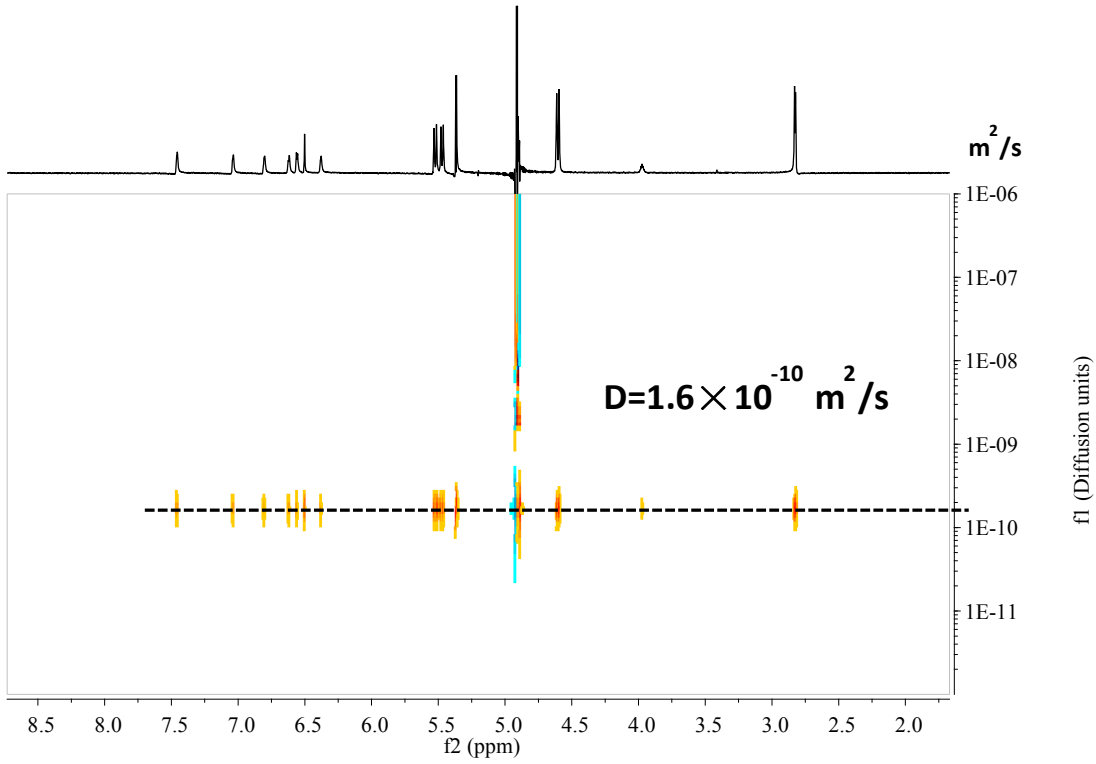


Figure S9. DOSY-NMR spectrum (500 MHz) of the solution of **T1** and CB[8] (1:1, 1.0 mM) in D_2O at 25 ^oC.

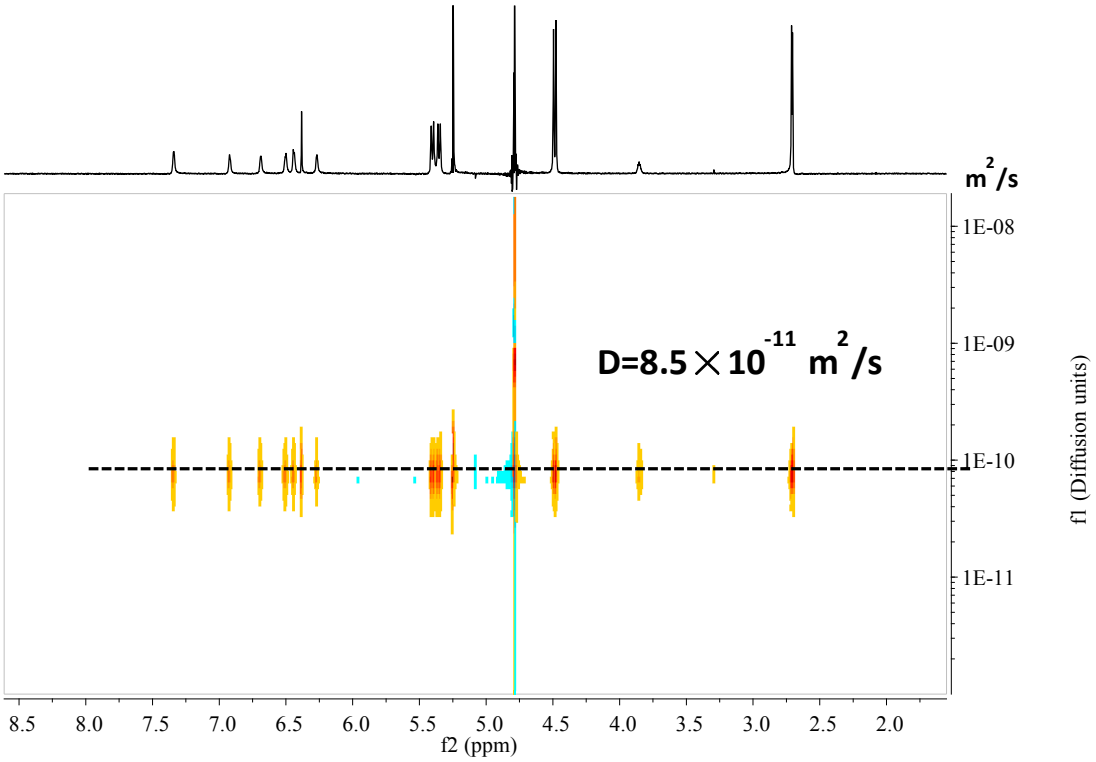


Figure S10. DOSY-NMR spectrum (500 MHz) of the solution of **T1** and CB[8] (1:1, 6.0 mM) in D_2O at 25 °C.

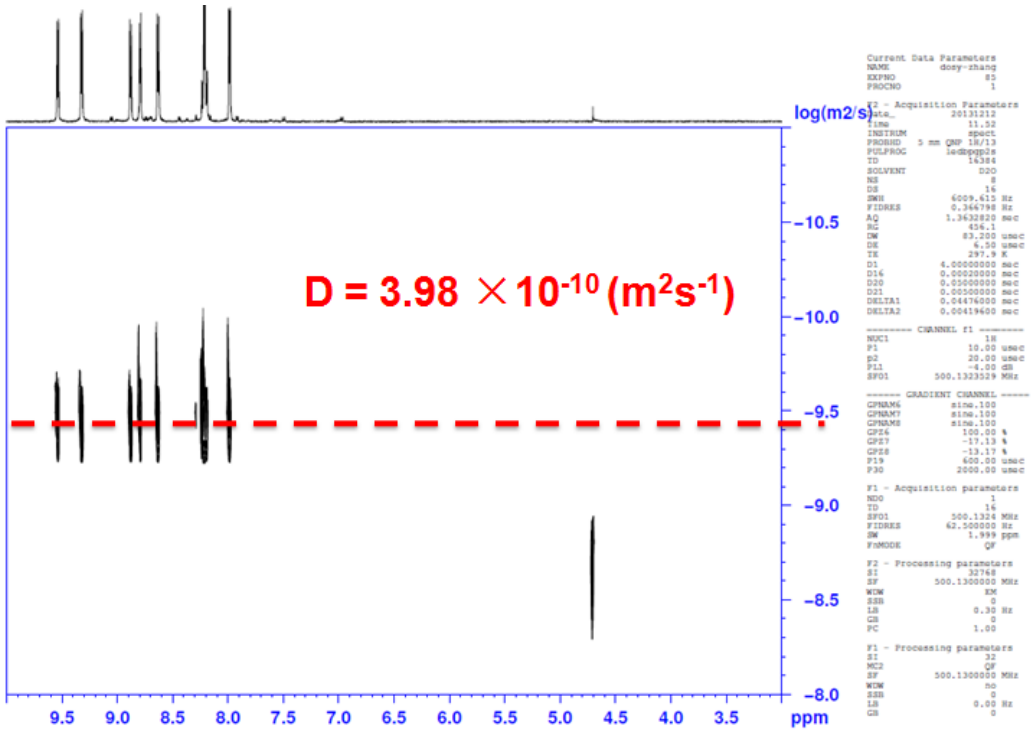


Figure S11. DOSY-NMR spectrum (500 MHz) of the solution of **T2** (5.0 mM) in D_2O at 25 °C.

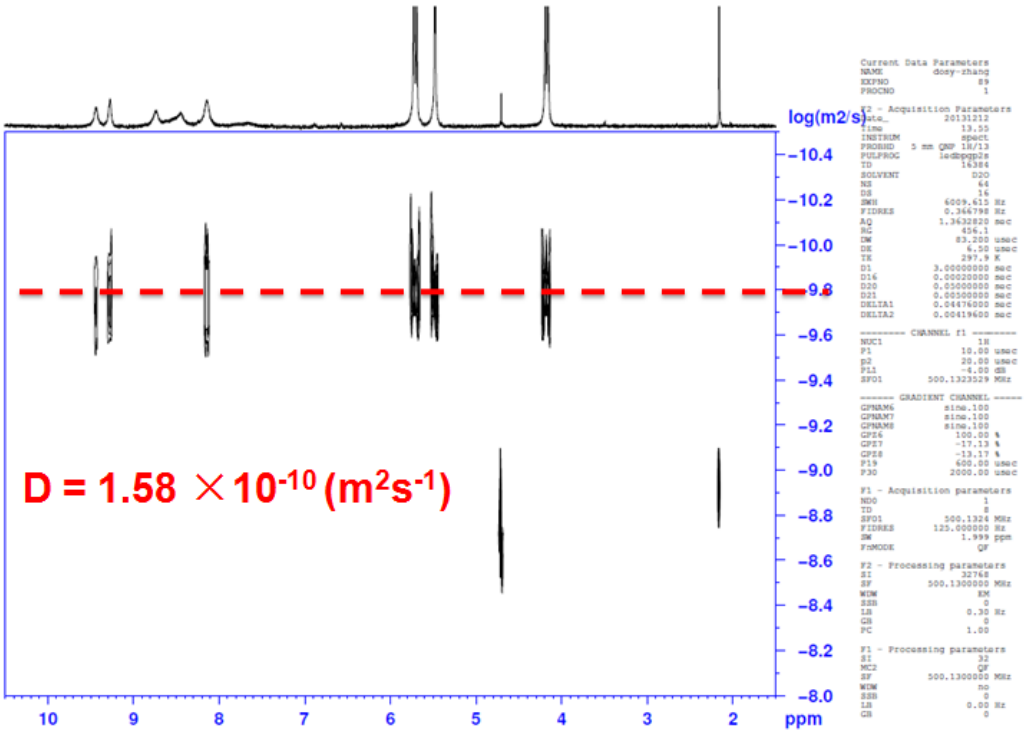


Figure S12. DOSY-NMR spectrum (500 MHz) of the solution of **T2** and CB[8] (1:1, 1.0 mM) in D_2O at 25 ^oC.

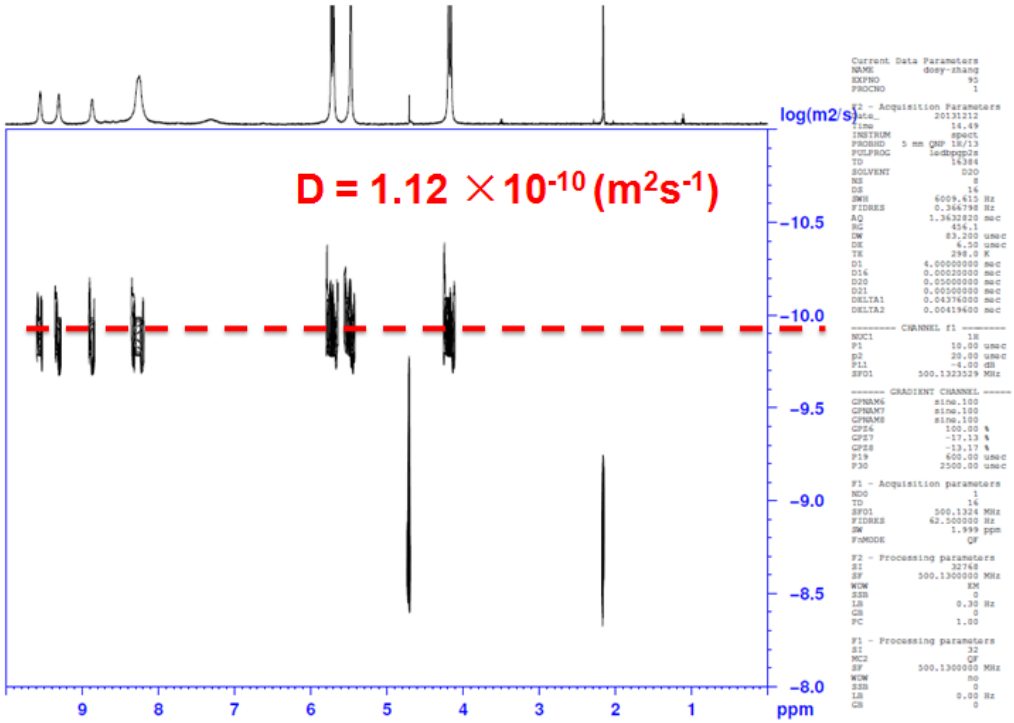


Figure S13. DOSY-NMR spectrum (500 MHz) of the solution of **T2** and CB[8] (1:1, 5.0 mM) in D_2O at 25 ^oC.

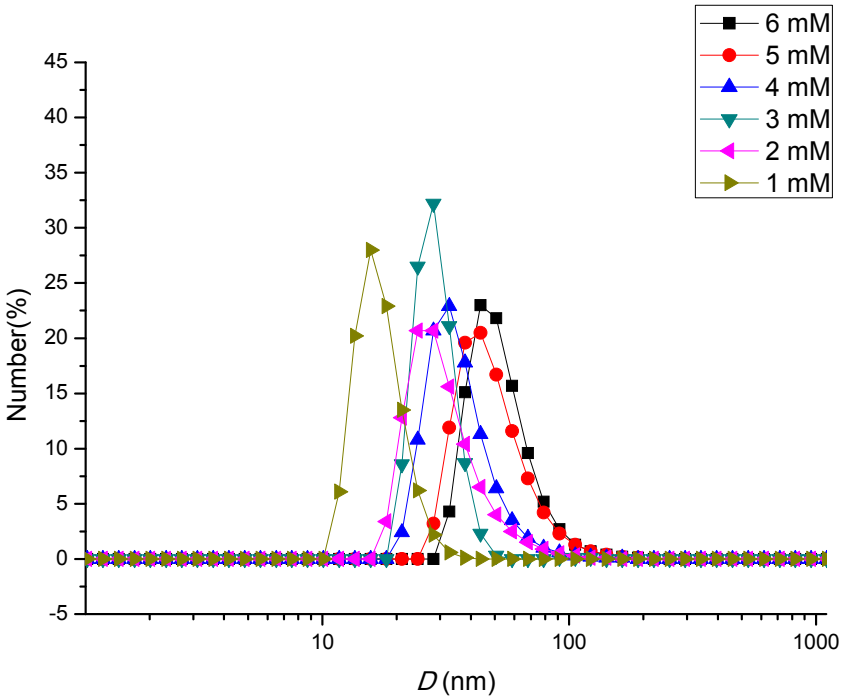


Figure 14. DLS profile of the mixture of **T1** and CB[8] (1:1) at different concentrations in water at 25 °C.

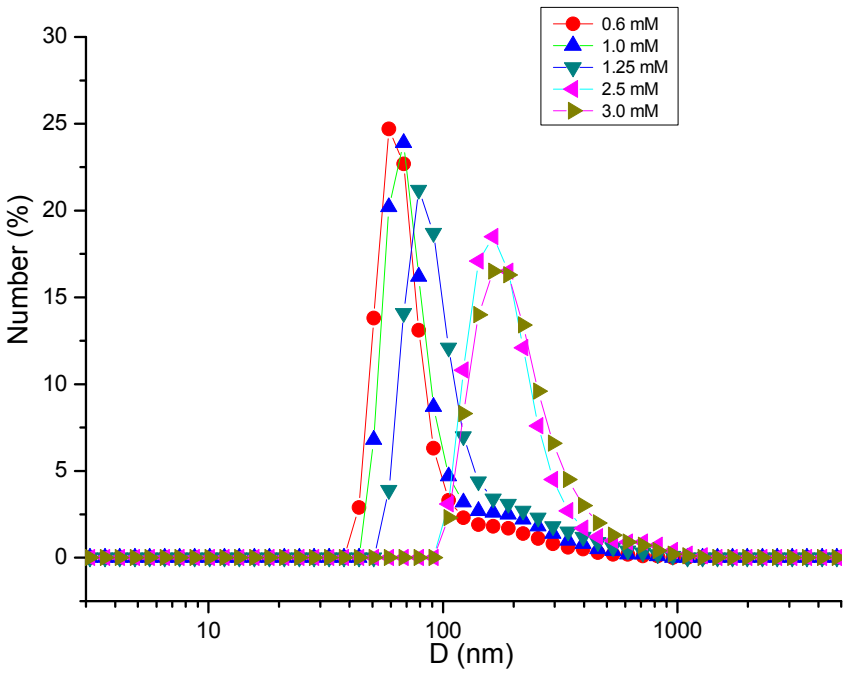


Figure 15 DLS profile of the mixture of **T2** and CB[8] (1:1) at different concentrations in water at 25 °C.

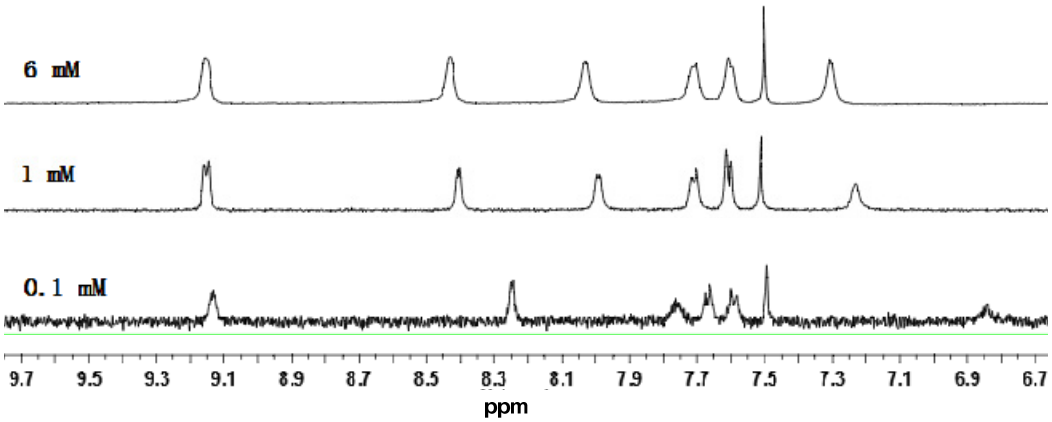


Figure 16. Partial ^{1}H NMR spectra of the mixture of **T1** and CB[8] (1:1) at different concentrations in D_2O at 25 ^{o}C.

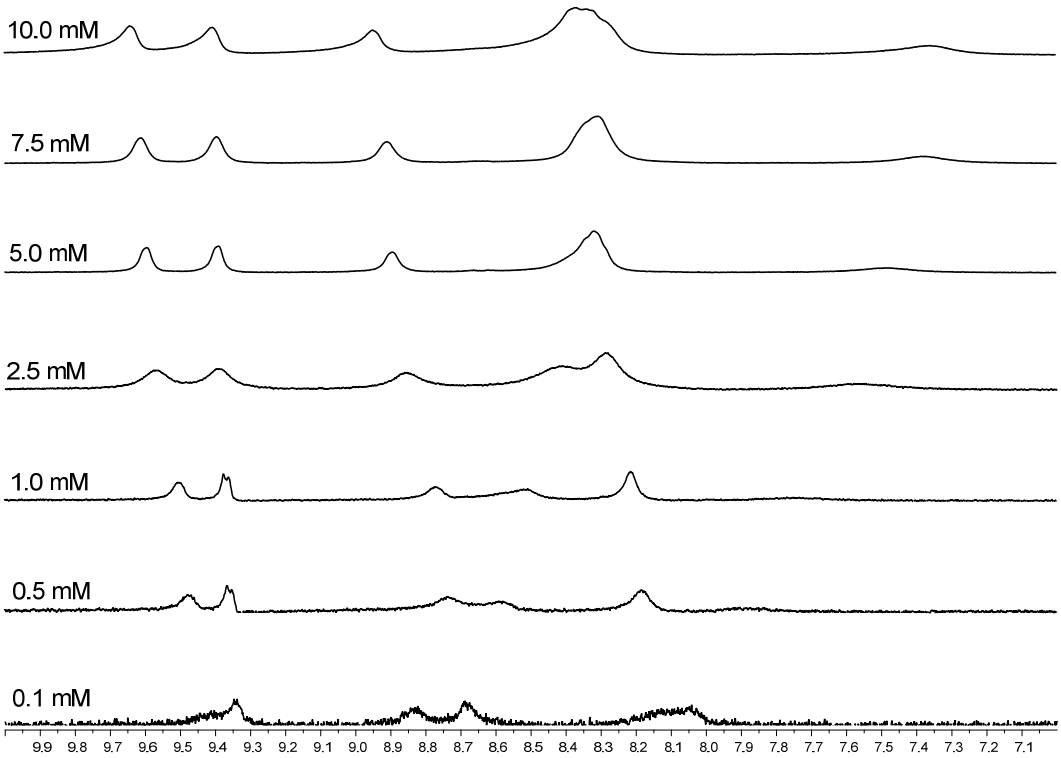


Figure 17. Partial ^{1}H NMR spectra of the mixture of **T2** and CB[8] (1:1) at different concentrations in D_2O at 25 ^{o}C.

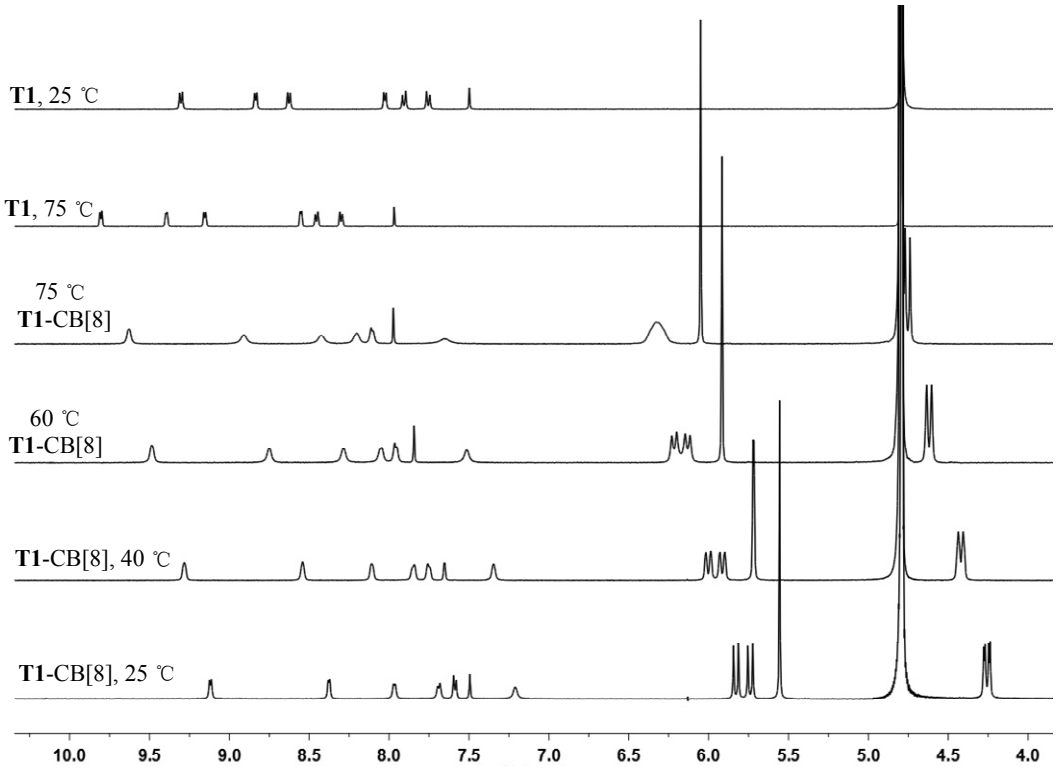


Figure 18. Partial ^{1}H NMR spectra of **T1**–CB[8] (1:1) and **T1** in D_2O at different temperatures. The concentration of **T1** was 3.0 mM.

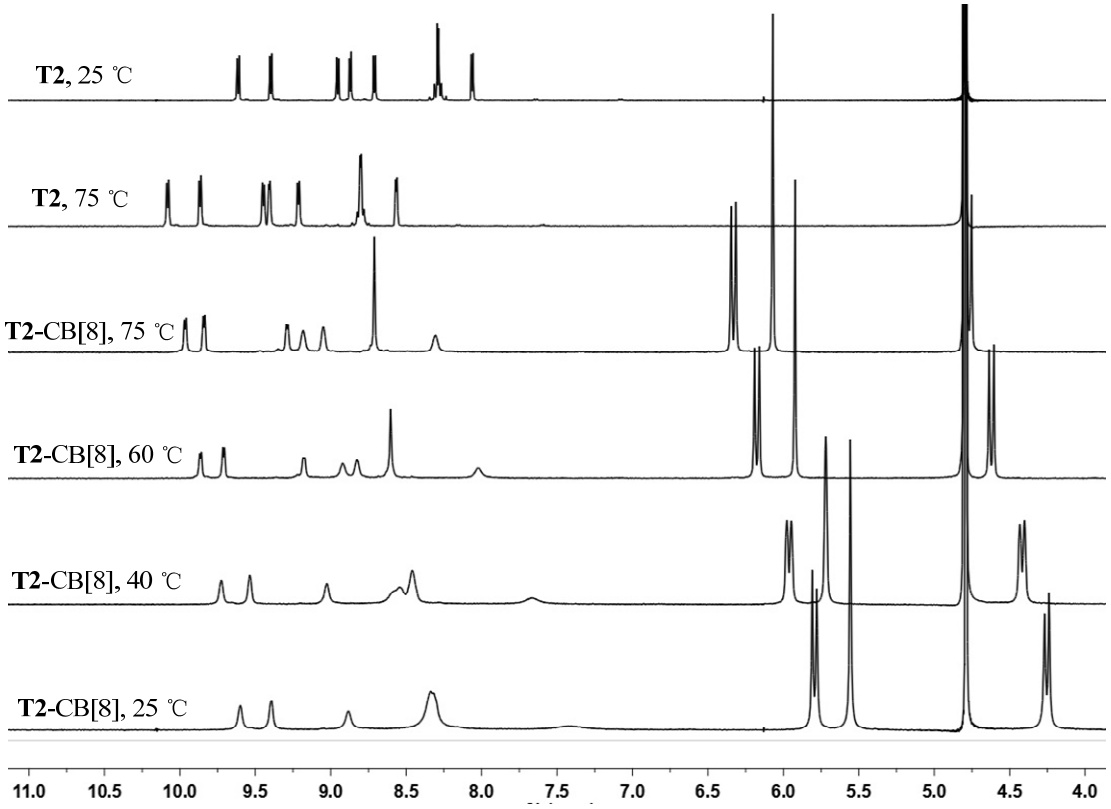


Figure 19. Partial ^{1}H NMR spectra of **T2**–CB[8] (1:1) and **T2** in D_2O at different temperatures. The concentration of **T2** was 3.0 mM.

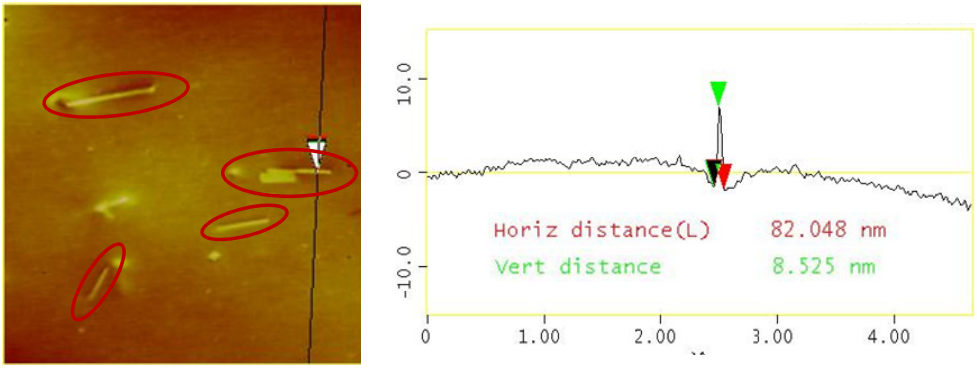


Figure 20. Tapping-mode AFM image and cross-section analysis of the sample fabricated from a mixture of **T1** and CB[8] (1:1, 6.0 mM) in water on mica surface.

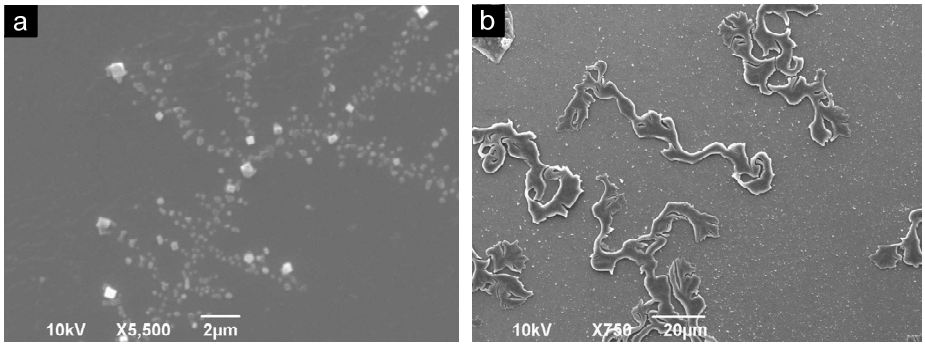


Figure 21. SEM images of samples fabricated from aqueous solutions of (a) **T1** (2.0 mM) and (b) **T2** (5.0 mM) on mica surface.

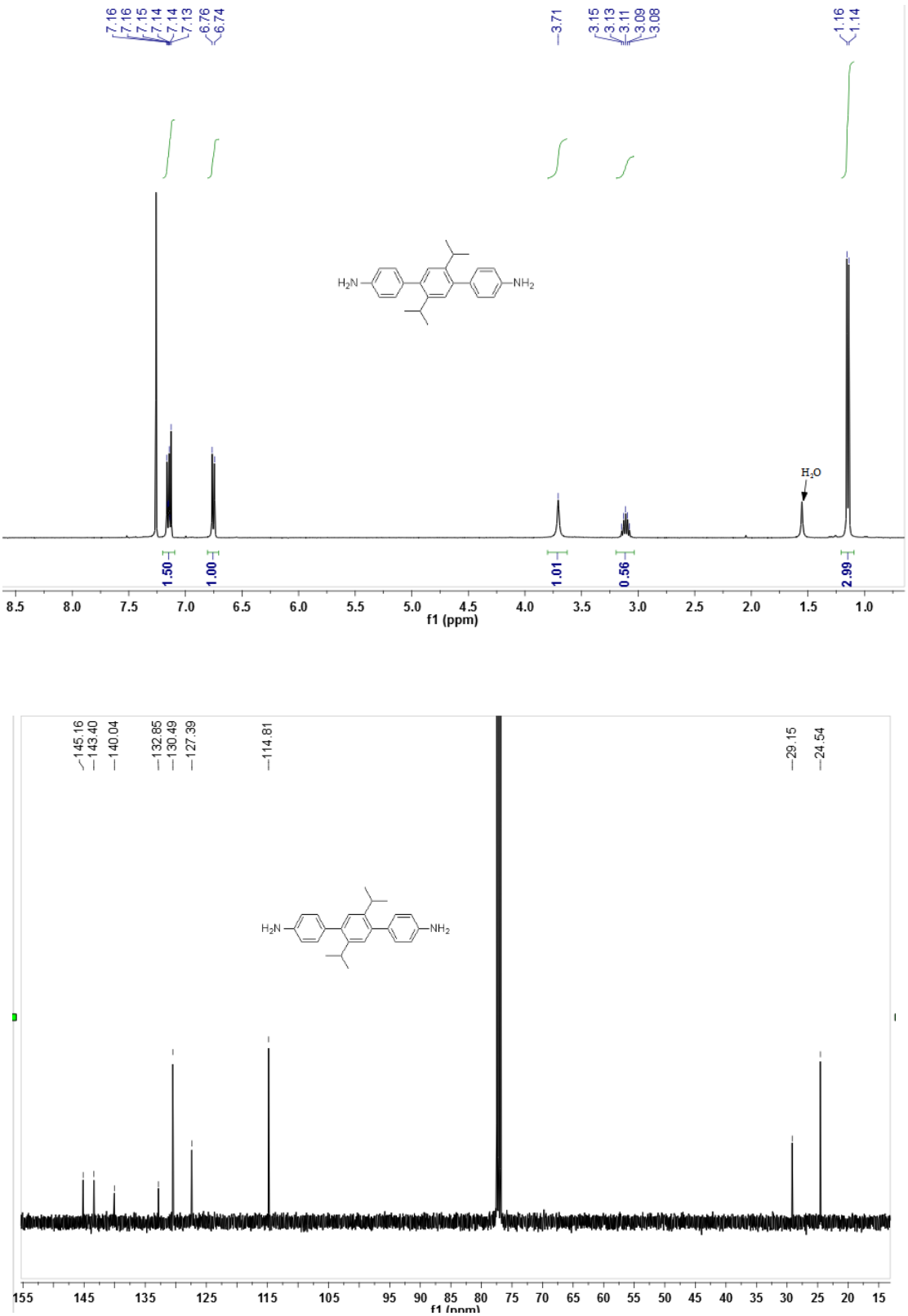


Figure S22. ^{1}H NMR and ^{13}C NMR spectra of compound **5** in $CDCl_3$.

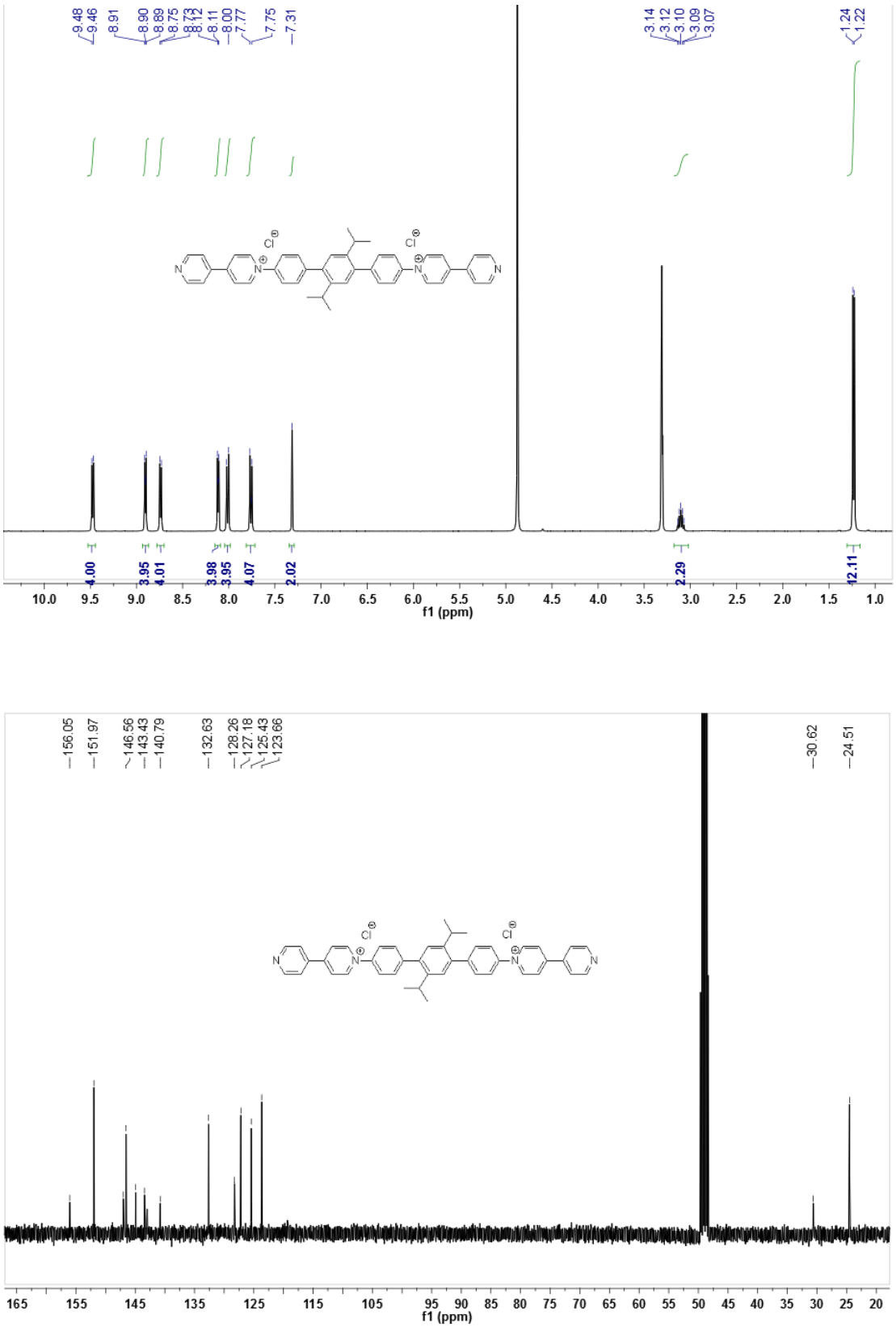


Figure S23. ^{1}H NMR and ^{13}C NMR spectra of **T1** in CD_3OD.

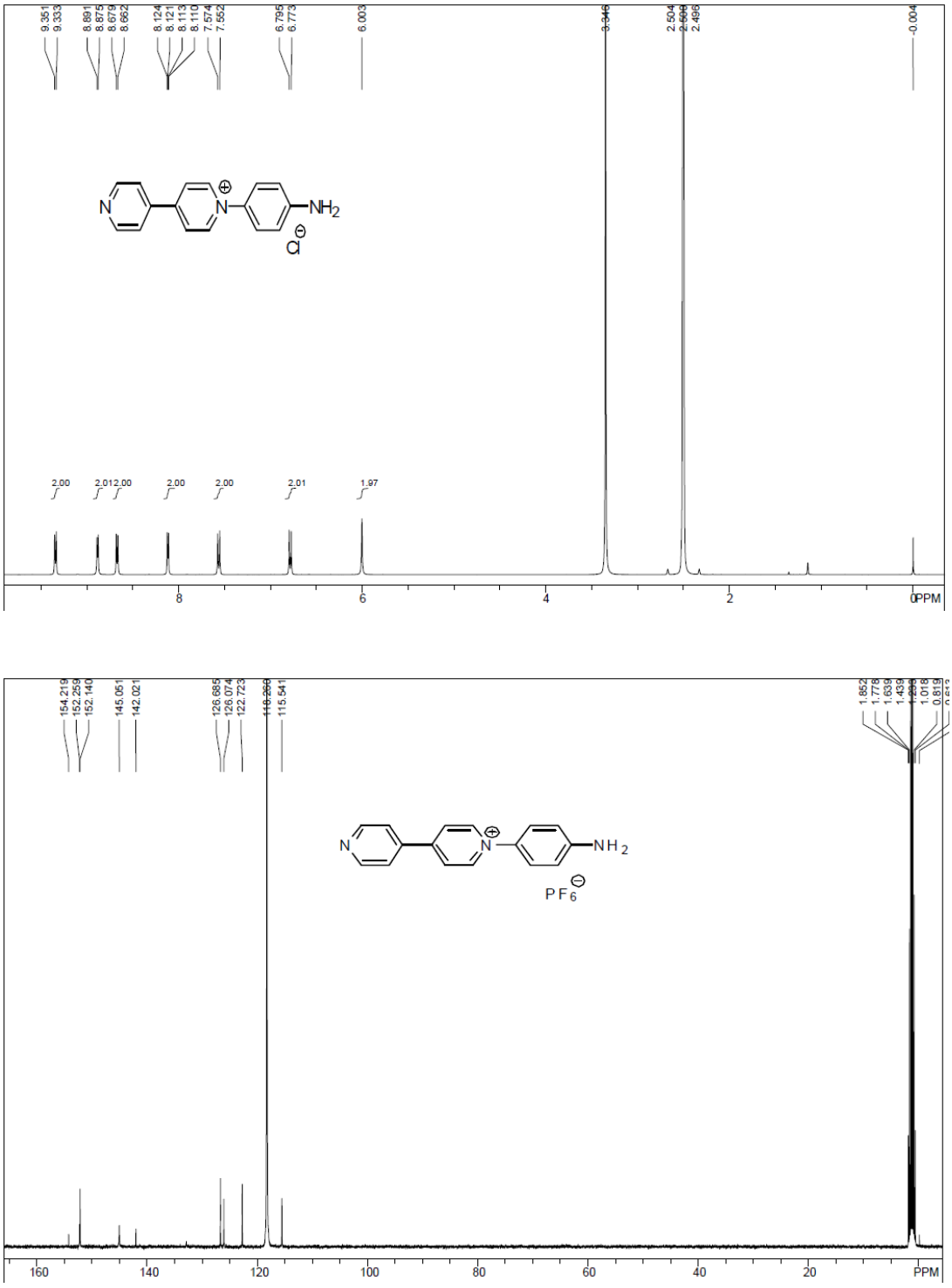


Figure S24. ^{1}H NMR (in DMSO-d_6) and ^{13}C NMR (in CD_3CN) spectra of compound **9**.

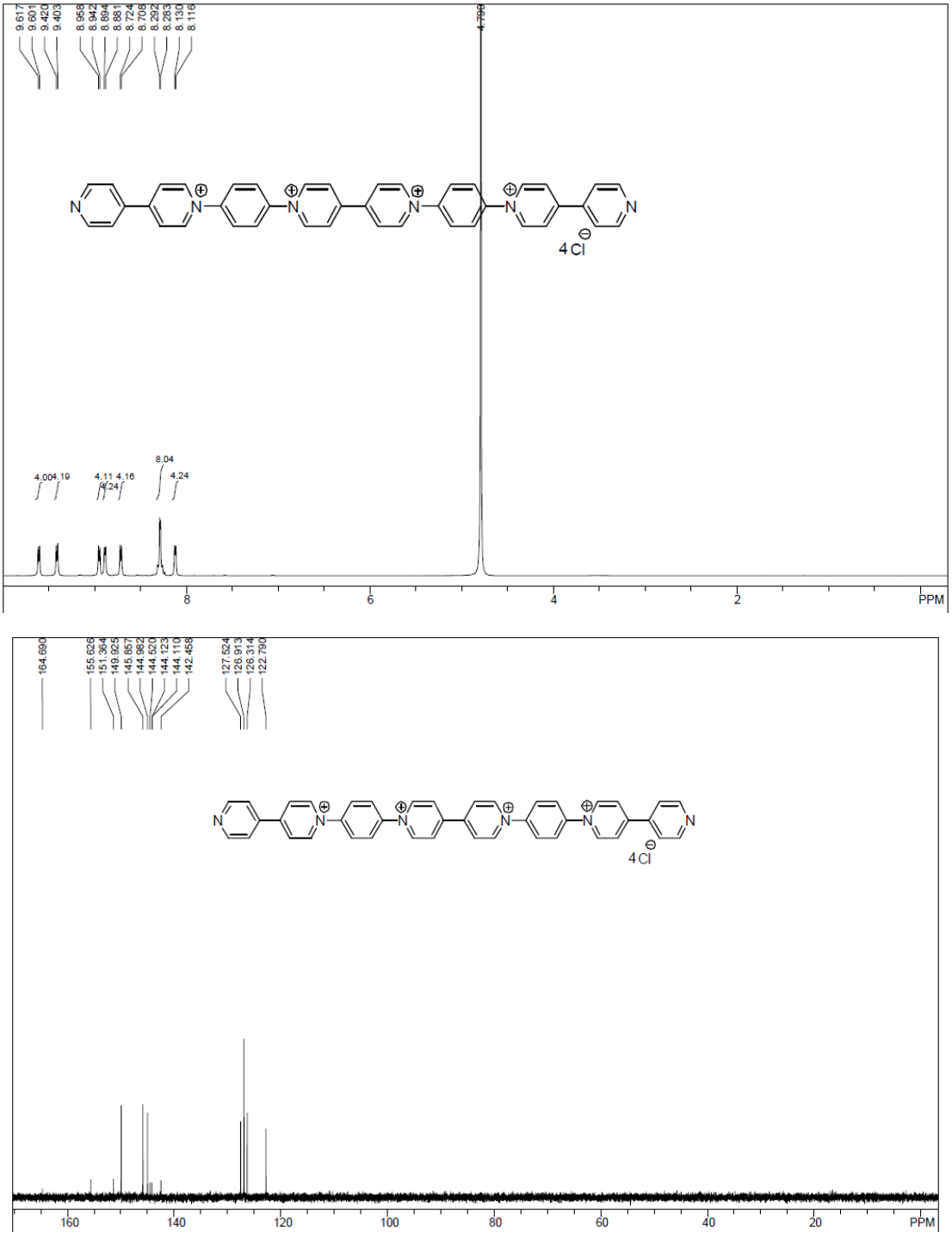


Figure S25. ^{1}H NMR and ^{13}C NMR spectra of **T2** in D_2O.

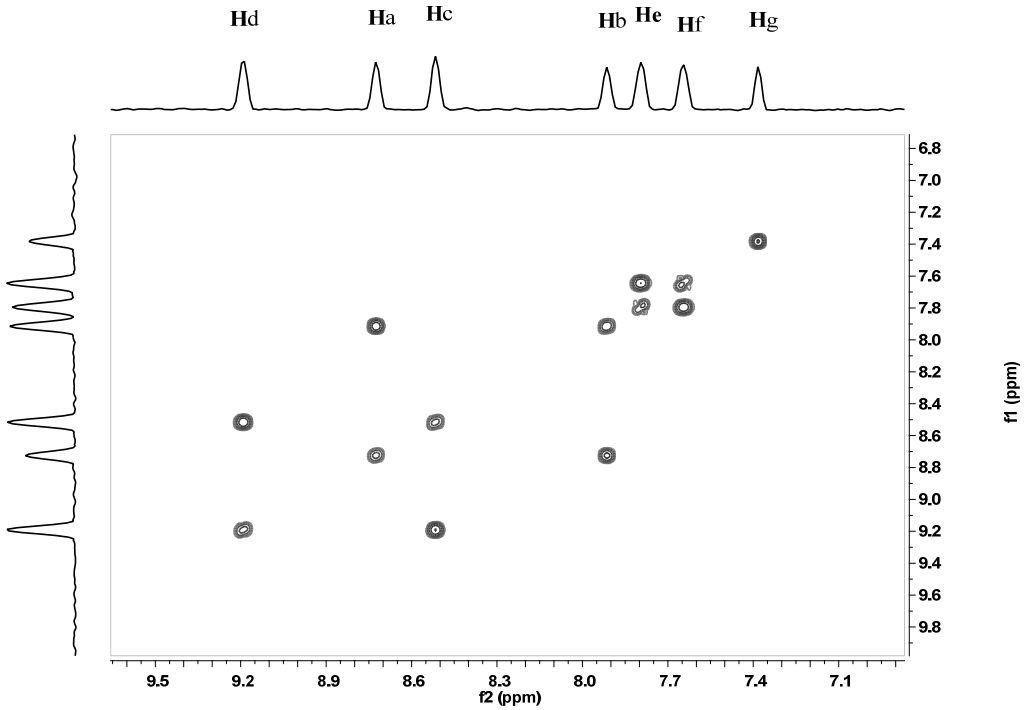


Figure S26. 2D ^{1}H NMR COSY spectrum (500 MHz) of **T1** in D_2O.

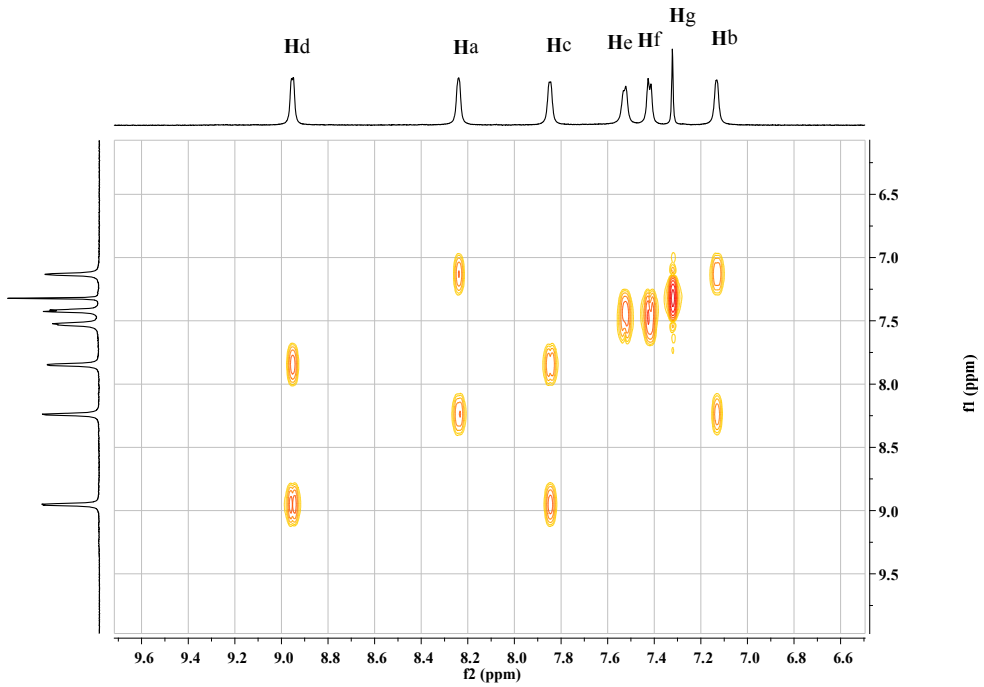


Figure S27. 2D ^{1}H NMR COSY spectrum (600 MHz) of **T1**+ CB[8] (1:1) in D_2O.

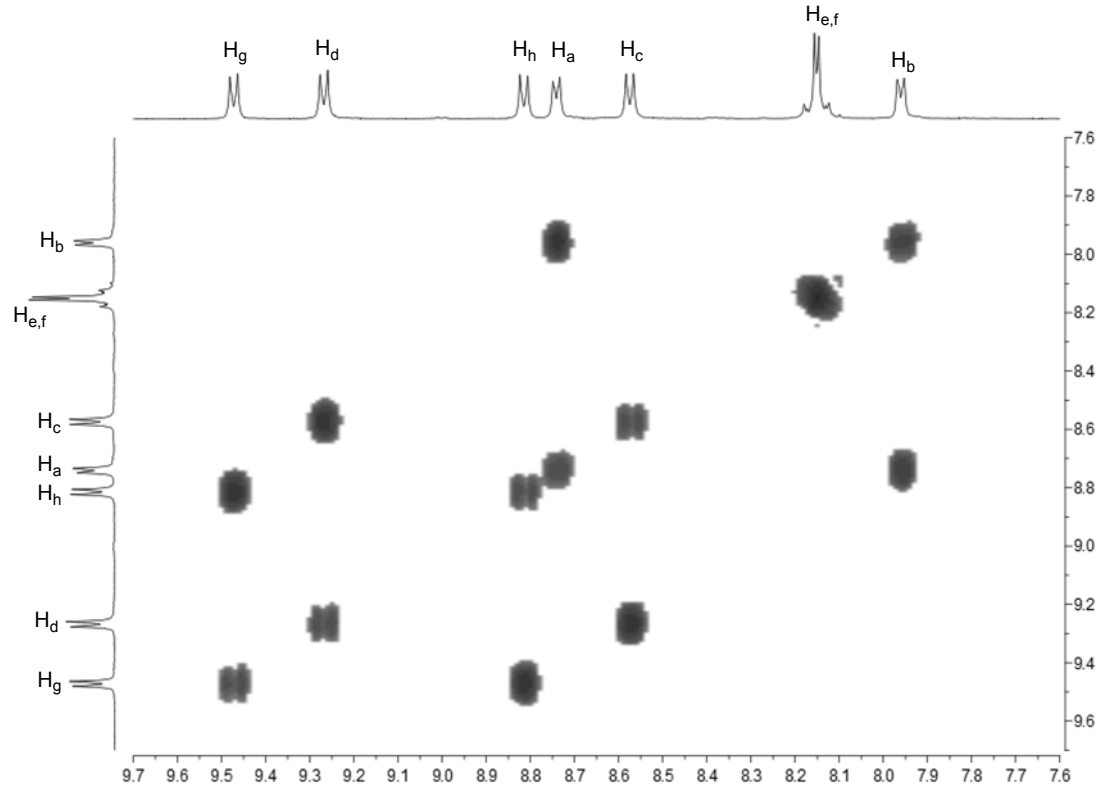


Figure S28. 2D ^{1}H NMR COSY spectrum (500 MHz) of **T2** in D_2O.

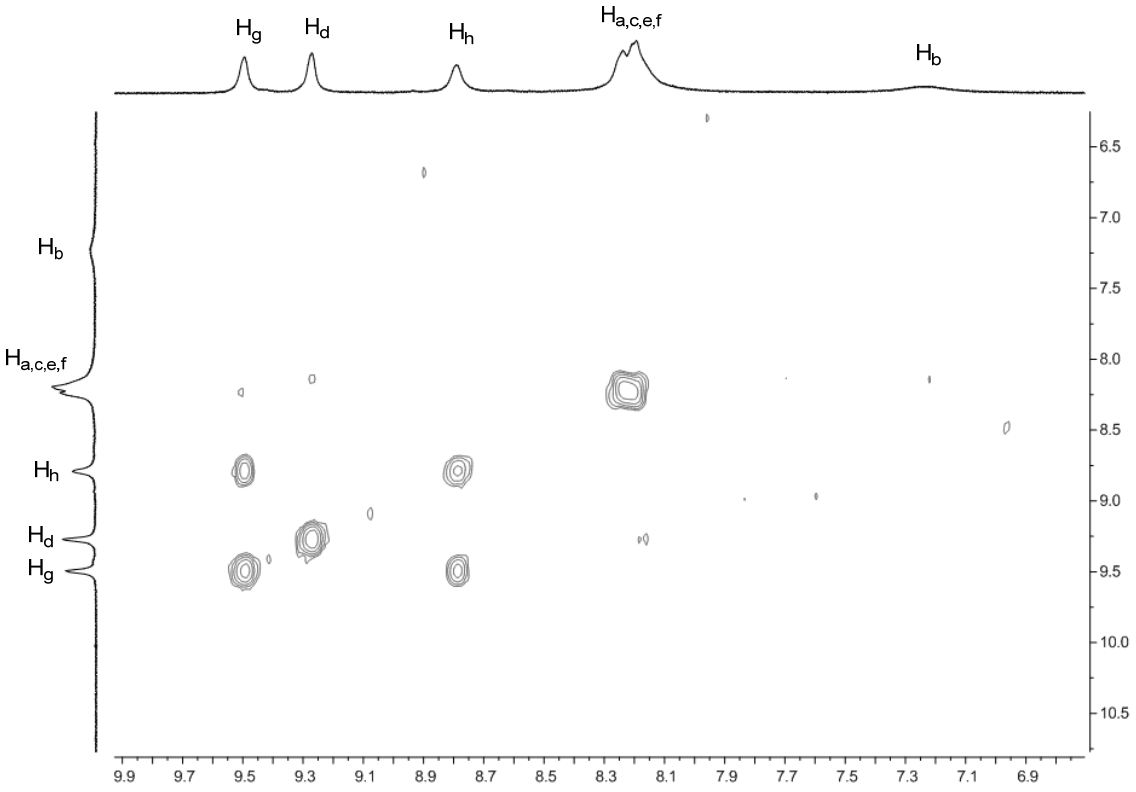


Figure S29. 2D ^{1}H NMR COSY spectrum (500 MHz) of **T2**+ CB[8] (1:1) in D_2O.