Materials and methods

Tetraphenylmethane, titanium tetrabromide, bromomethyl methyl ether, 4,4'-bipyridine, 1-bromobutane and CB[8] were purchased and used as supplied without further purification. Compound **1** and **2** was prepared and purified according to previously published methods [1-2]. The NMR data of compound were recorded on a AVANCE III HD 400 MHz spectrometer (Bruker), and the spectra of nuclear magnetic experiments were recorded on a ASCEND™ 600 MHz spectrometer (Bruker).

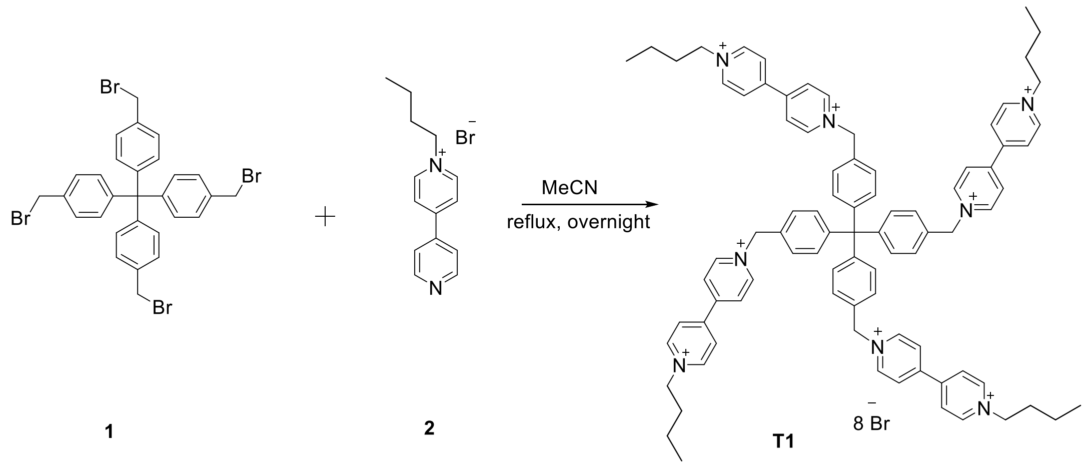
Single-crystal X-ray crystallography: Single crystals of compound T1@CB[8] were grown from water by vapor diffusion. The X-ray crystallographic analysis was obtained on a Bruker D8 VENTURE diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Data were corrected for absorption effects using the Multi-Scan method (SADABS). Data collection and reduction was performed using the APEX 3 software. The structure was solved and refined using the Bruker SHELXTL Software Package. The crystal structures were solved by direct methods and refined on F2 by full-matrix least- squares techniques using all unique data. CCDC 2039141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Isothermal titration calorimetry (ITC) experiments: The association constants and thermodynamic parameters for the inclusion complexation of T1 with CB[8] were determined by titration calorimetry with a ITC instrument (Nano ITC, TA, America) in aqueous solution. An aqueous solution (0.09 mM) of CB[8] was placed in the sample cell (1.3 mL). As a solution (0.5 mM) of the guest T1 was added in a series of 20 injections (5 μL), the heat evolved was recorded at T = 298.15 K. The heat of dilution was corrected by injecting the guest solution into deionized water and subtracting these data from those of the host-guest titration. Computer simulations (curve fitting) were performed using the Nano ITC analyze software.

Growth of single crystals: To a solution of **T1** (18.5 mg, 0.01 mmol) in water (2 ml), CB[8] (7.0 mg, 0.005 mmol) was added. The mixture was stirred at 80°C for 3 mins. Slow solvent evaporation of the solution in air over a period of about one month provided colorless crystals of **T1**@CB[8].

Dialysis experiments: The dialyzed eosin B, acid red 27, PTB in the absence and presence of **T1** or **Bu-SOF** in water or PBS solution (pH=7.4) at 37 °C. For preparing the solutions, eosin B, acid red 27, PTB was dissolved in pure water or PBS solution (pH=7.4) to obtain the control solution or in the solutions containing the **T1** or **Bu-SOF** and then diluting the solutions to the designed concentration ([eosin B] = [acid red 27] = [PTB] = 1 mM, [**T1**] = 1.86 mg/mL or **Bu-SOF** = 4.52 mg/mL). The solutions (0.5 mL) were added to a dialysis bag (cutoff MW: 1000 Da) that was immerged in pure water (20 mL). The solutions, being placed on a shaking orbital shaker, were subjected to dialysis for 4-6 hours. By recording the adsorption of eosin B, acid red 27, PTB at 517, 522, 518 nm, respectively, in the outside solution, the amount of the leaked eosin B, acid red 27 and PTB was calculated.

Nitrogen gas absorption experiments: The experiments were conducted according to reported methods [1].



Compound T1: A mixture of compounds **1** [2] (0.69 g, 1.0 mmol) and **2** [3] (2.35 g, 8.0 mmol) in acetonitrile (120 mL) was stirred under reflux for overnight and then cooled to room temperature. The resulting precipitate was filtrated and washed with acetonitrile (120ml) and dried under vacuum. The compound **T1** was obtained as a light yellow solid (1.67g，90%). M.p. 260-262 ℃. ^{1}H NMR (400 MHz, D_2O): δ 9.15-9.10 (q, 16H), 8.55-8.54 (d, J= 4.8 Hz, 16H), 7.53-7.45 (dd, J_1= 8.4 Hz, J_2= 21.8 Hz, 16H), 5.91 (s, 8H), 4.76-4.71 (m, 8H), 2.08-2.03 (m, 8H), 1.44-1.38 (m, 8H), 0.99-0.95 (t, 12H). ^{13}C NMR (400 MHz, D_2O): 150.45, 149.78, 147.82, 145.44,131.66, 130.42, 129.07, 127.16, 127.00, 64.18, 62.01, 32.56, 18.72, 12.61. HRMS (ESI): calcd for $[M-2Br]^{2+}$: 852.1248. Found: 852.1258.

References:

[1] Tian J, Zhou TY, Zhang SC, Aloni S, Altoe MV, Xie SH, Wang H, Zhang DW, Zhao X, Liu Y, Li ZT. *Nat Commun,* 2014, 5: 5574.
[2] Zhou C, Tian, J, Wang, JL, Zhang, DW, Zhao, X, Liu, Y, Li, ZT. *Chem Eur J,* 2014, 20: 575.
[3] Xiao X, Liu JX, Chen K, Zhu QJ, Xue SF, Tao Z. *Eur J Inorg Chem,* 2010, 2956.

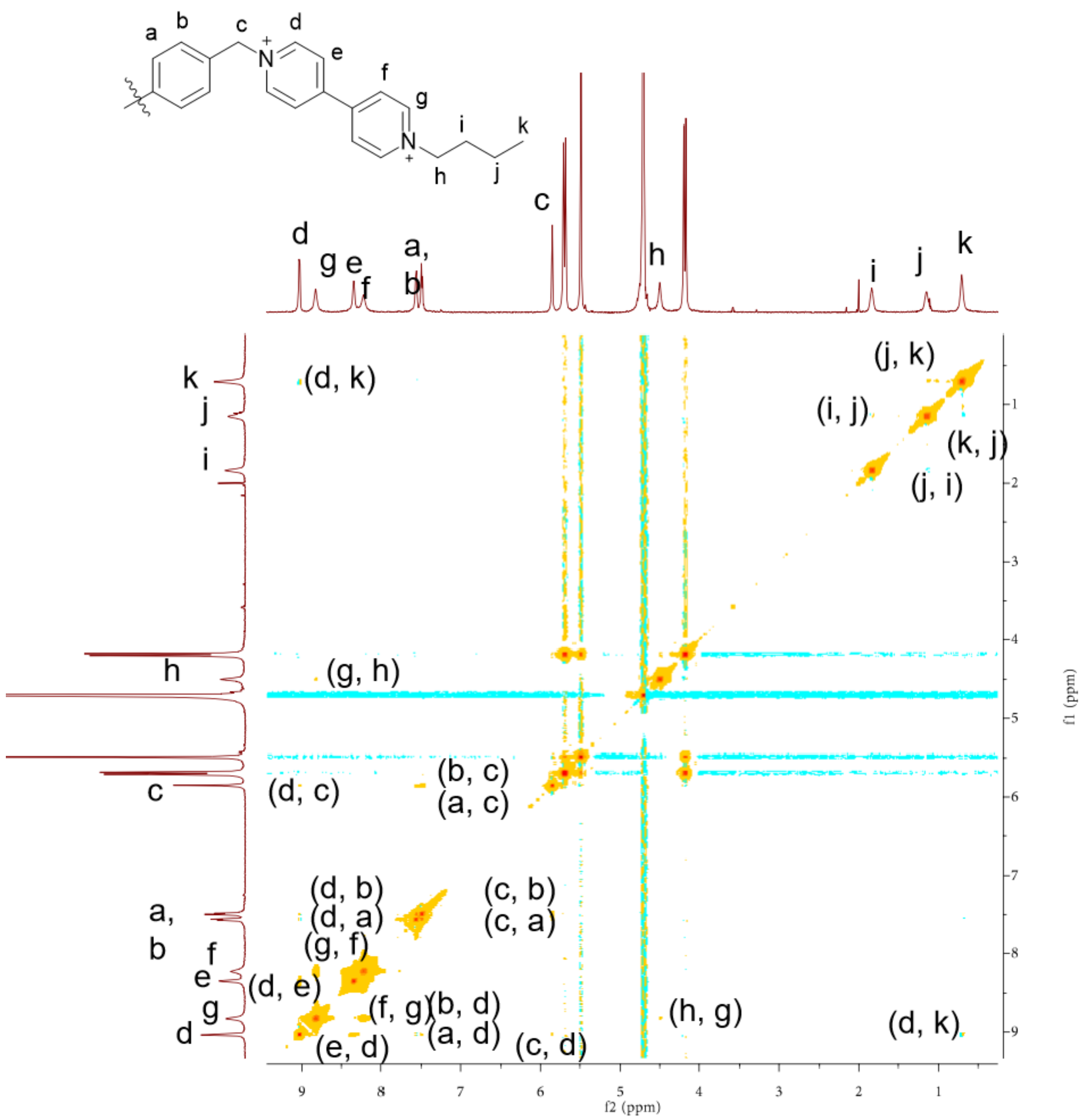


Figure S1 NOESY spectrum (500 MHz) of the solution of **T1** and CB[8] (1:2, [**T1**] = 1.0 mM) in D_2O.

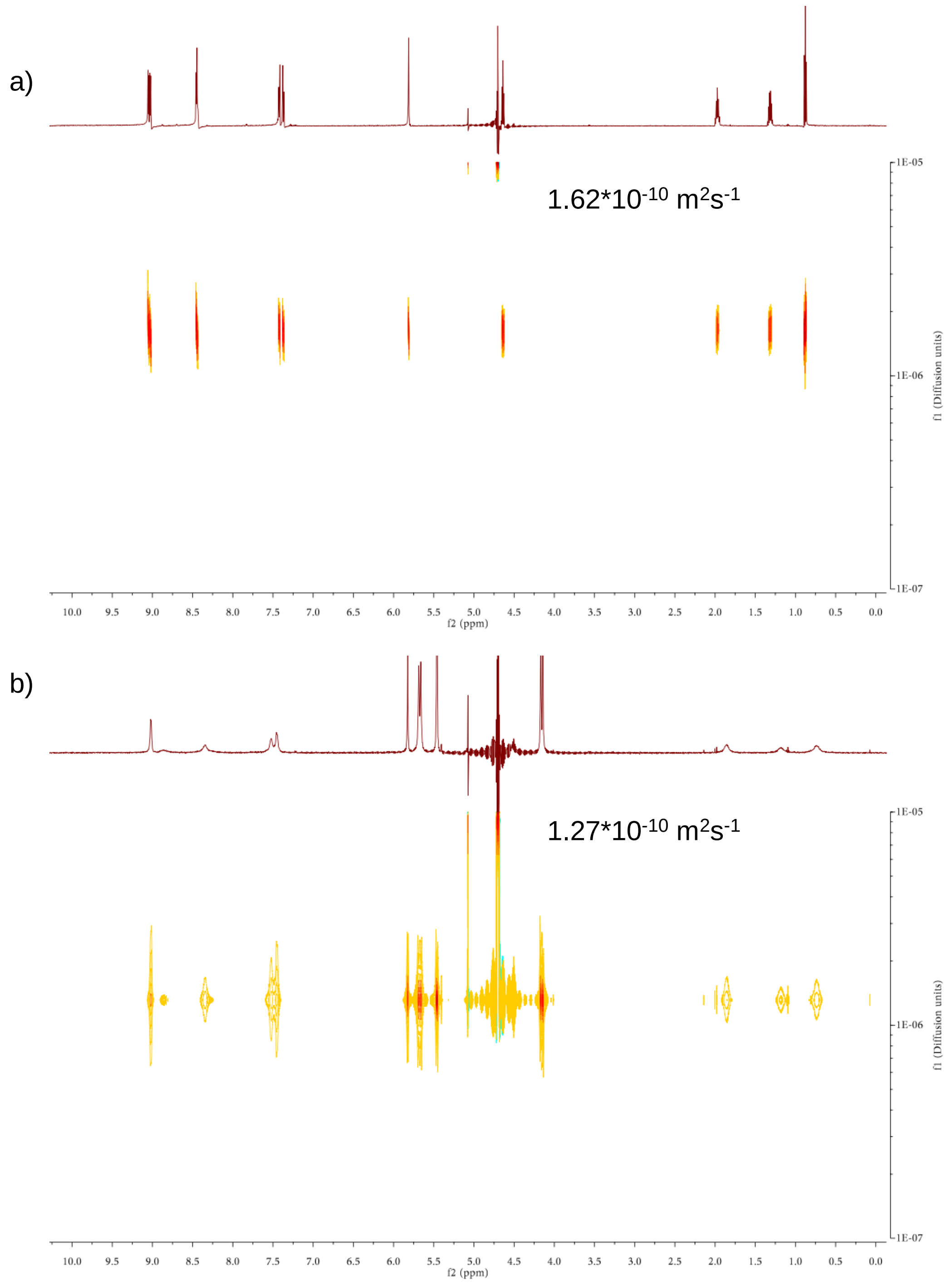


Figure S2 DOSY spectra (500 MHz): a) free guest **T1** and b) **T1**@CB[8] (1:2) in D_2O ([**T1**] = 0.5 mM).

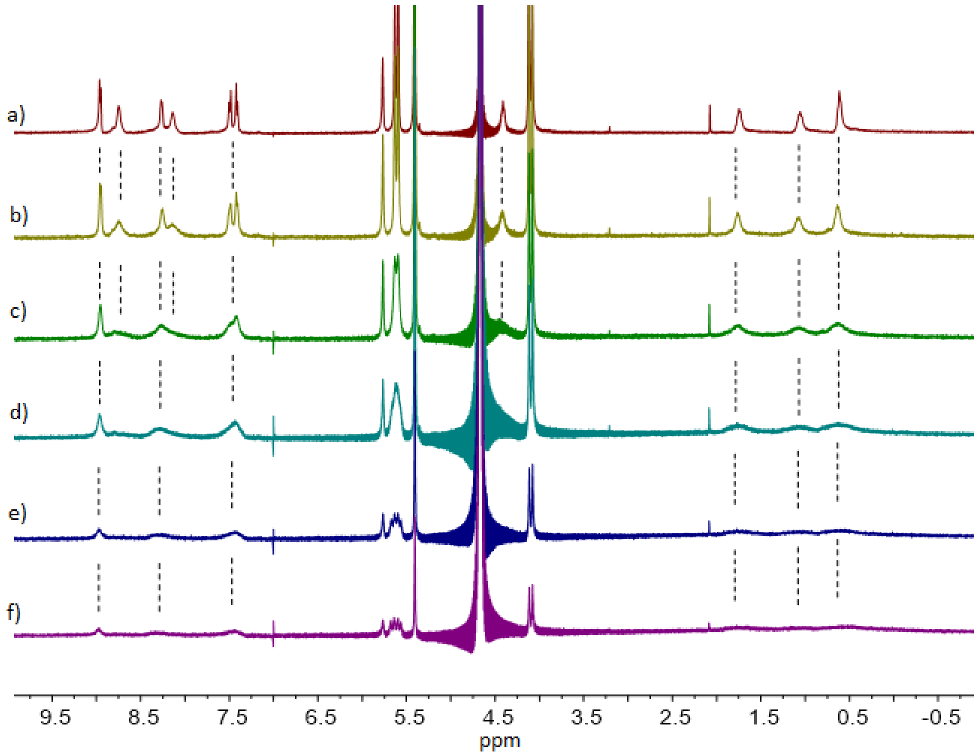


Figure S3 ^{1}H NMR spectra (400 MHz) of the solution of **Bu-SOF** in D_2O: [**T1**] = a) 1.0 mM, b) 0.5 mM, c) 0.25 mM, d) 0.12 mM, e) 0.06 mM, and f) 0.03mM.

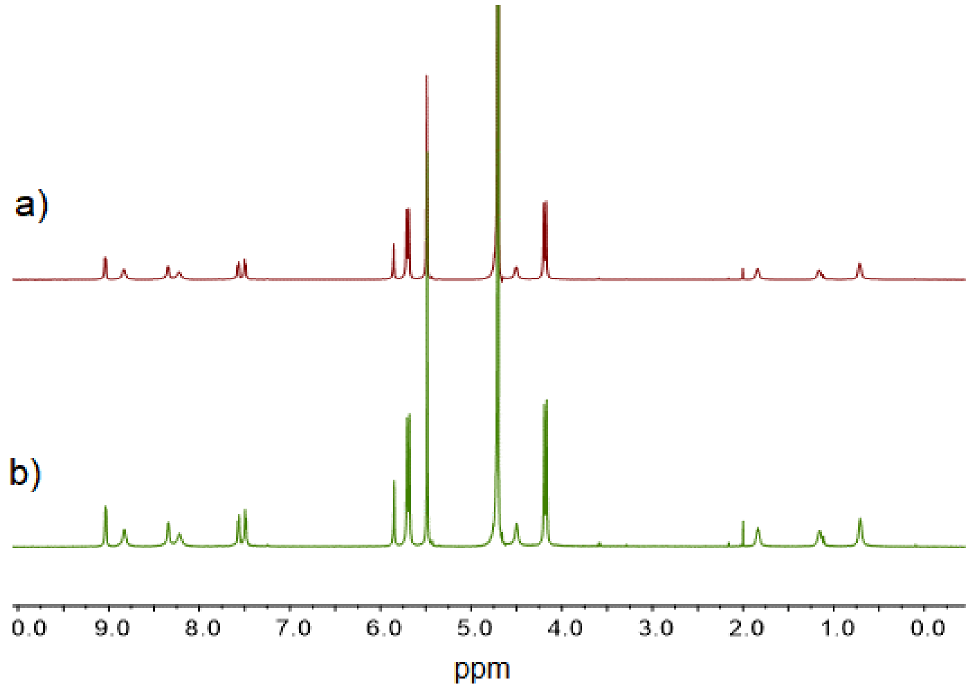


Figure S4 ^{1}H NMR spectra (600 MHz) of the solution of **Bu-SOF**（[**T1**] = 0.5 mM) in D_2O recorded after 1 h) and b) 96 h.

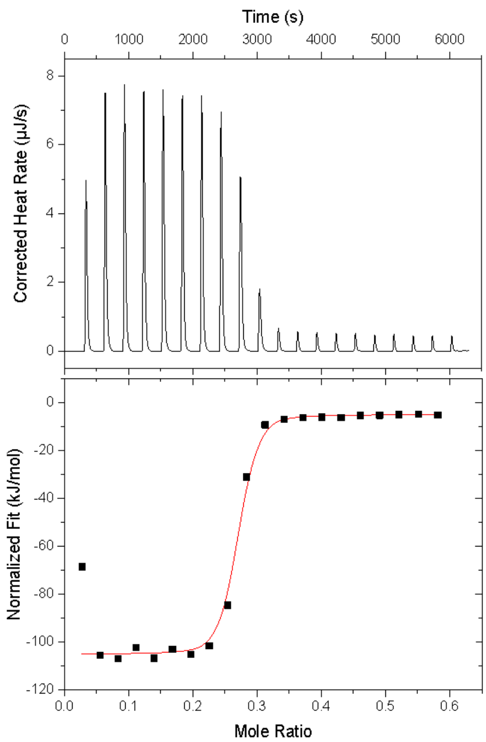


Figure S5 Isothermal titration calorimetry (ITC) profiles of CB[8] (0.09 mM) with the addition of guest **T1** at 298 K.

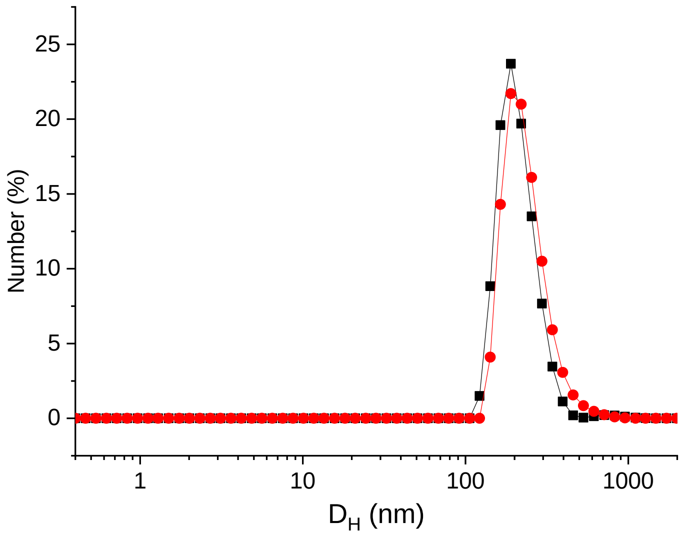


Figure S6 DLS profiles of **Bu-SOF** ([**T1**] = 0.03 mM) in water at 25 °C recorded after 1 hour (black) and 4 months (red).

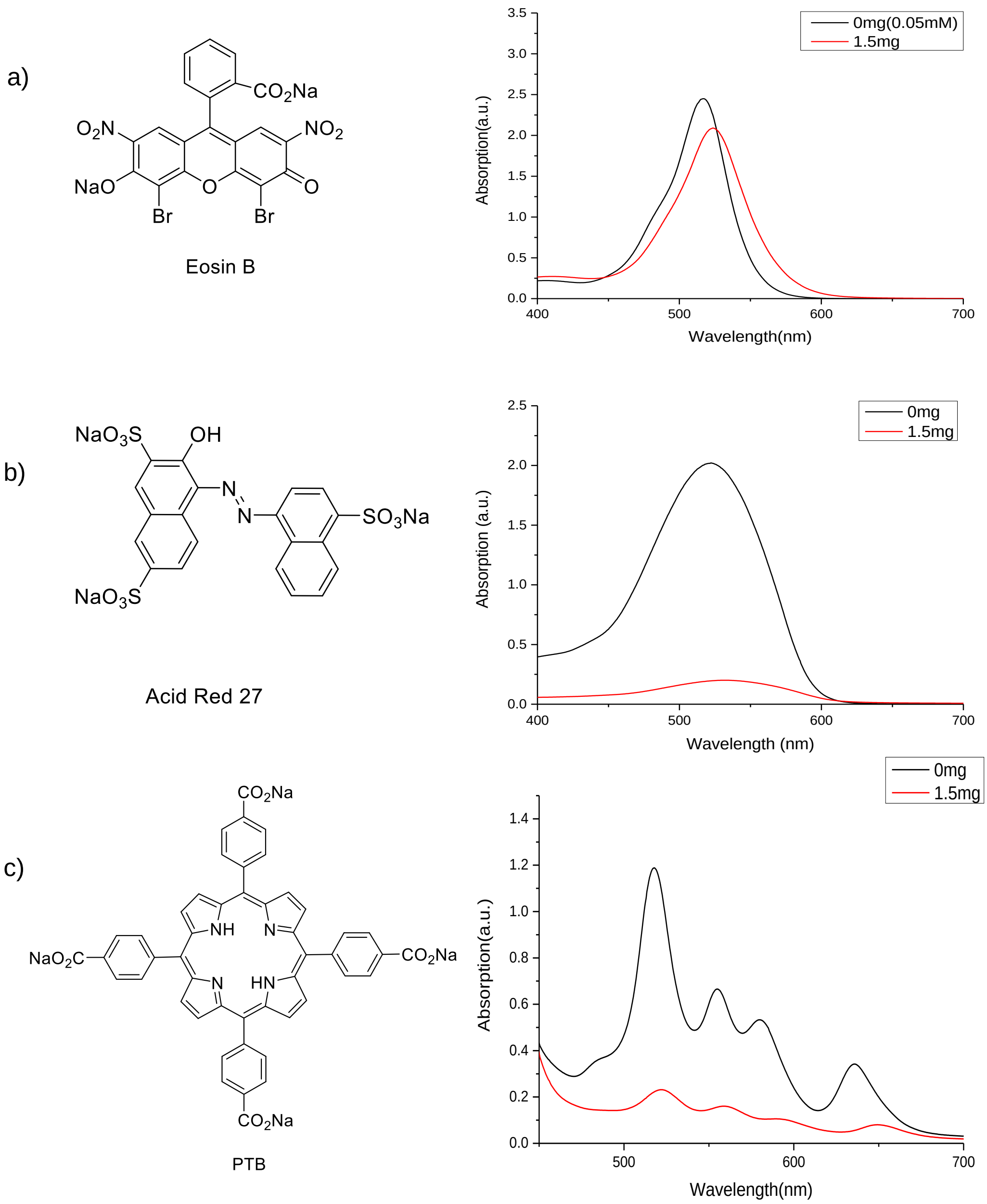


Figure S7 The absorbance of eosin B (0.1 mM), PTB (0.1mM) and acid red 27 (0.1mM) before and after the adsorption by the **Bu-SOF** power (1.5mg), prepared by freeze-drying its solution in water.

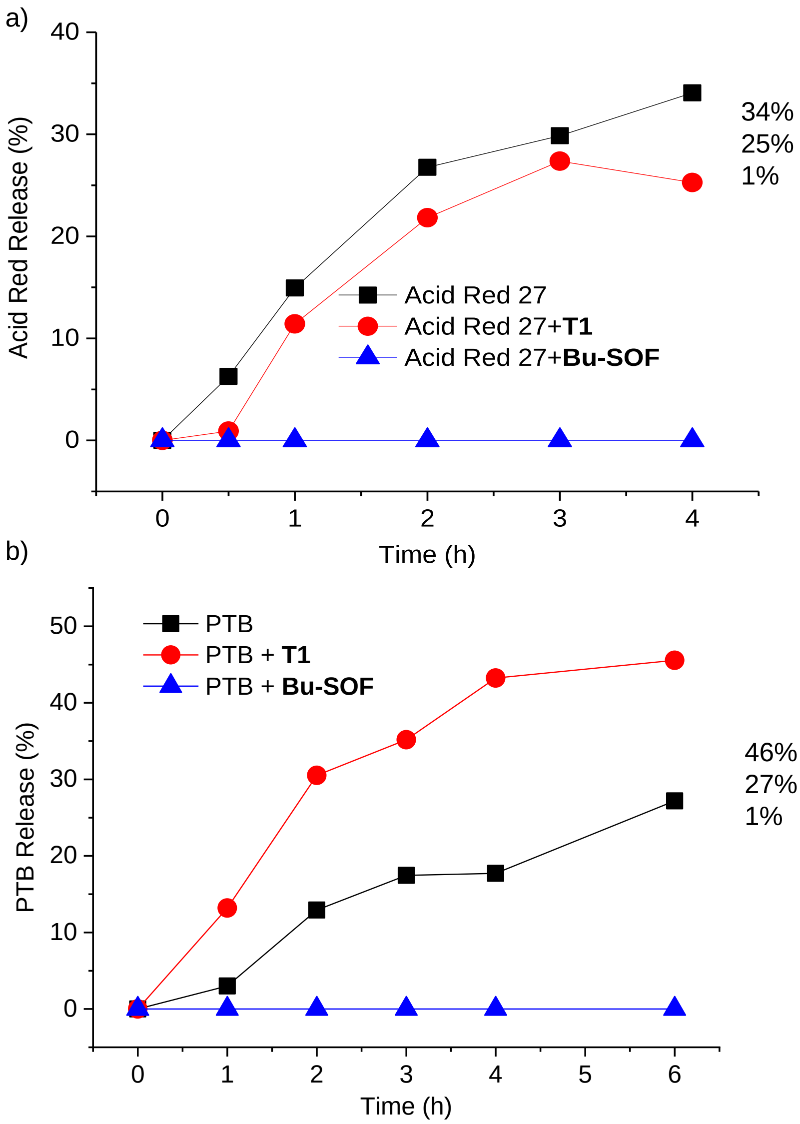


Figure S8 Dialysis experiments (molecular weight cut-off: 1000 Da) for the mixture solution: a) acid red 27, acid red 27 + **T1** and acid red 27 + **Bu-SOF** (H_2O, acid red 27=1mM, **T1**=1mM), (b) PTB, PTB+**T1** and PTB + **Bu-SOF** (PBS, pH=7.4, PTB=1mM, **T1**=1mM).

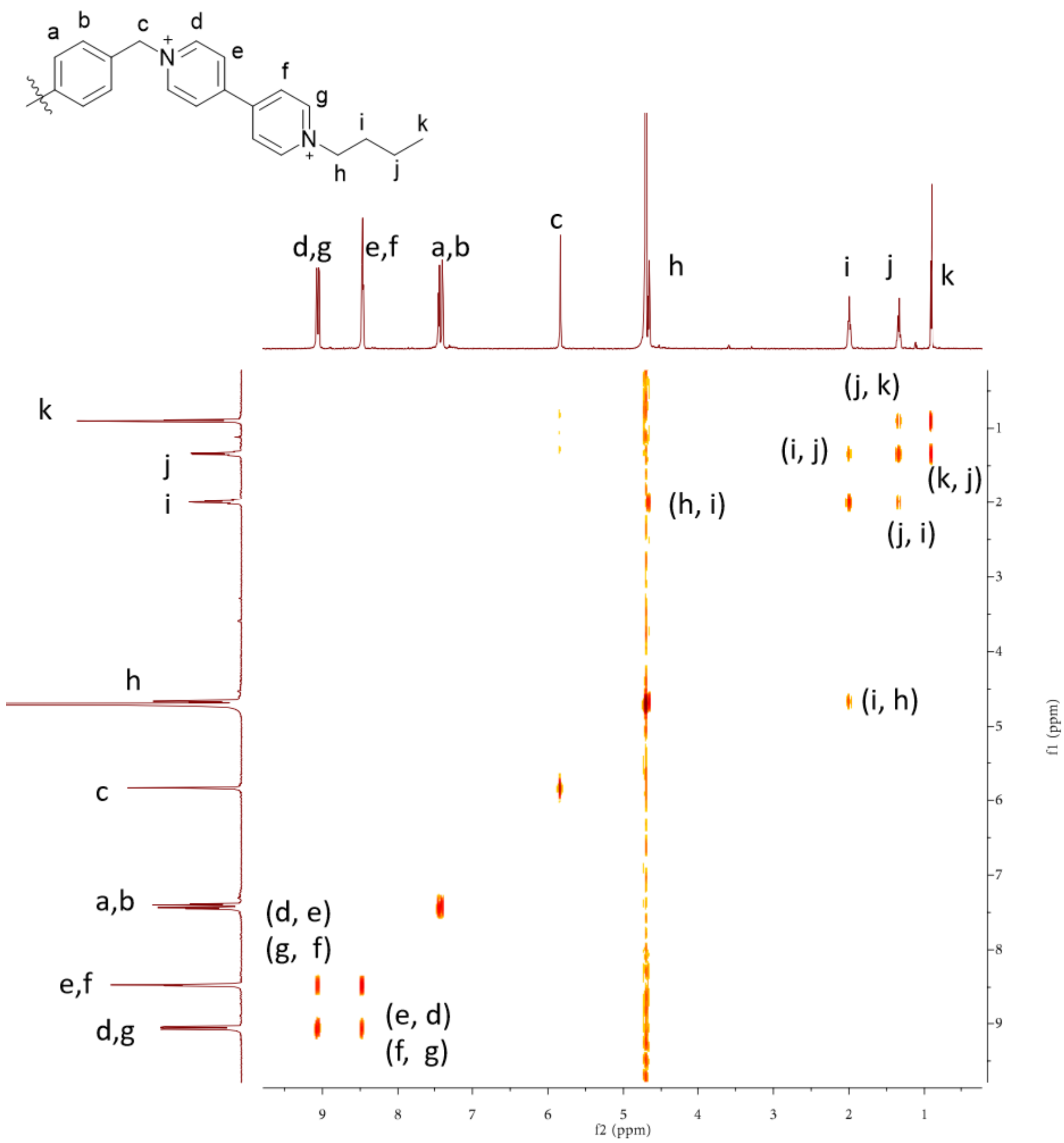


Figure S9 COSY spectrum (600 MHz) of **T1** (1.0 mM).

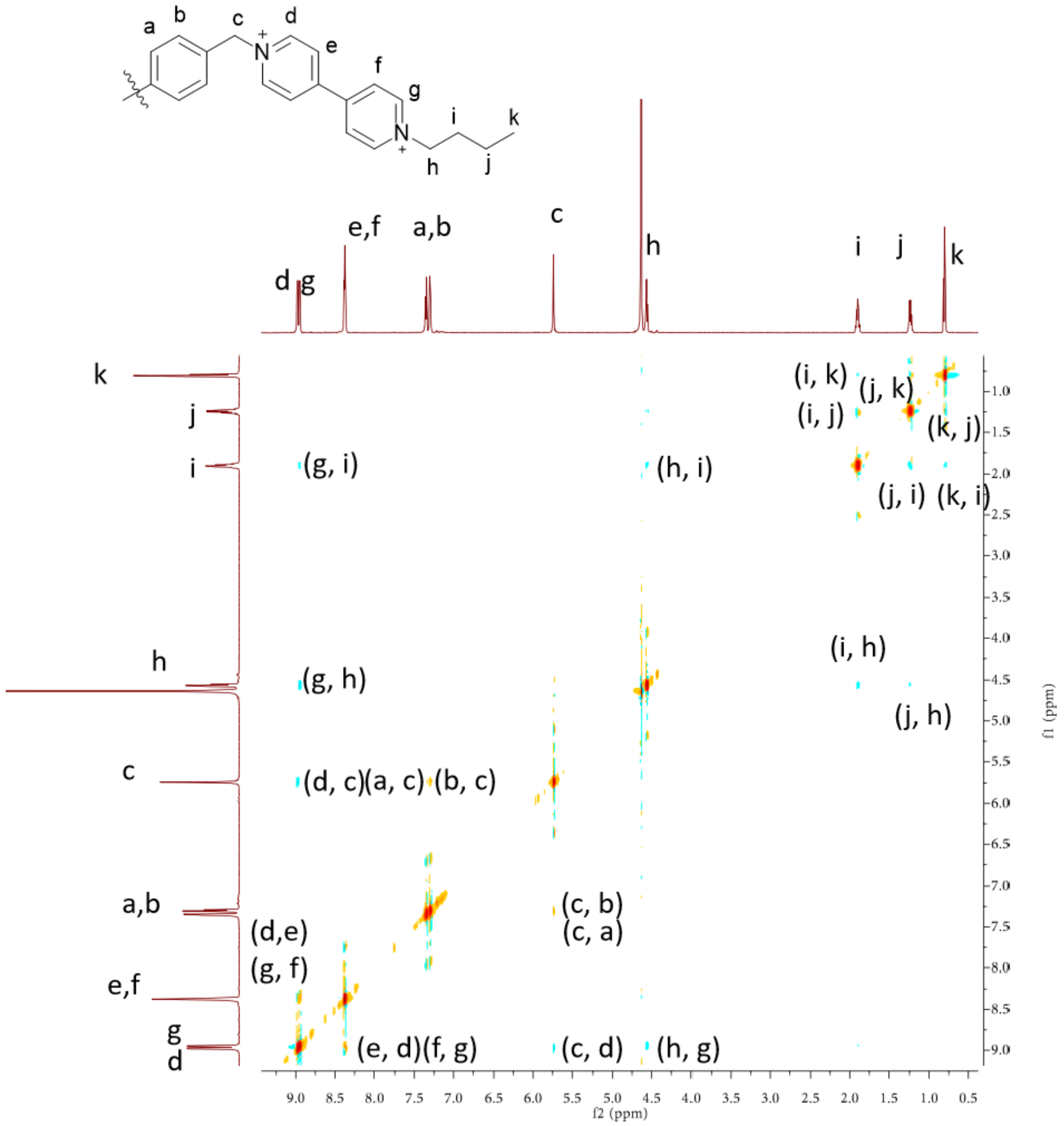


Figure S10 NOESY spectrum (600 MHz) of **T1** (1mM).

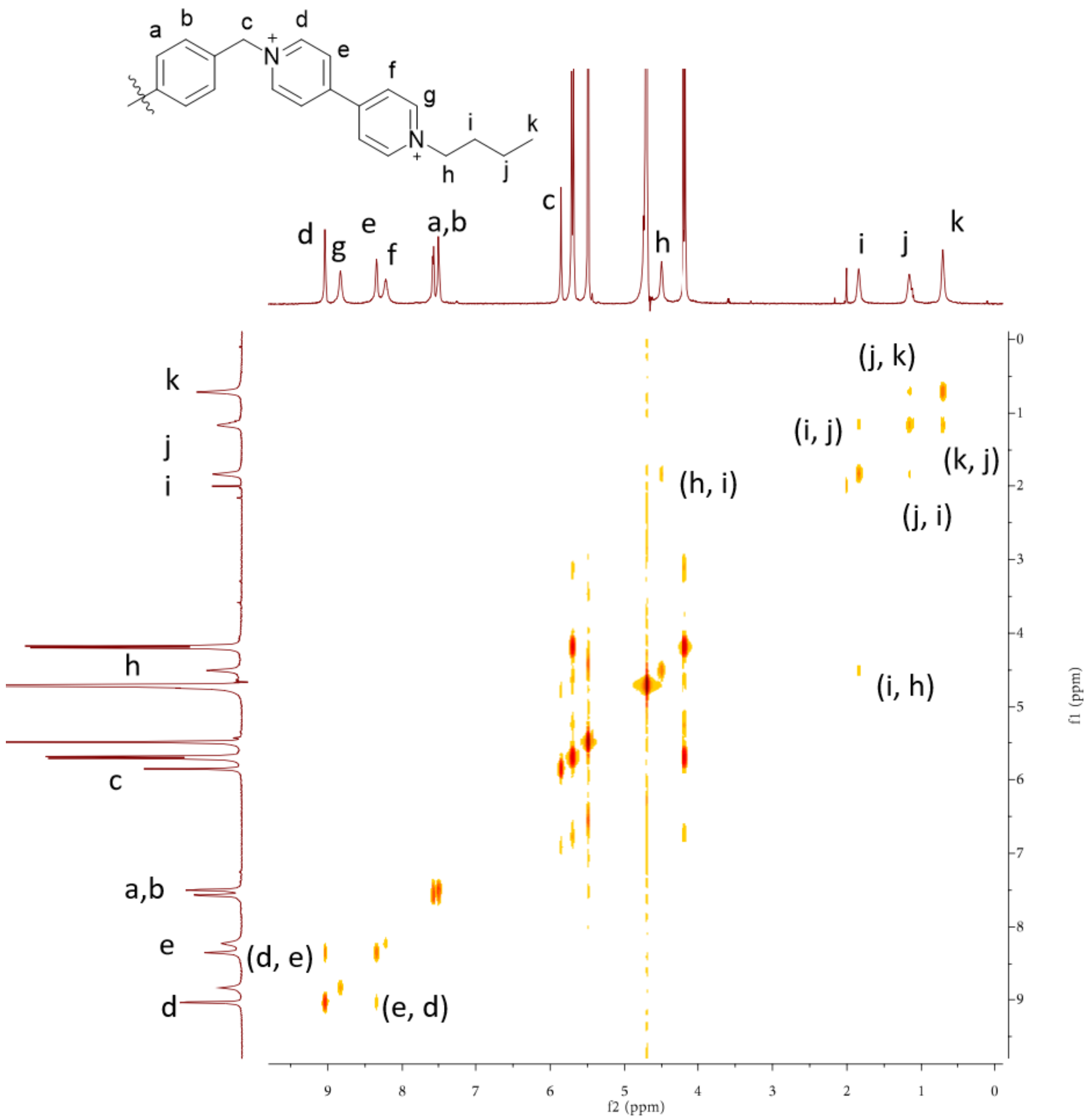


Figure S11 COSY spectrum (600 MHz) of **T1** with CB[8] (1:2) (1.0 mM).

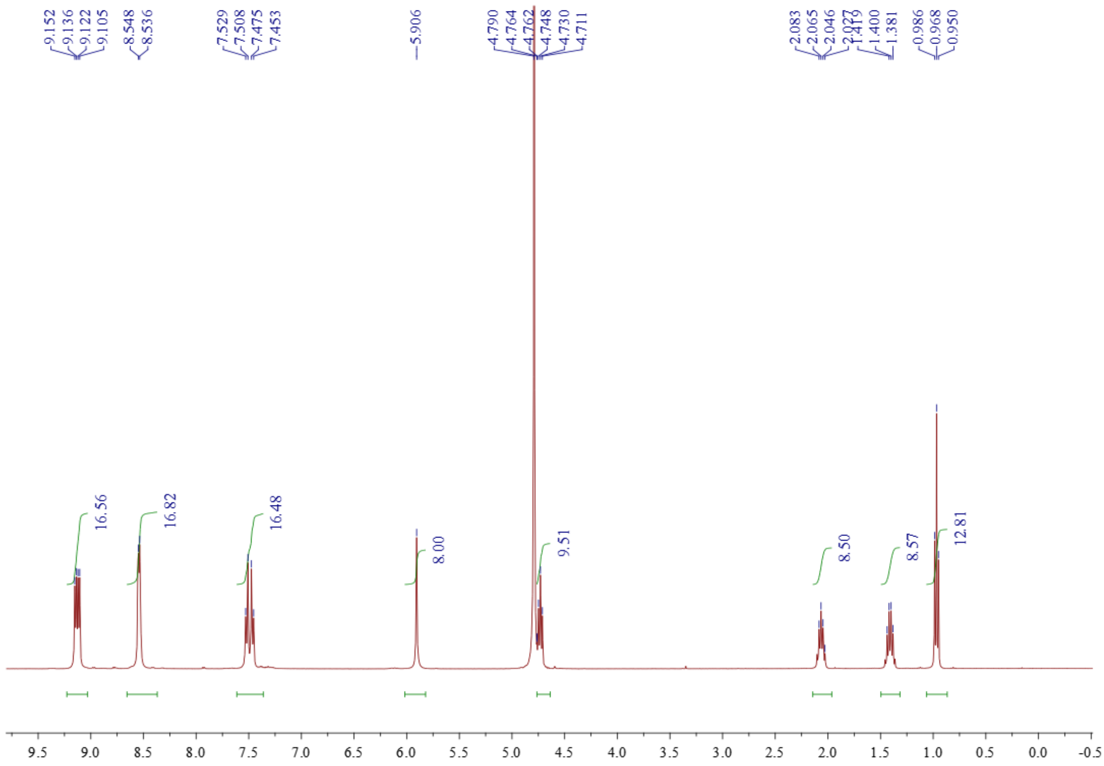


Figure S12 ^{1}H NMR (500 MHz) of **T1** (1.0 mM) in D_2O.

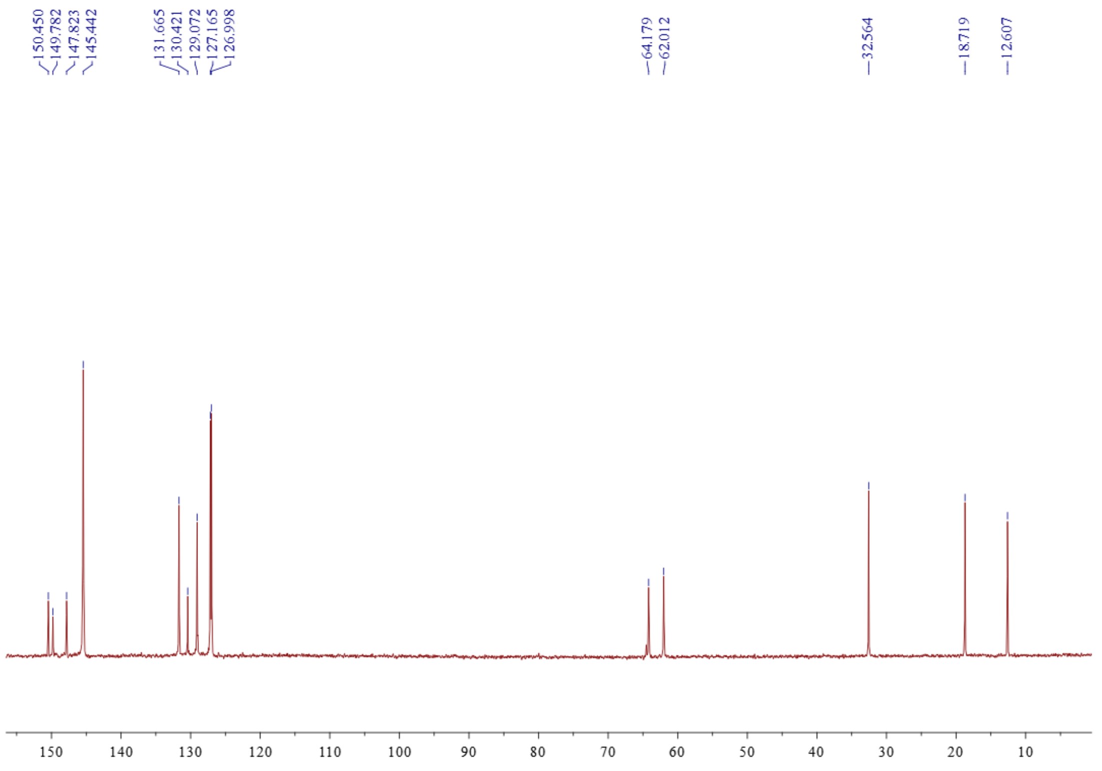


Figure S13 ^{13}C NMR (125 MHz) of **T1** (1.0 mM) in D_2O.

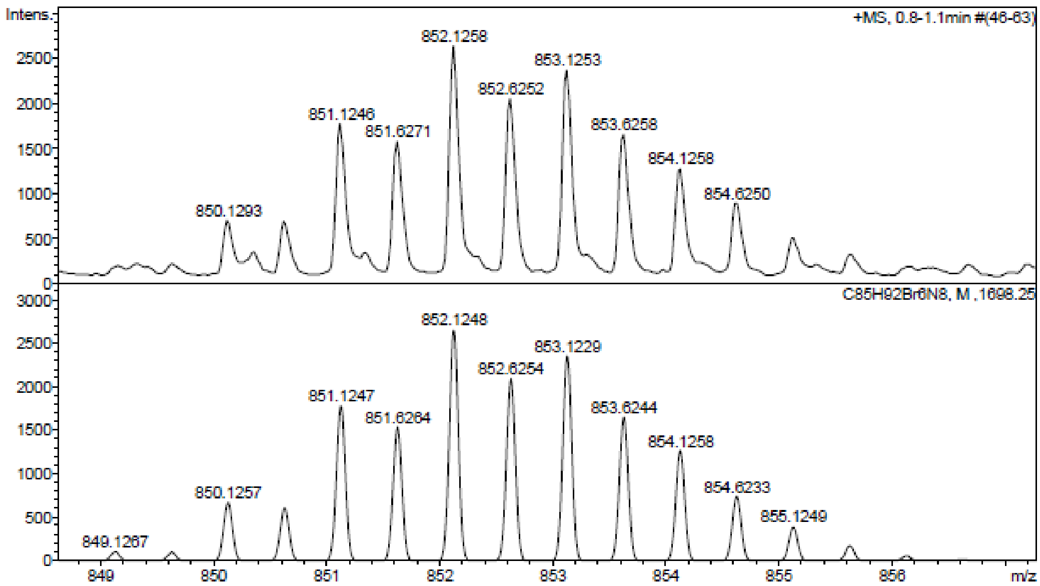


Figure 14 Mass spectrum of compound **T1**.