Alkaline Earth Caions-Mediated Photoluminescent Materials of Thioflavin with Twisted Cucurbit[14]uril

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Experimental

1.1. Materials.

*t*Q[14] was synthesized according to the procedure developed in our laboratory and characterized by ^{1}H NMR spectrometry. Thioflavin T (ThT) was obtained from Sigma–Aldrich (Shanghai, China); perchlorate salts and nitrate salts were obtained from Aladdin (Shanghai, China). All reagents were of analytical reagent grade and were used without further purification. Doubly-distilled water was used throughout.

1.2. Measurement of absorption and fluorescence spectra.

All UV/Vis spectra were recorded on an Agilent 8453 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) from solutions in 1 cm quartz cells. Fluorescence emission spectra were recorded on a VARIAN Cary Eclipse spectrofluorometer (Varian, Inc., Palo Alto, CA, USA). The fluorescence spectra were obtained by excitation at 414 nm with 5 nm emission and excitation bandwidths. Stock solutions of *t*Q[14] (2×10^{-3} mol L^{-1}), ThT (1×10^{-3} mol L^{-1}), and M^{n+} (1 mol L^{-1}) were prepared in doubly-distilled water. Working solutions were prepared by diluting the stock solutions to the required concentrations.

Aqueous solutions of ThT (2.00×10^{-5} mol L^{-1}) were prepared by diluting the stock solutions. For the absorption and fluorescence spectra, increasing concentrations ($0–30\times10^{-5}$ mol L^{-1}) of *t*Q[14] solution were added to the free ThT. The excitation and maximum emission wavelengths ($\lambda_{ex}/\lambda_{em}$) were 414 nm/491 nm for the complex *t*Q[14]–ThT with 5 nm emission and excitation bandwidths.

Aqueous solutions of *t*Q[14]–ThT complex (ThT: 2.00×10^{-5} mol L^{-1}) were prepared for characterization by fluorescence emission spectroscopy. To obtain fluorescence spectra, quantitative concentration (20 mM) of metal ion solutions (Mg^{2+},Ca^{2+},Sr^{2+}, Ba^{2+}) were added to the *t*Q[14]–ThT complex. Fluorescence spectra were obtained by excitation at 414 nm with 5 nm emission and excitation bandwidths and the emission intensity was monitored at 390–750 nm at room temperature. The maximum emission wavelength was λ_{em}=491 nm for the complex of *t*Q[14]–ThT. For each experiment, three replicate measurements were made.

1.3. ^{1}H NMR measurements.

^{1}H NMR spectra were recorded at 25°C on a WNMR-I 500 MHz NMR spectrometer (Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences). D_2O was used as a field-frequency lock and the observed chemical shifts are reported in parts per million (ppm) relative to that of the internal standard (TMS at 0.0 ppm).

1.4 Isothermal titration calorimetry (ITC) measurements

Thermodynamic parameters and binding constants (*K*) for the *t*Q[14]/ThT complex were determined by titration calorimetry using a Nano ITC instrument (TA, USA). All solutions were prepared in doubly distilled water and degassed prior to the titration experiments. The heat evolved was recorded at 298.15 K. The heat of dilution was corrected for by injecting the guest solution (free guest) into the aqueous solution and subtracting the values from the corresponding values obtained for the host–guest titration. Computer simulations (curve fitting) were performed using the Nano ITC analytical software. For ThT, the concentration of *t*Q[14] in the sample cell (1.3 mL) was 1×10^{-4} mol/L. A typical ITC titration was carried out by titrating the ThT solution (1×10^{-3} mol/L, 5 μL aliquots, at 200 s intervals) into a *t*Q[14] solution. For the remaining 4 metals (containing Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), the concentration of *t*Q[14] in the sample cell (1.3 mL) was 1×10^{-4} mol/L, and the concentration of ThT in the sample cell (1.3 mL) was 1×10^{-4} mol/L. The ITC titrations were carried out by titrating metals solution (2×10^{-3} mol/L, 10

μL aliquots, at 250 s intervals) into the *t*Q[14] solution, respectively.

1.5 DLS measurements

The sample solution for the DLS measurements was prepared by filtering the solution through a 450 nm millipore filter into a clean scintillation vial. It is worth noting that the aqueous solution of either *t*Q[14] or ThT was respectively prepared and then took the DLS measurements. Then both solutions were mixed together and the same DLS measurements were carried out. All the DLS measurements were performed at the scattering angle of 90° on a MGL-III-532nm-200mW-17061018 (Brookhaven Instruments) 25°C.

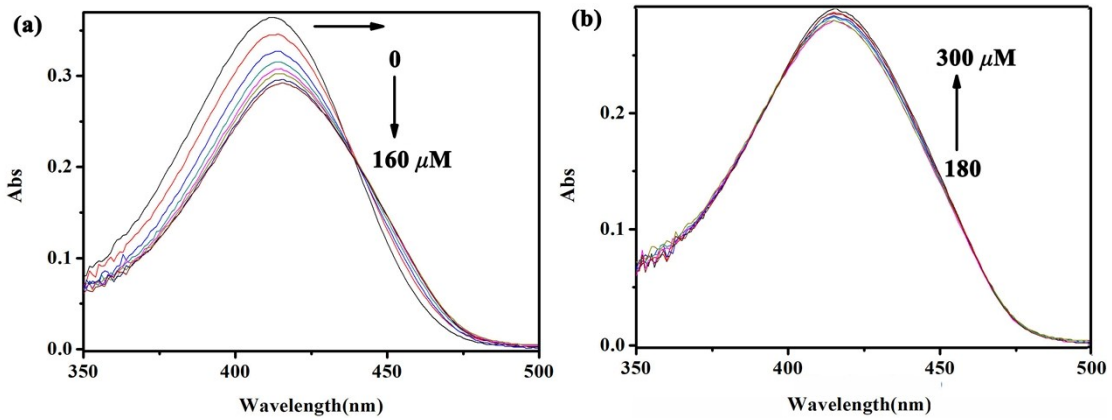


Fig . S1. Absorption spectra of ThT (20 μM) with increasing amount of *t*Q[14] from (a) 0, 20, 40, 60, 80, 100, 120, 140, 160, and (b) 180, 200, 220, 240, 260, 280, 300 μM in aqueous solutions, respectively.

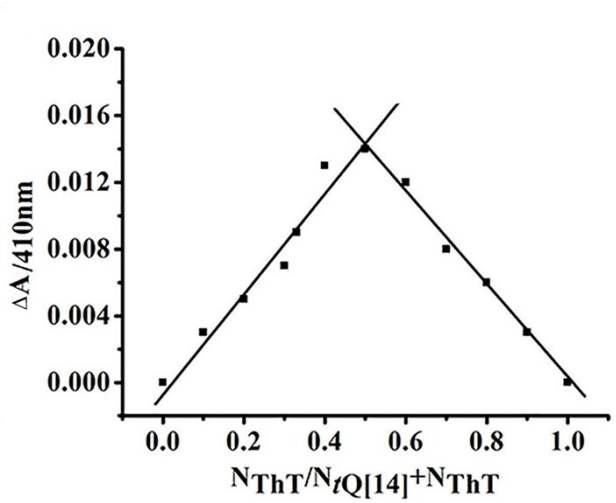


Fig . S2 Job plot for the formation of ThT/*t*Q[14] complex in water ($N_{tQ[14]} + N_{ThT} = 2.0 \times 10^{-4}$ mol/L) with a cuvette with a light path of 1 mm.

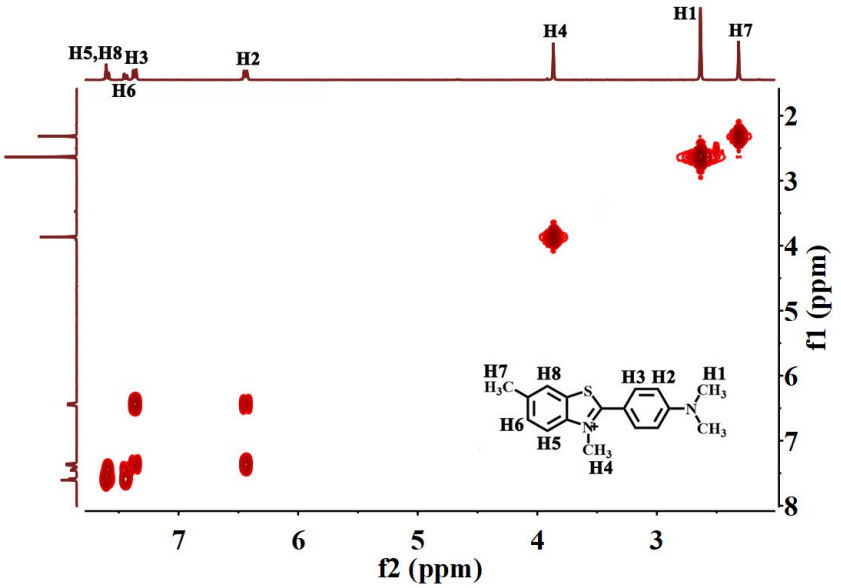


Fig. S3 COSY spectrum of ThT in D_2O

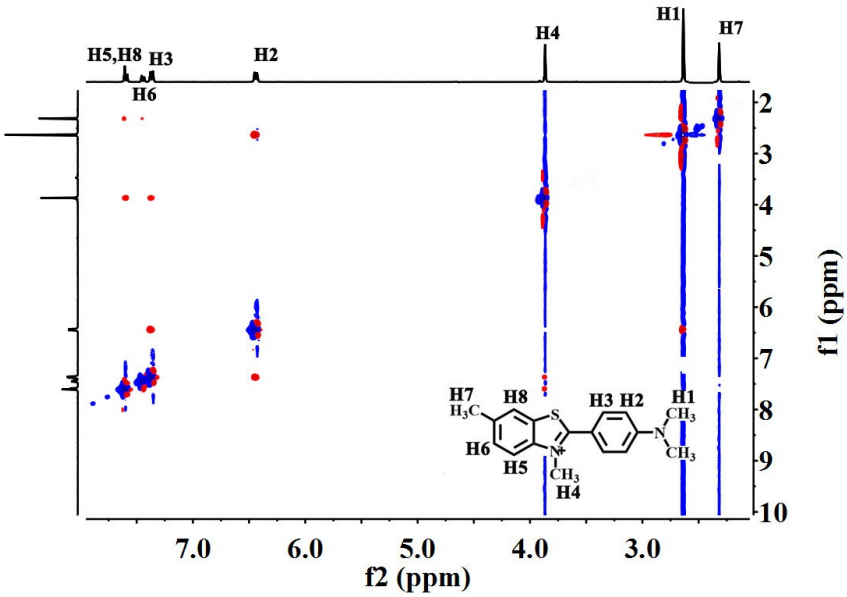


Fig. S4 ROSEY spectrum of ThT in D_2O

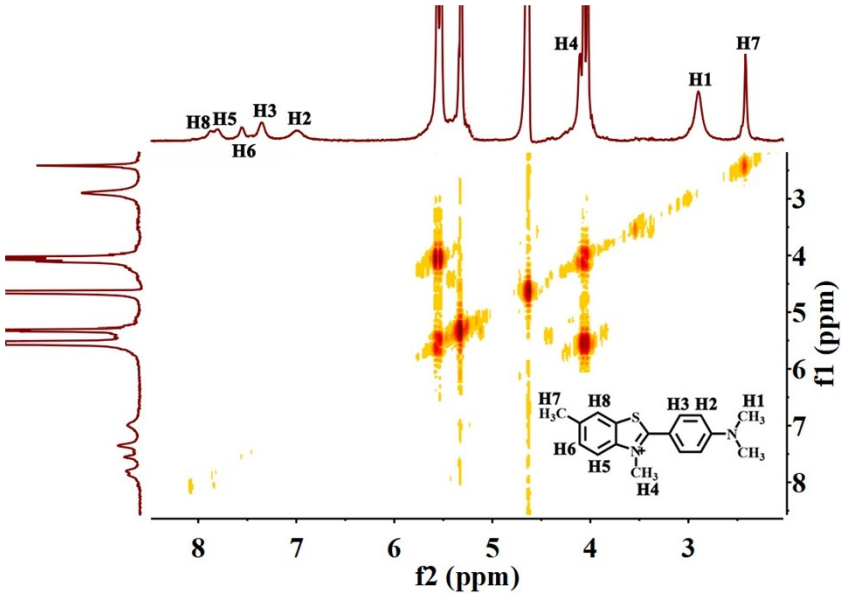


Fig. S5 COSY 2D spectrum of ThT/*t*Q[14] (1:1) in D_2O

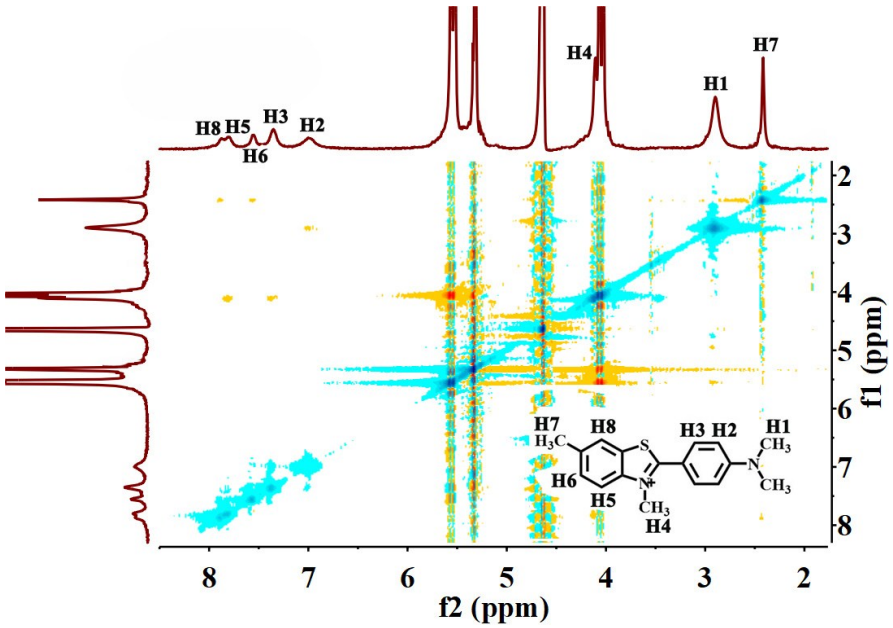


Fig. S6 ROSEY 2D spectrum of ThT/*t*Q[14] (1:1) in D_2O

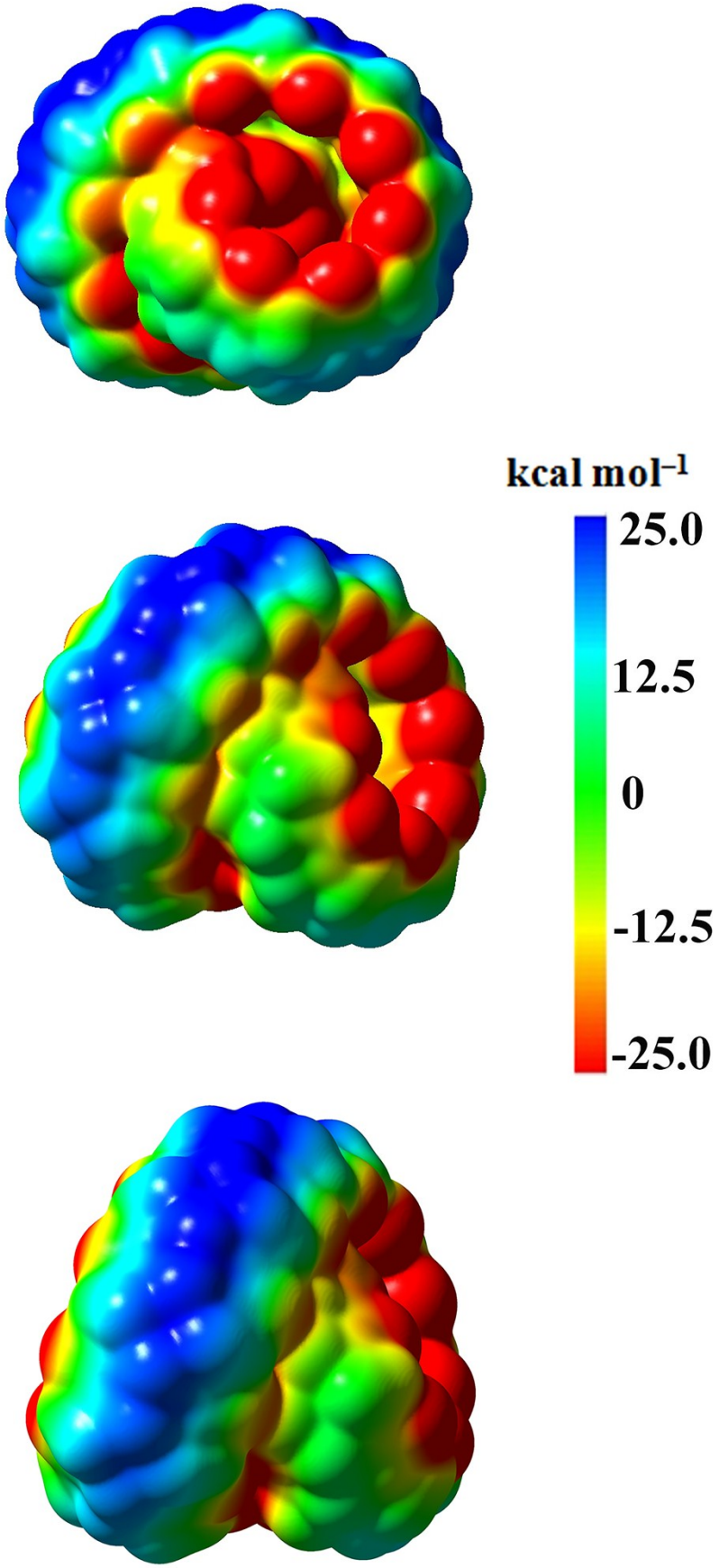


Fig. S7 Electrostatic potential maps (ESPs) for *t*Q[14]. ESPs are mapped on electron density isosurfaces (0.001 e/au^3) for *t*Q[14] at the B3LYP/6-311G (d, p) level of theory with Gaussian09.

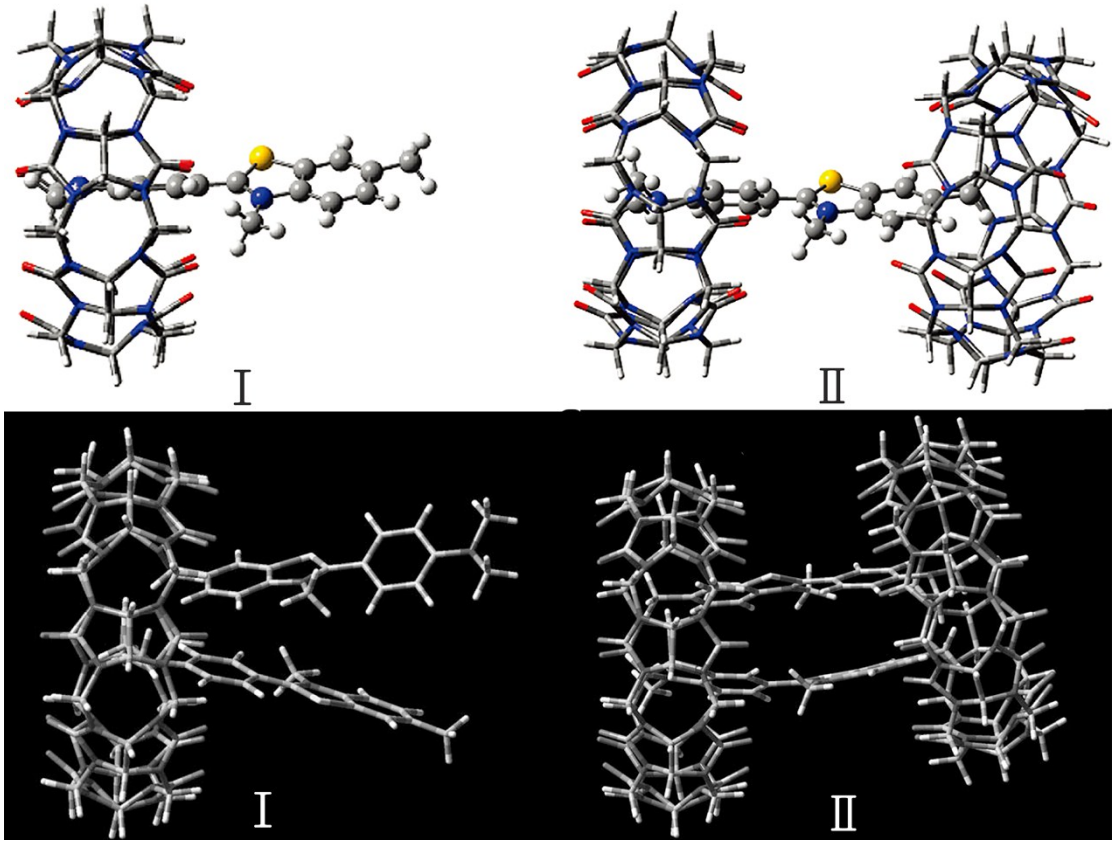


Fig. S8 Computationally optimized structures for (top) Q[7]-ThT system in 1:1 (I) and 2:1 (II) stoichiometries; (bottom) Q[8]-ThT system in 1:2 (I) and 2:2 (II) stoichiometries.

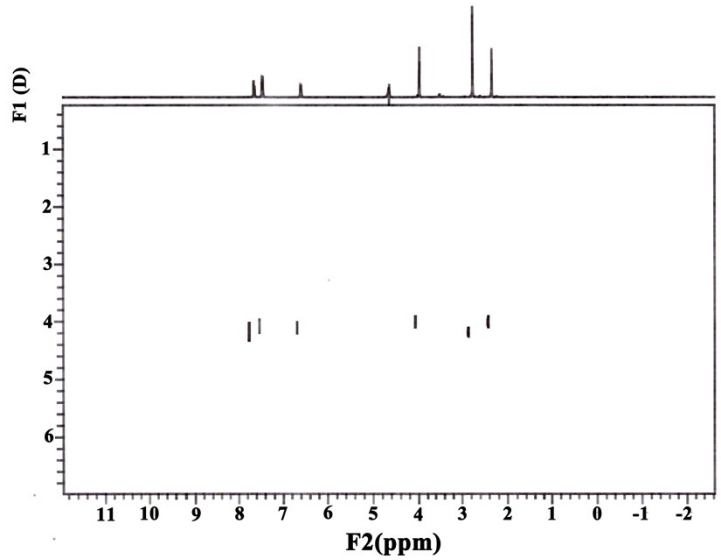


Fig. S9 DOSY NMR spectrum of ThT in D_2O

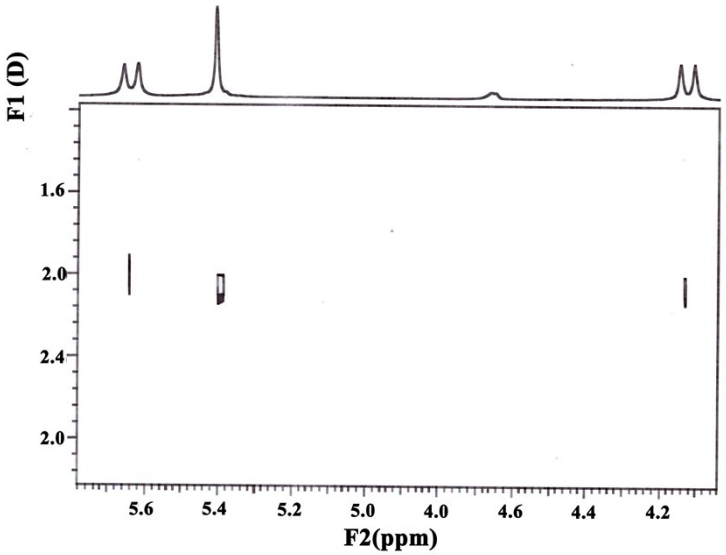


Fig. S10 DOSY NMR spectrum of *t*Q[14] in D_2O

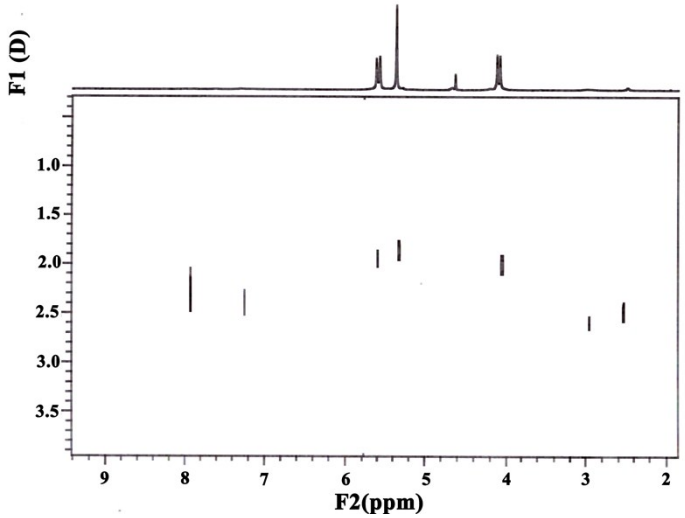


Fig. S11 DOSY NMR spectrum of ThT/*t*Q[14] (1:1) in D_2O

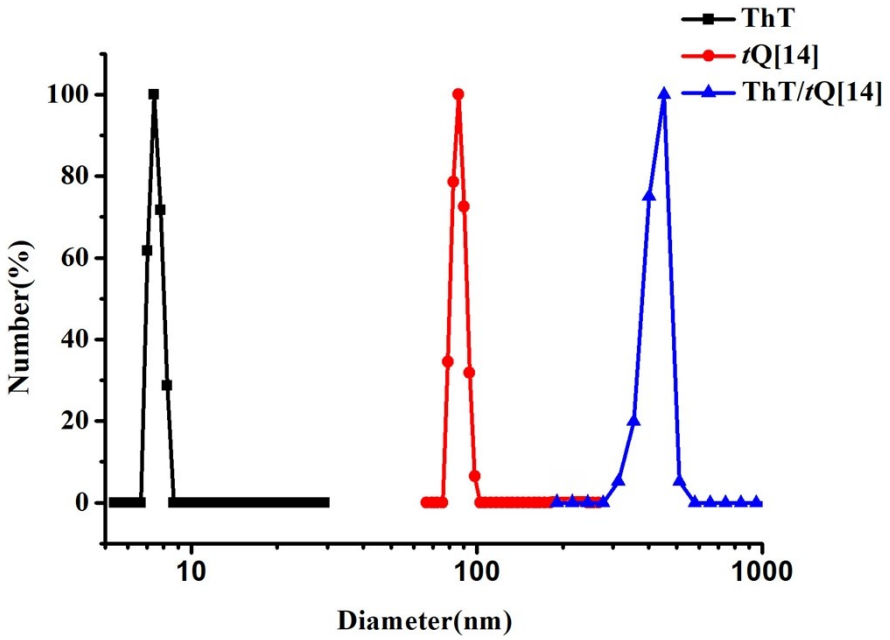
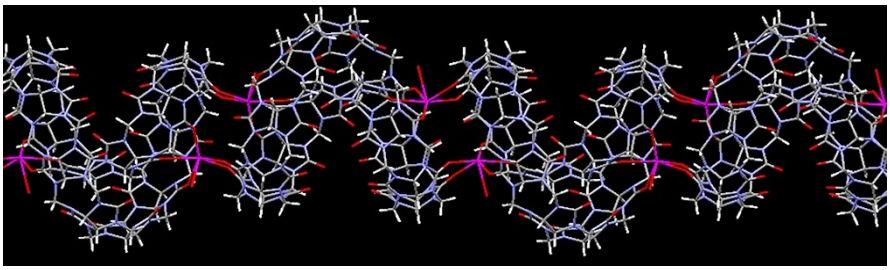
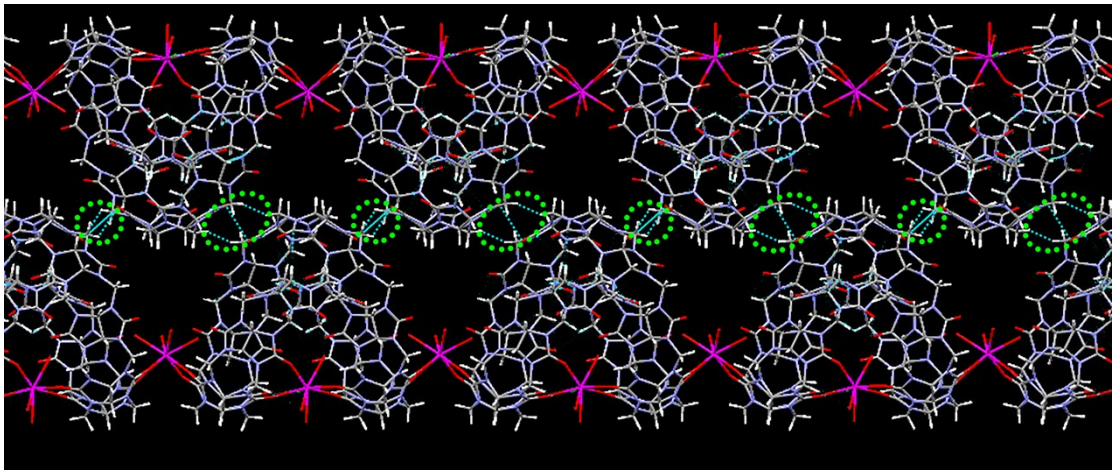


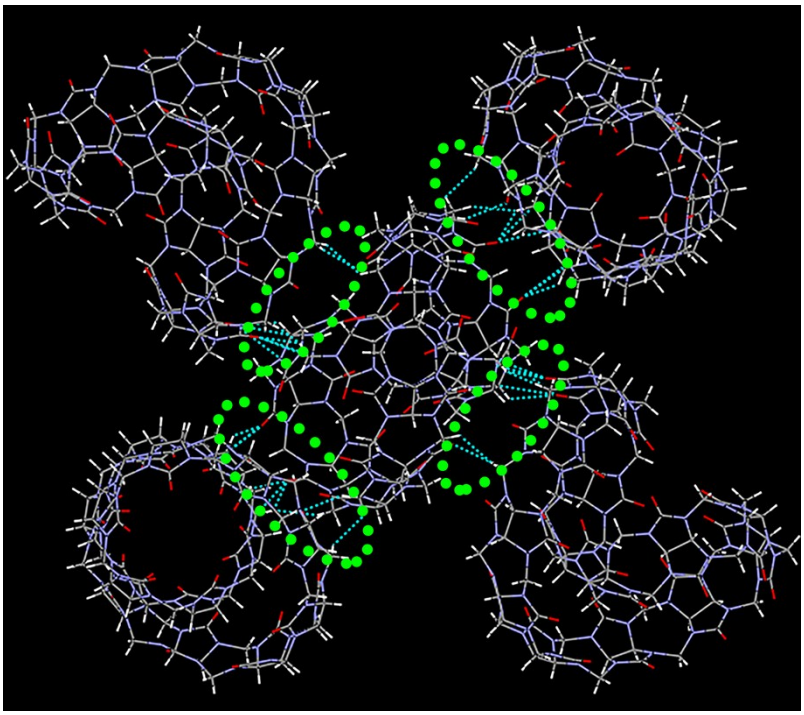
Fig. S12 DLS results of the aqueous solution of ThT ($C_{ThT,}$ = 1.0 × 10^{-3} mol/L), *t*Q[14] ($C_{tQ[14]}$ = 1.0 × 10^{-3} mol/L), ThT/*t*Q[14] (1:1, $C_{ThT,}$ = $C_{tQ[14]}$ = 1.0 × 10^{-3} mol/L).



Linear *t*Q[14]/Sr^{2+}-based coordination polymer



Interaction of *t*Q[14]/Eu^{3+}-based coordination polymers through the outer surface interaction of Q[*n*]s



Interaction between *t*Q[14] molecules in various manners through the outer surface interaction of Q[*n*]s

Fig. S13 (top) a *t*Q[14]-based chain linked by Sr^{2+} metal ions; (middle and bottom) interaction between *t*Q[14] molecules in different manner through the outer surface interaction of Q[*n*]s.

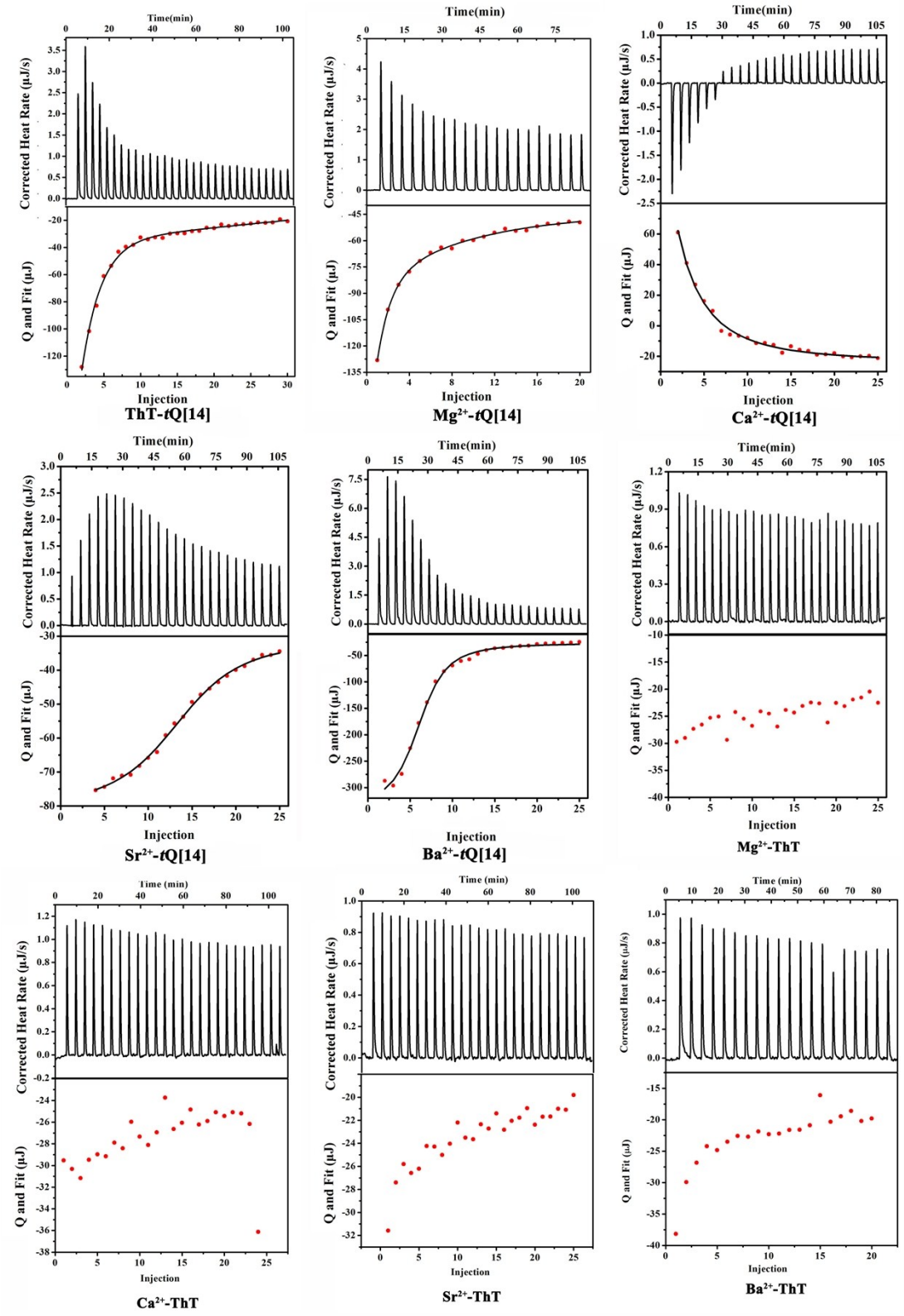


Fig. S14 ITC profiles of interaction of *t*Q[14] with ThT and Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} metal ions, and ThT with Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} metal ions respectively, in aqueous solution at 25°C

Table S1. Binding constants K_a (M^{-1}) and thermodynamic parameters ΔH and TΔS (kJ/mol) for complex formation of ThT and the selected 4 metal ions with the twisted cucurbit[14]uril in aqueous solution at 25ºC.

Metal	$K_a(M^{-1})$	ΔH (kJ/mol)	TΔS(kJ/mol)
ThT- *t*Q[14]	1.06×10^5	−57.28	28.59
Mg^{2+}- *t*Q[14]	6.44×10^3	−43.36	-21.62
Ca^{2+}- *t*Q[14]	1.05×10^4	75.53	98.47
Sr^{2+}- *t*Q[14]	3.86×10^4	−2.52	23.66
Ba^{2+}- *t*Q[14]	4.33×10^5	−71.43	−39.26
Mg^{2+}- ThT	—	—	—
Ca^{2+}- ThT	—	—	—
Sr^{2+}- ThT	—	—	—
Ba^{2+}- ThT	—	—	—

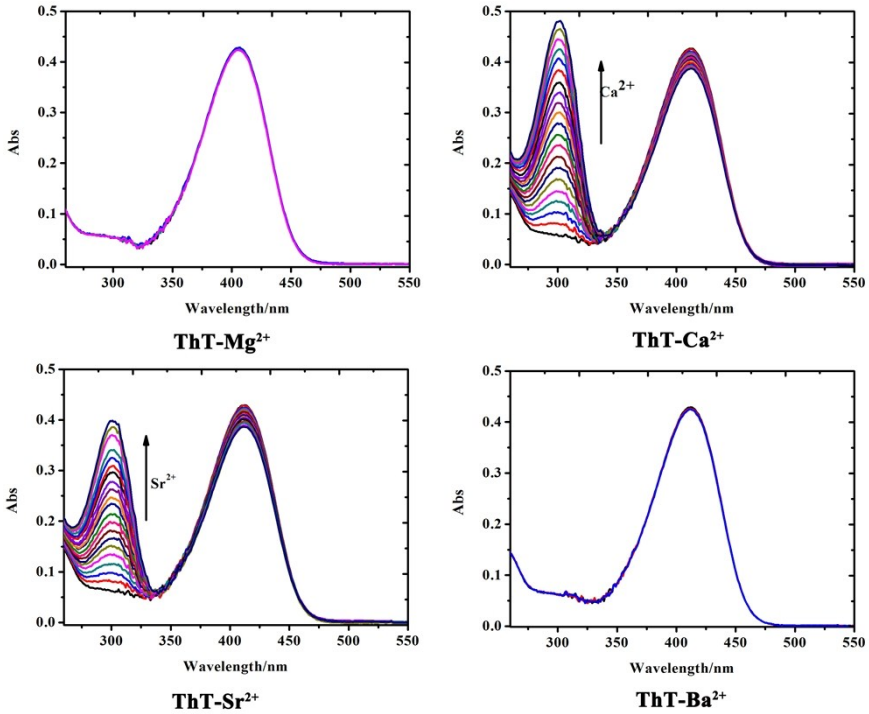


Fig. S15 Absorption spectra of ThT (20 μM) in the presence of different concentrations of in the presence of 1000 equiv. of various metal ions.

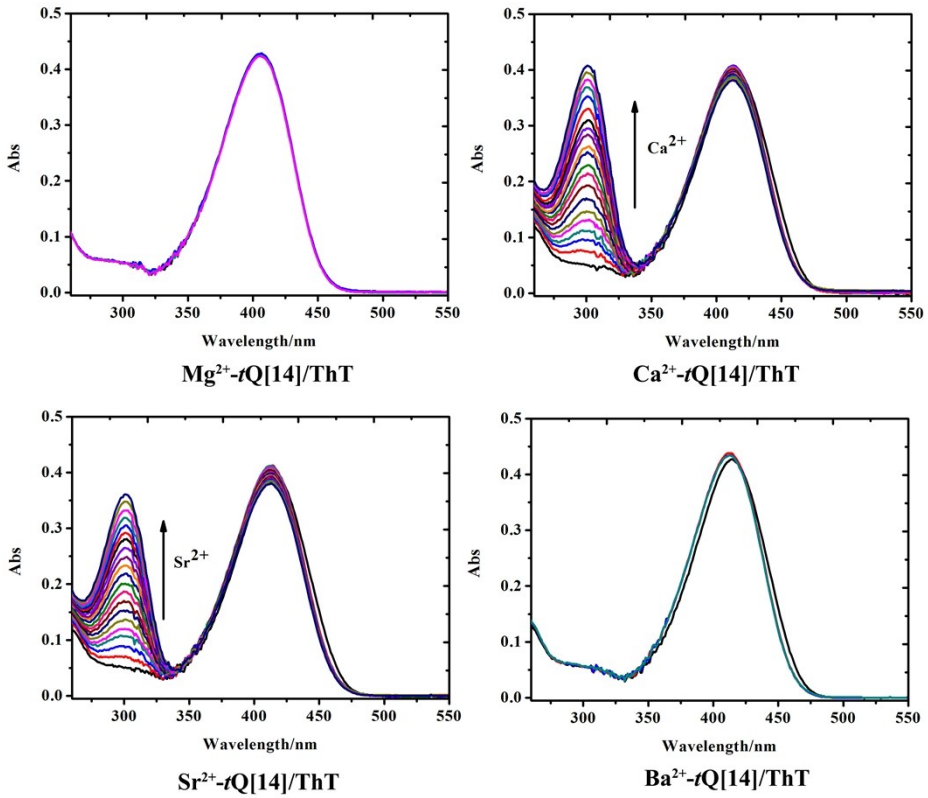


Fig. S16 Absorption spectra of *t*Q[14]/ThT (20 μM) in the presence of different concentrations of in the presence of 1000 equiv. of various metal ions.

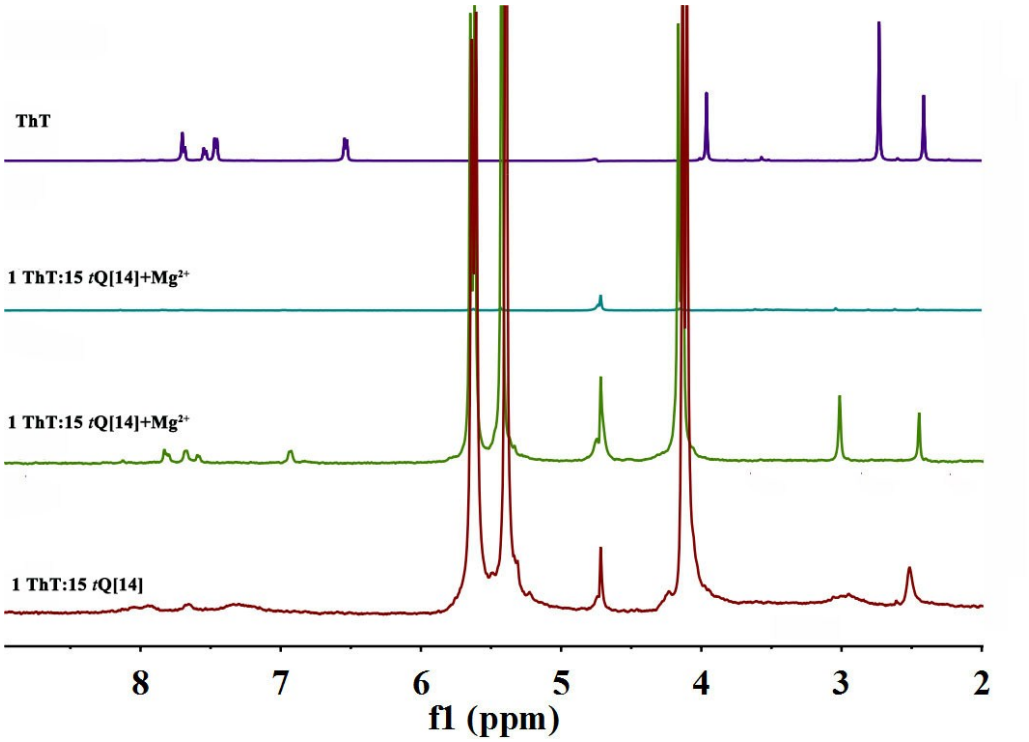


Fig. S17 Titration ^{1}H NMR spectra (500 MHz, D_2O) of *t*Q[14]/ThT with increase of Mg^{2+} compared to the free ThT at D_2O at 25ºC.

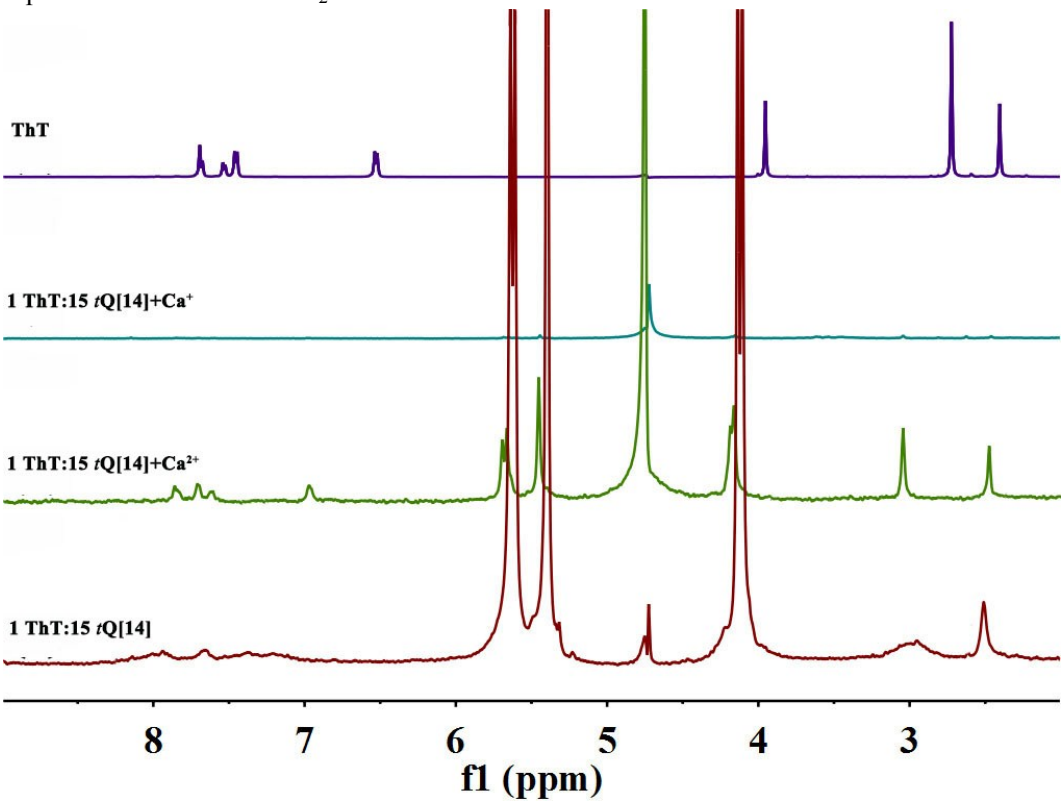


Fig.S18 Titration ^{1}H NMR spectra (500 MHz, D_2O) of *t*Q[14]/ThT with increase of Ca^{2+} compared to the free ThT at D_2O at 25ºC.

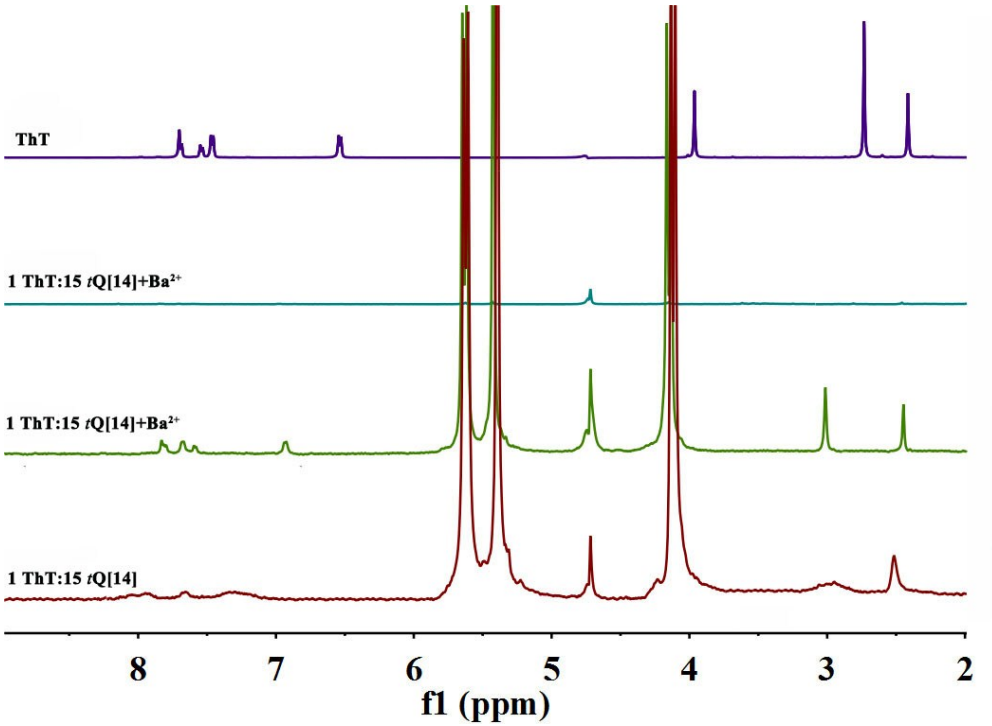


Fig. S19 Titration ^{1}H NMR spectra (500 MHz, D_2O) of *t*Q[14]/ThT with increase of Ba^{2+} compared to the free ThT at D_2O at 25ºC.

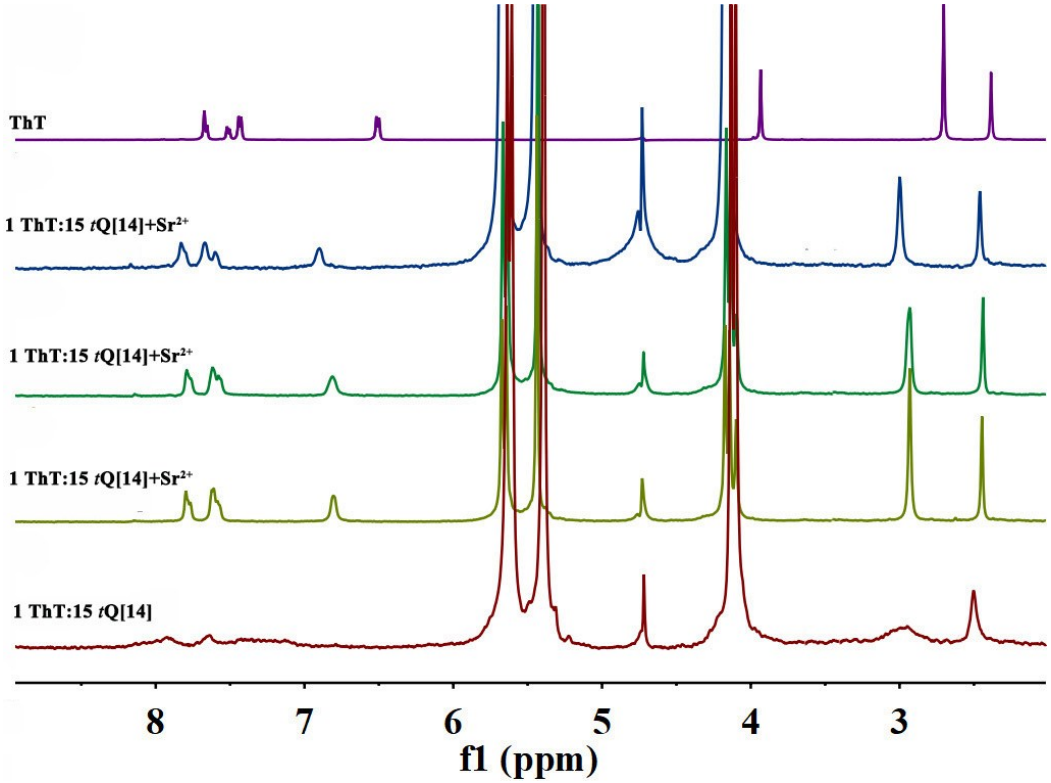


Figure S20. Titration ^{1}H NMR spectra (500 MHz, D_2O) of *t*Q[14]/ThT with increase of Sr^{2+} compared to the free ThT at D_2O at 25ºC.