Electronic Supplementary Material (ESI) for ChemComm.

The smallest cucurbituril analogue with high affinity for Ag^+

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Supporting information

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1. General methods

^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The molecular mass spectra were recorded on a 4800 Plus M-TOF/TOF Analyzer (AB SCIEX, USA) and a Waters LCT Premier XE mass spectrometer. Thermal stability were measured by thermogravimetric analysis with model SDT Q600 V8.3 Build 101. The ITC experiments were carried out on a GE MicroCal iTC 200.

Materials: 2,2-Dimethyl-1,3-propanediol was purchased from Aldrich and was used directly；Other commercially available chemicals were used without further purification.

2. Experimental section

1) Synthesis of dimethylpropanediurea(Me_2TD)

A solution of dry dimethyl sulfoxide (9.6 mL, 135.2 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise at -78 °C to oxalyl chloride (5.8 mL, 67.6 mmol) in dry CH_2Cl_2 (40 mL). After stirring for 30 min at this temperature, 2,2-Dimethyl-1,3-propanediol (3.2 g, 30.7 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise at a temperature of -78 to -70 °C. After stirring for 90 min at -70 °C, the mixture was cooled to -78 °C, Et_3N (30.6 mL, 215mmol) was added slowly, and the mixture was stirred for 30min at this temperature. The reaction mixture was allowed to warm

to room temperature over the course of 1 h. The reaction was terminated by addition of saturated NH_4Cl solution (75 mL), and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic layers were washed with 2 M HCl (5 ×70 mL) and saturated NaCl solution (2 × 70 mL). The solution was dried over Na_2SO_4, and the solvent was evaporated to obtain the crude malonic dialdehyde, which was used directly for the next reaction.

The crude dialdehyde and urea (4.3 g, 0.074 mol) were added in the mixture of acetic acid (30 ml) and concentrated sulfuric acid (1.5 ml). After stirring the mixture at 95℃ for 12h, the solution was allowed to cool down to room temperature and water (200 ml) was added. The precipitate was filtered and washed with acetone. The product was dried under vacuum to give Me_2TD as a white powder. （2.8 g, 50%） dimethylpropanediurea: ^1H NMR (400 MHz, DMSO, 298 K): δ 6.98 (d, J = 4.1Hz, 4H), 3.86 (t, J = 4.1Hz, 2H), 1.24 (s, 6H).

2）Synthesis of **Me_8TD[4]**

To a mixture of Me_2TD (1.84 g, 10.0 mmol), calcium chloride (0.22g, 2mmol) and paraformaldehyde (0.72 g, 24.0 mmol) was added 37% HCl (5 mL). The mixture was then heated to 90 °C under stirring for 48 h. The resulting solid after cooling was collected by filtration. The crude product was dissolved in methanol (200ml) and then ethyl acetate (250ml) was added to precipitate a solid. The precipitate was filtered and dried under

vacuum to give **Me_8TD[4]** as a white powder (131mg, 5%). ^{1}H NMR (400 MHz, D_2O, 298 K): δ 6.42 (d, *J* = 15.1Hz, 8H), 4.74 (s, 8H), 4.11(d, *J* = 15.1Hz, 8H), 1.05 (s, 24H). ^{13}C NMR (100 MHz, D_2O): δ 152.25, 77.76, 62.05, 32.88, 20.72. MALDI-TOF MS m/z 855.3736 $[M+Na]^+$. (calcd 855.3739)

3. Removal of Ca^{2+}

Me_8TD[4] with Ca^{2+} (105mg, 0.1mmol) was dissolved in water (10ml). To this solution was added EDTA (58.4mg, 0.2mmol) and $(CH_3)_4N^+OH^-$ (72mg, 0.8mmol). White precipitate was collected by filtration and washed thoroughly with H_2O. Drying the product at 80℃ yielded 27mg, 32.8%.

4. Calorimetric Titration

log K, ΔH, and TΔS values for the interactions of the metal ions with Me_8TD[4] were determined by titration calorimetry at 25.0±0.1 °C in deionized water using a GE MicroCal iTC 200. Concentrations of metal ion solutions were 8M, except for Ba^{2+}, $Pb^{2+}$and Ag^+, and that of Me_8TD[4] ligands were 0.4M. In the case of Ba^{2+}, $Pb^{2+}$and Ag^+, concentrations were 8M in the first place and then decreased to 4M after 1:1 complexes were observed. The metal-ion solutions were titrated into the ligand solutions. The heat of dilution was corrected for by injecting

the metal ion solution into neat solution and substracting this data from that of the host-guest titration. The data were analyzed and fit by the Origin software (MicroCal).

5. Preparation of the single crystal of Me_8TD[4]

The single crystals of Me_8TD[4] (0.05 mmol in the form of Ca^{2+} complexes obtained from the template-direct synthesis and 0.05 mmol Me_8TD[4] removed of Ca^{2+}) were prepared from their water solutions (10ml) by the slow diffusion of acetone vapor at room temperature. Colorless crystals were obtained after several weeks.

6. The solubility measurements of the Me_8TD[4]

Excessive amounts of **Me_8TD[4]** in a deuterated solvent (0.2 mL) was stirred in a constant temperature water bath (25 °C) for 24 hours. After the removal of undissolved **Me_8TD[4]** by centrifuge, a 0.1 mL aliquot of the saturated **Me_8TD[4]** solution was diluted with 0.4 mL of D_2O, and then a standard solution of tetraethylammonium bromide in D_2O (0.20 M, 20 μL) was added. Tetramethylammonium chloride was used instead of tetraethylammonium bromide in those measurements using methanol-d_4 or DMSO-d_6. The amount of dissolved **Me_8TD[4]** in the solution was estimated by comparing the intensities of its signals with that of the tetraethylammonium ion (or tetramethylammonium ion) in ^{1}H NMR

spectrum which was recorded at 25 °C.

7. Supplementary Figures

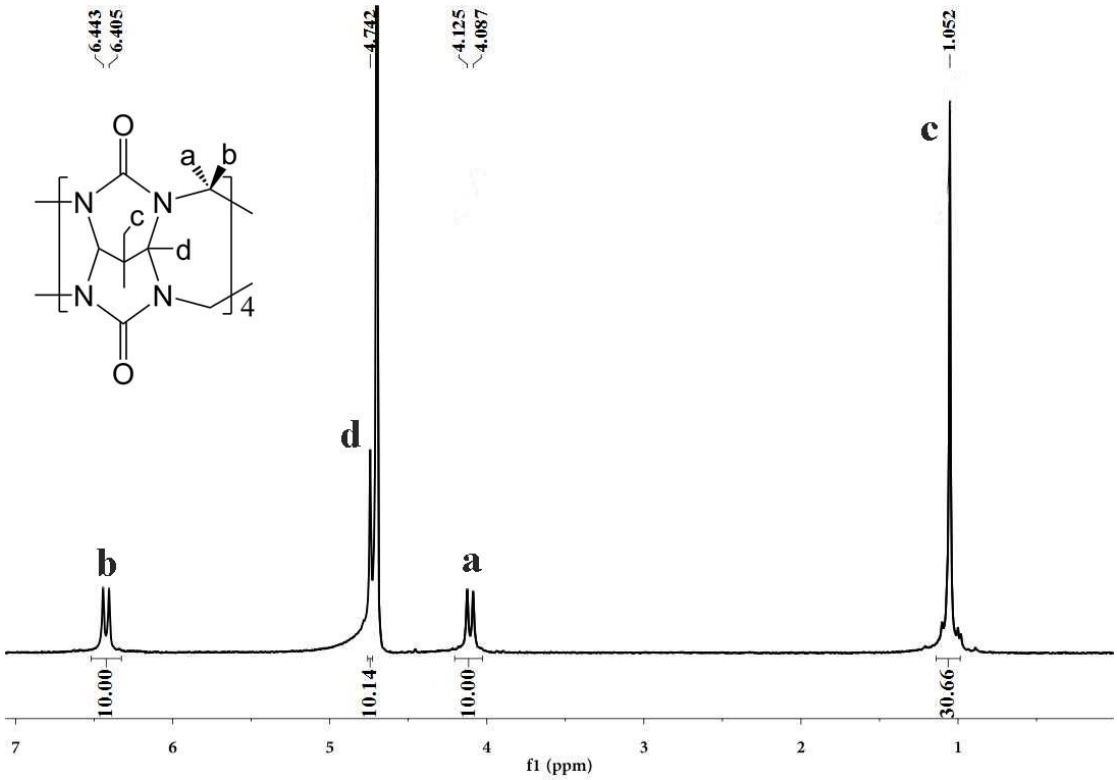


Fig. S1 ^{1}H NMR spectra (400MHz, 99% D_2O, 298 K) of **Me_8TD[4]** in the presence of Ca^{2+}.

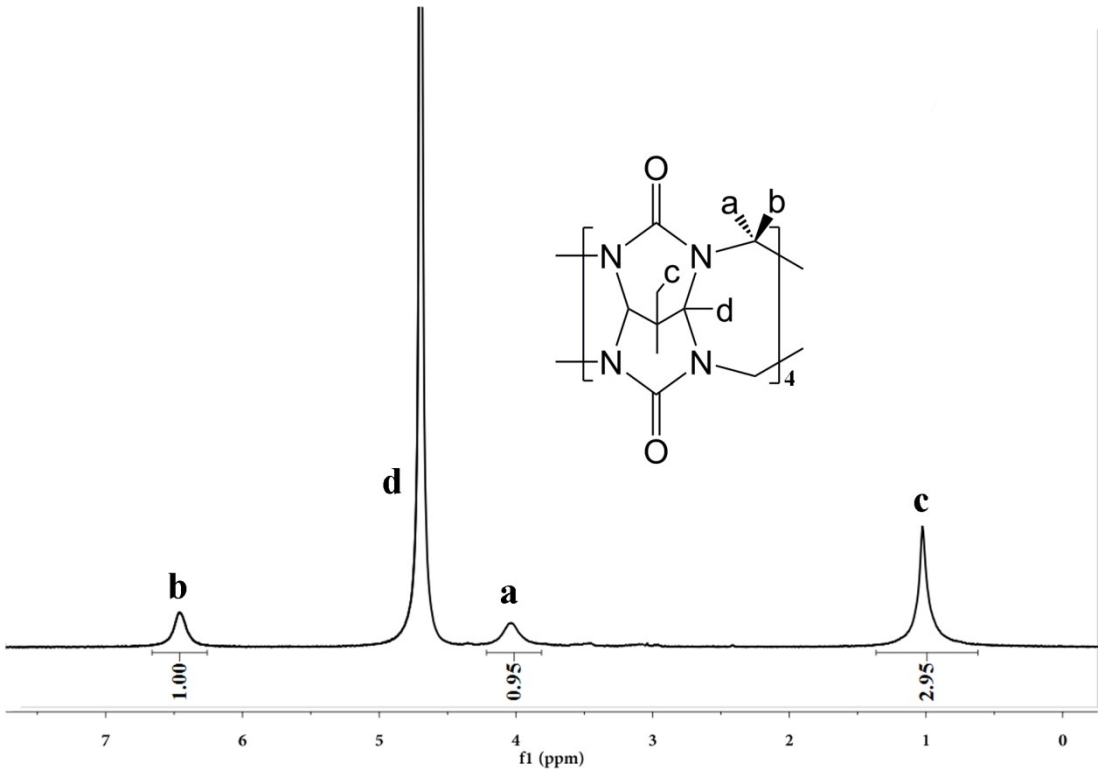


Fig. S2 ^{1}H NMR spectra (400MHz, 99% D_2O, 298 K) of **Me_8TD[4]**.

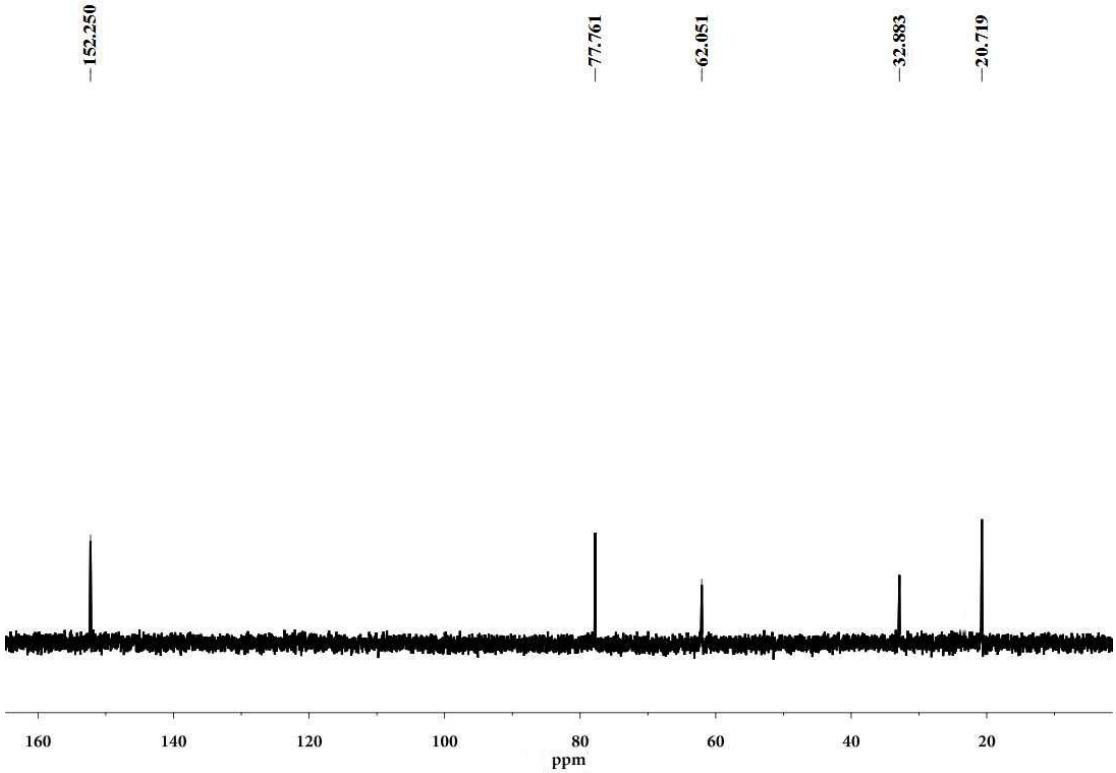


Fig. S3 ^{1}C NMR spectra (100MHz, 99% D_2O, 298 K) of **Me_8TD[4]**.

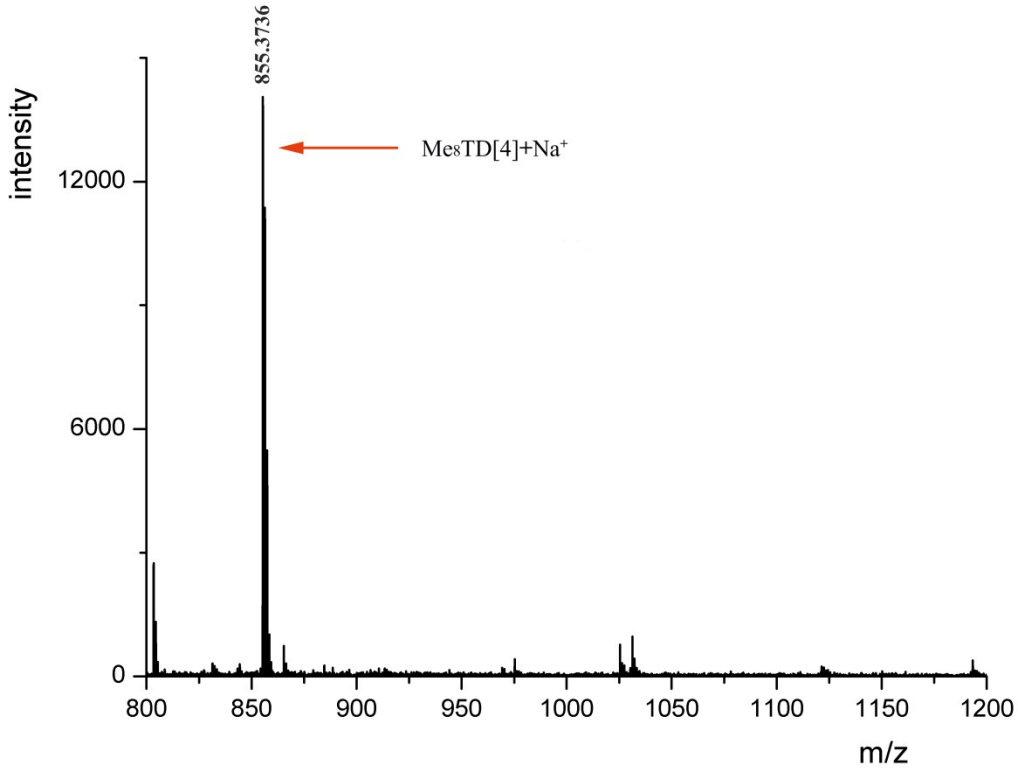


Fig. S4 MALDI-TOF of **Me_8TD[4]**: m/z 855.3736 $[M+Na]^+$.

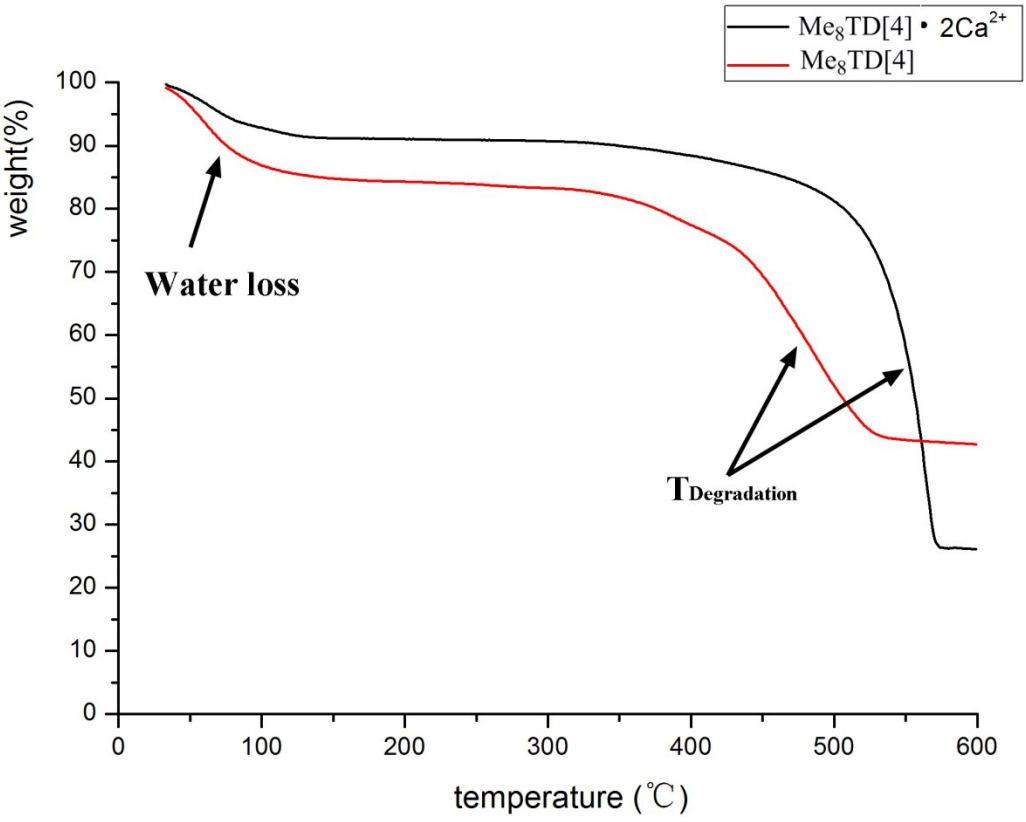


Fig. S5 Thermogravimetric analysis of **Me_8TD[4]•2Ca^{2+}** and **Me_8TD[4]**

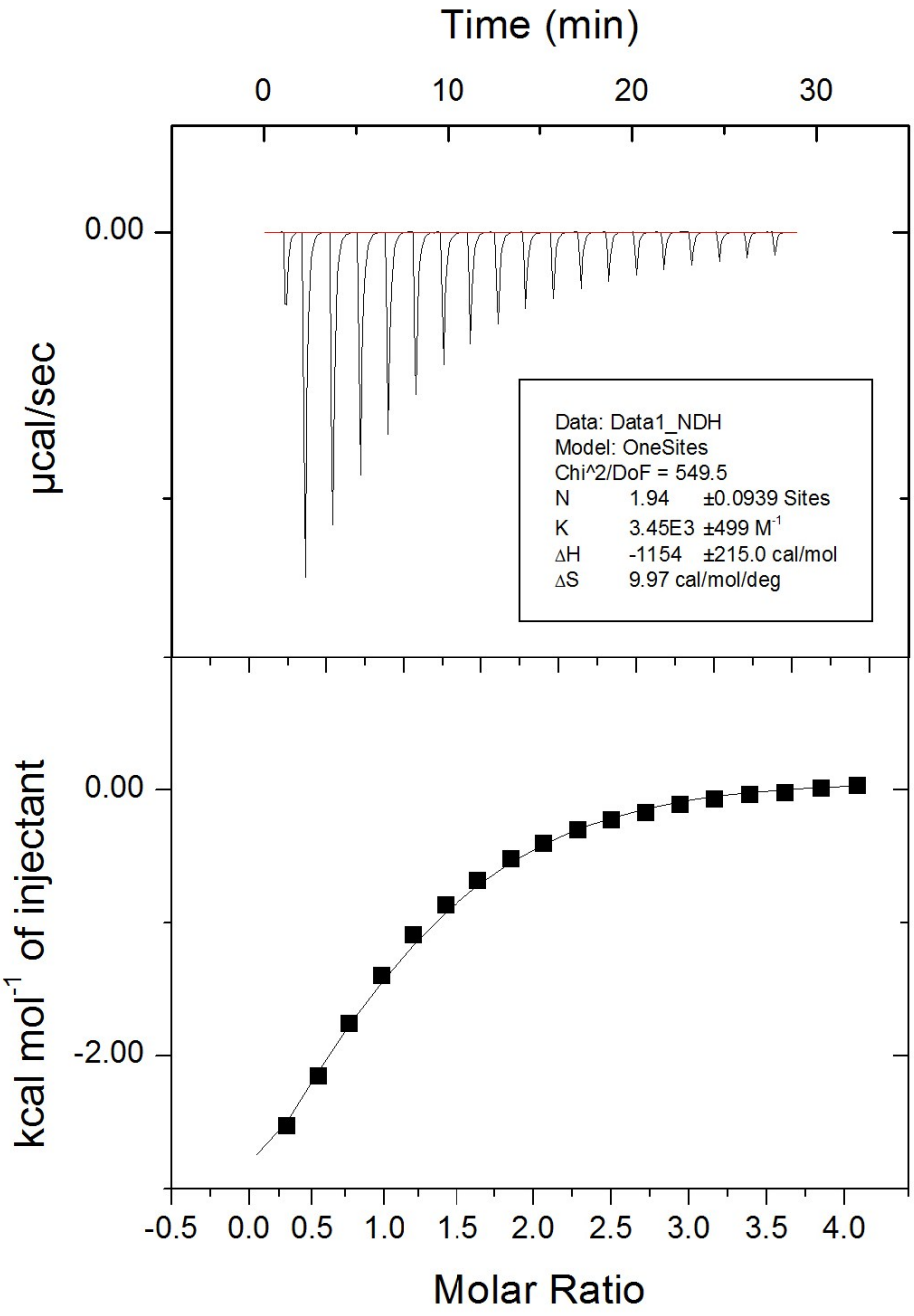


Fig. S6 ITC results for the complexation of **Me_8TD[4]** with Na^+ in deionized water at 25℃.

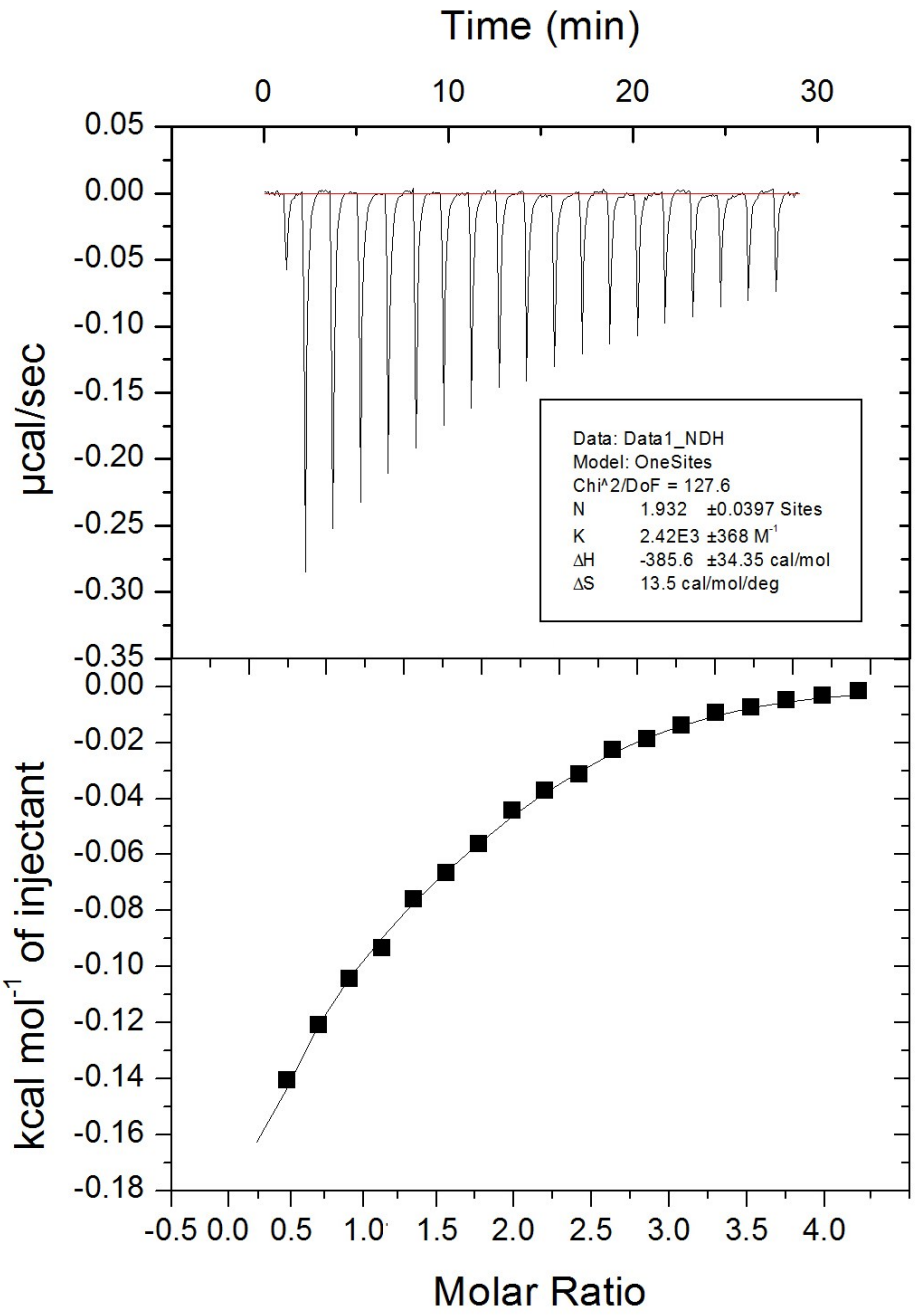


Fig. S7 ITC results for the complexation of **Me_8TD[4]** with K^+ in deionized water at 25℃.

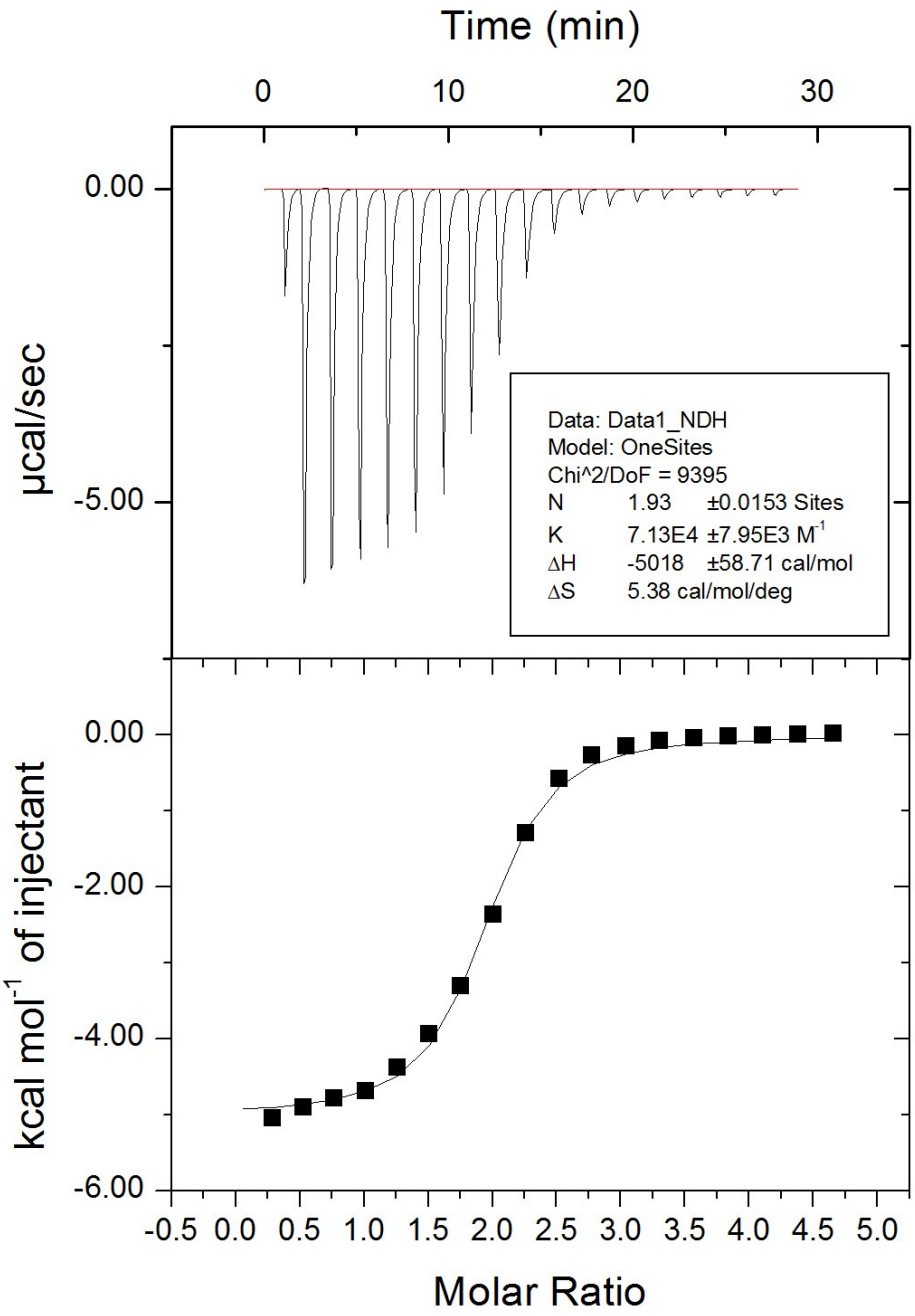


Fig. S8 ITC results for the complexation of **Me_8TD[4]** with Ca^{2+} in deionized water at 25℃.

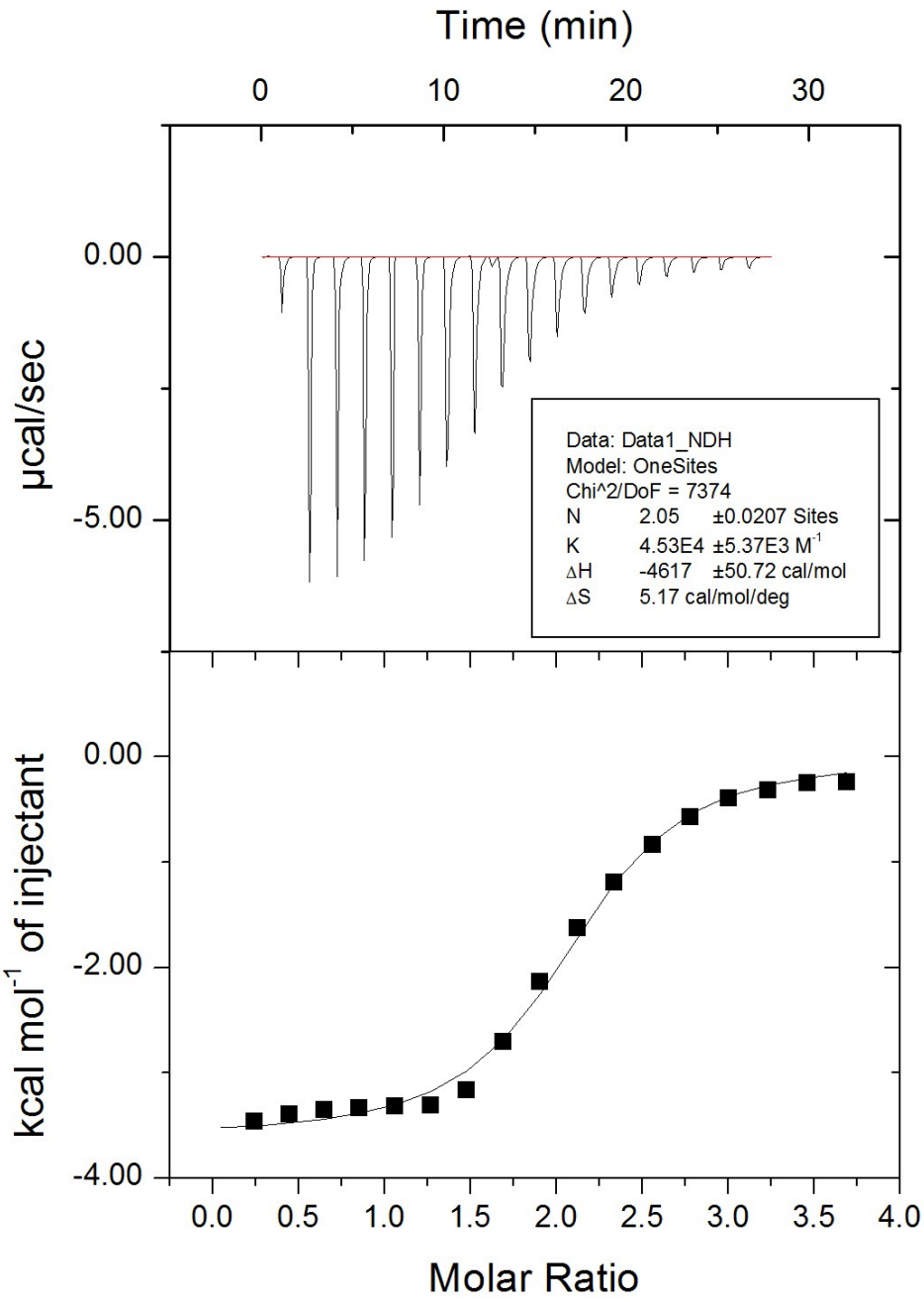


Fig. S9 ITC results for the complexation of **Me_8TD[4]** with Sr^{2+} in deionized water at 25℃.

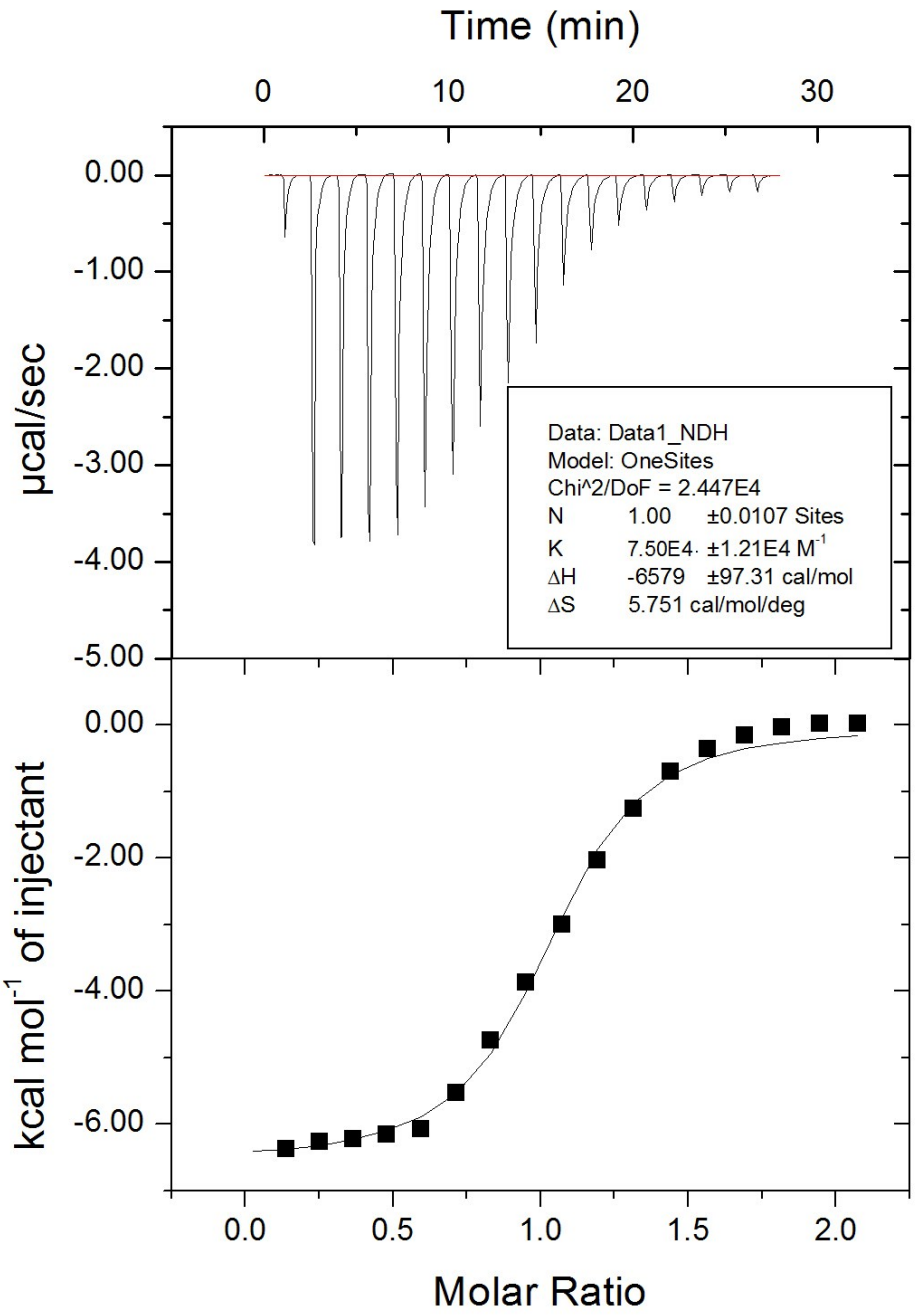


Fig. S10 ITC results for the complexation of **Me_8TD[4]** with Ba^{2+} in deionized water at 25℃.

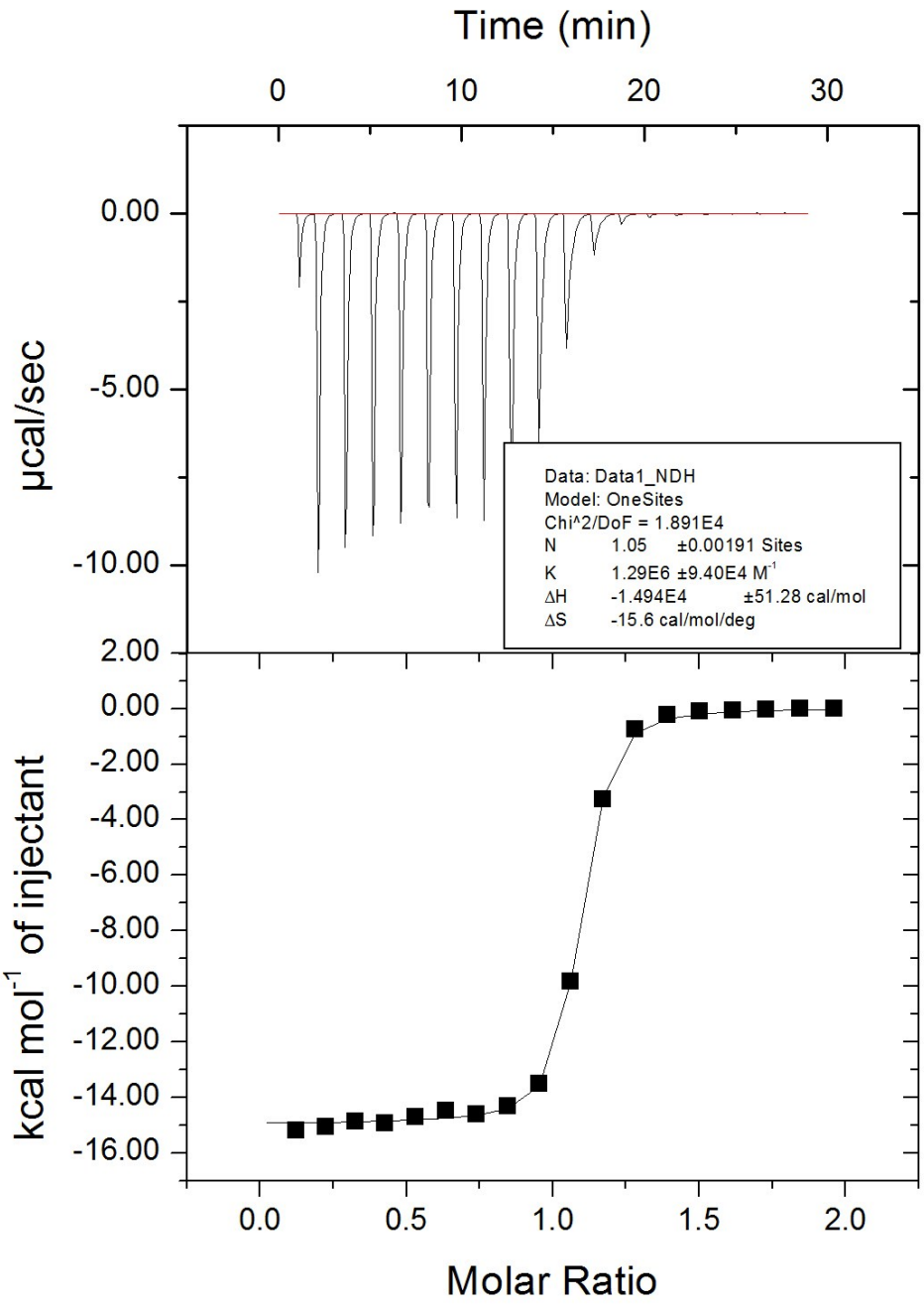


Fig. S11 ITC results for the complexation of **Me_8TD[4]** with Ag^+ in deionized water at 25℃.

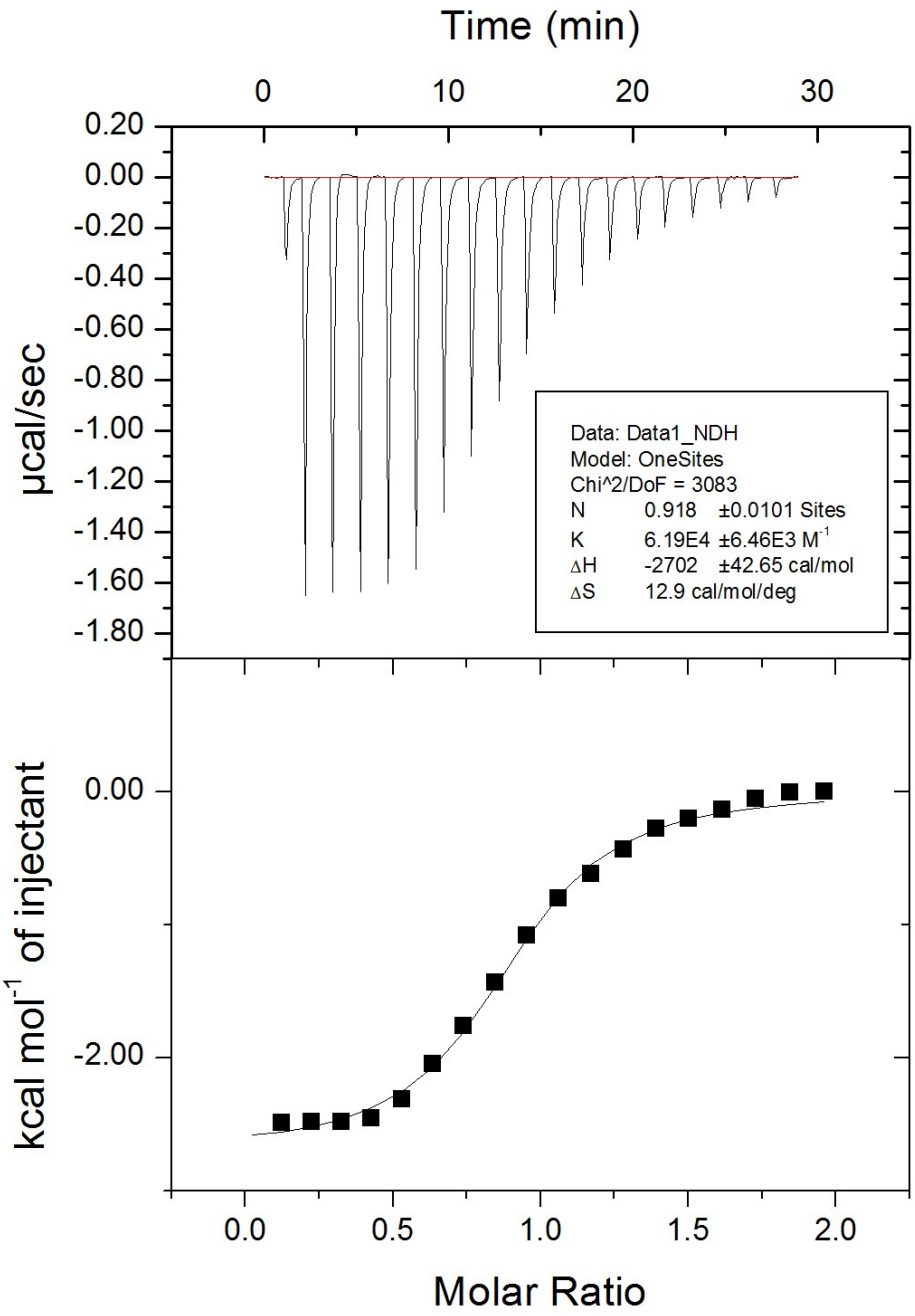


Fig. S12 ITC results for the complexation of **Me_8TD[4]** with Pb^{2+} in deionized water at 25℃.

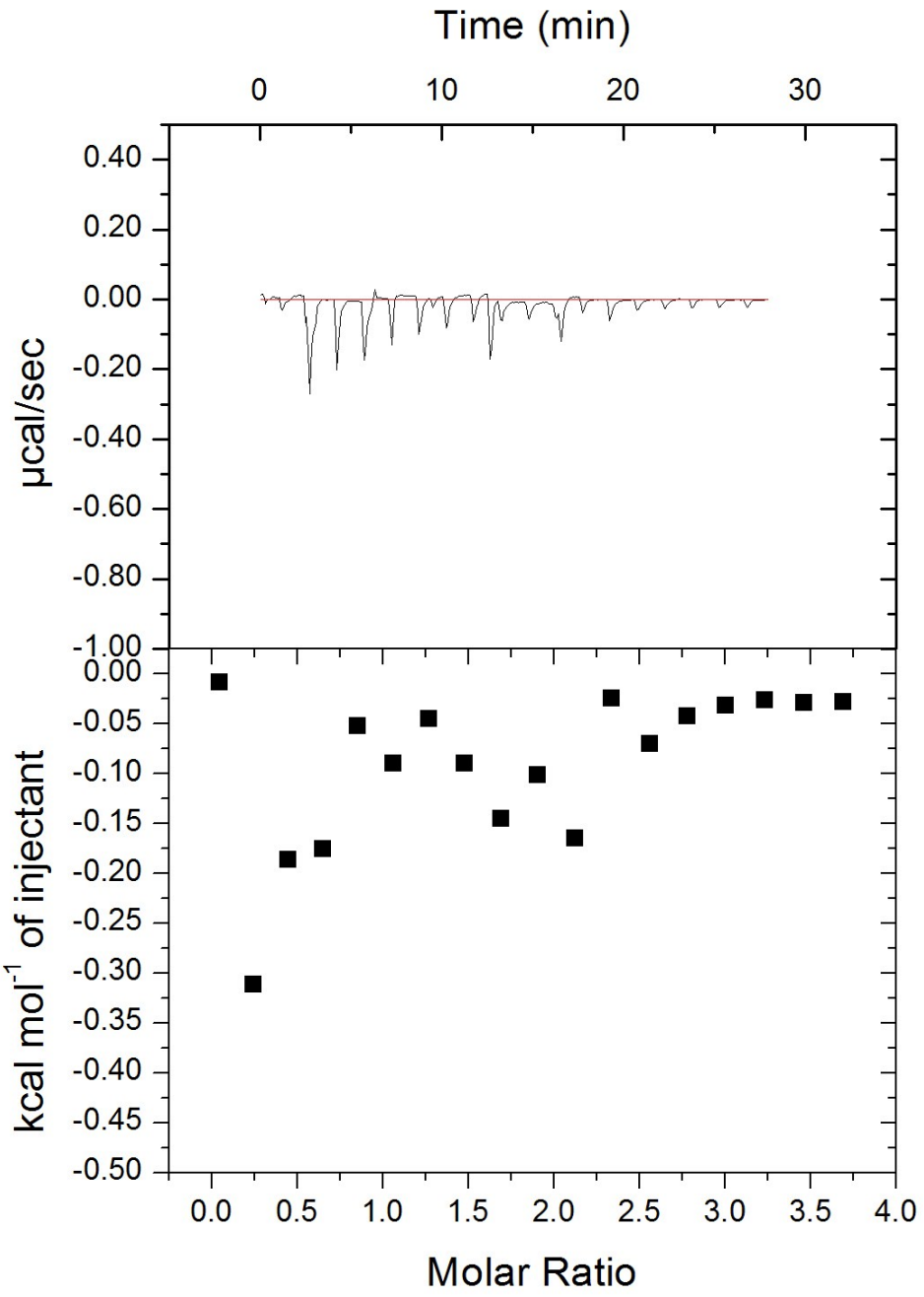


Fig. S13 ITC results for the complexation of **Me_8TD[4]** with Li^+ in deionized water at 25℃.

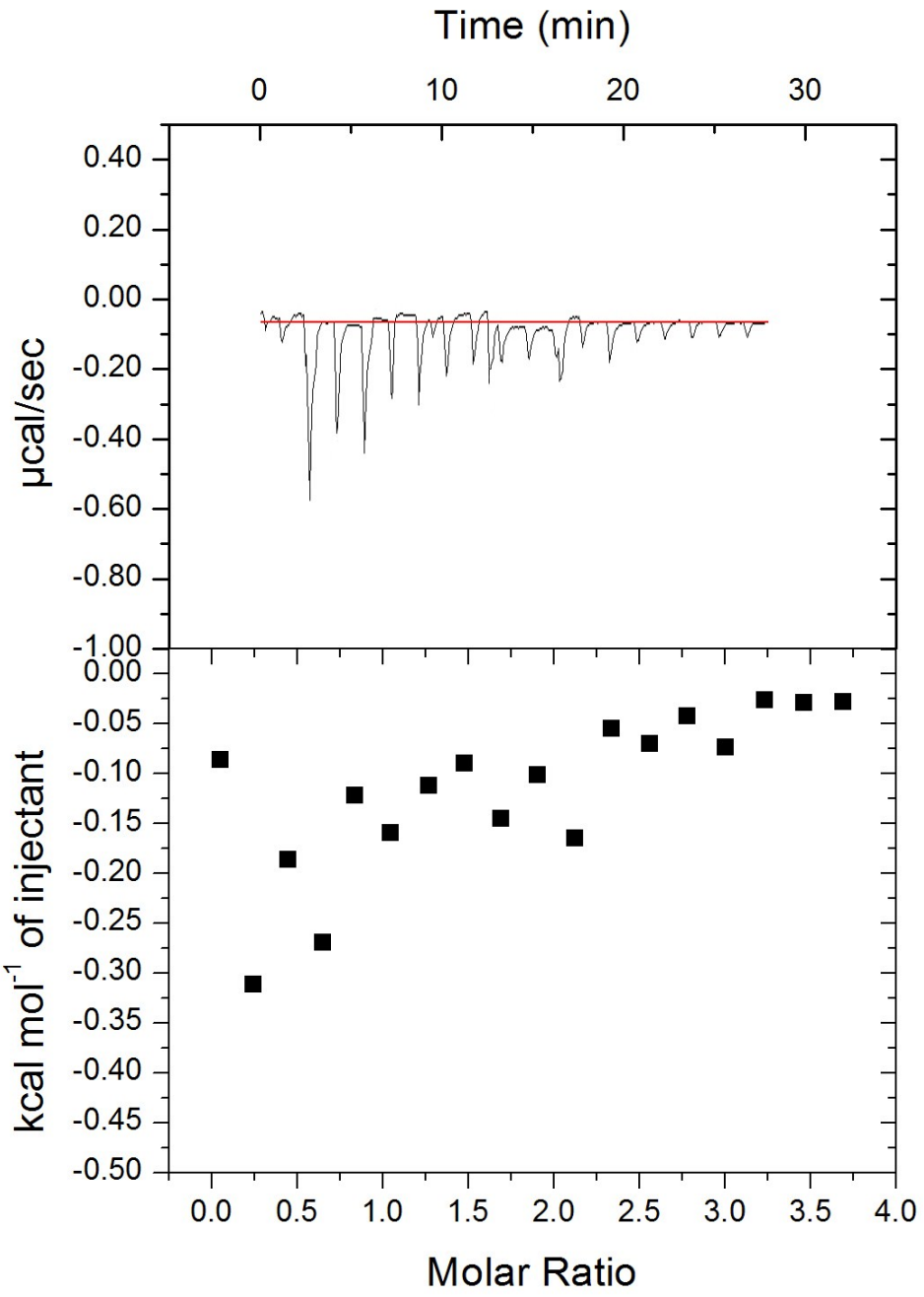


Fig. S14 ITC results for the complexation of **Me_8TD[4]** with Cs^+ in deionized water at 25℃.

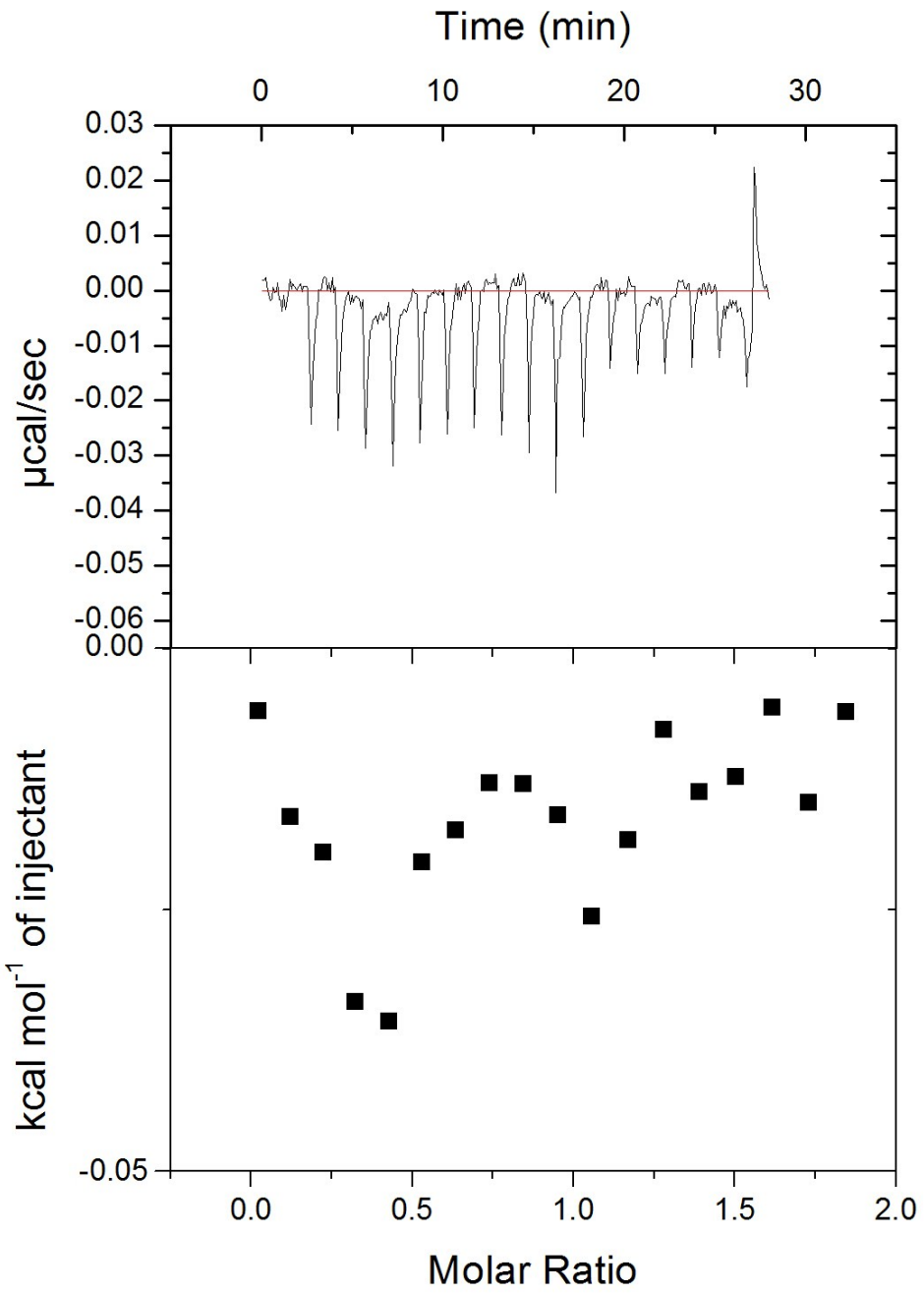


Fig. S15 ITC results for the complexation of **Me_8TD[4]** with Mg^{2+} in deionized water at 25℃.

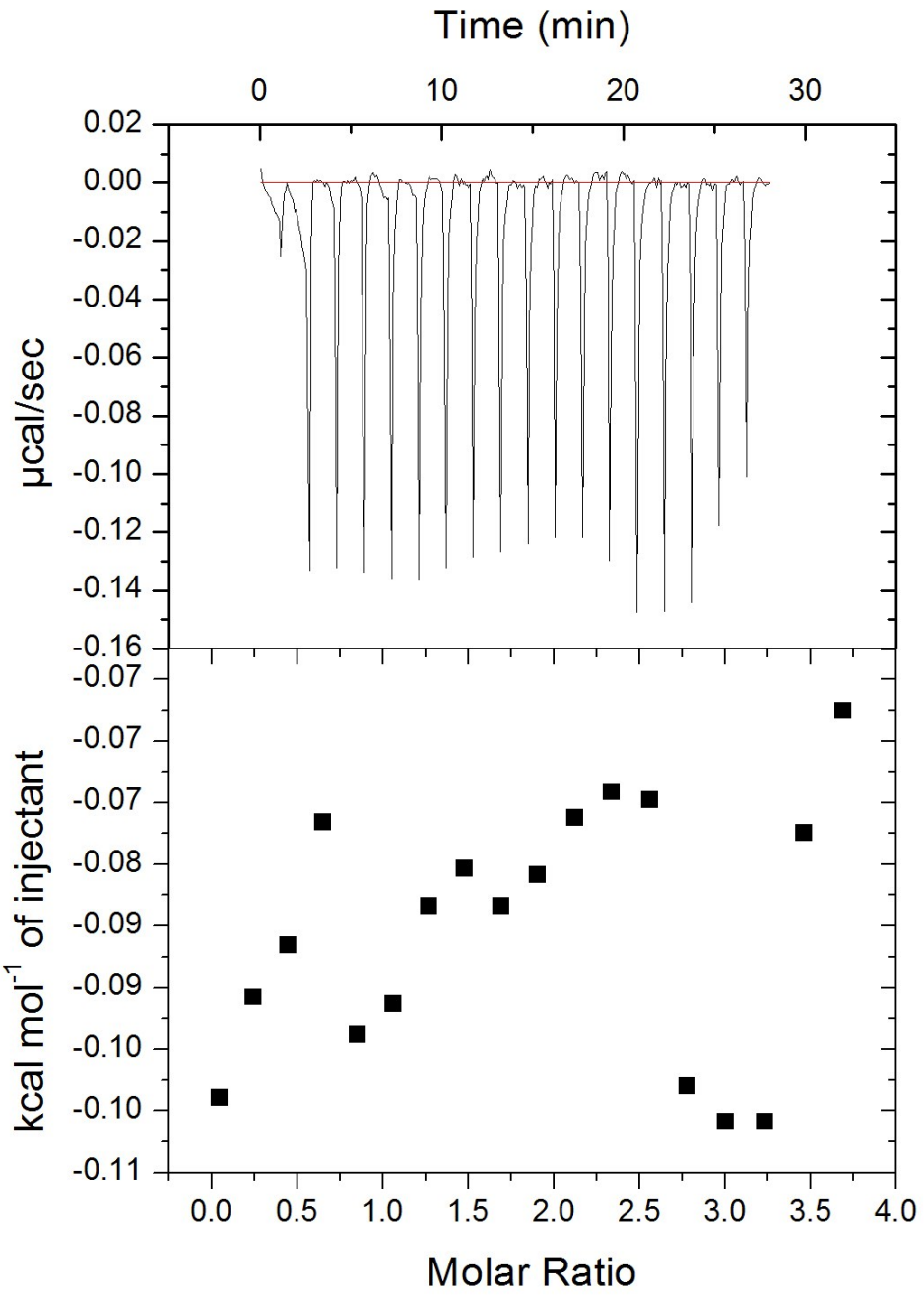


Fig. S16 ITC results for the complexation of **Me_8TD[4]** with Zn^{2+} in deionized water at 25℃.

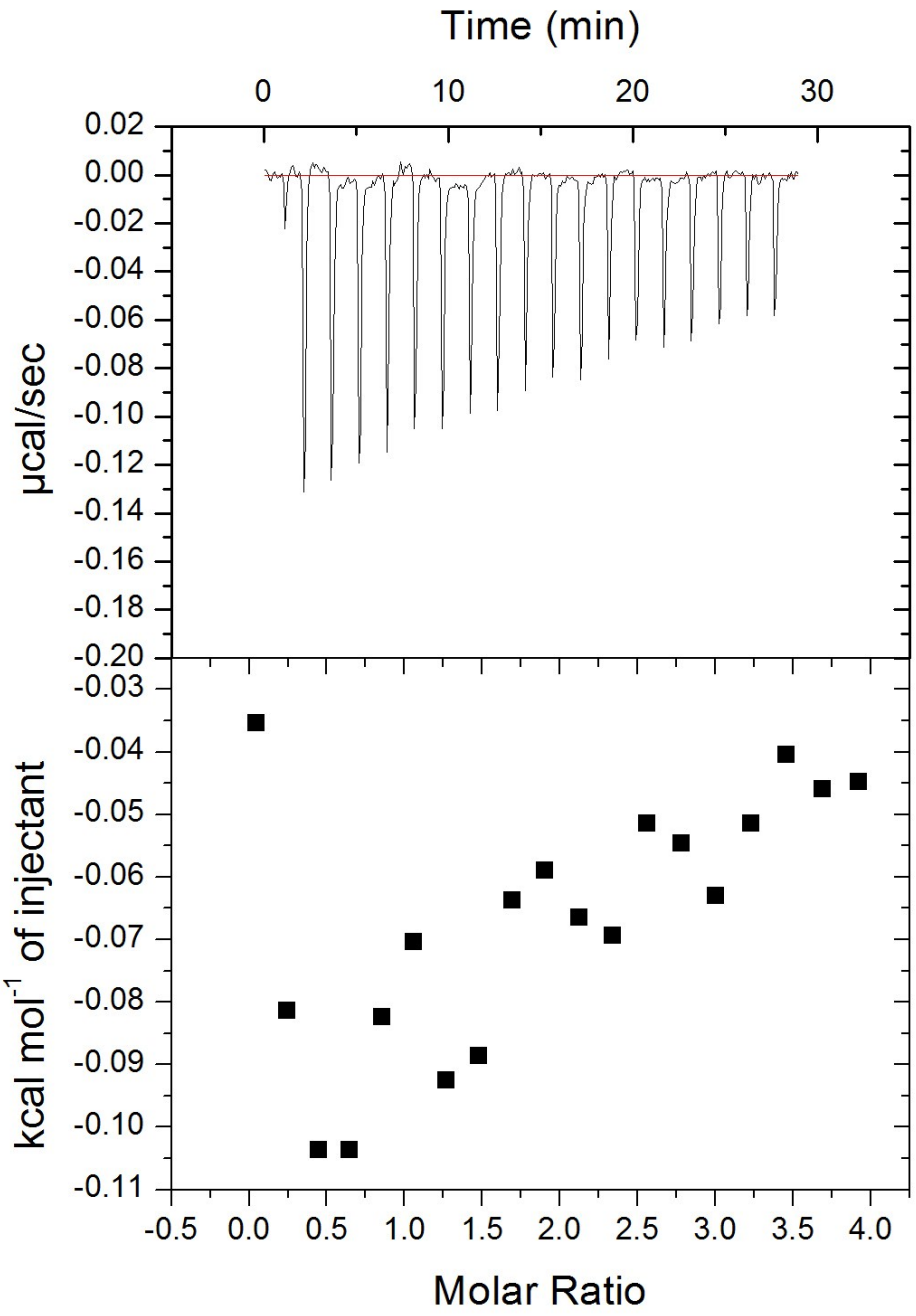


Fig. S17 ITC results for the complexation of **Me_8TD[4]** with Co^{2+} in deionized water at 25℃.

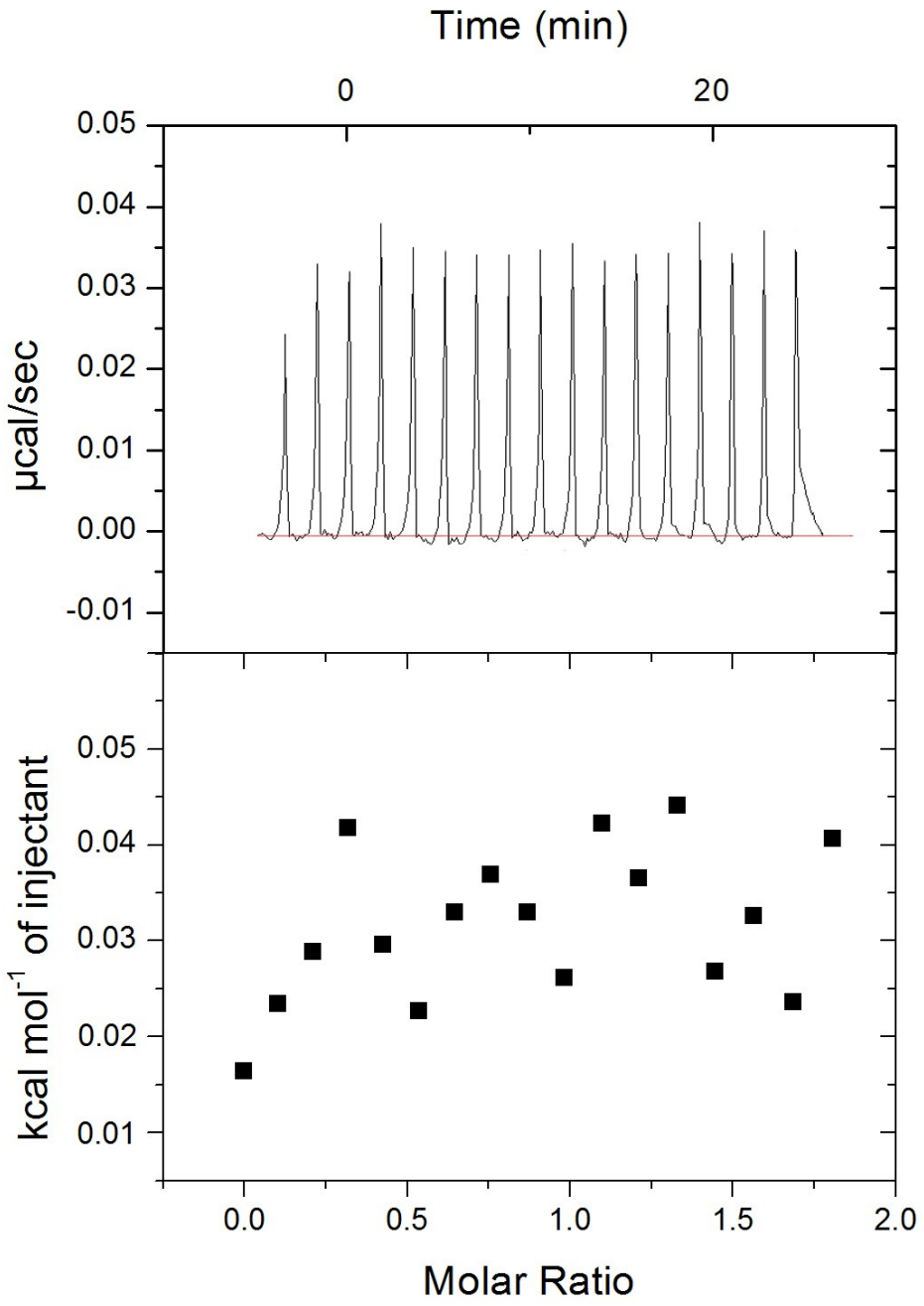
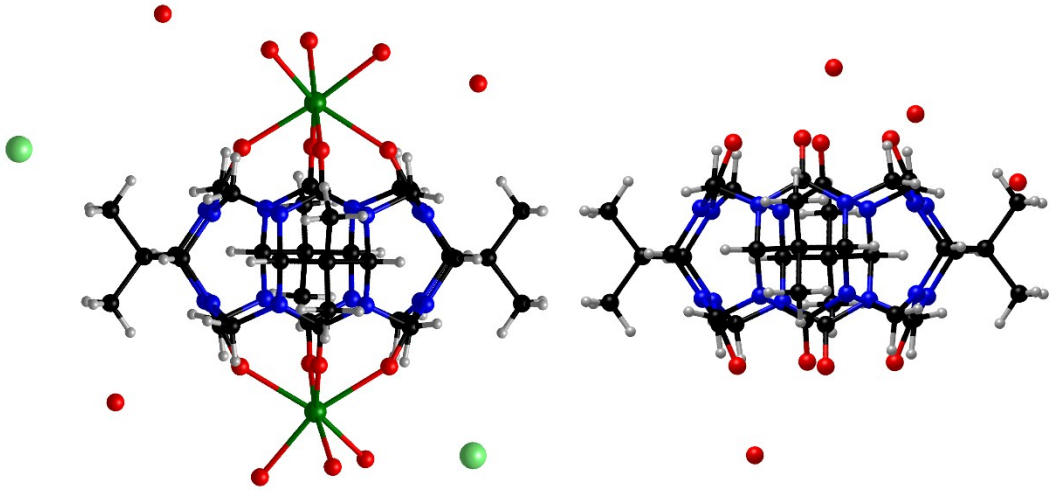
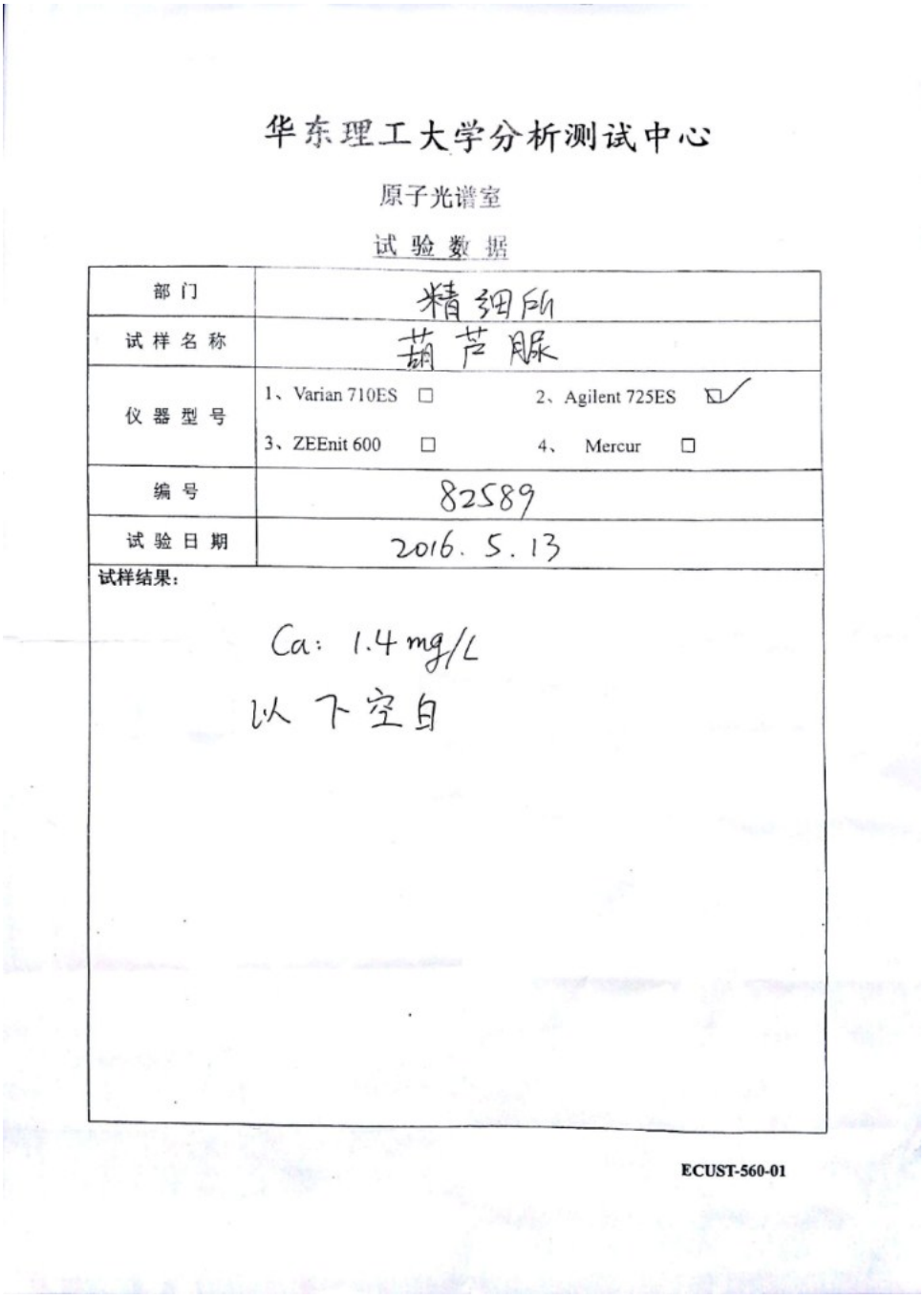


Fig. S18 ITC results for the complexation of **Me_8TD[4]** with Cu^{2+} in deionized water at 25℃.



a) b)

Fig. S19 The single crystal structures of a) **Me_8TD[4]-$CaCl_2$** and b) **Me_8TD[4].** Color codes: Carbon, black; Nitrogen, blue; Oxygen, red; Hydrogen, Grey; Calcium, green; Chloride, light green.



华东理工大学分析测试中心

原子光谱室

试验数据

部门	精细所
试样名称	葫芦脲
仪器型号	1、Varian 710ES □ 2、Agilent 725ES ☑ 3、ZEEnit 600 □ 4、Mercur □
编号	82589
试验日期	2016.5.13

试样结果：

Ca：1.4 mg/L

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ECUST-560-01

Fig. S20 The result of the atomic absorption spectrum test for the calcium content of **Me_8TD[4]** solution (1.6×10^{-5}mol/L). The concentration of Ca^{2+} was 1.4mg/L (3.5×10^{-5}mol/L), indicating an about 1:2 complexation between **Me_8TD[4]** and Ca^{2+} .

8. Details of the X-ray Crystal Structure

	$Me_8TD[4]•2Ca^{2+}$	$Me_8TD[4]$
Chemical formula	$C_{36}H_{62}Ca_2C_{l4}\ N_{16}O_{22}$	$C_{36}H_{64}N_{16}O_{16}$
Formula weight	1292.97	977.03
Temperature	296(2) K	296(2) K
Wavelength	0.71073Å	0.71073Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	C 2/m
Unit cell dimensions	a=12.207(4) Å b=21.254(6) Å c=22.602(7) Å α=90 ° β=101.677(5) ° γ=90 °	a=10.972(2) Å b=18.773(4) Å c=11.281(4) Å α=90 ° β=101.677(5) ° γ=90 °
Volume	5743(3) $Å^3$	2265.0(9) $Å^3$
Z	4	2
Density (calculated)	1.496 Mg/cm^3	1.433 Mg/cm^3
Absorption coefficient	0.472 mm^{-1}	0.114 mm^{-1}
F(000)	2696	1040
Crystal size	0.200×0.100× 0.040 mm^3	0.180 x 0.150 x 0.120 mm^3
Theta range for data collection	1.840 to 25.250°	1.852 to 26.997°
Index ranges	-14<=h<=14, -25<=k<=25, -27<=l<=23	-10<=h<=14, -23<=k<=22, -14<=l<=12
Reflections collected	34356	8054
Independent reflections	10352 [R(int) = 0.1124]	2533 [R(int) = 0.0368]
Completeness to theta = 25.242°	99.5 %	99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.646	0.746 and 0.687
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10352 / 0 / 729	2533 / 0 / 159
Goodness-of-fit on F^2	1.018	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0942, wR2 = 0.2427	R1 = 0.0816, wR2 = 0.2479
R indices (all data)	R1 = 0.1591, wR2 = 0.2938	R1 = 0.1172, wR2 = 0.2930
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.930 and -0.662 e.$Å^{-3}$	1.972 and -0.42 e.$Å^{-3}$