Experimental Section

Materials. The three sulfonated calixarene host molecules, *p*-sulfonatocalix[4]arene (SC4A),[1] *p*-sulfonatocalix[5]arene (SC5A),[2] and *p*-sulfonatothiacalix[4]arene (STC4A),[3] and the two phenanthroline-diium guest molecules, 5,6-dihydropyrazion[1,2,3,4-*lmn*][1,10]phenanthroline-4,7-diium (DP^{2+})[4] and 6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-4,8-diium (PPQ^{2+}),[5] were synthesized and purified according to previously reported procedures. These compounds were identified by ^1H and ^{13}C NMR spectroscopy in D_2O, performed on a Varian 300 spectrometer, and elemental analysis, performed on a Perkin-Elmer 2400C instrument. All other chemicals were commercially available and used without further purification.

The phosphate buffer solution of pH 7.2 was prepared by dissolving disodium hydrogen phosphate ($Na_2HPO_4\cdot12H_2O$, 25.79 g) and sodium dihydrogen phosphate ($NaH_2PO_4\cdot2H_2O$, 4.37 g) in distilled, deionized water (1000 mL) to make a 0.1 M solution. The phosphate D_2O buffer solution of pD 7.2 was prepared by dissolving disodium hydrogen phosphate (Na_2HPO_4, 0.2045 g) and sodium dihydrogen phosphate (NaH_2PO_4, 0.0672 g) in 20.00 mL D_2O to make a 0.1 M solution. The pH and pD values of buffer solutions were verified on a Sartorius pp-20 pH meter calibrated with two standard buffer solutions. pH readings were converted to pD by adding 0.4 units.[6]

Measurements. *Isothermal Titration Calorimetry (ITC).* A thermostatted and fully computer-operated isothermal calorimetry (VP-ITC) instrument, purchased from Microcal Inc. (Northampton, MA) was used for all microcalorimetric experiments. The VP-ITC instrument was calibrated chemically by the measurement of the complexation reaction of β-cyclodextrin with cyclohexanol, and the obtained thermodynamic data were in good agreement (error < 2%) with the literature data.[7] All microcalorimetric titrations between hosts and guests were performed in aqueous phosphate buffer solution (pH 7.2) at atmospheric pressure and 298.15 K. Each solution was degassed and thermostatted by a ThermoVac accessory before the titration experiment. Twenty-five successive injections were made for each titration experiment. A constant volume (10 μL/injection) of guest (or host) solution in a 0.250 mL syringe was injected into the reaction cell (1.4227 mL) charged with host (or guest) in the same aqueous phosphate buffer solution. A representative titration curve is shown in Figure S1. As can be seen from Figure S1, each titration of PPQ^{2+} into the sample cell gave an apparent reaction heat caused by the formation of inclusion complex between STC4A and PPQ^{2+}. The reaction heat decreases after each injection of PPQ^{2+} because less and less host molecules are available to form inclusion complexes. A control experiment was carried out in each run to determine the dilution heat by injecting a guest (or host) aqueous phosphate buffer solution into a pure aqueous phosphate buffer solution containing no host (or guest) molecules. The dilution heat determined in these control experiments was subtracted from the apparent reaction heat measured in the titration experiments to give the net reaction heat.

The net reaction heat in each run was analyzed by using “one set of binding sites” model (ORIGIN software, Microcal Inc.) to simultaneously compute the binding stoichiometry (N), complex stability constant (K_S), standard molar reaction enthalpy ($\Delta H°$), and standard deviation from the titration curve. Generally, the first point of titration curve was disregarded, as some liquid mixing near the tip of the injection needle is known to occur at the beginning of each ITC run. Knowledge of the complex stability constant (K_S) and molar reaction enthalpy ($\Delta H°$) enabled calculation of the standard free energy ($\Delta G°$) and entropy changes ($\Delta S°$) according to

$$\Delta G° = -RT \ln K_S = \Delta H° - T\Delta S°$$

where R is the gas constant and T is the absolute temperature.

A typical curve fitting result for the complexation of PPQ^{2+} with STC4A at pH 7.2 is shown in Figure S2. To check the accuracy of the observed thermodynamic parameters, two independent titration experiments were carried out to afford self-consistent thermodynamic parameters, and their average values with associated errors are listed in Table 1.

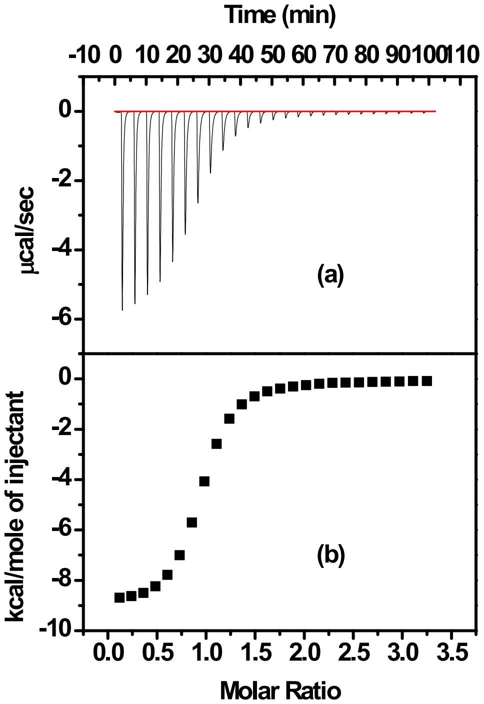


Figure S1. Microcalorimetric titration of STC4A with PPQ^{2+} in phosphate buffer solution (pH 7.2) at 298.15 K. (a) Raw data for sequential 25 injections (10 μL per injection) of PPQ^{2+} solution (2.04 mM) injecting into STC4A solution (0.12 mM). (b) Apparent reaction heat obtained from the integration of calorimetric traces.

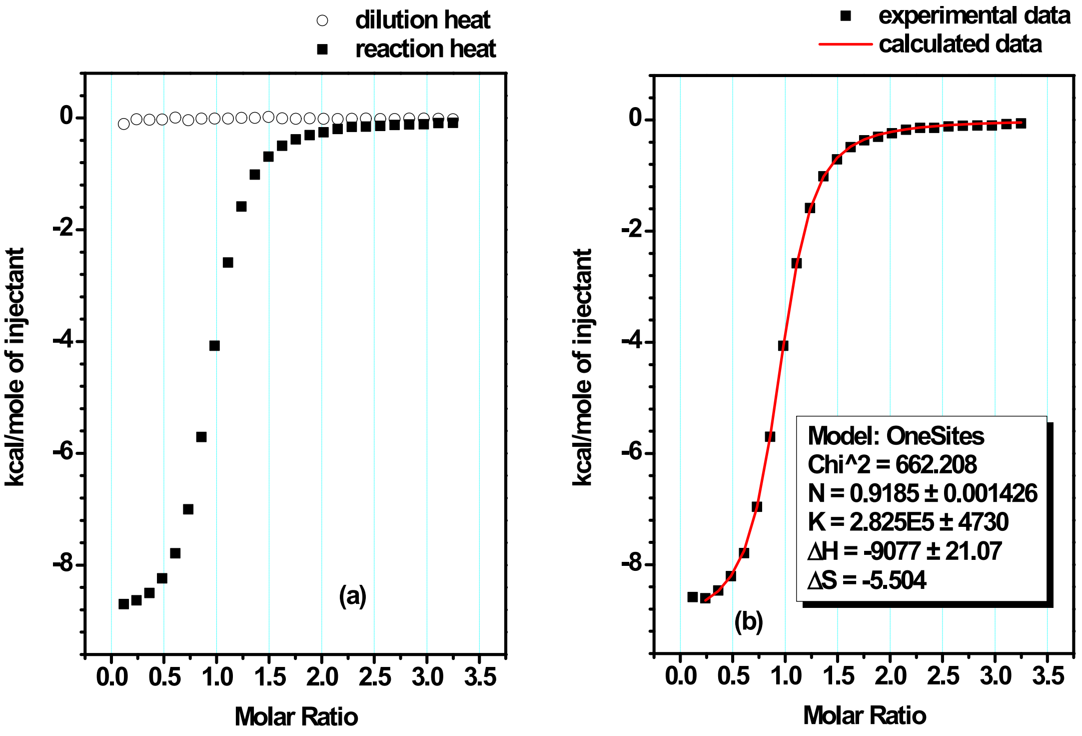


Figure S2. (a) Heat effects of the dilution and of the complexation reaction of PPQ^{2+} with STC4A at pH 7.2 for each injection during titration microcalorimetric experiment. (b) "Net" heat effects of complexation of PPQ^{2+} with STC4A for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model.

Cyclic Voltammetry. The cyclic voltammetric measurements were carried out on a BAS Epsilon electrochemical analyzer with C3 cell stand. All the solutions were prepared in pH 7.2 phosphate buffers (0.1 M) at 25 °C, and deoxygenated by purging with dry nitrogen for at least 15 min before each experiment. The glassy carbon working electrode was polished with 0.05 μm BAS alumina suspension on a brown Texmet polishing pad, sonicated in distilled water for a few minutes to remove any residual alumina particles, and then rinsed with ethanol before use. A platinum wire was used as the counter electrode. The measured potentials were recorded with respect to an Ag/AgCl (immersed in a solution containing 3 M sodium chloride) reference electrode.

NMR Spectroscopy. ^{1}H NMR spectra were recorded at pD 7.2 with a Varian Mercury VX300 spectrometer by using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an external reference. The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

Molecular Mechanics Calculation. The minimum-energy structures between sulfonated calixarene hosts and DP^{2+} guest were optimized by the molecular mechanics method with a Dreiding force field.

^{1}H NMR Spectra of SC4A, SC5A, STC4A, DP^{2+}, and PPQ^{2+} in D_2O:

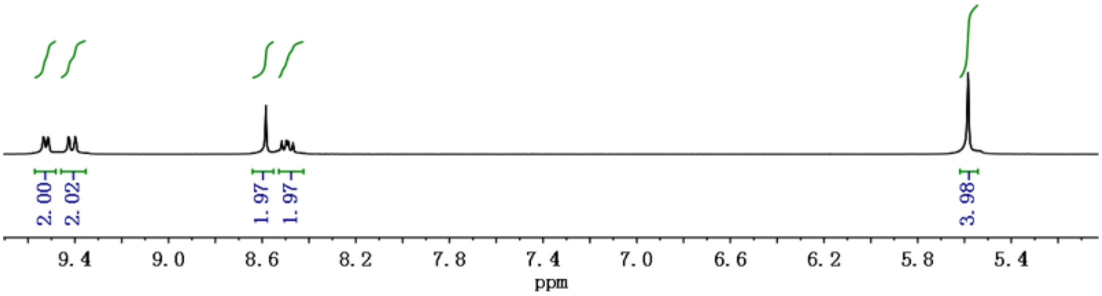


Figure S3. ^{1}H NMR spectrum of DP^{2+} in D_2O.

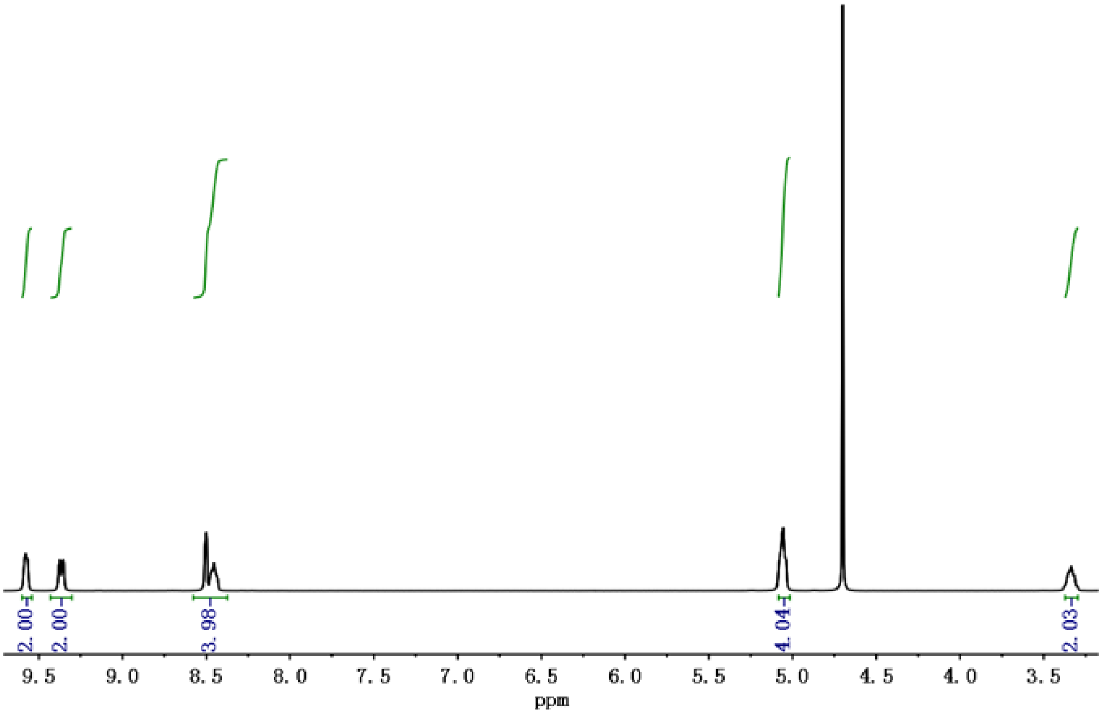


Figure S4. ^{1}H NMR spectrum of PPQ^{2+} in D_2O.

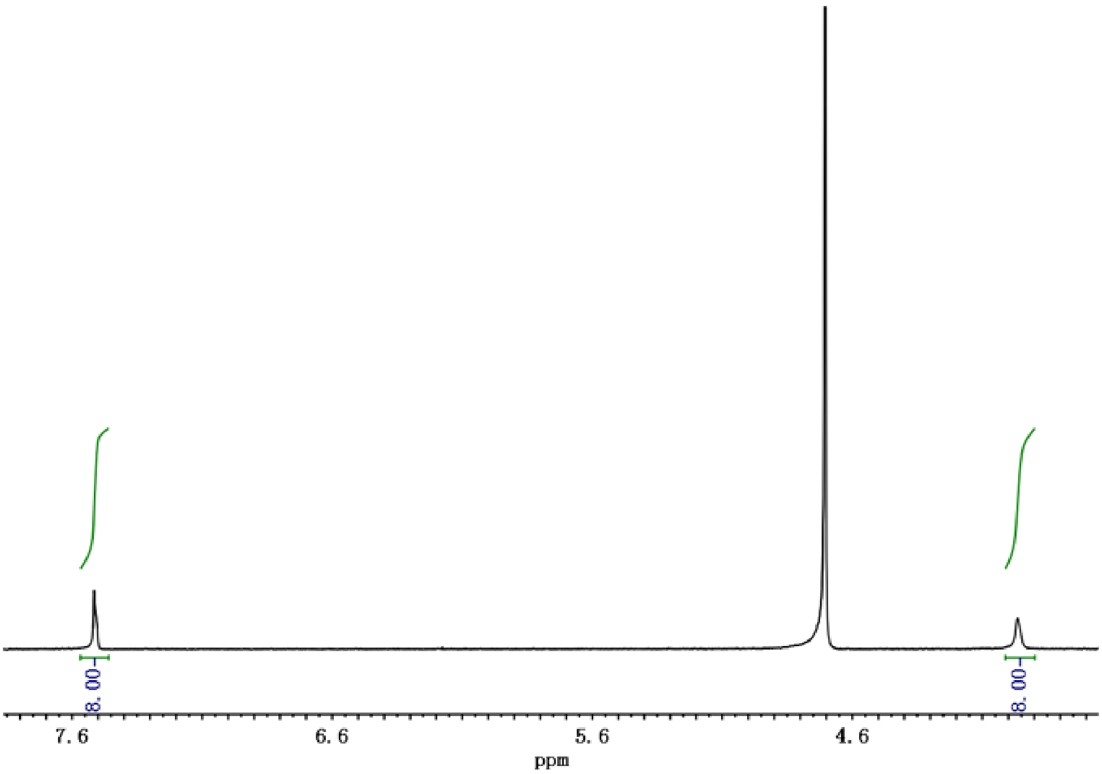


Figure S5. ^{1}H NMR spectrum of SC4A in D_2O.

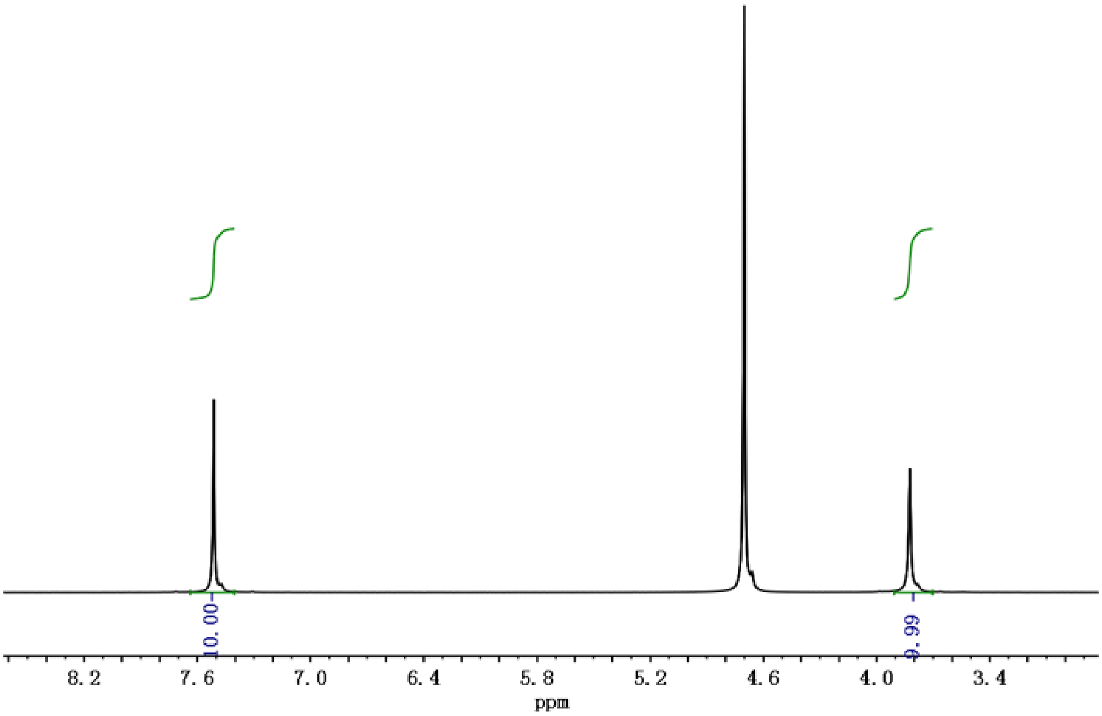


Figure S6. ^{1}H NMR spectrum of SC5A in D_2O.

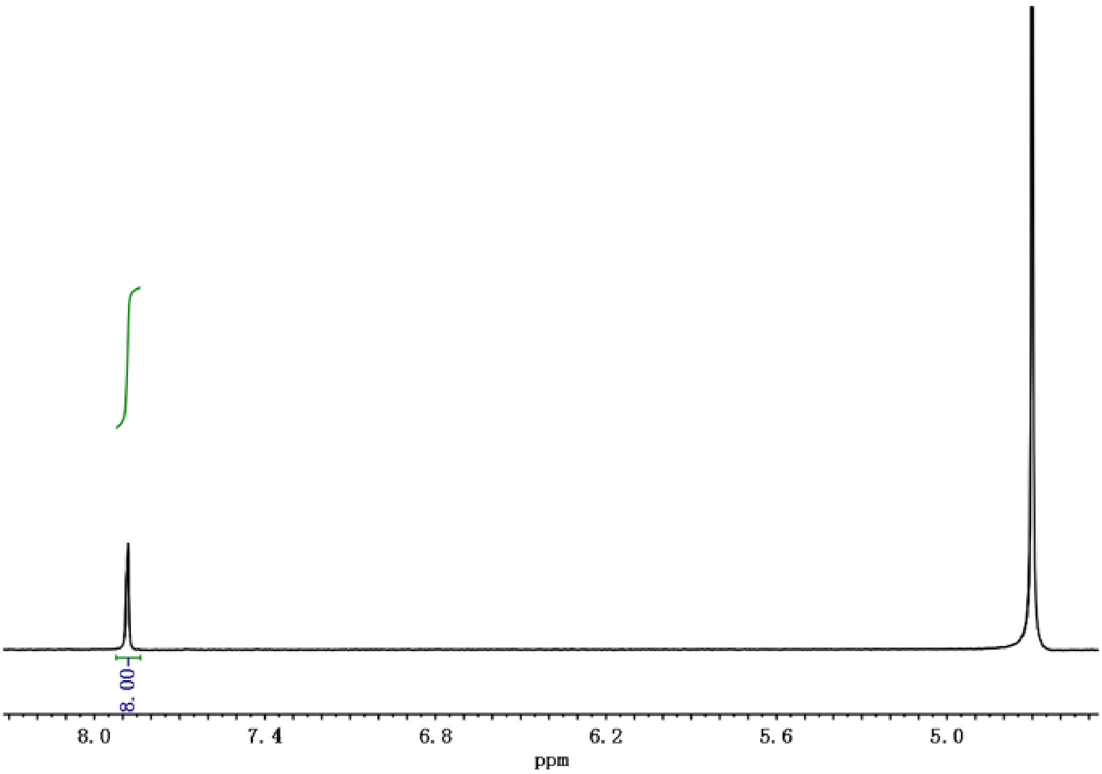


Figure S7. ^{1}H NMR spectrum of STC4A in D_2O.

^{13}C NMR Spectra of SC4A, SC5A, STC4A, DP^{2+}, and PPQ^{2+} in D_2O:

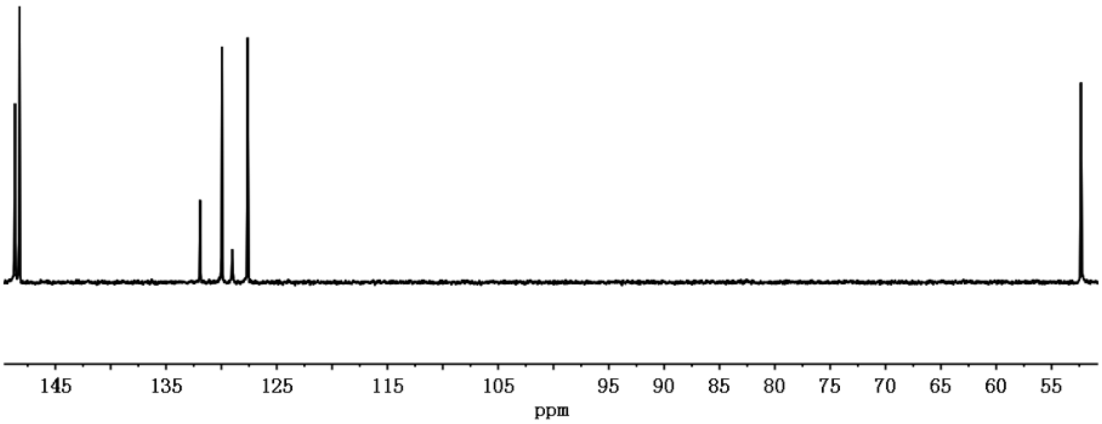


Figure S8. ^{13}C NMR spectrum of DP^{2+} in D_2O.

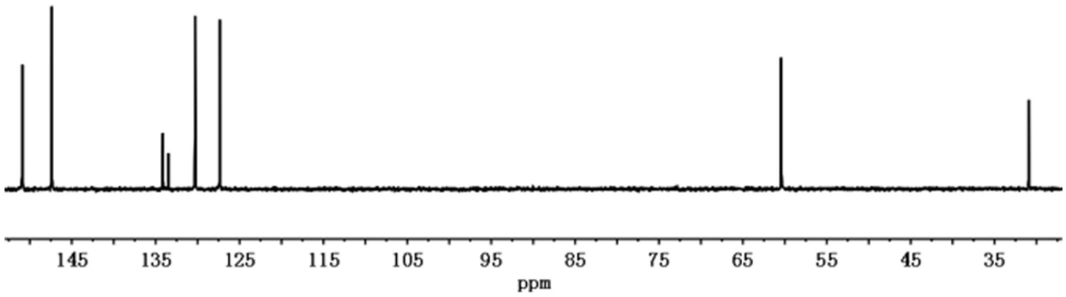


Figure S9. ^{13}C NMR spectrum of PPQ^{2+} in D_2O.

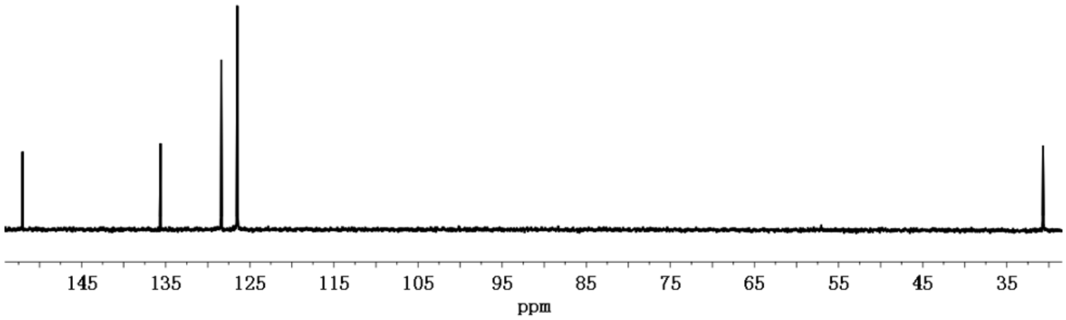


Figure S10. ^{13}C NMR spectrum of SC4A in D_2O.

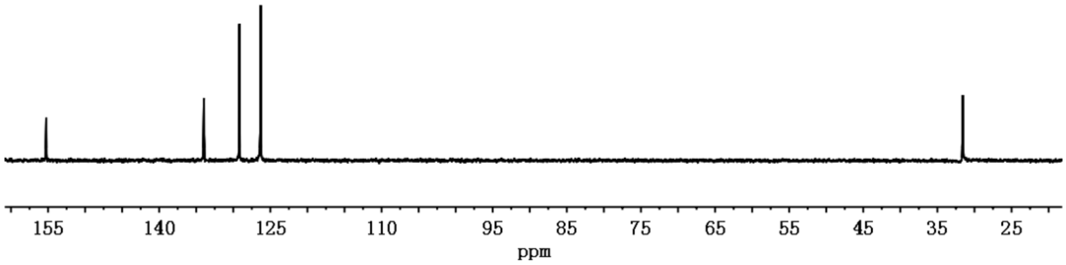


Figure S11. ^{13}C NMR spectrum of SC5A in D_2O.

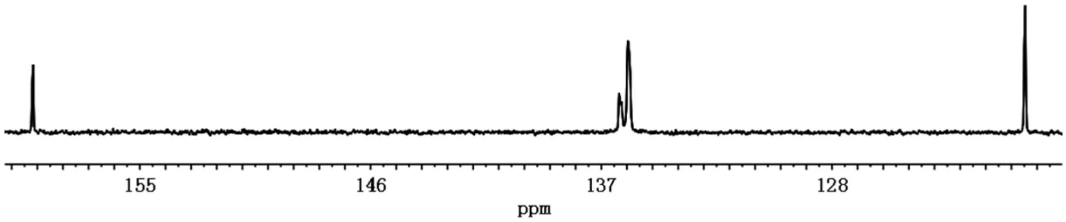


Figure S12. ^{13}C NMR spectrum of STC4A in D_2O.

Elemental Analysis Data of SC4A, SC5A, STC4A, DP^{2+}, and PPQ^{2+}:

Anal. Calcd (%) for $C_{14}H_{12}N_2^{2+}$•$2Br^-$ (DP^{2+}•$2Br^-$): C, 45.68; H, 3.29. Found (%): C, 45.52; H, 3.42.

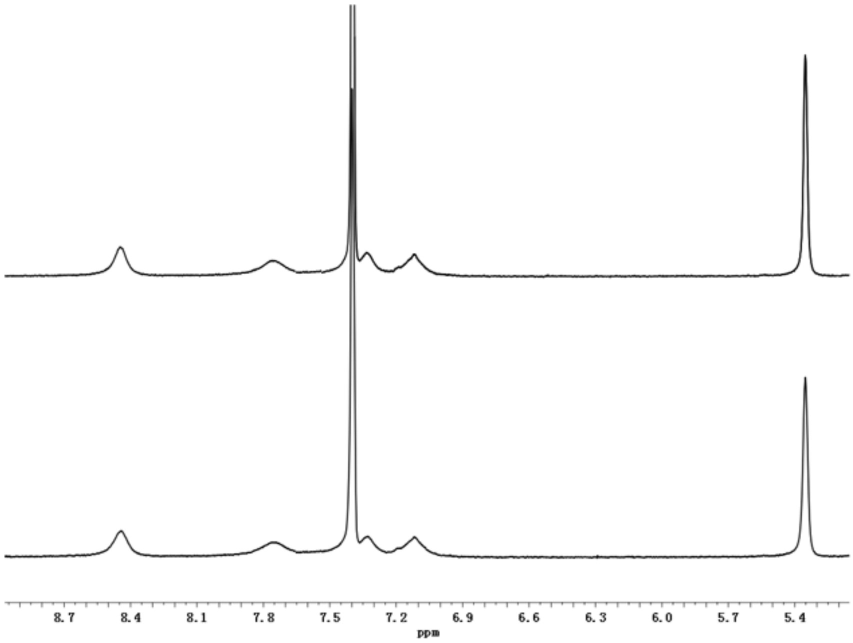
Anal. Calcd (%) for $C_{15}H_{14}N_2^{2+}$•$2Br^-$ (PPQ^{2+}•$2Br^-$): C, 47.15; H, 3.69. Found (%): C, 47.01; H, 3.87.

Anal. Calcd (%) for $C_{28}H_{20}O_{16}S_4Na_4$•$8H_2O$ (SC4A•$8H_2O$): C, 34.43; H, 3.71. Found (%): C, 34.21; H, 4.01.

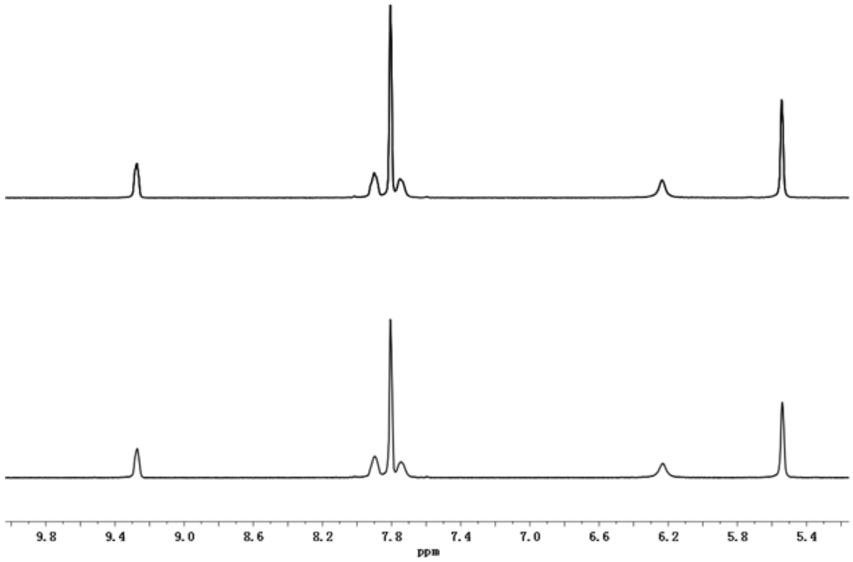
Anal. Calcd (%) for $C_{35}H_{25}O_{20}S_5Na_5$•$5H_2O$ (SC5A•$5H_2O$): C, 37.17; H, 3.12. Found (%): C, 37.01; H, 3.22.

Anal. Calcd (%) for $C_{24}H_{12}O_{16}S_8Na_4$•$6H_2O$ (STC4A•$6H_2O$): C, 28.46; H, 2.39. Found (%): C, 28.23; H, 2.68.

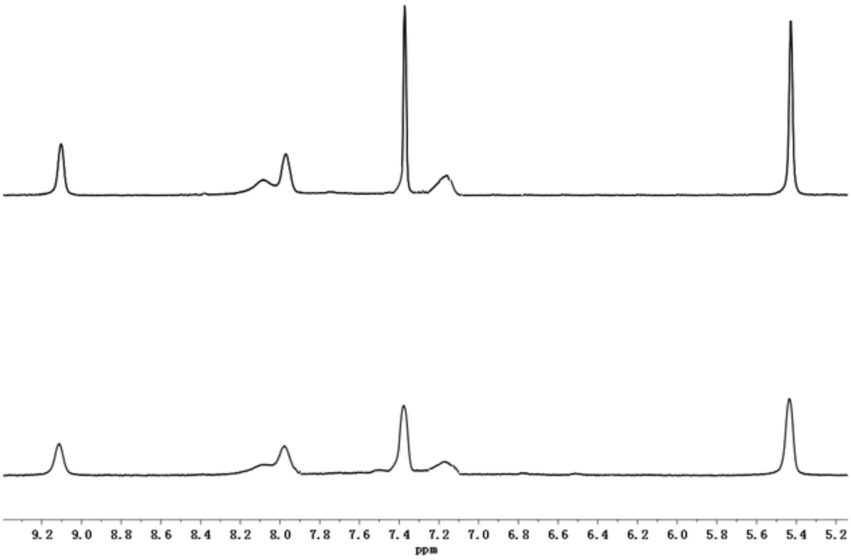
Figure S13. Pictures showing the color of DP^{2+} solutions upon complexation with 1 equiv of sulfonated calixarenes (10 mM in pD 7.2 phosphate D_2O buffer solution), (a) SC4A + DP^{2+}, (b) STC4A + DP^{2+}, and (c) SC5A + DP^{2+}.


8.7
8.4
8.1
7.8
7.5
7.2
6.9
6.6
6.3
6.0
5.7
5.4
ppm

(a)


9.8
9.4
9.0
8.6
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
ppm

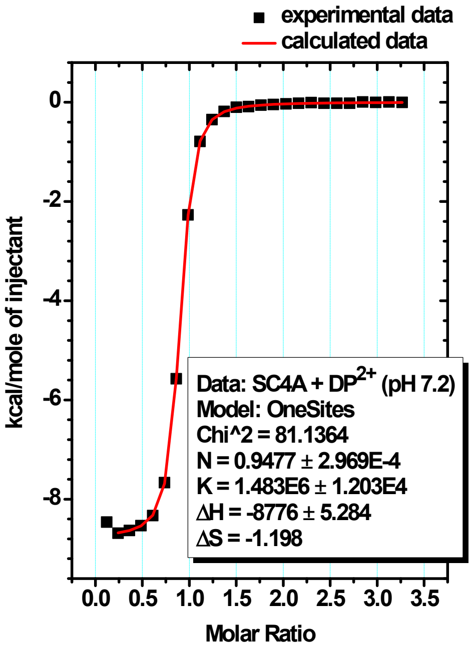
(b)



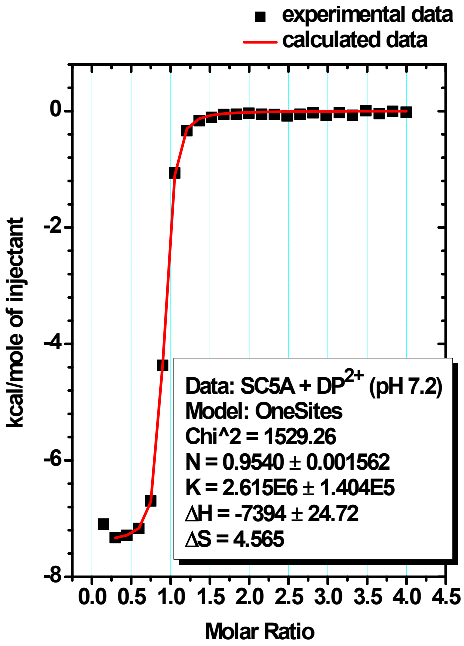
(c)

Figure S14. ^{1}H NMR spectra of SC4A + DP^{2+} complex (a), STC4A + DP^{2+} complex (b), and SC5A + DP^{2+} complex (c) at 25 °C (top) and around 0 °C (bottom). The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

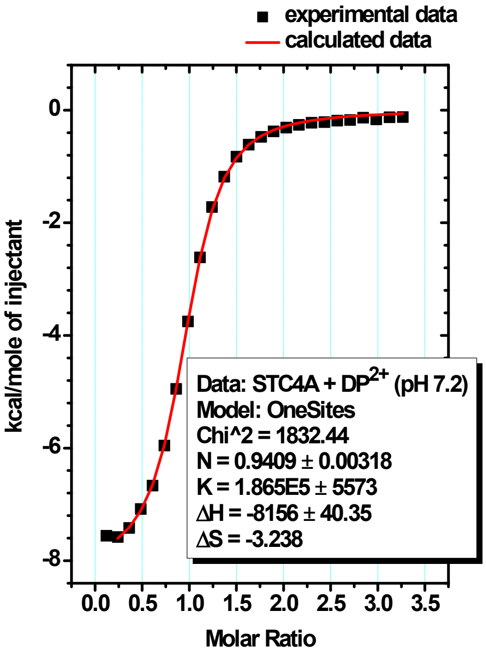
ITC Curves:



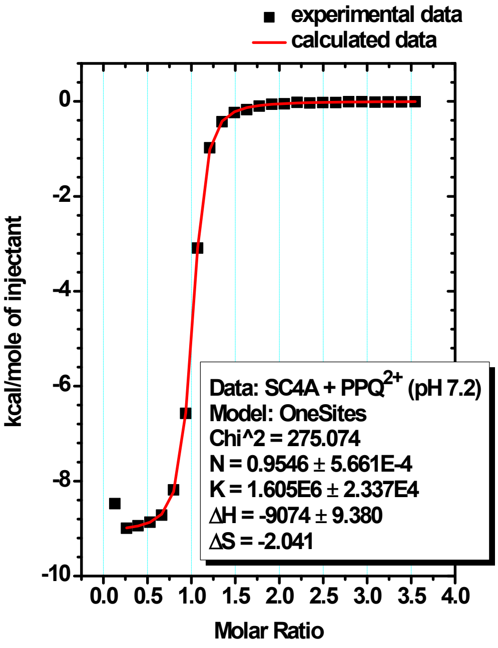
(a)



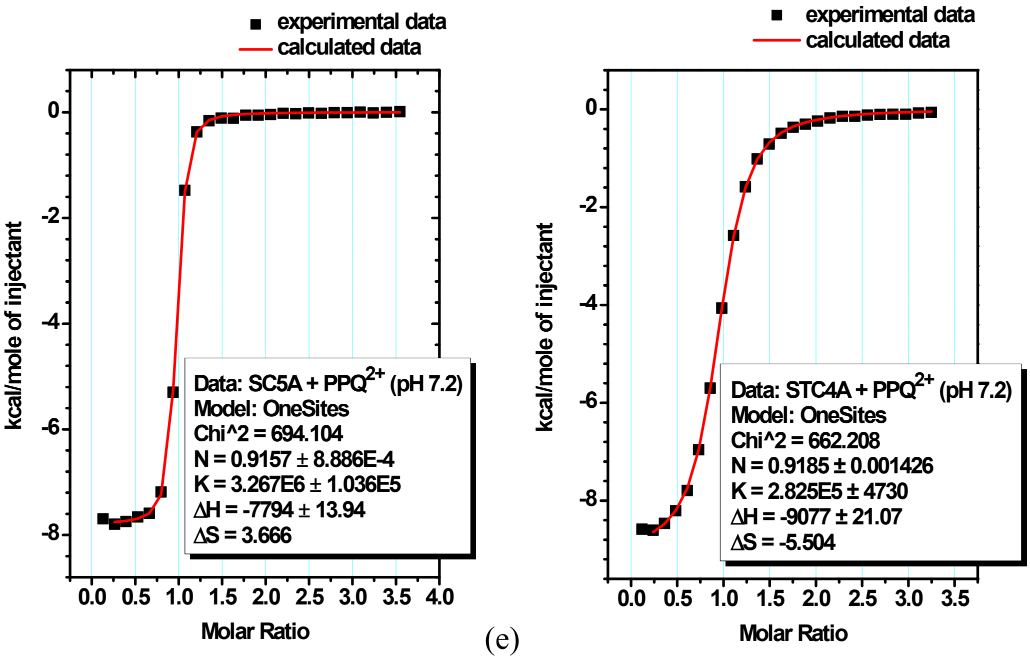
(b)



(c)



(d)



(e) (f)

Figure S15. “Net” heat effects of complexation of DP^{2+} and PPQ^{2+} with SC4A, SC5A, and STC4A for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the “one set of binding sites” model.

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