Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Electrochemical Stimulus-responsive Supramolecular Polymer Based on Sulfonatocalixarene and Viologen Dimers

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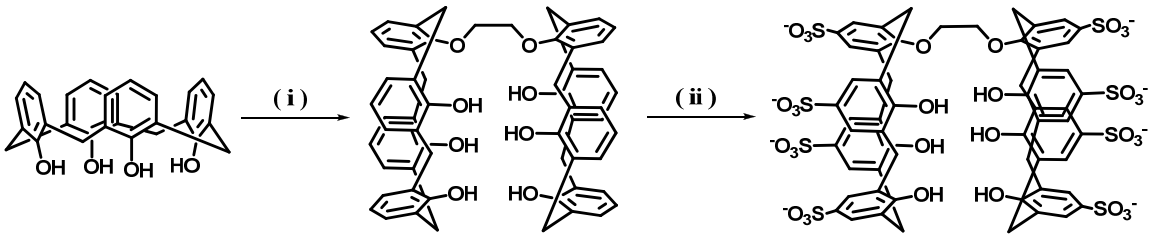
Synthesis



***bis*-C4A** ***bis*-SC4A**

***bis*-C4A:** ***bis*-C4A** was synthesized referring to the literature process.[1] A mixture of *p*-H-calix[4]arene (1.7 g, 4 mmol) and NaOMe (0.28 g, 5mmol) was refluxed in acetonitrile (60 ml) for 0.5h under a nitrogen atmosphere. The $TsOCH_2CH_2OTs$ (0.74 g, 2 mmol) was added, and the solution was refluxed for two more days. After being cooled to room temperature, the solvent was removed by rotating evaporation. The residue was dissolved in CH_2Cl_2, washed with 0.1 M HCl solution (3×50 ml), dried over anhydrous $MgSO_4$ and concentrated in vacuum. The crude solid was purified by chromatography on silica gel using CH_2Cl_2/petroleum ether (60-90°C) as eluent to give a white pure produce in 33% yield (0.74 g). ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 8.96 (s, 4H, ArOH), 8.90 (s, 2H, ArOH), 7.16 (d, 4H, J = 7.5 Hz, Ar-H), 7.09 (d, 4H, J = 7.5 Hz, Ar-H), 7.01 (d, 4H, J = 7.3 Hz, Ar-H), 6.90 (m, 6H, Ar-H), 6.70 (t, 4H, J = 7.5 Hz, Ar-H), 6.62 (t, 2H, J = 7.5 Hz, Ar-H), 4.73 (s, 4H, OCH_2CH_2O), 4.6 (d, 4H, J = 13.1 Hz, $ArCH_2Ar$), 3.74 (d, 4H, J = 13.9 Hz, $ArCH_2Ar$), 3.65 (d, 4H, J = 13.1 Hz, $ArCH_2Ar$), 3.26 (d, 4H, J = 14.1 Hz, $ArCH_2Ar$) ppm,dichloromethane (δ = 5.30 ppm); ESI, Ms: m/z 874.1 $[M - H]^-$; Elemental analysis: calcd (%) for $(C_{58}H_{50}O_8)_2 \cdot (CH_2Cl_2)_3$: C 71.29, H 5.33; found C 70.88, H 5.32.

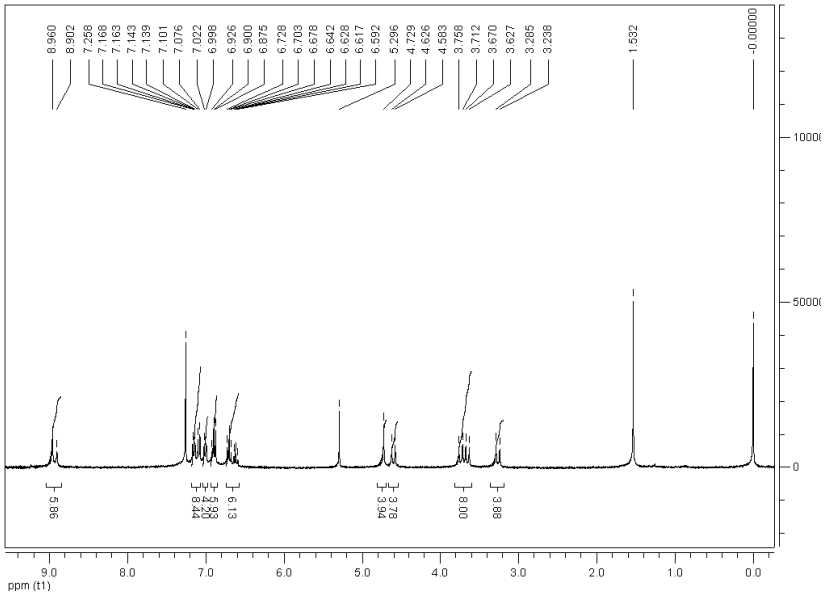


Fig. S1 ^{1}H NMR spectrum of ***bis*-C4A**.

***bis*-SC4A**: ***bis*-SC4A** was obtained according to the similar procedure previously reported by our group.[2] ***bis*-C4A** (1.0 g, 1.1 mmol) suspended in conc. H_2SO_4 (3 ml, 98%) was stirred at 50 °C for 24 h. After being cooled to room temperature, the solution was added to cold diethyl ether dropwise. The sticky precipitate was collected by filtration, washed 3 times with diethyl ether and dissolved in 50 ml distilled water. Neutralized by 1M NaOH solution to pH 7, the solvent was removed in vacuum. The obtained crude solid was later subjected to recrystallization (water:ethanol) to give a light yellow powder as the title product (0.9 g, 50% yield); ^{1}H NMR (300 MHz, D_2O, DSS): δ = 7.80 (s, 4H, Ar-H), 7.65 (s, 4H, Ar-H), 7.49 (s, 4H, Ar-H)，7.33 (s, 4H, Ar-H), 4.59–4.54 (m, 8H, $ArCH_2Ar$ and OCH_2CH_2O), 3.88 (d, 4H, J = 13.8 Hz, Ar-CH_2-Ar), 3.42 (s, 8H, Ar-CH_2-Ar) ppm, ethanol (δ_{CH3} = 1.10, δ_{CH2} = 3.58 ppm); ^{13}C NMR (300 MHz, D_2O): δ = 154.97, 154.92 (C-SO_3^-), 139.2, 134.4, 134.0, 133.8, 129.1, 128.6, 128.4, 126.8, 126.4, 126.2 (CH-Ar), 74.6 (O-CH_2CH_2-O), 31.3 (Ar-CH_2-Ar) ppm; Elemental analysis: calcd (%) for $(C_{58}H_{40}O_{32}S_8Na_{10})\cdot(C_2H_5OH)\cdot(H_2O)_{15}$: C 35.45, H 3.85; found C 35.09, H 3.79; Atomic Absorption Spectrophotometer (AAS): calcd (%) for $(C_{58}H_{40}O_{32}S_8Na_{10})\cdot(C_2H_5OH)\cdot(H_2O)_{15}$: Na 11.12; found Na 11.36.

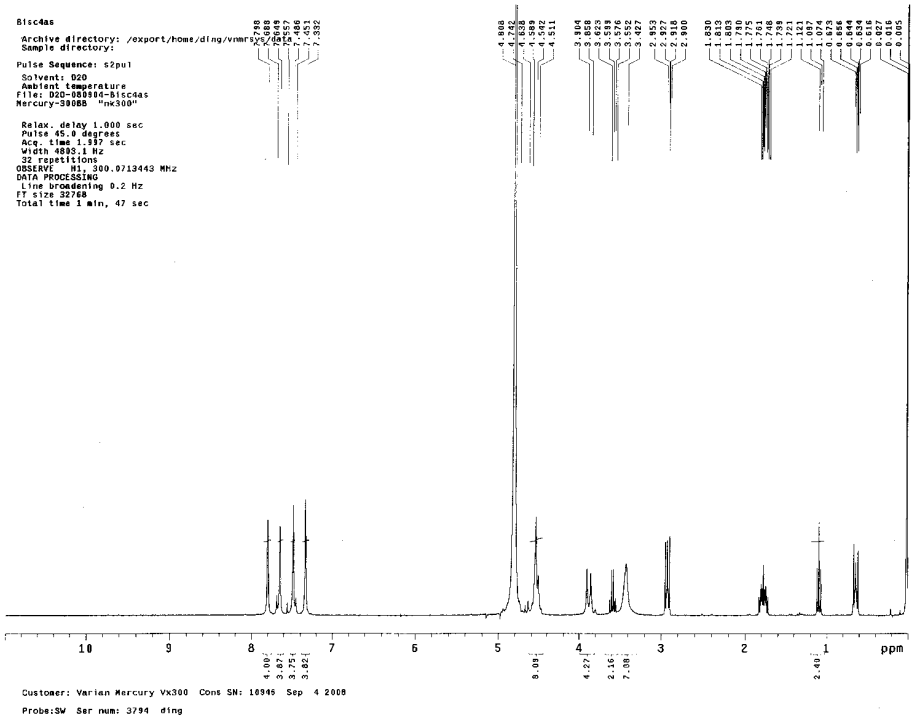


Fig. S2 ^{1}H NMR spectrum of ***bis*-SC4A**.

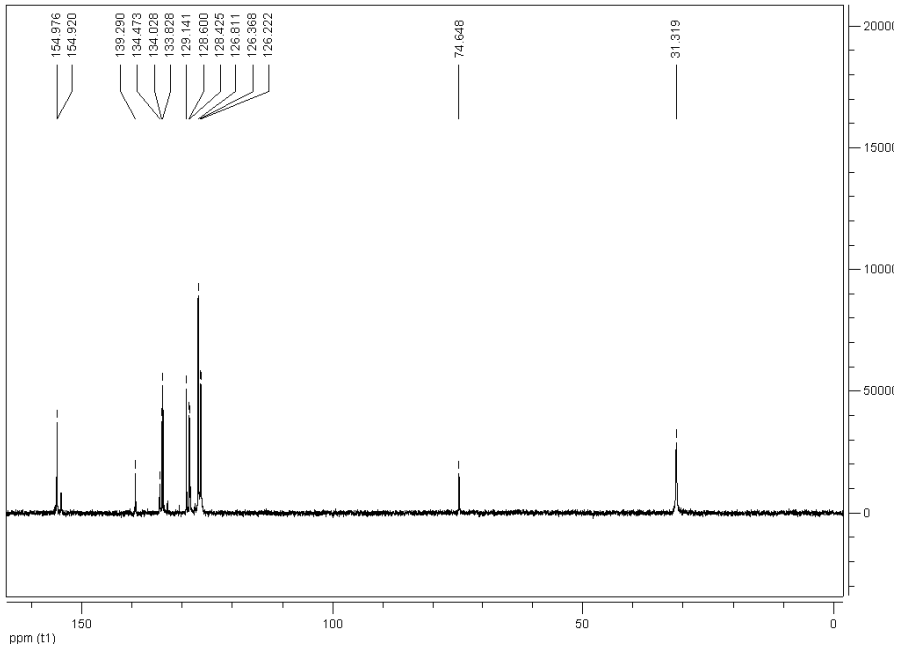


Fig. S3 ^{13}C NMR spectrum of ***bis*-SC4A**.

***bis*-MV^{4+}**: ***bis*-MV^{4+}** was prepared according to the literature method.[3] To a solution of 4,4'-bipyridine (1.56 g, 10 mmol) in 5 ml DMF was added 1,2-dibromoethane in 15 ml of DMF dropwise over a period of 24h, while the temperature of reaction mixture was maintained at 70 °C. After cooling to room temperature, diethyl ether was added to give a yellow precipitate of [bipyridine-$(CH_2)_2$-bipyridine]$^{2+}\cdot(Br^-)_2$ (1.8 g, 3.6 mmol). This compound was further treated with 4 equiv iodomethane in 5 ml of DMF and heated at 90 °C for 12h. The resulting red precipitate was filtered, washed with acetonitrile and dried under vacuum to give the pure product (2.2 g), yield 56%. ^{1}H NMR (300 MHz, D_2O): δ = 9.19 (d, 4H, J = 6.1 Hz), 9.02 (d, 4H, J = 5.7 Hz), 8.62 (d, 4H, J = 5.9 Hz), 8.51 (d, 4H, J = 6.1Hz), 5.49 (s, 4H), 4.45 (s, 6H) ppm.

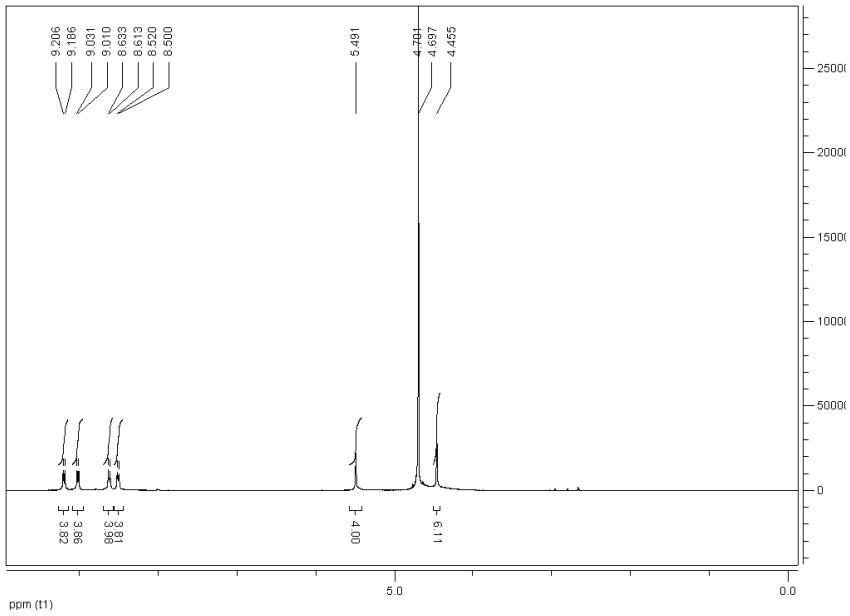


Fig. S4 ^{1}H NMR spectrum of ***bis*-MV^{4+}**.

Measurements

^{1}H NMR spectra were recorded in D_2O solution (pH adjusted by DCl or NaOD) at 25 °C. Chemical shifts (δ, ppm) in water were externally referenced to 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in order to avoid any possible interaction with host as well as with the guest molecule.

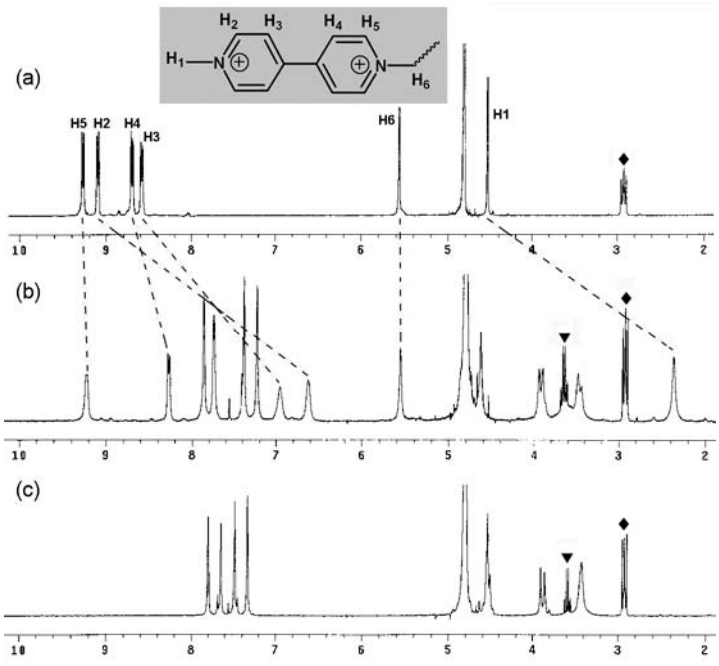


Fig. S5 ^{1}H NMR spectra in D_2O of *bis*-MV^{4+} (a), the 1:1 mixture of *bis*-MV^{4+} and *bis*-SC4A (b), and *bis*-SC4A (c). "▼" represents the signal of ethanol protons, and "♦" represents the signal of DSS protons.

Atomic force microscopy (AFM) was performed using a multi-mode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature, and samples were prepared by dropping an aqueous solution on mica.

The dynamic light scattering (DLS) was performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm. The measurement of weight-average molecular weights (M_W) was performed on a triple detection size exclusion chromatograph (Tri-SEC) containing a Waters 1525 separation module (Waters Corp.) connected with M302 triple detector array (Viscotek Corp., Houston, Texas), a combination of refractive index, light scattering (LS angle, 7° and 90°, laser wavelength, λ = 670 nm), and viscosity detector. Two mixed bed SEC columns (GMH_{HR}-M, GMH_{HR}-H, Viscotek Corp.) were used. Water was used as mobile phase at a flow rate of 1.0 mL/min and an operating temperature of 30 °C.

The cyclic voltammetry (CV) measurements were carried out on a BAS Epsilon electrochemical analyzer with C3-cell stand. All solutions were prepared in phosphate buffer (pH 7.2, 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 to a mirror with 0.05 mm 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 usage. 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.

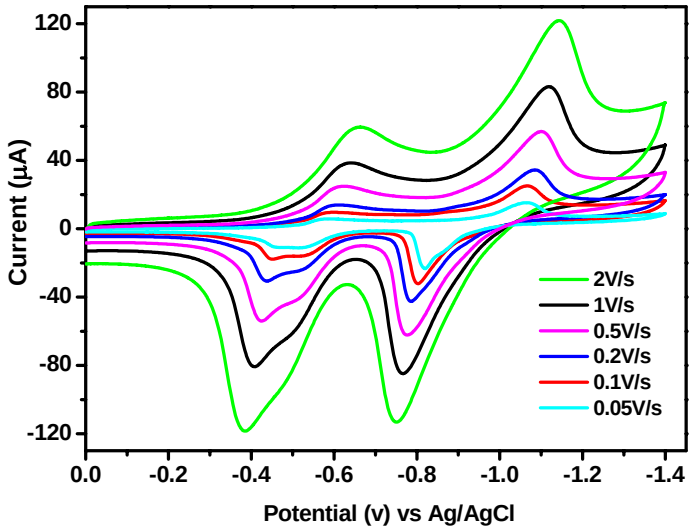


Fig. S6 CV curves of *bis*-MV^{4+} (1.0 mM in pH 7.2 phosphate buffer solution) in the presence of 1 equiv of *bis*-SC4A from 0.0 to –1.4 V as a function of scan rate (from 0.05 V/s to 2 V/s).

Isothermal Titration Calorimetry (ITC): A thermostated 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 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. All microcalorimetric titrations between *bis*-SC4A and *bis*-MV^{4+} were performed in phosphate buffer solution (pH 7.2) at atmospheric pressure and 298.15 K. Each solution was degassed and thermostated 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 solution in a 0.250-mL syringe was injected into the reaction cell (1.4227 mL) charged with host molecule solution in the same aqueous solution. A representative titration curve was shown in Fig. 1. As can be seen from Fig. 1, each titration of *bis*-MV^{4+} into the sample cell gave an apparent reaction heat caused by the formation of inclusion complex between *bis*-SC4A and *bis*-MV^{4+}. The reaction heat decreases after each injection of *bis*-MV^{4+} 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 aqueous solution into a pure aqueous solution containing no host 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 removed considering that the concentration of host in the cell far exceeded the concentration of the

guest. 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 *bis*-MV^{4+} with *bis*-SC4A at pH 7.2 was shown in Fig. S7. 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 were listed in Table S1.

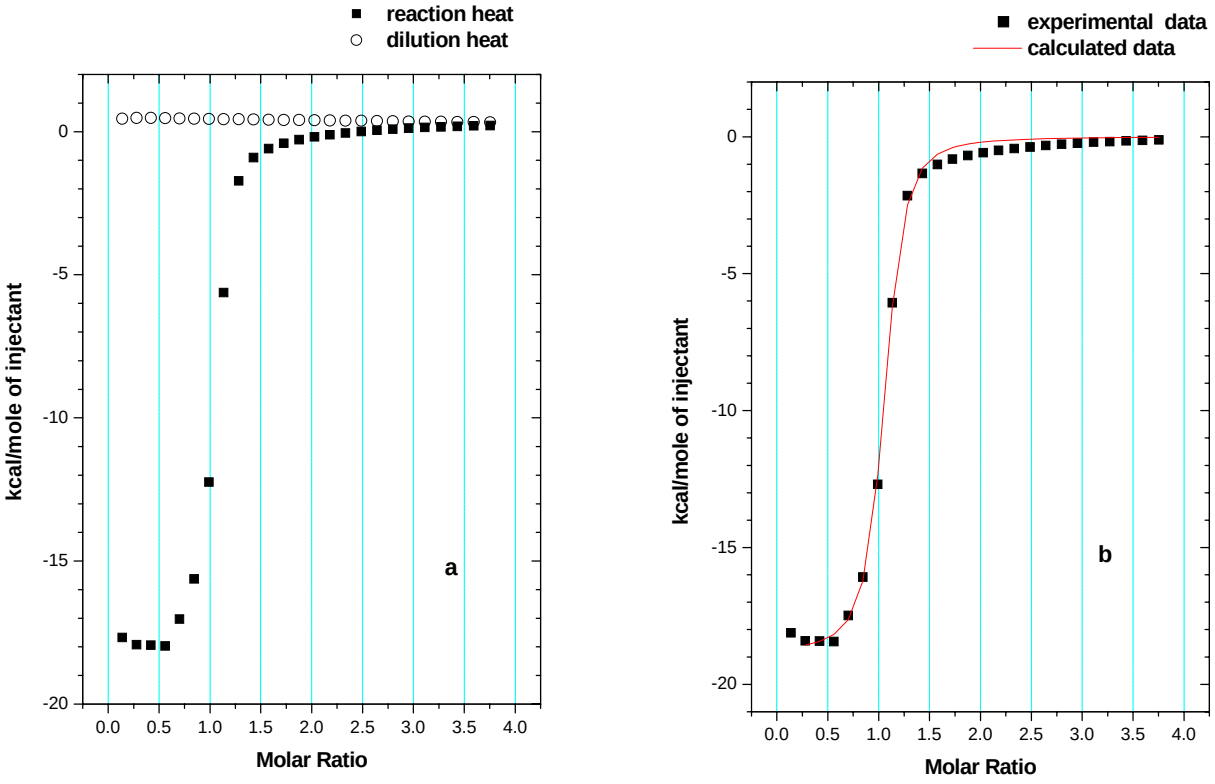


Fig. S7 (a) Heat effects of the dilution and of the complexation reaction of *bis*-SC4A with *bis*-MV^{4+} for each injection during titration microcalorimetric experiment. (b) "Net" heat effects of complexation of *bis*-SC4A with *bis*-MV^{4+} for each injection, obtained by

subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model.

Table S1. Complex Stability Constant (K_S/M^{-1}), Enthalpy [$\Delta H°/(kJ·mol^{-1})$], and Entropy Changes [$T\Delta S°/(kJ·mol^{-1})$] for the Intermolecular Complexation of of *bis*-SC4A with *bis*-MV^{4+} in Phosphate Buffer Solution (pH 7.2) at 298.15K.

Condition	Complex	K_S	$\Delta H°$	$T\Delta S°$
pH = 7.2	*bis*-SC4A+*bis*-MV^{4+}	$(4.27\pm0.01)\times10^5$	−39.47±0.02	−7.36±0.01

Gel Permeation Chromatograph (GPC): The molecular weight were measured on a Vescotek TDA 302 gel permeation chromatograph (GPC) instrument equipped with a Agilent Technologies 1200 Series pump, a TSK GMPWxl column, and a refractive index detector. Polyethylene Oxide (PEO) was used as calibration standard and water was used as the eluent at a flow rate of 1 ml/min at 30 °C.

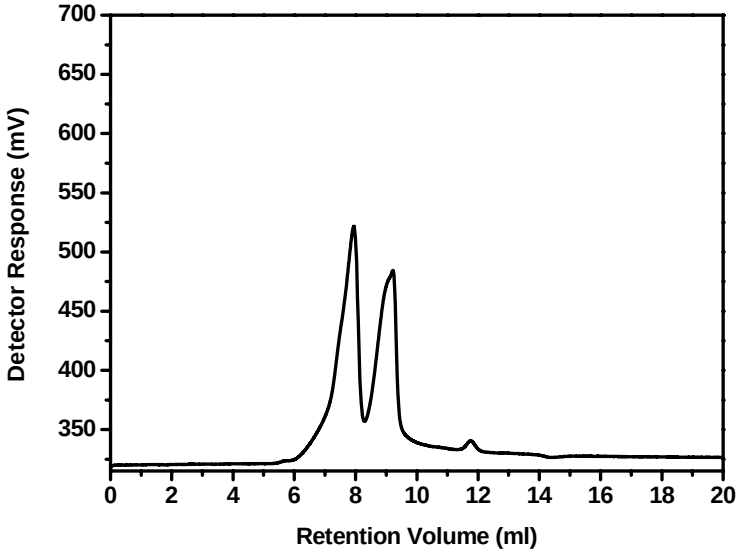


Fig. S8 GPC trace of the 1:1 mixture of *bis*-MV^{4+} and *bis*-SC4A (1.0 mM in water).

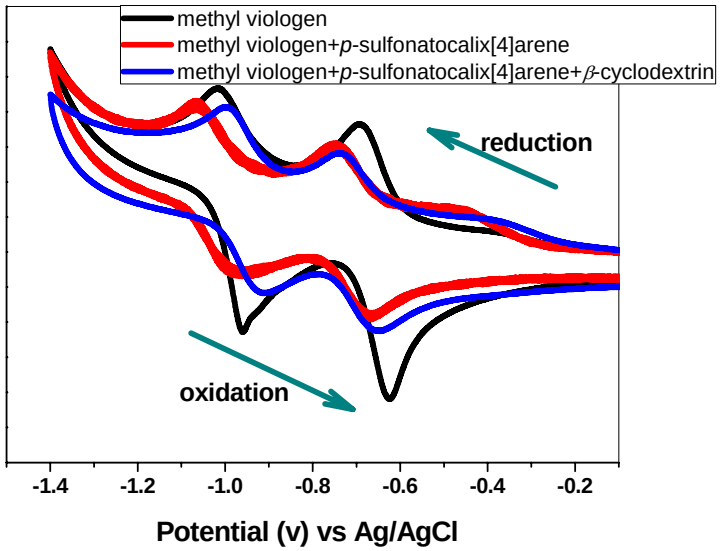


Fig. S9 CV curves of methyl viologen (1 mM), methyl viologen (1 mM) + *p*-sulfonatocalix[4]arene (1 mM), and methyl viologen (1 mM) + *p*-sulfonatocalix[4]arene (1 mM) + *β*-cyclodextrin (11 mM). Scan rate is 0.1 V/s.

We also performed the CV measurements for methyl viologen, methyl viologen + *p*-sulfonatocalix[4]arene, and methyl viologen + *p*-sulfonatocalix[4]arene + *β*-cyclodextrin to prove that. As shown in Fig. S9, for the first reduction potentials, the blue curve is similar to the red curve, and both of them shift to more negative values (more difficult to be reduced) compared with the black curve, which indicates that methyl viologen cation radical is included into the cavity of *p*-sulfonatocalix[4]arene regardless of *β*-cyclodextrin. In contrast, for the second reduction potentials, the red curve shifts to more negative value (more difficult to be reduced) compared with the black curve while the blue curve shifts to more positive value (much easier to be reduced) compared with the black curve, which indicates that the interaction between noncharged methyl viologen and *p*-sulfonatocalix[4]arene is so weak, and after reduction, noncharged methyl viologen will be included by *β*-cyclodextrin. We can get the same conclusion from the re-oxidation potentials. For the blue curve, its second

re-oxidation potential shifts to more positive value (more difficult to be oxidated) due to the inclusion of noncharged methyl viologen into the cavity of *β*-cyclodextrin. After that, the complex of *β*-cyclodextrin with methyl viologen cation radical will break up and methyl viologen cation radical will further be included by *p*-sulfonatocalix[4]arene, as a result, the blue curve is similar to the red curve for the first re-oxidation potential and both of them shift to more negative values (much easier to be oxidated) compared with the black curve. All these results are consistent with the reported studies about the interactions between *β*-cyclodextrin and viologens in their three oxidation states.[4]

Referrences

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(2) D.-S. Guo, K. Chen, H.-Q. Zhang and Y. Liu, *Chem. Asian J.*, 2009, **4**, 436–445.

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(4) (a) A. Mirzoian and A. E. Kaifer, *Chem. Commun.*, 1999, 1603–1604; (b) A. Mirzoian and A. E. Kaifer, *Chem. Eur. J.*, 1997, **3**, 1052–1058.