Supporting Information for

A Novel Supramolecular Ternary Polymer with Two Orthogonal Host-Guest Interactions

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Experimental Section

Materials:

Bis(p-sulfonatocalix[4]arene) octasodium (bisSC4A·8Na$^+$) was synthesized and purified referring to the literature process.[1] The dibromide salt of N-methyl-N'-adamantane carbomethyl-4,4'-bipyridinium (Ad-Vio·2Br$^-$) was prepared according to the literature procedure with counter ion exchanged by PF$_6^-$ and then Br$^-$.[2]

Preparation of Naphthyl-bridge-bis(β-cyclodextrin) (bisCD): To a solution of 1,5-propargyloxynaphthalene (100 mg, 0.424 mmol) in THF (20 mL) was added 6-deoxyl-6-azido-β-CD (1.1 g, 0.949 mmol) in H$_2$O (10 mL) with stirring. To the resulting solution were added CuSO$_4$·5H$_2$O (430 mg) and then sodium ascorbate (900 mg) dissolved in water (10 mL). The mixture was heated at about 60 °C for 48 h. The mixture was then dried under reduced pressure, and the residue was dissolved in DMF. Insoluble precipitates were removed by filtration, the crude product obtained was further purified by MPLC (reversed phase) with a water-alcohol eluent, and the collected fraction was freeze-dried to obtain a colorless powder in 67% yield: ^{1}H NMR (D$_2$O, 400 MHz, ppm) δ 7.96 (d, 1H), 7.73 (s, 1H), 7.49 (d, 1H), 7.37 (dd, 2H), 7.05 (t, 2H), 6.93 (s, 1H), 5.55–5.40 (m, 4H), 5.12–4.85 (m, 14H), 3.99–3.20(m, 86H); MALDI-MS m/z 2578.8250 ([M + Na]$^+$). Anal. Calcd for C$_{100}$H$_{150}$N$_6$O$_{70}$·16H$_2$O: C, 42.22; H, 6.45; N, 2.95. Found: C, 42.14; H, 6.46; N, 3.35.

All other chemicals were commercially available and were reagent grade without further purifications.

Transmission Electron Microscopy (TEM) measurements. 1.0×10^{-6} M (calculated from the repeat units) sample solutions were dropped onto a copper grid. The grid was then air-dried. The samples were examined by a high-resolution TEM (Tecnai G2 F20 high-resolution TEM) operating at an accelerating voltage of 300 kV.

Atomic Force Microscopy (AFM) measurements. The samples were performed using a multi-mode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature 2.0×10^{-6} M (calculated from the repeat units) sample solutions were dropped onto newly clipped mica and then air-dried.

Dynamic light-scattering (DLS) measurements. The samples were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm and 636 nm at 25 °C. All DLS measurements were performed at the scattering angle of 90°. The sample solutions were prepared by filtering each component solution (2 mL in total volume) respectively through a 220 or 450 nm Syringe filter into a clean scintillation vial at the different concentrations.

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,[3] and also by measurement of the complexation reaction of SC4A with methyl viologen, and the obtained thermodynamic data were in good agreement (error < 5%) with the

literature data.[4] All microcalorimetric titrations were performed in aqueous solution 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 per injection) of host solution in a 0.250 mL syringe was injected into the reaction cell (1.4227 mL) charged with guest molecule solution in the same aqueous solution. A representative titration curve was shown in Figure S15. As can be seen from Figure S15, each titration of *bis*CD into the sample cell gave an apparent reaction heat caused by the formation of inclusion complex between *bis*CD and Ad-Vio⊂*bis*SC4A.

The reaction heat decreases after each injection of *bis*CD because less and less guest complexes Ad-Vio⊂*bis*SC4A are available to form ternary complexes. A control experiment was carried out in each run to determine the dilution heat by injecting a host aqueous solution into a pure aqueous solution containing no guest complexes. 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 the 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 bisCD with Ad-Vio⊂bisSC4A is shown in Figure S16. The representative titration curves of complexation of bisCD with Ad-Vio and bisSC4A with Ad-Vio were shown in Figures S11 and S13. The typical curve fitting results for the complexation of bisCD with Ad-Vio and bisSC4A with Ad-Vio were shown in Figures S12 and S14. 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 were listed in Table 1.
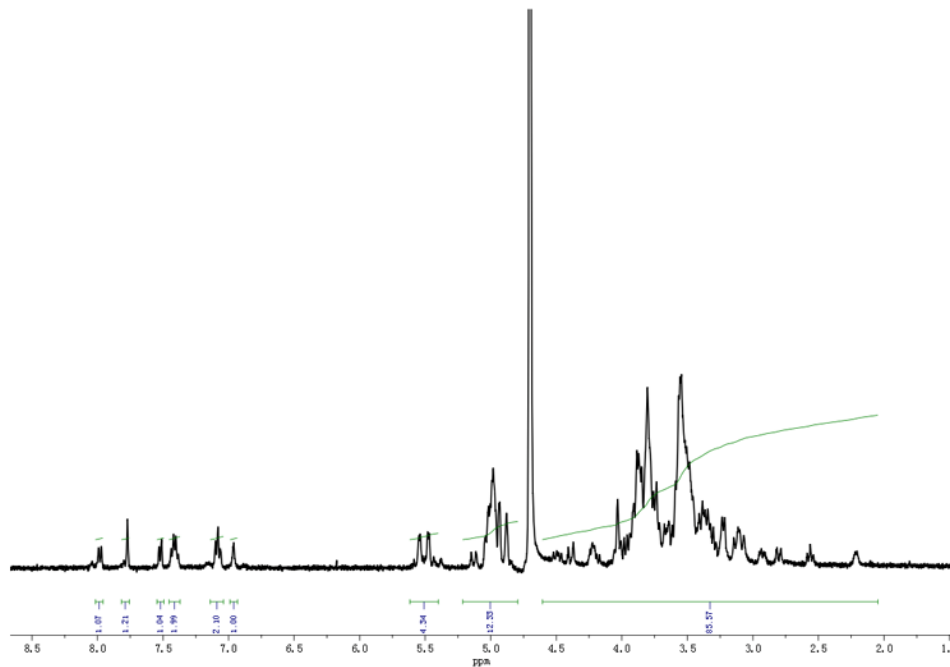
Figure S1. Partial ¹H NMR spectrum (400 MHz, D₂O, 298.15K) of bisCD.
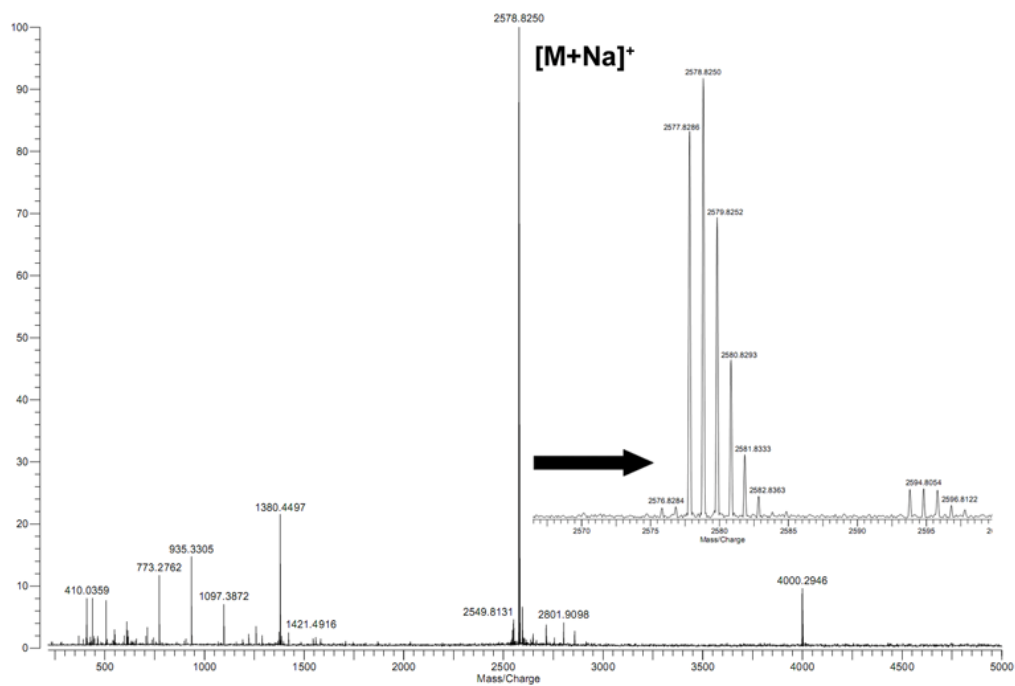
Figure S2. MALDI-HRMS spectrum of *bis*CD.
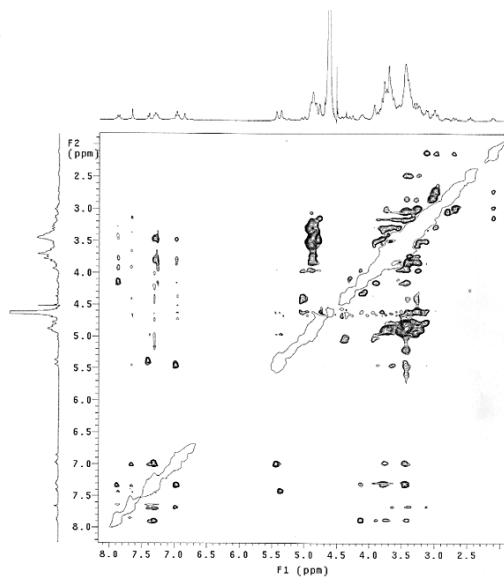
Figure S3. ROESY spectrum (300 MHz) of *bis*CD (4.0 mmol) in D_2O at 298.15K

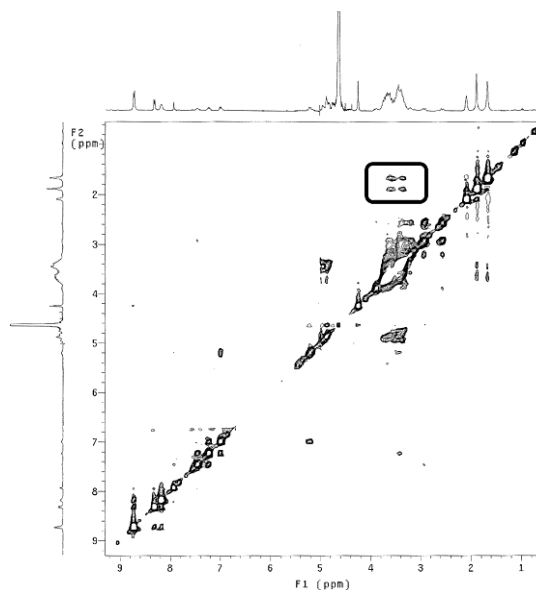with a mixing time of 230 ms.

Figure S4. NOESY spectrum of the *bis*CD (2.0 mM) with 2.0 equiv. Ad-Vio in D$_2$O at 298.15 K with a mixing time of 230 ms.
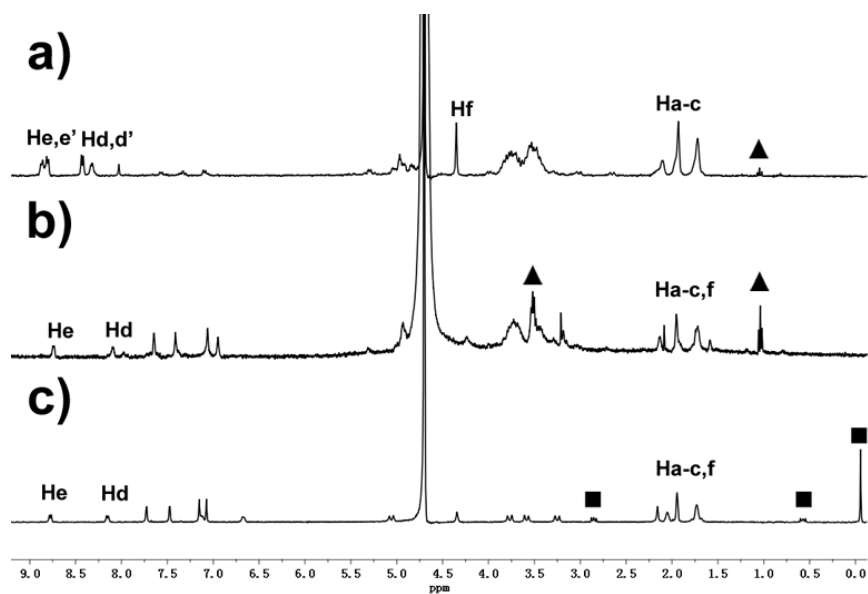

Figure S5. ^{1}H NMR spectra (400 MHz, D$_2$O, 298.15K) of a) 0.1 mM *bis*CD⊃Ad-Vio, b) 0.1 mM *bis*CD⊃Ad-Vio⊂*bis*SC4A, c) 0.1 mM Ad-Vio⊂*bis*SC4A. The solvent is D$_2$O and "▲" represents the signal of ethanol protons, "■" represents the proton of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), which was added as an external reference.
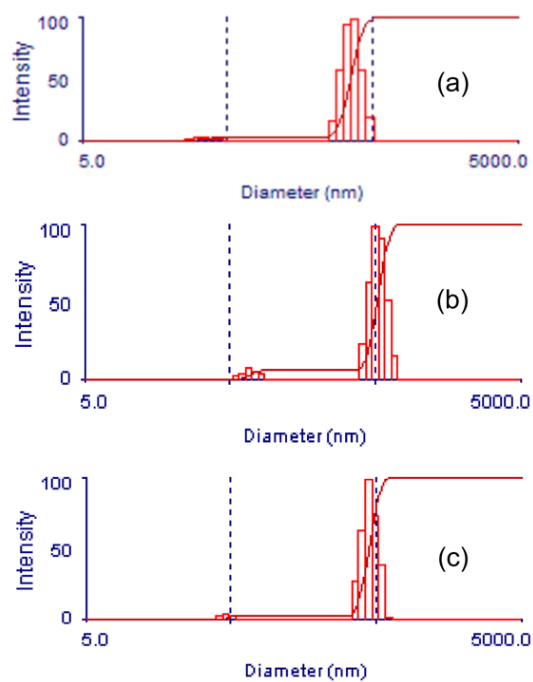
Figure S6. Hydrodynamic diameter distribution of 0.1 mM *bis*SC4A aqueous solution with 1.0 equiv. *bis*CD and 2.0 equiv. Ad-Vio at 298.15 K.
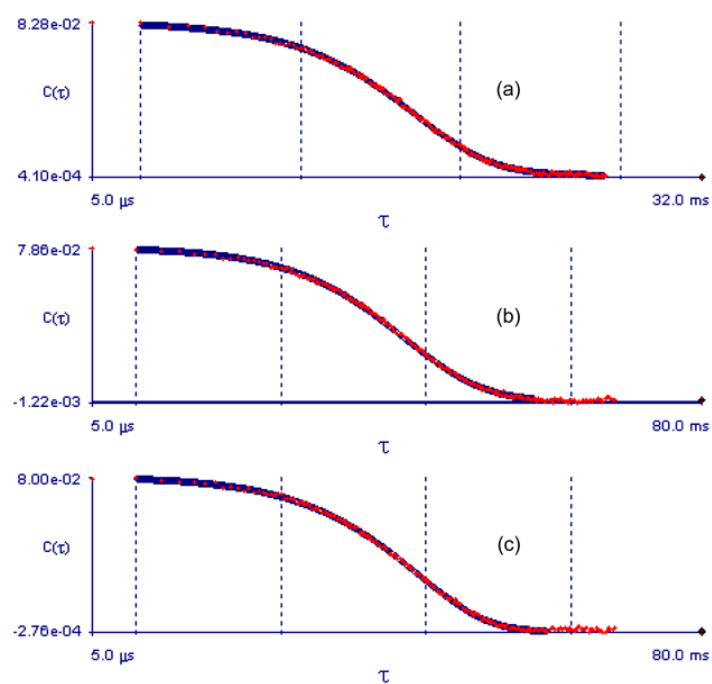
Figure S7. Representative dynamic light scattering data for (a) 0.05mM (b) 0.08mM (c) 0.1 mM aqueous solution of ternary assembly *bis*CD⊃Ad-Vio⊂*bis*SC4A.
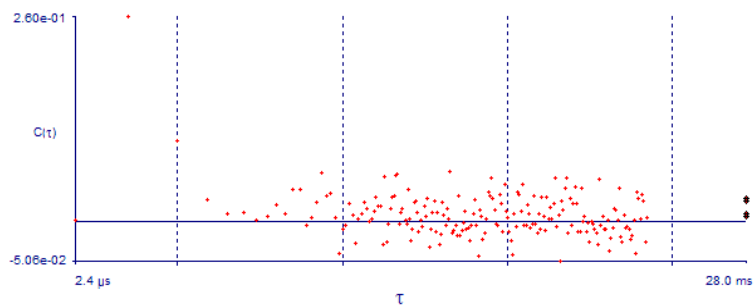
Figure S8. Representative dynamic light scattering data for 0.1 mM aqueous solution of binary complex Ad-Vio⊂*bis*SC4A.
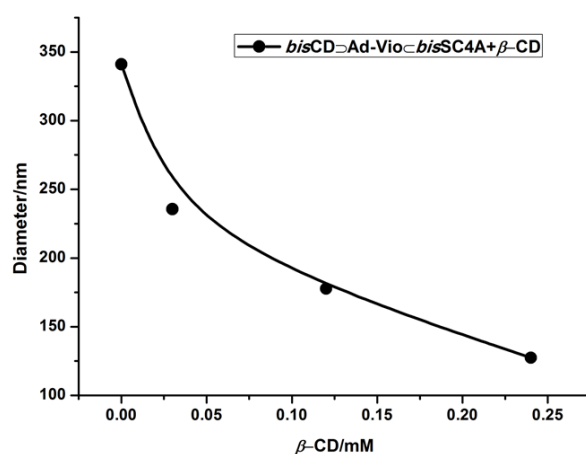

Figure S9. The hydrodynamic diameter of supramolecular ternary polymer *bis*CD⊃Ad-Vio⊂*bis*SC4A decreased, upon increasing the concentration of the β-CD (from 0.5 to 4 equiv) to 0.06 mM *bis*SC4A aqueous solution with 1.0 equiv. *bis*CD and 2.0 equiv. Ad-Vio. It seems to be that the assembly was not thoroughly disrupted by the excess β-CD, and still showed DLS signal of 127 nm. One reasonable explanation is that DLS is a highly sensitive technique to detect the nano-assembly or aggregation, and therefore, one can observe the DLS signal although there are very small amounts of aggregates in the system. Moreover, we noticed that the scattering intensity with 4 equiv. β-CD has been much lower than that of the ternary polymer, which indicates that most of the polymers have been disassembled.
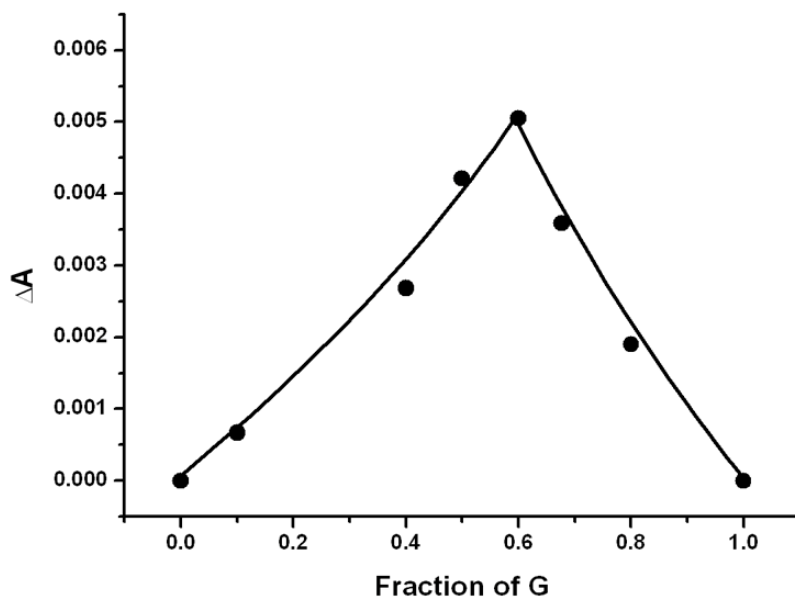
Figure S10. Job plot for Ad-Vio upon complexation with *bis*CD in aqueous solution

at 298.15K. Absorption change recorded at 396.5 nm. The sum of the total

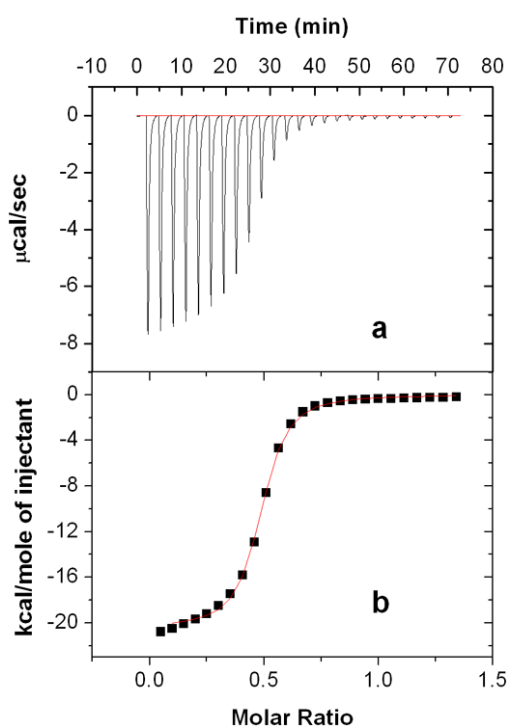concentration of host and guest is constant (4.0×10^{-5} M).

Figure S11. Microcalorimetric titration of *bis*SC4A with Ad-Vio in aqueous solution

at 298.15 K. (a) Raw ITC data for sequential 25 injections (10 µL per injection) of

*bis*SC4A solution (1.26 mM) injecting into Ad-Vio (0.18 mM) solution. (b) Apparent

reaction heat obtained from the integration of calorimetric traces.
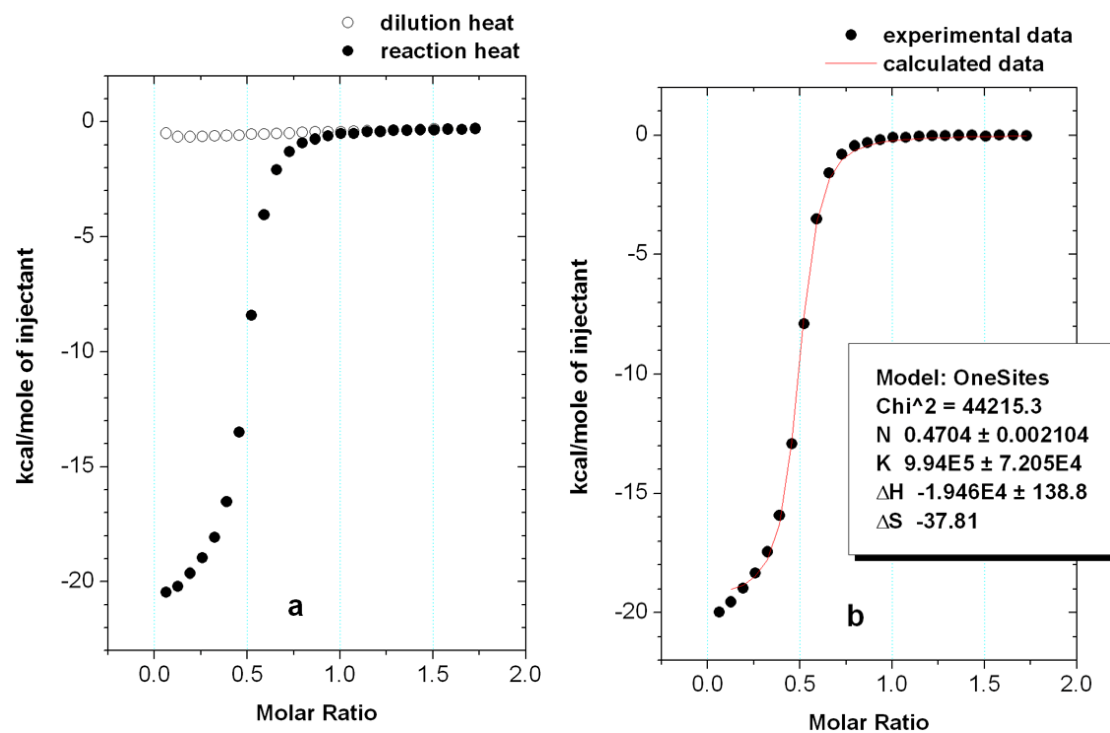

Figure S12. (a) Heat effects of the dilution and of the complexation reaction of *bis*SC4A with Ad-Vio for each injection during titration microcalorimetric experiment. (b) "Net" heat effects of complexation of *bis*SC4A with Ad-Vio for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model.
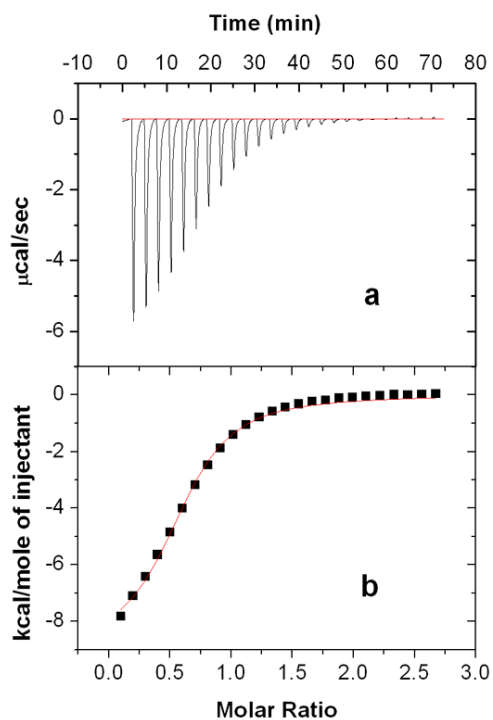
Figure S13. Microcalorimetric titration of *bis*CD with Ad-Vio in aqueous solution at 298.15 K. (a) Raw ITC data for sequential 25 injections (10 μL per injection) of *bis*CD solution (2.80 mM) injecting into Ad-Vio (0.20 mM) solution. (b) Apparent reaction heat obtained from the integration of calorimetric traces.
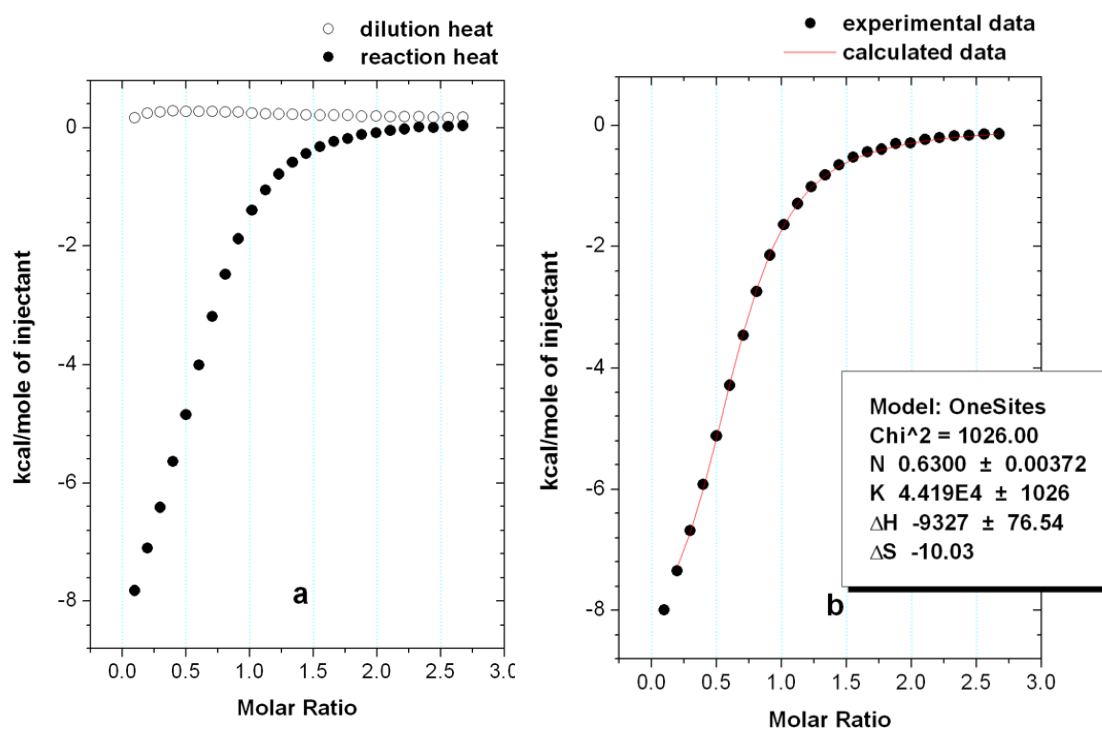

Model: OneSites
Chi^2 = 1026.00
N 0.6300 ± 0.00372
K 4.419E4 ± 1026
ΔH -9327 ± 76.54
ΔS -10.03

Figure S14. (a) Heat effects of the dilution and of the complexation reaction of *bis*CD

with Ad-Vio for each injection during titration microcalorimetric experiment. (b)

"Net" heat effects of complexation of *bis*CD with Ad-Vio for each injection, obtained

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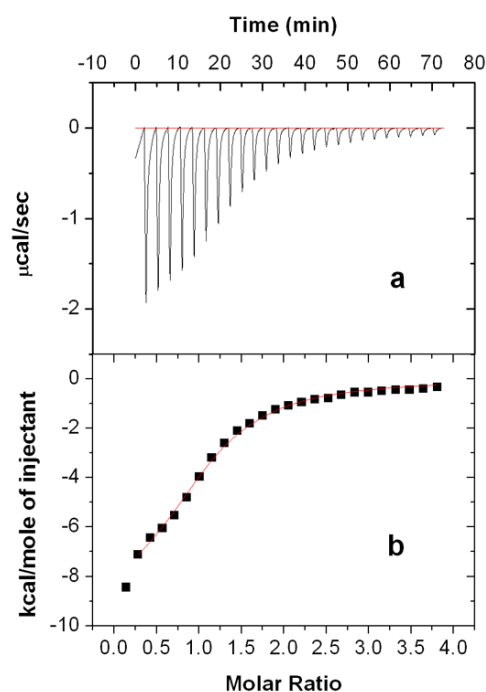
simulation using the "one set of binding sites" model.

Figure S15. Microcalorimetric titration of *bis*CD with Ad-Vio⊂*bis*SC4A in aqueous

solution at 298.15 K. (a) Raw ITC data for sequential 25 injections (10 μL per

injection) of *bis*CD solution (1.00 mM) injecting into 0.1 mM Ad-Vio with 1.0 equiv.

*bis*SC4A solution. (b) Apparent reaction heat obtained from the integration of
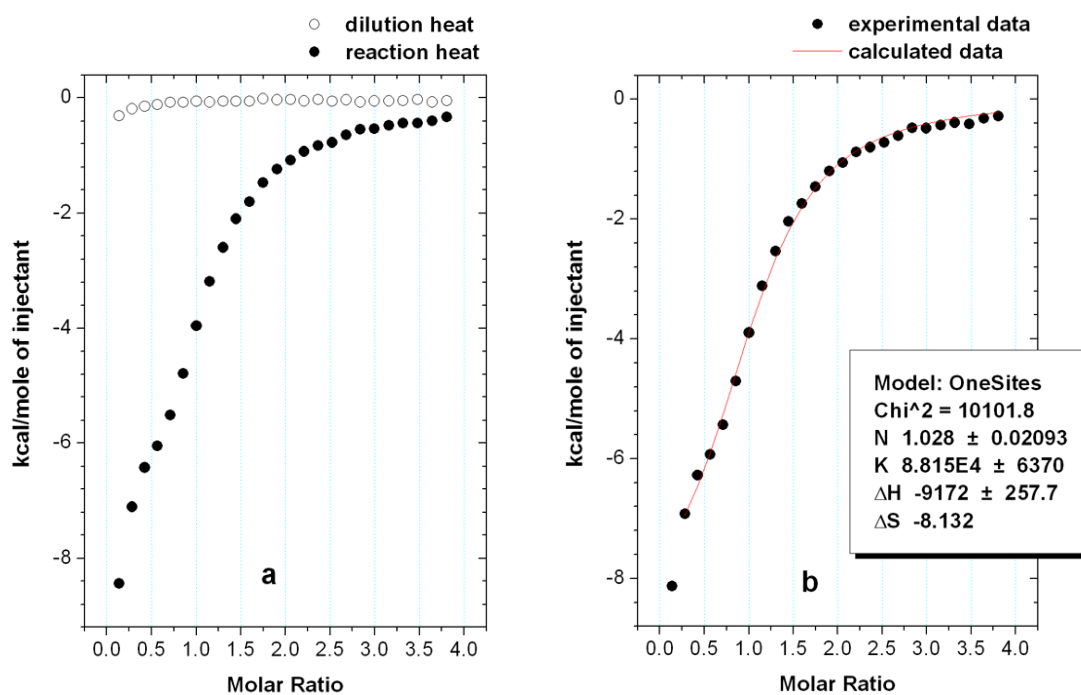
calorimetric traces.

Figure S16. (a) Heat effects of the dilution and of the complexation reaction of *bis*CD with Ad-Vio⊂*bis*SC4A for each injection during titration microcalorimetric experiment. (b) "Net" heat effects of complexation of *bis*CD with Ad-Vio⊂*bis*SC4A 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.
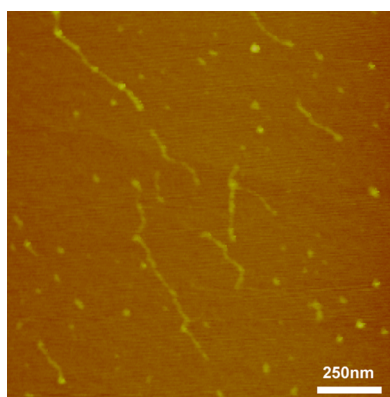

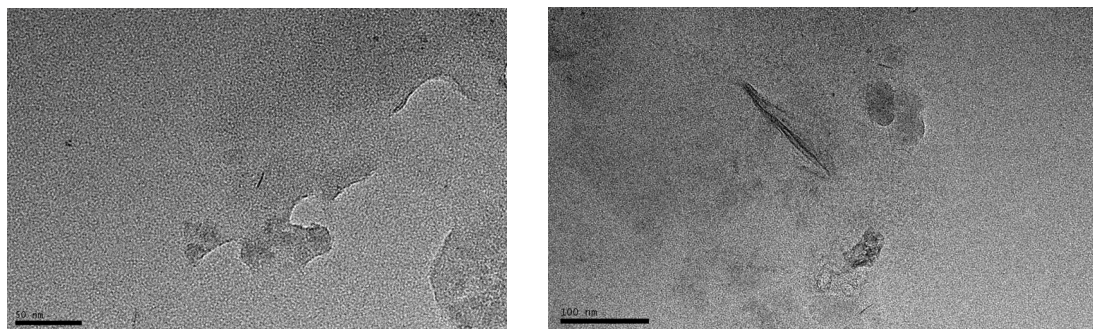**Figure S17.** AFM image of the linear supramolecular ternary polymer *bis*CD⊃Ad-Vio⊂*bis*SC4A.

Figure S18. TEM images of the linear supramolecular ternary polymer

*bis*CD⊃Ad-Vio⊂*bis*SC4A (scale bar = 50 nm or 100nm).

[1] D.-S. Guo, S. Chen, H. Qian, H. Q. Zhang, Y. Liu, *Chem. Commun*. **2010**, *46*, 2620−2622.

[2] K. Ohga, Y. Takashima, H. Takahashi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *Macromolecules*. **2005**, *38*, 5897−5904.

[3] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875–1917.

[4] D.-S. Guo, L.-H. Wang, Y. Liu, *J. Org. Chem.* **2007**, *72*, 7775–7778.