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Supramolecular ternary polymer mediated by cucurbituril and cyclodextrin†

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A novel supramolecular ternary polymer mediated by macrocyclic molecules cucurbit[8]uril (CB[8]) and cyclodextrin was successfully constructed, based on the CB[8]-stabilized charge-transfer (CT) interaction and cyclodextrin–adamantane host–guest interaction. Herein, we synthesized a naphthol-modified β-cyclodextrin (Np-β-CD) and an adamantane–viologen ditopic guest to obtain a ditopic host–guest complex with a preorientational donor–acceptor pair. Furthermore, after addition of CB[8] to the complex, the donor–acceptor pair of naphthol–viologen was encapsulated into the cavity of CB[8] leading to a linear supramolecular polymer which was well characterized by various methods, including DOSY, DLS, SEM, TEM and AFM. This work enriches the field of supramolecular polymers and provides a novel method to fabricate supramolecular architectures with multiple macrocyclic host molecules.

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Introduction

Supramolecular polymers, a class of supramolecular architectures in which monomeric units are assembled *via* directional and reversible non-covalent interactions, have attracted more and more attention due to their fascinating chemical and physical properties that are different from those of original covalent polymers.[1] In the early construction of supramolecular polymers, the driving forces are usually multiple-hydrogen bonds or hydrogen bonds supported by additional forces,[2] strong π–π (or arene–arene) interactions of discotic molecules,[3] as well as metal coordination.[4] Recently, various host–guest interactions based on macrocyclic compounds such as crown ethers, calixarenes, cyclodextrins, cucurbiturils and pillararenes have been used in the construction of a number of supramolecular polymers.[5]

Cyclodextrins (CDs), a class of cyclic oligosaccharides that have molecular-compatible cavities, are the most widely used macrocyclic compounds in supramolecular chemistry and have been widely used as building blocks to construct various advanced supramolecular polymers. Generally, owing to the satisfactory water solubility, environmental friendliness and low toxicity of CDs, the CD-based supramolecular polymers exhibit good water-solubility, stability, biocompatibility, biodegrability, as well as photoelectronic properties leading to potential applications in drug carriers, tissue scaffolds, light-harvesting and so on.[6] Moreover, cucurbituril-based supramolecular polymers also attract a significant amount of interest of chemists[7] due to the considerable binding abilities of cucurbiturils towards many cationic guests which make them widely used in the fabrication of various supramolecular species.[8] Along with a large enough cavity, CB[8] is a useful molecular connector. As early as 2001, Kim *et al.* firstly reported that CB[8] could form a highly stable 1 : 1 : 1 ternary complex with the electron-deficient 4,4-bipyridinium derivatives and electron-rich aromatics, which is driven and stabilized by a CT interaction between the electron-rich and electron-deficient guests.[9] Since then, such selected inclusion of an electron-deficient/rich guest pair in the CB[8] cavity provides a powerful and effective platform for supramolecular polymers.[10] Scherman and co-workers have utilized this host-stabilized CT interaction to realize the polymer–polymer,[11] protein–polymer,[12] monosaccharide–polymer,[13] and gold nanoparticle–polymer[14] conjugations, further construction of the vesicles,[15] hydrogels,[16] and microcapsules.[17] Recently, Zhang and co-workers constructed a supramolecular polymer from a small-molecule monomer and CB[8] based on multiple host-stabilized CT interactions.[18] However, a supramolecular polymer based on the combination of the CB[8]-stabilized CT interaction with other host–guest interactions has not been reported.

In our previous work, we reported a novel heterowheel [3]-pseudorotaxane by integrating two binary inclusion complexes of β-CD with hydroxynaphthalene and CB[8] with a viologen derivative in which the driving forces come from simultaneous molecular recognition of adamantane by β-CD and the CT interaction of hydroxynaphthalene with viologen in the CB[8] cavity.[8b] Based on that work, we employed a naphthol-modified β-CD (Np-β-CD) and an adamantane–viologen ditopic guest **1** to obtain a ditopic host–guest complex **2** with a preorientational donor–acceptor pair, which inhibits the oligomeric

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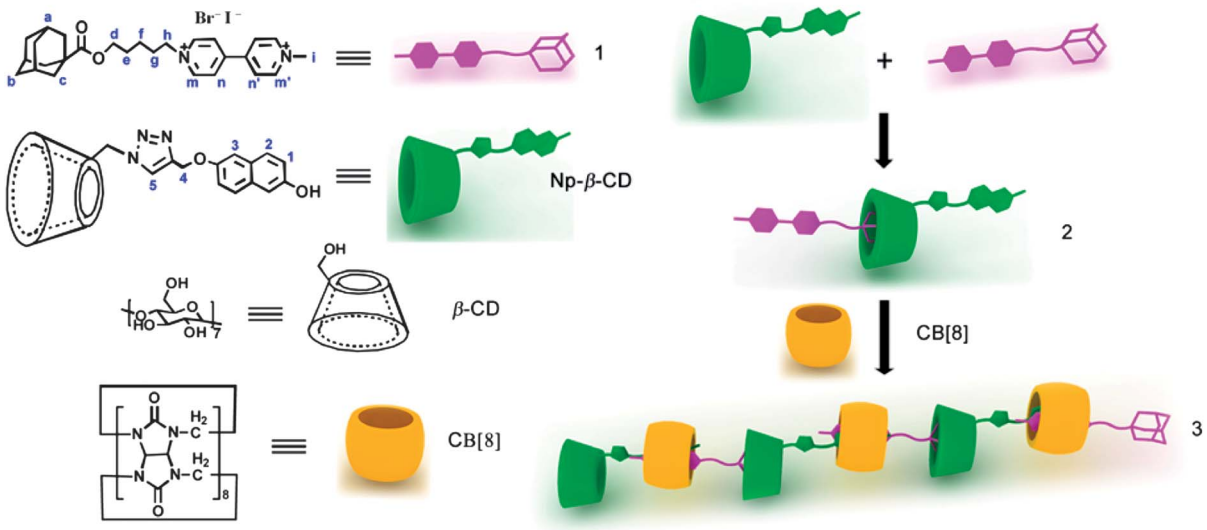


Scheme 1 Structural illustration of Np-β-CD, CB[8], **1** and formation of supramolecular ternary polymer **3**.

cyclic complex in further supramolecular polymerization by addition of CB[8] (Scheme 1). Besides the ordered array of building blocks, relatively high molecular weight, complexity of the resulting architecture, and the ease of self-assembly process through non-covalent interactions, this kind of supramolecular ternary polymer possesses several additional inherent advantages. Firstly, the supramolecular ternary polymer combines several kinds of macrocyclic host molecules having satisfactory binding abilities towards various neutral and/or ionic substrates. Secondly, the introduction of strong charge transfer interaction, along with the high affinity of the cyclodextrin–adamantane pair, jointly leads to a high degree of polymerization.

Results and discussion

The formation of the Np-β-CD/**1**/CB[8] ternary complex can be conveniently monitored by ^{1}H NMR in D_2O. As can be seen from Fig. 1c, upon the addition of Np-β-CD, signals of adamantyl protons (H_a–H_c) of **1** gave an appreciable downfield shift, accompanied by broadening of signal peaks. In addition, signals of H_1–H_5 protons of Np-β-CD split into 8 pieces. This information, along with the clear NOE cross-peaks between adamantyl protons of **1** and interior protons of β-CD in the ROESY spectrum (Fig. S7†), jointly indicated that **1** is bound to Np-β-CD with its adamantane moiety included in the cavity of β-CD. After the addition of CB[8] (Fig. 1d), signals of $H_{m,m'}$ and

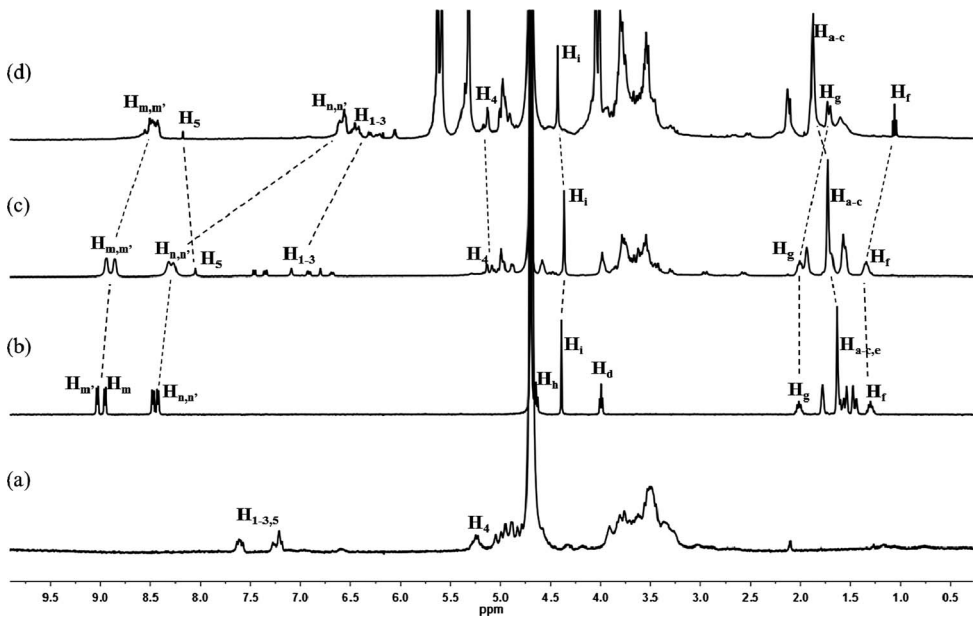


Fig. 1 ^{1}H NMR spectra (400 MHz, D_2O, 298.15 K) of (a) Np-β-CD, (b) compound **1**, (c) Np-β-CD + equimolar **1**, and (d) Np-β-CD·**1** + 1.6 equiv. of CB[8].

$H_{n,n'}$ protons of the viologen part of **1** exhibited remarkable upfield shifts of 0.45 ppm and 1.7 ppm respectively, which convincingly demonstrated the accommodation of the viologen part of **1** into the cavity of CB[8]. Moreover, signals of H_f and H_g protons in **1** showed apparent upfield shifts of 0.27 ppm and 0.31 ppm respectively, indicating that the alkyl chain between the adamantane moiety and the viologen moiety of **1** was partially included into the cavity of CB[8]. In addition, signals of H_{1-3} protons of the naphthol group in Np-β-CD underwent pronounced upfield shifts while H_4 and H_5 protons showed downfield shifts, owing to the inclusion of the naphthol group into the CB[8] cavity. The signals of H_a–H_c protons of **1** showed a more downfield shift. All of these phenomena demonstrated that CB[8] accommodated the viologen moiety of **1** and the naphthol substituent of Np-β-CD, while the adamantane moiety of **1** was encapsulated into the cavity of Np-β-CD.

As can be seen from the ROESY spectrum (Fig. S8†), with the addition of CB[8] to the Np-β-CD/**1** system, CB[8] protons showed strong NOE cross-peaks with $H_{m,m'}$ and $H_{n,n'}$ protons of the viologen subunit in **1** as well as H_{1-3} protons of the naphthol group of Np-β-CD (peaks B and C), providing strong evidence for the encapsulation of viologen and naphthol. Also, we can easily find the NOE cross-peaks between $H_{m,m'}$ protons of the viologen and H_{1-3} protons of the naphthol group (peak D). Moreover, NOE correlations between the adamantyl protons and interior protons of the β-CD cavity were also observed (peak F), indicating the capture of the adamantane moiety in **1** by Np-β-CD. However, for the Np-β-CD/**1** system without CB[8], no NOE cross-peaks between H_{1-3} protons of the naphthol group and $H_{m,m'}$ protons of the viologen moiety could be observed (Fig. S7†) which further confirmed the co-inclusion of viologen and naphthol into the CB[8] cavity. The formation of the ternary complex Np-β-CD/**1**/CB[8] is also evidenced by high resolution ESI-MS (Fig. S9†). In addition, isothermal titration calorimetry (ITC) experiments were performed to quantitatively determine the association constant (K_S) of Np-β-CD with **1** as 3.2×10^5 M^{-1} (Fig. 6 and 7) which makes sure the formation of the supramolecular ternary polymer **3** along with the very strong binding of CB[8] to viologen and naphthol.[8b,10]

Additionally, we executed a comparable analysis of the absorption spectra of **1**, Np-β-CD, CB[8], **1**/Np-β-CD, **1**/CB[8], and Np-β-CD/**1**/CB[8] (Fig. 2), where an unremarkable shoulder peak around 470 nm in the spectrum of **1**/Np-β-CD indicated a slight CT interaction between the electron-rich naphthol group of Np-β-CD and the electron-deficient viologen moiety of **1** (Fig. 2e).[8b] Significantly, when 1.0 equiv. of CB[8] was added, a distinctly different photophysical behavior was observed (Fig. 2f). A strong CT absorption band emerges at about 580 nm which is greatly red-shifted ($\Delta\lambda = 110$ nm) and with a concomitant high increase in the intensity relative to that of a 1 : 1 mixture of Np-β-CD and **1**.[8b,19] The highly enhanced CT interaction between viologen and naphthol arises from their close contact within the cavity of CB[8] which is coincident with the results confirmed from ^{1}H NMR and ROESY spectra.

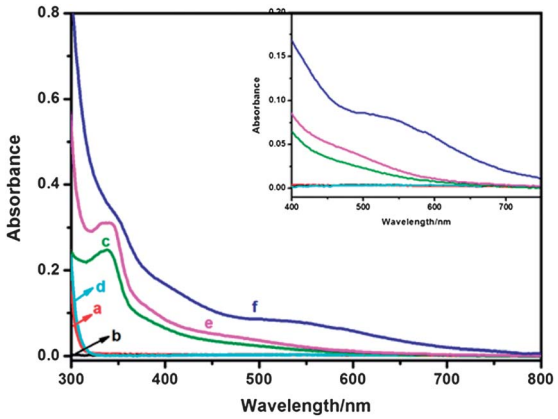


Fig. 2 Absorption spectra of (a) **1** (0.10 mM), (b) CB[8] (0.10 mM), (c) Np-β-CD (0.10 mM), (d) CB[8]/**1** (0.10 mM), (e) Np-β-CD/**1** (0.10 mM), and (f) Np-β-CD/**1**/CB[8] (0.10 mM) in H_2O, at 298 K.

Diffusion ordered ^{1}H NMR spectroscopy (DOSY) is a useful technique to investigate the size of aggregates in solution.[20] As can be seen in Fig. S11,† the equimolar mixture solution of Np-β-CD, **1** and CB[8] in D_2O gave a diffusion constant of 1.36×10^{-10} m^2 s^{-1}, while **1**/Np-β-CD and **1**/CB[8] in D_2O presented much larger diffusion constants of 2.51×10^{-10} m^2 s^{-1} and 3.35×10^{-10} m^2 s^{-1}, respectively. These results clearly indicated the formation of a large supramolecular architecture among Np-β-CD, **1** and CB[8].

Furthermore, we used dynamic light scattering (DLS) and electronic microscopy to confirm the formation of the supramolecular polymer in water. As can be seen in Fig. 3, one relatively wide peak was observed from 700 to 1000 nm at 0.5 mM with an average hydrodynamic diameter of 776 nm,[21] indicating the formation of large supramolecular assemblies. The other was centered at 93 nm, which is ascribed to the existence of oligomeric chains with a low degree of polymerization. Additionally, Fig. S17† shows that the hydrodynamic diameter of the supramolecular polymer increased from 149 to 776 nm when the concentration increased from 0.02 to 0.5 mM, indicating that the formation of the supramolecular polymer was

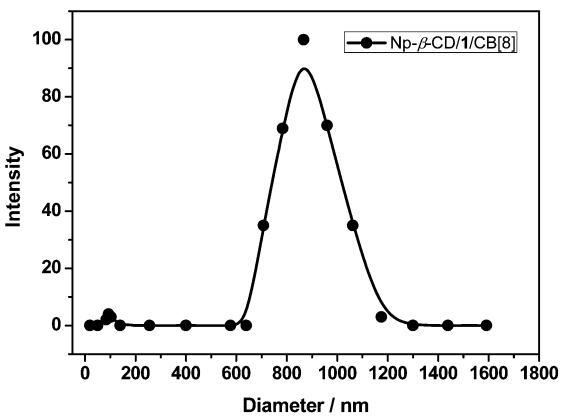


Fig. 3 Hydrodynamic diameter distribution of supramolecular ternary polymer **3**: 0.5 mM Np-β-CD/**1**/CB[8] aqueous solution.

intrinsically concentration-dependent; the higher the concentration, the larger the polymer size. GPC measurement gives the molecular weight of the supramolecular ternary polymer at 0.5 mM, where M_w and M_n (Da) values were obtained (28.3×10^4 and 23.2×10^4 respectively, Fig. S18†), indicating high polymerization degree of the supramolecular polymer. Due to the concentration-dependency of the supramolecular polymer, the number of repeating units obtained from GPC should be smaller than those obtained from DLS, because the GPC analysis involving high dilution and eluent flushing may inevitably result in the decrease of polymerization degree to some extent. Meanwhile, scanning electron microscopy (SEM) gave a rough insight into the morphology of the supramolecular polymer, showing a number of linear structures that were located close to each other to form a fiber-like array, which are likely formed during the process of sample preparation for microscopy observations (Fig. 4b). Atomic force microscopy (AFM) images displayed a fine structure of the supramolecular polymer as curving linear structures (Fig. 4a and S21†), and the average height of linear structures (*ca.* 1.7 nm) was basically consistent with the outer diameter of CB[8] (1.8 nm) and β-CD (1.6 nm).[6c] In addition, transmission electron microscopy (TEM) images (Fig. 4c and S23†) also showed a morphology of linear arrays with different lengths, among which the longer ones are approximately 150 nm while the shorter ones are dozens of nanometers, indicating that the polymers may have strong tendency to aggregate to each other.

One of the advantages of supramolecular assembly is the controlled disassembly resulting from the non-covalent nature of supramolecular interactions. For instance, the CB[8]-stabilized CT complex could be dissociated upon the addition of a competitive guest such as 1-adamantaneamine (ADA).[8a,15] In the present case, the addition of excess ADA to the Np-β-CD/**1**/CB[8] system led to the disassembly of the supramolecular polymer, which was evidenced by ^{1}H NMR experiments (Fig. 5). Comparing with Fig. 5b where the viologen moiety in **1** and the naphthol substituent of Np-β-CD are accommodated together in the cavity of CB[8], the chemical shifts of proton signals of the viologen moiety and naphthol group in Fig. 5c are all back to the original state as those in Fig. 5a, attributing to the replacement of viologen and naphthol by excess ADA.

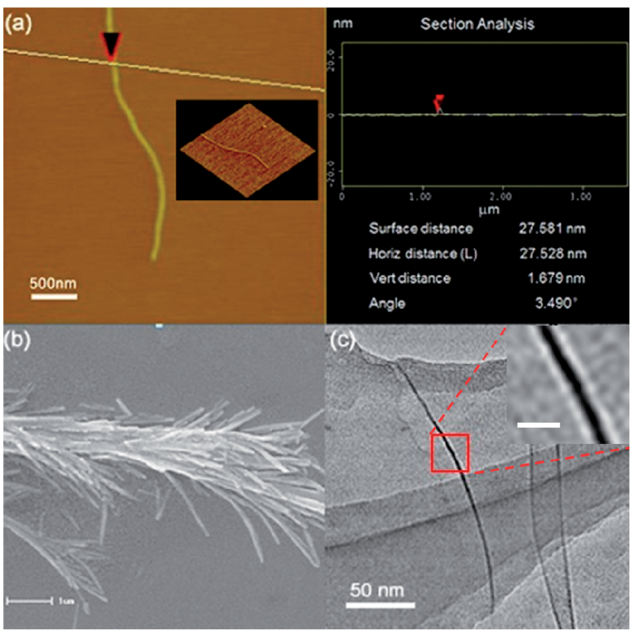


Fig. 4 (a) AFM ([Np-β-CD] = [**1**] = [CB[8]] = 1×10^{-6} M^{-1}), (b) SEM ([Np-β-CD] = [**1**] = [CB[8]] = 5×10^{-6} M^{-1}) and (c) TEM ([Np-β-CD] = [**1**] = [CB[8]] = 5×10^{-6} M^{-1}; the scale bar of the inset figure is 8 nm) images of the ternary polymer **3**.

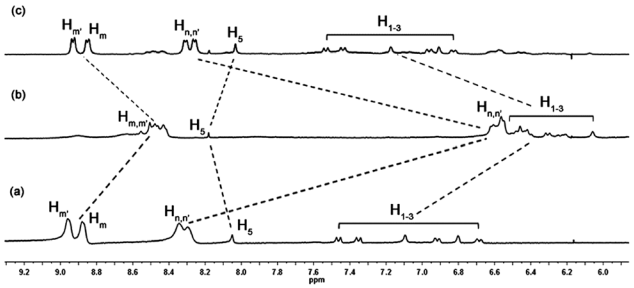


Fig. 5 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of (a) Np-β-CD (1.0 mM) + **1** (1.0 mM), (b) Np-β-CD·**1** (1.0 mM) + 1.6 equiv. of CB[8], and (c) Np-β-CD·**1** (1.0 mM) + CB[8] (1.6 mM) + excess ADA.

Conclusions

In this contribution, a novel supramolecular ternary polymer has been successfully constructed employing two orthogonal host–guest interactions. The collaborative contributions of hydrophobic interactions of adamantane with β-CD, viologen and naphthol with CB[8], and the CT interaction of viologen with naphthol are the main driving forces for the formation of this supramolecular polymer. In addition, benefiting from the non-covalent nature of supramolecular interactions, we can control the assembly/disassembly of the supramolecular polymer by adding a competitive guest to the system which can expel both the viologen moiety and naphthol group from the cavity of CB[8]. Compared with previously reported supramolecular polymers, this supramolecular ternary polymer provides the mutual advantages of ordered array of building blocks, relatively high molecular weight and complexity of the resulting architecture, as well as the ease of self-assembly process through non-covalent interactions. Furthermore, there are some additional inherent advantages of the present supramolecular ternary polymer, that is, the supramolecular ternary polymer not only combines different kinds of macrocyclic host molecules,[21] but also introduces the strong CT interaction which inevitably leads to a high degree of polymerization.[18] Therefore, this work enriches the field of supramolecular polymers and provides a novel method to fabricate supramolecular architectures with multiple macrocyclic host molecules.

Experimental

Materials and general methods

The synthesis route to compound **1** is shown in Scheme 2. Np-β-CD was synthesized according to ref. 22. 1-Adamantanecarboxylic

acid chloride and 5-bromo-1-pentanol were purchased from Aladdin, and CB[8] was purchased from Sigma-Aldrich, and all of them were used without further purification. Tetrahydrofuran (THF) was dried over metallic sodium. Acetonitrile was dried over CaH_2. All other chemicals were commercially available and were of reagent grade and they were used without further purification. ^{1}H NMR spectra were recorded at 298.15 K on a Bruker AV400 spectrometer operating at 400 MHz in $CDCl_3$ and D_2O. 2D ROESY experiments were performed at 298.15 K on a Varian Mercury VX300 spectrometer operating at 300 MHz in D_2O.

Preparation of compound 4

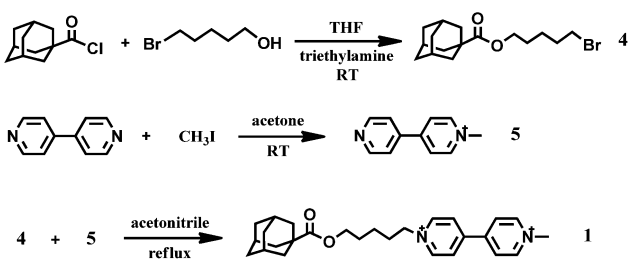
To a mixture solution of 1-adamantanecarboxylic acid chloride (662 mg, 5 mmol) and triethylamine (0.44 mL, 5 mmol) in THF (25 mL) was dropwise added a solution of 5-bromo-1-pentanol (835 mg, 5 mmol) in THF (30 mL) with stirring under a N_2 atmosphere in an ice-bath. The mixture was kept at room temperature for 24 h. Then the mixture was dried under reduced pressure and further purified by flash column chromatography using CH_2Cl_2-PE (1 : 1, v : v) as the eluent to give the product as transparent grease in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.09 (t, J = 6.4 Hz, 2H), 3.45 (t, J = 6.7 Hz, 2H), 2.05 (s, 3H), 1.98–1.50 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 176.6, 62.7, 39.7, 37.8, 37.6, 35.6, 35.4, 32.5, 31.3, 27.0, 26.8, 23.6. ESI-MS (m/z): 362.9 for $[M + Cl]^-$.

Preparation of compound 1

A mixture solution of compound **4** (450 mg, 1.4 mmol) was dissolved with acetonitrile (20 mL) and then compound **5** was added[23] (420 mg, 1.4 mmol). The mixture was refluxed with stirring for 36 h and then filtered to get yellow powder in 75% yield. ^{1}H NMR (400 MHz, D_2O, ppm): δ 9.03 (d, J = 6.6 Hz, 2H), 8.95 (d, J = 6.6 Hz, 2H), 8.45 (dd, J = 18.8, 6.5 Hz, 4H), 4.64 (t, J = 7.1 Hz, 2H), 4.39 (s, 3H), 3.99 (t, J = 6.0 Hz, 2H), 2.07–1.95 (m, 2H), 1.78 (s, 3H), 1.68–1.40 (m, 14H), 1.36–1.23 (m, 2H). ^{13}C NMR (100 MHz, D_2O, ppm): δ 181.0, 149.9, 149.5, 146.4, 145.6, 127.0, 126.6, 64.3, 62.1, 48.4, 40.8, 38.3, 35.7, 30.0, 27.5, 27.2, 21.7. ESI-MS (m/z): 210.3 for $[M]^{2+}/2$.

UV/Vis measurements

UV/Vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C.



Scheme 2 Synthesis route to compound **1**.

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. As the tri-component system, the DLS sample was prepared as follows: the aqueous solutions of Np-β-CD and CB[8]/**1** were prepared respectively, and these two solutions were respectively filtered through 450 nm filters and then mixed together. The samples were examined on a laser-light-scattering spectrometer (BI-200SM) which was equipped with a digital correlator (BI-9000AT) at 634 nm at 25 °C. All DLS measurements were performed at the scattering angle of 90°.

TEM measurements

5.0×10^{-6} M (calculated from the repeating units) sample solutions were dropped onto a copper grid. The grid was then air-dried and then examined using a high-resolution TEM (Tecnai G^2 F20 high-resolution TEM) operating at an accelerating voltage of 200 kV.

SEM measurements

SEM images were recorded on a Hitachi S-3500N SEM. The sample for SEM measurements was prepared by dropping the solution of 5.0×10^{-6} M onto a coverslip, followed by evaporating the liquid in air.

AFM measurements

A sample solution of 1.0×10^{-6} M (calculated from the repeating units) was dropped onto a newly clipped mica foundation and then air-dried. The sample was performed using a multi-mode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature.

GPC measurements

The measurement of weight-average and number-average molecular weights (M_w and M_n) was performed on a size exclusion chromatograph connected with Module 302 TDA Detectors. A column of model $GMPW_{XL}$ (TSK-GEL) was used. Poly(ethylene oxide) was used as the calibration standard and water was used as the mobile phase at a flow rate of 1.0 mL min^{-1} and an operating temperature of 30 °C.

ITC measurements

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 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.[24] All microcalorimetric titrations were performed in aqueous solution at atmospheric pressure and 298.15 K. Each solution was degassed and thermostatted using a ThermoVac accessory

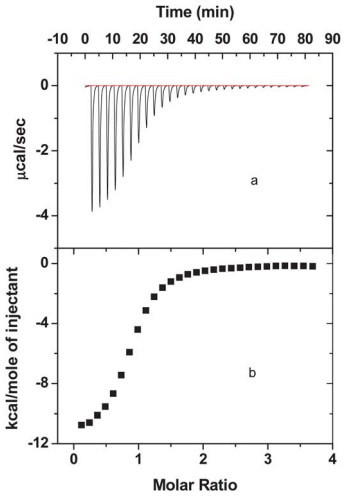


Fig. 6 Microcalorimetric titration of Np-β-CD with **1** in aqueous solution at 298.15 K. (a) Raw ITC data for sequential 28 injections (10 μL per injection) of compound **1** solution (1.89 mM) injecting into a Np-β-CD solution (0.07 mM). (b) Apparent reaction heat obtained from the integration of calorimetric traces.

before the titration experiment. Twenty-eight successive injections were made for each titration experiment. A constant volume (10 μL per injection) of guest solution in a 0.250 mL syringe was injected into the reaction cell (1.4227 mL) charged with a host molecule solution in the same aqueous solution. A representative titration curve is shown in Fig. 6. As can be seen from Fig. 6, each titration of guest molecule **1** into the sample cell gave an apparent reaction heat caused by the formation of an inclusion complex between Np-β-CD and **1**.

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 molecule. 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 the "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 (ΔH°) 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 (ΔH°) enabled calculation of the standard free energy (ΔG°) and entropy changes (ΔS°) according to

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

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

A typical curve fitting result for the complexation of **1** with Np-β-CD is shown in Fig. 7. To check the accuracy of the observed thermodynamic parameters, two independent titration experiments were carried out to afford self-consistent thermodynamic parameters.

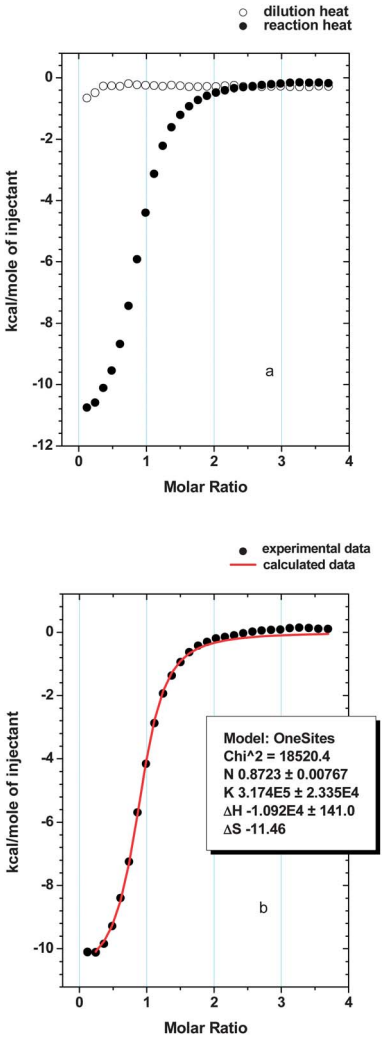


Fig. 7 (a) Heat effects of the dilution and of the complexation reaction of **1** with Np-β-CD for each injection during the titration microcalorimetric experiment. (b) "Net" heat effects of complexation of **1** with Np-β-CD for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model.

Acknowledgements

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