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Synthesis of A Bis-Macrotricyclic Host and Its Complexation with Secondary Ammonium Salts: An Acid–Base Switchable Molecular Handcuff

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A novel triptycene-derived bis-macrotricyclic host was designed and synthesized. The host was shown to form a 1:4 stable complex with 4 equiv. of dibenzylammonium salt in solution and in the solid state. Moreover, it was found that the host with multicavities could also self-assemble with 2 equiv. of bis-secondary ammonium salt to form a handcuff-like structure under the tested condition ($[\mathbf{1}]_0$ = 3.0 mM). The complexation and decomplexation of the assembly could be further chemically controlled by the stimuli of acid and base.

Introduction

Macrocyclic hosts have undoubtedly played key roles in host–guest chemistry, and they have been also one of the key sources for the development of new supramolecular systems with specific structures and properties.[1] Since Pedersen first reported the synthesis and cation-complexing characteristics of the crown ethers in 1967,[2] various macrocyclic hosts have been hitherto developed. Especially, macrocyclic hosts with multiple cavities and multiple recognition sites have attracted increasing interest because they are not only fundamental in understanding the molecular recognition and self-assembly processes pertinent to the origin of life and evolution, but also helpful for developing specific supramolecular systems and designing new classes of materials and devices for future technologies.[3] Recent successful examples in this regard included the wide applications of the hosts in the construction of molecular machines,[4] higher order interlocked structures,[5] and other specific supramolecular assemblies.[6,7] However, such macrocyclic hosts are limited, and the design and synthesis of new classes of the hosts with multicavities are still thrilling and challenging topics in host–guest chemistry.

In 1995, Stoddart and co-workers first reported that dibenzo-24-crown-8 (DB24C8) could be threaded by a secondary ammonium ion to form a [2]pseudorotaxane,[8] which resulted in the synthesis of various interlocked molecules.[9] Recently, we[10] synthesized novel triptycene-based macrotricyclic host **2** containing one central cylindrical cavity and two lateral circular cavities and demonstrated that the host could exhibit interesting guest-dependent complexation with different guests. Especially, it was found[10c] that host **2** could form a 1:2 complex with 2 equiv. of secondary ammonium salts, which could subsequently provide some opportunities for developing specific supramolecular assemblies. Herein, we report the synthesis of novel triptycene-derived bis-macrotricyclic host **1** (Figure 1), complexation between **1** and dibenzylammonium salts in solution and in the solid state, formation of a handcuff-like molecular assembly, and switchable process of the molecular handcuff by the stimuli of acid and base.

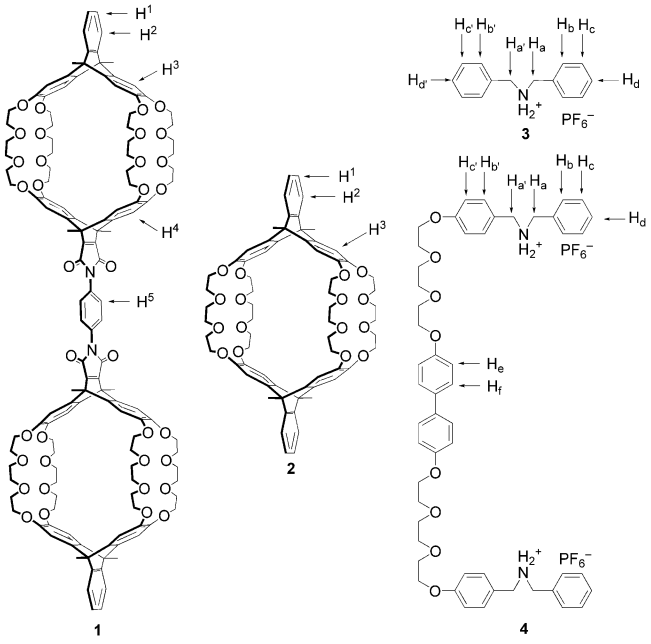

Figure 1. Structures and proton designations of hosts **1** and **2** and guests **3** and **4**.

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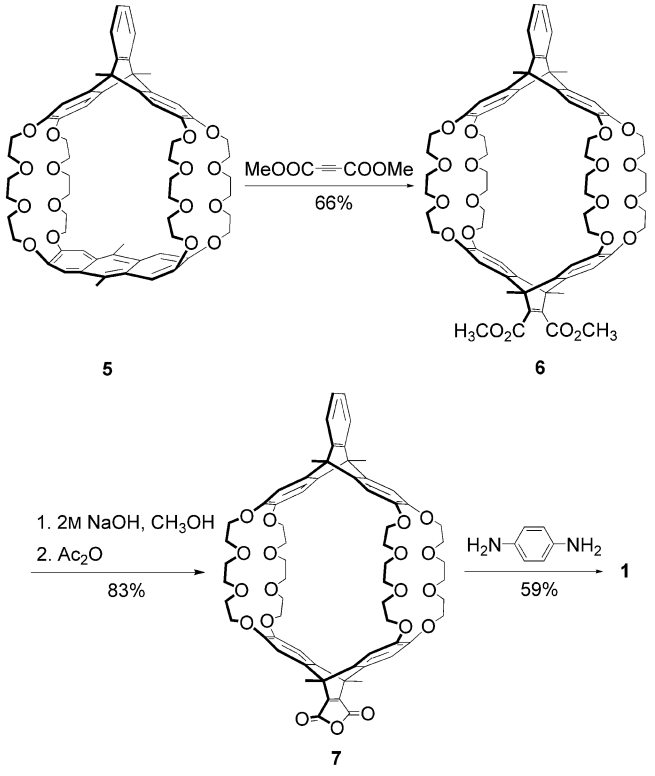
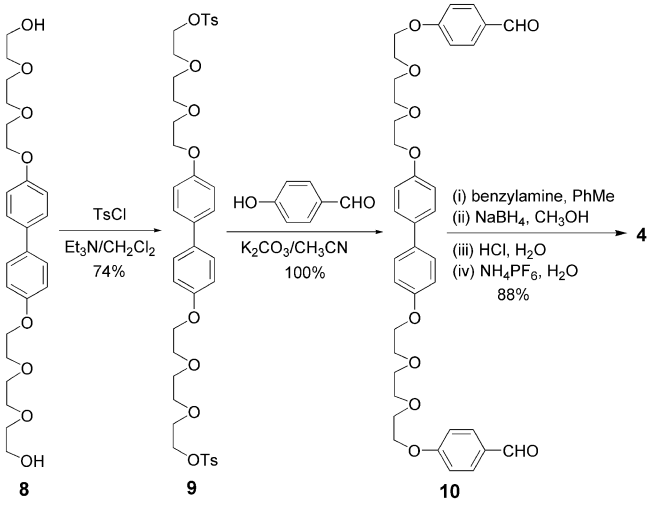
Results and Discussion

Synthesis of Triptycene-Derived Bis-Macrotricyclic Host 1 and Bis-Dibenzylammonium Salt 4

Synthesis of host **1** is depicted in Scheme 1. Cylindrical macrotricyclic diester **6** was obtained in 66% yield by the reaction of macrocyclic compound **5**[11] and dimethyl acetylenedicarboxylate. Hydrolysis of **6** in sodium hydroxide solution followed by dehydrolysis in acetic anhydride gave **7** in 83% yield over two steps. Anhydride **7** was further treated with *p*-phenylenediamine to afford **1** in 59% yield.



Scheme 1. Synthesis of host **1**.



Scheme 2. Synthesis of guest **4**.

Synthesis of guest **4** is outlined in Scheme 2. Ditosylation of diol **8**[12] and then reaction with 4-hydroxybenzaldehyde gave **10**. Condensation of **10** with benzylamine, reduction with $NaBH_4$, protonation of the resulting amine, and counterion exchange with NH_4PF_6 formed target guest **4** in 88% yield over the four steps.[13] All new compounds were confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Complexation between 1 and Dibenzylammonium Salt 3 in Solution and in the Solid State

First, we investigated the complexation between host **1** and dibenzylammonium salt **3** in solution. As shown in Figure 2, the ^1H NMR spectrum of a 1:4 mixture of **1** and **3**, recorded in $CDCl_3/CD_3CN$ (5:1) showed a dispersed array of well-defined resonances and a major difference from those of host **1** and guest **3**. The resonances of the complex were assigned by its ^1H–^1H COSY 2D NMR spectrum.[13] The benzyl proton signals of **3** located outside the cavities of **1** were shifted downfield, whereas those of the benzyl protons inside the cavities were shifted upfield. In particular, striking upfield shifts ($\Delta\delta$ = –1.35 to –1.91 ppm) for the inner phenyl proton (H_b~H_d) signals were observed, and this may be attributed to the strong shielding effect of the macrocycle. The signal of the outer benzylic methylene proton $H_{a'}$ adjacent to the NH_2^+ center exhibited a large downfield shift ($\Delta\delta$ = 0.55 ppm), which was attributed to the hydrogen-bonding interactions and the deshielding effect of the aromatic rings in **1**. Moreover, upfield shifts for aromatic protons H^3 ($\Delta\delta$ = –0.18 ppm) and H^4 ($\Delta\delta$ = –0.16 ppm) of **1** and significant changes in the chemical shifts of the protons in the crown ether units were also observed. These observations suggested that **1** and **3** combined to form the 1:4 complex **1**·$\mathbf{3}_4$.

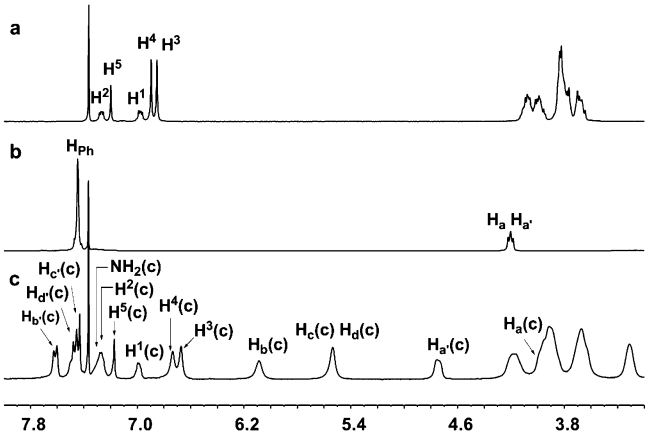


Figure 2. Partial ^1H NMR spectra (300 MHz; $CDCl_3/CD_3CN$, 5:1) of (a) free host **1**, (b) free guest **3**, and (c) **1** and 4.0 equiv. of **3**. $[\mathbf{1}]_0$ = 3.0 mM.

As shown in Figure 3, when guest **3** was gradually added into the solution of host **1**, it was found that the ^1H NMR spectra showed two sets of signals for the protons H^3 (5.64 and 5.41 ppm) and H^4 (5.67 and 5.47 ppm) of host **1**, indi-

cating a slow exchange complexation between host **1** and guest **3**. The electrospray ionization mass spectrum (ESI-MS) provided more evidence for the formation of complex **1**·$\mathbf{3}_4$. Consequently, peaks at *m*/*z* = 1116.4, 1001.9, and 801.3 for $[\mathbf{1}\cdot\mathbf{3}_4\text{-}3PF_6^-]^{3+}$, $[\mathbf{1}\cdot\mathbf{3}_3\text{-}3PF_6^-]^{3+}$, and $[\mathbf{1}\cdot\mathbf{3}_4\text{-}4PF_6^-]^{4+}$, respectively, were observed.[13]

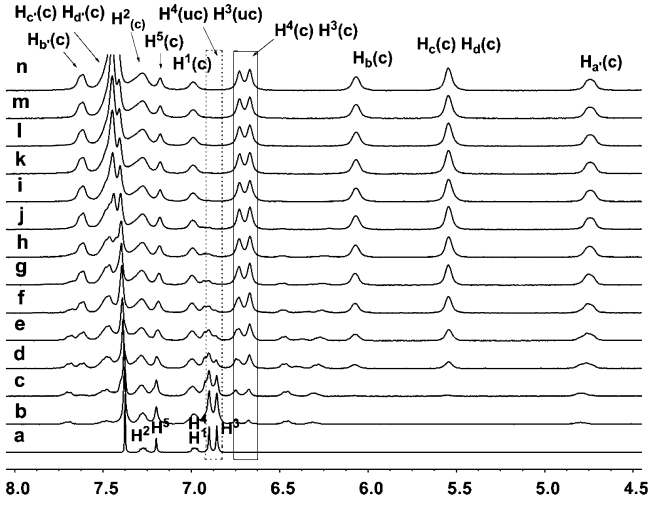


Figure 3. Partial ^{1}H NMR spectra (300 MHz; $CDCl_3/CD_3CN$, 5:1) of host **1** upon the addition of **3**: (a) 0, (b) 0.6, (c) 1.2, (d) 1.8, (e) 2.4, (f) 3.0, (g) 3.6, (h) 4.0, (i) 4.2, (j) 4.8, (k) 5.4, (l) 6.0, (m) 6.6, and (n) 7.2 equiv. $[\mathbf{1}]_0$ = 3.0 mM.

Further support for the formation of complex **1**·$\mathbf{3}_4$ came from its X-ray crystal structure.[14] As shown in Figure 4, host **1** contains two symmetrical macrotricyclic moieties,

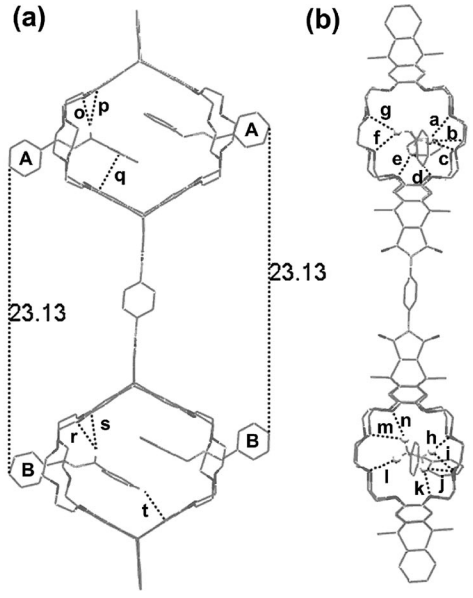


Figure 4. Top view (a) and side view (b) of the crystal structure of complex **1**·$\mathbf{3}_4$. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the interactions are omitted for clarity. Hydrogen bond lengths [Å]: a = 2.55, c = 2.44, d = 2.44, e = 2.23, h = 2.00, i = 2.52, j = 2.52, k = 2.09 for N–H···O; b = 2.89 for N–H···C; f = 2.33, g = 2.52, l = 2.33, m = 2.63, n = 2.47, o = 2.15, r = 2.63 for C–H···O; p = 2.86, s = 2.81, t = 2.73 for C–H···π; q = 3.29 for π···π stacking interaction.

and two dibenzylammonium ions are threaded through the center of the DB24C8 cavities of each macrotricycles in host **1**, which results in 1:4 complex **1**·$\mathbf{3}_4$. Interestingly, it was found that two central cavities formed in host **1** are along the same axis, whereas the dihedral angle/centroid–centroid distance between the aromatic rings A and B of the guest situated outside of the cavities are all 9.68°/23.13 Å. There are multiple hydrogen-bonding interactions between the polyether oxygen atoms and the NH_2^+ hydrogen atoms and the benzylic methylene hydrogen atoms located both inside and outside the cavities. Also, C–H···π interactions are evident between host **1** and the guests with distances of 2.86 (p), 2.81 (s), and 2.73 Å (t), respectively. Moreover, an offset face–face π···π stacking interaction between the inner phenyl ring of the guest and one of the aromatic rings of the host with the dihedral angle/centroid–centroid distance of 3.53°/3.29 Å (q) was also observed. These multiple non-covalent interactions might play an important role in the formation of stable complex **1**·$\mathbf{3}_4$, which is also consistent with the result observed in solution.

Formation of a Handcuff-Like Molecular Assembly

The formation of complex **1**·$\mathbf{3}_4$ encouraged us to further design and construct a handcuff-like assembly. The first evidence for the formation of the handcuff-like assembly in solution came from its ^{1}H NMR spectrum. As shown in Figure 5, when a solution of **1** in $CDCl_3/CD_3CN$ (5:1) was mixed with 2 equiv. of **4**, only one set of peaks was found (Figure 5c). With the aid of 2D NMR (^{1}H–^{1}H COSY) experiments, almost all the resonances could be assigned to an assembly of **1**·$\mathbf{4}_2$. Similar to those of complex **1**·$\mathbf{3}_4$, the host–guest exchange is also slow on the ^{1}H NMR timescale at different temperatures (Figure S19, Supporting Information) and significant upfield shifts for the inner phenyl protons and downfield shifts for the benzylic methylene protons $H_{a'}$ were observed. Moreover, large chemical shifts for the signals of protons H^3, H^4, and the protons of the crown rings of host **1** were also observed. However, it was

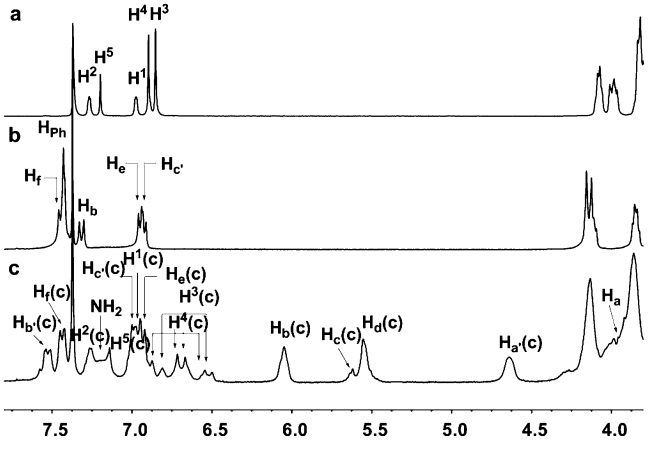


Figure 5. Partial ^{1}H NMR spectra (300 MHz; $CDCl_3/CD_3CN$, 5:1) of (a) free host **1**, (b) free guest **4**, and (c) **1** and 2.0 equiv. of **4**. $[\mathbf{1}]_0$ = 3.0 mM.

noted that the signals of protons H^3 and H^4 split into three set of peaks, which may be attributed to the asymmetry of the phenyl rings inside the cavities and the asymmetry of two macrotricyclic moieties arising from the linking of each of the two ammonium salts on the two sides. Particularly, it was different from complex **1**·3_4 in which the proton H^5 of host **1** showed a relatively obvious upfield shift ($\Delta\delta$ = –0.06 ppm), which might be due to the shielding effect of the aromatic rings in **4**. These observations suggested that a new handcuff-like assembly was formed.

To further ascertain the formation of the molecular handcuff at the tested concentration, a diffusion-ordered NMR (Figure 6) experiment of the 1:2 mixture of **1** ([$\mathbf{1}_0$] = 3.0 mM) and **4** in a $CDCl_3/CD_3CN$ (5:1) solution was performed. The result showed that only one species with the hydrodynamic radius[15] (or Stokes radius) of 20.45 Å was observed in the solution, which agreed well with the measurement obtained from the crystal structure of **1**·3_4 with a length of 21.70 Å at its longest points. This result led us to conclude that the single species in solution should be the handcuff-like assembly. The ESI-MS results provided more evidence for the formation of the 1:2 complex between **1** and **4**. As a result, the peaks at *m*/*z* = 1413.37, 1024.1, and 987.6 for [**1**·$\mathbf{4}_2$-3PF_6^-]$^{3+}$, [**1**·$\mathbf{4}_2$-4PF_6^-]$^{4+}$, and [**4**-PF_6^-]$^+$, respectively, were observed (Figure S21, Supporting Information).

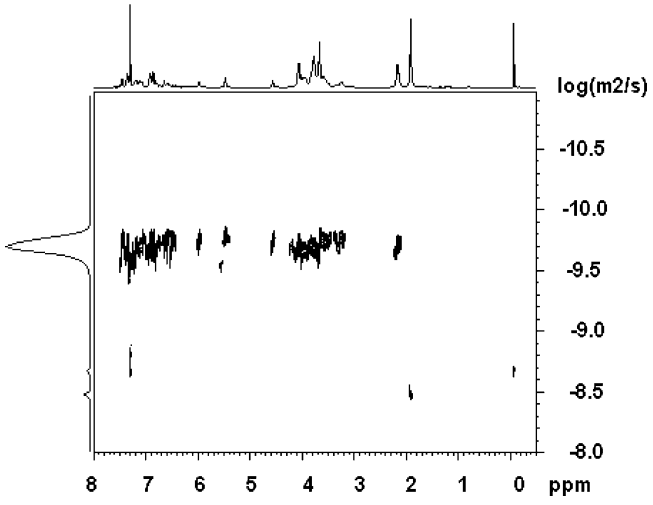


Figure 6. DOSY NMR spectrum (600 MHz; $CDCl_3/CD_3CN$, 5:1; 298 K) of **1** and 2.0 equiv. of **4**. [$\mathbf{1}]_0$ = 3.0 mM (plotted using the log values of the diffusion constant).

Switchable Process of the Molecular Handcuff by the Stimuli of Acid and Base

Inspired by the fact that the association and disassociation of the complex between DB24C8 and the secondary ammonium ion can be chemically controlled by pH, we deduced that the complexation process between host **1** and guests **3** and **4** could also be switched by acid and base. We first studied the complexation process between host **1** and guest **3**. As shown in Figure 7, host **1** and 4 equiv. of guest **3** formed a stable complex **1**·3_4, but when 6 equiv. of tributylamine (TBA) was added into the solution of **1**·3_4 in $CDCl_3/CD_3CN$ (5:1), it was found that the proton signals of complex **1**·3_4 totally disappeared, whereas the signals for protons H_b, H_c, and H_d shifted downfield and the signals of protons $H_{a'}$, $H_{b'}$, $H_{c'}$, and $H_{d'}$ shifted upfield. Moreover, the aromatic proton and crown ether proton signals of host **1** shifted almost to the original positions. These observations indicated that the disassociation of complex **1**·3_4 had occurred. When 12 equiv. of trifluoroacetic acid (TFA) was added to the above solution, the characteristic proton signals of complex **1**·3_4 reappeared, which indicated the complex was formed again.

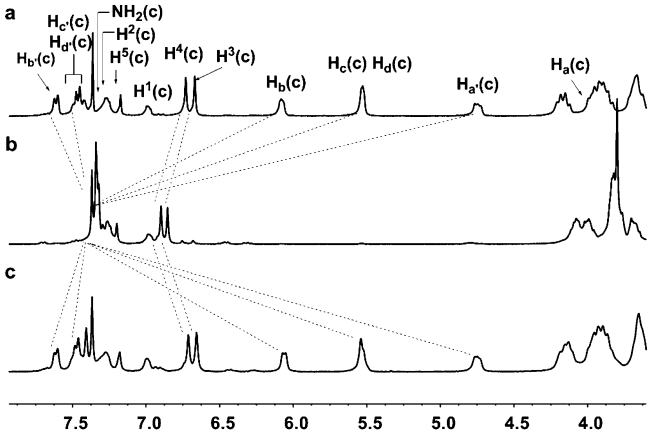


Figure 7. Partial ^{1}H NMR spectra (300 MHz; $CDCl_3/CD_3CN$, 5:1) of (a) complex **1**.3_4, (b) complex $\mathbf{3}_4$ upon the addition of 6 equiv. of TBA, and (c) complex $\mathbf{3}_4$ in the presence of TBA (6 equiv.) upon the addition of 12 equiv. of TFA.

Because the association and disassociation of complex **1**·3_4 could be controlled by pH, we reasoned that the "molecular handcuff" assembly could also be switched "on" or "off" by the addition of acid and base. As shown in Fig-

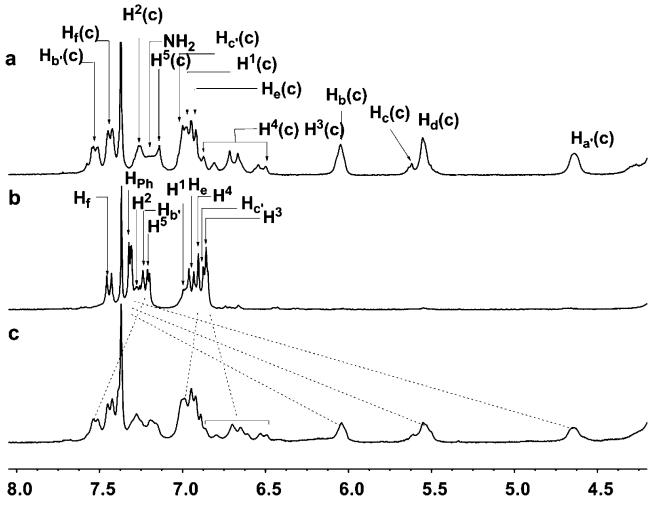


Figure 8. Partial ^{1}H NMR spectra (300 MHz; $CDCl_3/CD_3CN$, 5:1) of (a) complex **1**·$\mathbf{4}_2$, (b) complex **1**·$\mathbf{4}_2$ upon the addition of 6 equiv. of TBA, and (c) complex **1**·$\mathbf{4}_2$ in the presence of TBA (6 equiv.) upon the addition of 12 equiv. of TFA.

ure 8, when 6 equiv. of TBA was added to the solution, the characteristic signals of assembly $\mathbf{1}\cdot\mathbf{4}_2$ disappeared and the proton signals of host **1** shifted to relevant positions characteristic of the free species (Figure 8b). The resonances of these free species were assigned by using ^{1}H–^{1}H COSY 2D NMR spectroscopy.[13] The subsequent addition of 12 equiv. of TFA could further regenerate assembly $\mathbf{1}\cdot\mathbf{4}_2$. Consequently, the switchable process of the molecular handcuff could be achieved by the stimuli of acid and base (Figure 9).

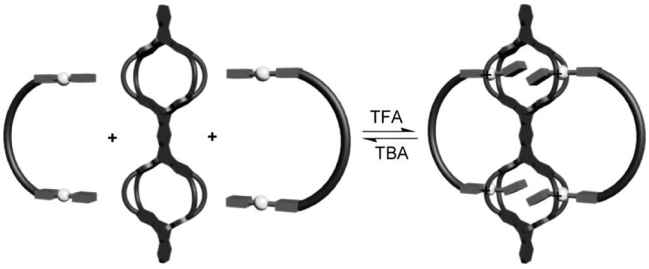


Figure 9. Schematic representation of the acid–base switchable molecular handcuff.

Conclusions

In summary, we have synthesized a novel triptycene-derived bis-macrotricyclic host and also demonstrated that it could form a 1:4 stable complex with 4 equiv. of dibenzylammonium salt in solution and in the solid state. Moreover, we have shown that a handcuff-like assembly could be formed by complexation between the host and 2 equiv. of bis-secondary ammonium ions, and the molecular handcuff could further be switched by the stimuli of acid and base. Our future work will focus on exploring the applications of the host in constructing other specific supramolecular assemblies such as molecular ladders[16] and molecular locks.[17]

Experimental Section

General Information: Melting points were measured with an electrothermal melting point apparatus. NMR spectra were recorded with a Bruker AV 300 NMR or Bruker AV 600. MALDI-TOF mass spectra were obtained with a Bruker BIFLEX III mass spectrometer with CCA. ESI mass spectra were obtained with a FT-ICR MS spectrometer. Elemental analyses were carried out with an Elemental FLASH EA1112 instrument. Materials obtained commercially were used without further purification.

Compound 6: A solution of macrotricycle **5**[11] (0.59 g, 0.55 mmol) and dimethyl acetylenedicarboxylate (0.3 g, 2.12 mmol) in diethylene glycol dimethyl ether (6 mL) was stirred at 110 °C for 22 h under an argon atmosphere. The crude product obtained after evaporation of the organic solvent was dissolved in methanol (5 mL) and heated under reflux for 30 min. After cooling to room temperature, the mixture was filtered, and the solid was recrystallized from dichloromethane and methanol to afford **6** (0.44 g, 66%) as a pale-yellow solid. M.p. 262–264 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (s, 2 H, Ar*H*), 6.97 (s, 2 H, Ar*H*), 6.82 (s, 8 H, Ar*H*), 4.06–3.67 (m, 56 H, OCH_2CH_2O, OCH_3), 2.24 (s, 6 H, CCH_3), 2.10 (s, 6 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.0, 150.7, 148.8, 145.9, 145.8, 142.3, 141.6, 124.5, 119.9, 109.5, 109.3, 71.0, 69.9, 51.8, 49.1, 47.8, 13.7 ppm. MS (MALDI-TOF): *m*/*z* = 1237.4 [M + Na]$^+$, 1253.4 [M + K]$^+$. $C_{68}H_{78}O_{20}\cdot 3H_2O$ (1268.54): calcd. C 64.34, H 6.67; found C 64.56, H 6.91.

Compound 7: Hydrolysis of **6** (0.44 g, 0.36 mmol) in methanol/10% NaOH (5:7, 96 mL) at 80 °C for 8 h. The mixture was cooled to ambient temperature, acidified with 10% hydrochloric acid, and extracted with dichloromethane (3 × 30 mL). The combined extract was dried with anhydrous sodium sulfate and concentrated. The residue was dissolved in acetic anhydride (20 mL) and stirred under reflux for 6 h. The crude product obtained after evaporation of the organic solvent was recrystallized from dichloromethane and isopropyl ether to obtain anhydride **7** (0.35 g, 83%) as a yellow solid. M.p. 212–214 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25 (d, *J* = 4.9 Hz, 2 H, Ar*H*), 6.98 (dd, *J* = 5.4, 3.1 Hz, 2 H, Ar*H*), 6.86 (s, 4 H, Ar*H*), 6.83 (s, 4 H, Ar*H*), 4.10–3.68 (m, 48 H, OCH_2CH_2O), 2.24 (s, 12 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.1, 160.0, 148.8, 146.1, 145.7, 142.3, 140.5, 124.6, 119.9, 109.8, 109.0, 71.1, 71.0, 70.0, 69.9, 69.9, 69.8, 48.8, 47.8, 13.7, 11.7 ppm. MS (MALDI-TOF): *m*/*z* = 1191.3 [M + Na]$^+$, 1207.2 [M + K]$^+$. $C_{66}H_{72}O_{19}\cdot H_2O$ (1186.48): calcd. C 66.77, H 6.28; found C 66.75, H 6.10.

Host 1: To a stirred solution of *p*-phenylenediamine (13 mg, 0.12 mmol) in anhydrous DMF (2.5 mL) was added anhydride **7** (0.35 g, 0.3 mmol) at room temperature under an argon atmosphere. The mixture was stirred at 25 °C for 1 h and to this was added acetic anhydride (3.5 mL), pyridine (1.75 mL), and DMF (1.25 mL). After stirring for 1 h, the mixture was heated at 90 °C for 10 h. A solid precipitated after the reaction mixture was cooled. The product was collected as a pale-yellow solid (170 mg, 59%) after filtration and washing with methanol. M.p. >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25 (d, *J* = 5.2 Hz, 4 H, 2-*H*), 7.21 (s, 4 H, 5-*H*), 6.97 (dd, *J* = 5.4, 3.1 Hz, 4 H, 1-*H*), 6.87 (s, 8 H, 4-*H*), 6.83 (s, 8 H, 3-*H*), 4.13–3.65 (m, 96 H, OCH_2CH_2O), 2.27 (s, 12 H, CCH_3), 2.24 (s, 12 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.1, 157.5, 148.8, 145.9, 145.7, 142.3, 141.5, 130.7, 126.5, 124.6, 119.9, 109.7, 109.1, 71.1, 70.0, 69.9, 69.8, 48.6, 47.8, 13.7, 12.1 ppm. MS (MALDI-TOF): *m*/*z* = 2431.3 [M + Na]$^+$. $C_{138}H_{148}N_2O_{36}\cdot 2H_2O$ (2445.00): calcd. C 67.74, H 6.26, N 1.14; found C 67.84, H 6.12, N 1.27.

Compound 9: A solution of **8**[17] (1.10 g, 2.45 mmol), TsCl (1.12 g, 5.88 mmol), Et_3N (0.74 g, 7.35 mmol), and DMAP (30.5 mg, 0.25 mmol) in anhydrous dichloromethane (80 mL) was stirred under reflux for 12 h. After cooling to room temperature, the reaction mixture was neutralized with 10% hydrochloric acid and then washed with water (3 × 60 mL) after the addition of dichloromethane (70 mL). The combined organic phase was concentrated and purified by column chromatography (ethyl acetate/petroleum, 5:1) to give **9** (1.36 g, 74%) as a white solid. M.p. 56–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.78 (d, *J* = 6.7 Hz, 4 H, Ar*H*), 7.45 (d, *J* = 7.0 Hz, 4 H, biphenyl Ar*H*), 7.31 (d, *J* = 7.0 Hz, 4 H, Ar*H*), 6.95 (d, *J* = 7.0 Hz, 4 H, biphenyl Ar*H*), 4.15 (d, *J* = 2.2 Hz, 8 H, OCH_2CH_2O), 3.83 (s, 4 H, OCH_2CH_2O), 3.67 (m, 8 H, OCH_2-CH_2O), 3.62 (s, 4 H, OCH_2CH_2O), 2.41 (s, 6 H, $ArCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.9, 144.8, 133.6, 133.1, 129.8, 128.0, 127.7, 114.9, 70.8, 69.8, 69.3, 68.7, 67.5, 21.6 ppm. MS (MALDI-TOF): *m*/*z* = 781.6 [M + Na]$^+$, 797.5 [M + K]$^+$. $C_{38}H_{46}O_{12}S_2$ (758.24): calcd. C 60.14, H 6.11; found C 60.16, H 6.13.

Compound 10: A mixture of compound **9** (1.36 g, 1.79 mmol), *p*-hydroxybenzaldehyde (0.44 g, 3.58 mmol), and K_2CO_3 (1.48 g, 10.8 mmol) in anhydrous CH_3CN (50 mL) was heated at reflux under an argon atmosphere for 16 h. After cooling to room temperature, the reaction mixture was filtered and the solid was washed with CH_3CN (30 mL). The combined organic filtrate was concentrated, and crude compound **10** was then dissolved in dichloromethane (80 mL), washed with dilute HCl, and dried with $MgSO_4$. Solvents were removed under reduced pressure, and the crude product was purified by column chromatography (CH_2Cl_2/ethyl acetate, 10:1) to afford **10** (1.18 g, 100%) as a white solid. M.p. 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.86 (s, 2 H, C*H*O), 7.80 (d, J = 8.8 Hz, 4 H, Ar*H*), 7.44 (d, J = 8.8 Hz, 4 H, Ar*H*), 7.00 (d, J = 8.7 Hz, 4 H, Ar*H*), 6.95 (d, J = 8.7 Hz, 4 H, Ar*H*), 4.24–4.11 (m, 8 H, OCH_2CH$_2$O), 3.89 (m, 8 H, OCH_2CH$_2$O), 3.76 (s, 8 H, OCH_2CH$_2$O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 190.7, 163.9, 157.9, 133.6, 131.9, 130.1, 127.6, 114.9, 114.9, 71.0, 70.9, 69.9, 69.5, 67.8, 67.6 ppm. MS (MALDI-TOF): m/z = 658.6 $[M]^+$, 681.6 $[M + Na]^+$, 697.5 $[M + K]^+$. $C_{38}H_{42}O_{10}$ (658.28): calcd. C 69.29, H 6.43; found C 69.16, H 6.34.

Compound 4: A solution of **10** (1.18 g, 1.8 mmol) and benzylamine (0.385 g, 3.6 mmol) in toluene (60 mL) was stirred at reflux in a Dean–Stark apparatus for 12 h. After cooling the mixture to room temperature, the solvent was removed in vacuo, and the residue was added to a solution of $NaBH_4$ (1.36 g, 36 mmol) in THF (40 mL). Methanol (20 mL) was added in small portions to the reaction mixture, which was heated at reflux with stirring for 8 h. It was then allowed to cool and dilute HCl was added (pH < 2). After evaporation of the solvent, the residue was suspended in H_2O (60 mL) and extracted with dichloromethane (4 × 50 mL). The combined extract was washed with 5% aqueous $NaHCO_3$ (2 × 50 mL) and H_2O (50 mL) and then dried with $MgSO_4$. Removal of the solvent under vacuum afforded a pale solid, which was dissolved in methanol (50 mL). Concentrated HCl was added (pH < 2), and the reaction mixture was stirred for 5 h. Evaporation of the solvent afforded a pale solid, which was suspended in acetone (40 mL). An aqueous solution of NH_4PF_6 was added until dissolution occurred. Evaporation of acetone afforded compound **4** as a white solid, which was isolated, washed with H_2O, and dried in vacuo (1.8 g, 88%). M.p. 98–100 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.43 (s, 4 H, NH_2), 7.86–7.22 (m, 18 H, Ar*H*), 7.01 (dd, J = 8.7, 6.4 Hz, 8 H, Ar*H*), 4.57 (d, J = 8.8 Hz, 8 H, OCH_2CH$_2$O), 4.30–4.08 (m, 8 H, OCH_2CH$_2$O), 3.84 (m, 8 H, OCH_2CH$_2$O), 3.70 (s, 8 H, OCH_2CH$_2$O) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 161.0, 159.1, 134.1, 132.7, 132.0, 131.0, 130.5, 130.0, 128.3, 123.8, 115.9, 115.8, 71.5, 70.4, 70.3, 68.6, 68.5, 52.4, 52.3 ppm. MS (MALDI-TOF): m/z = 841.6 $[M – H – 2PF_6]^+$. $C_{52}H_{62}F_{12}N_2O_8P_2$ (1132.38): calcd. C 55.12, H 5.52, N 2.47; found C 55.37, H 5.50, N 2.37.

CCDC-744055 (for **1·3$_4$**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra of new compounds; ^{1}H–^{1}H COSY, ^{1}H NMR titration and variable-temperature ^{1}H NMR experiments; mass spectra (ESI) of complexes **1·3$_4$** and **1·4$_2$**.

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[13] See the Supporting Information for details.
[14] Crystal data for **1**·**3**$_4$·2CH_2ClCH_2Cl: $C_{99}H_{110}Cl_2F_{12}N_3O_{18}P_2$, M_w = 1990.74, crystal size 0.18 × 0.16 × 0.14 mm^3, monoclinic, space group $P2_1/c$, a = 16.397(6) Å, b = 27.887(10) Å, c = 30.957(11) Å, β = 98.431(4)°, V = 14003(8) Å^3, Z = 4, $D_{calcd.}$ = 0.944 Mg m^{-3}, T = 113(2) K, μ = 0.133 mm^{-1}, 83153 reflections measured, 24645 unique (R_{int} = 0.0716), final R indices [$I > 2\sigma(I)$]: R_1 = 0.1221, wR_2 = 0.3123, R indices (all data): R_1 = 0.1676, wR_2 = 0.3489.
[15] The hydrodynamic radius refers to a hypothetical hard sphere that diffuses at the same rate as the molecule; it does not give the exact size of nonspherical species.

$$R = \frac{k_B T}{6\pi\eta D} = \frac{1.38\times10^{-23}\times298}{6\times3.14\times0.54\times1.99\times10^{-10}}\text{Å} = 20.45\text{Å}$$

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