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Complexation of Triptycene-Based Macrotricyclic Host toward (9-Anthracylmethyl)benzylammonium Salt: A Ba^{2+} Selective Fluorescence Probe

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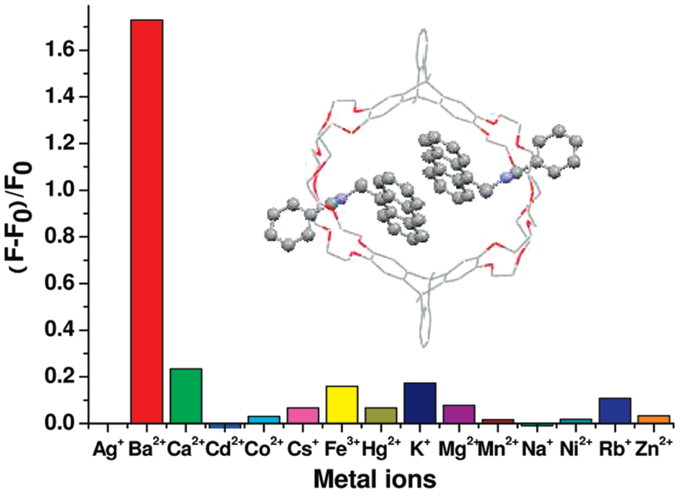

A new triptycene-based macrotricyclic host containing two dibenzo-30 crown-10 moieties (**1**) has been synthesized. It could form a 1:2 stable complex $\mathbf{1}\cdot\mathbf{3}_2$ with (9-anthracylmethyl)benzylammonium salt (**3**) in both solution and solid state, in which the 9-anthracyl groups were selectively positioned inside the cavity of the host. Moreover, the complexation and disassociation of complex $\mathbf{1}\cdot\mathbf{3}_2$ could be chemically controlled by the addition of base and acid. It was also found that Ba^{2+} ion could considerably induce the fluorescence enhancement of complex $\mathbf{1}\cdot\mathbf{3}_2$, which might thus be utilized as a selective supramolecular fluorescence probe for Ba^{2+} ion. Fluorescence and ^1H NMR spectroscopic titrations further showed that the complexation between complex $\mathbf{1}\cdot\mathbf{3}_2$ and barium ions underwent a two-step process.

Introduction

In host−guest chemistry, a permanent and challenging topic is to develop novel macrocyclic hosts with the capability of binding substrate species strongly and selectively.[1,2] Since Stoddart et al.[3] first reported that the dibenzo-24-crown-8 ether (DB24C8) could form 1:1 stable [2]pseudorotaxane-type complexes with secondary dialkylammonium ions in 1995, various DB24C8-based supramolecular systems with specific structures and properties have thus been developed.[4]

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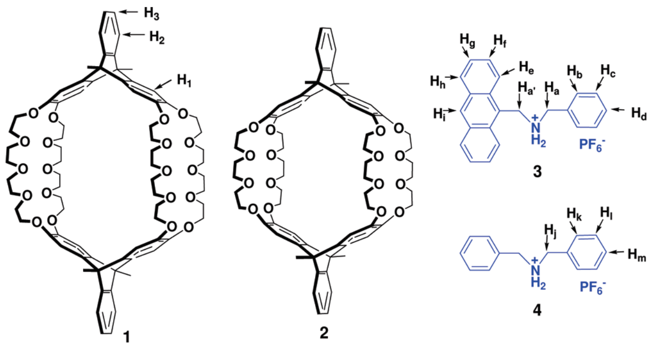


FIGURE 1. The chemical structures and proton designations of the macrocycles **1** and **2**, and the guests **3** and **4**.

Recently, we have synthesized a novel triptycene-based cylindrical macrotricyclic host **2** containing two dibenzo-24-crown-8 moieties (Figure 1), and found that the host could form stable complexes in different complexation modes with different functional paraquat derivatives and secondary ammonium salts.[5] In particular, we interestingly found that host **2** could form a 1:2 complex with two 9-anthracylmethylbenzylammonium salts, in which the 9-anthracyl groups were selectively positioned outside the lateral crown cavities.[5c] Herein, we report the synthesis of a new triptycene-based macrotricyclic host **1** containing two dibenzo-30-crown-10 moieties (Figure 1), and its complexation with guests **3** and **4** in solution and in the solid state. It was noteworthy that host **1** can selectively form a 1:2 stable complex $\mathbf{1}\cdot\mathbf{3}_2$ with two guests of **3**, and the 9-anthracyl groups in $\mathbf{1}\cdot\mathbf{3}_2$ are all positioned inside the lateral crown cavities, which is different from that of complex $\mathbf{2}\cdot\mathbf{3}_2$. It is also found that the complexation and disassociation of the complex $\mathbf{1}\cdot\mathbf{3}_2$ can be chemically controlled by the addition of base and acid. Moreover, Ba^{2+} ion can considerably induce the fluorescence enhancement of complex $\mathbf{1}\cdot\mathbf{3}_2$, which might thus be utilized as a selective supramolecular fluorescence probe for Ba^{2+} ion. Although some fluorescence sensors for Ba^{2+} were reported,[6] to the best of our knowledge, this is the first example of a host–guest complex based fluorescence chemosensor for Ba^{2+} ion.

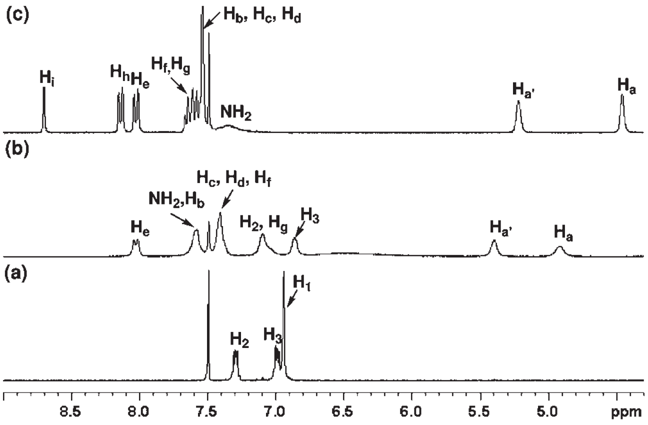
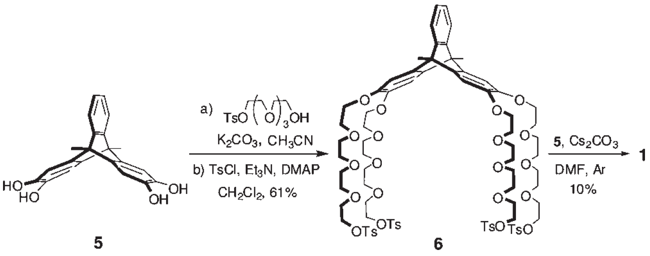


FIGURE 2. Partial ^1H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ = 1:1, v/v, 295 K) of (a) free host **1**, (b) **1** and 2.0 equiv of **3**, and (c) free guest **3**. $[\mathbf{3}]_0$ = 8.0 mM.

SCHEME 1. Synthesis of Host 1



Results and Discussion

Synthesis of Host 1. Synthesis of host **1** is depicted in Scheme 1. According to the same approach as described previously,[5a] host **1** as a white solid was conveniently synthesized in three steps starting from the triptycene derivative **5**. The structure of **1** was confirmed by ^1H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis.[7]

Complexation Studies of Host 1 with Guests 3 and 4. Complexation between host **1** and guest **3** was first studied in solution by the ^1H NMR spectroscopic method. As shown in Figure 2, the ^1H NMR spectrum of a 1:2 mixture of **1** and **3** in $CDCl_3/CD_3CN$ (1:1, v/v) showed only one set of signals, and great differences from the separated host and guest, which indicated that the complexation between **1** and **3** was a fast exchange process, and it was different from the slow exchange process of complex $\mathbf{2}\cdot\mathbf{3}_2$.[5c] The resonances of complex $\mathbf{1}\cdot\mathbf{3}_2$ were assigned by its $^1H-^1H$ COSY and ROESY 2D NMR spectroscopy.[7] The ROESY spectrum revealed the cross-peaks between proton H_e in the anthracyl ring of guest **3** and protons in crown ether units of **1**, indicating the close contacts between these protons. It was found that the proton H_i and H_h signals of **3** and the proton H_1 signal of **1** disappeared, which might be caused by restricted molecular motion of the guests incorporated into the host cavity and the strong shielding effect between the

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(7) See the Supporting Information for details.

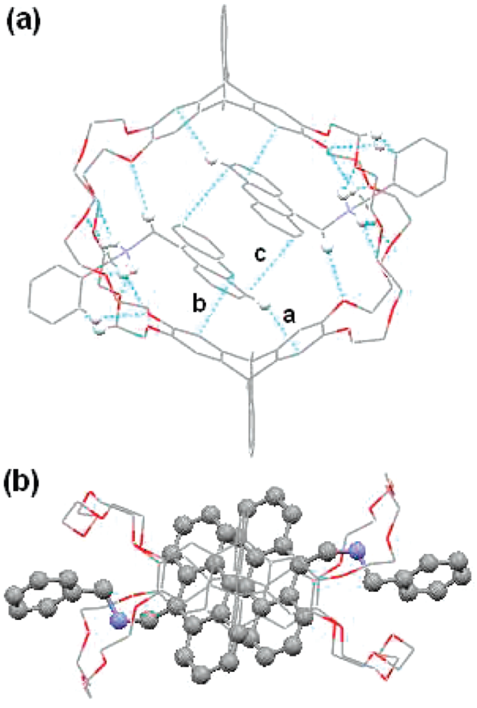

FIGURE 3. Top view (a) and side view (b) of the crystal structure of complex $1 \cdot 3_2$. Blue lines denote the noncovalent interactions between the host and the guests. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

host and the guests.[8] The proton H_g signal of the anthracyl ring shifted upfield significantly and broadened probably due to the $\pi \cdots \pi$ stackings between the two anthracyl rings of the guests. However, the proton signals of anthracyl rings in the complex $2 \cdot 3_2$ exhibited large downfield shifts, which were probably attributed to hydrogen bonding interactions and the deshielding effect of the aromatic rings in host **1**. Moreover, the protons H_2 and H_3 of host **1** showed large upfield shifts compared to those of complex $2 \cdot 3_2$, which might be affected by the shielding effect of anthracyl rings in the cavities. It was also noteworthy that the ^1H NMR spectrum of complex $1 \cdot 3_2$ was nearly unchanged after four months in the dark.[7] These observations suggested that host **1** and guest **3** formed a stable complex in solution. Furthermore, ^1H NMR spectroscopic titrations were carried out by monitoring the chemical shift of the proton $H_{a'}$ of guest **3**. Consequently, the stoichiometry of the complex was determined to be 1:2 by a mole ratio plot,[7,9] and the average association constant K_{av} for the complex was calculated to be $6.8(\pm 0.2) \times 10^3$ M^{-1} by the Scatchard plot.[7,10]

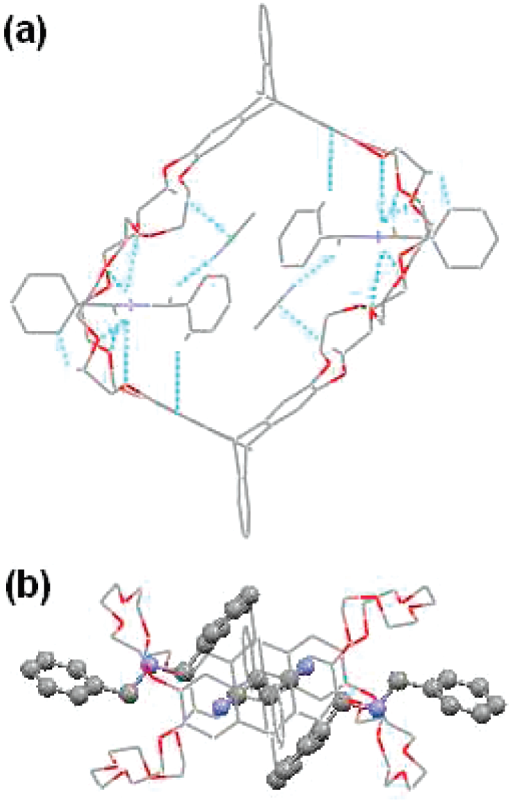

FIGURE 4. Top view (a) and side view (b) of the crystal structure of complex $1 \cdot 4_2$. Blue lines denote the noncovalent interactions between the host and the guests. PF_6^- counterions and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

We also obtained the light yellow single crystals of complex $1 \cdot 3_2$ suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of **1** and **3** in $CHCl_3$ and CH_3CN (1:1, v/v). As shown in Figure 3, two ammonium guests were threaded symmetrically through the lateral crown cavities of host **1**. Interestingly, it was found that the two anthracyl groups were selectively positioned inside the crown cavities, which is completely different from the case of complex $2 \cdot 3_2$ with the anthracyl groups outside the cavities.[5c] There existed multiple N$-$H$\cdots$O and C$-$H$\cdots$O hydrogen bonds between the host and the guests. Moreover, a pair of C$-$H$\cdots\pi$ interactions between the protons of the anthracyl group and the phenyl rings of the triptycene subunits with a distance of 2.73 Å (a) and a pair of $\pi \cdots \pi$ interactions between the anthracyl rings and the phenyl rings of the triptycene subunits with a distance of 3.37 Å (b) were also observed. In particular, it was found that the two anthracyl rings were almost parallel, and a pair of $\pi \cdots \pi$ interactions between them with a distance of 3.35 Å (c) was shown. These multiple noncovalent interactions resulted in the selective formation of the stable 1:2 complex $1 \cdot 3_2$.

Similar to the case of complex $1 \cdot 3_2$, we found that host **1** and guest **4** could also form a 1:2 stable complex in solution. Consequently, the ^1H NMR spectrum of a 1:2 mixture of **1** and **4** recorded in $CDCl_3/CD_3CN$ (1:1, v/v) showed one new set of signals,[7] which indicated that the complexation between **1** and **4** was also a fast exchange process. The stoichiometry of the complex between host **1** and guest **4** was further determined to be 1:2 in solution by mole ratio plot.[7] The average association constant (K_{av}) of the 1:2 complex $1 \cdot 4_2$ was calculated to be $1.9(\pm 0.1) \times 10^3$ M^{-1} by the ^1H NMR spectroscopic titrations,

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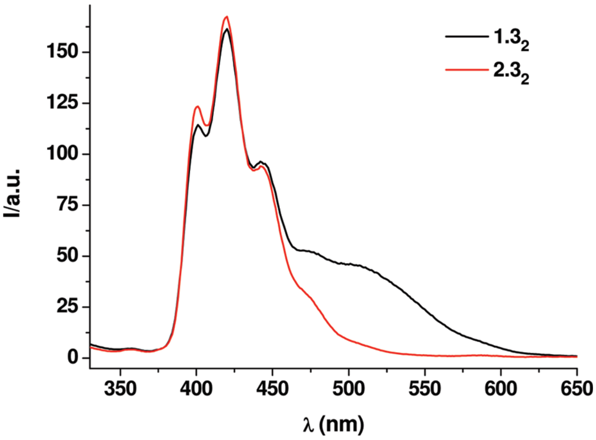

FIGURE 5. The comparison of fluorescence emission spectra of $1\cdot3_2$ and $2\cdot3_2$ ($CHCl_3/CH_3CN$ = 1:1, v/v, 295 K), excitation at 294 nm. $[3]_0 = 1.0 \times 10^{-4}$ M.

which is less than one-third of that of complex $1\cdot3_2$. This result implied that the positive cooperativity of the interactions between the anthracene moieties of the two guests in $1\cdot3_2$ may play an important role in the stability of the complex. Moreover, we obtained the single crystals suitable for X-ray analysis by vapor diffusion of diethyl ether into a 1:2 mixture solution of **1** and **4** in $CHCl_3/CH_3CN$ (1:1, v/v). The crystal structure showed that two guest molecules thread through the lateral crown ether cavities to form a [3]pseudorotaxane-type complex (Figure 4). Interestingly, it was found that two acetonitrile molecules were also included in the central cavity of host **1**, which could act as a bridge to connect the guest and the host. There also existed multiple C−H···N and C−H···O hydrogen bonding interactions between the host and the guests. Moreover, a pair of C−H···π interactions between the aromatic protons of guest **4** and the phenyl rings of the triptycene subunits in host **1** were also shown. However, no face-to-face $\pi\cdots\pi$ stacking interactions between the aromatic rings of the two guests in complex $1\cdot4_2$ were observed, which is different from those of complexes $2\cdot4_2$ and $1\cdot3_2$.

The electrospray ionization mass spectra (ESI MS) provided more evidence for formation of the 1:2 stable complexes $1\cdot3_2$ and $1\cdot4_2$. Consequently, the strong peaks at *m*/*z* 960.7 for $[1\cdot3_2\text{-}2PF_6^-]^{2+}$ and 861.2 for $[1\cdot4_2\text{-}2PF_6^-]^{2+}$ were observed, respectively.[7]

The complexation between host **1** and guest **3** was also investigated by the fluorescence emission experiments. When it was excited at 294 nm, it was found that the fluorescence of the anthracene unit in both complexes quenched up to 80% compared with the value when guest **3** was excited alone.[7] Moreover, a comparison between the emission spectra of the complexes $1\cdot3_2$ and $2\cdot3_2$ was made to provide further evidence for their different complexation modes. As shown in Figure 5, a new broad band from 470 to 650 nm was observed in the spectrum of complex $1\cdot3_2$, which is consistent with the excimer[11] formation in a specific cavity. However, this broad band was not observed in the spectra of the complexes $2\cdot3_2$ and DB30C10$\cdot$**3**,[12] which might be mainly attributed to the different location of the anthracene unit relative to the hosts.

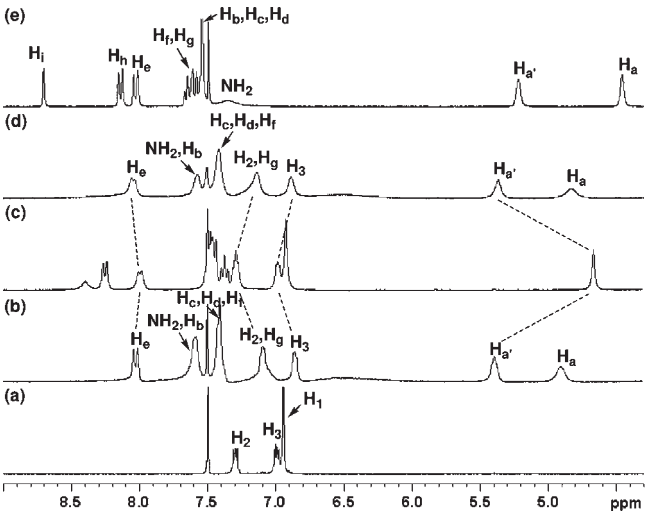

FIGURE 6. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ = 1:1, v/v, 295K) of (a) free host **1**, (b) **1** and 2.0 equiv of **3**, (c) to the solution of b was added 2.0 μL tributylamine, (d) to the solution of c was added 1.0 μL trifluoroacetic acid, and (e) free guest **3**. $[3]_0$ = 8.0 mM.

Chemically Controlled Binding and Releasing of Guest 3 in Complex $1\cdot3_2$. We further examined the chemically controlled binding and releasing of guest **3** in complex $1\cdot3_2$. Consequently, a series of ^{1}H NMR experiments were performed. As shown in Figure 6, when 2.0 μL of tributylamine was added into the solution of complex $1\cdot3_2$, the proton signals of the complex disappeared, while the proton signals of the deprotonated guest **3** and host **1** were observed. When 1.0 μL of trifluoroacetic acid was added into the above system, it was found that the proton signals of complex $1\cdot3_2$ recovered, which suggested that complex $1\cdot3_2$ formed again.

The above switchable process also could be monitored by the fluorescence spectra.[7] Upon the addition of 2 equiv of tributylamine into the $CHCl_3/CH_3CN$ (1:1, v/v) solution of complex $1\cdot3_2$, it was found that the fluorescence intensity of the anthracene unit of **3** dramatically decreased, while the broad band also disappeared, which implied that guest **3** was deprotonated,[13] while the complex thus disassociated. When excess trifluoroacetic acid was added into the above mixture, the fluorescence of the anthracene unit almost recovered, while the broad band appeared but could not totally come back to the original level. This reversible process could be performed repeatedly over more than five cycles, indicating the complexation and decomplexation of the complex could be efficiently controlled by addition of the acid and the base.

Complexation Studies of Host 1 and Complex $1\cdot3_2$ with Ba^{2+} Ion. It was known that crown ethers could bind certain metal ions, which inspired us to test the presence of special metal ions by inspecting the change of fluorescence intensity of complex $1\cdot3_2$ in the presence of metal ions. Consequently,

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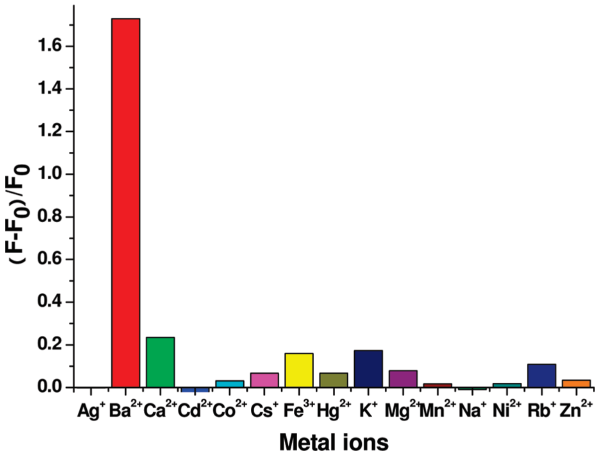

FIGURE 7. Fluorescence enhancement ratio of a solution of $\mathbf{1}\cdot\mathbf{3}_2$ in $CHCl_3/CH_3CN$ (1:1, v/v) in the presence of equimolar metal ions. $[\mathbf{1}\cdot\mathbf{3}_2]_0 = 5.0 \times 10^{-5}$ M. Perchlorate salts were used, except KPF_6. Excitation was performed at 294 nm; emission was monitored at 421 nm.

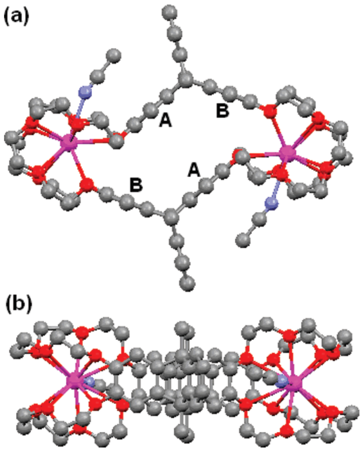

FIGURE 8. (a) Top view and (b) side view of the crystal structure of complex $\mathbf{1}\cdot 2Ba^{2+}$. ClO_4^- counterions, hydrogen atoms, and solvent molecules not involved in the interactions are omitted for clarity.

it was found that upon addition of 1 equiv of Ba^{2+} ion to the $CHCl_3/CH_3CN$ (1:1, v/v) solution of $\mathbf{1}\cdot\mathbf{3}_2$, the fluorescence intensity dramatically increased.[7] However, under the same conditions, no obvious changes were observed for other widely tested metal ions.[7] These results suggested that Ba^{2+} ions might bind much stronger with host **1** than those of other tested metal ions (Figure 7). Thus, complex $\mathbf{1}\cdot\mathbf{3}_2$ could act as a Ba^{2+} selective supramolecular fluorescence probe.

To gain insight into the recognition behavior of host **1** and Ba^{2+} ion, the fluorescence emission spectral experiments were carried out.[7] Consequently, it was found that upon the addition of Ba^{2+} ion to host **1**, the emission band at 319 nm gradually increased when the ion concentrations were below 1 equiv of the host. But when the titrations proceeded with the concentration of Ba^{2+} ion more than 1 equiv of host **1**, the intensity of emission band at 319 nm decreased with concomitance of the emerging of a new band at 589 nm. These observations indicated that host **1** may bind two Ba^{2+} ions through two steps. To further confirm the stepwise binding behavior, ^{1}H NMR spectroscopic titrations were also conducted.[7] It was found that the proton signals of host **1** and $\mathbf{1}\cdot Ba^{2+}$ overlap each other partially in the period of the first binding step, but proton H_1 signals in two species were discernible. Thus, formation of $\mathbf{1}\cdot Ba^{2+}$ could be evidenced by the emergence and increase of a new signal at 6.90 ppm accompanied by a decrease of the signal at 6.91 ppm. In the second binding step, the proton H_1 and the bridgehead methyl proton signals could be used to distinguish $\mathbf{1}\cdot Ba^{2+}$ and $\mathbf{1}\cdot 2Ba^{2+}$. Moreover, on the basis of fluorescence emission titrations, the association constants for the 1:1 and 1:2 complexes

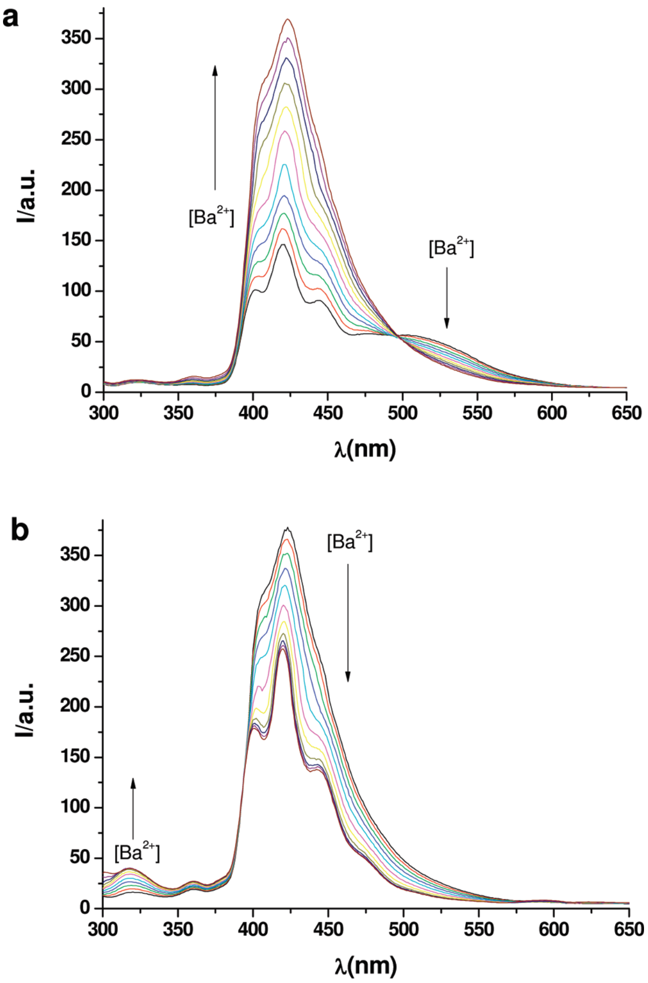

FIGURE 9. Fluorescence emission spectra of $\mathbf{1}\cdot\mathbf{3}_2$ in the presence of Ba^{2+} in $CHCl_3/CH_3CN$ (1:1, v/v) at 295 K. Excitation at 294 nm, $[\mathbf{1}\cdot\mathbf{3}_2]_0 = 5.0 \times 10^{-5}$ M. (a) The concentration of Ba^{2+} (from bottom to top) are 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 $\times 10^{-5}$ M; (b) the concentrations of Ba^{2+} (from top to bottom) are 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5$\times 10^{-5}$ M.

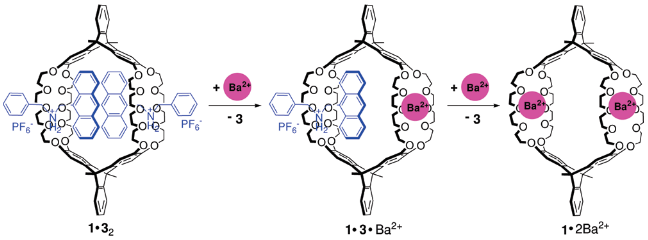

FIGURE 10. Graphic representation of the displacement of guest **3** in $\mathbf{1}\cdot\mathbf{3}_2$ by Ba^{2+} ion.

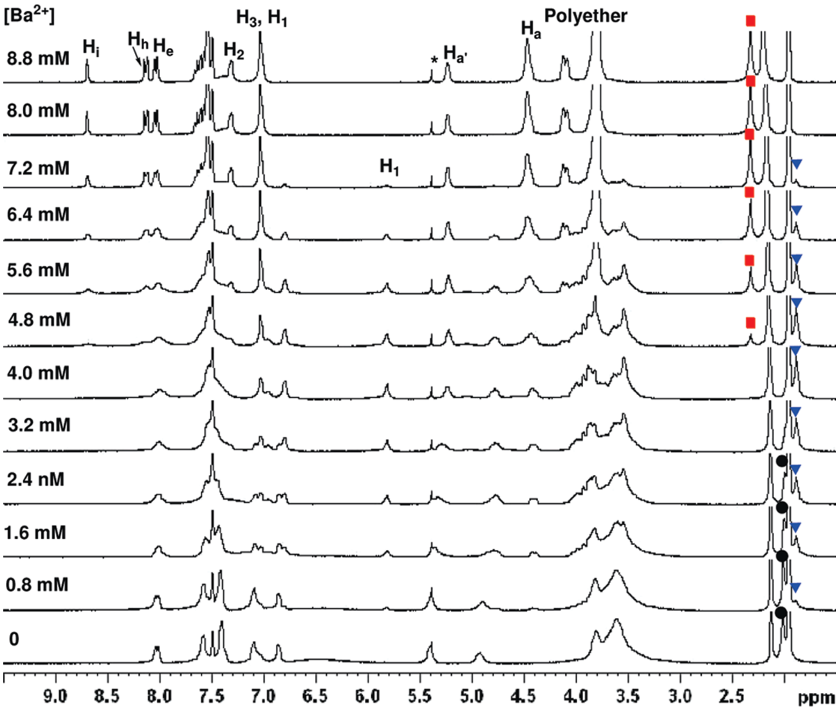

FIGURE 11. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ = 1:1, v/v, 295 K) of $\mathbf{1}\cdot\mathbf{3}_2$ in the presence of Ba^{2+}. $[\mathbf{3}]_0$ = 8.0 mM. The asterisk denotes the residue signals of CH_2Cl_2. (Black circles) proton H_1 signals of **1** in $\mathbf{1}\cdot\mathbf{3}_2$; (blue triangles) proton H_1 signals of **1** in $\mathbf{1}\cdot\mathbf{3}\cdot Ba^{2+}$; (red squares) proton signals at bridgehead methyl of **1** in $\mathbf{1}\cdot 2Ba^{2+}$.

of host **1** and Ba^{2+} were calculated to be $1.6(\pm0.2) \times 10^5\ M^{-1}$ for K_1 and $3.3(\pm0.2) \times 10^4\ M^{-1}$ for K_2, respectively, by using a Hyperquad 2003 program. Moreover, ESI MS spectrum showed a base peak at m/z 401.1 for $\mathbf{1}\cdot 2Ba^{2+}$, which also suggested formation of the complex $\mathbf{1}\cdot 2Ba^{2+}$.

Fortunately, we obtained the colorless single crystal of $\mathbf{1}\cdot 2Ba^{2+}$ suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of **1** and $Ba(ClO_4)_2$ in a 1:1 chloroform/acetonitrile solution. As shown in Figure 8, the crystal structure showed that all ten oxygen atoms of each crown ether unit of host **1** coordinated to the center of two barium ions, respectively. The bond lengths between oxygen atoms and barium ions ranged from 2.82 to 3.06 Å, which is similar to the reported values.[14] Interestingly, an acetonitrile molecule located outside the cavity of host **1** was bound to the Ba^{2+} ion as the eleventh ligand. Moreover, it was found that the distance between the parallel phenyl rings of the triptycene subunits is 5.14 Å for A−A and 7.57 Å for B−B, respectively, which are much shorter than the corresponding distances in complexes $\mathbf{1}\cdot\mathbf{3}_2$ (A−A: 10.09 Å; B−B: 10.33 Å) and $\mathbf{1}\cdot\mathbf{4}_2$ (A−A: 11.09 Å; B−B: 13.20 Å). Thus, the cavity of host **1** in complex $\mathbf{1}\cdot 2Ba^{2+}$ is much smaller than those of $\mathbf{1}\cdot\mathbf{3}_2$ and $\mathbf{1}\cdot\mathbf{4}_2$, which makes the limited cavity no longer able to accommodate other molecules inside.

To explore the recognition property of complex $\mathbf{1}\cdot\mathbf{3}_2$ to Ba^{2+} ions, we have also carried out fluorescence titration experiments. As shown in Figure 9a, upon the addition of Ba^{2+} into the solution of complex $\mathbf{1}\cdot\mathbf{3}_2$ in $CHCl_3/CH_3CN$ (1:1, v/v), the emission band in the region of 495−600 nm decreased, while the emission at 421 nm gradually increased. The fluorescence emission intensity arrived at maximum when the ratio of barium ions to complex $\mathbf{1}\cdot\mathbf{3}_2$ was changed to 1:1. Then, with the continuous increase of the concentration of Ba^{2+} ion, the emission at 421 nm gradually decreased (Figure 9b). After the addition of 2 equiv of Ba^{2+} ions, the fluorescence did not decrease any more when Ba^{2+} ions were continuously added. Additionally, we have also proved that the Ba^{2+} ion could not quench the fluorescence of guest **3**.[7] Thus, the decrease of fluorescence was probably ascribed to the formation of complex $\mathbf{1}\cdot 2Ba^{2+}$, which was further evidenced by the fluorescence titrations of **3** in the presence of $\mathbf{1}\cdot 2Ba^{2+}$. Consequently, it was found that the fluorescence intensity of guest **3** gradually decreased with the increase of the additional complex $\mathbf{1}\cdot 2Ba^{2+}$, which indicated that similar to that of host **1**, complex $\mathbf{1}\cdot 2Ba^{2+}$ could also expectedly quench the fluorescence of guest **3**.[7] These observations suggested that the displacement of guest **3** could undergo a two-step binding process (Figure 10).

We further investigated the interaction between complex $\mathbf{1}\cdot\mathbf{3}_2$ and Ba^{2+} by ^{1}H NMR spectroscopic titrations. As shown in Figure 11, upon the addition of Ba^{2+} into a solution of complex $\mathbf{1}\cdot\mathbf{3}_2$ in $CDCl_3/CD_3CN$ (1:1, v/v), a new signal at 1.89 ppm assigned to the bridgehead methyl group of the triptycene unit in $\mathbf{1}\cdot\mathbf{3}\cdot Ba^{2+}$ emerged upfield compared to the corresponding signal in $\mathbf{1}\cdot\mathbf{3}_2$. With the increase of the concentration of Ba^{2+} ion, proton H_1 signal of host **1** appeared while protons H_2 and H_3 split into two set of signals, respectively, which also suggested the formation of an unsymmetric ternary complex $\mathbf{1}\cdot\mathbf{3}\cdot Ba^{2+}$. After the ratio of Ba^{2+} ion and host reached 1:1, the proton signals of guest **3** and $\mathbf{1}\cdot 2Ba^{2+}$ appeared, and then increased as the proton signals of $\mathbf{1}\cdot\mathbf{3}\cdot Ba^{2+}$ decreased gradually. When the ratio reached 1:2, only the proton signals of guest **3** and $\mathbf{1}\cdot 2Ba^{2+}$ were shown. These observations further

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[14] (a) Li, Z.-Q.; Xu, H.-W.; Wang, X.-W.; Fan, Y.-P. *Chin. J. Struct. Chem.* **1989**, *8*, 273–277. (b) Masci, B.; Thuéry, P. *Cryst. Eng. Chem.* **2007**, *9*, 582–590.

indicated that the complexation between complex $1\cdot 3_2$ and barium ions underwent a two-step process, which is in agreement with the results of the fluorescence titrations.

Conclusion

In conclusion, we have synthesized a new macrotricyclic host containing two dibenzo-30-crown-10 moieties, and proved that the host could selectively bind two (9-anthracylmethyl)benzylammonium ions to form a 1:2 stable complex $1\cdot 3_2$ in both solution and solid state, in which the two 9-anthracyl groups were all positioned inside the cavity. Moreover, the complexation and disassociation of complex $1\cdot 3_2$ also could be chemically controlled by the addition of base and acid. We further found that Ba^{2+} ion could considerably induce the fluorescence enhancement of complex $1\cdot 3_2$, which might thus be utilized as a selective supramolecular fluorescence probe for Ba^{2+} ion. Fluorescence and ^1H NMR spectroscopic titrations showed that the complexation between complex $1\cdot 3_2$ and barium ions underwent a two-step process. The results presented here will be helpful in developing new supramolecular systems with specific structures and properties, which is underway in our laboratory.

Experimental Section

The guests **3**[12] and **4**,[3] and compound **5**[5a] were prepared according to the published procedures.

Compound 6. To a stirred solution of **5** (2.5 g, 7.2 mmol) and tetra(ethylene glycol) monotosylate (11.1 g, 31.8 mmol) in dried CH_3CN (120 mL) was added K_2CO_3 (7.9 g, 57.6 mmol). The reaction mixture was stirred at reflux for 40 h, cooled to ambient temperature, and then filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved in dried CH_2Cl_2 (80 mL) and TsCl (6.7 g, 35.0 mmol), Et_3N (4.8 g, 47.7 mmol), and DMAP (77 mg, 0.64 mmol) were added. The reaction mixture was stirred at reflux for 12 h. CH_2Cl_2 (60 mL) was added and the solution was washed with diluted HCl and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by column chromatography (SiO_2: 3:1 EtOAc/CH_2Cl_2) yielded **6** (7.4 g, 61%) as a pale yellow oil. Mp 73−74 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 6H), 2.41 (s, 12H), 3.54−3.68 (m, 40H), 3.74−3.78 (m, 8H), 4.07−4.14 (m, 16H), 6.94 (s, 4H), 6.98−7.00 (m, 2H), 7.26−7.32 (m, 10H), 7.77 (d, J = 8.0 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 21.6, 47.9, 68.6, 69.3, 69.7, 69.9, 70.5, 70.6, 70.7 109.9, 120.0, 124.6, 128.0, 129.9, 132.9, 142.4, 144.8, 145.8, 148.8; MALDI-TOF MS m/z 1666.5 (M^+). Anal. Calcd for $C_{82}H_{106}O_{28}S_4$: C 59.05, H 6.41. Found: C 58.81, H 6.40.

Compound 1. A suspension of cesium carbonate (3.9 g, 12 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **5** (519 mg, 1.5 mmol) and **6** (2.5 g, 1.5 mmol) in anhydrous DMF (80 mL) over 12 h. The reaction mixture was stirred at 100 °C for another 3 d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (100 mL). The filtrate was concentrated under reduced pressure, then the residue was dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography (SiO_2: 60:1 CH_2Cl_2/MeOH) to yield **1** (198 mg, 10%) as a white solid. Mp > 300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 12H), 3.59−3.65 (m, 32H), 3.72−3.75 (m, 16H), 4.02−4.12 (m, 16H), 6.91 (s, 8H), 6.98−7.01 (m, 4H), 7.27−7.29 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 47.9, 69.7, 69.8, 70.8, 70.9, 109.5, 120.0, 124.6, 142.4, 145.7, 148.7; MALDI-TOF MS m/z 1324.5 (M^+). Anal. Calcd for $C_{76}H_{92}O_{20}$: C 68.86, H 7.00. Found: C 68.51, H 7.00.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra for new compounds, ESI-MS and $^1H-^1H$ COSY spectra for complexes $1\cdot 3_2$, $1\cdot 4_2$, and $1\cdot 2Ba^{2+}$, determination of the association constants, fluorescence spectra of the complexes, and X-ray crystallographic files (CIF) for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.