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# Unidirectional Threading into a Bowl-Shaped Macrocyclic Trimer of Boron–Dipyrrin Complexes through Multipoint Recognition

*Takashi Nakamura, Gento Yamaguchi, and Tatsuya Nabeshima**

***Abstract:*** *Bowl-shaped macrocycles have the distinctive feature that their two sides are differentiated, and thus can be developed into elaborate hosts that fix a target molecule in a controlled geometry through multipoint interactions. We now report the synthesis of a bowl-shaped macrocyclic trimer of the boron–dipyrrin (BODIPY) complex and its unidirectional threading of guest molecules. Six polarized* $B^{\delta+}{-}F^{\delta-}$ *bonds are directed towards the center of the macrocycle, which enables strong recognition of cationic guests. Specifically, the benzylbutylammonium ion is bound in a manner in which the benzyl group is located at the convex face of the bowl and the butyl group at its concave face. Furthermore, adrenaline was strongly captured on the convex side of the bowl by hydrogen bonding, Coulomb forces, and C−H⋯π interactions.*

Unidirectional guest binding is an important and challenging topic, not only in terms of precise molecular recognition, but also for the development of elaborate artificial nanomachines that achieve regulated motions.[1] Macrocyclic compounds have often been employed as components of molecular machines, such as rotaxanes, and their shape is a fundamental factor to create the functions.[2] In contrast to planar molecules, nonplanar macrocyclic hosts can interact in a different way with guests on the two sides. Classical examples of nonplanar bowl-shaped macrocycles are cyclodextrins[3] and calixarenes.[4] Their unsymmetrical structures gave rise to unidirectional threading of designed axle molecules of (pseudo)rotaxanes.[5,6] However, they often suffer from inversion of the bowl because of their flexibility, or from the two sides of the macrocycles being very similar. These issues adversely affect the binding ability and precisely regulated molecular motions.

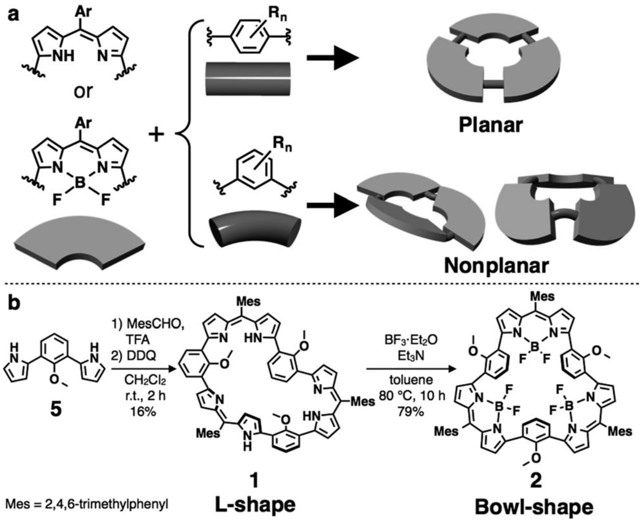

***Figure 1.*** a) Difference in shape of *para*-phenylene-linked cyclic dipyrrin/BODIPY trimers and *meta*-phenylene-linked ones. b) *Meta*-phenylene-linked L-shaped dipyrrin trimer **1** and bowl-shaped BODIPY trimer **2**. TFA = trifluoroacetic acid, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

We focused on boron–difluoride complexes of dipyrrins (BODIPY)[7] as a constituent unit of the macrocycles.[8] We previously reported trimeric macrocycles of dipyrrin/BODIPY linked through its 3,5-positions by *para*-phenylene moieties.[9] The macrocycles had planar triangular shapes as a corollary of the angle of each unit (Figure 1 a). We envisaged that the employment of *meta*-phenylene linkers (ca. 120°)[10] instead of *para*-phenylene ones (ca. 180°)[9,11] would result in trimeric macrocyclic frameworks with nonplanar, distorted shapes, because the sum of the interior angles of the macrocycle would not be suitable for the formation of planar polygons (Figure 1 a). Herein, we report the synthesis of a *meta*-phenylene-linked dipyrrin trimer **1**, and a bowl-shaped BODIPY trimer **2** formed by the reaction of **1** with $BF_3{\cdot}Et_2O$ (Figure 1 b). We also investigated the ability of **2** to form an oriented [2]pseudorotaxane by unidirectionally threading an ammonium guest.

A dipyrrin trimer **1** was synthesized in 16 % yield by the TFA-catalyzed condensation of a 2,6-bis(2-pyrrolyl)anisole (**5**) and mesitaldehyde. The $^1H$ NMR spectrum of **1** recorded at 238 K showed three signals for the methoxy protons, thus suggesting that the cyclic trimer lost its apparent $C_3$ symmetry (Figure 2 a,b). A single-crystal X-ray diffraction analysis revealed the unique L-shaped structure of **1** (Figure 2 c,d). The two dipyrrin moieties (denoted as units 2 and 3 in Figure 2 a,b and depicted in blue and red, respectively) and one methoxyphenyl ring (unit 3) deviated significantly from the plane. Another characteristic is that one pyrrole ring of a dipyrrin (unit 3) was inverted. All the $^1H$ NMR signals of **1** were assigned on the basis of $^1H$-$^1H$ COSY and ROESY NMR measurements (see Figures S4 and S5 in the Supporting Information). Characteristic transannular ROE effects (e.g. $a_3$-$b_2'$) indicated that the solution structure of **1** is basically the same as that obtained by the X-ray analysis.

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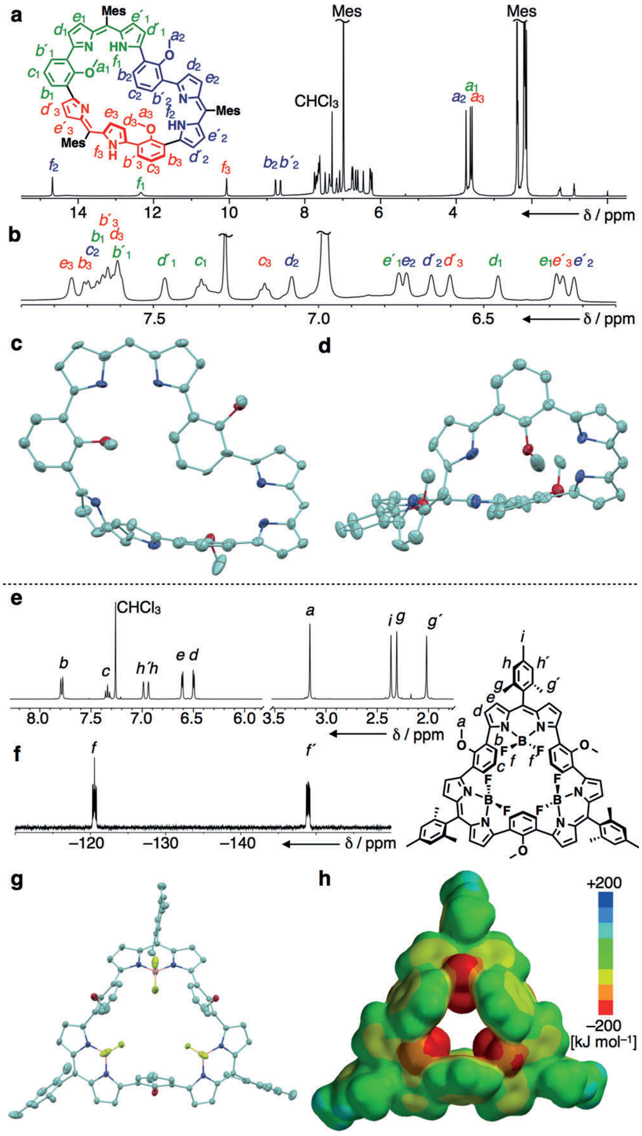


***Figure 2.*** a,b) $^{1}$H NMR spectra of L-shaped dipyrrin trimer **1** (600 MHz, CDCl$_3$, 238 K). c,d) The X-ray crystal structure of **1**, with ellipsoids at 50% probability. c) Top view. d) Side view. Hydrogen atoms, solvents, and Mes groups are omitted for clarity. C: light green, N: blue, O: red. e) $^{1}$H NMR (400 MHz) and f) $^{19}$F NMR (376 MHz) spectra of bowl-shaped BODIPY trimer **2** (CDCl$_3$, 298 K). g) The X-ray crystal structure of **2**, with ellipsoids at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. C: light green, N: blue, O: red, B: pink, F: yellow-green. h) Electrostatic potential surfaces of **2** obtained by DFT calculations at the B3LYP/6-31G* level (the atomic coordinates of the crystal structure of **2** were used).

The dipyrrin trimer **1** was converted into the BODIPY trimer **2** in 79% yield on reaction with $BF_3{\cdot}Et_2O$. Figure 2e shows the $^{1}$H NMR spectrum of **2**. Two signals were observed for each proton of the mesityl groups (*g*,*g′* and *h*,*h′*), which suggests that **2** has $C_{3v}$ symmetry. The $^{19}$F NMR spectrum showed two separated signals (−120.5, −148.9 ppm), which also indicated that the two faces of the macrocycles were differentiated (Figure 2f). A single-crystal X-ray analysis of **2** clearly revealed the bowl-shaped macrocyclic structure (Figure 2g). The three BODIPY units were tilted by about 20–40° from the plane perpendicular to the apparent $C_3$ axis. Free rotation of the phenylene spacers was restricted by steric hindrance of the B−F units, thus the conformation was fixed into a bowl shape. The central cavity was surrounded by F atoms of the boron difluoride units. The distances between any two of the three inner F atoms were 4.62–4.78 Å. The two sets of $^{1}$H signals (*g*,*g′* and *h*,*h′*) of the mesityl groups did not coalesce in the $^{1}$H NMR measurement at 115 °C in 1,1,2,2-[D$_2$]tetrachloroethane, and no EXSY cross-peaks were observed between them in the NOESY NMR spectrum at the same temperature (mixing time, 1000 ms; see Figure S11). This observation suggested that the rate of the bowl inversion of **2** was slower than 0.02 s$^{-1}$ at 115 °C and its activation energy ($\Delta G^{\ddagger}$) higher than 108 kJ mol$^{-1}$. The slow bowl inversion renders **2** a promising candidate for a new kind of nonplanar macrocyclic receptor.

The fluorine atoms of **2** accumulated in the cavity possess partial negative charges resulting from polarized $B^{\delta+}{-}F^{\delta-}$ bonds (Figure 2h). This feature enables **2** to serve as an excellent receptor for a cationic guest. Secondary ammonium ions, in particular, were tightly bound to **2** to form a [2]pseudorotaxane. A $^{1}$H NMR titration experiment of the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) salt of the dibutylammonium cation **6**$^{+}$ against **2** in CDCl$_3$ unambiguously determined its binding mode to be **2**:**6**$^{+}$ = 1:1 (Figure S13), and the binding constant ($K_a$ [M$^{-1}$]) was determined to be log$K_a$ = 5.49(3) from a UV/Vis titration measurement (Table 1, see Figures S14 and S15). Two sets of signals were observed for the butyl groups of **6**$^{+}$ in the $^{1}$H NMR spectrum of [**6**@**2**]$^{+}$ (Figure 3c). This observation indicated that **6**$^{+}$ threaded through the bowl-shaped **2**, with one butyl group positioned on the concave face of **2**, while the other was positioned on its convex face. $^{1}$H-$^{1}$H ROESY NMR measurements of [**6**@**2**]$^{+}$ (Figure 3a) showed ROE cross-peaks between the protons of one butyl group (H5–H8) of axle **6**$^{+}$ and those of the *meta*-phenylene spacers (*b*,*c*) of the macrocyclic ring **2**. Thus, the [2]pseudorotaxane formation shown in Figure 3b was confirmed. Its formation was further supported by a $^{1}$H DOSY NMR measurement, which gave the same diffusion coefficient for **6**$^{+}$ and **2** ($D = 4.3\times10^{-10}$ [m$^{2}$s$^{-1}$]; Figure S19).

The bowl-shaped **2** has the potential to form an orientated rotaxane with unsymmetrical axles by utilizing the difference in the local environment of the convex and concave faces. Benzylbutylammonium ion **3**$^{+}$ was chosen as the axle for this purpose. The $^{1}$H NMR and UV/Vis titration experiments

***Table 1:*** Binding of ammonium guests to **2** (CHCl$_3$ or CDCl$_3$, 298 K).

| Guest | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | log$K_a$ [log(M$^{-1}$)] |
|---|---|---|---|
| none | 514 | 606 | - |
| **3**$^{+}$ | 514 | 604 | 5.48(3)[a] |
| **6**$^{+}$ | 514 | 603 | 5.49(3)[a] |
| **7**$^{+}$ | 512 | 596 | 4.36(7)[a,c] |
| **8**$^{+}$ | –[e] | –[e] | 2.6(2)[d] |
| **9**$^{+}$ | 511 | 590 | 6.57(7)[a] |
| **10**$^{+}$ | 510 | 587 | 7.2(1)[a] |
| **4**$^{+}$ | 511 | 597 | 8.0(1)[b] |

[a] Determined by UV/Vis titration. [b] Determined by competitive $^{1}$H NMR titration in the presence of 40 equiv of **3**$^{+}$. [c] No threading. [d] Determined by $^{1}$H NMR titration. [e] Not measured.

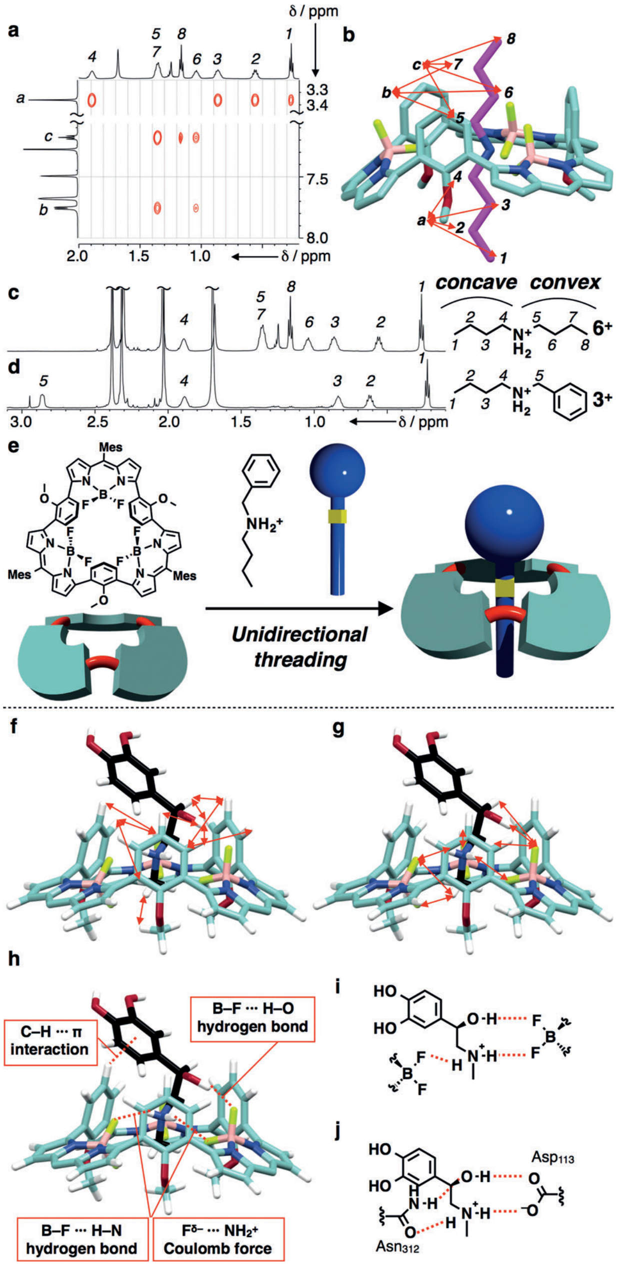
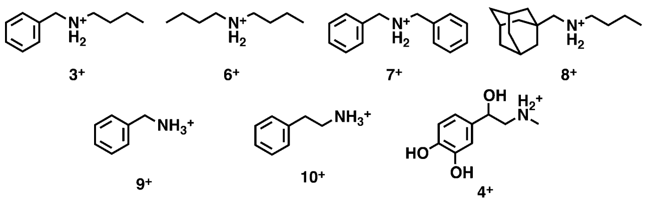


***Figure 3.*** a) $^1$H-$^1$H ROESY NMR spectrum of [**6@2**](TFPB) ($CDCl_3$, 600 MHz, 263 K). b) The structure of [**6@2**]$^+$ obtained by DFT calculations at the B3LYP/6-31G* level. The Mes groups and hydrogen atoms are omitted for clarity. C of **2**: light green; C of **6**: magenta, O: red, N: blue, B: pink, F: yellow-green. Pairs of protons between which ROE cross-peaks were observed are highlighted. c,d) $^1$H NMR spectra of [2]pseudorotaxanes (600 MHz, 263 K, $CDCl_3$): c) [**6@2**](TFPB), d) [**3@2**](TFPB). e) Schematic representation of the unidirectional threading of benzylbutylammonium ion **3**$^+$ into the bowl-shaped BODIPY trimer **2**. f–h) The structure of [**4@2**]$^+$ obtained by DFT calculations at the B3LYP/6-31G* level. C of **2:** light green, C of **4**: black, O: red, N: blue, B: pink, F: yellow-green, H: white. Mes groups are omitted for clarity. f) Pairs of $^1$H-$^1$H atoms between which cross-peaks were observed in the ROESY NMR spectrum (Figure S35). g) Pairs of $^{19}$F-$^1$H atoms between which cross-peaks were observed in the HOESY NMR spectrum (Figure S36). h) Intermolecular interactions between adrenaline **4**$^+$ and BODIPY trimer **2**. i,j) Comparison of the intermolecular hydrogen bonding of adrenaline **4**$^+$ with i) BODIPY trimer **2** and j) a $\beta_2$-adrenaergic receptor protein.[12]

confirmed the 1:1 binding between **3**$^+$ and **2,** with a binding constant ($\log K_a = 5.48(3)$) similar to that of **6**$^+$ and **2** (Figures S21 and S22). The $^1$H NMR spectrum of [**3@2**]$^+$ showed signals characteristic of **3**$^+$ threaded into **2**. Remarkably, only one set of signals was observed for [**3@2**]$^+$, which suggests the selective formation of one conformational isomer. Comparison of the $^1$H NMR chemical shifts of [**3@2**]$^+$ with those of [**6@2**]$^+$ (Figure 3 c,d) revealed that the benzyl group of **3**$^+$ was on the convex side of **2**, while the butyl group of **3**$^+$ was contained within its concave cavity (Figure 3 e). The selectivity of the threading direction was as high as 97 %, as determined from the integral ratios of the $^1$H NMR signals.

The recognition feature of the bowl-shaped BODIPY trimer **2** was revealed by binding experiments with other ammonium guests (Scheme 1, Table 1). The dibenzylammonium ion **7**$^+$ interacted with **2** ($\log K_a = 4.36(7)$) but did not thread into it (Figure S24). It is considered that the benzyl group of **7**$^+$ is too large to pass through the cavity of **2**. The binding of (admantylmethyl)butylammonium ion **8**$^+$ was also weak ($\log K_a = 2.6(2)$), probably because the bulky adamantyl group near the ammonium group destabilizes the formation of the pseudorotaxane. Primary ammonium species, such as benzylammonium ion **9**$^+$ and phenethylammonium ion **10**$^+$, were more strongly bound ($\log K_a = 6.57(7)$ and 7.2(1), respectively) than the secondary ones (**3**$^+$ and **6**$^+$). This result is explained by the increased number of hydrogen bonds between the ammonium NH group and the BODIPY B−F moieties.



***Scheme 1.*** The investigated guests (used as TFPB salts). A racemic DL-adrenaline **4**$^+$ was used in the experiment.

Interestingly, adrenaline **4**$^+$ was bound the strongest of the investigated ammonium guests. The interaction was so strong that its association constant ($\log K_a = 8.0(1)$) could not be determined by ordinary UV titration experiments; it was thus determined by a competition experiment in the presence of an excess amount of **3**$^+$ (Figure S34). Since the binding of secondary ammonium species is generally weaker than primary ones (Table 1), it is remarkable that adrenaline **4**$^+$ (secondary ammonium) exhibited such a strong association constant. The detailed structure of the adrenaline/macrocycle complex was unambiguously determined by $^1$H-$^1$H ROESY and $^{19}$F-$^1$H HOESY NMR measurements, together with the structure obtained by DFT calculations (Figure 3 f,g). As in the case of benzylbutylammonium ion **3**$^+$, the benzene ring of **4**$^+$ was positioned at the convex face of **2**, and the methyl group of **4**$^+$ at the concave face. Several intermolecular interactions contributed to the strong binding of **4**$^+$ (Figure 3 h): 1) Hydrogen bonding between the ammonium NH group of $4^+$ and the BODIPY B−F groups; 2) hydrogen bonding between the hydroxy group of $4^+$ and the BODIPY B−F groups; 3) Coulomb interaction between the cationic ammonium group $NH_2^+$ of $4^+$ and the polarized $B^{\delta+}$−$F^{\delta-}$ bonds of BODIPY; and 4) C−H⋅⋅⋅π interactions between the benzene ring of $4^+$ and the *m*-Ph spacer of **2**. In terms of points (1) and (2), one $BF_2$ moiety undergoes a double hydrogen bonding with the hydroxy and ammonium groups of $4^+$ (Figure 3h,i). This hydrogen bonding was supported by strong correlations between the corresponding $^1$H-$^{19}$F pairs in the $^{19}$F-$^1$H HOESY NMR (Figure S36) as well as no chemical exchange of the ammonium and hydroxy protons with $H_2O$ in the ROESY NMR spectrum (Figure S35). This multiple hydrogen bonding is reminiscent of the recognition mode of adrenaline $4^+$ by the aspartic acid and asparagine residues in the natural $\beta_2$-adrenergic receptor protein (Figure 3j).[12] Several artificial host molecules aiming at recognition of adrenaline $4^+$ and other phenethylamine derivatives have been reported, but it has been difficult to achieve selective recognition through multiple intermolecular interactions modes.[13] In this sense, **2** is a fresh departure from simple artificial macrocycles that recognize guests through nonselective interactions.

In conclusion, the L-shaped dipyrrin macrocycle **1** and bowl-shaped BODIPY macrocycle **2** were synthesized and their unique shapes were unambiguously determined by various NMR techniques and single-crystal X-ray diffraction measurements. **2** formed an oriented [2]pseudorotaxane by unidirectionally threading ammonium guests such as benzylbutylammonium ion $3^+$ and adrenaline $4^+$. Multiple interaction modes, such as hydrogen bonding with the BODIPY B−F bonds and C−H⋅⋅⋅π interactions with the aromatic scaffold, are key to realizing the significantly strong and regiospecific binding. This research should contribute to the design of functional host molecules utilizing multiple interaction modes. In addition, the bowl-shaped ring, whose two faces are desymmetrized, has the potential to realize one-way movement of a molecular machine along the axle fueled by random thermal energy. The study of such sophisticated molecular devices is now in progress.

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**Keywords:** boron · host–guest systems · macrocycles · molecular recognition · supramolecular chemistry

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## Communications

### Molecular Recognition

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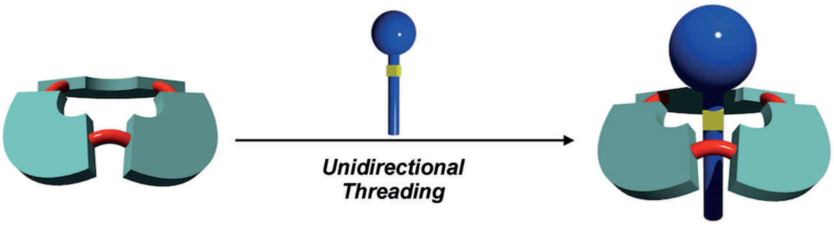
Unidirectional Threading into a Bowl-Shaped Macrocyclic Trimer of Boron–Dipyrrin Complexes through Multipoint Recognition



**Going in to bowl:** A bowl-shaped macrocyclic trimer of a boron–dipyrrin complex has been synthesized in which six polarized B–F bonds are directed towards the center of the macrocycle for strong recognition. Cationic ammonium guests are strongly captured from the convex side of the macrocycle by hydrogen bonding, Coulomb forces, and C–H⋯π interactions and thread unidirectionally through the complex.