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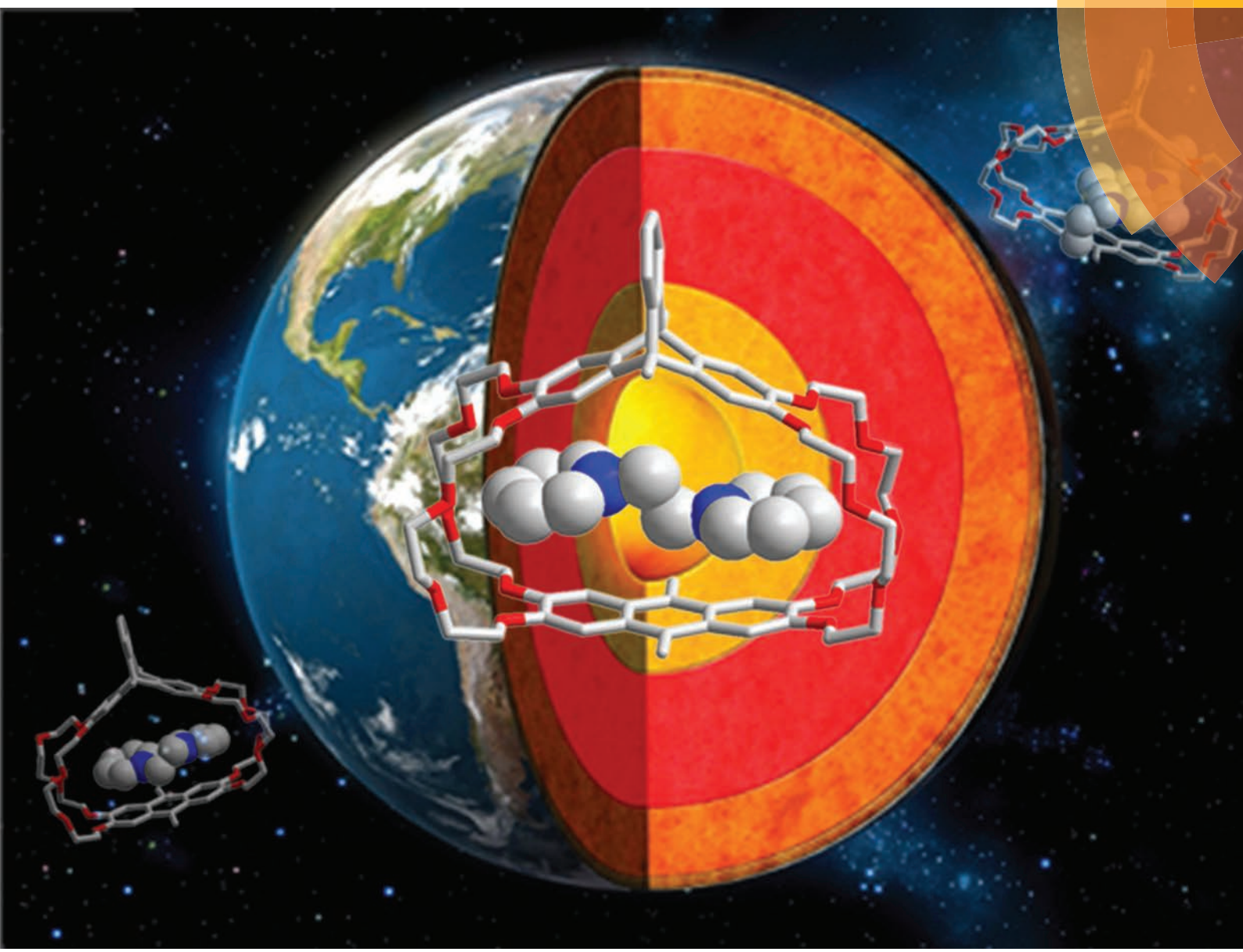

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Triptycene-derived macrotricyclic polyether containing an anthracene unit as a powerful host for 1,2-bis(pyridium)ethane, diquat and 2,7-diazapyrenium salt†

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Triptycene-derived macrotricyclic polyether containing an anthracene unit is a powerful host for 1,2-bis(pyridium)ethane, diquat and 2,7-diazapyrenium salt with association constants of the 1 : 1 complexes at >10^5 M^{-1}. Crystal structures showed that π–π stacking interactions between the host and the guests play an important role in the formation of the stable complexes.

The development of efficient host–guest recognition systems with controllable binding properties has been one of the major goals in the areas of molecular switches, supramolecular assembly and supramolecular catalysis.[1] Developing new classes of hosts and selecting appropriate guests are two of the permanent topics in host–guest chemistry.[2] Special attention has been devoted to the binding between supramolecular hosts and electron-deficient cations through π–π stacking and other noncovalent interactions.[3]

Guests including 1,2-bis(pyridium)ethane (BPE^{2+}), diquat (DQ^{2+}) and 2,7-diazapyrenium (DAP^{2+}) derivatives with different structural features have been widely studied in host–guest chemistry.[4] BPE^{2+} can bind with simple crown ethers, which has been used to construct different interlocked molecules and MOF structures by Loeb, Liu and other groups.[5] But the binding constants of 1 : 1 complexes between BPE^{2+} and crown ethers are only 10^2 M^{-1}. DQ^{2+} as a guest can bind with a variety of hosts including cryptands, calixarenes, pillararenes and cucurbituril,[6] and the binding constants of the complexes vary from 10^2 to 10^5 M^{-1} in organic solvents. DAP^{2+} derivatives with large π-electron systems could have effective binding abilities with macrocyclic hosts; however, reports on the complexation related to this class of guests are still limited.[7] Therefore, exploring an appropriate host to construct highly stable complexes with these guests is theoretically and practically meaningful for their wide potential applications in supramolecular chemistry.

Recently, we[2c,8] have demonstrated that triptycene can be used as a useful building block for the construction of different kinds of macrocyclic hosts with specific structures and properties. As a result, we reported a triptycene-derived macrotricyclic host **1**[9] containing an anthracene unit, which can form cascade complexes with pyromellitic diimide and anthraquinone in the presence of lithium and potassium, respectively. Herein, we report the complexation between host **1** and electron-deficient guests BPE^{2+} (**2a**), DQ^{2+} (**2b**) and $DPDAP^{2+}$ (**2c**) both in solution and in the solid state (Fig. 1). It was found that macrocycle **1** proved to be a powerful host for the three guests with association constants (K_a) of the 1 : 1 complexes at >10^5 M^{-1}. Moreover, different binding modes depending on the guests were also observed. Controllable binding and release of the guests in the complexes were further achieved by adding and removing the potassium ion.

Firstly, we tested the binding abilities of host **1** and guests **2a–2c** in solution. Due to the charge transfer between the electron-rich host and the electron-poor guest, the colorless solution changed into a yellow one in a short period of time when guest **2a** was added into the solution of host **1**. The ^1H NMR spectrum of an equimolar (3.0 mM) mixture of host **1** and

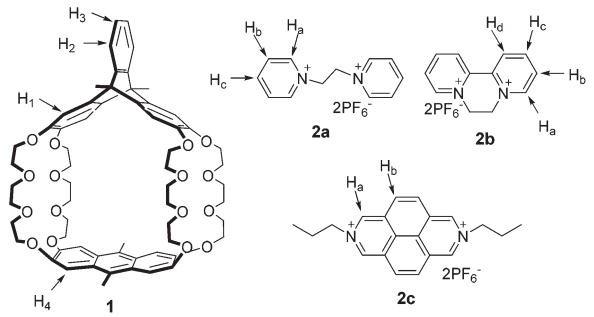

Fig. 1 Chemical structures and proton designations of host **1** and guests **2a–2c**.

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†Electronic supplementary information (ESI) available: Mole ratio plots, ^1H–^1H COSY, ESI-MS spectra, X-ray crystallographic files for **1·2a–1·2c**. CCDC 979732–979734. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob00310a

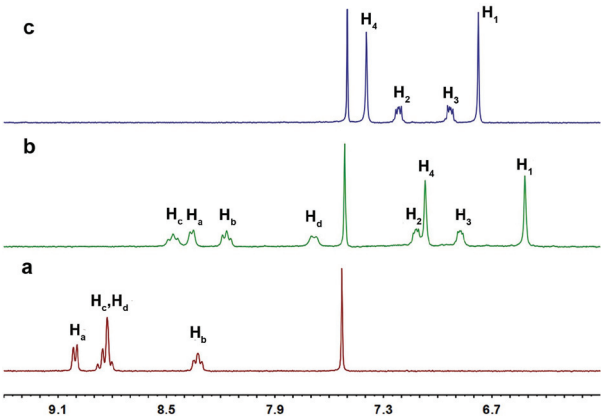

Fig. 2 Partial ^{1}H NMR spectra (300 MHz, CD_3CN–$CDCl_3$ = 1 : 1, v/v, 295 K) of (a) free guest **2a**, (b) **1** and 1.0 equiv. of **2a**, and (c) free host **1**. $[\mathbf{1}]_0$ = 3.0 mM.

aromatic cation **2a** in $CDCl_3$–CD_3CN (1 : 1 v/v) showed only one set of resonances, which suggested that a new stable complex **1**·**2a** was formed, and the binding was a fast exchange process (Fig. 2). The significant upfield shift ($\Delta\delta$ −0.95 ppm) of H_a proton signal of guest **2a** was observed, which could be attributed to the strong shielding effect of the aromatic rings of **1**. A similar effect of aromatic cation **2a** also resulted in the upfield shift of protons H_1–H_4 of host **1**. Because of the strong shielding effect of the aromatic rings of **1**, upfield shifts of the aromatic protons for both **1**·**2b** and **1**·**2c** were also observed.[10] Similar to the case of **1**·**2a**, complexes **1**·**2b** and **1**·**2c** exhibited typical charge transfer with the color of the final solutions in green-brown and tan, respectively.

Furthermore, we quantitatively estimated the binding properties between host **1** and guests **2a–2c** through ^{1}H NMR spectroscopic titrations. The results showed that host **1** could form 1 : 1 complexes with guests **2a–2c** by the mole ratio plot. Correspondingly, association constants $K_{\mathbf{1}\cdot\mathbf{2a}}$, $K_{\mathbf{1}\cdot\mathbf{2b}}$ and $K_{\mathbf{1}\cdot\mathbf{2c}}$ for the three complexes were further calculated to be 1.06 (±0.01) × 10^5, 6.37(±0.02) × 10^5 and 1.51(±0.01) × 10^6 M^{-1}, respectively, by fitting the data using a nonlinear regression algorithm.[11] It was noteworthy that $K_{\mathbf{1}\cdot\mathbf{2b}}$ was almost 200 times larger than the association constant of a similar complex previously reported.[12] Moreover, to our knowledge, these binding constants are also the largest ones among the known complexes based on guests **2a–2c** in organic solvents.[5–7]

In order to analyze the binding constants of the three complexes, we further analyzed the electron charge density of the guests by DFT(B3LYP) calculations using the 6-31G* basis set. As shown in Fig. 3, these cationic guests have similar electron-deficient distributions. The interaction between the two pyridinium rings is weak in **2a** because of the long distance. In **2b**, the distance between two pyridine rings was shorter than in **2a**, which augmented the π–π conjugation between the adjacent pyridine rings. Therefore, the electron densities in both pyridine rings were reduced. This effect made **2b** a more effective π-electron acceptor than **2a**.[13] As a result, the reduced π-electron in pyridine ring of **2b** lowered the exchange-repulsion[14] and enhanced the π–π stacking interaction with triptycene and anthracene units of host **1**. Consequently, host **1** had a more efficient binding ability for **2b** than for **2a**. Furthermore, complex **1**·**2c** with the largest association constant was due to the larger number of π-electron systems within **2c** than those in **2a** and **2b**, which makes **2c** form much stronger π–π stacking interactions with host **1**.

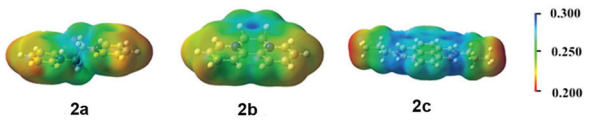

Fig. 3 DFT calculated electron charge distributions (Å^{-3}) of **2a–2c**.

Formation of the stable 1 : 1 complexes between host **1** and the three guests was also demonstrated by the electrospray ionization mass spectrometry. Consequently, the strongest peaks at m/z 1403.6 for $[\mathbf{1}\cdot\mathbf{2a}\text{-}PF_6]^+$, 628.3 and 681.3 for $[\mathbf{1}\cdot\mathbf{2b}\text{-}2PF_6]^{2+}$ and $[\mathbf{1}\cdot\mathbf{2c}\text{-}2PF_6]^{2+}$ in 1 : 1 (v/v) chloroform and acetonitrile were observed.[10]

Furthermore, suitable single crystals of complex **1**·**2a** for X-ray diffraction were obtained by vapor diffusion of isopropyl ether into a 1 : 1 (v/v) $CHCl_3$–CH_3CN solution containing a mixture of the two components. The crystal structure revealed formation of the 1 : 1 complex between **1** and **2a**. As shown in Fig. 4a, guest **2a** was located in the center of the cavity of host **1**, and the two pyridine rings of **2a** exhibited a dihedral angle of 11.79°. This binding mode is totally different from that of the complex between guest **2a** and the simple [24]-crown-8 ether,[15] which might be attributed to that host **1** contains a three-dimensional electron-rich cavity; thus guest **2a** has a greater tendency to be encapsulated inside the central cavity rather than threading the cavity of lateral [24]-crown-8 ether. In complex **1**·**2a**, there existed not only multiple C–H···O hydrogen bonding interactions, but also π–π stacking interactions between the two pyridinium rings of the guest and the aromatic rings of the anthracene ($d_{\pi-\pi}$ = 3.52 Å for AC and 3.81 Å for BD) and triptycene moieties ($d_{\pi-\pi}$ = 3.82 Å for BF) (Fig. 4b).

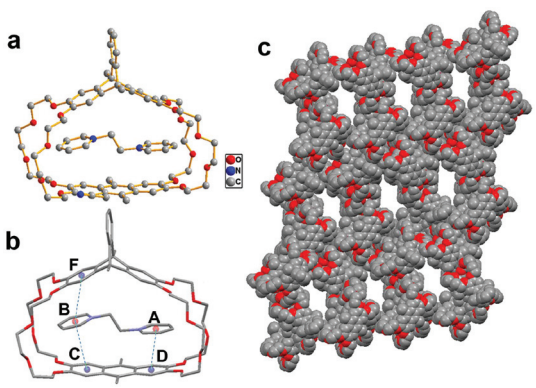

Fig. 4 (a, b) Crystal structure of **1**·**2a**, the dash lines denote the non-covalent interactions between **1** and **2a**. (c) Packing of **1**·**2a** with a 3D microporous structure. Solvent molecules, PF_6^- counterions, and hydrogen atoms were omitted for clarity.

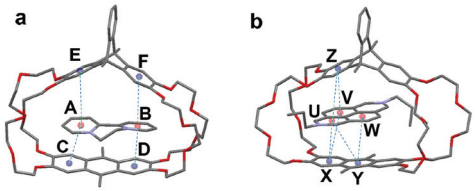

Fig. 5 Crystal structures of (a) **1·2b** and (b) **1·2c**. The distances (Å) for the π–π stacking interactions: AC = 3.55, BD = 3.53, AE = 3.92. UX = 3.58, UY = 3.89, VX = 3.88, WY = 3.62. Solvent molecules, PF_6^- counter-ions, and hydrogen atoms were omitted for clarity.

These multiple non-covalent interactions play an important role in the formation of stable complex **1·2a**. Moreover, the crystal packing of the complex also showed a 3D microporous supramolecular structure (Fig. 4c) with solvent molecules and PF_6^- anions situated inside the channels.

Formation of 1 : 1 complexes of **1·2b** and **1·2c** was also confirmed by their X-ray crystal structures (Fig. 5). Similar to the structure of complex **1·2a**, guest **2b** was also located at the center of the host cavity, and π–π stacking interactions between the host and the guest were observed. For complex **1·2c**, it was found that guest **2c** threaded the central cavity of host **1** to form a [2]pseudorotaxane-type complex, which is different from the complex modes of **1·2a** and **1·2b**. Because of the strong electron-deficient properties of guest **2c**, it could form the most stable complex with host **1** compared with two other complexes. These results are consistent with those of the theoretical evaluation.

It has been proved that host **1** could form a 1 : 2 stable complex with K^+ ions by complexation with two dibenzo[24]-crown-8,[9] which could introduce electrostatic repulsion into the organic guest to dissociate the previously formed complex. Therefore, we further investigate the ion-controlled binding and release of the guests in the complexes. When 4.0 equivalents of KPF_6 were added into the solution of **1·2a**, the color of the solution turned from yellow to colorless immediately. Meanwhile, the ^{1}H NMR spectrum showed that the aromatic proton signals in **1·2a** shifted downfield to almost the original positions of free host **1** and guest **2a** (Fig. 6d), suggesting that decomplexation of **1·2a** occurred while the crown cavities coordinate with potassium ions. When 6.0 equivalents of KPF_6 were added into the above system, the yellow solution reappeared. Correspondingly, the ^{1}H NMR spectrum displayed the proton signals of **1·2a**. Thus, the binding and release of **2a** in the complex could be easily induced by adding and removing the potassium ion. Similarly, K^+-ion-controlled binding and release of **2b** and **2c** in their host–guest complexes could also be achieved.[10]

Conclusions

In conclusion, we have demonstrated that the triptycene-derived macrotricyclic polyether containing an anthracene unit is a powerful host for 1,2-bis(pyridium)ethane, diquat and

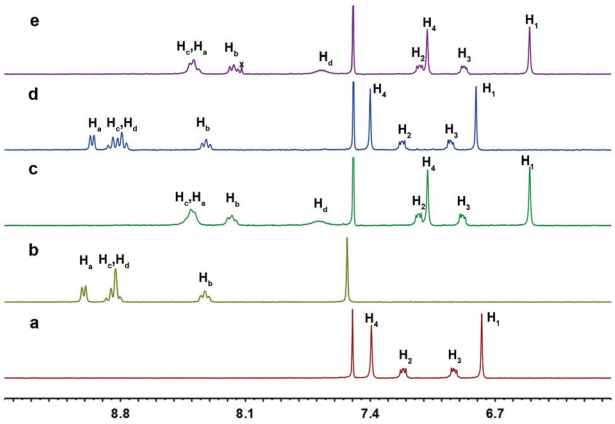

Fig. 6 Partial ^{1}H NMR spectra (300 MHz, CD_3CN–$CDCl_3$ = 1 : 1, v/v, 295 K) of (a) free host 1, (b) free guest **2a**, (c) 1 and 1.0 equiv. of **2a**, (d) to the solution of (c) was added 4.0 equiv. of KPF_6, and (e) to the solution of (d) was added 6.0 equiv. of [18]-crown-6. $[\mathbf{1}]_0$ = 3.0 mM.

2,7-diazapyrenium salt. The host and the guests could form 1 : 1 stable complexes in $CHCl_3$–CH_3CN (1 : 1, v/v) solution with association constants of more than 10^5 M^{-1}, which represented the largest ones among the known complexes based on these three guests in organic solvents. Crystal structures showed that different binding modes depending on the guests with different structural features were observed, and multiple non-covalent interactions, especially the strong π–π stacking interactions between the host and the guests, play an important role in the formation of the stable complexes. Moreover, the binding and release of the guests in the complexes could also be controlled by the addition and removal of potassium ions.

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