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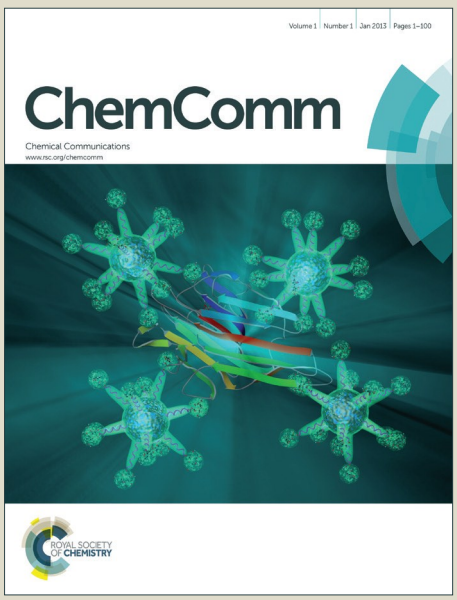

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ARTICLE TYPE

Acid/base controllable complexation of triptycene-derived macrotricyclic host and protonated 4,4'-bipyridinium/pyridinium salts

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A new acid/base controllable host-guest system based on triptycene-derived macrotricyclic host and protonated 4,4′-bipyridinium/pyridinium salts was developed. Moreover, a competition complexation process between the host and two different kinds of 4,4′-bipyridinium salts could also be chemically controlled by acid and base.

Host−guest systems[1] which can respond to external stimuli have attracted much attention due to their wide applications in such as molecular machines,[2] responsive supramolecular polymers,[3] and self-healing materials.[4] Development of novel responsive host-guest systems in specific complexation modes is always a very important and attractive topic. It was known that 1,1′-disubstituted 4,4′-bipyridinium salts[5] and 1-substituted pyridinium salts[6] are ones of the most common guests, and they have been utilized for construction of different kinds of responsive host-guest systems. However, applications of protonated 4,4′-bipyridinium and protonated pyridinium salts as guests in host-guest chemistry are very limited.[7] Protonated 4,4′-bipyridinium and 4-pyridinium salts are easily deprotonated to be 4,4′-bipyridine and pyridine, and vice versa, which could make the association and disassociation of the complexes based on the protonated 4,4′-bipyridinium and protonated pyridinium salts be easily chemically controlled by acid and base, which is very different from those of the complexes based on the 1,1′-disubstituted 4,4′-bipyridinium and 1-substituted pyridinium salts, in which ion-controlled processes were usually performed.[8] However, to the best of our knowledge, no acid-base controlled association/disassociation processes of the complexes based on protonated 4,4′-bipyridinium salts and protonated pyridinium salts have been reported so far.

Previously, we reported a novel triptycene-derived macrotricyclic host **1** containing two dibenzo-24-crown-8 moieties, and found that the host could form complexes with various 1,1′-disubstituted 4,4′-bipyridinium salts, such as guest **6**.[9] Moreover, the binding and release of the guests in the complexes could be controlled by potassium ions. Herein, we report a novel responsive host-guest system based on macrotricyclic host **1** and protonated 4,4′-bipyridinium salts **2-3**, and protonated 4-substituted pyridinium salts **4-5** (Fig. 1) in both solution and solid state. It was found that host **1** can form 1:1 complex with diprotonated 4,4′-bipyridinium **2**, but 1:2 complexes with mono-protonated 4,4′-bipyridinium **3** and pyridinium salts **4-5** in different complexation modes. Notably the binding and release of the guests in the complexes can be easily controlled by acid and base. Moreover, the competitio complexation process between the host with two different kind of 4,4′-bipyridinium salts (**2** and **6**) can also chemically controlled.

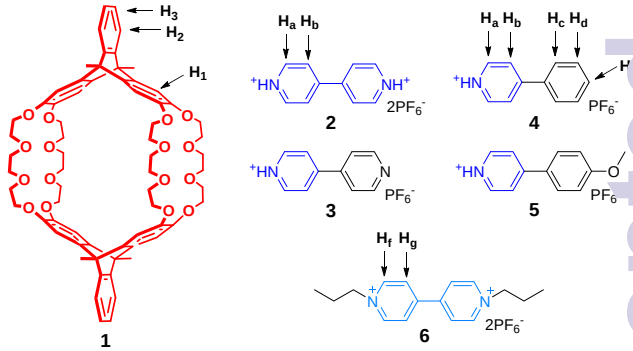

Fig. 1 Structures and proton designations of host **1**, and guests **2-6**.

First, we tested the complexation between host **1** an guests **2-5** in solution by the ^{1}H NMR spectroscopic method. As shown in Fig. 2, the ^{1}H NMR spectrum of a 1:1 de yellow mixture of **1** and **2** in $CDCl_3$ and CD_3CN (1:1, v/v) exhibited a well-defined set of signals, and they are different from those for the separated host and guest, which suggested that a new complex **1·2** was formed, and the complexatio between **1** and **2** was a fast exchange process. Especially, was found that the proton H_a of the bipyridinium ring showed a upfield shift ($\Delta\delta$ = 0.10 ppm) due to the shielding effect c aromatic rings in **1**, and H_1 and H_b proton signals also shifte upfield. Moreover, the 2D NMR spectrum (Fig. S16) showe the cross-peaks between proton H_a in the bipyridinium ring of **2** and the protons in crown ether units of **1**, which suggeste that the guest could thread the two crown ether cavities of host **1**. Furthermore, ^{1}H NMR spectroscopic titrati ns afforded a quantitative estimate between **1** and **2** monitoring the changes of the chemical shift of proton H_1. A mole ratio plot showed that a 1:1 complex **1·2** was formed Moreover, the association constant K_a for **1·2** was calculate to be 1.8(±0.12)×10^4 M^{-1} by nonlinear curve-fitting method (Fig. S22).[10,11]

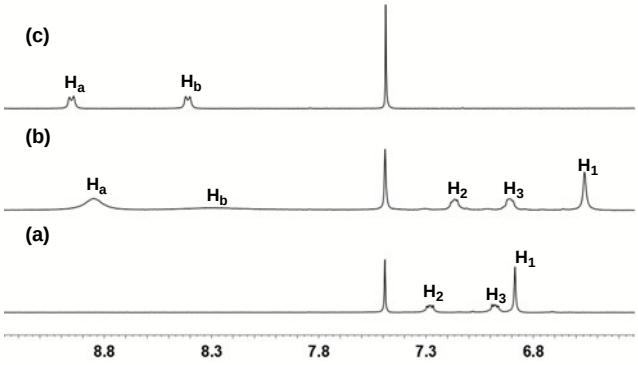

Fig. 2 Partial ^{1}H NMR spectra (300 MHz, 298 K, $CD_3CN/CDCl_3$ = 1:1, v/v) of (a) free **1**, (b) **1** and 1.0 equiv of **2**, (c) free **2**. $[\mathbf{1}]_0$ = 3.0 mM.

For mono-protonated 4,4′-bipyridinium salt **3**, it was interestingly found that its complexation with host **1** was also a fast exchange process (Fig. S9), but the stoichiometry of the complex was determined to be 1:2 by a mole ratio plot, which is very different from 1:1 complex **1·2**. According to the ^{1}H NMR spectroscopic titrations, the association constants K_{a1} and K_{a2} for **1·3**$_2$ were calculated to be 420(±25) and 100(±8) M^{-1}, respectively, by the nonlinear curve-fitting method (Fig. S27).[12] Similarly, host **1** also formed 1:2 complexes with pyridinium salts **4** and **5**, respectively. The association constants K_{a1} and K_{a2} were calculated to be 410(±11) and 340 (±28) M^{-1} for **1·4**$_2$, and 560(±61) and 160(±19) M^{-1} for **1·5**$_2$.[10]

The electrospray ionization (ESI) mass spectra provided more evidence for formation of the complexes.[10] As a result, the strong peaks at *m/z* 653.3, 1451.5 for $[\mathbf{1{\cdot}2}\text{-}2PF_6^-]^{2+}$ and $[\mathbf{1{\cdot}2}\text{-}PF_6^-]^+$ were found by using a solution of **1** and **2** in 1:1 (v/v) $CHCl_3$ and acetonitrile, which supported the formation of the 1:1 complex. Similarly, formation of the complexes between host **1** and guests **4** and **5** were also supported by the ESI mass spectra, in which the strong peaks at *m/z* 1605.6, 1665.6 for $[\mathbf{1{\cdot}4}_2\text{-}2PF_6]^{2+}$ and $[\mathbf{1{\cdot}5}_2\text{-}2PF_6]^{2+}$, were observed, respectively.[10] For complex **1·3**$_2$, the peak at *m/z* 653.3 for $[\mathbf{1{\cdot}3}\text{+H-}PF_6^-]^{2+}$ instead of $[\mathbf{1{\cdot}3}_2\text{-}2PF_6]^{2+}$ was found, which might be due to the easily protonation of the pyridine group in **3** so that the complexation could be changed into the same 1:1 mode as that of complex **1·2** under the tested conditions.

By vapor diffusion of diisopropyl ether into a solution of **1** and the guests in CH_3CN and $CHCl_3$ (1:1, v/v), we obtained single crystals suitable for X-ray diffraction analysis. As shown in Fig. 3a, guest **2** is encapsulated in the center of the macrotricyclic host, and the two pyridinium rings of **2** are nearly coplanar. Moreover, the two NH groups in **2** are positioned in the two crown ether cavities, which results in 1:1 complex **1·2** in solid state, which is consistent with that in solution. There existed multiple π-π interactions between the bipyridinium ring of **2** and the aromatic rings of the triptycene moieties of **1** with the distances of 3.30 (a), 3.24 (b), 3.28 (c) and 3.30 Å (d), and multiple C-H···O hydrogen bondings between the protons of bipyridinium ring and ether oxygen atoms of the host with the distances of 2.70 (A), 2.59 (B), 2.53 (C), 2.38 (D), 2.38 (E), 2.53 (F), 2.59 (G), and 2.70 Å (H). These multiple interactions play an important role in the formation of complex **1·2**.

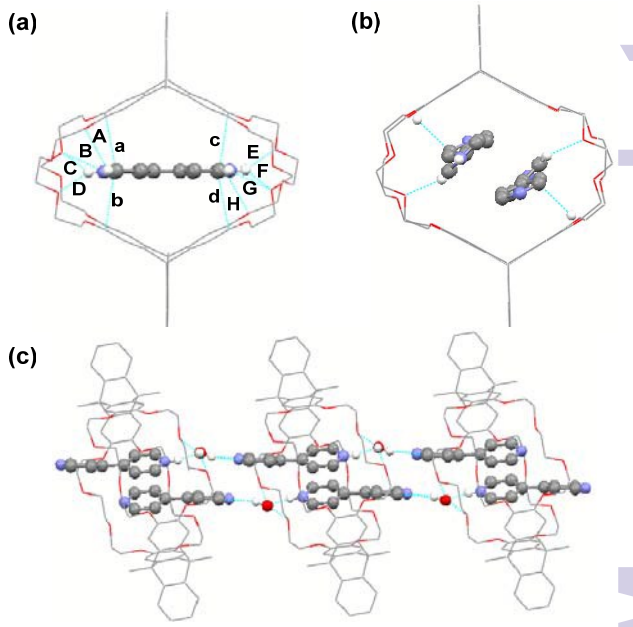

Fig. 3 Crystal structures of complexes **1·2** (a) and **1·3**$_2$ (b). (c) 1D linear structure by linking complex **1·3**$_2$ with water. Solvent molecules, PF_6^- counterions and hydrogen atoms not involved in the non-covalent interactions are omitted for clarity.

It is obviously different from **1·2** that host **1** formed 1:2 complex **1·3**$_2$ with guest **3** in the solid state, in which two guests threaded the central cavity of the host by a staggered mode (Fig. 3b). We also found that the two guests were distorted by the dihedral angles between the pyridinium rings of 24.59˚ and 24.38˚, respectively. There also existed C-H···O hydrogen bonding between the protons of pyridinium ring and ether oxygen atoms of the host, and the π-π stacking interactions between the bipyridinium ring and the aromatic rings of the triptycene moieties. Interestingly, it was also found that water molecules could connect the adjacent complexes to form a 1D linear structure by virtue of multiple C-H···π interactions, C-H···O hydrogen bonding, and N-H hydrogen bonding between water and the complex (Fig. 3c).[10] The different complexation between host **1** and guests **2** and **3** suggested that a small structural change in the guest could result in the formation of a complex with different structure and complexation mode, which might be useful in developing new supramolecular systems.

Similar to complex **1·3**$_2$, it was found that host **1** could also form 1:2 complexes **1·4**$_2$ and **1·5**$_2$ with protonated pyridinium salts **4** and **5**, respectively, in the solid state. As shown in Fig. 4, two guests **4** or **5** threaded symmetrically the central cavity of host **1** to form 1:2 complexes. Interestingly, it was found that due to the different electrostatic effect between benzene ring and pyridine ring, the two guest located in the central cavity of host **1** to form "head to tail" structure, which could provide an opportunity to construct the assemblies with specific structures and properties.[13]

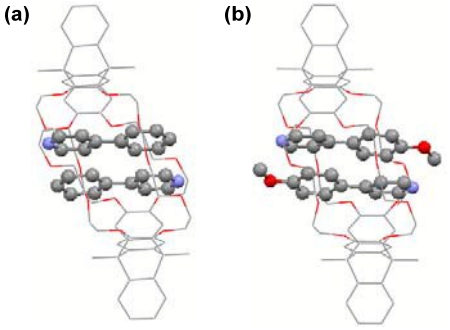

Fig. 4 Crystal structures of complexes **1**·4_2 (a) and **1**·5_2 (b). Solvent molecules, PF_6^- counterions and hydrogen atoms are omitted for clarity.

Since 4,4′-bipyridine and pyridine are easily protonated to be protonated 4,4′-bipyridinium and pyridinium salts, and vice versa, we found that the association and disassociation of the complexes between host **1** and protonated 4,4′-bipyridinium salt **2** (Fig. 5a) or guests **3**-**5** could all be chemically controlled by acid and base (Fig. S46 and Fig. S47), which could not be achieved for the complexes based on 1,1′-disubstituted 4,4′-bipyridinium and 1-substituted pyridinium salts.[9,14]

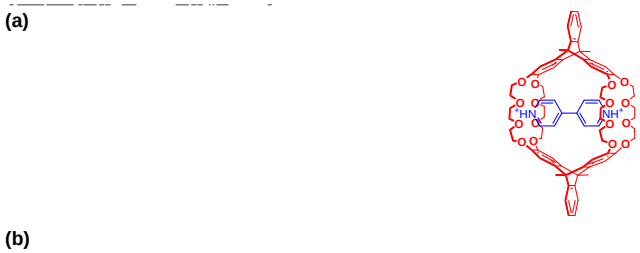

Fig. 5 (a) Schematic representation of acid-base controlled complexation process, and (b) acid-base controlled competitive complexation process.

The easy protonation of 4,4′-bipyridine also inspired us to further examine the competitive binding abilities of the host toward different kinds of guests (Fig. 5b). Firstly, we mixed host **1** (3.0 mM) and 1.0 equiv of 4,4′-bipyridine in 1:1 (v/v) $CD_3CN/CDCl_3$, and found no complexation occurred (Fig. 6b). When 1 equiv of **6** was added to the above solution, a stable complex **1**•**6** formed (Fig. 6c). After excess TFA was added to the above solution, H_a, H_b of guest **2** shifted downfield, and H_g, H_f of guest **6** shifted downfield almost to the original position (Fig. 6d), which indicates that complex **1**•**2** formed, while complex **1**•**6** disassociated. To the above solution was added excess Et_3N, and guest **2** was deprotonated, which resulted in the disassociation of **1**•**2**, and reformation of complex **1**•**6** (Fig. 6e). These results showed that the competition complexation process between the host and two different 4,4′-bipyridinium salts could be chemically controlled by acid and base. The reversible complexation process provides a on-off switch which can be used in the construction of controllable molecular switches.

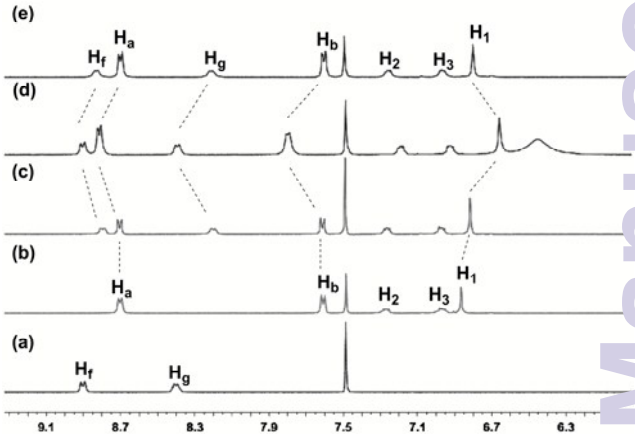

Fig. 6 Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **6**, (b) **1** and 1.0 equiv of 4,4'-bipyridine, (c) to the solution of b was added 1.0 equiv. of **6**, (d) to the solution of c was added 4.0 equiv. of TFA, and (e) to the solution of c was added 6.0 equiv. of Et_3N. $[\mathbf{1}]_0$ = 3.0 mM.

In conclusion, we have developed a new responsive host-guest system based on the triptycene-derived macrotricyclic host and protonated 4,4′-bipyridinium/pyridinium salts. It was found that the triptycene-derived macrotricyclic host could form 1:1 complex with diprotonated 4,4′-bipyridinium salt but 1:2 complexes with mono-protonated 4,4′-bipyridinium and protonated pyridinium salts in different complexation modes in both solution and solid state. Especially, two guests **4** or **5** could form "head to tail" assemblied structure in the complex. Moreover, the association and disassociation of the complexes could be chemically controlled by acid and base which could not be achieved in the complexes based on 1,1′-disubstituted 4,4′-bipyridinium salts and 1-substituted pyridinium salts. Furthermore, it was found that a competition complexation process between the host and two different 4,4′-bipyridinium salts could also be chemically controlled. The results presented here can provide us an opportunity to further design and construct new supramolecular assemblies with specific structures and responsive properties, which are now underway.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization data of new compounds. Determination of the association constants. ESI-MS for the complexes. X-ray crystallographic files (CIF) for complexes **1·2**, **1·3**$_2$, **1·4**$_2$ and **1·5**$_2$. For the ESI and crystallographic data in CIF, see DOI: 10.1039/b000000x/

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