



# Crown ether-based cryptand/tropylium cation inclusion complexes



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## ABSTRACT

Host–guest complexation between crown ether-based cryptand hosts and a carbonium ion, tropylium hexafluorophosphate was studied. <sup>1</sup>H NMR, NOESY NMR, and electrospray ionization mass spectrometry were employed to characterize these inclusion complexes. The contrast tests of <sup>1</sup>H NMR and association constants indicated that cryptands are much better hosts for tropylium hexafluorophosphate than the corresponding simple crown ethers. C–H⋯O hydrogen bonding, face-to-face π-stacking interactions, and charge-transfer interactions are thought to be the main driving forces for the formation of these host–guest complexes. These multiple non-covalent interactions may jointly contribute to the complex formation and considerably reinforce the complex stability. Moreover, the complexation between dibenzo-24-crown-8-based cryptand **4** and tropylium hexafluorophosphate **7** can be reversibly controlled by adding KPF<sub>6</sub> and then DB18C6 in 1:1 acetonitrile/chloroform, providing a new cation-responsive host–guest recognition motif for supramolecular chemistry.

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## 1. Introduction

During the past decades, supramolecular chemistry, chemistry beyond the covalent bond, has developed rapidly with the purpose of imitating the complex self-assembled structures in the natural world.<sup>1</sup> As an active and important part of supramolecular chemistry, host–guest chemistry, which aims at developing sophisticated chemical systems with novel topologies and/or important functions by molecular recognition and self-organization of components based on non-covalent interactions, has played a significant role in the development of supramolecular chemistry due to its wide applications in the fabrication of artificial molecular machines,<sup>2</sup> supramolecular polymers,<sup>3</sup> and other advanced supramolecular materials.<sup>4</sup> It was first demonstrated by Stoddart and co-workers in 1987 that crown ethers could bind paraquat (*N,N'*-dimethyl-4,4'-bipyridinium) dications in acetone.<sup>5</sup> Later, Loeb and co-workers found that 24-crown-8 can complex 1,2-bis(pyridinium)-ethane derivatives.<sup>6</sup> Then, these host–guest recognition motifs have been widely used in the efficient preparation of various threaded structures including pseudorotaxanes, rotaxanes, and metal–organic rotaxane frameworks (MORFs), which has vastly promoted the development of supramolecular chemistry.<sup>7</sup> Therefore, designing and preparing new macrocyclic hosts and various guest molecules and establishing novel host–guest recognition motifs, especially the

ones, which can respond to external stimuli have been a topic of great current interest.<sup>8</sup>

Cryptands, a kind of crown ether derivatives, which were first reported in 1968 and gained a wide range of interests during the past decade, are three-dimensional bicyclic hosts with adequate cavities that are suitable for encapsulating ions and small molecules.<sup>9</sup> By virtue of a significant contributions made by Gibson, Huang, and co-workers, cryptands have been demonstrated to be much better hosts for organic salts compared with simple crown ether counterparts because of the introduction of additional binding sites and the preorganization of the host structures during the association process.<sup>10</sup> Therefore, the design and investigation of new recognition motifs based on cryptands will undoubtedly push forward not only the development of cryptand-based host–guest chemistry but also the research on threaded structures.

The tropylium cation, which possesses a positive center and planar rigid structure, is a typical aromatic system. These interesting characteristics make it an effective π-acceptor and ideal guest for charge-transfer complexation with various π-electron-rich counterparts, thereby facilitating the construction of advanced supramolecular architectures. Even so, the reports on the host–guest recognition of macrocyclic hosts to tropylium cation are still rare. A recent example is that Li and co-workers reported the charge-transfer inclusion complex of pillararenes with tropylium cation.<sup>11</sup> It was demonstrated that tropylium cation can selectively associate with a pillar[6]arene with an association constant of  $1.8 \times 10^3 \text{ M}^{-1}$ .

Herein, we report three novel inclusion complexes based on the recognition of crown ether-based cryptands to tropylium cation

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with high binding abilities and stimuli-responsiveness. In this paper, we select *cis*-dibenzo-24-crown-8 (DB24C8)-based cryptand **4**, bis(*m*-phenylene)-26-crown-8 (BMP26C8)-based cryptand **5**, and bis(*m*-phenylene)-32-crown-10 (BMP32C10)-based cryptand **6** as the hosts and tropylium hexafluorophosphate **7** as the guest (Fig. 1). Meanwhile, the host–guest complexations of the corresponding simple crown ethers DB24C8 diol **1**, BMP26C8 diol **2**, and BMP32C10 diol **3** with tropylium hexafluorophosphate **7** were also studied as a comparison (Fig. 1). It is worth mentioning that the host–guest inclusion complex **4**⊃**7** can be reversibly controlled by adding and removing potassium cation in 1:1 acetonitrile/chloroform.

complexes (**4**⊃**7**, **5**⊃**7**, and **6**⊃**7**) were of 1:1 stoichiometry in solution (Fig. 2). The Job plots of **1**⊃**7**, **2**⊃**7**, and **3**⊃**7** showed the same results too (Fig. S1).

## 2.2. Electropray ionization mass spectrometry

Electrospray ionization mass spectra (ESI-MS) of the solutions of **4**–**6** and **7** in 1:1 acetonitrile/chloroform provided further support for the formation of 1:1 complexes between cryptands **4**–**6** and tropylium hexafluorophosphate **7** in solution. As shown in Fig. 3, all equimolar mixtures of **4** and **7**, **5** and **7**, and **6** and **7** have strong mass fragments of  $[\text{H}\text{D}\text{G}-\text{PF}_6]^+$ :  $m/z$  730.4 (100%) for

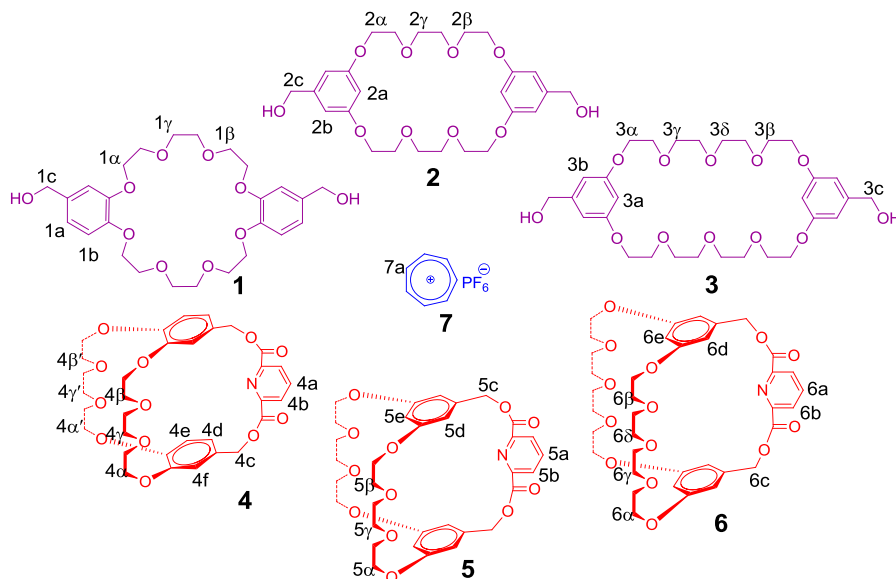


Fig. 1. Chemical structures of crown ethers **1**–**3**, cryptands **4**–**6**, and tropylium hexafluorophosphate **7**.

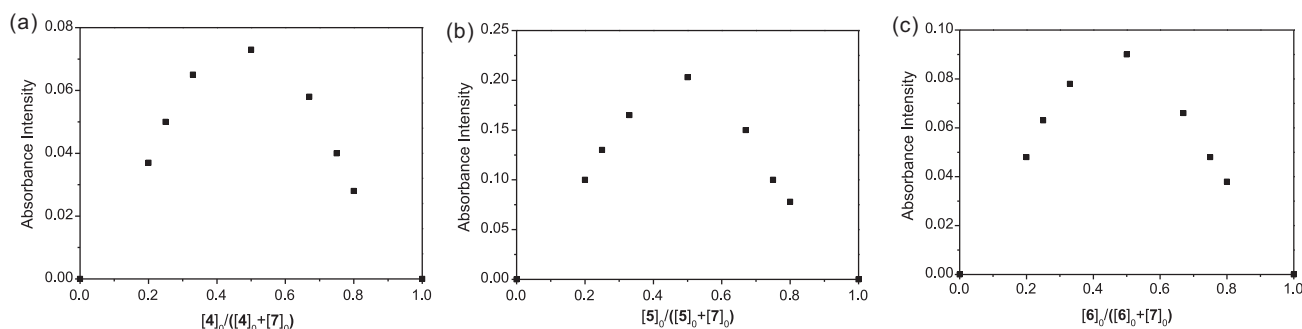


Fig. 2. Job plots showing the 1:1 stoichiometries of the complexations between **4** and **7** (a), between **5** and **7** (b), and between **6** and **7** (c) in 1:1 acetonitrile/chloroform: (a)  $[\mathbf{4}]_0 + [\mathbf{7}]_0 = 0.500$  mM; (b)  $[\mathbf{5}]_0 + [\mathbf{7}]_0 = 0.500$  mM; (c)  $[\mathbf{6}]_0 + [\mathbf{7}]_0 = 0.500$  mM.  $[\mathbf{4}]_0$ ,  $[\mathbf{5}]_0$ ,  $[\mathbf{6}]_0$ , and  $[\mathbf{7}]_0$  are the initial concentrations of **4**, **5**, **6** and **7**, respectively.

## 2. Results and discussion

### 2.1. Determination of stoichiometries of the complexations between cryptands **4**–**6** and tropylium hexafluorophosphate **7**

Equimolar 1:1 acetonitrile/chloroform solutions of each of the cryptands **4**, **5**, and **6** with tropylium hexafluorophosphate **7** were yellow due to charge-transfer interactions between the electron-rich aromatic rings of the cryptand hosts and the electron-poor tropylium ring of the guest **7**, giving direct evidence for complexation. Job plots<sup>12</sup> based on UV–vis absorption spectroscopy of the charge-transfer band demonstrated that all these host–guest

$[\mathbf{4}\text{D}\mathbf{7}-\text{PF}_6]^+$ ,  $m/z$  730.3 (100%) for  $[\mathbf{5}\text{D}\mathbf{7}-\text{PF}_6]^+$ , and  $m/z$  818.3 (32.5%) for  $[\mathbf{6}\text{D}\mathbf{7}-\text{PF}_6]^+$ . No peaks with other complexation stoichiometries were found. Electropray ionization mass spectra of equimolar 1:1 acetonitrile/chloroform solutions of **1** (or **2**, **3**) with **7** were studied at the same time (Figs. S7–S9).

### 2.3. Determination of association constants of **1**⊃**7**, **2**⊃**7**, **3**⊃**7**, **4**⊃**7**, **5**⊃**7**, and **6**⊃**7**

Then association constants ( $K_a$ ) of complexes **1**⊃**7**, **2**⊃**7**, **3**⊃**7**, **4**⊃**7**, **5**⊃**7**, and **6**⊃**7** were determined in 1:1 acetonitrile/chloroform by probing the charge-transfer band of the complexes by

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