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Digest paper

Supramolecular systems constructed by crown ether-based cryptands

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ABSTRACT

Cryptands, seen as a kind of crown ether derivatives, have attracted much attention because of their three dimensional spatial structures and additional binding sites. Moreover, by changing functional groups on the third arm, various stimuli-responsive host–guest systems were obtained, which have played key roles in the construction of functional supramolecular systems. The recent advances in supramolecular systems constructed by crown ether-based cryptands, and further applications, especially in supramolecular polymers are summarized in this digest paper.

Contents

Introduction

The development of new kind of hosts is one of the most important topics in host–guest chemistry. Crown ethers as the first generation of synthetic hosts have been extensively used in various fields, such as supramolecular polymers,[1] molecular machines[2] and drug delivery materials.[3] However, the flexible structures and relatively monotonous complexation modes of simple crown ethers have limited their further applications in the efficient fabrication of advanced supramolecular architectures. Thus, designing and synthesizing novel crown ether-based hosts with specific structures and properties have attracted increasing attentions so far.

Crown ether-based cryptands, a kind of crown ether derivatives, have received great attentions due to their three dimensional spatial architectures and potential applications in the construction of advanced supramolecular systems. Moreover, in many cases, crown ether-based cryptands have been proved to be more influential hosts than the corresponding simple crown ethers for the

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introduction of additional binding sites and the preorganization during the association process. More importantly, the different additional arms on cryptands played crucial roles in constructing host–guest systems responsive to various external stimuli, which was crucial for the fabrication of functionalized supramolecular systems.

In the past two decades, a series of crown ether-based cryptands were elegantly designed and prepared, serving as one of the major driving forces for the accelerated development of host–guest chemistry.[4] In this digest paper, we will highlight recent advances in the functional supramolecular systems constructed by crown ether-based cryptands. Although many wonderful cryptand-based supramolecular systems have been reported so far, not all of them can be included in this digest paper due to the space limitation.

General synthetic methods of crown ether-based cryptands

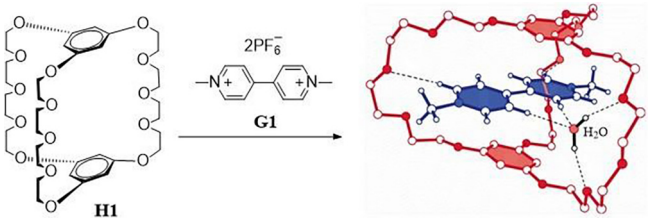
There are many methods to construct different crown ether-based cryptands. In general, crown-ether derivatives were obtained as the starting materials firstly, and then, the different third arm on cryptands were constructed. A representative example was the synthesis of cryptand **H1**. As shown in Scheme 1, bis(5-hydroxy-1,3-phenylene)-32-crown-10 was obtained firstly and reacted with tetra(ethyleneglycol) ditosylate to give **H1** in 38% yield by a highly diluted method.[5]

Basic host–guest systems

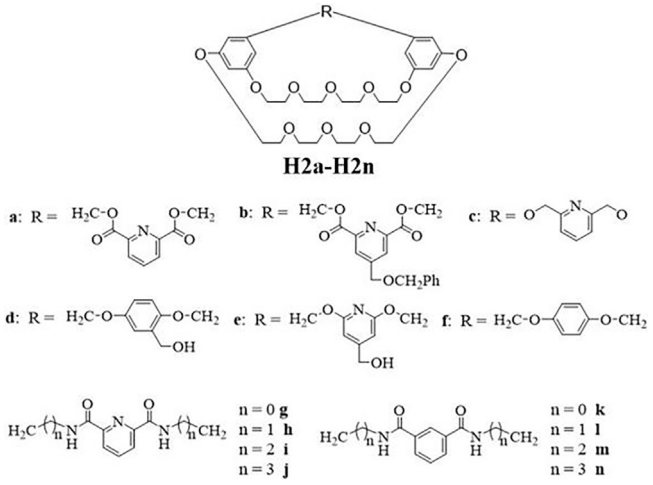
Pseudorotaxanes[6] were seen as basic units of complex supramolecular systems, in which macrocyclic components were threaded onto axles. In order to build pseudorotaxanes more effectively, high binding strengths of the host–guest interaction were necessary, and crown ether-based cryptands were the appropriate candidate hosts to construct pseudorotaxanes owing to 3D spatial architectures and the high binding capacity.

Inspired by the sandwich-type structures of the complexes between bis(*m*-phenylene)-32-crown-10 (BMP32C10) and paraquat derivatives, Gibson et al. reported the first BMP32C10-based cryptand **H1**.[5] The cryptand has three dimensional cavity structure and multiple binding sites, which has strong complexing ability with paraquat guest **G1** (Scheme 2). The association constant of the host–guest system in acetone solution is $6.1 \times 10^4\ M^{-1}$, 100 times stronger than simple BMP32C10 derivatives. More importantly, **H1** ⊃ **G1** complex exhibited a "pseudorotaxane-like" structure according to the crystal analysis results, which was different from the taco structures that BMP32C10 derivatives usually formed. This work has played the milestone role in the development of crown ether-based cryptands and their supramolecular assemblies.

After that, Gibson et al. also synthesized a series of BMP32C10-based cryptands (Scheme 3).[7] All of the results revealed that these cryptands have higher association constants with paraquat derivatives than conventional crown ethers due to the preorganization of the host and the introduction of the optimized binding sites. For instance, the association constant of cryptand host **H2a** and guest **G1** was $5.0 \times 10^6\ M^{-1}$, which had been the largest value of the association constant with paraquat derivatives so far. Moreover, crystal structures of complexes formed by these cryptands with guests were more likely to be pseudorotaxanes, not sandwich-type structures. Lately, Gibson et al. reported two types of crown ether-based pyridyl cryptands also have the familiar structures.[8]



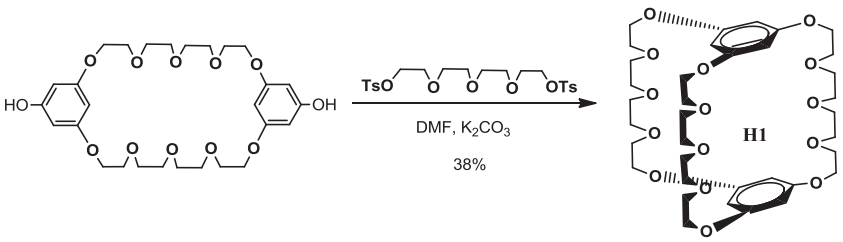
Scheme 2. Chemical and crystal structure of complex **H1** ⊃ **G1**.



Scheme 3. Chemical structures of **H2a-H2n**.

Yan et al.[9] synthesized a BMP32C10-based cryptand **H3** with a pyridine nitrogen atom outside on the third arm (Scheme 4), which was confirmed by the crystal structure of the **H3** ⊃ **G2** complex. By using host–guest interaction based on **H3** and metal coordination ability, a novel [3]pseudorotaxane was obtained.

Our group[10] designed and synthesized two BMP32C10-cryptands **H4a** and **H4b** by bridging P═O functional groups in the third arms, in which the locations of the P═O groups has a minor differences, and those two cryptands **H4a** and **H4b** could form [2]pseudorotaxanes with paraquat guest **G1** both in solution and solid state. More interestingly, by analyzing the packed crystal structures of these two complexes **H4a** ⊃ **G1** and **H4b** ⊃ **G1**, two supramolecular poly[2]pseudorotaxanes could be obtained in



Scheme 1. Synthetic method of crown ether-based cryptands **H1**.