

Cucurbit[6]uril-Based Supramolecular Assemblies: Possible Application in Radioactive Cesium Cation Capture

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S Supporting Information

ABSTRACT: Multidimensional supramolecular assemblies based on cucurbit[*n*]uril (*n* = 6 or 7) were constructed via the outer-surface interactions of cucurbit[*n*]urils with the polyaromatic compound 4,4',4''-benzene-1,3,5-triyl-tribenzoate as a structure-directing agent. Most impressively, the cucurbit[6]uril-based assembly exhibits high selectivity for capture of cesium cations among the common alkali metal ions in a basic medium and releases the cesium cations under acidic conditions. This reversible process enables possible applications in cesium cation capture.

With increasing concerns for protection of the environment, efficient treatment of radioactive wastes has emerged as one of the great challenging areas of present research. One of the important elements in radioactive waste is ¹³⁷Cs, one of the major products of ²³⁵U fission and a radionuclide with a relatively long radioactive half-life ($T_{0.5} = 30$ years).¹ Hence, studies of extraction and separation of radioactive Cs⁺ have attracted great attention of chemists. Previous reports indicate that various techniques such as chemical precipitation, evaporation, extraction, and ion exchange can be applied for the treatment of aqueous waste solutions containing cesium ions.²

To date, great efforts have been devoted to the development of processes and materials suitable for the effective separation of Cs⁺ from aquatic environments. Among them, it is well-known that alkali metal cations can be selectively included and separated by using suitable hosts such as crown ethers through host–guest interactions.³ As a new generation of host, cucurbit[*n*]urils (Q[*n*]s) have attracted remarkable attention in recent years because of their specific structures comprising a rigid hydrophobic cavity of low polar accessibility through two open polar portals lined with carbonyl groups.⁴ They readily form various host–guest inclusion complexes or coordinate with metal ions to provide supramolecular frameworks.^{5,6} The driving forces are attributed to interactions of the hydrophobic cavity of Q[*n*]s as well as ion–dipole and hydrogen-bonding interactions of portal carbonyl groups of Q[*n*]s with guests⁵ or coordination to metal ions.⁶ The electrostatic potential (ESP) profiles of Q[*n*]s can be used to explain such behaviors.^{5b} However, it is not well recognized that the electrostatically positive outer surface of Q[*n*]s can provide an important driving force, resulting in the formation of Q[*n*]-based supramolecular assemblies and coordination polymers. Very

recently, Tao and co-workers summarized the function of the electrostatically positive outer surface of Q[*n*]s,⁷ in particular the interactions of the outer surface of Q[*n*]s with aromatic compounds via $\pi \cdots \pi$ and/or C–H $\cdots\pi$ interactions, in the construction of novel Q[*n*]-based supramolecular assemblies and coordination polymers, which could present not only novel structural features but also potential applications in catalysis, sensing, polymer materials, and so on.^{8–10}

On the other hand, non-covalent interactions, especially those related to aromatic groups, are weak but important in molecular/ionic recognition as well as in the formation of supramolecular assemblies.¹¹ For example, aromatic carboxylate compounds have been demonstrated to be able to participate in $\pi \cdots \pi$ and C–H $\cdots\pi$ interactions.^{12–14} However, it is still a great challenge to employ $\pi \cdots \pi$ and C–H $\cdots\pi$ interactions as directional forces in a predictable manner.¹⁵ Therefore, understanding these weak interactions is paramount in designing and synthesizing new crystalline architectures and materials. Following this context, we focus our attention on Q[*n*]-based assemblies formed through non-covalent interactions as environmentally friendly, technologically viable adsorbents for Cs⁺ removal from aqueous media.

In this work, the polyaromatic compound 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB) was employed as structure-directing agent, and two novel three-dimensional (3D) supramolecular assemblies with Q[*n*] (*n* = 6 or 7) were successfully obtained. In particular, the Q[6]-based assembly shows high selectivity for cesium cations. In a basic medium, the Q[6]-based assembly can selectively trap cesium cations, and furthermore, the trapped cesium cations can be released from the assembly by elution with dilute HCl solution (Scheme 1), implying reusability of the Q[6]-based assembly materials.

Mixing Q[6] or Q[7] and H₃BTB in an aqueous ammonia solution (pH ~12) under hydrothermal conditions yielded colorless crystals with formulas of {(NH₄)₃Q[6]_{1.5}BTB} (1) and {(NH₄)₃Q[7]_{1.5}BTB} (2), respectively.¹⁶ Single-crystal X-ray diffraction analysis revealed that both 1 and 2 have poly-Q[*n*]-based layers (*n* = 6 or 7) linked by layers of BTB³⁻ anions. As a representative example, Figure 1a shows the structure of assembly 1, in which Q[6] molecules are sandwiched by BTB³⁻ anions (also see Figure SI-1 in the Supporting Information). A close inspection reveals that two BTB³⁻ anions stack together through $\pi \cdots \pi$ (3.530 Å) and C–H $\cdots\pi$ (2.951 Å) interactions (Figure 1b), whereas each BTB³⁻

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Scheme 1. Construction of a Multidimensional Q[6]-Based Supramolecular Assembly Using BTB^{3-} as a Structure-Directing Agent; The Q[6]-Based Assembly Exhibits High Selectivity for Cs^+ Cations

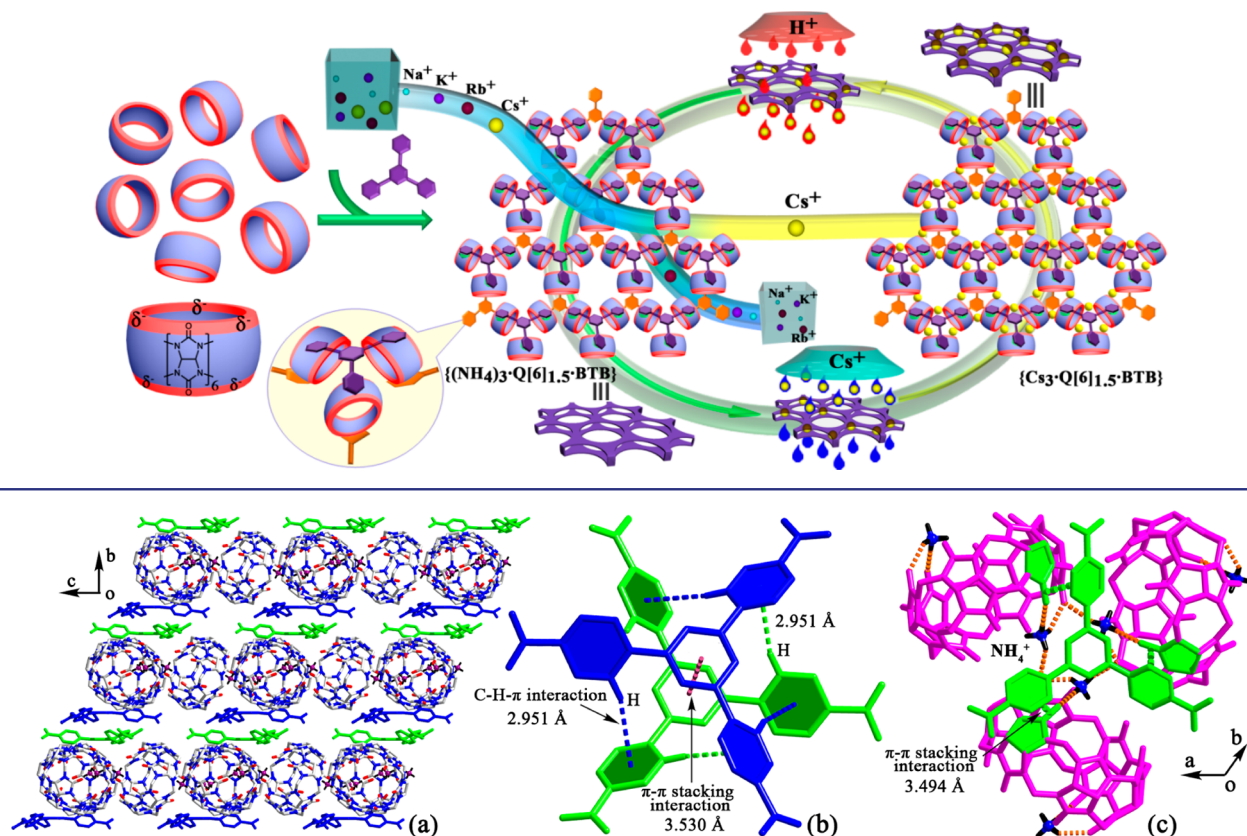


Figure 1. (a) Structure of assembly **1** with alternating Q[6] and BTB^{3-} layers. (b) Interactions in the BTB^{3-} pairs. (c) Interactions between BTB^{3-} and Q[6] and among Q[6], BTB^{3-} , and NH_4^+ .

catches three Q[6] molecules through interactions between the outer surface of Q[6] and the aromatic rings of BTB^{3-} , including (1) $\pi\cdots\pi$ interactions between benzoate moieties of BTB^{3-} and the carbonyl groups of Q[6]s (3.494 Å; Figure 1c) and (2) C–H $\cdots\pi$ interactions between electronegative BTB^{3-} and the methylene groups on the outer surface of Q[6]s. Basically, they arise from interactions between the electropositive outer surface of Q[6] and electronegative BTB^{3-} .⁷ Moreover, ion–dipole and hydrogen-bonding interactions between the NH_4^+ cations and the portal carbonyl oxygen atoms of Q[6]s further strengthen the assembly (Figure 1c). Thus, the combination of these interactions resulted in the formation of the novel Q[6]-based 3D supramolecular assembly **1**. Similar structural features can be observed in the Q[7]-based assembly **2**, suggesting that the driving forces are also the interactions between the outer surface of Q[7] and the aromatic rings of BTB^{3-} .⁷ The detailed structural information on **2** is given in Table SI-1 and Figures SI-2 and SI-3 in the Supporting Information. The results suggest that using polyaromatic compounds as structure-directing agents is a useful strategy for the construction of Q[*n*]-based supramolecular assemblies and that the driving forces are primarily due to interactions between the outer surface of Q[*n*]s and the aromatic moieties of the polyaromatic compound.

Previous studies have shown that Q[6] can coordinate with alkali metal ions to form Q[6]– $\text{M}_{\text{alkali}}^+$ complexes and/or coordination polymers.^{17,18} Thus, we examined the affinity of the Q[6]-based supramolecular assembly for alkali metal ions

by introducing Na^+ , K^+ , Rb^+ , or Cs^+ into the mixture of Q[6] and H_3BTB under the same synthetic conditions. Single-crystal X-ray diffraction analysis revealed that only a new compound **3** containing Cs^+ was obtained, while the compounds **1a**, **1b**, and **1c** from the Na^+ , K^+ , and Rb^+ systems are the same as compound **1**. Therefore, the Q[6]– BTB^{3-} system can selectively bind Cs^+ to give assembly **3**, while in the presence of Na^+ , K^+ , or Rb^+ , only assembly **1** without binding of Na^+ , K^+ , or Rb^+ was obtained. The crystal structure of **3** shows structural features similar to those of **1** except that NH_4^+ is replaced by Cs^+ (Tables SI-1 and SI-2 and Figure SI-4 in the Supporting Information). Each Cs^+ fully covers a portal of a Q[6] molecule (Figure 2a), with bond lengths in the range 3.306(10)–3.645(12) Å (Table SI-2), and also coordinates to a portal

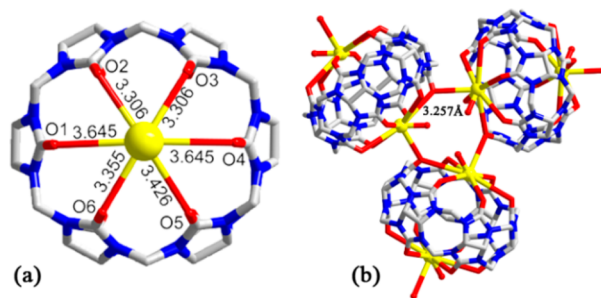


Figure 2. (a) Coordination of Cs^+ with Q[6] and (b) the trinuclear subunit in **3**.

carbonyl oxygen of a neighboring Q[6] with a bond length of 3.256(9) Å, resulting in the formation of a trinuclear subunit (Figure 2b).¹⁹ The selective replacement of NH₄⁺ in **1** by Cs⁺ to form **3** is attributed to the suitable size of Cs⁺, which has the largest ionic radius (1.67 Å) among the common alkali metal ions, since assembly **2** with Q[7] did not show such selective binding of Cs⁺ because of the larger portal size of Q[7]. The results imply the precise size-dependent selectivity. In addition, no selective binding of Cs⁺ was observed without the presence of BTB³⁻, indicating that the interactions between the outer surface of Q[6] and the polyaromatic BTB³⁻ anions, resulting in the formation of the Q[6]-based supramolecular assembly, are also important for selective binding of Cs⁺.

The selective binding of Cs⁺ was also confirmed by energy-dispersive spectrometry (EDS). As shown in Figure 3, only a

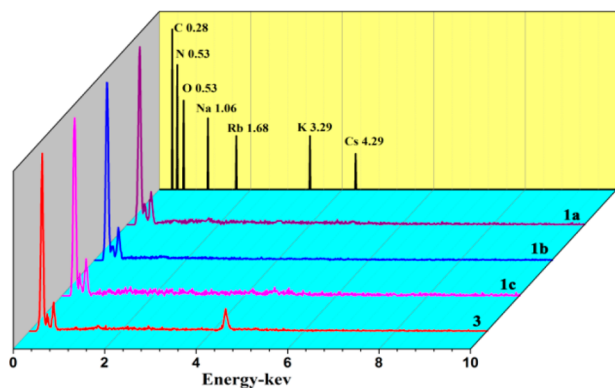


Figure 3. EDS spectra of compounds **1a**, **1b**, **1c**, and **3**.

Cs⁺ peak at 4.29 keV was observed in the EDS spectrum of **3**, while no signals corresponding to Na⁺, K⁺, or Rb⁺ were detected in the EDS spectra of **1a–c**. Inductively coupled plasma (ICP) measurements further showed that no change in the concentration of Na⁺, K⁺, or Rb⁺ occurred upon isolation of **1a–c** (Figure SI-5). The similar single-crystal cell parameters and similar powder X-ray diffraction (PXRD) patterns suggested that **1a**, **1b**, **1c**, and **3** are isomorphous and have crystal structures similar to that of **1** (Figure SI-6). A series of experiments further confirmed that **1** can selectively capture Cs⁺ from mixtures of alkali metal ions (Figures SI-7 and SI-8). More interestingly, leaving solid **3** in a dilute HCl solution (1 mmol/L) leads to release of the Cs⁺ ions from the crystals, and again putting the weathered solid in a solution containing Cs⁺ resulted in the recovery of compound **3**. The corresponding EDS, PXRD, and energy-dispersive X-ray fluorescence (ED-XRF) results are shown in Figures SI-9–SI-11. Both compounds with and without Cs⁺ remained stable after three cycles of capture and release (Figures SI-12 and SI-13).

Further experiments revealed that **1** and **3** can be obtained not only under hydrothermal conditions as mentioned above but also under convenient conditions (for details, see the Supporting Information). The PXRD patterns of the crystals obtained under convenient conditions are the same as those of the crystals obtained under hydrothermal conditions (Figures SI-14 and SI-15). The combination of the above results suggests that the Q[6]-based supramolecular assembly can selectively catch Cs⁺ and that the assembly material is reusable and recyclable, which enables possible applications in capture of radioactive cesium cation (¹³⁷Cs⁺).

In summary, we have demonstrated a strategy for the construction of multidimensional Q[*n*]-based supramolecular assemblies in the presence of BTB³⁻ as a structure-directing agent. The driving forces are the interactions between the outer surface Q[*n*]s and the aromatic rings as well as the electrostatic interactions between the electropositive outer surface of Q[6] and the electronegative BTB³⁻. By means of this strategy, two novel supramolecular assemblies containing Q[6] and Q[7] were obtained. In particular, the Q[6]-based assembly shows high selectivity for Cs⁺ cations. Moreover, the reversible ability to capture and release Cs⁺ makes the assembly a useful material for possible applications in extraction and separation of radioactive ¹³⁷Cs⁺.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and characterization details; additional figures; and PXRD, EDS, and XRF data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Figure 1 was corrected on December 3, 2014.