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Self-Assemblies Based on the “Outer-Surface Interactions” of Cucurbit[*n*]urils: New Opportunities for Supramolecular Architectures and Materials

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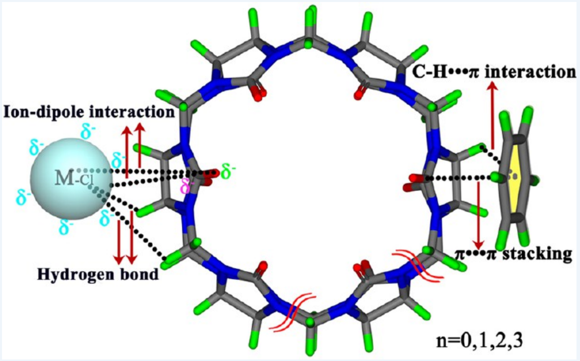

CONSPECTUS: Supramolecular architectures and materials have attracted immense attention during the last decades because they not only open the possibility of obtaining a large variety of aesthetically interesting structures but also have applications in gas storage, sensors, separation, catalysis, and so on. On the other hand, cucurbit[*n*]urils (Q[*n*]s), a relatively new class of macrocyclic hosts with a rigid hydrophobic cavity and two identical carbonyl fringed portals, have attracted much attention in supramolecular chemistry. Because of the strong charge−dipole and hydrogen bonding interactions, as well as hydrophobic and hydrophilic effect derived from the negative portals and rigid cavities of Q[*n*]s, nearly all research in Q[*n*]s has been focused on utilizing the portals and cavities to construct supramolecular assemblies similar to other macrocyclic receptors such as cyclodextrin and calixarenes. Interestingly, a recent study revealed that other weak noncovalent interactions such as hydrogen bonding and $\pi\cdots\pi$ stacking, as well as C−H$\cdots\pi$ and ion−dipole interactions, could also be defined as “outer-surface interactions”, which are derived from the electrostatically positive outer surface of Q[*n*]s. These interactions could be the driving forces in the formation of various novel Q[*n*]-based supramolecular architectures and functional materials. In this Account, we provide a comprehensive overview of supramolecular self-assemblies based on the outer-surface interactions of Q[*n*]s. These outer-surface interactions include those between Q[*n*]s, Q[*n*]s and aromatic molecules, Q[*n*]s and calixarenes, Q[*n*]s and inorganic complex ions, and Q[*n*]s and polyoxometalates. Pioneering work has shown that such weak noncovalent interactions play very important roles in the formation of various Q[*n*]-based functional materials and supramolecular architectures. For example, hydrogen bonds in outer-surface interactions between Q[*n*] molecules not only function as the sole driving force in the formation of one-dimensional Q[*n*] porous channels but also assist the bonding forces of the channels in capturing and accommodating acetylene molecules and carbon dioxide in the channel cavities. Moreover, upon introduction of a third species such as an aromatic molecule or inorganic anion into the Q[*n*]/metal system, “outer-surface interactions” could lead to Q[*n*]/metal-based self-assemblies from simple finite supramolecular coordination complexes to infinite polydimensional supramolecular architectures and other structures.

Overall, this Account focuses on the novel self-assembly driving force derived from Q[*n*]s including (i) concepts of the outer-surface interactions of Q[*n*]s, (ii) providing plausible explanations of the mechanisms of the outer-surface interactions of Q[*n*]s, and (iii) introduction of an overview of the developments and practical applications of outer-surface interactions of Q[*n*]s in supramolecular chemistry. It is hoped that this study based on the outer-surface interactions of Q[*n*]s can enrich the field of molecular engineering of functional supramolecular systems and provide new opportunities for the construction of functional materials and architectures.

1. INTRODUCTION

Cucurbit[*n*]urils (Q[*n*]s or CB[*n*]s) are a family of macrocyclic compounds self-assembled from an acid catalyzed condensation reaction of glycoluril and formaldehyde (Scheme 1). Cucurbit[6]uril[1] (Q[6]) was first synthesized by Behrend and co-workers in 1905. However, it was not until 1981 that Mock structurally characterized Q[6] as comprising six glycoluril units linked by 12 methylene bridges.[2] Afterward, in the early 2000s, the pioneering work of Kim and Day enabled chemists to synthesize different homologues of Q[*n*]s (n = 5, 7, 8, 10, 14).[3−6] These pumpkin-shaped containers have a characteristic rigid hydrophobic cavity accessible through two polar portals rimmed with carbonyl groups. In particular, their superior molecular recognition and coordination properties in aqueous medium have attracted much attention in supramolecular chemistry in the last decades. A wide variety of supramolecular species such as host−guest interactions, supramolecular assemblies, and molecular machines incorporating Q[*n*]s have been reported.[7−11] Other applications of Q[*n*]s such as in

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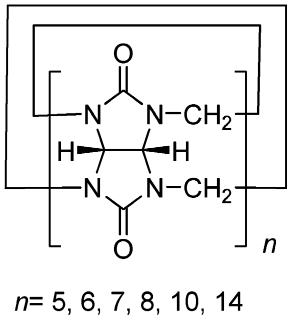
Scheme 1. Chemical Structures of Cucurbit[*n*]urils



catalysis,[12] sensing,[13] drug delivery,[14] biomolecular recognition,[15] and polymer materials[16] have also been demonstrated.

Interestingly, our recent study revealed that the coordination of Q[*n*]s with metal ions in the presence of a third species (such as aromatic molecules and inorganic anions), that is, a structure inducer, can result in the formation of various cucurbit[*n*]uril-based polydimensional supramolecular coordination architectures and polymers.[17] Weak noncovalent interactions derived from the "outer-surface interactions" of Q[*n*]s, such as hydrogen bonding, $\pi\cdots\pi$ stacking, and C−H$\cdots\pi$ and ion−dipole interactions, have important roles in those systems. Detailed investigations have indicated that such noncovalent interactions can be the main driving forces in the formation of Q[*n*]-based supramolecular assemblies and functional materials.

2. GENERAL PROPERTIES OF OUTER-SURFACE INTERACTIONS OF Q[*n*]s

Electrostatic potential surface calculations on Q[*n*]s (Figure 1) indicated that the regions around the portal carbonyl groups on Q[*n*]s are significantly negatively charged. The inner surface of the cavities is also negatively charged, whereas the outer surface is somewhat electrostatically positive. Because of the strong charge−dipole and hydrogen bonding interactions, as well as hydrophobic and hydrophilic effect derived from the negative portals and rigid cavities of Q[*n*]s, it is not surprising that almost all research in this field has been focused on utilizing the portals and cavities to construct supramolecular assemblies similar to macrocyclic receptors such as cyclodextrins and calixarenes. In fact, Chen and co-workers first proposed that the chemical behavior of the convex outer walls of Q[*n*]s could be explored to develop novel structures and functional materials when they investigated iodine-assisted supramolecular assemblies of helical coordination polymers of Q[6] and asymmetric copper(II) complexes.[18]

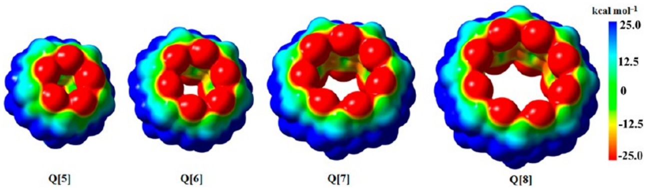


Figure 1. Electrostatic potential maps (ESPs) for Q[5], Q[6], Q[7], and Q[8], respectively. ESPs are mapped on electron density isosurfaces (0.001 e/au^3) for cucurbit[*n*]urils at the B3LYP/6-311G (d, p) level of theory with Gaussian09.

Close inspection reveals that the convex glycoluril surface bones of Q[6] exhibit much higher affinity for the aromatic moieties of the copper(II) complex anions than for the other Q[6] units; we call the resulting interactions outer-surface interaction of Q[*n*]s. Figure 2 shows the comprehensive outer-surface interactions between Q[6] and copper(II) complex anions. In such supramolecular assemblies, each Na$^+$-coordinated Q[6] molecule is surrounded by five copper(II) complex anions (Figure 2a). Each copper(II) complex anion is surrounded by five Na$^+$-coordinated Q[6] molecules (Figure 2b) through outer-surface interactions, including (1) the unusual hydrogen bonding of the equatorial methine or bridge methylene groups on the outer surface of Q[6] molecules with oxygen and iodine chloride from the copper(II) complex anions, (2) $\pi\cdots\pi$ interactions of carbonyl groups of Q[6] molecules with aromatic moieties of the copper(II) complex anion, (3) C−H$\cdots\pi$ interactions of the methine or methylene groups on the outer surface of Q[6] molecules with aromatic moieties of the copper(II) complex anion, and (4) electrostatic interaction of the Na$^+$-coordinated Q[6] molecules with copper(II) complex anions. A combination of these outer-surface interactions of Q[6] results in the formation of novel honeycomb-like supramolecular assemblies in which one-dimensional (1D) Na-Q[6] based coordination polymers fill the cells constructed from asymmetric copper(II) complexes (Figure 2c,d).

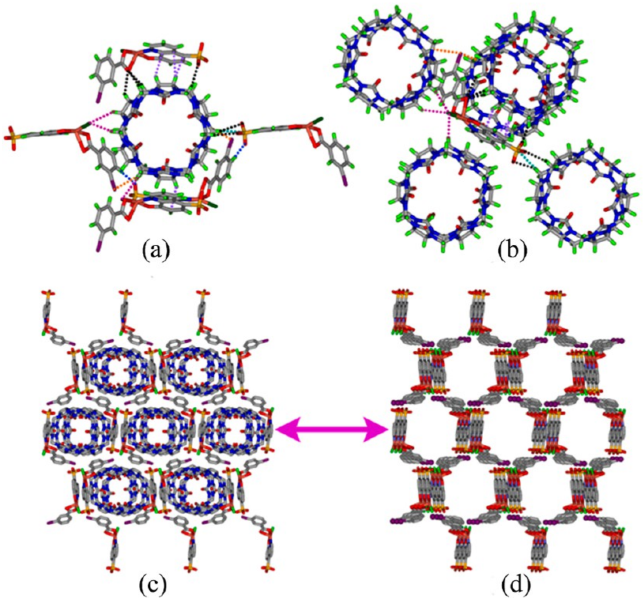
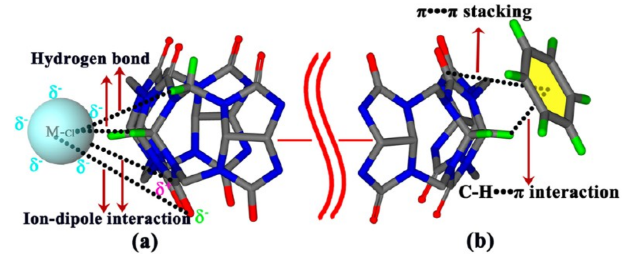


Figure 2. X-ray crystal structures of supramolecular assemblies of Q[6] and asymmetric copper(II) complexes: (a, b) features of the interaction between Q[6] and copper(II) complex anions; honeycomb-like supramolecular assemblies constructed from asymmetric copper(II) complexes (c) filled with and (d) without one-dimensional Na-Q[6]-based coordination polymers in the cells.

Our recent studies, along with related results from other researchers, suggest that the electrostatically positive outer-surface of Q[*n*]s could provide a balance of various supramolecular driving forces, such as those involved in C−H$\cdots\pi$, hydrogen bonding, and ion−dipole interactions, which could generate numerous novel Q[*n*]-based supramolecular assemblies. Thus, a new branch of Q[*n*] chemistry based on outer-surface interactions can be established as shown in Scheme 2.

Scheme 2. (a) Outer-Surface Interactions between Q[*n*]s and Inorganic Molecules and (b) Outer-Surface Interactions between Q[*n*]s and Aromatic Molecules



3. OUTER-SURFACE INTERACTIONS BETWEEN Q[*n*]s AND THE CORRESPONDING SUPRAMOLECULAR ASSEMBLIES

Recently, studies on hydrogels prepared by using the well-established host–guest chemistry of macrocyclic cavitands have been reported.[19,20] However, simple macrocycles have never been considered as hydrogelators. Kim and co-workers first demonstrated that a pH-triggered hydrogel exhibiting guest-induced stimuli-responsive behavior could be formed from simple Q[7] molecules. The driving force for gelation may be the propensity of Q[7] to aggregate through strong hydrogen bonding interactions between Q[7] portals and hydronium ions, as well as between Q[7] molecules.[21] Figure 3 shows the fiber-like Q[7]-based supramolecular assemblies and the unusual hydrogen bonding of methine or methylene groups on the outer surface of Q[7] molecules with carbonyl oxygens from neighboring Q[7] molecules in the Q[7]-based hydrogel (the dashed lines in black and in pink).

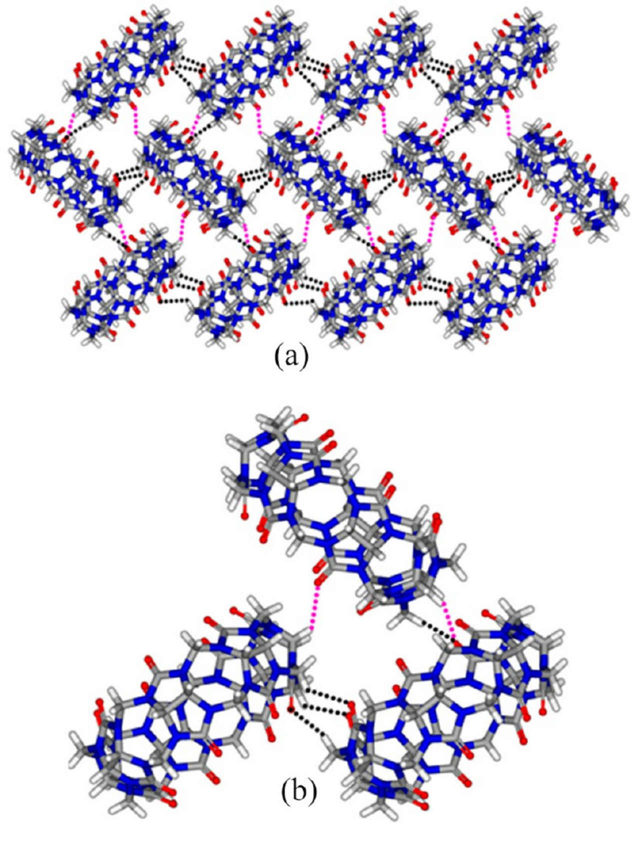


Figure 3. X-ray crystal structures of (a) the fiber-like Q[7]-based supramolecular assemblies; (b) the unusual hydrogen bonding of methine or methylene groups on the outer surface of Q[7] molecules with carbonyl oxygens from neighboring Q[7] molecules.

Later, Kim and co-workers discovered that hydrogen bonding in outer-surface interactions between Q[6]s could not only function as the sole driving force in the formation of 1D Q[*n*] porous channels but also assist the bonding force of the channels in capturing acetylene molecules[22] and carbon dioxide.[23] Experimental results suggest that the hydrogen-bonding-assisted Q[6]-based porous material exhibits high thermal stability, permanent porosity, and remarkable gas sorption properties. Figure 4a,b shows the Q[6]-based honeycomb-like 1D porous material with linear cells, and Figure 4c,d shows each cell filled with acetylene and carbon dioxide under the assistance of ion–dipole interactions and hydrogen bonding from the Q[6] molecules. More recently, the same group further demonstrated that both Q[6]- and Q[8]-based porous materials bear structures similar to the aforementioned Q[6] porous channels and show anisotropic proton conductivity.[24] Close inspection reveals that the driving force in the formation of these structures is also the unusual hydrogen bonding of portal carbonyl oxygens of the Q[*n*] molecule with methine or methylene groups on the outer surface of a neighboring Q[*n*] (*n* = 6, 8) molecule (Figure 4e,f).

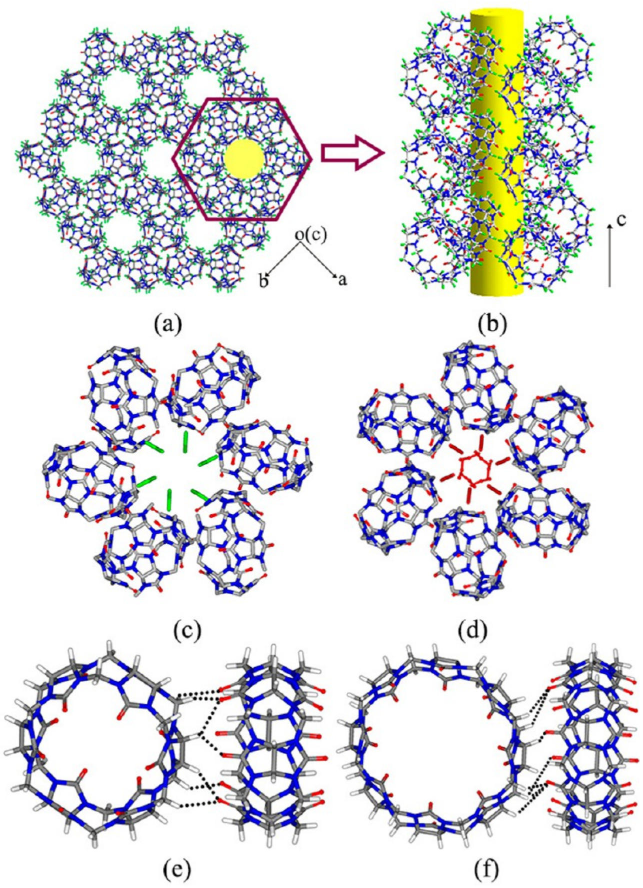


Figure 4. X-ray crystal structures of (a, b) the Q[6]-based honeycomb-like material with linear cells, that of the material with each cell filled with (c) acetylene or (d) carbon dioxide, and (e, f) the detailed interactions between the two neighboring Q[*n*] (*n* = 6, 8) molecules.

Li and co-workers also showed a rapid and facile method to access in high yield one-molecule-thick free-standing organic nanosheets with regular shape by self-assembly of Q[8] and small organic molecules.[25] By scanning tunneling microscopy, the arrangement of Q[8] molecules in the sheets was confirmed. In this arrangement, the Q[8] molecule has its carbonyl-lined portals pointing toward the sidewalls of neighboring Q[8] molecules, and its own sidewalls are adjacent to the portals of neighboring Q[8]s. The unusual hydrogen bonding of portal carbonyl oxygens of the Q[8] molecules with methine or methylene groups on the outer surface of neighboring Q[8] molecules in this Q[8]-based supramolecular assembly is unusual.

4. OUTER-SURFACE INTERACTIONS BETWEEN Q[*n*]s AND AROMATIC MOLECULES AND THE CORRESPONDING SUPRAMOLECULAR ASSEMBLIES

Recently, our group focused on the coordination of Q[*n*]s with metal ions in the presence of small aromatic molecules as structure inducers, since we found that Q[5] could induce room-temperature phosphorescence (RTP) of α- and β-naphthol. The key interactions between the convex outer walls of Q[5] and the plane of aromatic naphthols, namely, $\pi\cdots\pi$ stacking and C−H$\cdots\pi$ interactions, may be essentially maintained. They thus lead to a microenvironment that holds the luminophore and the heavy-atom perturber together. Such a model is supported by the observed Q[5]-complex-induced RTP of the above naphthols.[26] For example, we discovered the formation of a novel K^+-coordinated Q[5]-based supramolecular assembly with stable and accessible channels in the presence of *p*-hydroxybenzoic acid (Hyb) as a structure inducer.[27] The template molecule Hyb is located centrally over each trigonal branched junction through $\pi\cdots\pi$ stacking between the carbonyl groups of Q[5] molecules and the aromatic moiety of Hyb, and through C−H$\cdots\pi$ interactions between of methylene groups on the outer surface of Q[5] molecules with the aromatic moiety of Hyb (Figure 5a). The trigonal branches link a layer of molecular network with hexagonal holes constructed from Q[5] "beaded" six-membered rings (Figure 5b). The holes appeared to absorb small organic molecules such as methanol and 1,4-dioxane. Results of our further experiment suggest that other aromatic molecules such as phenol or its derivatives could lead also to novel Q[5]/metal-based coordination polymers and architectures.[17] In particular, a detailed study of supramolecular assembles of Q[5][28] resulting from a Q[5]/metal, Q[5]/aromatic molecule, or Q[5]/metal/aromatic molecule system (Figure 6) provided unequivocal proof of the important effect of the outer-surface interaction between aromatic molecules and Q[5]s on the construction of these assemblies.

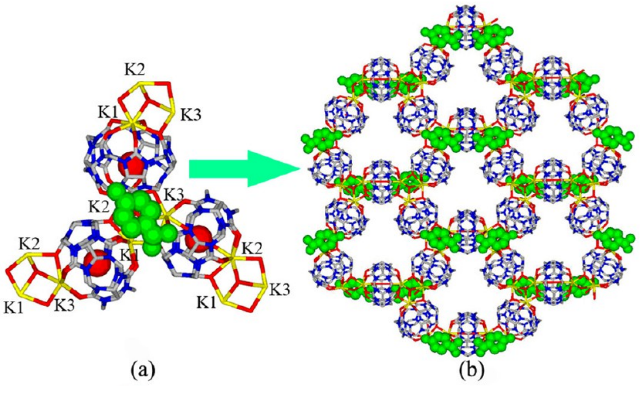


Figure 5. (a) Trigonal junctions of three Q[5] molecules coordinated to potassium ions (yellow) and (b) six-membered Q[5] beaded rings with molecules of *p*-hydroxybenzoic acid (green) in a single layer.

Interestingly, when we investigated the coordination of Q[5] with lanthanide cations in the presence of hydroquinone as an organic structure inducer, we found that coordination polymers of Q[5] with heavy lanthanide cations ($Ln^{3+} = Dy^{3+}$, Er^{3+}, Yb^{3+}, or Lu^{3+}) were distinctly different from those with light lanthanide cations.[17] For example, the coordination of light lanthanide cations to Q[5] leads to the formation of linear 1D coordination polymers, whereas coordination of intermediate lanthanide cations such as Eu(III) or Gd(III) with Q[5] leads to the formation of Q[5] pairs. Coordination of heavy lanthanide cations to Q[5] leads to the formation of homochiral helical 1D coordination polymers.[29] On the basis of the above results, we can therefore conclude that the $\pi\cdots\pi$ stacking and the C−H$\cdots\pi$ interactions occurring between aromatic molecules and Q[5]s play important roles in the formation of such supramolecular assemblies.

5. OUTER-SURFACE INTERACTIONS BETWEEN Q[*n*]s WITH CALIXARENES AND THE CORRESPONDING SUPRAMOLECULAR ASSEMBLIES

In the preceding, we have shown some aromatic organic molecules that could form Q[*n*]-based supramolecular assemblies through outer-surface interactions of Q[*n*]s. Herein, we further introduce typical macrocyclic compounds, namely, calixarenes, that behave as structure inducers in the construction of Q[*n*]-based supramolecular assemblies; calixarenes also consist of aromatic moieties. Figure 7 shows a complex of Q[6]−calixarene in which the calixarene is 4-sulfocalix[4]arene.[30] In this system, a three-dimensional (3D) framework (Figure 7a) is formed by stacking of two-dimensional (2D) networks (Figure 7b) constructed from alternating Q[6] and 4-sulfocalix[4]arene in linear assemblies through outer-surface interactions of Q[6]. Figure 7c,d show the detailed outer-surface interactions around each Q[6] and 4-sulfocalix[4]arene molecule, respectively. They include (1) $\pi\cdots\pi$ stacking interactions of the carbonyl group of Q[6] with the phenyl rings of 4-sulfocalix[4]arene molecules, (2) C−H$\cdots\pi$ interactions between the methine or methylene groups of Q[6] and the phenyl rings of 4-sulfocalix[4]arene molecules, and (3) the unusual hydrogen bonding of methine or methylene groups of Q[6] with sulfo moieties from 4-sulfocalix[4]arene molecules. A combination of these intermolecular interactions results in the formation of the Q[6]-4-sulfocalix[4]arene-based supramolecular assembly.

Interestingly, when 4-sulfocalix[6]arene was used to replace 4-sulfocalix[4]arene, a novel Chinese-knot-like 2D network could be obtained (Figure 8a,b).[30] The basic intermolecular interactions are also outer-surface interactions of Q[6] molecules with aromatic rings or sulfo moieties of the 4-sulfocalix[6]arene molecules. Figure 8c−f shows the detailed interactions between Q[6] molecules and 4-sulfocalix[6]arene molecules.

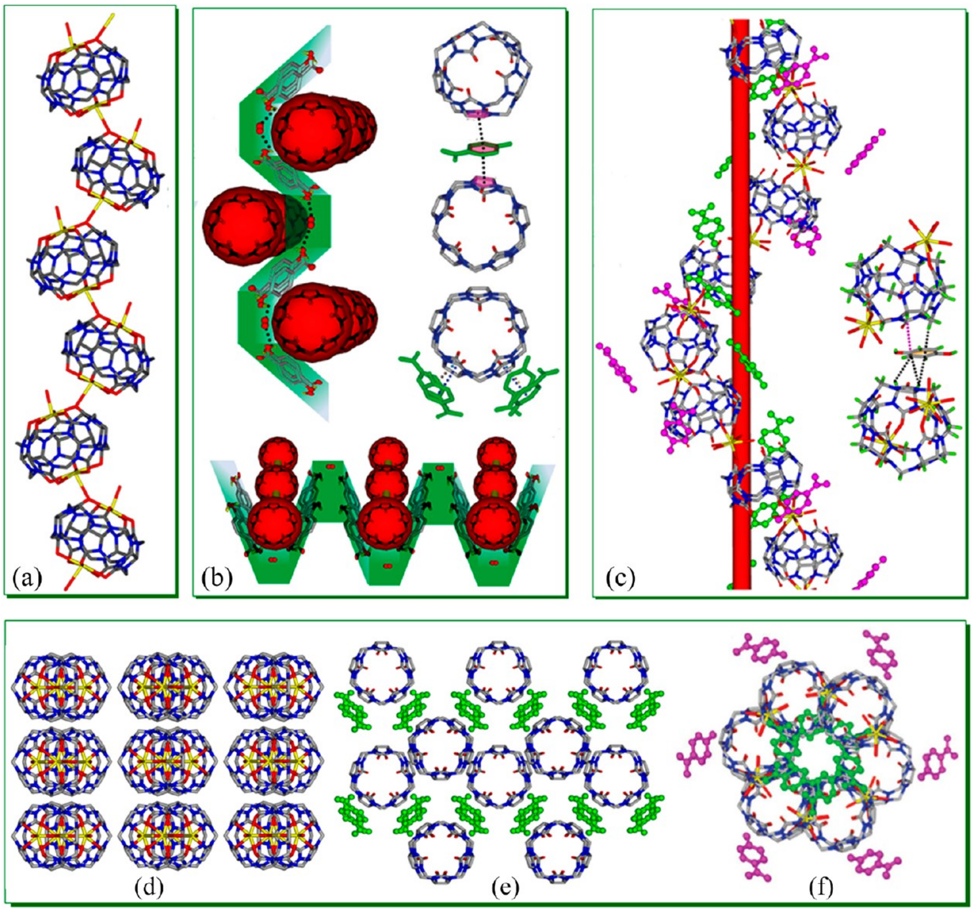


Figure 6. X-ray structures of Q[5] complexes: (a) side and (d) top views of a linear supramolecular chain constructed from Q[5]/Ca^{2+} through direct metal coordination; (b) side and (e) top views of a linear supramolecular chain constructed from Q[5]/hydroquinone through outer-surface interactions in $\pi\cdots\pi$ stacking; (c) side and (f) top views of the chiral helical Q[5]/Ca^{2+} coordination polymer formed through outer-surface interactions ($\pi\cdots\pi$ stacking and C−H$\cdots\pi$ interactions) of hydroquinone-based left-handed helixes.

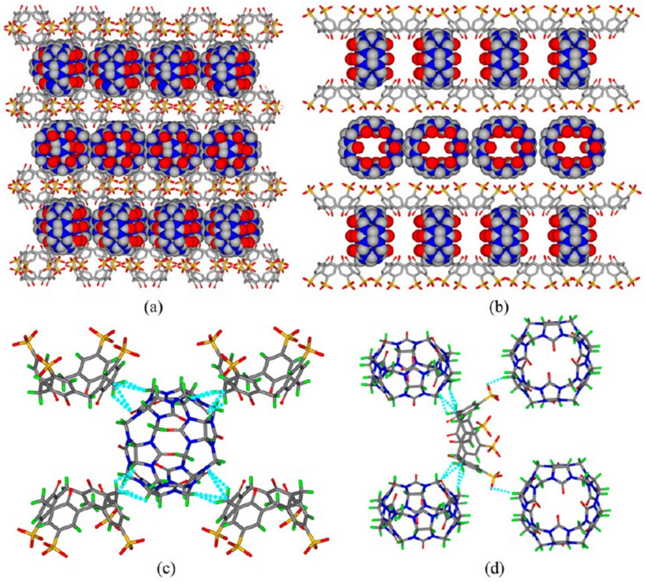


Figure 7. X-ray crystal structures of Q[6]-4-sulfocalix[4]arene: (a) the 3D structure, (b) 2D structure, and (c, d) the detailed outer-surface interactions around each Q[6] and 4-sulfocalix[4]arene molecule, respectively.

6. OUTER-SURFACE INTERACTIONS BETWEEN Q[*n*]s AND INORGANIC ANIONS AND THE CORRESPONDING SUPRAMOLECULAR ASSEMBLIES

Bardelang et al. demonstrated that metal-free Q[6] and Q[8] hydrate crystals with water-filled channels consist of perfectly aligned 1D macrocycle nanotubes (Figure 9).[31] The water molecules link Q[*n*]s through classical hydrogen bonding between portal carbonyl oxygens and water molecules and form 1D macrocycle nanotubes (Figure 9c, f). Chloride or nitrate anions link the 1D macrocycle nanotubes through unusual hydrogen bonding (Figure 9b, e), and form novel Q[*n*]-based supramolecular assemblies (Figure 9a, d). Each Q[6] and Q[8] molecule is surrounded by 6 chloride anions and 16 nitrate anions in the Q[6]- and Q[8]-based supramolecular assemblies, respectively. Outer-surface interactions between Q[6] molecules and chloride anions are simple, occurring between methylene groups on the outer surface of Q[6] molecules and the surrounding chloride anions. Each chloride anion attracts three Q[6] molecules. The outer-surface interactions between Q[8] molecules and nitrate anions include (1) the unusual hydrogen bonding of methylene or methine groups on the outer surface of the Q[8] molecule with surrounding nitrate anions and 2) ion−dipole interaction between nitrate anions and carbonyl carbon on the outer surface of the Q[8] molecules. Numerous water molecules in the channels interact

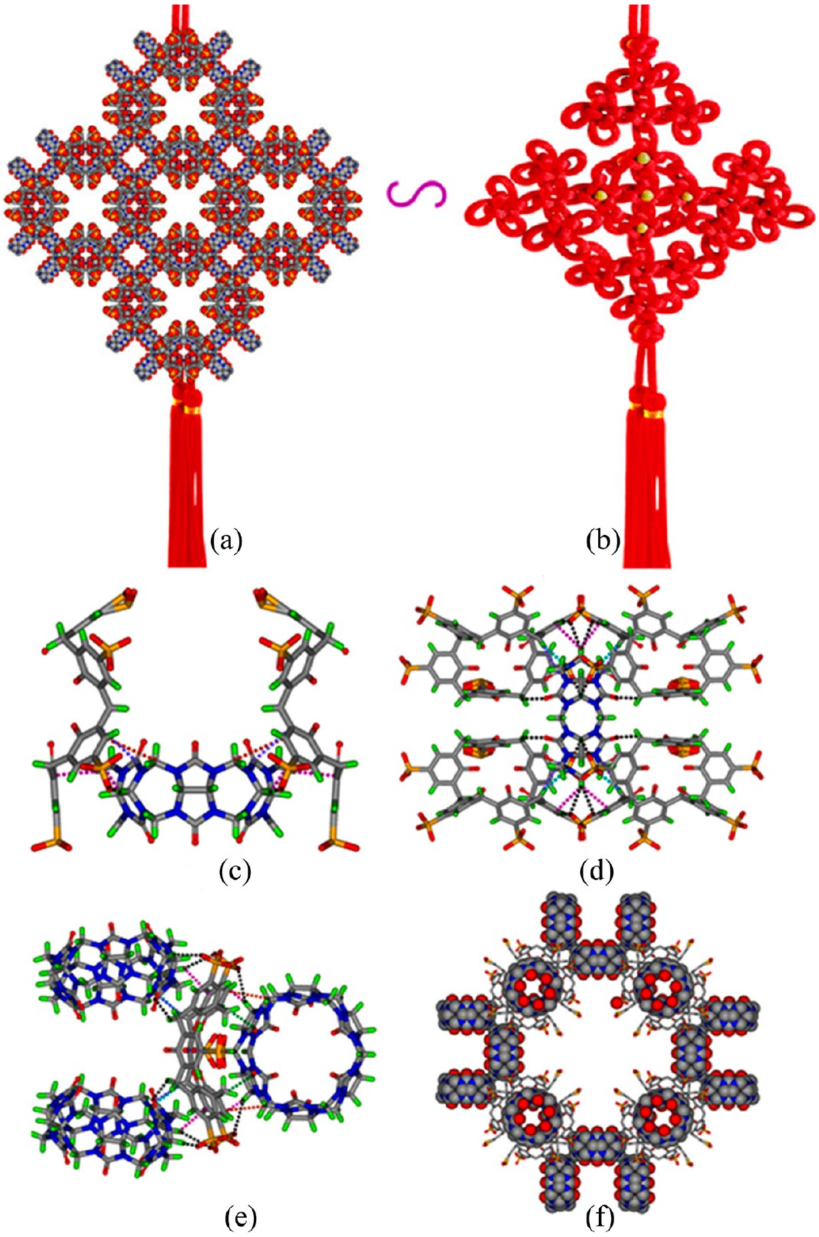


Figure 8. X-ray crystal structures of Q[6]-4-sulfocalix[6]arene: (a) a novel Chinese-knot-like 2D network and (b) a typical Chinese knot; (c−e) detailed interactions between Q[6]s and 4-sulfocalix[6]arenes; (f) a combination of all interactions results in the formation of each basic building block.

with the anions and form complicated hydrogen bonding networks, which also aid in forming the supramolecular assemblies.

Our recent studies suggested that tetrachloride transition-metal anions ($[M_{trans}Cl_4]^{2-}$, M_{trans} = Cd, Zn, Cu, Co, Ni, etc.) as the third species could produce the *honeycomb effect* and lead to the formation of various Q[*n*]-based 1D supramolecular coordination polymers (Scheme 3).[17] We propose that the driving forces of the outer-surface interactions include (1) the unusual hydrogen bonding of methine or methylene groups on the outer surface of Q[*n*] molecules with $[M_{trans}Cl_4]^{2-}$ anions or portal carbonyl oxygens of Q[*n*] molecules and (2) ion−dipole interaction of $[M_{trans}Cl_4]^{2-}$ anions or portal carbonyl oxygens with portal carbonyl carbons of the adjacent Q[*n*] molecule and of the satellite $[M_{trans}Cl_4]^{2-}$ anions around the Q[*n*] molecule. The negative honeycomb thus attracts metal ions, leading to their coordination to the portal carbonyl oxygens and formation of 1D coordination polymers.

There is an apparent preference of outer-surface interactions between ($[M_{trans}Cl_4]^{2-}$ anions and Q[*n*]s for the honeycomb effect over direct metal coordination. To obtain more detailed information on this phenomenon, we carried out experiments in the presence of only the tetrachloride transition-metal anions ($[M_{trans}Cl_4]^{2-}$, M_{trans} = Cd, Zn, Ni) in Q[*n*] solutions. Features of the interaction between the Q[8] molecule and $[CdCl_4]^{2-}$ anions are shown in Figure 10 as a representative example.[32] Each Q[8] molecule is surrounded by seven $[CdCl_4]^{2-}$ anions through dipole interaction between portal carbonyl carbons and chlorine from $[CdCl_4]^{2-}$ anions and through hydrogen bonding of chlorine from $[CdCl_4]^{2-}$ with methine or methylene on the outer surface of Q[8] molecules (Figure 10a). Additional interactions in these Q[8]-based porous supramolecular

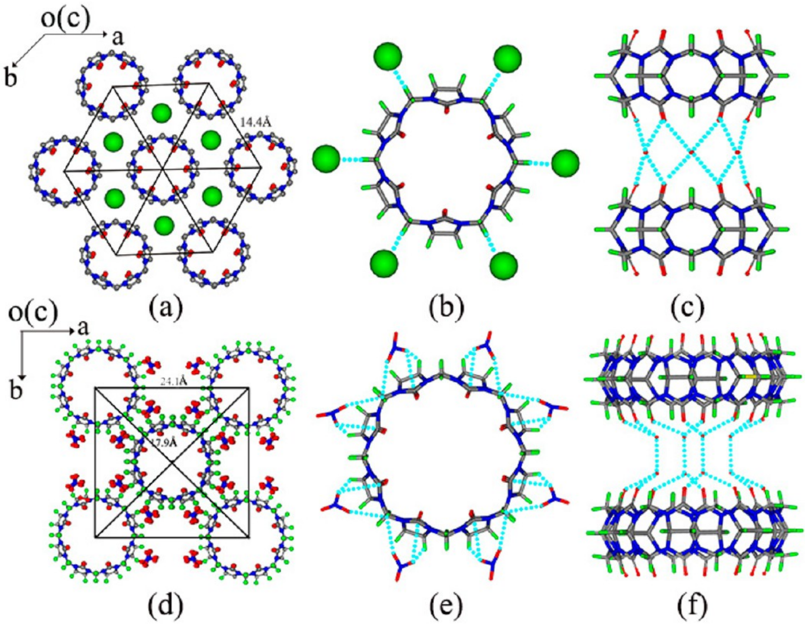
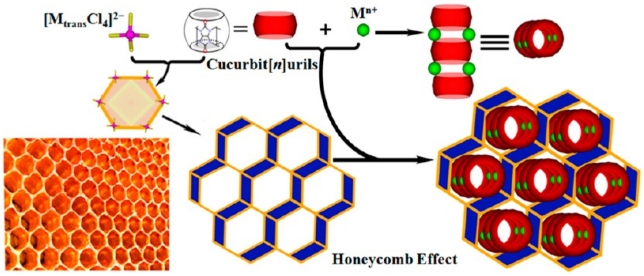


Figure 9. Crystal packing and interchannel distances within (a, b) Q[6]- and (d, e) Q[8]-based crystals, as displayed along the *c* and *a* axes, respectively. Hydrogen bonding between neighboring (c) Q[6] and (f) Q[8] molecules, respectively.

Scheme 3. Representation of the Honeycomb Effect Derived from Q[*n*]-Based Coordination



assemblies between two adjacent Q[8] molecules occur through dipole interaction and hydrogen bonding (Figure 10b). On the other hand, formation of the Q[8]-based supramolecular assembly (Figure 10c) is the combined effect of $[CdCl_4]^{2-}$-induced honeycomb-shaped cells (Figure 10d) and the zigzag Q[8] molecule chain filling the honeycomb cells along the *c* axis. Thus, a novel Q[8]-based porous material with 1D parallelogram channels with an average cross-sectional area of ∼83 Å^2 (along the *a* axis, Figure 10c) could be formed without direct metal coordination. Moreover, the tests of potential applications show that these porous materials not only can capture organic molecules but also can adsorb larger organic molecules with different selectivity.

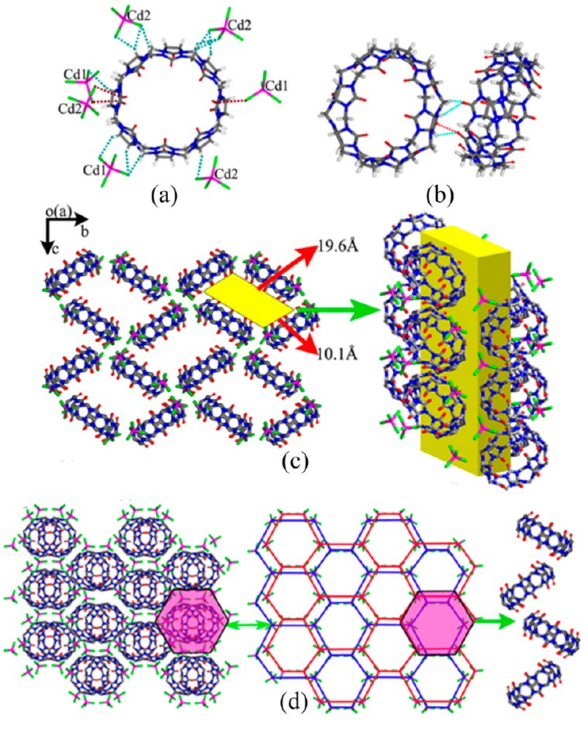


Figure 10. X-ray crystal structures of a $[CdCl_4]^{2-}$-induced Q[8]-based porous supramolecular assembly: (a) features of the interaction between the Q[8] molecule and $[CdCl_4]^{2-}$ anions; (b) interactions between two adjacent Q[8] molecules; (c) overall view of the Q[8]-based porous supramolecular assembly; (d) $[CdCl_4]^{2-}$-based honeycomb-shaped cells and a zigzag Q[8] molecule chain.

7. OUTER-SURFACE INTERACTIONS BETWEEN Q[*n*]s AND POLYOXOMETALATES AND THE CORRESPONDING SUPRAMOLECULAR ASSEMBLIES

Polyoxometalates (POMs), a wide class of metal oxide clusters generally characterized by large molecular structures, present a wide range of anion forms in normal media. In this section, we introduce it as another kind of inorganic anion in the construction of Q[*n*]-based supramolecular assemblies. Although POMs are generally too large to be included in Q[*n*] molecules as normal guests, their interaction with the outer surface of Q[*n*]s has drawn extensive attention because the hybridization of redox-active inorganic anions with organic Q[*n*] molecules could provide not only novel Q[*n*]-based supramolecular architectures but also a versatile route to POM-based multifunctional materials with enhanced magnetic, catalytic, zeolitic, and recognition properties. Kögerler and co-workers first demonstrated two hybrid complexes of $[H_2O@V^{IV}{}_{18}O_{42}]^{12-}$ based on Q[6] and Q[8] molecules.[33] These complexes have characteristic large channels constructed from Q[6] or Q[8] molecules and $[H_2O@V^{IV}{}_{18}O_{42}]^{12-}$ anions, formed through combined ion−dipole interactions of $V{=}O_{POMs}\cdots C{=}O_{carbonyl\text{-}carbon}$ and hydrogen bonding of methine groups on the outer surface of Q[*n*] molecules with O from $[H_2O@V^{IV}{}_{18}O_{42}]^{12-}$ anions. Figure 11 shows the crystal structure of the $Q[6]/[H_2O@V^{IV}{}_{18}O_{42}]^{12-}$ supramolecular assembly with large square channels. The driving forces involve the opposite end of the carbonyl dipole and the electron-deficient carbon sites with V=O oxygen from polyoxometalate, as well as hydrogen bonding of V−O or V=O of polyoxometalate with methine or methylene groups on the outer surface of neighboring Q[6] or Q[8] molecules (Figure 11).[33]

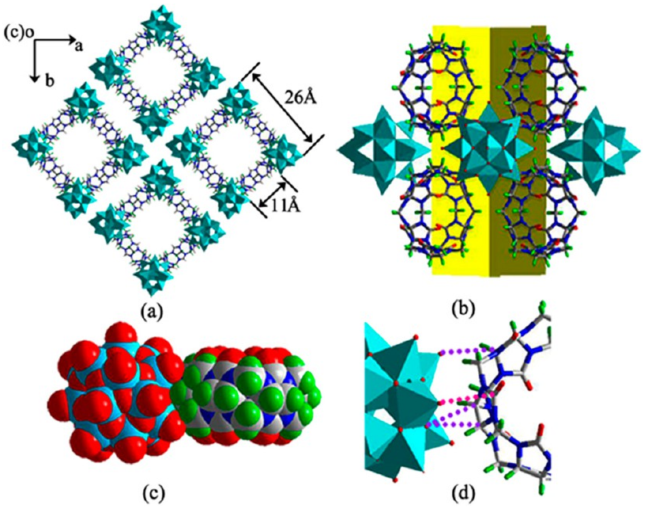


Figure 11. (a) Extended structures of Q[6] complex by packing along the *c* axis; (b) side view of a 1D square channel (highlighted in yellow); (c) neighboring $\{V_{18}\}$ and Q[6] units of the complex in space-filling mode; (d) magnified view showing supramolecular contacts (dotted lines): ion−dipole interaction in orange and hydrogen bonding in purple.

More recently, Cao and co-workers, as well as other groups, prepared a series of hybrid Q[*n*]/POM complexes through outer-surface interaction of Q[*n*]s.[34] Among these hybrid complexes are water-insoluble $Q[6]-[SiW_{12}O_{40}]^{4-}$ or decamethylcucurbit[5]uril complexes ($(Me_{10}Q[5])/[P_2W_{18}O_{62}]^{6-}$), which are active photocatalysts for the degradation of methyl orange under visible light. These catalysts afford highly reproducible photocatalytic degradation that may be carried out through a simple recycling procedure without obvious loss of catalytic activity.[35,36]

An effective approach to the preparation of polydimensional porous supramolecular assemblies is the incorporation of multidentate organic bridging ligands with various coordination orientations into the coordination systems. Our recent works revealed that the equatorial perhydroxycucurbit[5]uril, $(HO)_{10}Q[5]$,[37] could coordinate with metal ions through not only the portal carbonyl oxygens but also the equatorial hydroxyl groups, resulting in formation of novel polydimensional coordination polymers.[38] This discovery has prompted us to introduce $(HO)_{10}Q[5]$ into Q[*n*]−POM systems. We thus synthesized $(HO)_{10}Q[5]$-based porous supramolecular assemblies using $[PMo_{12}O_{40}]^{3-}$ as the structure inducer (Figure 12).[39]

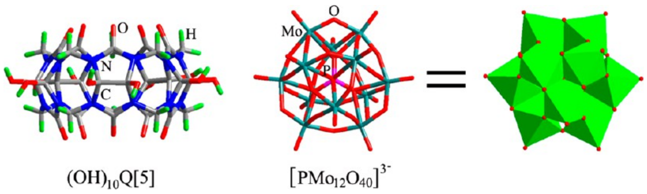


Figure 12. Structure of the $(HO)_{10}Q[5]$ molecule and $[PMo_{12}O_40]^{3-}$ anion.

Figure 13 shows an overall view of the honeycomb-like porous supramolecular assembly constructed from $[PMo_{12}O_{40}]^{3-}$ anions and $(HO)_{10}Q[5]$ molecules. Further crystal structure analysis revealed that each $(HO)_{10}Q[5]$ molecule is surrounded by six $[PMo_{12}O_{40}]^{3-}$ anions in three slightly different ways (Figure 13c). Each $[PMo_{12}O_{40}]^{3-}$ anion in turn interacts with six $(HO)_{10}Q[5]$ molecules in also three slightly different ways (Figure 13d). The formation of $(HO)_{10}Q[5]/[PMo_{12}O_{40}]^{3-}$ hydride is primarily driven by classical hydrogen bonding (light-blue dashed lines) of functionalized OH groups on the outer surface of Q[5] molecules with Mo=O or Mo−O groups on the outer surface of $[PMo_{12}O_{40}]^{3-}$ anions. The hydride is also formed by (1) ion−dipole attraction (red dashed lines, Figure 13c,d) of electron-deficient carbon of $(HO)_{10}Q[5]$ carbonyl groups with

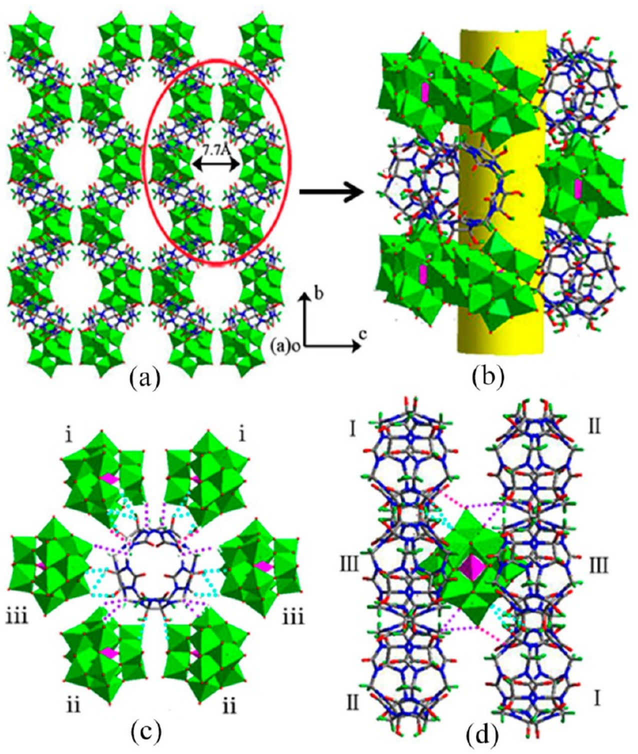


Figure 13. X-ray crystal structures of $(HO)_{10}Q[5]$ complex: (a) an overall view of a $(HO)_{10}Q[5]/[PMo_{12}O_{40}]^{3-}$-based supramolecular assembly; (b) an isolated $(HO)_{10}Q[5]/[PMo_{12}O_{40}]^{3-}$-based "cell" along the crystallographic *a*-axis; (c) the detailed interactions between $[PMo_{12}O_{40}]^{3-}$ anions and the center $(HO)_{10}Q[5]$ molecule; (d) the detailed interactions between $(HO)_{10}Q[5]$ molecules and the center $[PMo_{12}O_{40}]^{3-}$ anions.

electron-rich Mo−O oxygen sites of $[PMo_{12}O_{40}]^{3-}$ and (2) the unusual hydrogen bonding (purple dashed lines, Figure 13c,d) of Mo═O or Mo−O groups of $[PMo_{12}O_{40}]^{3-}$ with methylene groups on the outer surface of neighboring Q[5] molecules.

Comparison of $(HO)_{10}$Q[5]/POM hydrides with unsubstituted Q[*n*]/POM hydrides shows a marked difference between the interaction of $O_{Mo=O}$ or O_{Mo-O} of $[PMo_{12}O_{40}]^{3-}$ with hydroxyl group of $(HO)_{10}$Q[5] and methine of unsubstituted Q[*n*]. The former interaction features classical hydrogen bonding ($O_{Mo=O}$ or $O_{Mo-O}\cdots H-O$) and the latter features unusual hydrogen bonding ($O_{Mo=O}$ or $O_{Mo-O}\cdots H-C_{methine}$). In addition, each hydroxyl group of the $(HO)_{10}$Q[5] molecule interacts with at least one Mo═O or Mo−O group of the $[PMo_{12}O_{40}]^{3-}$ anions. Based on this observation, our more recent experiment results suggest that the coordination assemblies of potassium/lanthanide cations to perhydroxycucurbit[5]uril in the presence of $[PMo_{12}O_{40}]^{3-}$ anions as the structure inducer through outer-surface interactions show significantly different selectivity behaviors. In particular, these differences can be used for the isolation of light lanthanides from their heavier counterparts.[40]

8. SUMMARY AND PERSPECTIVES

In this Account, we summarize a novel noncovalent interaction, the outer-surface interaction of Q[*n*]s with other species. This interaction may occur between Q[*n*]s, Q[*n*]s and aromatic molecules, or Q[*n*]s and inorganic molecules (polychloride transition-metal anions). Outer-surface interactions between Q[*n*]s are mainly hydrogen bonding between methine or methylene groups on the outer surface of Q[*n*] molecules and carbonyl oxygens from neighboring Q[*n*] molecules. They may occasionally include ion−dipole interactions between portal carbonyl oxygens of adjacent Q[*n*] molecules. Outer-surface interactions between Q[*n*] molecules and aromatic organic molecules could include (1) $\pi\cdots\pi$ interactions between carbonyl groups of Q[*n*] molecules and aromatic moieties of organic molecules and (2) $C-H\cdots\pi$ interactions of methine or methylene groups on the outer surface of Q[6] molecules with aromatic moieties of organic molecules. Outer-surface interactions between Q[*n*] molecules and inorganic anions include (1) hydrogen bonding of methine or methylene groups on the outer surface of Q[*n*] molecules with inorganic anions and (2) ion−dipole interaction between inorganic anions with the portal carbonyl carbons of an adjacent Q[*n*] molecule. Such outer-surface interactions of Q[*n*]s not only may result in the formation of novel supramolecular architectures but may also yield various functional materials. Studies on the outer-surface interaction of Q[*n*]s could establish a new branch in Q[*n*] chemistry, namely, Q[*n*]-based outer-surface interaction chemistry. It could be added to other areas of macrocycle chemistry, such as calixarene, cyclodextrin, and polyoxometalate chemistry. We believe that extensive studies on Q[*n*]-based outer-surface interaction chemistry will contribute to further development of supramolecular architectures and functional materials.

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