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Tetrachloridometallate Dianion-Induced Cucurbit[8]uril Supramolecular Assemblies with Large Channels and Their Potential Applications for Extraction Coating on Solid-Phase Microextraction Fibers

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Supporting Information

ABSTRACT: Q[8]-based porous materials were synthesized in the presence of $[M_{\text{d-block}}Cl_4]^{2-}$ anions as structure inducers. The driving forces of the structure-directing effect of the $[M_{\text{d-block}}Cl_4]^{2-}$ anions may be due to the ion−dipole interaction and hydrogen bonding between the $[M_{\text{d-block}}Cl_4]^{2-}$ anions and ≡CH or =CH$_2$ groups on the backs of Q[8] molecules. Moreover, the tests of potential applications show that these porous materials can not only capture organic molecules through the cavity of Q[8] moieties but also adsorb larger organic molecules with different selectivities.

Cucurbituril[1] and its isolated homologues[2] and derivates[3] characteristically have a fairly rigid hydrophobic cavity of low polarity accessible through two polar portal openings rimmed with carbonyl groups. They can not only function as hosts and include various guests but also act as ligands and coordinate with various metal ions, clusters, and so on, resulting in the establishment of Q[*n*]-based host−guest chemistry[4] and Q[*n*]-based coordination chemistry.[5,6]

In recent years, a branch of investigation involving supramolecular assemblies of cucurbit[*n*]urils has quietly evolved. For example, Kim and co-workers first demonstrated a pH-triggered hydrogel constructed of a simple Q[7], which exhibits guest-induced stimuli-responsive behavior. The driving force for gelation was suggested to be the propensity of Q[7] to aggregate through strong interactions between Q[7] portals and hydronium ions as well as between Q[7] molecules themselves.[7] Bardelang and co-workers demonstrated metal-free Q[6] and Q[8] hydrate crystals with water-filled channels consisting of perfectly aligned one-dimensional macrocycle nanotubes.[8] In particular, Kim and co-workers also discovered a Q[6]-based porous material exhibiting high thermal stability, permanent porosity, and remarkable sorption properties for acetylene[9] and dioxide carbon,[10] and they also discovered Q[8]-based porous materials exhibiting anisotropic proton conductivity.[11] These interactions between Q[*n*] molecules themselves may involve the dipole interaction between portal carbonyl oxygens with portal carbonyl carbons of neighboring Q[*n*] molecules as well as hydrogen bonding of portal carbonyl oxygens with methine (≡CH) or methylene (=CH$_2$) on the back of neighboring Q[*n*] molecules.[8]

A recent investigation showed that, in the presence of a second species, either an organic or inorganic molecule, one can still obtain Q[*n*]-based porous materials. For example, Lin and co-workers demonstrated Q[6]-based supramolecular complexes in the presence of calixarenes. These novel supramolecular compounds clearly show the role of hydrophobic−hydrophobic and hydrophilic−chydrophilic interactions in directing the supramolecular assembly.[12] Li and co-workers showed a rapid and facile method to access one-molecule-thick free-standing organic nanosheets with high yield and regular shape by the self-assembly of Q[8] and small organic molecules.[13] Fang and co-workers first demonstrated the hybrid porous materials based on the interaction of Q[6] or Q[8] with polyoxometalates (POMs). The driving forces were thought to involve the very opposite end of the carbonyl dipole, the electron-deficient carbon sites with oxygen of V=O from POM, and hydrogen bonding of V−O or V=O from POM with ≡CH or =CH$_2$ groups on the backs of neighboring Q[6] or Q[8] molecules.[14]

In recent years, our group has extensively studied the coordination of Q[*n*] with metal ions in the presence of a third species as structure inducers, in particular, the tetrachloridometallate ($[M_{\text{d-block}}Cl_4]^{2-}$, where $M_{\text{d-block}}$ = Cd, Zn, Cu, Co, Ni, etc.), which produced the so-called "honeycomb effect" and resulted in the formation of various coordination polymers.[15] The driving forces were again suggested to be the ion dipole interaction of the portal carbonyl carbons with Cl from $[M_{\text{d-block}}Cl_4]^{2-}$ anions and hydrogen bonding of carbonyl oxygens or Cl from $[M_{\text{d-block}}Cl_4]^{2-}$ anions with ≡CH or =CH$_2$ groups on the backs of neighboring Q[*n*] molecules. In the present work, we present some typical Q[8]-based porous materials in the presence of the above-mentioned inorganic structure inducers: $[M_{\text{d-block}}Cl_4]^{2-}$ anions, herein, $M_{\text{d-block}}$ = Cd, Zn, Ni. The crystal structures of these Q[8]-based porous supramolecular assemblies show that they are isomorphous with a common formula: $Q[8]\cdot 2[M_{\text{d-block}}Cl_4]\cdot 4H_3O\cdot aH_2O$ ($51 \le a \le 68$). A view of the interaction features between the Q[8] molecule with $[CdCl_4]^{2-}$ anions is given in Figure 1a as a representative example. One can

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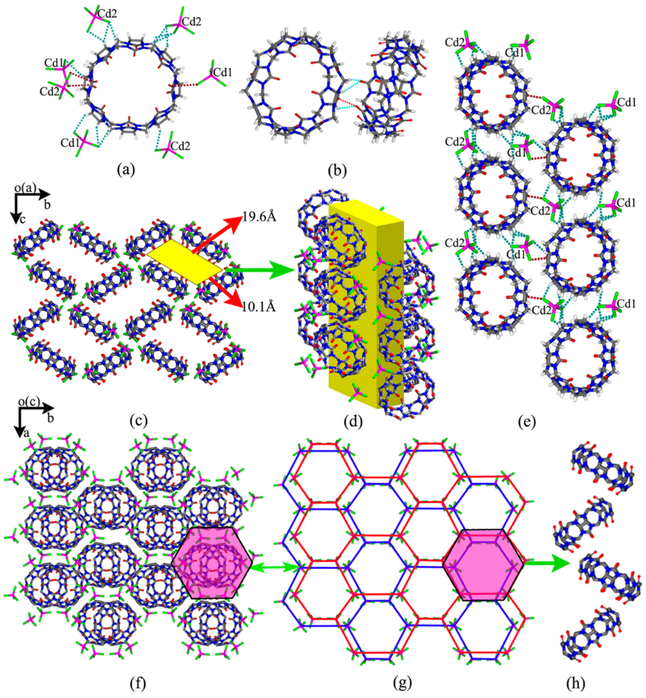
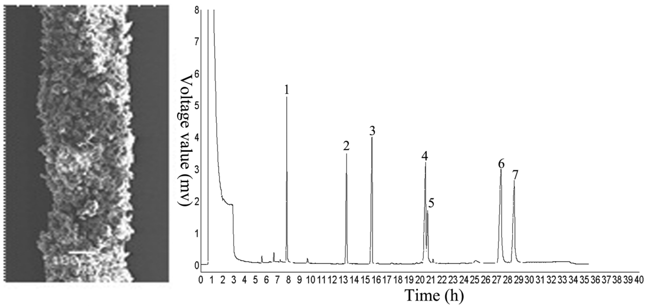


Figure 1. X-ray crystal structures of the $[CdCl_4]^{2-}$-induced Q[8]-based porous supramolecular assembly: a) the interaction features between the Q[8] molecule with $[CdCl_4]^{2-}$ anions; b) interactions between two adjacent Q[8] molecules; c) overall view of the Q[8]-based porous supramolecular assembly along the *a* axis; d) a parallelogram channel constructed of Q[8] molecules and $[CdCl_4]^{2-}$ anions; e) two adjacent Q[8]-based walls of the parallelogram channel; f) overall view of the Q[8]-based porous supramolecular assembly along the *c* axis; g) $[CdCl_4]^{2-}$-based honeycomb-shaped cells; h) a zigzag Q[8] molecule chain.

see that each Q[8] molecule is surrounded by seven $[CdCl_4]^{2-}$ anions through the ion dipole interaction between portal carbonyl carbons with Cl from $[CdCl_4]^{2-}$ anions (O=C···Cl, where the C···Cl distance in dark-red dashed lines = 3.36–3.40 Å) and hydrogen binding of Cl from $[CdCl_4]^{2-}$ anions with methine or methylene on the backs of Q[8] molecules (Cl···H–C, where the Cl···C distance in blue dashed lines = 3.60–3.84 Å). According to Figure 1a, one can imagine that each $[CdCl_4]^{2-}$ anion is, in turn, surrounded by Q[8] molecules (three for $[Cd_1Cl_4]^{2-}$ and four for $[Cd_2Cl_4]^{2-}$). Some extra interactions in these Q[8]-based porous supramolecular assemblies exist between two adjacent Q[8] molecules through dipole interaction between portal carbonyl oxygens with portal carbonyl carbons (O=C···O=C, where the C···O distance in red dashed lines = 3.02 Å) and hydrogen bonding of carbonyl oxygens with ≡CH or $=CH_2$ groups on the backs of neighboring Q[8] molecules (C=O···H–C, where the O···C distance in light-blue dashed lines = 3.11–3.53 Å). Thus, the combination of all of these interactions results in the formation of a novel Q[8]-based porous material with one-dimensional parallelogram channels with an average section of 83.2 $Å^2$ along the *a* axis (Figure 1c), which are filled with large amounts of water molecules. To the best of our knowledge, it is the largest Q[*n*]-based channel constructed of Q[8] molecules and $[CdCl_4]^{2-}$ anions (Figure 1d).[14,16] A close inspection reveals that the four Q[8]-based walls of the parallelogram channel are exactly the same, and the insides of the four walls are decorated with portal carbonyl oxygens, suggesting a strong polarity of the parallelogram channels (Figure 1e). On the other hand, along the *c* axis, one can also interpret the Q[8]-based porous supramolecular assembly (Figure 1f) as a combination of $[CdCl_4]^{2-}$-based honeycomb-shaped cells (Figure 1g) and the zigzag Q[8] molecule chains along the *c* axis (Figure 1h), which fill the honeycomb cells. In our previous works, the $[M_{d\text{-}block}Cl_4]^{2-}$ anions are present with the so-called "honeycomb effect" and induce Q[*n*] molecules directly to coordinate with metal ions, resulting in the formation of various coordination polymers.[15] Herein, one can see the different effect of the $[M_{d\text{-}block}Cl_4]^{2-}$ anions, which result in the formation of novel Q[8]-based porous materials (refer to Table S1 and Figures S1–S3 in the SI).

Above, we described the solid structure of the Q[8]-based porous supramolecular assembly in the presence of $[CdCl_4]^{2-}$ anions in detail. The channels and molecular cavities of Q[8] are estimated to fill with 54 and 18 water molecules per Q[8], respectively. Basically, the elemental analysis data of these Q[8]-based porous materials are consistent with their chemical formulas. The free volumes of the channels and molecular cavities are estimated to be 38 and 12%, respectively, of the total crystal volume. Gas (N_2) sorption isotherms for Q[8]–$[CdCl_4]^{2-}$ porous materials were measured up to 0.88 atm at 77.3 K, and the Brunauer–Emmett–Teller surface area of the Q[8]–$[CdCl_4]^{2-}$ porous materials calculated from the isotherm is 93.5 $m^2\,g^{-1}$ (Figure S4 in the SI). The pore volume is 0.083 $cm^3\,g^{-1}$, and the pore width is 3.169 nm. Curiously, what kinds of compounds can fill the channels and cavities of Q[8] molecules have not been fully investigated. Our previous work proved that the Q[8] molecule can include a series of phenanthrolines and methyl derivatives and the form of 1:2 inclusion host–guest complexes;[17] therefore, diffusion of these phenanthrolines into HCl solutions containing Q[8] and $M_{d\text{-}block}Cl_2$ ($M_{d\text{-}block}$ = Cd, Zn, Ni) could yield compounds with the same one-dimensional parallelogram channels, in which these phenanthrolines could fill the cavities of Q[8] molecules or channels. While the 1,10-phenanthroline is found to be included in the cavity of Q[8] molecule, no 1,10-phenanthroline is found in the channels as in the mentioned Q[8]-based porous materials (referring to Table S1 and Figures S5 in the SI). Each Q[8] molecule can only include one disordered 1,10-phenanthroline molecule in the 6 M HCl solution in the presence of $[ZnCl_4]^{2-}$ anions. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry of this Q[8]-based porous material clearly yielded an ion that was equivalent to a 1,10-phenanthroline@Q[8] species (for the 1,10-phenanthroline@Q[8] ion, *m*/*z* 1509.2, as shown in Figure S6 in the SI). The ^1H NMR spectrum of this compound further confirmed that 1,10-phenanthroline is included in the cavity of the Q[8] molecule, because the unbound Q[8] is not soluble in the neutral D_2O (refer to Figure S7 in the SI). The broadness of the resonances indicates a relatively fast exchange on the NMR time scale.[17]

The Q[8]-based porous materials were further investigated as extraction coatings on solid-phase microextraction (SPME) fibers to examine their other possible utilities. The SPME fiber comprises a supporting substrate and a thin layer of sorbent material.[18] Fused-silica fiber was used as the supporting substrate, and the Q[8]-based porous crystals were affixed onto the surface of the fused-silica fiber with high-temperature epoxy. The surface structure of the SPME fiber was investigated by scanning electron microscopy (SEM), as shown in Figure 2a; the microstructured coating is rough, porous, and uniform. The thickness of the coating is about 46 μm. Coupled to gas chromatography, the fiber was investigated with seven polycyclic



(a) (b)

Figure 2. (a) SEM image of the Q[8]-based porous crystal-coated SPME fiber with magnification 300×. (b) GC-FID chromatograms of seven PAHs extracted by the novel fiber with Q[8]-based porous crystal as its extraction coating. Peaks: naphthalene (1); acenaphthene (2); fluorene (3); phenanthrene (4); anthracene (5); fluoranthene (6); pyrene (7).

aromatic hydrocarbons (PAHs) in aqueous samples in the headspace mode. The linear range of detection of the proposed method was 50−5000 and 250−5000 $\mu g\ L^{-1}$ with coefficients of determination between 0.991and 0.998. Limits of detection for seven PAHs were 0.96−9.63 $\mu g\ L^{-1}$. The novel fiber with Q[8]-based porous crystals as its extraction coating exhibited excellent extraction efficiency and stability and could be applied in the analysis of trace PAHs in real water samples (Figure 2b).

In conclusion, we not only introduced a strategy to synthesize Q[8]-based porous materials by introducing $[M_{\text{d-block}}Cl_4]^{2-}$ anions as structure inducers, but we also demonstrated the potential selective sorption applications of these porous materials. The driving forces of the structure-directing effect of the $[M_{\text{d-block}}Cl_4]^{2-}$ anions may be due to the ion−dipole interaction and hydrogen bonding between the $[M_{\text{d-block}}Cl_4]^{2-}$ anions and ≡CH or $=CH_2$ groups on the backs of Q[8] molecules. Moreover, the tests for potential applications show that these porous materials can not only capture organic molecules through the cavity of Q[8] moieties but also adsorb larger organic molecules with different selectivities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file in CIF format and analytical 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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