ORIGINAL ARTICLE

Substituted cucurbit[*n*]uril rings, catenanes and channels

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Abstract The developments into the synthesis of networked rings, and channels generated in crystalline structures of substituted cucurbit[*n*]uril with metal ions and organic cations are reviewed. Pertinent chemical features and characteristics are discussed in the context of structural design and supramolecular architecture when utilizing substituted cucurbit[*n*]uril as building blocks.

Keywords Cucurbituril · MOF · Channel structures · Supramolecular rings

Introduction

Since the discovery of the family of molecules known as cucurbit[*n*]uril, Q[*n*] there have been a number of studies on the formation of solid state frameworks where these molecules are used as fundamental building blocks for supramolecular architecture [1–4]. More recently substituted cucurbit[*n*]uril, SQ[*n*] have resulted in an extension of this study, which has modified the influences of each of the driving forces that interplay in the construction of the supramolecular frameworks. Here in, we review the developments in the recent literature of frameworks that are formed from partially substituted SQ[*n*] to construct rings, catenanes and channels. Understanding what drives the formation of any of these three

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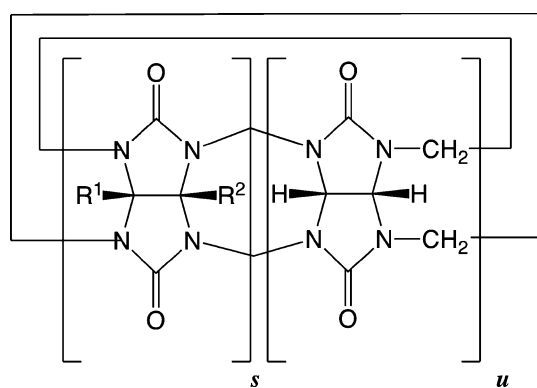Institute of Applied Chemistry, Guizhou University, Guiyang 550025, People's Republic of China

forms should enable the construction of such frameworks by design. Part of our exploration into this area has been motivated by the possibility of creating structures that contain channels between Q[*n*] or SQ[*n*] building blocks, that are essentially clear of molecules or ions, other than solvent molecules. Clear-channeled structures have the potential to act as absorption materials for gases and volatiles [5, 6]. Unsubstituted Q[6] in one of its polymorphic forms has been demonstrated to have porosity of the type described above and has been shown to absorb gases [7, 8]. Similarly an unsubstituted Q[5] in the presences of trifluoromethanesulfonic acid forms a channeled structure [9]. The interaction of trifluoromethanesulfonic acid with Q[5] is described as a series of direct hydrogen bonds between C–H···O (portal O), C–H···F (anion F) and indirect hydronium ion portal interactions. The consequence of these interactions is that the Q[5] stack into 1D supramolecualr chains and the columns of stacks create channels filled with the anion. The Q[7] under similar conditions also forms a structure through a series of hydrogen bonds comparable to those of Q[5]. The result is that the larger Q[7] forms helical chains in a 3D hexagonal packed column with a channel at the centre [9]. Other unsubstituted Q[5] structures with metal ions such as Hg^{2+} and Pb^{2+} also form channels but in general the channels are blocked with anions and therefore can not serve as porous structures [10]. In contrast to the linear chains that most Q[5] metal coordinated structures adopt, partially substituted SQ[5] (Fig. 1) have been shown to form coordination rings and not chains [11–17].

Metal ion coordination structures with substituted Q[5]

Four SQ[5]'s (Fig. 1) have been demonstrated to form metal organic frameworks (MOFs) and these frameworks are rings of two types—catenated and discrete.

Fig. 1 A representation of partially substituted SQ[n] where $n = s + u$; s = substituted glycoluril moieties and u = unsubstituted glycoluril moieties. A *Greek letter* identifies the relative position of each s. SQ[n] discussed in the text—CyH₅Q[5] ($R^1=R^2=(CH_2)_4$ and $u = 0$); α,β,δ-Me₆Q[5] ($R^1=R^2=$Me); α,β,δ-CyH₃Q[5] ($R^1=R^2=(CH_2)_4$); α-Me₂Q[5] ($R^1=R^2=$Me); α,δ-Me₄Q[6] ($R^1=R^2=$Me)

Fig. 2 Catenated 10-membered 'beaded' ring structures. Only two rings are shown to highlight the relative interrelationship. In its entirety the structure is complex with 10 trigonal branches from each ring to form two 3D networks of interlocking 10-membered ring systems

Catenated rings

When the substitution is of a high order such as the fully substituted pentacyclohexanocucurbit[5]uril (CyH₅Q[5]) or partial substitution where at least 3 glycoluril moieties carry substituents such as α,β,δ-hexamethylcucurbit[5]uril and α,β,δ-tricyclohexanocucurbit[5]uril (Fig. 1. α,β,δ-Me₆Q[5] and α,β,δ-CyH₃Q[5] respectively) the frameworks for all three are polycycles of 10-membered SQ[5] 'beaded' rings [15, 16].The channels created by these 10-membered SQ[5] 'beaded' rings are filled by an equal set of 10-membered SQ[5] 'beaded' rings which culminates in catenated frameworks (Fig. 2 catenation). This catenated structure occurs with the K^+ ions as the coordinating metal and would appear to be independent of the counter ion Cl^- or I^-. The K^+ ion is formally octacoordinate to O where six of these O are portal carbonyl O's and the remainder are water molecules. The direct coordination of a K^+ ion to the portal O's and a trigonal planar junction arrangement of three SQ[5] portals and three K^+ ions is a key feature leading to catenated ring formation. The accommodation of ten SQ[5] as 'beads' in the ring is probably a function of the hydrophobic nature of the equatorial substituents and the average diameter of the respective SQ[5] of ~ 12Å, fitting inside an equally hydrophobic 10-membered 'beaded' ring of ~ 19Å. Another important feature favoring ring formation and stability is the increased electronegativity of the carbonyl O of the substituted glycoluril moiety. The suggestion of increased electronegativity is supported by—theoretical calculations showing the Mulliken atomic charges on the O of the respective substituted glycoluril moieties are more negative [16] and—the measured higher binding of cations on Me₁₀Q[5] compared to unsubstituted Q[5] also points to this conclusion [18, 19].
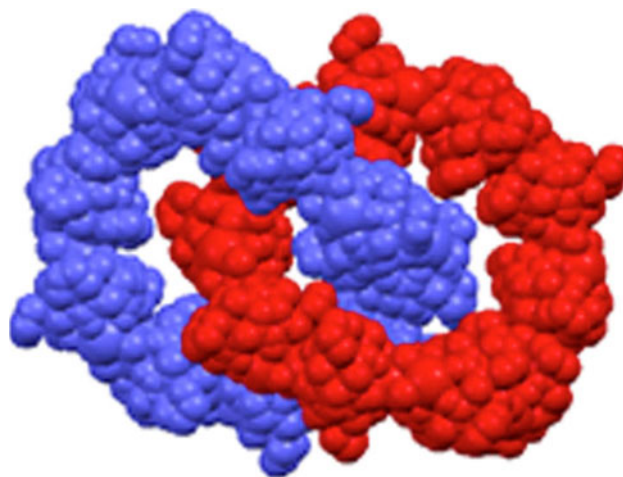
Discrete rings

At a lower order of substitution such as α-dimethylcucurbit[5]uril (α-Me₂Q[5]), 6-membered SQ[5] 'beaded' rings are formed [18]. These are discrete rings where each 'bead' in the ring is linked by of two Sr^{2+} ions directly coordinated to the SQ[5] portals (MOF ring). Each of these 6-membered rings is stacked upon one another forming channels. These channels are blocked by Cl^- ions, which are located in line with the channel but sandwiched between the stacked rings. The original publication's principle focus was on MOF formation of rings and with this, attention was drawn to the channel that is formed by the MOF ring stacks. Within the structure there are however, four channels of different cross sectional dimension. Three channels of different types (one is the MOF ring stack) all run in parallel with each other and a fourth channel is found perpendicular to the other three (Fig. 3). All of the channels contain water molecules and all except one are blocked by Cl^- ions. The Cl^- ion free channel (channel C) has a flat elliptical cross section $\sim 2.7 \times 15$ Å. The three channels (A, B and C) that open to the same face (bc face) of the structure (Fig. 3) are all formed from the arrangement of 6 SQ[5] 'beads' but this occurs in three different ways. There are three different construction components derived from SQ[5] found within the lattice, these are: (1) the 6-membered SQ[5] 'beaded' ring (MOF ring); (2) pairs of SQ[5] linked by two Sr^{2+} ions, and; (3) SQ[5] as individual units coordinated to a Sr^{2+} ion (Fig. 4a–c, respectively). Each of these as components, function as building blocks to form each of the hexagonal channels A, B and C. Within the face of the unit cell the
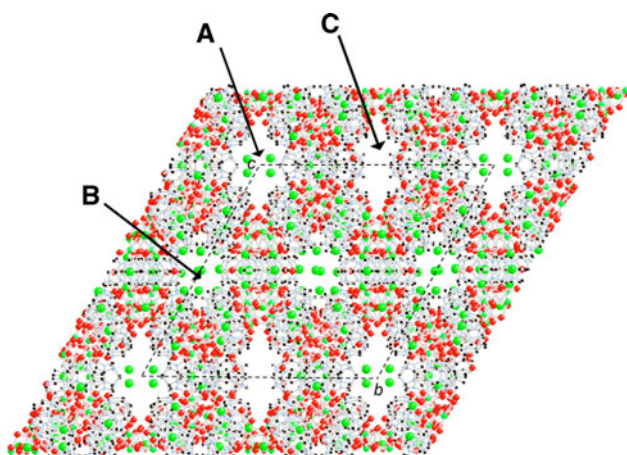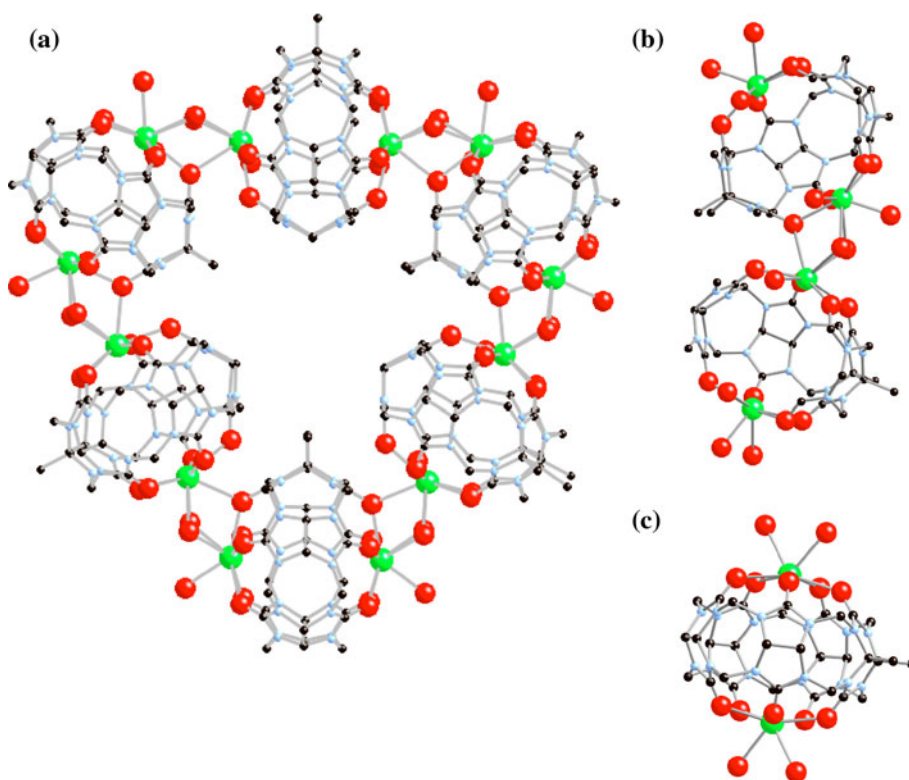
Fig. 3 Showing openings to three channel types *A*, *B* and *C* on the bc unit cell face (4 *A*'s, 2 *C*'s and 3 *B*'s). The unit cell face is indicated by the *dotted line*. The fourth channel type on the ac face is not shown. Channel water molecules have been omitted for clarity

opening to nine hexagonal channels can be found (see Fig. 3 bc face). Four of these hexagonal channels (A) are derived from the MOF rings, which are centered at the corners of the unit cell face. Three slightly smaller hexagonal channels (B) are also found on the same unit cell face, one face centered and two at parallel edges. These are derived from a hexagonal arrangement of single SQ[5], pairs of SQ[5] and the outer surface of 6-membered MOF

rings. And to complete the set of nine, two flat elliptical hexagonal channels (C) are found centered at the remaining opposite parallel edges. The C channels are derived from only, pairs of SQ[5] and the outer surface of 6-membered MOF rings.

What is perhaps surprising about α-Me$_2$Q[5] as a SQ[5] building block is that it does not form trigonal junctions. This is at least the case for the Sr^{2+} ion, which differs from the K$^+$ ion. It may be concluded that this is a consequence of the differences in the metal ion to O bond lengths where on average the K$^+$ to carbonyl O are $\sim$2.8Å and the Sr^{2+} to carbonyl O are $\sim$2.5–2.6Å. In addition, and as a likely consequence of the shorter Sr^{2+}–O bonds the portal openings are angled slightly closer to each other, $\sim$58° and $\sim$65° (Sr^{2+} ion junction compared to a K$^+$ ion mediated junction).

Recently, we published an example of a K$^+$ ion mediated junction of unsubstituted Q[5] and in this case the junction was a planar trigonal junction where the Q[5] formed hexagonal MOF rings that formed a network of hexagonal rings in a single layer [17]. This structure was achieved by templating the junctions on *p*-substituted phenols with functional groups such as COOH, CN or NO$_2$. The remarkable feature of this structure was that the MOF hexagonal channels where filled only with water molecules, producing a material that was found to be highly porous to volatile organic molecules [17].

Fig. 4 a discrete 6-membered SQ[5] (Me$_2$Q[5]) 'beaded' ring (MOF ring); **b** pairs of SQ[5] linked by two Sr^{2+} ions; **c** single SQ[5] unit coordinated to Sr^{2+} and water

Channels in a structure of tetramethyl Q[6] with an organic dication

The electronegative portals of Q[n] or SQ[n] clearly lend themselves to ion–dipole interactions with metal ions as discussed in the previous section and numerous published examples [1–4, 20]. In this section we review the resultant structure of α,δ-tetramethylcucurbit[6]uril (α,δ-Me$_4$Q[6], Fig. 1) and the organic dication bispyridiniumdecane (Bipda^{2+}) [21]. The focus here is on the formation of potential clear channels within the structure. The major driving force for a framework derived from α,δ-Me$_4$Q[6] and Bipda^{2+} is presumably an ion–dipole interaction between the α,δ-Me$_4$Q[6] portals and the pyridinium cation. However, given that a decane chain ties the two cation centers together, there should also be a hydrophobic driving force from the methylene chain. It appears that both of these driving forces are in play and an interesting channeled system is generated from these two components when they are crystallized from water.

As can been seen in Fig. 5, the openings to four channels are located at the center of each edge of the unit cell. These channels are elliptical ($\sim 5.2 \times \sim 10$Å) and filled with water molecules of low structural arrangement. The potential for these channels to create a porous structure is indicated by the location of the Br$^-$ ions, which are situated against the inner surface of the channel and do not obstruct the channel. This gives a clear column of water, which could potentially be displaced or evacuated as we have previously demonstrated with the Q[5] MOF structure discussed above [17].

The strongest driving force to this channeled structure is likely to be the ion–dipole interaction between the pyridinium cation and the electronegative portals. There are three possible modes of portal interaction for a pyridinium cation. These include: (a) an exterior association where the cation resides near the portal; (b) cavity encapsulation of the pyridinium ring with the N$^+$ interior and closest to the portal; (c) threading of the methylene chain through the cavity and the N$^+$ exterior and closest to the portal (Fig. 6 for binding modes—a, b and c). The third mode c has been reported for the 6 or 8 carbon chain equivalents to Bipda^{2+}, and here the chain spans the cavity where α,δ-Me$_4$Q[6] threads over the bispyridinium guest so that each pyridinium cation resides near each portal of the same SQ[6] [21, 22]. Alternatively, short 3 or 4 methylene carbon chains are found in combination with each of the modes a and b, represented in a solid structure (Fig. 6). However, the 10-carbon chain is too long to be accommodated by the cavity of a α,δ-Me$_4$Q[6] and therefore does not provide maximum ion–dipole interaction but the chain is long enough to allow adequate separation between two different SQ[6] portals. The pyridinium cation at each end of the chain is accommodated within a cavity with the N$^+$ located nearest the portal O's (association mode b Fig. 6). The hydrophobic chain is then packed closely to the outside surface of two α,δ-Me$_4$Q[6] molecules, specifically near methyl substituted glycoluril moieties (Fig. 7). As a consequence the methylene chain has minimal exposure to the water in the channel. The supramolecular unit of Bipda^{2+}@ (α,δ-Me$_4$Q[6])$_2$ forms a channeled structure through a series of networked hydrogen bonding interactions with only three water molecules involved OW (1, 2 and

Fig. 5 The structure of {Bipda^{2+} @ (α,δ-Me$_4$Q[6])$_2$}Br$_2^-$ showing the channel openings on the *ab face* of the unit cell. The water molecules have been omitted for clarity. The *brown (larger)* atoms are the Br$^-$ ions. (Color figure online)
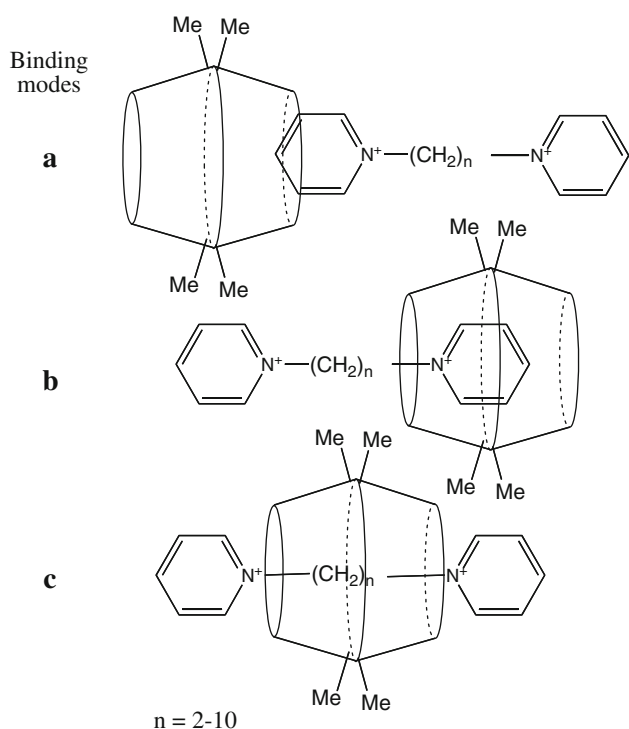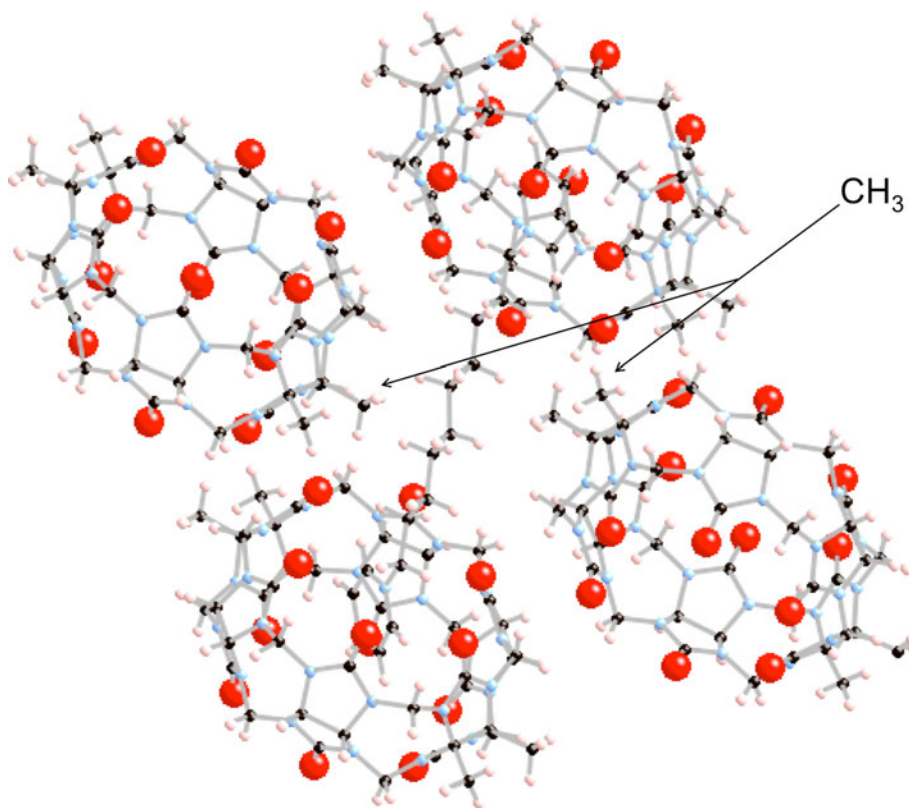
Binding modes

a

b

c

n = 2-10
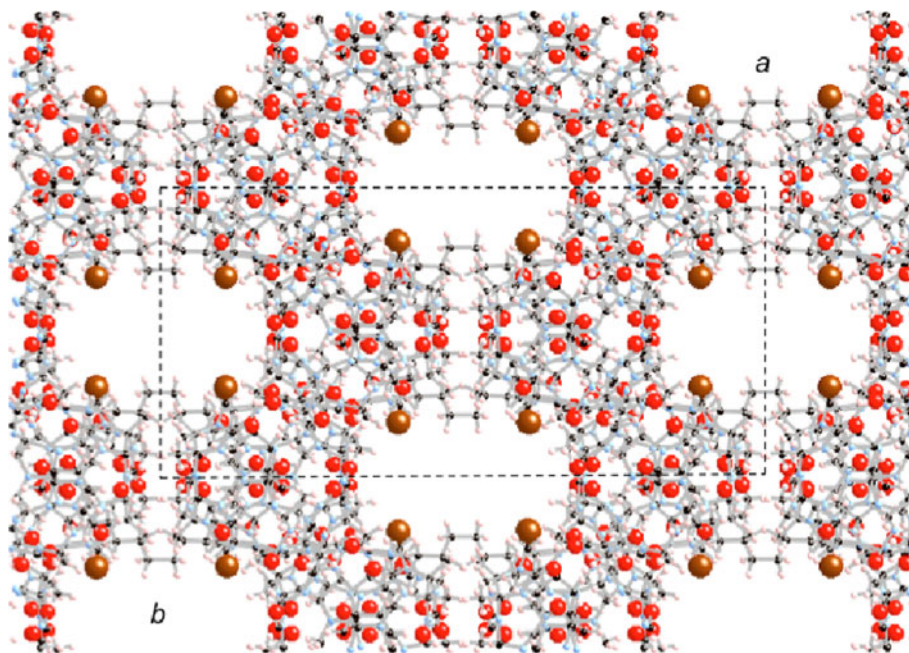
Fig. 6 Depiction of the three possible arrangements of the pyridinium ion relative to the electronegative portals of α,δ-Me₄Q[6]

3). O3 W for example forms H-bonds to the para proton of the pyridinium ring, a carbonyl O (O5) of the host ring and a neighboring α,δ-Me₄Q[6] methine H (H30). The remaining fifteen water molecules OW (4–18) form the loosely structured water of the channel.

The thermal stability of this type of structure has not been tested but given the reported stability of an H-bonded Q[6] structure, it is reasonable to expect that this structure could have a high thermal stability also [7]. The potential porosity of this structure warrants further exploration to evaluate its stability, absorption capabilities and its molecular absorption selectivity. Molecular absorption selectivity is likely to be different to the MOF structures previously discussed, compared to these organic structures derived from larger organic cations and SQ[n].

Conclusion

The relatively rigid empty barrel-shaped family of macrocycles Q[n] have provided a new building block for solid state construction and the substituted relatives SQ[n] have expanded these construction possibilities. The effect of a substituent group through the simple occupation of space

Fig. 7 Shows the hydrophobic methylene chain nestled between the methyl substituents of two other α,δ-Me₄Q[6]

by a substituent, or polarity differences both at the substituent group and an increased negative dipole of the carbonyl O have added an extra dimension to this area of solid state design. The dipole differentials between carbonyl O of glycolurils of the substituted and unsubstituted moieties have been exploited in MOF construction to create rings and channels. Organic cationic components and SQ[n] can also form channels through a combination of H-bonding networks and hydrophobic effects. Future structural design could also take advantage of cavity encapsulated organic dications, that adopt a specific orientation within a SQ[n] cavity such as α,δ-Me$_4$Q[6] which is ellipsoid in shape. This could be especially interesting where the linked dication has less flexibility and therefore would be dictated to pack differently.

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