Self-assembly principles in molecular crystals

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Abstract - The control of self-assembly during the crystallization of molecular solids is crucial for the design and synthesis of these materials. Consideration of self-assembly principles during the crystallization process should facilitate the development of rational approaches to supramolecular structures with desirable electronic properties. Described herein are strategies employing organometallic polycations that serve as templates for charge-transfer and hydrogen-bonded anion networks. The topology of the anion networks is directed by the spatial orientation of cation centers in the polycations, resulting in predictable dimensionalities. The observations suggest that this approach can lead to new materials with interesting electrical conductivity behavior.

The design and synthesis of molecular crystalline solids with desirable properties requires understanding of the factors that control the formation of different supramolecular structures. One of the larger obstacles to this goal is that control of crystal packing, which is the result of numerous weak intermolecular interactions such as van der Waal's, hydrogen bonding and charge transfer interactions, can be rather elusive. If crystal packing can be directed in a rational manner, it is likely that properties such as superconductivity, ferromagnetism, non-linear optical behavior and bioavailability can be controlled. Accordingly, "crystal engineering" strategies[1] that rely on intermolecular interactions in the solid state such as hydrogen bonding,[2] Cl···Cl interactions[3] and charge transfer[4] to direct crystal packing have been explored. The goal of these strategies generally involves optimizing these interactions to achieve the most thermodynamically stable structure. The common occurrence of polymorphs, however, suggests small energy differences between alternative crystal packing motifs. In these circumstances, it is reasonable to consider the self-assembly mechanisms that occur prior to the nucleation leading to a crystalline phase. The nucleation and growth of molecular crystals generally has not been considered in these terms, although recent studies indicate that appreciation for molecular recognition during crystallization is growing.[5] If the relationship between self-assembly and supramolecular structure can be better understood the rational design and synthesis of molecular solids may be realized.

Our approach has focused on a conceptualization of the crystallization process which involves the self-assembly of molecules into aggregates (Fig. 1). When the size of these aggregates exceeds the critical size for nucleation, crystal growth is initiated with the resulting macroscopic crystal exhibiting a supramolecular structure based on the self-assembled structure of the aggregates. This process can account for previous
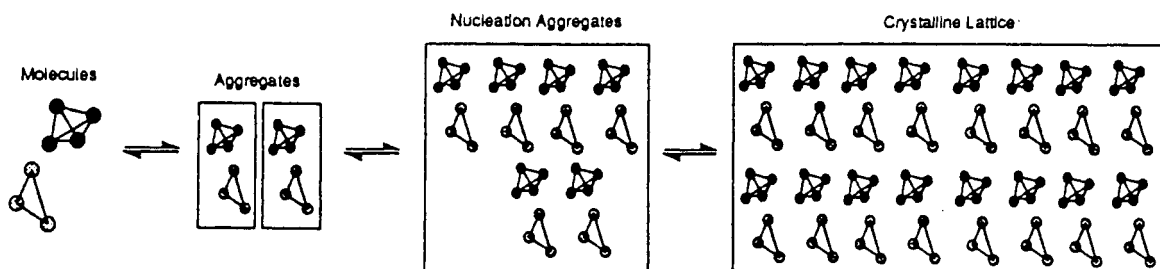

Fig. 1. Schematic representation of the evolution of self-assembled aggregates toward a macroscopic crystal.

successes in "crystal engineering." In these cases, crystal packing generally relies on molecular recognition between functionality on molecular components to direct the self-assembly process into a desirable motif. The role of electrostatic interactions between ionic molecular components during self-assembly and crystallization, however, has been relatively ignored. This is perhaps not surprising when one considers that the forces associated with electrostatic interactions are expected to be long-range compared to hydrogen bonding or van der Waal's interactions. It generally has been assumed that short range interactions are most important for crystal packing. If the motif formed during self-assembly of the prenucleation aggregate is responsible for the ultimate crystal packing, however, long range forces may be significant as they may govern the initial orientation of the molecules in the aggregate. Also, because the energetic differences between different possible polymorph motifs typically is small the force of electrostatic interactions may guide self-assembly toward a unique motif, especially if the ionic centers have an anisotropic topology.

In order to explore the effect of electrostatic interactions on self-assembly and crystal packing, we have explored the condensation of organic anions with organometallic polycations. While organic cations are also reasonable components, organometallic reagents provide for flexible design and a corresponding rich diversity of molecular shapes, sizes and topologies. In addition, the presence of d-states in organometallic systems can provide for unique electronic properties, such as that observed in ferromagnetic molecular solids prepared from ferrocene and manganocene charge-transfer salts.[6]

We have explored systems in which the organometallic polycations have various numbers of cationic centers per molecule with different spatial arrangements, providing unique topologies dictated by the arrangement of cationic centers. These cations include $(\eta\text{-}C_6Me_6)_2M^{2+}$ and $(\eta\text{-}C_6Me_3H_3)_2M^{2+}$ (M = Fe(1a,2a), Ru(1b,2b)), $Cp^*Ru(\eta\text{-}C_6Me_6)^+$ (3), $(Cp^*Ru)_2(\eta^6,\eta^6\text{-}[2_2](1,4)$ cyclophane)$^{2+}$(4), and $[Cp^*Ru(\eta\text{-}C_6Me_5)]_4C^{4+}(5)$.[7] Each of the compounds possesses a cationic metal center(s) capable of exerting an electrostatic force on negatively charged counterions. We have focused on anions that exhibit tendency to self-associate into stacks by either charge-transfer or hydrogen bonding. Our purpose was to partially restrict the degrees of freedom available to the anions so that the effects of cation topology on self-assembly could be studied more easily. The anions we have chosen include polycyanoanions and bifunctional hydrogen-bonding aromatic anions. The former, including $C_3[C(CN)_2]_3^{n-}$ (n=1,2) (6), iso-$[C(CN)_2]_3^{2-}$ (7) and tetracyanoquinodimethane (TCNQ, 8), commonly form organic conductors. Hydrogen bonded anions such as $HO_2C(C_6H_4)CO_2^-$ (9) may provide understanding of the role of this interaction in self-assembly.

1a,1b　　　2a,2b　　　3　　　4　　　5

6　　　　　　7　　　　　8　　　　　9
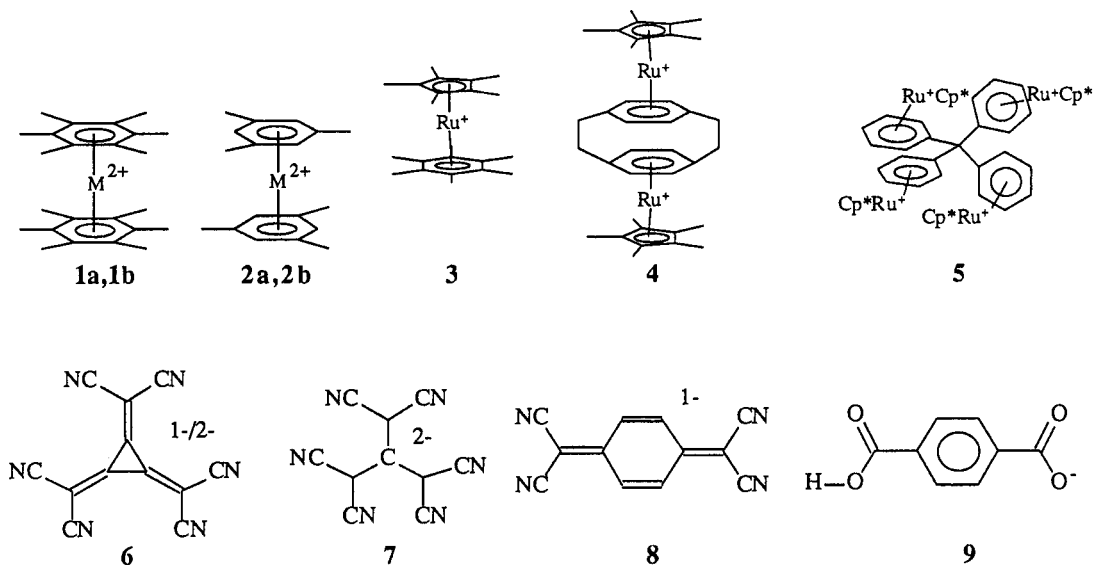
The strategy of this work is summarized in Fig. 2. Several alternative structures are feasible during assembly of monocations and anions. Confinement of two positive charges along a single axis such as in 4, however, would force alignment of planar charge-transfer anions parallel to the dication axis as aggregates form in solution. The length of the dication would dictate whether neutral forms of the anions could be accomodated in order to maximize packing density (this would results in different electron occupancy of the band structure that forms in these extended stacks). Finally, the topology of the tetracation, comprising two orthogonal axes of dipositive charge would be expected to guide the self-assembly of anions into orthogonal stacks to maximize electrostatic attraction.
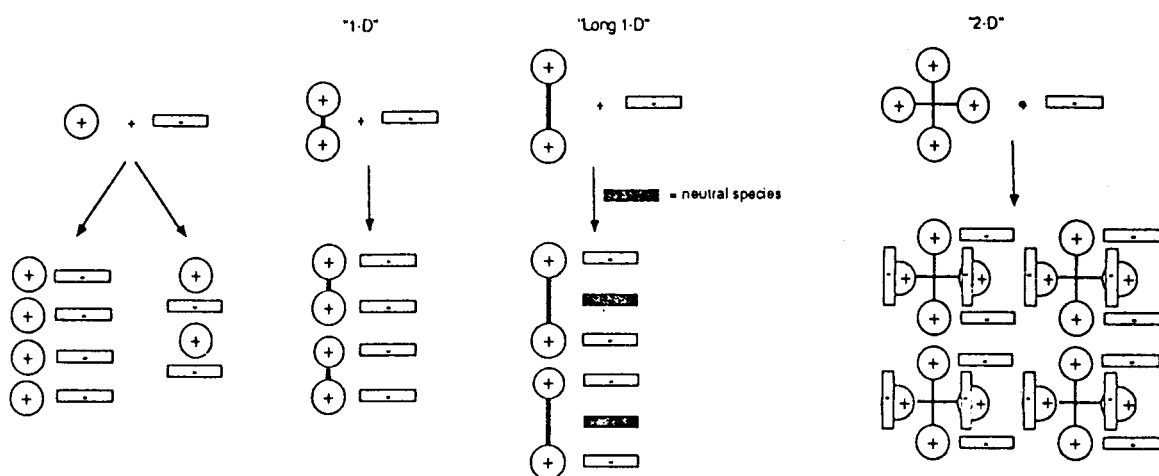
Fig. 2. Schematic representation of different self-assembled motifs for organometallic polycations and anions.

One particularly interesting example of electrostatic effects is the formation of the highly-colored charge-transfer salt $1a^{2+}6^{2-}$ and $1b^{2+}6^{2-}$. This compound crystallizes in the rhombohedral space group R3(bar), reflecting the three-fold symmetry of the cation and anion.[8] The single crystal X-ray structure reveals extended "mixed' stacks of cations and anions in an ...ABAB... pattern (Fig. 3a). This motif is believed to result from electrostatic and charge-transfer interactions between the dications and dianions. A segregated stack motif with extended anion chains is not possible owing to the closed shell nature of the dianions which does not allow for energetically favorable charge transfer interactions between dianions. Intermolecular charge transfer interactions are evident from the intense optical absorbance in the visible region that arises from excitation from anion-based states to cation-based states. The superposition of the anion and cation rings responsible for the orbital mixing required for these charge-transfer interactions is a common geometry for charge-transfer adducts formed in solution,[9] suggesting that during self-assembly electrostatics drives the formation of ion-pairs but that charge-transfer favors the geometry with superposition of the rings. The lattice motif, however, reveals the importance of electrostatic enforcement in self-assembly. Each anion is surrounded by six dications, undoubtedly the result of energy minimization in prenucleation aggregates by electrostatic interactions between the ions. Similar results obtain for the charge-transfer solids $2a^{2+}7^{2-}$ and $2b^{2+}7^{2-}$, which exhibit zig-zag ...ABAB... chains with the non-planar anions closely associated with the dication rings.[10] Electrostatic interactions between stacks are evident from the crystal packing that reveals each dianion is surrounded by four nearest neighbor dications. In this context, these motifs are not unlike those observed in inorganic ionic lattices that tend to maximize Madelung stabilization by maximizing oppositely charged nearest neighbors.
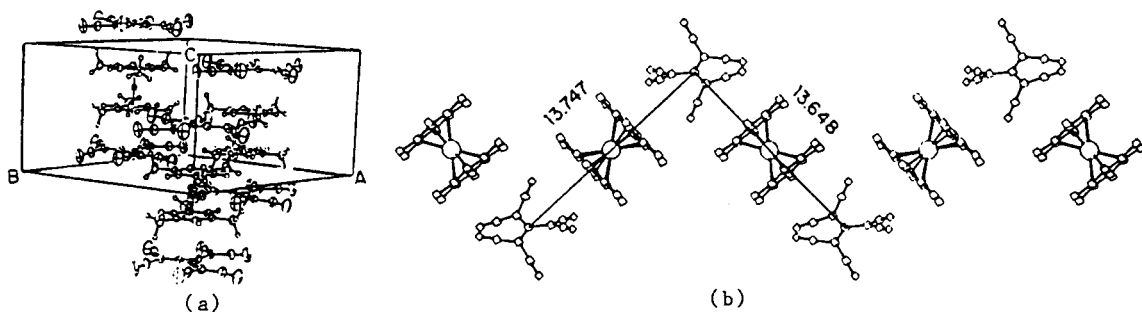

(a)   (b)

Fig. 3. (a) Single crystal X-ray structure of $1a^{2+}6^{2-}$ viewed normal to the stacking axis.
(b) Zig-zag chains of of $1b^{2+}7^{2-}$ normal to the chain axis.

The effect of polycation topology is especially evident in charge-transfer salts of the 6^{1-} monoanion. Condensation of two equivalents of this anion with $1a^{2+}$ forms extended segregated chains of cations and anions, with all the chains parallel (Fig. 4a).[11] Unlike the aforementioned compound with the 6^{2-} dianions, this structure indicates the strong tendency of the singly charged anion to form continuous chains

as a result of the charge-transfer interactions between these <u>open shell</u> species. Close inspection of the structure reveals that each anion chains is surrounded by four nearest neighbor dication chains, suggesting once again electrostatic interactions during self-assembly. It also should be noted that the cations are arranged side-to-side in their chains and the anions pack against the rings of the dications; this suggests that the positive charge of the dication is directed more along the ring-metal-ring axis. The single crystal X-ray structure of $4^{2+}(6^{1-})_2$ also reveals <u>parallel</u> anion stacks adjacent to six dication stacks (Fig. 4b).[12] Similarly, the compound $4^{2+}(8^{0.5-})_4$, which possesses semi-reduced anions and exhibits significant electrical conductivity (prepared by electrochemical reduction of 8 in the presence of 4), has parallel linear stacks of anions adjacent to the dication stacks (Fig. 4c). This suggests that this parallel enforcement is applicable to different anions.
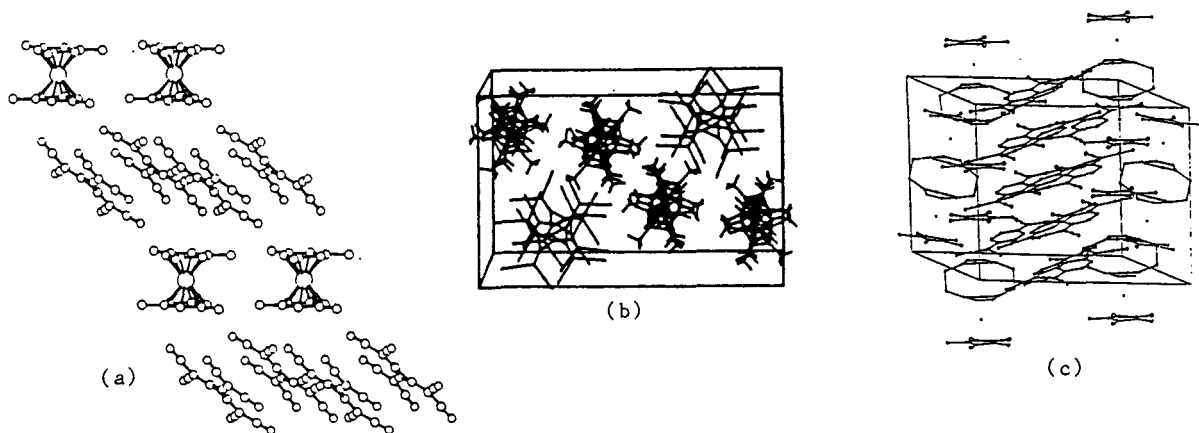

Fig. 4. (a) Projection normal to the stacking axis of $1a^{2+}(6^{1-})_2$. (b) View along the stacking axis of $4^{2+}(6^{1-})_2$. (c) View normal to the stacking axis of $4^{2+}(8^{0.5-})_2$.

The role of polycation topology becomes evident from the X-ray crystal structure of the charge-transfer salt prepared from 5^{4+} and four equivalents of 6^{1-}. This compound crystallizes in the monoclinic C2/c space group because of the presence of <u>orthogonal</u> extended anion stacks. This supramolecular structure is enforced by the topology of the tetracation. Inspection of the structure reveals that the anion stacks are actually parallel to the orthogonal axes of dipositive charge present in the tetracation. Therefore, the structural enforcement is no different than in the three previous examples, but the spatial arrangement of cation centers in 5^{4+} dictates the observed topology.
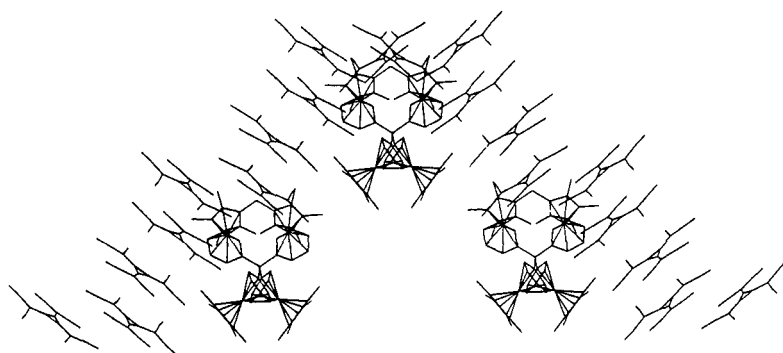

Fig. 5. View normal to the stacking axes in $5^{4+}(6^{1-})$.

The results described above demonstrate clearly the concept of electrostatic enforcement in the crystallization of compounds containing polycations and open-shell anions that tend to form extended stacks by charge-transfer interactions. We have observed aggregates of these anions in solution. It is therefore likely that this electrostatic enforcement occurs in the prenucleation aggregates preceding crystal growth. We have found that that self-associated hydrogen bonded networks also exhibit topology enforced by organometallic polycations. For example, condensation of 4^{2+} with two equivalents of the bifunctional

9^{1-} gives $4^{2+}(9^{1-})_2$, which contains ribbons of anions held together by the strong -C(=O)O·····HO-C(=O)-(Fig. 6a). These ribbons pack tightly around adjacent parallel to chains of dications. Once again, the tendency of the dication is to enforce the alignment of negatively charged anion chains along its one-dimensional axis. We currently envision the presence of hydrogen-bonded aggregates in solution that are associated with the dications to form prenucleation aggregates.
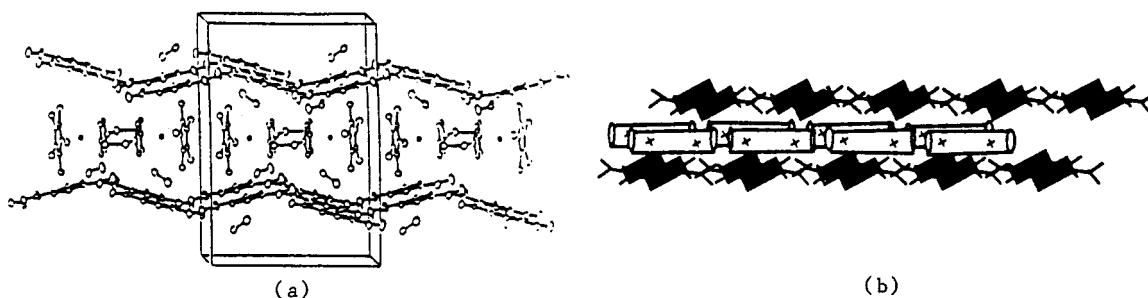

(a)   (b)

Fig. 6. (a) Single crystal X-ray structure of $4^{2+}(9^{1-})_2$. (b) Schematic representation of a possible supramolecular motif resulting from electrostatic enforcement of self-associated charge transfer acceptor anions.

These observations suggest interesting molecular engineering strategies involving self-assembly with these electrostatic "templates." One intriguing possibility would be to introduce hydrogen bonding functionality to charge-transfer acceptor anions such as TCNQ (**8**). It is expected that such anions would form hydrogen-bonded chains along an axis in the same plane as the long molecular axis, with the chains stacking in a direction normal to this axis. In the presence of polycations such as 3^{2+} one may expect lameller structures containing unusual two-dimensional conducting anion sheets. Interesting electronic properties are bound to result from unusual topologies such as this. More importantly, consideration of molecular-level self-assembly principles promises to facilitate the synthesis of new molecular solids.

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