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REVIEWS

Engineering of Lattice Inclusion Based on Dimer Synthon-Mediated Hierarchical Self-Assembly of Carboxylic Acids

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Abstract | The macroscopic properties of organic solids are largely dictated by organization of the constituent molecules in the crystal lattice. It is thus possible to control bulk properties of organic solids in a bottom-up approach by programming the constituent molecules to undergo self assembly in a specific fashion. Molecular recognition lies at the heart of lattice inclusion chemistry, and the study of lattice inclusion compounds allows in-depth insights into the fundamental aspects of host-guest chemistry. The phenomenon of lattice inclusion of guests as the functional property of solids, we have attempted to demonstrate how molecular building blocks with certain geometric disposition of COOH groups permits their self-assembly via the acid dimer synthon into hierarchical 0- to 3-dimensional superstructures that accommodate guests in the crystal lattice.

1 Introduction

Nature utilizes a variety of noncovalent weak interactions for diverse fundamental biological processes. Chemists have been endeavoring to emulate nature in controlling highly complex chemical systems by exploiting noncovalent interactions. The process by which molecules interact with each other through noncovalent interactions, under equilibrium conditions, to spontaneously form stable and structurally well-defined aggregates, as nature does, is molecular *self assembly*.[1–3] The formation of molecular crystals, colloids, self-assembled monolayers, association of ligands with receptors, folding of polypeptide chains into proteins and the folding of nucleic acids into their functional forms are all examples of molecular self assembly. The field of chemistry which aims at developing complex chemical systems from components interacting by noncovalent intermolecular forces is known as *supramolecular chemistry*,[1–3] and the resulting systems are known as *supermolecules*. The most common noncovalent intermolecular interactions are hydrogen bonds (both strong and weak), ion-ion interactions, weak coordination bonds, dipole-dipole interactions, cation-π interactions, π-π stacking, van der Waals forces and hydrophobic effects.[4–6]

Hydrogen bonding is by far the immensely exploited noncovalent interaction in creating structural aggregates due to its strength and directionality. In particular, the properties of solids, which represent an extreme of molecular aggregation, solely depend on the organization of constituent molecules.[7,8] Consequently, it is possible to control the properties of solids by programming the constituent molecules via functionalization with certain molecular subgroups to undergo self-assembly in a particular fashion. This indeed is *crystal engineering*,[7] which is defined as "*the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties*". The approach of engineering aggregation through certain molecular subunits is applicable in a variety of areas such as molecular recognition, catalysis, nonlinear optical materials, magnetic materials, development of drugs, etc. Herein, we are concerned with the use of hydrogen bonding as a glue to accomplish molecular order in the solid state. In particular, we shall try to exemplify how

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noncovalent hydrogen bonds in carboxylic acids can be exploited to develop *lattice inclusion compounds* based on rational design of constituent molecular modules.

The chemistry of lattice inclusion compounds has grown tremendously in the last 50 years.[9–11] Its importance is due to the fact that molecular recognition lies at the heart of lattice inclusion. The inclusion chemistry allows the size, shape and electronic complementarity between the host and the guest, which are integral to the phenomenon of molecular recognition, to be analyzed more meaningfully in the solid state. Given that porous systems that can include guest species reversibly may serve as solid-state reservoirs,[12] rational design of new host compounds that include guest species in the solid state essentially constitutes development of functional materials.

1.1 *Supramolecular synthons and self-assembly of carboxylic acids*

In general, not all atoms in a given molecule are important in molecular aggregation, but certain group(s) or grouping(s) of a few atoms, that is, functional groups, direct molecular organization by behaving as site(s) at which the molecules interact. The noncovalent interactions between functional groups manifest as recognition motifs, which have been referred to as '*supramolecular synthons*' by Desiraju.[13] The knowledge as to the robustness and reproducibility of these synthon(s) for a given functional group in the crystal structures of diverse compounds can be invaluable in the context of crystal structure prediction and crystal engineering. Based on Cambridge crystal structure database analyses, the supramolecular synthons have now been firmly understood for all functional groups that engage in noncovalent interactions, and have been categorized as *homosynthons* and *heterosynthons.*[14,15] The former are the self-association motifs that are composed of identical complementary functional groups in the form of dimers, chains, etc., and are observed for functional groups such as carboxylic acids, amides, alcohols, pyrazoles and oximes; while the latter, that is, *heterosynthons,* are composed of two or more different but complementary functional groups such as acid–aromatic nitrogen, acid–amide, hydroxyl–aromatic nitrogen, etc. In Figure 1 are shown some of these synthons based on O/N-H···O/N hydrogen bonds.

The carboxylic acids with both strong hydrogen bond donor (O–H) and acceptor (C = O) groups constitute one important class of functional group compounds that are widespread in nature. Their ability to assemble via H-bonding has led to rich supramolecular chemistry. The homosynthons observed heretofore for carboxylic acids are shown separately in Figure 1. The tetrameric[16] and helical synthons[17] are the rarest, and are virtually inconsequential in the context of crystal engineering. The dimer synthon with two hydrogen bonds is the most prevalent and robust synthon. The database analyses of the structures of carboxylic acids in which competing interactions due to other functional groups are absent reveal that the dimer motif is observed in more than 90% of the cases.[15] Depending on the conformations adopted by the interacting acids, there are other variants of the catemeric synthon,[18] namely *syn-syn*, *syn-anti* and *anti-anti,* which incidentally are very infrequent. Exceptionally, the catemeric motif has been shown to be observed under special conditions when auxiliary C-H···O hydrogen bonds aid the crystal packing.[18] Be this as it may, the robustness associated with the acid dimer motif has indeed paved way for demonstration of hierarchical molecular self-assembly based on geometric disposition of the acid functional groups in a given molecule.[19] In this brief review, we shall demonstrate how 0- to 3-dimensional assemblies—generated by the acid dimer synthon—of carboxylic acids with specific structural attributes allow the phenomenon of solid state guest inclusion to be observed. The choice of examples considered is purely our own, and omission of presumably better examples should not be misconstrued to undermine their importance.

1.2 *Lattice inclusion based on self-assembly of acids into 0-D discrete structures*

The 0-dimensional assemblies exhibiting guest inclusion are rare, and any demonstration of such a phenomenon requires very diligent approach and design. We discuss here three examples of molecular systems that aggregate to create voids in which guest molecules are included.

First is an impressive example reported by Nangia and co-workers,[20] who designed 4-tritylbenzoic acid **1** as a 'surrogate supermolecule' to mimic wheel-and-axle class of host compounds[21] that have a long linear axis with large rigid substituents at both ends; bulky terminal groups (wheels) prevent close packing around the central spacer thereby creating voids in which the guest species get included. The benzoic acid with the triphenylmethyl group at the *para* position was shown to self assemble with adoption of the dimer synthon to yield a wheel-and-axle type supermolecule, which crystallizes out with inclusion of a variety of aromatic guests such as *o*-, *m*- and *p*-xylenes,

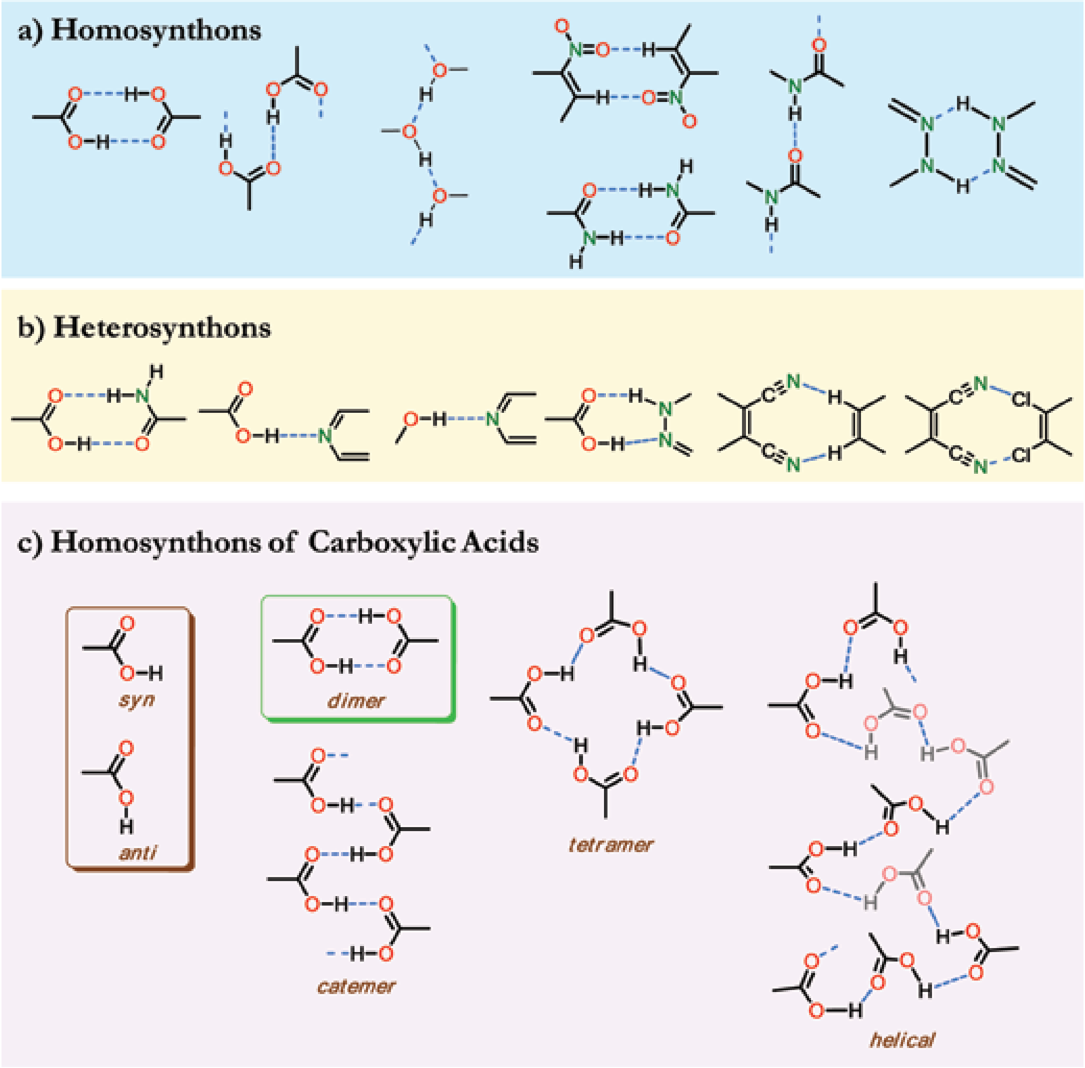
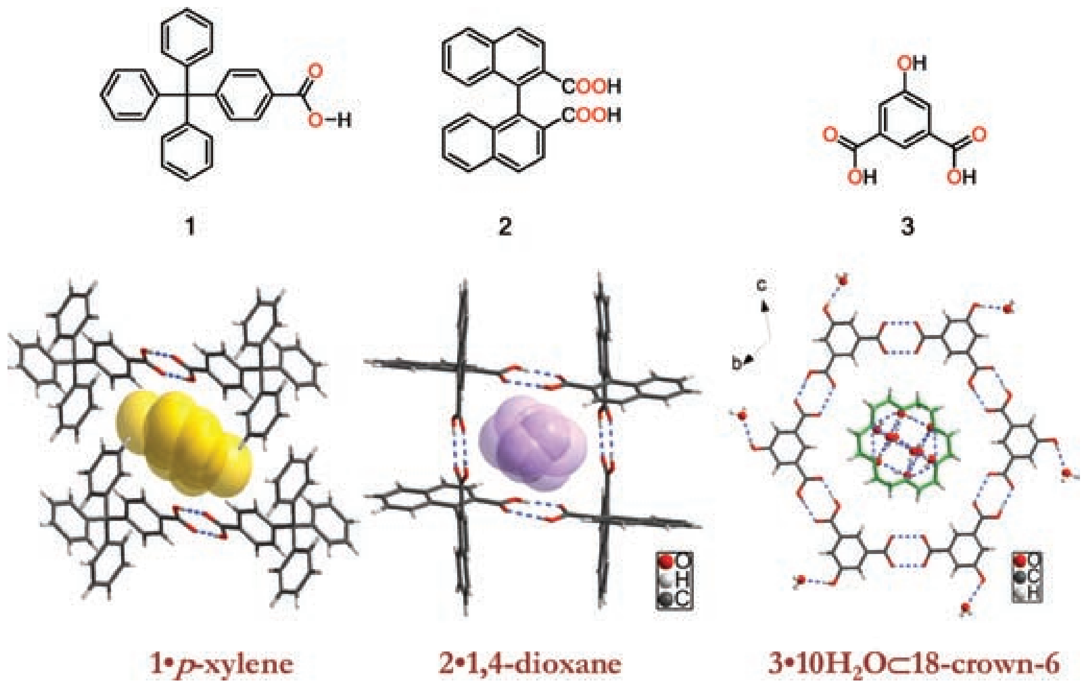


Figure 1: Some examples of homo- (a) and heterosynthons (b), and the conformations of carboxylic acids (*syn* and *anti*) and their homosynthons (c).

chlorobenzene, bromobenzene, mesitylene, anisole and nitrobenzene. In Figure 2 is shown the assembly observed in which the dimeric association of 4-tritylbenzoic acid leads to the inclusion of one of the guest molecules, i.e., *p*-xylene. Clearly, the dimeric association of 4-tritylbenzoic acid to mimic the lattice inclusion phenomenon of a unique class of inclusion host compounds should constitute a brilliant example of crystal engineering, whereby the solid state behavior, namely lattice inclusion, is achieved by a rational design of molecular module that exploits the acid dimer motif.

The second example is the case of self-assembly of 1,1′-binaphthyl-2,2′-dicarboxylic acid **2**. In fact, it has been found to be a versatile host system for inclusion of a variety of guest molecules.[22,23] The inclusion behavior has been attributed to the "amphoteric molecular backbone".[22] The bulky and twisted aromatic rings restrict the molecules from undergoing close packing leading to looser aggregation of molecules, while the COOH groups act as binding sites that aid in the propagation of the network via acid dimer motif forming a host matrix for inclusion of suitable guest molecules. In its inclusion compound with dioxane, four molecules of the diacid **2** are found to form a hydrogen-bonded tetramer via the acid dimer synthon, Figure 2. The resultant supramolecular macrocycles are filled by the disordered dioxane guests.[22]

The third constitutes the case of an isophthalic acid derivative **3**. Although the preferred self-assembly of isophthalic acid in the solid state should lead to a zigzag ribbon (vide infra), it has been demonstrated that insulated hexagonal honeycomb cages



$1 \cdot p$-xylene $2 \cdot 1,4$-dioxane $3 \cdot 10H_2O \subset 18$-crown-6

Figure 2: Structures of the lattice inclusion hosts **1-3** and their 0-dimensional self-assemblies with void spaces occupied by guest species.

formed by acid dimer-mediated aggregation of six building blocks have been shown to be engineered with 5-hydroxyisophthalic acid; in the cavities of the resultant aggregates, hydrated 18-crown-6 guests species are shown to be nested (Figure 2).[24] The water is found to be a decameric cluster that is centrosymmetric and fully ordered with the connectivity resembling that of the carbon skeleton of a bishomocubane with the methylene bridges replacing opposite C-C bonds of cubane.

1.3 *Lattice inclusion based on self-assembly of acids into 1-D polymers*

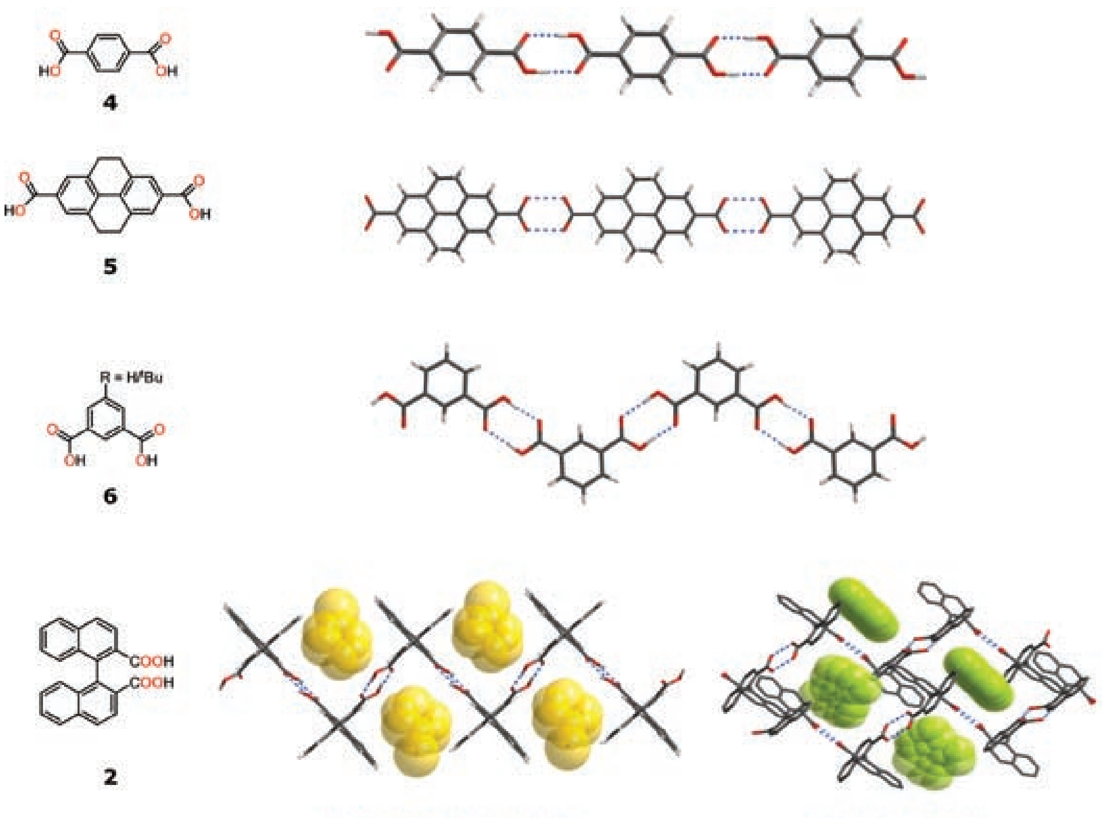
Depending on how the COOH groups in planar and rigid diacids are oriented with respect to each other, 1-dimensional chains that are linear or zigzag can be distinguished. For example, rigid planar terephthalic acid **4**,[25] 4,5,9,10-tetrahydropyrene-2,7-dicarboxylic acid **5**,[26] etc., adopt acid dimer motif in the solid state leading to 1-dimensional chains. However, in systems that are characterized by a kink defined by some angle between the COOH groups, e.g., 60° in phthalic acid,[27] 120° in isophthalic acid **6**[28,29] and 130° in furan-α-α'-dicarboxylic acid,[30] one observes the formation of zigzag 1-dimensional chains,[19] Figure 3.

It is difficult to fathom how 1-dimensional chains may lead to voids for guest inclusion. An interesting host system that permits inclusion of guests within 1-dimensional chains that are generated is the case of 1,1′-napththalene-2,2′-dicarboxylic acid **2**. This property comes about as a result of unique feature that renders the molecular system to be loosely packed in its crystal lattice. In Figure 3 are shown the lattice inclusion compounds of the diacid **2** formed with 4-bromobenzene[22] and *o*-xylene.[23] In all cases, the diacid **2** adopts the dimer motif leading to zigzag arrangement, which offers the possibility to create apolar cleft-like environment within the chains. For example, in the case of the inclusion compound formed with bromobenzene, the Br atom is located asymmetrically with respect to the oxygen atoms of the COOH groups to enable hydrogen bonding with the Br atom. The loose attachment of the bromobenzene molecule gives rise to the observed disorder.

Crystallization of the diacid **2** from xylene isomers at room temperature is found to yield three different inclusion compounds. In all the compounds, the guest molecules are incorporated within the infinite zigzag chains created by the acid dimer synthon as shown in Figure 3.

1.4 *Self-assembly of acids into 2-D porous network structures*

Hydrogen-bonded 2-D networks with void spaces for guest inclusion are exemplified by the self-assembly of building blocks with multiple



2•bromobenzene 2•*o*-xylene

Figure 3: The linear and zigzag 1-dimensional chains generated by acid-dimer mediated self-assembly of diacids **4-6** with different orientations of the COOH groups. At the bottom is shown how the self-assembly of **2** leading to zigzag chains allows guest species to be incorporated in the voids.

complementary terminal carboxyl groups that are suitably disposed. The 2-dimensional porous network structures have indeed been realized with a number of building blocks. We shall discuss a few cases of the self-assembly of triacids that lead to hexagonal pores and one case each of tetra- and hexaacids that yield rectangular and triangular void spaces, respectively. Insofar as the triacids are concerned, the self-assembly of trimesic acid, i.e., benzene-1,3,5-tricarboxylic acid **7**, represents a prototype for molecular self-assembly in general. The triacid **7** possesses trigonal exodentate functionality that facilitates self-assembly into two dimensions. In the solid state, this molecular system has been found to predictably undergo hydrogen-bonded self-assembly into hexagonal networks; further, it has been shown to lend itself to a variety of phenomena such as polymorphism, catenation, interpenetration and guest inclusion. The crystal structure of the α-polymorph of trimesic acid **7** was reported by Duchamp and Marsh in 1969.[31] The structure formed based on the acid dimer motif was found to contain pleated chicken-wire motif with voids of ca. 14 Å. The latter evidently are closed up by triple concatenation such that independent networks are interpenetrated. After a long hiatus, Herbstein documented a series of non-catenated chicken-wire structures mediated by the acid dimer as well as solvent-interrupted dimer synthons with the pores filled by a variety of guests.[32] In Figure 4 is shown a typical honeycomb sheet formed by triacid **7** with hexahelicene occupying the pores perfectly. The sheets are found to be bit puckered to permit C-H···O hydrogen bonding between the helicene and the oxygens of the triacid **7**.[33]

The extended sterically-rigidified derivatives of trimesic acid, namely 1,3,5-tris(4-carboxyphenyl) mesitylene **9** and 1,3,5-tris(2,6-dimethyl-4-caboxyphenyl)benzene **10**, have been demonstrated by us to undergo 2-dimensional self-assembly via the acid dimer synthon into honeycomb structures with a pore diameter of ca. 24-28 Å;[34,35] it should be mentioned that the guest inclusion phenomenon with the sterically unhindered benzene tribenzoic acid **8** has been noted to be unsuccessful.[36,37] To achieve close packing, both network structures have been found to be highly interpenetrated.

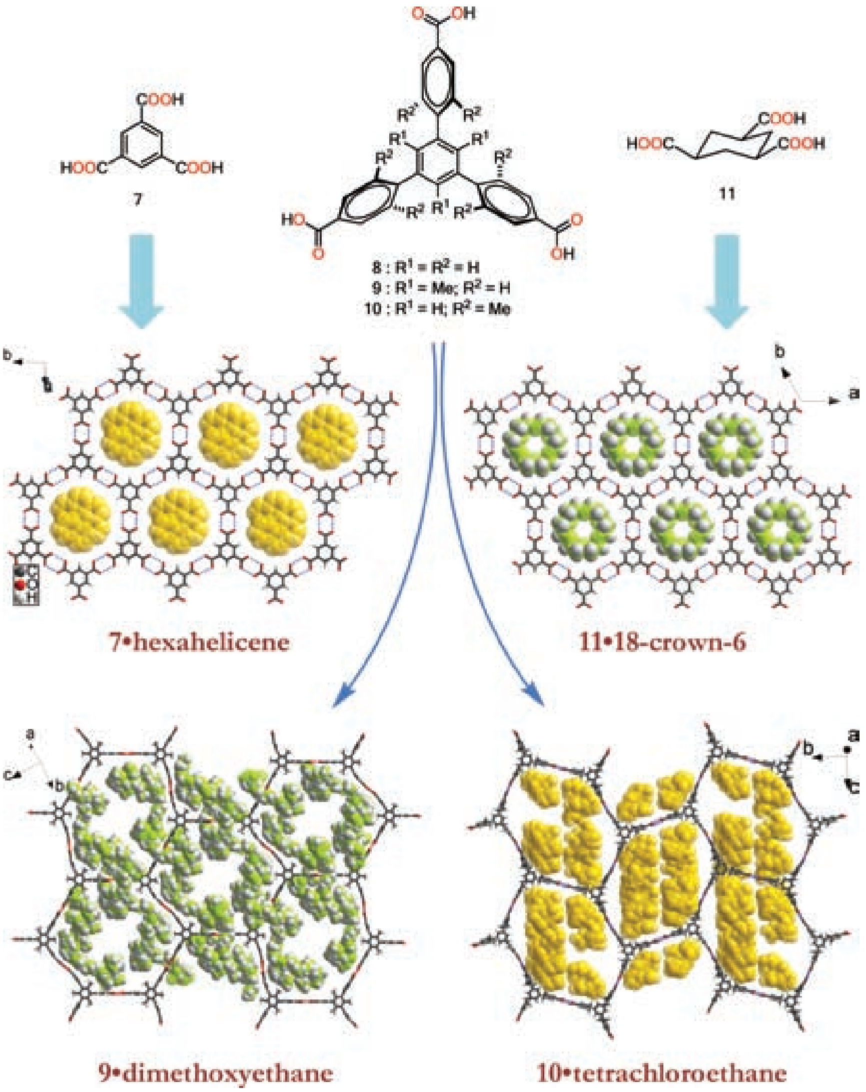


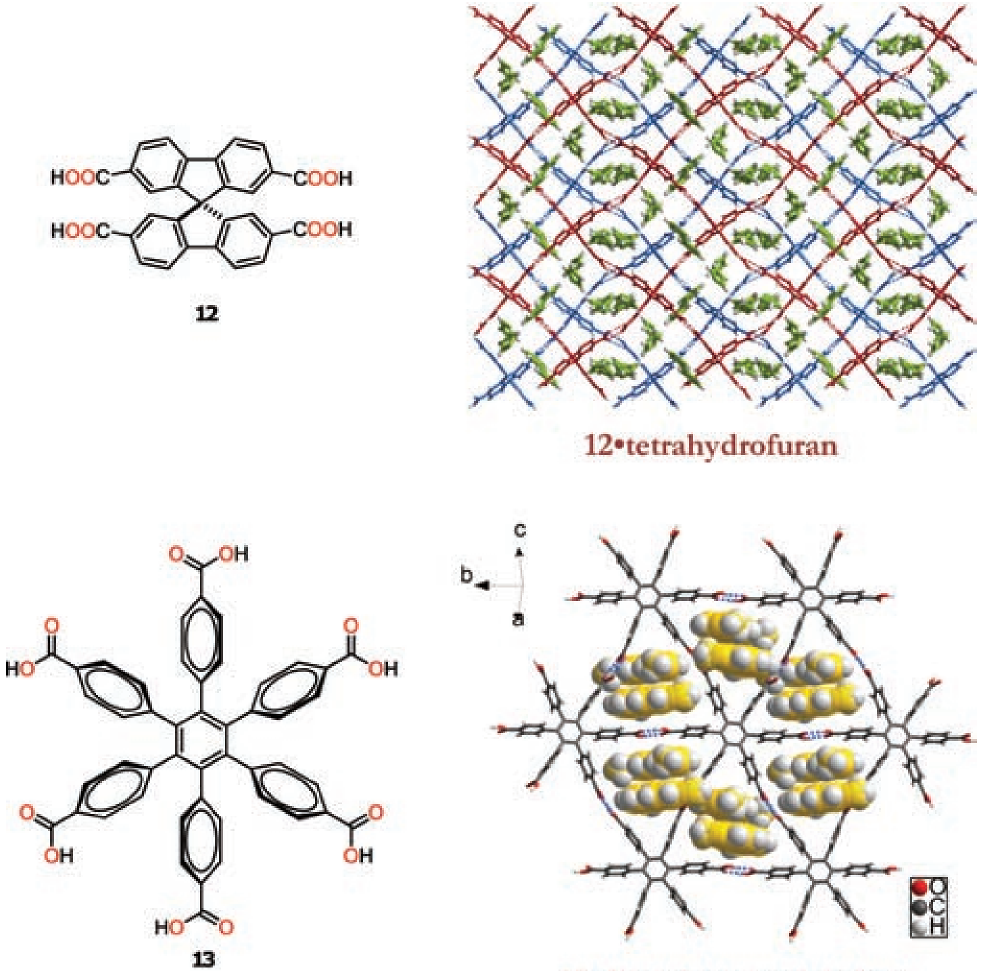
Figure 4: Acid dimer-mediated self-assembly of triacids **7-11** into honeycomb networks that include guest molecules.

Despite interpenetration, guests such as dimethoxyethane and tetrachloroethane have been found to be included in the crystal lattices of **9** and **10**, respectively.

The hexagonal structure formed by hydrogen bond-mediated self-assembly of cyclohexane-1,3,5-tricarboxylic acid **11** resembles the structure of **3** described previously. The highly symmetric network of triacid **11** in the crystal structure is stabilized by 12 C-H···O hydrogen bonds between the crown macrocycle and O atoms of six COOH dimers.[38]

Successful guest inclusion in the square-grid sheets constructed by the acid dimer-mediated self-assembly has been shown for 9,9′-spirobifluorene-2,2′,7,7′-tetracarboxylic acid **12** (Figure 5).[39] It turns out that two layers undergo interpenetration to preclude significant porosity. Otherwise, tetrahydrofuran has been shown to be included in the void spaces that still remain.

An excellent example of the self-assembly of a hexacarboxylic acid based on the acid dimer synthon was demonstrated by Kobayashi and co-workers sometime ago.[40] The latter showed that the aggregation of C_6-symmetric 1,2,3,4,5,6-hexakis(*p*-carboxyphenyl)benzene **13** leads to trigonal voids; each hydrogen-bonded hexacarboxylic acid has six nearest neighbors such that a non-interpenetrated 2D hexagonal hydrogen-bonded network is generated with large triangular cavities surrounded by three walls of the aromatic carboxylic acid dimers (Figure 5). Within the triangular cavities, 2,7-dimethoxynaphthalene has been shown to be included as a guest.



12

12•tetrahydrofuran

13

13•dimethoxynaphthalene

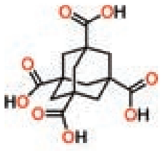
Figure 5: Square grid and triangular cavities generated by the self-assembly of tetraacid **12** and hexaacid **13**. Note that the void spaces are occupied by the guest species in both cases.

1.5 *Lattice inclusion based on self-assembly of acids into 3-D network structures*

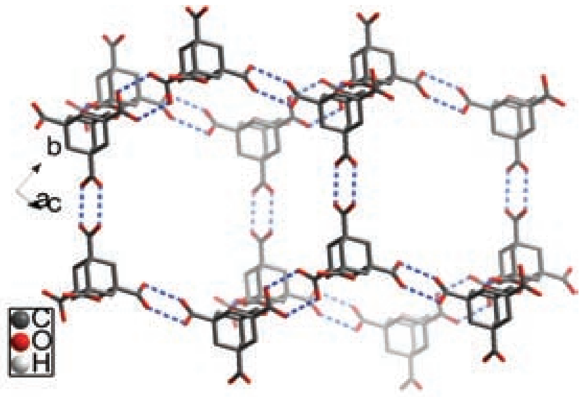
Hierarchical self-assembly of molecular building blocks into higher order complex and macroscopic structures in a predictable manner is the ultimate goal of supramolecular chemistry. Creation of 3-dimensional ordered structures based on linear acid dimer motif, conceivably, should be possible via molecular building blocks that are programmed to self-assemble in three dimensions. In other words, polyacids with disposition of the COOH groups in three dimensions should be a priori expected to lead to 3-dimensional assemblies. Of course, further attention to the structural attributes may impart the features for guest inclusion in the assemblies.

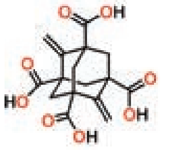
A fantastic example of 3-dimensional aggregation of a tetraacid that leads to super-diamondoid networks was reported by Otto Ermer.[41] The structural characterization of adamantane-1, 3,5,7-tetracarboxylic acid **14** and its implications have formed a strong basis for crystal engineering of molecular ordering in 3-dimensions. Following Ermer's studies, one observes a hectic activity in the literature on design of both organic and metal-organic diamondoid networks from first principles. The self-assembly of tetraacid **14** via acid dimer synthon leads to 3-D network, which has been found to be doubly interpenetrated with no possibility for guest inclusion. However, its derivative, i.e., 2,6-dimethylidene adamantane-1,3,5,7-tetracarboxylic acid **15**, has been shown likewise to undergo self-assembly and yield 2-fold 'double-diamondoid' structure as that observed for **14** (Figure 6), but with sufficient void space to permit inclusion of guests such as mesitylene, *t*-butylbenzene, etc.[42]

Incidentally, self-assembly of polyacids into porous architectures created purely based on the

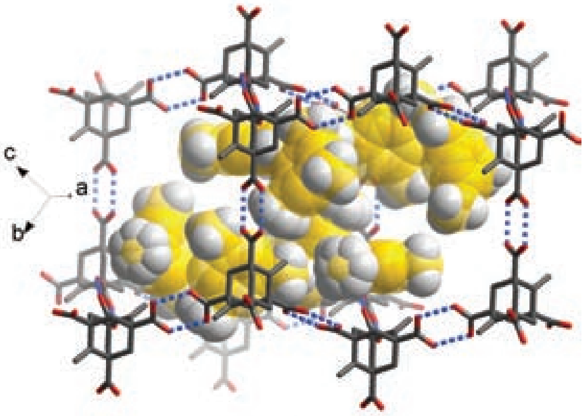


14





15



15•mesitylene

Figure 6: Acid dimer-mediated 3-dimensional self-assembly of adamantane tetracarboxylic acid **14** into diamondoid structure, which is doubly interpenetrated (top). Its dimethylene analog **15** undergoes self-assembly likewise, but with some void spaces, which are occupied by mesitylene guests (bottom).

acid dimer motif cannot be easily found in literature. Although a variety of porous hydrogen-bonded lattice inclusion compounds based on other functional groups has been reported,[43–46] those based on the dimer synthon of the acid are unknown subsequent to the reports by Ermer.

2 Conclusions

The fundamental precept of crystal engineering is that all the information necessary for 0-, 1-, 2- and 3-D structures is embodied in the molecular structure of the chemical species. The understanding of supramolecular chemistry and supramolecular synthons is being aided presently by the advent of CCD diffractometers coupled with sophisticated analytical and visualization tools. With ever-increasing understanding of molecular self-assembly and influence of subtle factors, a rational design of building blocks should be deciphered as being important to realize higher order complex assemblies with pre-defined properties. It is evident from the examples described herein that self-assembly of acids into 0-, 1-, 2- and 3-D crystals that include guest species, could be hierarchically engineered based on the acid dimer motif based on building blocks with suitable attributes. Clearly, diligent choice of building blocks in conjunction with functional groups that manifest in robust synthons should pave way for complex assemblies with pre-defined functions. As mentioned earlier, creation of 3-dimensional assemblies is a challenge, and should be best accomplished via building blocks that lend themselves to propagation of supramolecular synthons in three dimensions. Of course, the scope is abundant for explorations in this direction just as the creation of 3-dimesional lattice inclusion compounds based on the acid dimer motif. The formation of 3-dimensional complex assemblies for pre-defined function is certainly limited by innovative design of molecular building blocks.

Acknowledgments

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