# From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids

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## I. Introduction

Whereas single-crystal X-ray crystallography has represented an active area of research since shortly after the discovery of X-rays, the subjects of crystal design and crystal engineering have developed rapidly only in recent years. This is presumably an



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artifact of a number of factors. For example, the development of relatively low-cost and powerful computers has not only enhanced crystal structure determination, but also crystal structure visualiza-

tion, database development and analysis, and reflection analysis and processing. Simply put, X-ray crystallographic analysis has become less time consuming, relatively inexpensive, and more readily available, even for larger and/or difficult structures. The growth of crystal engineering has also coincided with advances in our understanding of intermolecular interactions and supramolecular chemistry and the realization that several aspects of solid-state chemistry are of increasing relevance and can only be resolved with a better understanding of structure—function relationships. It is the latter that will be the primary focus of this review, which is to present an overview of how advances in supramolecular chemistry have impacted the manner in which chemists view the existence of single crystals and, perhaps even more importantly, the design of new crystalline phases.

## A. From Molecules to Crystal Engineering

"*One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.*" This provocative comment by Maddox[1] illuminates an issue that continues to represent a challenge of the highest level of scientific and technological importance. Simply put, to quote Feynman, "*What would the properties of materials be if we could really arrange the atoms the way we want them?*"[2] Such a dream generally remains to come to fruition, at least in terms of molecular self-assembly in the crystalline state. However, it has spawned and fuelled a seemingly exponential growth in research activity devoted to the subjects of crystal design and crystal engineering. Furthermore, the implications go beyond materials science since structure—function relationships in the solid state are of relevance to opportunities in the context of areas of interest that are as diverse as solvent-free synthesis and drug design and development. The term crystal engineering was first coined in a contribution by G. M. J. Schmidt concerning the subject of organic solid-state photochemistry.[3] Schmidt's article marked a thought evolution in at least two important ways. First, as implicit by use of the term crystal engineering, it became clear that, in appropriate circumstances, crystals could be thought of as the sum of a series of molecular recognition events, self-assembly, rather than the result of the need to "avoid a vacuum". It has subsequently become clear that crystal engineering, especially in the context of organic solids, is intimately linked to concepts that have been developed in supramolecular chemistry, another field that has undergone explosive growth in recent years. Supramolecular chemistry, defined by Lehn as chemistry beyond the molecule,[4,5] and "supramolecular assemblies" are inherently linked to the concepts of crystal engineering. In this context, crystals might be regarded as being single chemical entities and as such are perhaps the ultimate examples of supramolecular assemblies or supermolecules. Dunitz referred to organic crystals as "supermolecule(s) *par excellence*".[6,7] As revealed herein, this interpretation

is fully consistent with the approaches to crystal engineering practiced by ourselves and others who are presently active in the field.

Second, Schmidt's work emphasized that the physical and chemical properties of crystalline solids are as critically dependent upon the distribution of molecular components within the crystal lattice as the properties of its individual molecular components. Therefore, crystal engineering has implications that extend well beyond materials science and into areas as diverse as pharmaceutical development and synthetic chemistry. In the context of the former, there are important processes and intellectual property implications related to polymorphism.[8-12] In the context of the latter, solid-phase organic synthesis can be solvent free and offer significant yield and regioselectivity advantages over solution-phase reactions. In other words, crystals should not be regarded as chemical graveyards. To the contrary, it is becoming increasingly clear that binary or inclusion compounds can be used to effect a diverse range of thermal and photochemical reactions in the solid state,[13-16] including some that cannot be effected in solution.[17-19]

In this contribution we concentrate upon advances that were spawned by a series of papers and monographs in the 1980s by Desiraju[20-22] and Etter[23-25] that concentrated upon using the Cambridge Structural Database[26] (CSD) for analysis and interpretation of noncovalent bonding patterns in organic solids. It should be noted that a considerable body of work devoted to the subjects of crystal nucleation, growth, and morphology was developed concurrently. This research, which could be perhaps termed "engineering crystals", is not the intended focus of this review and is exemplified by the work of research groups such as those of Cohen,[27] Green,[28] Addadi,[29-33] Mann and Heywood,[34,35] Thomas,[36,37] and Davey.[38,39] The seminal work by Desiraju and Etter in solid-state organic chemistry afforded the concept of *supramolecular synthons*[22] and led to hydrogen bonds being perhaps the most widely exploited of the noncovalent interactions in the context of crystal engineering. Their research programs addressed the use of hydrogen bonding as a design element in crystal design and delineated the nature (strength and directionality) of the interaction. It is now readily accepted that these forces include weak hydrogen-bonding interactions such as $C-H\cdots X$ and $CH\cdots\pi$. Although Professor Desiraju continues his valuable contributions to the discipline, Professor Etter passed away in 1992.

In this contribution, we attempt to address the challenges and opportunities represented by crystal engineering with particular emphasis upon how supramolecular concepts are important in helping us to understand supramolecular isomerism and superstructural diversity in the context of two classes of structure: coordination polymers and organic molecular networks.

## B. Crystal Engineering vs Crystal Structure Prediction

It is important to stress the significant conceptual difference between crystal engineering and crystal

structure prediction. In short, crystal structure prediction is precise (i.e., space group and exact details of packing are defined) and deals primarily with known molecules or compositions of molecules. Crystal engineering is less precise (e.g., network prediction) and most typically deals with entirely new phases, sometimes, but not necessarily, involving well-known molecules. Technological advances in experimental and computational methodology have accelerated the evolution of crystal engineering. In particular, the advent of CCD diffractometers facilitated the solution of crystal structures within hours or minutes rather than weeks or days and computational advances have made use of databases and visualization software inexpensive and straightforward. Therefore, although ab initio crystal structure prediction remains at best a significant challenge,[40−43] even for small molecules, crystal engineering has been able to develop rapidly because its objectives and *modus operandi* are distinctly different from crystal structure prediction. The *raison d'etre* and strategies of crystal engineering are somewhat different from those of crystal structure prediction since the former is primarily concerned with design and, although more restrictive in terms of molecular components that might be employed, is becoming increasingly synonymous with the concept of supramolecular synthesis of new solid-state structures. In other words, crystal engineering represents a paradigm for synthesis of new solid phases with predictable stoichiometry and architecture. In contrast, predicting a crystal structure requires analysis of the recognition features of a molecular component in the context of how they will generate crystallographic symmetry operations and optimize close packing, i.e., it requires space group determination.

Engineering and design are far less restrictive from a conceptual perspective since they focus more broadly upon the design of new and existing architectures. In effect, the principles of design are based upon a blueprint, in many cases a blueprint that is first recognized via a serendipitous discovery, and allow the designer to select components in a judicious manner. Therefore, a desired network structure or blueprint can be limited to chemical moieties, in many cases commercially available moieties, that are predisposed to a successful outcome.

## C. Supramolecular Isomerism

Closely related to the well-documented (but not necessarily well understood) subject of polymorphism in crystalline solids is the existence of supramolecular isomerism[44] in polymeric network structures. Supramolecular isomerism in this context is the existence of more than one type of network superstructure for the same molecular building blocks and is therefore related to structural isomerism at the molecular level. In other words, the relationship between supramolecular isomerism and molecules is similar to that between molecules and atoms. In some instances, supramolecular isomerism can be a consequence of the effect of the same molecular components generating different supramolecular synthons and could be synonymous with polymorphism. How-

ever, in other situations, supramolecular isomerism is the existence of different architectures (i.e., architectural isomerism[45]) or superstructures. In this context, the presence of guest or solvent molecules that do not directly participate in the network itself, especially in open framework structures, is important to note as it means that polymorphism represents an inappropriate term to describe the superstructural differences between network structures. Indeed, it is reasonable to assert that polymorphism can be regarded as being a type of supramolecular isomerism but not necessarily vice versa. Pseudopolymorphism is a related term that has been coined to categorize solvates,[46,47] especially in the context of pharmaceutical solids. Since solvent molecules are often integral parts of the resulting network structures, a pseudopolymorph is, at least from a supramolecular perspective, a binary phase and an entirely different class of compound.

The subject of supramolecular isomerism is important for a number of reasons. (1) Investigation of the relationship between supramolecular isomerism and polymorphism represents a fundamental scientific challenge. However, when one considers that bulk properties of solids are critically dependent upon architecture and that crystal structure confirms composition of matter from a legal perspective, the applied relevance also becomes immediately apparent. Polymorphism in molecular crystals represents a phenomenon that is particularly important and ubiquitous in the context of pharmaceuticals and is receiving increasing attention from a scientific perspective.[48−53] It should also be noted that McCrone was prompted to suggest that the "*number of forms known for a given compound is proportional to the time and money spent in research on that compound*".[54] However, the generality of McCrone's statement remains ambiguous despite indications that polymorphism is more general than expected from the CSD.[55] For example, Desiraju[47] demonstrated that the frequency of occurrence of polymorphic modifications is not necessarily uniform in all categories of substance. His analysis revealed that the phenomenon is probably more common with molecules that have conformational flexibility and/or multiple groups capable of hydrogen bonding or coordination. Coincidentally and importantly, this is inherently the situation for many pharmaceuticals and conformational polymorphism is a subject in its own right.[56,57] Desiraju also suggested that polymorphism can be strongly solvent-dependent. In summary, the relevance of polymorphism is clear but remains a subject that is not fully or widely understood at a fundamental level.

(2) Control over supramolecular isomers and polymorphs lies at the very heart of the concept of crystal engineering (i.e., design of solids). However, there is presently very little understanding concerning even the existence of supramolecular isomers, never mind how to control them.

(3) Supramolecular isomerism also lies at the heart of gaining a better understanding of supramolecular synthons and, by inference, how they develop and occur in other solid phases and even solution. The

**Scheme 1. Schematic Representation of Some of the Simple Network Architectures Structurally Characterized for Metal−Organic Polymers: (a) 2D Honeycomb, (b) 1D Ladder, (c) 3D Octahedral, (d) 3D Hexagonal Diamondoid, (e) 2D Square Grid, and (f) 1D Zigzag Chain**



　　　　(a)　　　　　　　(b)　　　　　　(c)　　　　　　　　(d)　　　　　　　(e)　　　　　　(f)
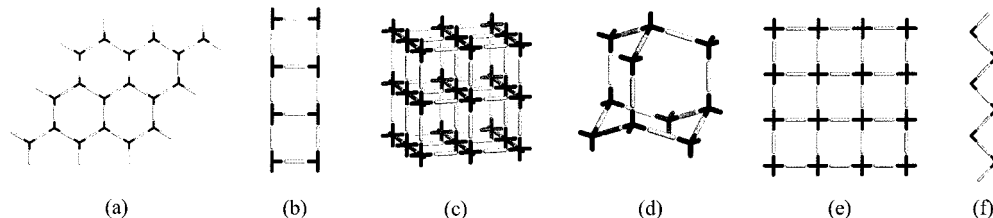
Cambridge Structural Database remains a very powerful tool in this context, but it must be remembered that even such a large database will not necessarily be reflective of the full range of compounds that will be isolated and characterized in future years.

The conceptual link between polymorphism and supramolecular isomerism in organic and metal−organic networks is not immediately apparent. However, since polymorphs can be rationalized on the basis of supramolecular interactions, polymorphism can be regarded as a type of supramolecular isomerism. Implicitly, all sets of polymorphs can therefore be regarded as being supramolecular isomers of one another but the reverse is not necessarily the case. It should also be noted that solvates are almost always different compounds from a crystal engineering perspective. The only exception would be in the case of inclusion compounds where the host framework remains intact in the presence of different solvent molecules, i.e., the solvent serves the function of being a guest molecule. Supramolecular isomerism as seen in metal−organic and organic networks may be classified based upon analogies drawn with isomerism at the molecular level. Thus far it is appropriate to categorize the following classes of supramolecular isomerism.

**Structural.** The components of the network (i.e., the metal moiety and the ligands the or exofunctional organic molecule) remain the same but a different superstructure exists.[44] In such a situation, the networks are effectively different compounds even though their empirical formula and chemical components are identical.

**Conformational.** Conformational changes in flexible ligands such as bis(4-pyridyl)ethane generate a different but often related network architecture.[44] Conformational polymorphism is a closely related subject.[56,57]

**Catenane.** The different manner and degrees in which networks interpenetrate or interweave can afford significant variations in overall structure and properties depending upon the molecular building blocks that are utilized.[58] Interpenetrated and non-interpenetrated structures are effectively different compounds because their bulk properties will be so different.

**Optical.** Networks can be inherently chiral and can therefore crystallize in chiral (enantiomorphic) space groups. Therefore, an analogy can be drawn with homochiral compounds. This type of supramolecular isomerism lies at the heart of an important issue: spontaneous resolution of chiral solids.[59−65]

The remainder of this contribution reviews the subject of supramolecular isomerism and how it leads to superstructural diversity in network solids. Emphasis is placed upon metal−organic or coordination polymers and organic solids, respectively. However, it should be noted that the subject matter is divided along these lines for convenience only since the basic concepts apply equally well to both classes of compound.

## II. Coordination Polymers

Coordination polymers exemplify how crystal engineering has become a paradigm for the design of new supramolecular structures. In this context, the work of Wells is exhaustive and seminal and can serve as a reference point. Wells was primarily concerned with the overall structure of solids, particularly inorganic compounds.[66,67] He defined crystal structures in terms of their topology by reducing them to a series of points (nodes) of a certain geometry (tetrahedral, trigonal planar, etc.) that are connected to a fixed number of other points. The resulting structures, which can also be calculated mathematically, can be either discrete (zero-dimensional) polyhedra or infinite (one-, two-, and three-dimensional) periodic nets.

It is perhaps surprising that it took until the 1990s for the approach of Wells to bear fruit in the laboratory. Robson[68−75] was primarily responsible for the initial studies that facilitated rapid development of the field of coordination polymers alongside that of crystal engineering of organic solids. Robson extrapolated Wells work on inorganic network structures into the realm of metal−organic compounds and coordination polymers. In this context, the resulting "node and spacer" approach has been remarkably successful at producing predictable network architectures. Scheme 1 illustrates some of the simplest architectures that can be generated by using commonly available metal moieties and linking them with linear "spacer" ligands. Whereas diamondoid networks represent a class of structure that could be described as mineralomimetic because there are many naturally occurring analogues, that is not the case for any of the other architectures illustrated in Scheme 1.

The nature of these novel structures and their organic analogues and the diversity exhibited by their *supramolecular isomers*[44] represent the primary focus for the remainder of this contribution. Such structures are of interest for both conceptual reasons and because of their interesting properties. They are

ideally suited to illustrate the concepts of crystal engineering for the following reasons. (1) The diversity of structures that can be obtained from the simplest of components is quite remarkable, not only in the context of coordination polymers but also in the context of organic solids and even, for that matter, discrete architectures. (2) Coordination polymers can be relevant in the context of inclusion chemistry. As should be clear from Scheme 1, a recurring feature of even the simplest network structures is the presence of voids or cavities that are inherently present because of the architecture itself and the dimensions of the spacer ligands. This feature is attracting considerable interest, and there are a number of recent reports concerning open framework coordination polymers that exhibit hitherto unprecedented levels of porosity and high levels of thermal stability. Indeed, there already exists a diverse range of coordination polymers with higher effective surface areas than zeolites and stability to loss of guest.[76-84] (3) From a design perspective, it should be clear from Scheme 1 that each of the networks illustrated is based upon at least two components (i.e., the node and the spacer) and, as will become clear herein, such components can be preselected for their ability to self-assemble. The network structures can therefore be regarded as examples of blueprints for the construction of networks that, in principle, can be generated from a diverse range of chemical components, i.e., they are prototypal examples of modular frameworks. It should be noted that the construction of networks from single-component systems also represents an important area of activity. Self-assembly of a single-molecular component, or "molecular tectonics", represents a different approach to crystal design, and it must be remembered that most existing crystal structures are based upon a single component. However, in order for single-component self-assembly to be directly relevant in the context of crystal engineering, all the molecular recognition features that lead to supramolecular synthons must be present in a single molecule. 1,3,5,7-Adamantanetetraacetic acid[85,86] and methanetetraacetic acid[87] can be regarded as being prototypal for self-assembled diamondoid architectures. Both structures are sustained by one of the most well recognized supramolecular synthons—the carboxylic acid dimer.[88] Pyridone dimers have been used in a fashion similar to build diamondoid networks, in this case from tetrahedral tetrakispyridones.[89] A number of well-known inorganic structures can also be regarded as examples of self-assembly (e.g., ice, potassium dihydrogenphosphate), and one might even consider covalent bonds as conceptually related: diamond, Si, Ge, ZnS, BP, GaAs, ZnSe, CdS, $CuInSe_2$, $CuFeS_2$ (chalcopyrite). However, this contribution will focus primarily upon the modular or multicomponent approach to crystal design. Coordination polymers and hydrogen-bonded structures with multiple complementary components can be regarded as being the consequence of modular self-assembly.[90]

The remainder of this section will be organized according to the dimensionality of the observed

**Scheme 2. 3D Models of the Regular (Platonic) and Semiregular (Archimedean) Solids**
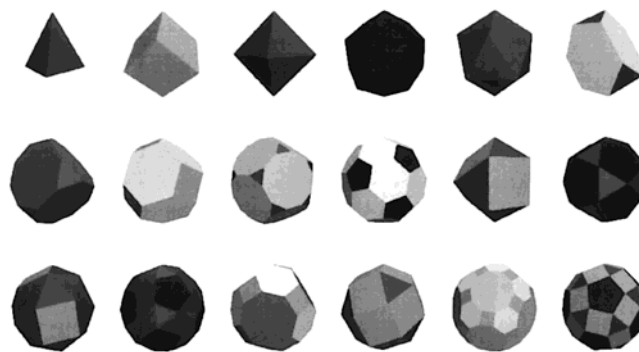


structures. However, it should be stressed that the modular self-assembly approach applies equally well to all levels of dimensionality since the dimensionality is often determined directly by the node. Therefore, it is appropriate to include discrete 0D structures in the discussion.
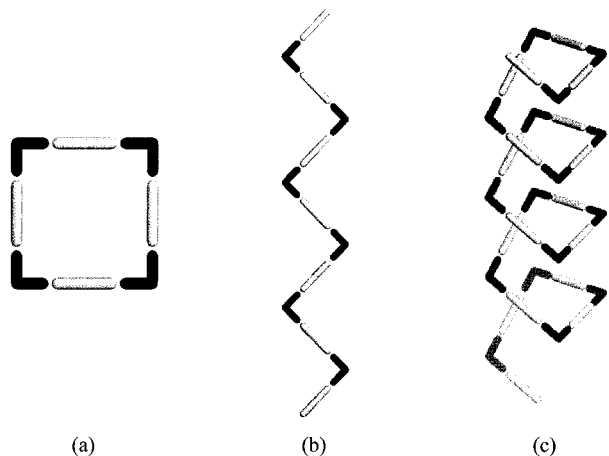
## A. 0D (Discrete) Architectures

In addition to research that has focused upon infinite structures, the principles of self-assembly have also been applied toward the design and isolation of discrete molecular structures. Such structures are exemplified by molecular squares[11,91-108] and, more recently, by striking examples of new high molecular weight compounds that can be described as spheroid architectures.[109-127] The design principles behind the isolation and development of these new classes of compounds are based upon the concept of self-assembly in the context of geometric considerations found in regular (Platonic) and semiregular (Archimedean) solids. Such structures are also known in zeolites (e.g., Linde A, which is based upon an edge-skeleton generated by fused truncated octahedra[128]) and in biological self-assembled systems such as mammalian picornaoviruses[93,99,129-131] and proteins.[132] The 5 Platonic and 13 Archimedean solids[133] are illustrated in Scheme 2. They can be constructed at the molecular level by sharing of the edges of molecular moieties that have the shape of regular polygons,[118] i.e., triangles, squares, pentagons, hexagons, and octagons, or by connecting molecular vertexes with linear bifunctional rodlike ligands.[100,112] In the case of the former closed convex surfaces are generated, whereas for the latter all the faces are open windows. This subject is highly topical, and several recent review articles have appeared.[100,112,114,117,134] We shall therefore provide no further details. The primary purpose of highlighting such structures is that they have been developed using the same principles as those used for generating the infinite structures described herein. Structures such as molecular squares are in effect supramolecular isomers of some of the infinite 1D structures described herein.

## B. 1D Coordination Polymers

### 1. Stoichiometry of Metal to Ligand = 1:1

Structural supramolecular isomerism is exemplified by the range of structures that has thus far been
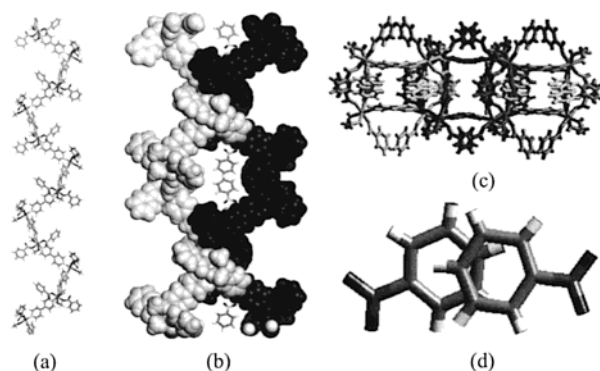
**Scheme 3. Schematic Representation of the Three Structural Supramolecular Isomers Observed for Angular Nodes Generated by *cis*-Substituted Metal Moieties: (a) 0D Square, (b) 1D Zigzag Chain, and (c) 1D Helix**



(a)          (b)          (c)



(a)          (b)          (c)          (d)

**Figure 1.** Illustration of the crystal structure for [Ni(bipy)-(PhCO$_2^-$)$_2$(MeOH)$_2$]·PhNO$_2$: (a) portion of a single helical chain, (b) space-filling model illustrating the packing of adjacent helices and the resulting cavities occupied by (nitrobenzene)$_2$ adducts, (c) overhead view of packing of helices, and (d) illustration of the dissymmetric nitrobenzene dimer.

observed in coordination polymers, in particular network structures that have been observed for some of the simplest building blocks and stoichiometries. Scheme 3 illustrates the possible structures that can result from self-assembly of either a *cis*-octahedral or a *cis*-square planar metal and a linear "spacer" ligand. There are three obvious architectures that might result, and they are dramatically different from one another. The "square box" or "molecular square" architecture represents a discrete species that has been developed extensively in recent years by the groups of Fujita,[106] Stang,[11,100,102−104,107,112,120] and Hupp.[92,94−96,98,101,135] The other two architectures are both examples of 1D coordination polymers, but they are quite different from one another. The zigzag polymer[136−146] has been fairly widely encountered, and such structures tend to pack efficiently and eschew open frameworks or cavities. The helix[147−158] remains quite rare in the context of coordination polymers, but there is added interest because it is inherently chiral regardless of what its components might be. The inherent chirality of this architecture comes from spatial disposition rather than the presence of chiral atoms, thereby illustrating an important aspect of the solid state: it is possible for achiral molecules to generate chiral crystals. To illustrate the potential for generation of chiral architectures from simple achiral building blocks, let us consider how one might design a homochiral crystal from simple molecular components.

There would appear to be at least four strategies for the design of polar crystals that are independent of the need for homochiral molecular components: (1) achiral building blocks that crystallize in a chiral space group, (2) achiral molecular building blocks to build a chiral framework, (3) achiral host framework built from achiral molecular components with chiral guest(s), and (4) achiral host framework built from achiral molecular components with achiral guest(s).

Whereas exploitation of homochiral components represents the most obvious approach because the absence of a crystallographic center of inversion is guaranteed, it in no way implies or affords any

control over molecular orientation and, therefore, bulk polarity. Furthermore, reliance upon the use of pure enantiomers raises the substantial problem of requiring control over stereochemistry at the molecular level without yet solving the problem of controlling stereochemistry at the supramolecular level. Indeed, strategy 1, which basically relies upon serendipity, offers just as much chance of optimal control of crystal packing as the use of homochiral components. However, there are three types of polar architecture that do not need to be sustained by homochiral molecular components: helical networks,[149,153,154,159−166] 1D acentric networks sustained by head-to-tail stacking of complementary molecules,[167−175] and host−guest networks which are polar because of the presence of acentric guest molecules or guest aggregates.[65,176,177]

Although the crystallization process for strategies 1−4 can inherently afford homochiral single crystals, only the use of homochiral components guarantees that all crystals in a batch will be of the same enantiomorph. Batches of crystals will often be heterochiral as both enantiomers tend to be formed equally during crystallization. Fortunately, it has been demonstrated that formation of homochiral bulk materials can be afforded by seeding with the desired enantiomer.[153]

[Ni(bipy)(benzoate)$_2$(MeOH)$_2$][154] (bipy = 4,4-bipyridine), **1**, illustrates the issues raised above. **1** self-assembles as a helical architecture that is sustained by linking of octahedral metal moieties with linear spacer ligands. Furthermore, it persists in the presence of several guests, even if 4-hydroxybenzoate ligands (i.e., ligands that are capable of forming strong hydrogen bonds) are employed. The crystal structure of the nitrobenzene clathrate is presented in Figure 1 and reveals the presence of large chiral cavities that induce the guest molecules to form chiral dimers. The guest molecules are trapped in a closed environment since helices from adjacent planes close off the 500 Å$^3$ cavities. The helical chains generated by **1** pack such that they are staggered but align in a parallel fashion. Therefore, the bulk crystal is polar as every helix in an individual crystal is of the same handedness.
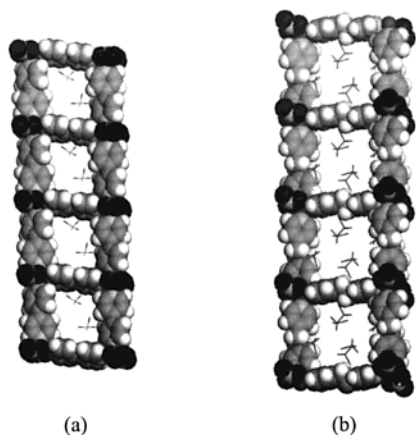
**Figure 2.** Illustration of the crystal structures two molecule ladders: (a) [Co(bipy)$_{1.5}$(NO$_3$)$_2$]·2CHCl$_3$ and (b) [Co(bipy-eta)$_{1.5}$(NO$_3$)$_2$]·3CHCl$_3$.

**1** illustrates the attractiveness of self-assembly and crystal engineering for generation of polar architectures. In particular, there is no prerequisite for homochiral molecular components and host−guest compounds have the potential to be modular and fine-tunable since the guest molecule might be used to impart functional properties. It should also be stressed that, at least in principle, all existing achiral moieties can be incorporated into polar structures. The problem that has yet to be solved is how reliably and predictably to avoid crystallographic centers of inversion and how to control alignment of molecular dipoles.

Another example of a coordination polymer that self-assembles into a helical architecture is represented by the result of complexation of a 2,2′-bipyridine-based exo-ditopic macrocyclic ligand with Ag$^+$ cations. The single-strand helical assembly is one of four possible arrangements and contains channels that run through the center of the assembly. These channels contain acetonitrile solvent molecules. The helices align antiparallel with respect to each other, and therefore, a racemic mixture of the right- and left-handed helices is obtained.[155]

### 2. Stoichiometry of Metal and Spacer Ligand = 1:1.5

Molecular ladders represent another type of 1D coordination polymer.[59,91,178−185] They differ in two important ways from molecular chains and helices. Most obviously, their stoichiometry is different since they are the result of self-assembly of 1.5 spacer ligands per metal. Therefore, the molecular building unit is effectively a "T-shape" moiety. Second, they necessarily contain cavities within the individual molecular ladders. These cavities are determined by the length, shape, and orientation of the spacer ligand. Simple examples of molecular ladders are represented by the coordination polymers [M($\mu$-L)$_{1.5}$-(NO$_3$)$_2$]$_n$ (L = bipy,[186] **2a**, or bis(4-pyridyl)ethane,[44] **2b**). Examples of these structures are illustrated in Figure 2, which reveals how **2a** and **2b** contain cavities that are large enough to sustain individual or pairs of molecules. The cavities are hydrophobic in nature, and their diagonal dimensions are defined by M−M separations of ca. 16 and 19 Å, respectively.

This means that the effective dimensions of the cavities are ca. 13 and 16 Å, respectively.

## C. 2D Coordination Polymers

The strategy of exploiting known coordination geometries of metals to propagate 2D structures via coordination with linear bifunctional spacer ligands has yielded many examples of coordination polymers with various metal moieties and architectures. The ratio of metal and ligand and the nature of the coordination of terminal ligands (i.e., degree of chelation) are the primary factors that determine the topology of the network. Scheme 4 illustrates some of the 2D network structures that have thus far been observed in coordination polymers.
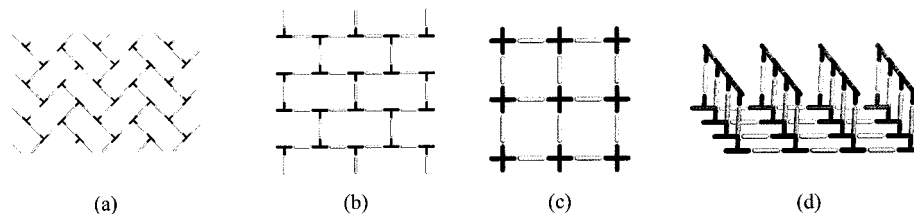
### 1. Square Grids

Square grid networks exemplify a particularly simple and commonly reported example of a predictable 2D metal−organic network. Square grid coordination polymers are based upon 1:2 metal:ligand complexes with linear bifunctional spacer ligands. They were first reported using cyano ligands[187−190] and have recently been expanded in terms of chemical type and cavity size to include pyrazines,[191−193] bipy,[78,194−199] and longer analogues of bipy.[197,200] These compounds can be regarded as being analogues of clays since they would be expected to have the ability to intercalate guest molecules. However, they have added features that are not likely to be present in clays. For example, cavities lie within the plane of the structure. These cavities are suitable for either interpenetration or enclathration of a possibly wide range of organic guest molecules. There also exists potential for incorporating catalytically active sites into such structures.[70] Furthermore, the cavities are tunable as the length and width of the spacer ligand controls the size of the cavities that occur within the polymeric structure, although interpenetration can mitigate against the existence of frameworks with very large cavities.[58]

Open framework square grid networks generated with bipy spacer ligands were first reported by Fujita et al.[70] Fujita's structures are based on Cd(II), and other examples have subsequently been reported based on a number of other transition metals, including Co(II), Ni(II), and Zn(II). Although these 2D coordination networks are isostructural within the coordination grid (effective dimensions of the diagonals are ca. 13 × 13 Å), the crystal structures of compounds can differ in the manner in which the networks stack with respect to each other (interlayer separations range from 6 to 8 Å).

The compounds [M(bipy)$_2$(NO$_3$)$_2$]·guest (M = Co, Ni) have been studied extensively[201] by us, and we have only observed three basic crystal structure types (Figure 3).

Type A compounds crystallize with similar cell parameters (monoclinic $C2/c$; $a$ = 21.5 Å, $b$ = 11.5 Å, $c$ = 13 Å; $\beta$ = 102°), have 2:1 guest:host stoichiometry and interplanar separations of ca. 6 Å. The crystal packing appears to be influenced by C−H···O hydrogen-bond interactions between the bipy ligands of one square grid and the nitrate anions of adjacent square

**Scheme 4. Schematic Representation of 2D Networks Recently Reported for Metal−Organic Polymers: (a) Herringbone or 'Parquet Floor', (b) Brick Wall, (c) Square Grid, and (d) Bilayer**



(a)        (b)        (c)        (d)

grids. The square grids do not align with a unit cell face, and adjacent grids are slipped in one direction by ca. 20%, i.e., every sixth layer repeats. The crystal packing of type B compounds is also controlled by weak interactions between adjacent layers. They generally crystallize with 2.5 guest molecules per metal center, and cell parameters are fairly consistent (monoclinic $P2_1/c$; $a = 16$ Å, $b = 14.75$ Å, $c = 16$ Å; $\beta = 100°$). The interlayer separation is ca. 8 Å. Type C compounds have interlayer separations that are similar to those seen for type B compounds. Four examples of type C compounds have 3:1 stoichiometry: three crystallize in space group $C2/c$ (monoclinic; $a = 16$ Å, $b = 11.5$ Å, $c = 23$ Å; $\beta = 100°$), and the other crystallizes in space group $Cc$. The latter compound exhibits similar cell parameters except that there is a tripling of the $a$-axis and the cell volume. Another example of a type C grid crystallizes in space group $Pn$ (monoclinic; $a = 11.4$ Å, $b = 22.8$ Å, $c = 15.9$ Å; $\beta = 93.3°$). Although these cell parameters are inconsistent with the previous four structures, the packing of the grids is appropriate for type C grids. The positioning of the grids facilitates inclusion of one guest molecule in the center of each grid. The other guest molecules lie between the grids and engage in stacking interactions between the bipy ligands and themselves.

In all of these compounds the proportion of the crystal that is occupied by guest molecule is ca. 50 vol %. In such a situation it becomes reasonable to question whether interactions between the guest molecules determine the cavity shape and crystal packing of the square grid polymers rather than vice versa. This issue is addressed later.
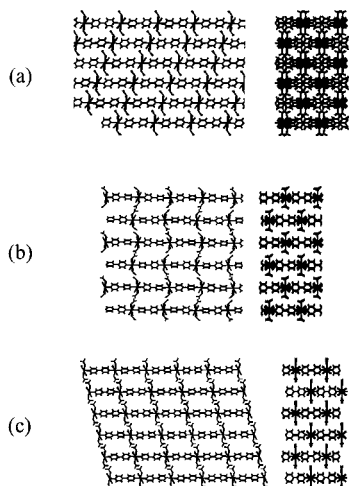


**Figure 3.** Perspective views of the stacking of square grid network architectures of formula [M(bipy)$_2$(NO$_3$)$_2$]: (a) A-type grids, (b) B-type grids, and (c) C- type grids.
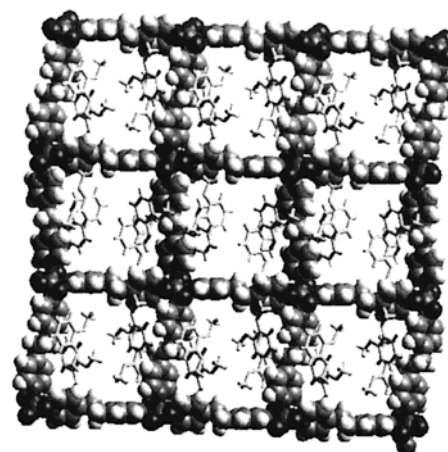


**Figure 4.** Illustration of the square grid architecture [Ni-(bipy-eta)$_2$(NO$_3$)$_2$]·2Ph(OMe)$_2$.
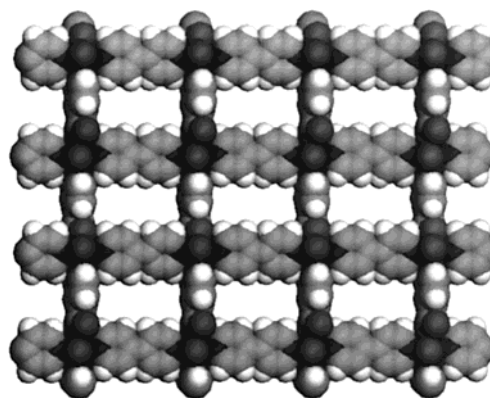


**Figure 5.** Space-filling illustration of [Co(pyca)(bipy)(H$_2$O)$_2$]-[NO$_3$]·(bipy)(H$_2$O)$_{1.5}$; an example of a rectangular grid resulting from the coordination of a metal to two types of spacer ligand.

As these square grid architectures are inherently modular, it should be possible to extend their dimensions by simply using longer spacer ligands. An example of such a structure, [Ni(1,2-bis(4-pyridyl)-ethane)$_2$(NO$_3$)$_2$]$_n$·2veratrole, is illustrated in Figure 4. This structure has grid dimensions ca. 20% larger than the smaller grids (diagonal dimensions are ca. 16 × 16 Å), large enough to enclathrate more than one aromatic guest. Larger grids (ca. 20 × 20 Å) have also been reported using tetra(4-pyridyl)porphyrin.[202]

Grids in which there are two types of spacer ligand have also been reported.[199,203] Figure 5 reveals the structure of such a compound, which is appropriately termed a rectangular grid.

### 2. Other 2D Architectures

Another metal geometry or node that is of particular interest because of its potential range of su-

**Scheme 5. Schematic Illustration of Calculated Tiling Patterns Characterized or Might Be Expected To Occur: (a) 1D Ladder (finite second dimension), (b) Brick Wall, (c) Herringbone, (d) Long and Short Brick, (e) Basket Weave. (d, e) Yet To Be Realized**

(a)　　　　　(b)　　　　　(c)　　　　　(d)　　　　　(e)
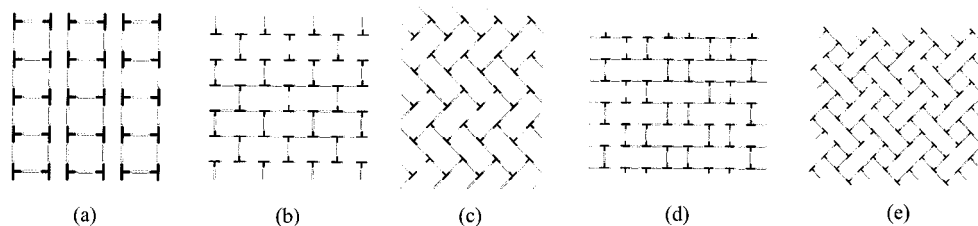
pramolecular isomers is the T-shaped geometry, i.e., a *mer*-substituted octahedral metal moiety or a trisubstituted square planar metal moiety with a 1:1.5 metal:spacer ligand ratio. This node has thus far produced examples of 1D, 2D, and 3D networks. Three distinct 2D supramolecular isomers have already been reported: brick wall,[78,178,180,204−209] herringbone,[78,210−212] and bilayer.[213−216] It is interesting to note that if one calculates the possible tiling patterns (i.e., all points lie in the same plane) that are possible for T-shaped nodes (Scheme 5), three of the five possibilities have already been realized.

The brick architecture (**5b**) is observed as the product of the reaction between heptacoordinate Cd(II) and 1,4-bis((4-pyridyl)methyl)-2,3,5,6-tetrafluorophenylene.[70] The T-shape geometry is the result of two terminal nitrate ligands chelating in a bidentate manner, thereby occupying four of the seven coordination sites. The structure is triply interpenetrated and, as such, does not possess channels or cavities. In a similar system using the nonfluorinated pyridyl-based ligand, a 1D ladder structure (**5a**) was observed. The brick architecture was also seen in [Ni(4,4′-azopyridine)$_{1.5}$(NO$_3$)$_2$]$_n$, which interpenetrates with two perpendicular [Ni(4,4′-azopyridine)$_2$-(NO$_3$)$_2$]$_n$ square grid networks.[208]

The herringbone or 'parquet floor' architecture (**5c**) has recently been observed by several groups.[204,210,211] In these structures, the coordination sphere is similar to that of the brick architectures: heptacoordinate Cd(II) or Co(II) with two terminal bidentate nitrate ligands and coordination to one end of three 4,4′-azopyridine bridging ligands; an isostructural example has also been reported with 1,2-bis(4-pyridyl)-ethyne as the bridging ligand.[214]

The bilayer architecture has been observed in at least three compounds.[213−215] It has been observed as the product from the reaction of Co(NO$_3$)$_2$ and bipy, which also generates ladder, square grid, and herringbone architectures. The bilayer form of [Co-(bipy)$_{1.5}$(NO$_3$)$_2$] is observed if crystallization occurs in the presence of CS$_2$ or H$_2$O. The bilayers pack by partial interdigitation, which allows 1D channels to run through the structure. This structure is particularly relevant since it represents one of the first reported examples of a compound that might be termed a "metal−organic zeolite", i.e., the structure is porous and stable to loss of guest.[215] The bilayer architecture has also been reported for systems using 1,2-bis(4,-pyridyl)ethane.[217]

The number of supramolecular isomers already observed in the Co(NO$_3$)$_2$/bipy system indicates how important selection of template and crystallization conditions are. It seems reasonable to assert that it is only a matter of time and effort before the weave (**5e**) and long-and-short brick (**5d**) motifs illustrated in Scheme 5 will also be realized.

In terms of topology, it should be noted that brick and herringbone motifs are both examples of (6,3) nets and can therefore be regarded as being closely related to honeycomb (6,3) nets.[67] Honeycomb networks are quite common in organic structures because of the availability of trigonal nodes (i.e., 1,3,5-trisubstituted benzenes such as trimesic acid and species such as the guanidinium cation) but they seldom occur in the context of metal−organic polymers because trigonal and trigonal bipyramidal coordination geometries are rare. However, [Cu-(pyrazine)$_{1.5}$]BF$_4$[218] is based upon trigonal Cu(I), and it should therefore be unsurprising that it crystallizes as a honeycomb (6,3) net. That a number of ligands with trigonal geometry[100,112,114,118,123,125,219−225] now exist means that it is likely that a wider range of honeycomb structures will be generated soon.

## D. 3D Coordination Polymers

It might be anticipated that the challenge of designing 3D network architectures represents an added level of complexity in comparison with 2D architectures, and it in many ways represents the ultimate challenge to crystal engineers since it leads most directly to crystal structure control and prediction. For example, in most situations, a finite number of structural isomers can be calculated if all nodes must lie in the same plane. However, a larger number of possibilities might exist when that limitation is relaxed. It is therefore perhaps ironic that two of the simplest examples of predictable networks are exemplified by 3D networks generated via self-assembly of tetrahedral or octahedral nodes.

Tetrahedral nodes are predisposed to generate diamond-like (diamondoid) architectures, whereas octahedral nodes are expected to afford octahedral networks. These architectures can be obtained for both organic (typically hydrogen bonded) and metal−organic (i.e., coordination polymer) systems. Interpenetration can occur in these compounds, thereby mitigating against enclathration and porosity. However, interpenetration can also be exploited as a potentially important design paradigm for rational transformation of some of the 2D networks described earlier into 3D frameworks. This principle is discussed in a later section with respect to interpenetration of identical networks (homocatenation) and

interpenetration of different networks (heterocatenation).

## 1. Diamondoid Networks

The diversity of components that are available for crystal engineering of diamondoid networks and the means by which they self-assemble spans the full range of chemistry. The breadth of chemical moieties that might be used for crystal engineering is particularly well illustrated by the range of diamondoid networks that have been reported in recent years. Diamondoid architectures using a tetrahedral metal (Zn or Cd) as the node and cyanide ligands ($CN^-$) as the spacer represent prototypal examples of diamondoid coordination polymers. $Zn(CN)_2$ and $Cd(CN)_2$ form diamondoid networks with 2-fold interpenetration.[71,73–75] However, $Cd(CN)_2$ can also be obtained as a single network with $CCl_4$ filling the cavity.[71] This result illustrates two principles that have broad implications for crystal engineering: (1) Interpenetration can be avoided in the presence of an appropriate template or guest molecule; (2) Such compounds might be regarded as catenated and noncatenated supramolecular isomers of each other.

A diamondoid architecture also results when $Zn(CN)_4^{2-}$ is reacted with Cu(I). The resulting anionic network might be viewed as consisting of tetrahedral zinc nodes that are linked to tetrahedral copper nodes by cyanide spacers. However, the nature of coordination at the copper and zinc ions remains ambiguous. Analysis of the structural data indicated that it is most appropriate to consider the coordination of the copper as 100% organometallic (Cu–C) and the coordination of the zinc 100% metal–organic (Zn–N). The ionic nature of this particular framework means that the presence of a counterion in the resulting cavities is required. $N(CH_3)_4^+$ fits comfortably inside the adamantoid cavity and precludes interpenetration.

A report[226] on the crystal structure and properties of [Cu(2,5-dimethylpyrazine)$_2$(PF$_6$)] represents one of the first examples of a metal–organic diamondoid structure, and the related compound [Cu(4,4′-bipy)$_2$](PF$_6$)] was reported shortly thereafter.[218] Both structures exemplify the modular assembly design strategy and contain anions in the cavities generated by the diamondoid structure. In the case of the latter, the intermetallic separations are 11.16 Å and result in cavities that are sufficiently large to facilitate 4-fold interpenetration as well as inclusion of the counterions. A diamondoid architecture propagated by silver(I) and bipy, [Ag(4,4′-bipy)$_2$](CF$_3$SO$_3$), was reported[227] shortly thereafter, and it also exhibits 4-fold interpenetration with anions in cavities. The Ag–Ag separations are 11.6 Å. The 4-cyanopyridine analogue was reported in the same article and exhibits metal–metal separations of 9.93 Å. Despite the variations observed in the dimensions of these networks, both exhibit 4-fold levels of interpenetration.

Subsequent studies resulted in a plethora of diamondoid metal–organic structures and 2-, 3-, 4-, 5-, 7-, and 9-fold levels of interpenetration.[228–231] It should be noted that although interpenetration reduces or eliminates porosity, there are at least two important properties that can be addressed with such structures. (1) They are predisposed to form acentric networks since there is no inherent center of inversion at a tetrahedral node. An odd level of interpenetration and an unsymmetrical ligand will definitely generate a structure that exhibits polarity.[90] (2) These structures could be useful for selective anion exchange.

In the context of the former, a series of neutral diamondoid architectures have been prepared with bridging ligands of varying size.[74,218,228,231–233] These compounds are of general formula $ML_2$ (M = $T_d$ metal; L = bridging anionic ligand), and it follows that a neutral network will be generated if a +2 metal is coordinated to two −1 anionic ligands. Zn(isonicotinate)$_2$ and Cd(*trans*-4-pyridylacrylate)$_2$ exhibit 3- and 5-fold degrees of interpenetration, respectively, and possess interesting properties in the context of polarity.[228] In the former compound, the Zn–Zn distance is ca. 8.8 Å. This is consistent with the previous structures that exhibit 4-fold interpenetration. The Cd–Cd distance is ca. 11.5 Å, similar to the intermetallic distances observed in the 4-fold interpenetrated structures that also contain counterions.

## 2. Octahedral Networks

Prototypal examples of octahedral networks are exemplified by iron cyano compounds. Such compounds are very well documented, and they have been used for centuries as pigments. An early X-ray study[234] of Berlin Green, [Fe$^{III}$Fe$^{III}$(CN)$_6$], Prussian Blue, [KFe$^{II}$Fe$^{III}$(CN)$_6$], and Turnbull's Blue, [K$_2$Fe$^{II}$Fe$^{II}$(CN)$_6$], demonstrated that the iron cations act as the node in octahedral arrays in which they are linked by linear cyano ligands. These compounds form isostructural networks that vary only in the degree of potassium inclusion and the oxidation states of the iron atoms. Berlin Green can therefore be regarded as being the prototypal example of an open framework octahedral network; however, the limited length and lack of chemical versatility of the cyano ligand means that it has little relevance in the context of porosity.

Synthetic metal–organic octahedral networks were first reported in 1995. [Ag(pyrazine)$_3$](SbF$_6$)[235] is sustained by octahedral Ag(I) cations and relatively short pyrazine ligands. The framework is necessarily cationic and is illustrated in Figure 6a. A neutral analogue is exemplified by [Zn(bipy)$_2$(SiF$_6$)].[195] In this structure (Figure 6b), the SiF$_6^{2-}$ counterions crosslink the square grids that are formed by Zn and bipy to form a rigid octahedral polymer. The structure cannot interpenetrate because the walls of the channels are blocked by bipy ligands. The resulting channels have an effective cross-section 8 × 8 Å and represent ca. 50% of the volume of the crystal. Solvent molecules are readily eliminated but the framework collapses irreversibly upon loss of solvent. Perhaps the most salient feature of this structure is that the structure is entirely predictable in terms of both shape and dimensions. [Zn(bipy)$_2$(SiF$_6$)] crystallizes in space group $P4/mmm$ with $Z = 1$. In other words, the point group at Zn, $D_{4h}$, is propagated into
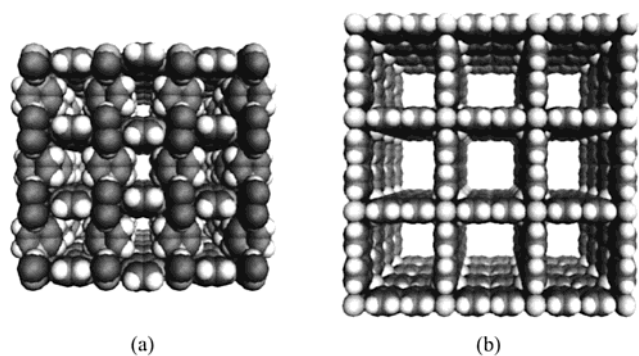
**Figure 6.** Space-filling models of two octahedral coordination polymers: (a) $[Ag(pyrazine)_3](SbF_6)$; (b) $[Zn(4,4'-bipyridine)_2(SbF_6)](DMF)_x$.
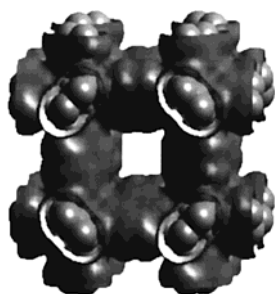


**Figure 7.** Space-filling illustration of $Zn_4O(BDC)_3$: an octahedral coordination polymer generated from a tetrahedral node (SBU). The structure is octahedral because the six edges of the tetrahedral SBU are linked by spacer ligands. The area outside the shaded surface represents the accessible surface area, approximately 60% of the total cell volume.

space group symmetry. Furthermore, the cell parameters are determined by the intermetallic separations. The Cu analogue of $[Zn(bipy)_2(SiF_6)]$ is isostructural and is of particular relevance since it has a higher capacity for methane adsorption than any previously studied porous material and is stable to loss of guest.[76] Octahedral coordination polymers remain much less common than their diamondoid counterparts, but a recent report revealed a novel metal−organic coordination polymer, $Zn_4O(BDC)_3$ (BDC = 1,3-benzenedicarboxylate), that suggests an exciting future for such compounds.[81] $Zn_4O(BDC)_3$ is a relatively simple and inexpensive material to prepare and is remarkably stable after loss or exchange of guest, remaining crystalline at temperatures above 300 °C. The key feature that makes $Zn_4O(BDC)_3$ special is that it exhibits a relative degree of porosity that is hitherto unprecedented in crystalline solids.

As revealed by Figure 7, the octahedral framework exhibits a large amount of surface area that remains accessible to guest molecules because it contains pores and cavities that are large enough to accommodate and release organic molecules such as chlorobenzene and dimethylformamide. Calculations and experimental data indicate that ca. 60% of the structure is available and accessible. This compares to the typical value of ca. 30% seen in zeolites. [128]

### 3. Other 3D Networks

In addition to the obvious, i.e., diamondoid and octahedral networks, there are numerous examples
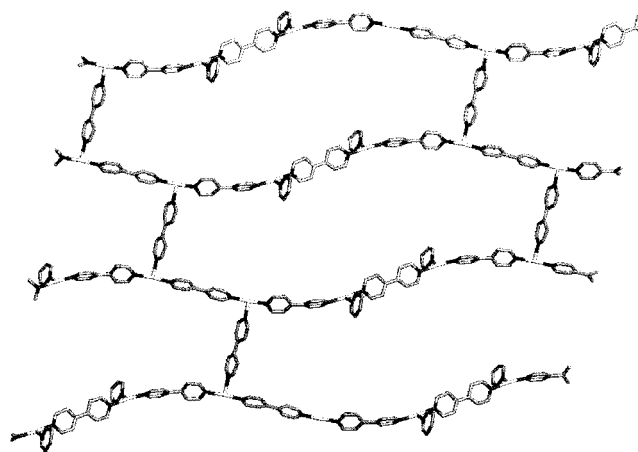


**Figure 8.** Illustration of the cross-section of a single network of $[Co(bipy)_{1.5}(NO_3)_2]\cdot1.5benzene$; effective dimensions of the cavity are ca. $8 \times 40$ Å.

**Scheme 6. Schematic Representation of the 3D-Frame Architecture: (a) Single Layer Illustrating the Large Cavities and the Relative Orientations of Adjacent T-Shaped Nodes and (b) Perspective View of the 3D Structure**
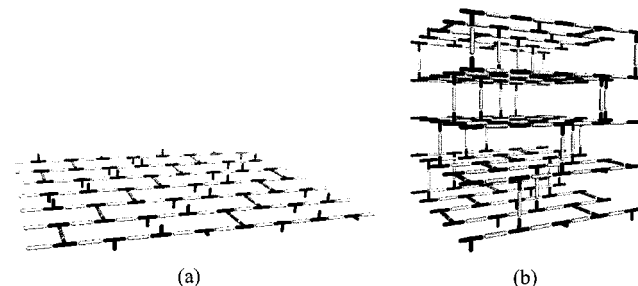


of novel 3D networks that have been observed in recent years. Many can be described as supramolecular isomers of low-dimensional structures. Two such structures are supramolecular isomers formed by self-assembly of T-shaped nodes. As discussed earlier, such self-assembly can afford 3D architectures that have not been seen in naturally occurring compounds. Scheme 6 reveals one of these structures: $[Co(bipy)_{1.5}(NO_3)_2]_n\cdot1.5benzene$.[177]

The cavities are revealed in Figure 8, and they are exceptionally large, having an effective cross-section of $8 \times 40$ Å. These large cavities are capable of sustaining both 3-fold interpenetration and inclusion of guest molecules in channels (Figure 9). Although the networks are inherently centrosymmetric, the crystal is polar because the guest molecules align in such a manner that their supramolecular structure cannot contain a center of inversion.

$[Ag(bipy)(NO_3)]_n$ generates another type of supramolecular isomer for self-assembly of T-shaped components. It self-assembles into linear Ag−bipy chains that cross-link via Ag−Ag bonds. This particular 3D structure has been described as a "Lincoln Log"-type structure and exhibits a 3-fold level of interpenetration that is open enough to facilitate ion exchange of the loosely bound nitrate anions.[236,237]

### 4. Hybrid Structures

An alternate approach to building 3D structures that seems to offer considerable potential is manipu-
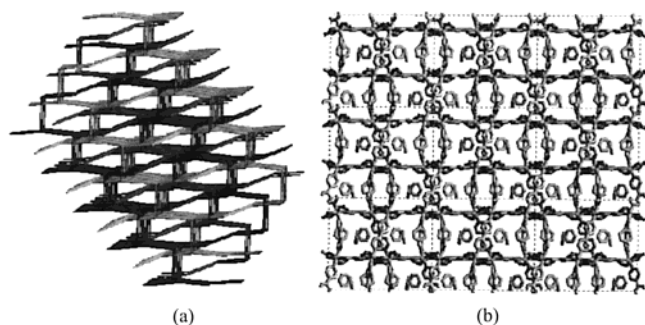
**Figure 9.** Crystal structure of [Co(bipy)$_{1.5}$(NO$_3$)$_2$]·1.5-benzene: (a) view illustrating the interpenetration of three networks and (b) illustration of the microchannels running parallel to the crystallographic $z$-axis. Polar 1D aggregates of benzene molecules are sustained by the channels.

**Scheme 7. Schematic Illustrating How Porosity Can Be Generated by Inclined Interpenetration of Square Grid Networks**
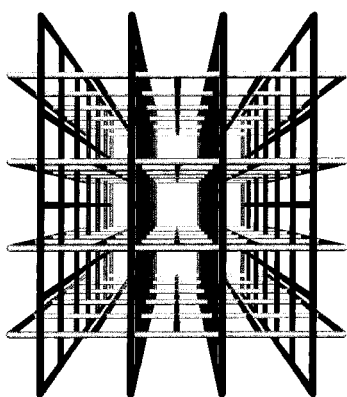


lation of existing 2D structures. There are two relatively simple strategies in this context: cross-linking of 2D structures and interpenetration of identical or different 2D networks.

Cross-linking becomes feasible if one selects an appropriate 2D structure that has functionality in the axial direction. Such an approach has been widely used by clay chemists, and hence, the term "pillaring" might be applied to describe such a process. [Zn-(bipy)$_2$(SiF$_6$)] could be used as a prototype in the context of coordination polymers since it can be regarded as having been generated from square grid coordination polymers that are cross-linked by $\mu$-SiF$_6$ anions. In the context of hydrogen-bonded structures, guanidinium sulfonates represent a class of compounds that have been cross-linked in a rational manner so as to generate infinite 3D structures.[45,176,238−240]

Interpenetration is a widely encountered phenomenon that mitigates against the existence of frameworks with very large cavities. However, Scheme 7 reveals that there are situations in which interpenetration can occur, generate porosity, and afford 3D structures. Square grid polymers that are based upon longer spacer ligands such as 1,2-bis(4-pyridyl)ethane (bipy-eta) or 1,2-bis(4-pyridyl)ethylene (bipy-ete) can interpenetrate in such a fashion.[58] However, an even more intriguing situation that could have important implications for design of new hybrid materials is exemplified by the crystal structure of the square grid coordination polymer {[Ni(bipy)$_2$(NO$_3$)$_2$]·2pyrene}$_n$.[241]
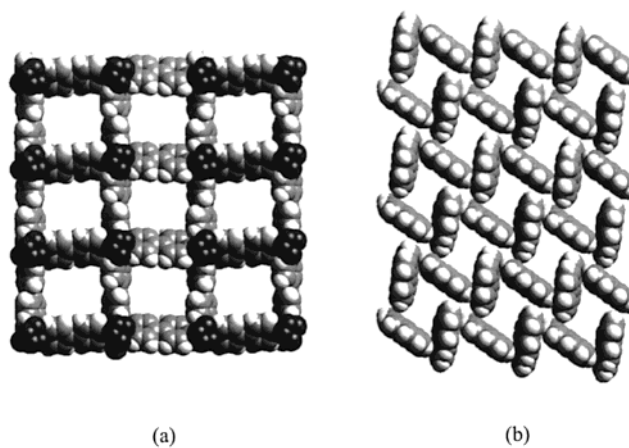


**Figure 10.** Space-filling illustrations of the two independent networks in [Ni(bipy)$_2$(NO$_3$)$_2$]·2C$_{10}$H$_8$: (a) metal−organic coordination polymer square grid and (b) noncovalent aromatic (4,4)-net.

Careful examination of the crystal packing in this compound reveals that the pyrene molecules form an independent noncovalent network that is complementary from a topological perspective with the square grid. The resulting crystal represents a compound in which two very different types of 2D net interpenetrate. The square grid coordination networks (Figure 10a) possess inner cavities of ca. 8 × 8 Å and stack in such a manner that they lie parallel to one another with an interlayer separation of ca. 7.9 Å. The pyrene nets (Figure 10b) are sustained by edge-to-face interactions and contain cavities of ca. dimensions 6.5 × 3.5 Å. The planes of the neighboring molecules intersect at an angle of ca. 60°, and there are no face-to-face stacking interactions between the molecules. The pyrene nets can be regarded as distorted (4,4) nets if the node is the point in space at which the vectors of the four pyrene planes intersect. An alternate interpretation is that nodes exist at the point of the edge-to-face interactions. The pyrene net could then be regarded as a distorted brick wall form of a (6,3) net. It is important to note that either a (4,4) or a (6,3) planar net is complementary from a topological sense with the (4,4) coordination polymer net and ensures that the coordination polymer nets must pack in a staggered manner. Given that cavity size within the pyrene nets is complementary with the width and height of a single aromatic ring, it should be unsurprising that the pyrene nets thread orthogonally with the bipy ligands of the coordination polymer via face-to-face and edge-to-face interactions and that the calculated volumes of the two nets are similar. This is to be expected based upon the observation that bipy square grids are self-complementary as they can interpenetrate in a 2-fold fashion.[196] The interpretation of this crystal structure as interpenetrating covalent and noncovalent nets is potentially important in the context of understanding the structure and stoichiometry of compounds that are based upon interpenetrated covalent and noncovalent nets. The structure also illustrates how polarity in crystals can be generated from subtle packing of achiral components, since the pyrene molecules form chiral nets.
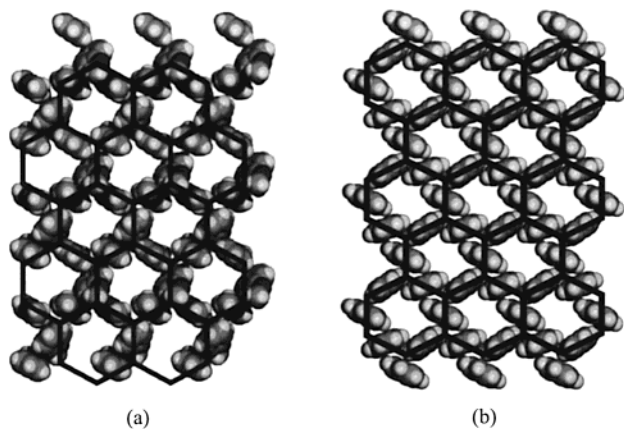
**Figure 11.** Space-filling illustrations of two hexagonal (6,3)-networks formed by (a) naphthalene and (b) veratrole in the intepentrated structures [Ni(bipy)$_2$(NO$_3$)$_2$]·aromatic.

**Scheme 8. Schematic Illustrating the Three Modes of Inclined Interpenetration Observed for Square Grid Networks: (a) Diagonal/Diagonal, (b) Parallel/Parallel, and (c) Parallel/Diagonal**
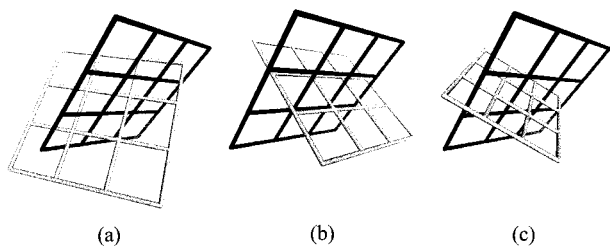


It should be noted that this type of packing is not found uniquely in {[Ni(bipy)$_2$(NO$_3$)$_2$]·2pyrene}$_n$. Its naphthalene analogue, {[Ni(bipy)$_2$(NO$_3$)$_2$]·3naph-thalene}$_n$, can be interpreted as being the result of interpenetration of hexagonal and square nets,[242] and a study of a series of more than 20 related compounds has revealed the presence of noncovalent nets in every one of these compounds.[243] The noncovalent hexagonal nets formed by anisole and veratrole are illustrated in Figure 11.

That interpenetration can vary and be influenced by subtle effects are exemplified by this class of compound. It has been reported that for coordination polymers in which (4,4) networks that are planar and identical interpenetrate, two types of interpenetration are typically observed, both of which are examples of *inclined interpenetration*.[58] The most commonly encountered form might be described as *diagonal/diagonal inclined interpenetration*[243] and was observed in the prototypal [M(bipy)$_2$X$_2$]$_n$ compound, [Zn(bipy)$_2$(H$_2$O)$_2$]SiF$_6$.[196] The other mode of interpenetration might be described as *parallel/parallel inclined interpenetration*.[208,244] These types of interpenetration are illustrated in parts a and b of Scheme 8, respectively, and differ in how the networks orient and cut through each other. *Parallel* refers to the structure in which a "spacer" ligand from one network threads through the cavity of the other; *diagonal* refers to the structure in which a "node" from one network (e.g., the metal moiety) is within the cavity of the other. One would anticipate that the structure that is adapted by a particular compound would be influenced by several geometric factors: the

relative size of the cavity, the distance between adjacent nodes within a network, the thickness of the layers and how this limits the interlayer separation of adjacent networks, and the steric bulk of the node. In this context, it is important to note that with all other things equal, the diagonal/diagonal mode of interpenetration facilitates an interlayer separation that is 41.4% greater than that of the parallel/parallel mode. Furthermore, the diagonal/diagonal mode ensures a staggered orientation of parallel layers, whereas an eclipsed orientation is necessary if the parallel/parallel structure is present. Therefore, in terms of steric considerations, the diagonal/diagonal mode would appear most likely to be favored. However, circumstances where the interlayer separation would ideally be shorter or where the metal atoms in adjacent layers would be eclipsed (e.g., to maximize interlayer interactions) could favor the parallel/parallel mode.

The structures we have studied that are based upon complementary covalent and noncovalent networks exhibit a new mode of inclined interpenetration that is a hybrid of the modes described above: *parallel/diagonal inclined interpenetration*.[243] The noncovalent (4,4) arene networks exhibit parallel inclined interpenetration with respect to the (4,4) metal−organic coordination networks, whereas the covalent coordination networks demonstrate diagonal inclined interpenetration with respect to the arene networks (Scheme 8c). This salient structural feature means that the nitrate groups of adjacent parallel coordination polymer grids are staggered and that the interlayer separation is a consequence of the size of the arene network. It should therefore be unsurprising that type A grids result when templated by the smallest arenes (benzene and derivatives) as they exhibit smaller interlayer separations than types B and C packing. Grid types B and C occur in the presence of larger or more arenes.

Given that cavity size within the aromatic networks is complementary with the width and height of a single aromatic ring, the self-assembly of aromatic molecules in the compounds reported herein is readily sustained by edge-to-face and face-to-face interactions with the hydrocarbon portion of the bipy moieties. These interactions are presumably a primary driving force for the clathration of the guests and a mitigating factor against interpenetration. Interpenetration was not encountered in the square grid coordination polymer networks described above, and stacking interactions are seen in all compounds. It is also interesting to note that only three packing modes are observed in 13 compounds of similar composition. However, a question that cannot yet be answered with certainty concerns whether the noncovalent networks of aromatic molecules can exist in the absence of the coordination polymers. In this context, the existence of a 1:1 binary compound between ferrocene and pyrene[245] represents an important prototype since pairs of ferrocene molecules are stacked inside a pyrene 2D network that is sustained by noncovalent C−H···$\pi$ interactions.

**Scheme 9. Representative Examples of Supramolecular Sythons**
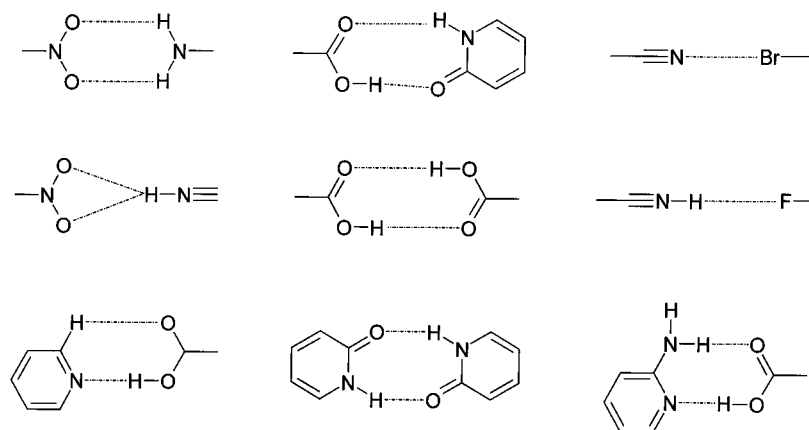


## III. Hydrogen-Bonded Networks

It would be inappropriate to attempt to present an exhaustive overview of crystal engineering of organic solids in this contribution. However, we feel that it is appropriate to highlight the analogies that can be drawn between hydrogen-bonded networks and co-ordination polymers. In particular, for hydrogen-bonded networks, the donor (i.e., a protic hydrogen atom) and the acceptor (i.e., a region of electron density) can be compared with metal atoms and ligands, respectively. Furthermore, as noted by Etter,[25] in cases where there are multiple hydrogen-bonding sites, there is a fair degree of predictability concerning which donors and acceptors will engage. Therefore, the "node and spacer" approach can be employed equally well with hydrogen bonds as with coordinate covalent bonds. Indeed, it is now realized that weak hydrogen bonds,[246-251] stacking interactions,[20,252,253] and halogen—halogen interactions[254-256] can also play a significant and predictable structure-determining role. However, we shall emphasize structures that are sustained by so-called strong hydrogen bonds, including ionic hydrogen bonds. For a more rigorous evaluation of the broader perspectives of hydrogen-bonded networks in the context of crystal engineering, one may consider looking at one of the many recent reviews on the subject.[22,90,257-264] In the context of this contribution, synthons that involve NH···O and/or OH···O hydrogen bonds, including those that exploit the carboxylic dimer or its depro-tonated form, will be highlighted. They represent reliable and ubiquitous supramolecular synthons that already have been applied in a broad range of systems and have analogues in the context of coor-dination polymers.

It is only natural to analyze existing crystal structures by breaking them down, at least as far as is reasonably possible, into discrete aggregates or 1D, 2D, or 3D networks. At the very least, rationalization of crystal structures then becomes greatly simplified since even the presence of a reliable 1D network, for example, for a given set of molecular recognition features or supramolecular synthons significantly restricts the number of possible packing modes. An exciting byproduct of this thought process is that design of new compositions and crystal structures can also be achieved by thinking in terms of network

design. The concept of using this *supramolecular synthesis* approach to design new generations of infinite network structures offers enticing targets for both scientific and technological reasons. The greatest degree of predictability occurs if 2D and 3D architectures can be generated from first principles. In the case of the latter, the only degree of unpre-dictability would appear to relate to whether subtle conformational effects can affect structure or, in the case of open framework structures, as to whether interpenetration occurs. This approach to crystal engineering offers the intriguing concept of inherent control over the dimensions and molecular recogni-tion features that are present in laminated or porous structures.

Scheme 9 illustrates some of the more common supramolecular synthons that have been exploited by crystal engineers to design and build organic molecular networks. The carboxylic acid moiety represents perhaps the most widely observed and exploited of these supramolecular synthons. This should be unsurprising since the carboxylic acid moiety is ubiquitous in organic chemistry. The car-boxylic acid moiety also represents an ideal illustra-tion of the problems associated with crystal structure prediction and design if one concentrates upon a molecular unit with a limited number of dimensions and molecular recognition sites. Monocarboxylic acids have been widely studied crystallographically, and it has been demonstrated[88] that there are two com-mon motifs observed in the solid state for carboxylic acids. These supramolecular isomers, which pro-foundly influence the crystal packing and bulk prop-erties, are illustrated in Scheme 10. As might be expected, the carboxylic dimer, A, is the most com-monly observed supramolecular isomer and, being inherently centrosymmetric, tends to afford nonpolar crystals. However, since it is effectively a discrete 0D aggregate, there is little information that might be used in order to facilitate prediction of the overall crystal structure. The other motif, B, affords a 1D chain that is polar because it is the result of "head-to-tail" self-assembly. This simplifies to some extent the problem of crystal structure prediction, but it still does not address how these 1D chains pack. There is almost random choice of parallel or antiparallel packing of these chains in observed crystal struc-

**Scheme 10. Schematic Diagram Illustrating the Two Supramolecular Isomers for the Carboxylic Acid Supramolecular Synthon: (a) 0D Dimer and (b) 1D Head-to-Tail Chain**

(a)

(b)
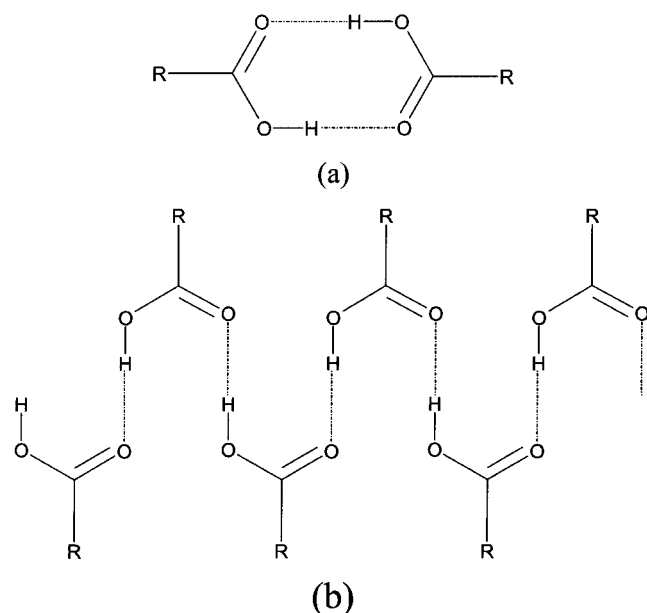
tures. This is a subtle but important distinction since, in the case of parallel packing of chains, there is no crystallographic center of inversion within the 2D layer and crystallization in polar space groups therefore occurs in approximately 50% of structures that have thus far been characterized, i.e., centers of inversion between layers appear to occur in a random fashion. A similar situation occurs in the case of benzenedicarboxylic acids such as terephthalic acid. That terephthalic acid is inherently predisposed to form infinite 1D chains is intuitive. However, one must still jump from chains to grids to frames in order to generate a crystal structure. Indeed, terephthalic acid exhibits two polymorphs that are based upon identical chains that pack in different orientations.[265,266] It is possible to summarize the situation in the context of monocarboxylic acids and 1D structures as follows. (1) A lot of information can be generated by analyzing the crystal packing in monocarboxylic acids, including confirmation that the presence of a centrosymmetric supramolecular synthon (i.e., the carboxylic acid dimer) strongly tends toward centrosymmetric crystals. (2) Unfortunately, we still have only really learned what not to do if one wishes to design polar crystals (i.e., one should avoid a centrosymmetric supramolecular isomer) rather than what one must aim for in order to ensure optimized bulk polarity. (3) It appears that multiple molecular recognition sites will be necessary in order to gain a greater degree of predictability over organic crystal structures. Furthermore, the orientation of these recognition sites should be suitable for generation of at least a 2D network.

For the above reasons, our primary focus in the context of hydrogen-bonded networks will be 2D and 3D networks, prefaced by a brief discussion of discrete aggregates and 1D polymers.
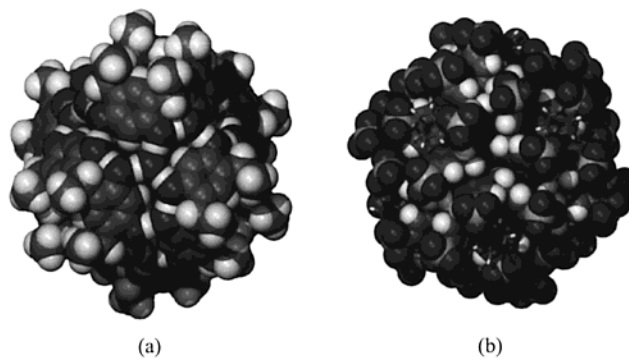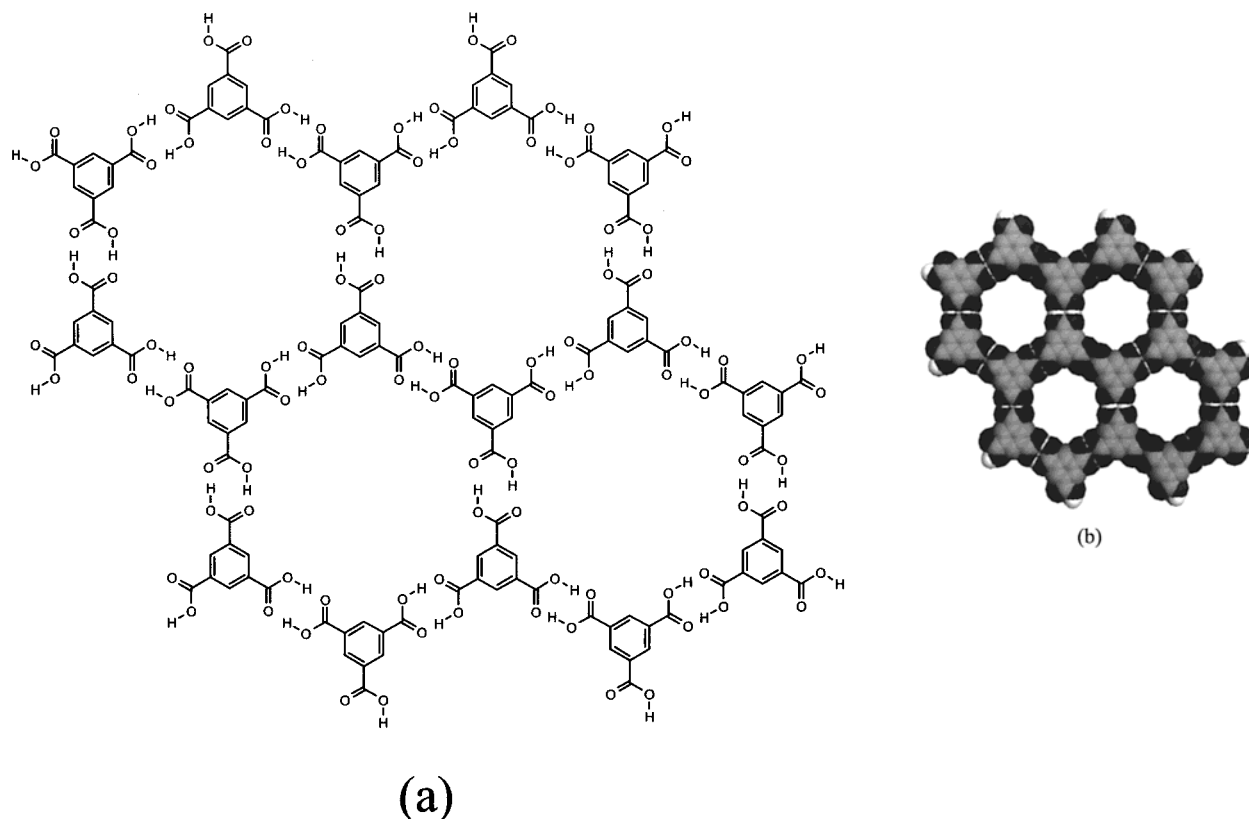


Figure 12. Space-filling representations of large self-assembled spherical assemblies: (a) [$C$-methylresorcin[4]-arene)$_6$(H$_2$O)$_8$], a snub cube, and (b) [($p$-sulfonatocalix[4]-arene)$_?$], a great rhombicuboctahedron.

## A. 0D (Discrete) Aggregates and 1D Networks

The structures that can result from self-assembly of a *cis*-octahedral or a *cis*-square planar metal and a linear "spacer" ligand have been previously discussed in section II in the context of coordination polymers. The important geometric constraint introduced by the *cis*-conformation is the 90° vector imposed by the coordination geometry, i.e., it represents an angular node which can direct self-assembly into either a 1D zigzag, 1D helical, or 0D discrete cyclic motif. A prototypal example of an angular "node" in the context of hydrogen-bonded networks is isophthalic acid, which subtends a 120° angle between its carboxylic acid moieties. Although the preferred solid-state structure of isophthalic acid is the zigzag motif,[267] it has been demonstrated that self-assembly of a discrete hexameric aggregate that also persists in solution can be invoked by the addition of a bulky substituent to the 5-position on the benzene core.[268,269]

The exploitation of bulky substituents to direct the formation of discrete aggregates over infinite structures has also been shown to be successful in binary hydrogen-bonded systems, as exemplified by a series of 1:1 complexes formed from cyanuric acid and disubstituted melamines.[270-275] The relative bulkiness of the melamine substituents determines whether the structure adopts a linear tape (1D), crinkled tape (1D), or rosette (0D) structure, in order of increasing steric contribution.

A different strategy that has recently been employed for the isolation and development of discrete structures is based upon generating molecular polyhedra by using geometric considerations as found in Platonic and Archimedean solids. A prototypal example of such a structure[121] is the self-assembled *snub cube*[276] that occurs when calix-$C$-methylresorcin-[4]arenes self-assemble with water molecules to form [$C$-methylresorcin[4]arene)$_6$(H$_2$O)$_8$]. The resulting structure forms a spheroid held together by hydrogen bonds, and it possesses a very large enclosed cavity, 1375 Å$^3$. A related structure[116] can be generated when $p$-sulfonatocalix[4]arenes self-assemble with pyridine-$N$-oxide, metal ions, and water. The resulting discrete structure is based upon a *rhombitruncated cuboctahedron*.[277] The two Archimedean structures are illustrated in Figure 12.

(a)



(b)

**Figure 13.** Honeycomb (6,3)-network observed for BTC (BTC = 1,3,5-benzenetricarboxylic acid): (a) schematic representation of the hydrogen-bonding pattern and (b) space-filling model illustrating the hexagonal channels that are formed.

Many viruses have an outer shell, or capsid, that can be described as a hydrogen-bonded polyhedron (icosahedron).[93] The above synthetic structures may provide chemists with insight as to how to design nanoscale polyhedra for application in biological systems. In this context, it should also be noted that Etter reported a series of discrete binary adducts between acyclic imides and a series of cocrystallization aids.[278] This work also represents an attempt to better understand and ultimately control the type of hydrogen-bonding interactions that play such an important role in molecular recognition of biological systems.[279] It seems reasonable to assert that the studies of hydrogen-bonding patterns in the systems described above might indeed eventually aid in the design of structures that will impact biological systems.

## B. 2D Networks

Hydrogen-bonded 2D networks are exemplified by organic molecular networks that are constituted from organic moieties with multiple complementary terminal functional groups that necessarily assemble into 2D arrays because of their geometric disposition.

### 1. Derivatives of Trimesic Acid

The well-known structure of trimesic acid (1,3,5-benzene tricarboxylic acid, H$_3$TMA), a polyfunctional carboxylic acid that is inexpensive and chemically robust, has long intrigued crystal engineers and represents a more suitable prototype for crystal structure prediction and design than mono- or dicarboxylic acids. It possesses trigonal exodentate func-
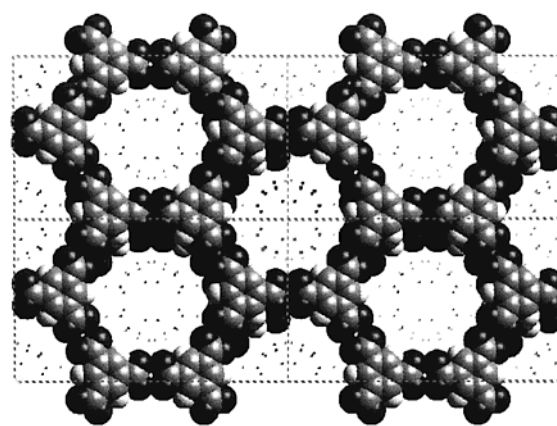


**Figure 14.** Space-filling illustration of the BTC·isooctane clathrate. The isooctane is disordered within the hexagonal channels.

tionality that facilitates self-assembly into two dimensions. Figure 13 illustrates how the hydrogen-bonding pattern in the 2D networks formed by H$_3$TMA generates cavities of predictable size (approximately 14 Å diameter). In pure H$_3$TMA[280] the honeycomb grid is puckered and the cavities are filled by self-inclusion, or interpenetration, of other networks. However, subsequent reports revealed that there are methods for preparing a noninterpenetrated or open framework form of H$_3$TMA.[281,282] If crystallized in the presence of alkanes, H$_3$TMA forms open framework honeycomb layers that align in such a manner that adjacent sheets are almost eclipsed with respect to each other (Figure 14). The resulting architecture observed in the crystal structure is essentially identical to that depicted in Figure 13.

(a)                                              (b)
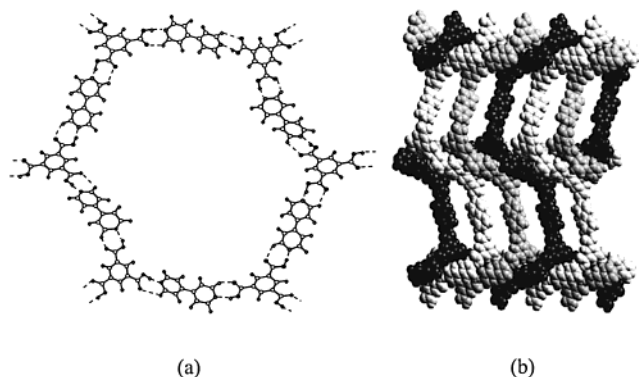
**Figure 15.**

H₃TMA represents an example of a motif that is the result of the assembly of a single component that is self-complementary. As discussed earlier, this means that there are limits in terms of supramolecular synthesis when compared to multiple-component modular systems. The H₃TMA network can be extended to generate larger holes and, therefore, larger channels and cavities by employing the modular self-assembly approach. The structure of [H₃TMA][bipy]$_{1.5}$ would be expected to exist as an expanded form of H₃TMA since the pyridine−carboxylic acid supramolecular synthon appears to be more stable than the carboxylic acid dimer itself.[283−285] As shown in Figure 15, the anticipated structure indeed occurs and the cavities are large (ca. 26 × 35 Å). However, these cavities are filled by the interpenetration of three independent networks (Figure 15b), thereby affording a close-packed structure with no cavities. This type of interpenetration, which can be termed parallel interpenetration,[10] resembles weaving and is facilitated by puckering of the pseudohexagons that form the network. The hexagons resemble the chair conformation of cyclohexane.

Rao et al. recently reported a related structure that is based upon modular self-assembly:[286] an organic network formed by trithiocyanuric acid (TCA) and bipy. Adjacent layers are aligned parallel to each other, but there is no interpenetration. The resulting open framework structure exhibits channels with an effective diameter of 10 Å. An interesting feature of this compound is that the cavities in the layers, and therefore the resulting channels, can vary in size depending on the solvent of crystallization that is used to template the modular self-assembly process. (Scheme 11). It should be noted that the two architectures that have thus been observed are not simply distorted or stretched variants of one another, they have distinct hydrogen-bonding patterns. Another salient feature is that there are sulfur atoms accessible in the cavities which could promote selective sorption or could facilitate desired chemical reactivity in the context of green chemistry.[287]

Network structures based upon metalloporphyrins with multiexodentate functionality (e.g., tetracarboxylic acid derivatives) have also yielded 2D networks sustained by hydrogen bonding.[288] An interesting feature of these structures is that the presence of a metal ion in the porphyrin ring can afford cross-linking of 2D layers by bidentate spacer ligands, thereby affording a 3D architecture.[288] Such an

**Scheme 11. Schematic of the Two Supramolecular Isomers Reported for the Modular Self-assembly of TCA and bipy**



(a)



(b)
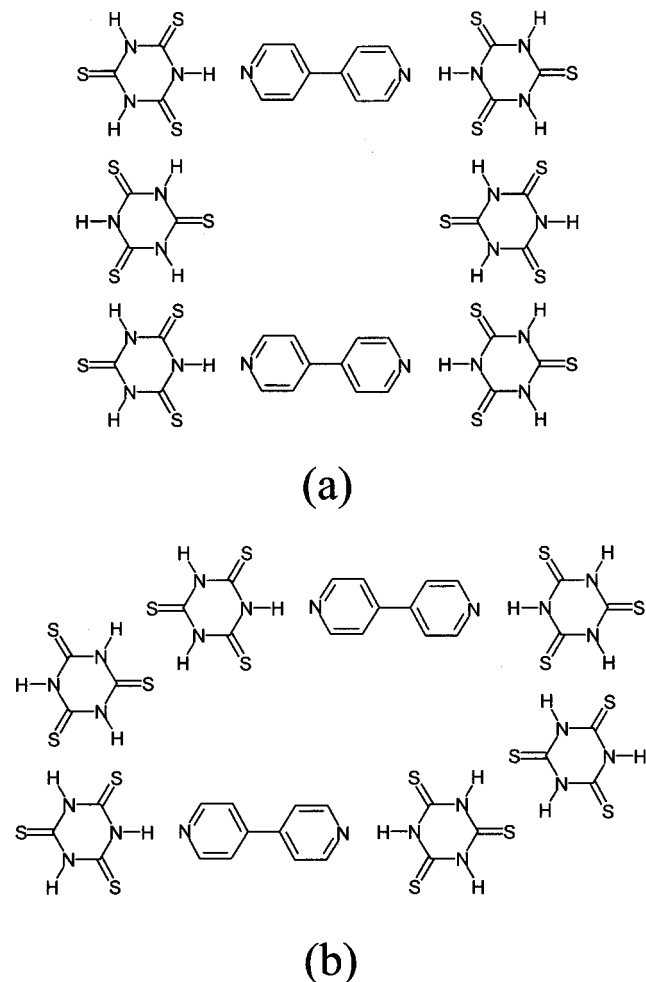
architecture is a hybrid form[289] of coordination polymer and organic network.

### 3. Hydrogen-Bonded Networks Sustained by Organic Ions

Salts that are based upon organic ions with complementary hydrogen-bonding sites represent an alternate approach to modular self-assembly of organic molecular components. H₃TMA also represents an appropriate precursor in this context, via formation of ammonium salts of the deprotonated forms of H₃TMA.[290−292] Although it might not at first be obvious how the ammonium moiety could extend anionic forms of H₃TMA into honeycomb networks, Scheme 12 illustrates two such motifs, the supramolecular isomers A and B, both of which facilitate linear propagation of carboxylate anions. In the case of TMA$^{3-}$ and dicyclohexylammonium, supramolecular isomers A and B have both been observed to generate laminated structures. The generation of A or B appears to be solvent dependent. It has also been shown that self-assembly of the lamellar structure can occur at surfaces.[293]

An important feature of architectures that are sustained by A and B is that some of their components and features can be fine-tuned without destroying the basic architecture. For example, the

**Scheme 12. Schematic Illustration of Two Motifs that Can Occur through Self-assembly of Dialkylammonium and Carboxylate Moieties. Both Motifs Effect Linear Propagation**



(a)                    (b)
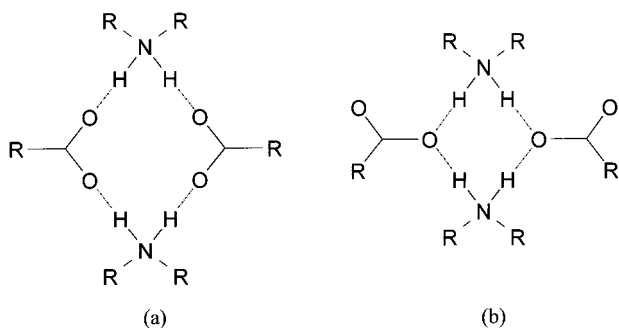
**Scheme 13. Schematic Illustration of the Interdigitation of the Alkyl Groups on Adjacent Layers in [(BTC²⁻)(NH₂(alkyl)₂⁺)₂] and the Possibility of Intercalation of Guest Molecules**
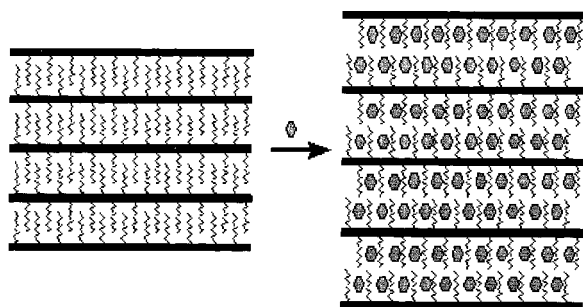


ammonium cation substituents can be changed without influencing the basic molecular recognition properties in the context of motifs A and B. For secondary amines, organic substituents would extend above and below the network and in appropriate circumstances would preclude interpenetration. Depending upon the nature of the substituents, adjacent layers might interdigitate and/or adopt clay-like intercalates in the presence of appropriate guest molecules (Scheme 13). Both $HTMA^{2-}$ and $TMA^{3-}$ can sustain laminar structures that result from crystallization of $H_3TMA$ in the presence of primary and secondary amines ($RNH_2$ and $R_2NH$).

Related laminar architectures have also been synthesized using other polyfunctional carboxylic acids such as trimellitic and pyromellitic acids.[294] Stoiochiometry has little influence over whether laminar structures are obtained, but it has a profound influence over the local hydrogen-bonding patterns and the molecular recognition features of the "organic clays" that are formed.

**Stoichiometry 1:2 (H₃TMA:amine).** The hydrogen-bond network within each sheet is hardly predictable, but it seems to be reproducible over a wide range of ammonium cations. The structure of the 2D network is illustrated in Figure 17, and it is composed entirely of ionic hydrogen bonds. If alkyl substituents are present on the ammonium cation, then the typical result is a laminated material with poor ability to adsorb molecules because of interdigitation of the alkyl substituents[291] (Figure 17). However, use of dibenzylamine (DBA), [(PhCh₂)₂NH], mitigates against interdigitation and promotes re-
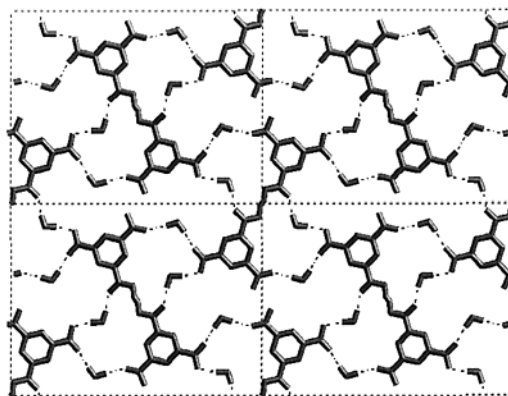


**Figure 16.** Illustration of the hydrogen-bonding pattern in [(BTC²⁻)(NH₂(CH₂Ph)₂⁺)₂]; benzyl groups are omitted for clarity.



(a)                    (b)



(c)                    (d)
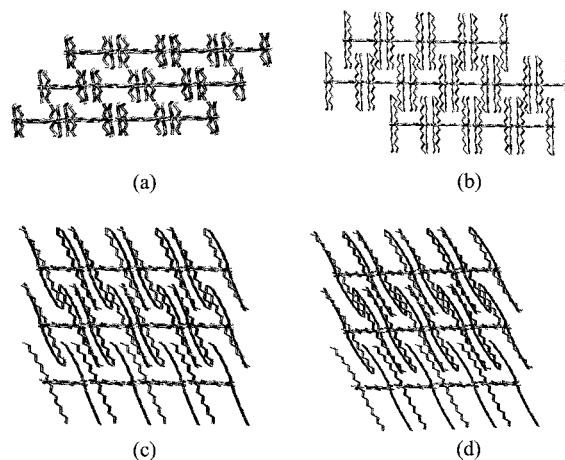
**Figure 17.** Illustrations of the packing interactions of the hydrogen-bonded 2D networks in [(BTC²⁻)(NH₂(alkyl)₂⁺)₂], alkyl = (a) propyl, (b) hexyl, (c) octyl, and (d) decyl.

versible incorporation of aromatic guest molecules.[290] The resulting compounds are structurally related to clays, but they are inherently hydrophobic and have affinity for aromatic guests over alcohols or water. In this series of compounds, there is some variation in the geometry of the hydrogen-bond layer and in the manner in which guest molecules are incorporated. In general, the benzyl groups form a plethora of aromatic C−H···π interactions to the surrounding guest molecules. The unit cell lengths are typically multiples of ca. 12 × 17 × 21 Å (stacking axis, short axis, and long axis, respectively). The length of the stacking axis represents the interlayer separation, and a doubling of the length of the stacking axis occurs when adjacent layers are not related by translation. Multiples of short and long axes also occur because of differences in the arrangement of guest molecules between benzyl groups. In effect, guest molecules and/or benzyl groups do not necessarily repeat with the asymmetric unit of the H-bonded layer. The crystal structures might be classified based upon the stacking axis as being of one of two types: (a) identical packing of adjacent layers (i.e., related by translation) or (b) adjacent layers which are different from each other. The hydrogen-bonded sheets can be either flat or corrugated. In effect, the host matrix is a flexible, generic host material for aromatic molecules. A representative
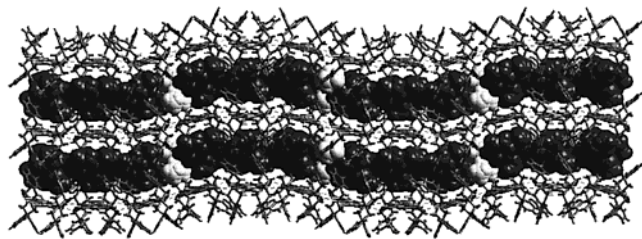
**Figure 18.** Illustration of the crystal packing of the hydrogen-bonded 2D networks in [(BTC$^{2-}$)(NH$_2$(CH$_2$Ph)$_2$$^+$)$_2$]. The benzyl moieties preclude interdigitation and facilitate reversible sorption of aromatic molecules.
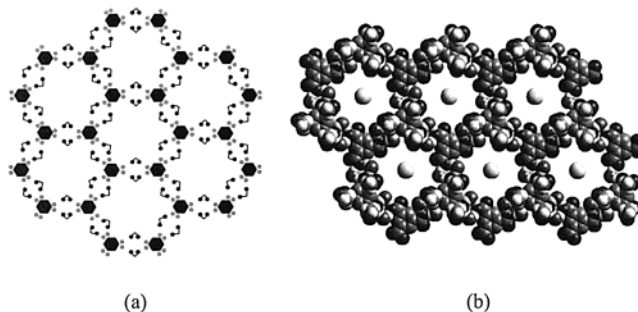


**Figure 19.** Illustration of the crystal packing in [(BTC$^{2-}$)(NH$_3$(CH$_2$Ph)$^+$)$_2$], a prototypal example of the network structures formed by BTC dianions and primary ammonium cations.



(a)　　　　　　　(b)

**Figure 20.** Modular honeycomb network sustained by BTC trianions and secondary alkylammonium cations: (a) schematic representation of the hydrogen-bonding pattern and (b) space-filling illustration of the crystal structure of [(BTC$^{2-}$)(NH$_3$(C$_6$H$_{12}$)$^+$)$_2$].

structure is illustrated in Figure 18, and as should be clear, there is no interdigitation of benzyl groups. The guest molecules interact with walls of the channels only, and the asymmetric unit is unusual: 3:3:1 for host:guest:solvent. In the presence of primary ammonium cations, similar structures are obtained but they are more appropriately termed bilayer architectures since there are alternating hydrophobic and hydrophilic regions. A typical structure is illustrated in Figure 19. Similar structures are obtained for both alkyl- and benzylammonium cations. It might be reasonable to describe such structures as being cytomimetic since there is a resemblance to the type of supramolecular synthons that exist in phospholipid membranes and in the solid phases of surfactants. The ancillary organic groups orient in the same direction and interdigitate with adjacent layers to generate hydrophobic regions. The hydrophilic faces of adjacent bilayers also face one another and can incorporate water molecules. The thickness of hydrophilic layers ranges from 3.2 to 3.4 Å, while the thickness of interdigitated layers increases with the size of the organic group.

**Stoichiometry 1:3 (H$_3$TMA:amine).** In principle, 1:3 stoichiometry offers the opportunity to generate honeycomb networks. As revealed by Figure 20a, motif A or B should be capable of propagating the trimesate anion into a honeycomb structure. Figure 20b reveals that the crystal structure of [TMA]-[dicylohexylammonium]$_3$ exists as the anticipated honeycomb array.[290] The cyclohexyl moieties, which are omitted for the sake of clarity, effectively prevent interpenetration by capping the 13 Å cavities that are present within the honeycomb structure. If the

solvent is changed, a honeycomb network based upon the other supramolecular synthon is generated,[293] and it has been reported that this form of the honeycomb network will self-assemble at the air−water interface. The modular nature of this structure permits replacement of the cyclohexyl moieties by other moieties. In this context, alkyl groups that are less sterically demanding (e.g., *n*-alkyl) have also been incorporated into the motif in Figure 20a. Interpenetration occurs in these structures.

**Guanidinium Sulfonates.** A series of related structures that are based upon two-dimensional layers resulting from hydrogen bonding of the trigonal guanidinium cation, C(NH$_2$)$_3$$^+$, and organic sulfonate ions RSO$_3$$^-$ has been extensively studied by the Ward group[176,238,240,295−302] (Scheme 14).

Interdigitation of the organic substituent of the sulfonate ions on adjacent layers and ionic hydrogen-bonding predictably leads to a broad series of laminar architectures. It should be noted that there are several key differences between guanidinium sulfonates and alkylammonium trimesates. (1) There exists only one ancillary organic functional group per sulfonate ion compared to up to two ancillary functional groups per ammonium cation. (2) The anion is functionalized rather than the cation. (3) In one sense, the alkylsulfonates are more versatile since they can exhibit architectural (i.e., supramolecular) isomerism so as to generate either bilayer or clay-like architectures. To generate a clay-like architecture, organic groups must orient above and below each layer as illustrated by Scheme 15. The steric demands of the organic group appear to determine whether they orient in the same direction (i.e., a bilayer structure) or alternate above and below the layer (i.e., a clay-like structure).

## C. 3D Networks

### 1. Self-Assembled Hydrogen-Bonded Diamondoid Networks

A report by Ermer[86] on the structural characterization of adamantane-1,3,5,7-tetracarboxylic acid and its implications represented a watershed for crystal engineering. Ermer's study was followed by a flurry of activity into design from first principles of both organic diamondoid networks and metal−organic diamondoid coordination polymers. The carboxylic

**Scheme 14. Schematic Illustration of the Key Structural Features of Guanidinium Sulfonates: (a) Hexagonal Channels that Form 2D Honeycomb Networks and (b) Two Extended Structures (2D and 3D) that Can Result from the Self-assembly of Guandinium Cations with Disulfonates Anions**



(a)

(b)
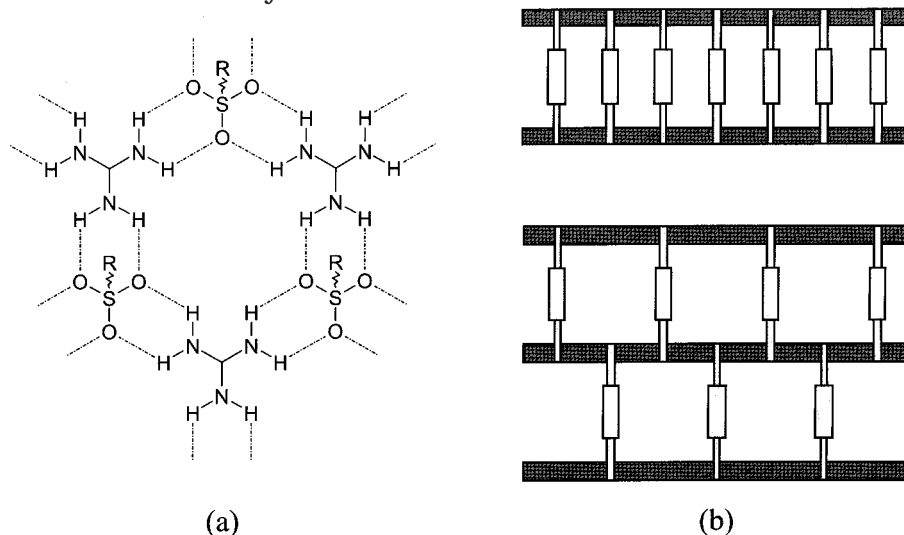
**Scheme 15. Schematic Illustrating Two Possible Modes of Interdigitation for Guanidinium Sulfonates: (a) Clay-like, Induced by Sterically Demanding Functional Groups and (b) Bilayer Architecture, Typically Observed for Smaller Functional Groups**



(a)

(b)

acid groups of adamantane-1,3,5,7-tetracarboxylic acid are tetrahedrally oriented. It is therefore unsurprising that they self-assemble via the hydrogen-bonded carboxylic dimer supramolecular synthon to afford an infinite diamond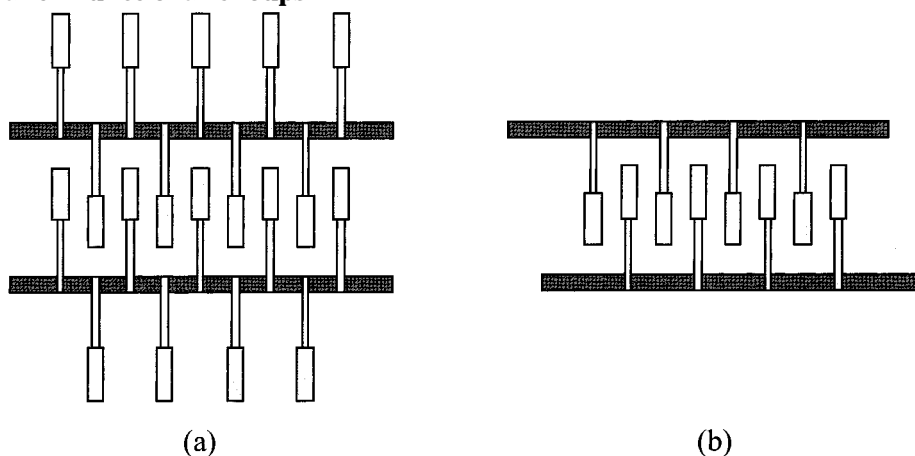oid network. Each network possesses cavities that could accommodate a large roughly spherical guest, or guest aggregate, of roughly 12 Å in diameter. However, these cavities are filled by five independent networks that interpenetrate in such a way that the crystal structure is densely packed, and consequently, guest inclusion is precluded. As subsequent studies have revealed, interpenetration is a widespread phenomenon in diamondoid networks and occurs in many other organic and metal–organic structures that would otherwise have large cavities or channels. An interpenetrated diamondoid architecture is also exhibited by methanetetraacetic acid, for which the cavities generated are approximately 10 Å in diameter.[87] As would be expected, methanetetraacetic acid exhibits a lower degree of interpenetration: 3-fold. 2,6-dimethylidine-adamantane-1,3,5,7-tetracarboxylic acid also forms a hydrogen-bonded diamondoid structure, but it exhibits a much lower degree of interpenetration

than its unsubstituted precursor. The 2-fold "double diamondoid" architecture is not as densely packed, and it can therefore act as a host and enclathrate guest molecules.[86]

Wuest demonstrated that the pyridone moiety also generates a hydrogen-bonded supramolecular synthon that is suitable for building extended arrays.[89,303,304] Remarkably, methanetetra(6-phenyl-ethynyl-2-pyridone) exhibits a diamondoid network, 7-fold interpenetration, and cavities large enough to enclathrate butyric or valeric acid.[89] Wuest introduced the concept of "tectons" to describe molecules that inherently possess the molecular structure and intermolecular recognition features to predictably self-assemble into crystalline networks. This study was followed by studies that demonstrated that there are several other examples of diamondoid networks that can be sustained by the pyridone moiety.[305,306]

### 2. Modular Self-Assembly of Hydrogen-Bonded Diamondoid Networks

As discussed earlier, modular self-assembly relies upon two molecular components that are not individually capable of self-assembly and can be invoked
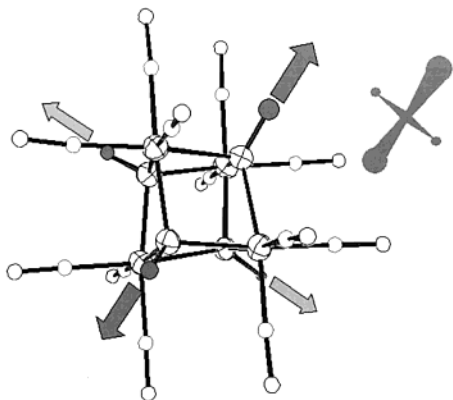
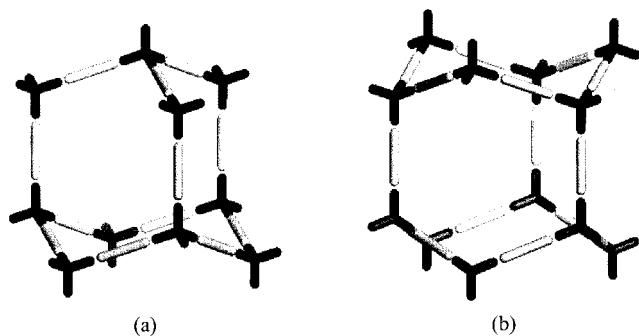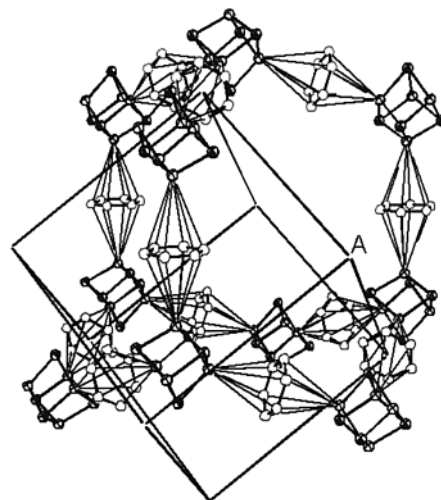**Figure 21.** [Mn($\mu_3$-OH)(CO)$_3$]$_4$: a cubane-like cluster possessing perfect $T_d$ symmetry that represents a prototypal example of a tetrahedral hydrogen-bond donor.

**Scheme 16. Schematic Illustration of the Two Types of Diamondoid Architecture: (a) Cubic and (b) Hexagonal**



(a)                                    (b)



**Figure 22.** Illustration of the crystal structure and diamondoid cavity generated in [Mn($\mu_3$-OH)(CO)$_3$]$_4$·2benzene.

to understand coordination polymers or multiple-component hydrogen-bonded networks.[90] There are significant differences between the types of tetrahedral moiety that can sustain networks that have been self-assembled from a single component vs networks that have been self-assembled from multiple components. The most fundamental difference between the two types of structure is that the tetrahedral component that sustains single-component self-assembled architectures would not ordinarily be able to sustain modular architectures and vice versa. In the case of the former, the tetrahedral moieties must be self-complementary and there is only one component necessary for self-assembly to occur. This means, for example, that both hydrogen-bond donors and hydrogen-bond acceptors must be present in the same molecule. In the case of the latter, the tetrahedral node must be either an acceptor or a donor of hydrogen bonds and the linker or spacer must be complementary. Both components are necessary, and there must be a 1:2 ratio in order for the diamondoid architecture to self-assemble. Scheme 16 illustrates the difference between the two types of diamondoid networks.

An example of a node that is suitable for modular self-assembly is the cubane cluster [Mn($\mu_3$-OH)(CO)$_3$]$_4$,[307] which possesses perfect $T_d$ symmetry and has four strong hydrogen-bond donors and no strong hydrogen-bond acceptors (Figure 21). This tetrahedral hydrogen-bond donor forms diamondoid cocrystals with a wide range of obvious and, in some cases, not so obvious spacer molecules. A "not so obvious"

structure is that formed when [Mn($\mu_3$-OH)(CO)$_3$]$_4$ is cocrystallized with benzene.[308] A 2-fold diamondoid structure is sustained by OH···$\pi$ hydrogen bonds, and the tetrahedral symmetry of the node is observed in the crystallographic sense since [Mn($\mu_3$-OH)(CO)$_3$]$_4$·2benzene crystallizes in the cubic space group $Pn$-$3m$ with $z = 2$. As revealed by Figure 22, which illustrates an adamantoid portion of the structure, a large cavity is generated and this facilitates interpenetration of a second diamondoid network.

The use of transition metals or transition-metal clusters to act as nodes for the modular self-assembly of diamondoid networks that are sustained by coordinate covalent bonds is also well established. Such architectures are of more than aesthetic appeal, and they have resulted in a class of compounds with interesting bulk and functional properties. Metal–organic diamondoid structures in which the spacer moiety has no center of inversion are predisposed to generate polar networks since there would not be an inherent center of inversion. Pyridine-4-carboxylic acid, isonicotinic acid, is such a ligand, and bis(isonicotinato)zinc exists as a 3-fold diamondoid structure that is both thermally stable and inherently polar.[228] It exhibits SHG activity that is three times higher than the commercially relevant NLO material KDP.[309,310]

There are also supramolecular synthons that do not rely upon hydrogen bonds. In this context, N···Br interactions were exploited to propagate a diamondoid network in the cocrystal formed by carbon tetrabromide and hexamethylenetetraaamine. This structure also represents a different but equally effective form of the modular approach: two tetrahedral nodes with one possessing donor functionality and the other acceptor functionality only. The structure of the cocrystal formed by carbon tetrabromide and hexamethylenetetraaamine exhibits 2-fold interpenetration and does not enclathrate solvent or guest.[311]

### 3. Other 3D Hydrogen-Bonded Networks

Although there are many examples of organic crystals that can be defined as 3D networks, few of

**Scheme 17. Schematic Illustrating Five Supramolecular Synthons Possible for Pyromellitate Dianions**



(a)          (b)          (c)

(d)          (e)
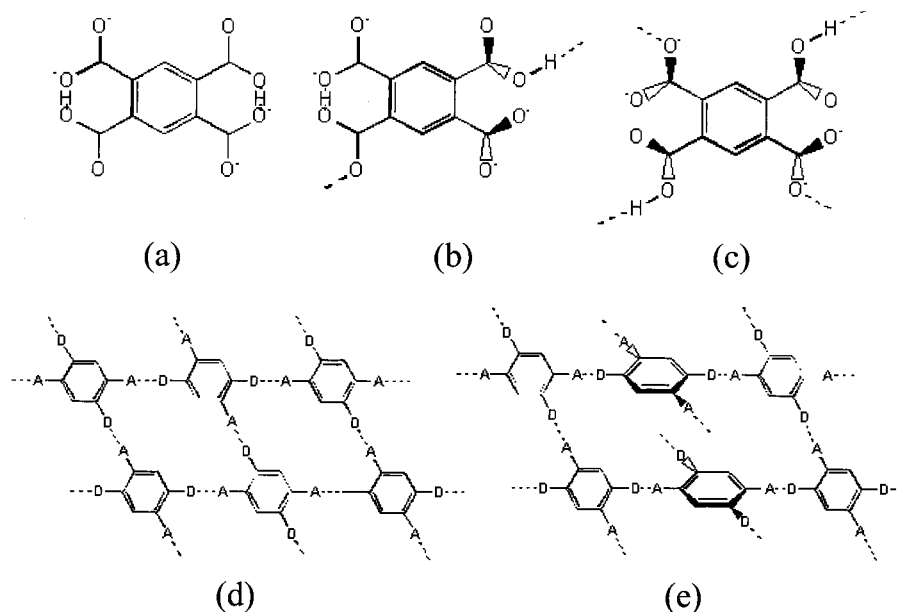
them are predictable or even rational in the same sense as diamondoid networks. Trimesic acid, $H_3$-TMA, is an interesting exception and was discussed earlier in the context of 2D structures. $H_3$TMA represents a prototypal molecule in the context of hydrogen bonding and generates extended structures when pure, partially deprotonated, in coordination polymers or in cocrystals. Anionic derivatives of $H_3$TMA self-assemble into honeycomb grids via $O-H\cdots O^-$ hydrogen bonds.[280-282,312,313] Pyromellitic acid, 1,2,4,5-benzenetetracarboxylic acid, $H_4$PMA, has been less widely explored than $H_3$TMA. It has been utilized as a ligand in coordination polymer networks,[294] and very few organic structures containing $H_4$PMA or its derivatives are known. We anticipated that doubly deprotonated $H_4$PMA would self-assemble via dicarboxylate hydrogen bonds to form 0D (two intramolecular hydrogen bonds), 1D (one intramolecular and one intermolecular hydrogen bond), or 2D/3D (two intermolecular hydrogen bonds) networks (Scheme 17). $H_2$PMA$^{2-}$ anions exhibit all four of these supramolecular isomers depending upon the polymorph or the counterion.[314] The 3D structure occurs because $H_2$PMA$^{2-}$ moieties orient in such a manner that they form hydrogen bonds to the next layer. The network can be described as a framework built from square building blocks that alternate parallel and perpendicular with respect to one another. This network can therefore be regarded as an organic analogue of NbO.[66]

It should be obvious that all 2D networks must, in the absence of solvent or intercalated guest, engage in noncovalent interactions with the layers above and below. The possibility of exploiting a combination of molecular recognition modes represents a particularly attractive approach to control crystal packing since it places no restrictions in terms of the type of chemical components that can be rationally incorporated into crystalline phases. In this context, Fowler and Lauher[19,315-320] illustrated how it is possible to use hydrogen bonding to control interactions between 1D networks, or á-networks, and to thereby yield

predictable 2D networks or α-networks. If the sheets are designed to be self-complementary in the third dimension, then a predictable 3D network or γ-network can result. Fowler and Lauher demonstrated not only that such a strategy is viable, but that it can offer a degree of control over stacking of layers such that the interlayer components are positioned within the limits of the topochemical principle. They were thereby able to effect solid-state reactions upon appropriate perturbation. When coupled with other advances in this context, including recent reports[17,19] that demonstrate how discrete aggregates may also afford components that are positioned within the topochemical boundaries, it should be clear that crystal engineering involving multiple types of molecular recognition offers significant implications for solid-state synthesis and solvent-free, green chemistry.

## IV. Supramolecular Isomerism and Polymorphism

The existence of supramolecular isomerism might be seen as a problem from a design perspective since it necessarily implies that there will be superstructural diversity for a given molecular building block. However, there is another way to look at this matter. It is also possible to view supramolecular isomerism as an opportunity to gain a better fundamental understanding of the factors that influence crystal nucleation and growth. Such a linkage can be justified as follows. (1) If one invokes the concept of supramolecular isomerism, then it should become apparent that it represents a significant limitation on the number of possible superstructures (i.e., discrete structures or 1D, 2D, or 3D networks) that can occur for a given molecular building block. Therefore, one can invoke a study on supramolecular isomerism or polymorphism with the assumption that self-assembly means that there will only be a finite number of architectures that are feasible for a given molecular species. This assumption will be based upon crystals being the result of directional

**Scheme 18. Schematic Illustration of the Six Supramolecular Isomers Reported for T-Shaped Nodes Linked by Linear Bifunctional Exodentate Ligands: (a) 1D Ladder, (b) 3D Lincoln Logs, (c) 2D Herringbone, (d) 2D Bilayer, (e) 2D Brick Wall, and (f) 3D Frame**

(a)   (b)   (c)

(d)   (e)   (f)
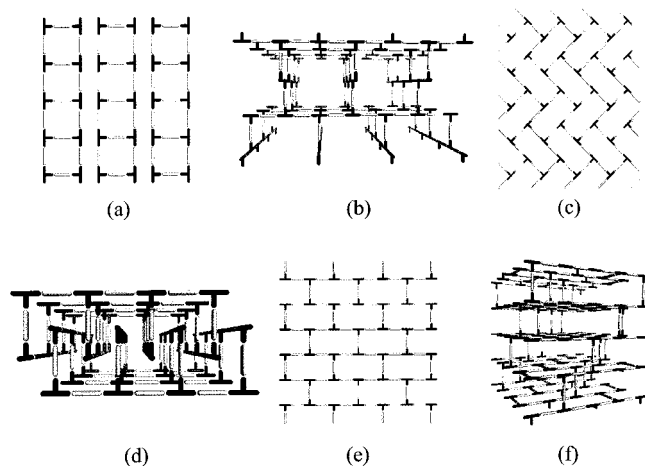
supramolecular synthons, the fundamental precept of crystal engineering. (2) The ability of the crystal engineer to design a molecular building block that is predisposed toward the formation of supramolecular isomers provides an ideal opportunity for design of supramolecular isomers and, perhaps more importantly, for learning how to control supramolecular isomers. At the very least, it will be possible to develop "recipes" that invoke crystallization conditions, templates, and/or solvents to favor or disfavor a particular supramolecular isomer.[321,322] (3) The concepts of self-assembly, crystal engineering, and networking provide clear implications for gaining a better fundamental understanding of polymorphism since polymorphism can be regarded as a subset of supramolecular isomerism. (4) It should be clear that to gain a better understanding of supramolecular isomerism and polymorphism, it is a requirement that full structural characterization of compounds be conducted. This means an in-depth analysis of crystal packing and intermolecular contacts as well as measurement of physical properties.

To illustrate the linkage between crystal engineering, supramolecular isomerism, and polymorphism, we shall consider three types of supramolecular isomerism and demonstrate how analogies can be readily drawn between coordination polymers and organic networks.

## A. Structural Supramolecular Isomerism

That structural supramolecular isomerism can have profound implications for structure and properties is exemplified by the range of structures that has thus far been observed in coordination polymers that are generated by one of the simplest building blocks and stoichiometries: 1:1.5 stoichiometry, mer-metal, and linear spacer ligand. These building blocks can be regarded as being based upon self-assembly of T-shaped nodes. There already exists a surprisingly diverse range of structures that have been observed in this context. Scheme 18 illustrates the supramo-

lecular isomers that have thus far been observed: ladder[91,178] (A), brick wall[204] (B), 3D frame or "Lincoln Logs"[236,237] (C), bilayer[213] (D), herringbone[210] (E),[78,211,212] and another version of a 3D frame[177] (F). Three of the isomers A,[178] D,[213] and F[177] have been observed for the same asymmetric unit for metal = $Co(NO_3)_2$ and ligand = bipy, and the other three have been seen in similar compounds which use bipy or extended analogues as "spacer ligands".

The following points should be noted about such structures. (1) These compounds are not true polymorphs since guest or solvent molecules are present in the lattice. However, neither are they solvates in the conventional sense. (2) The diversity of network structures and hence bulk properties is remarkable. (3) None of these architectures occurs naturally in minerals. (4) The network structures themselves are entirely predictable based upon simple structural considerations. (5) Some of these structures can occur from the same building blocks under almost identical crystallization conditions.

It is possible to draw direct analogies with polymorphism in organic crystals. For example, a similar approach based upon networks can be used to analyze the packing in organic compounds. A recent paper highlighted this situation in the context of 2-amino-5-nitropyrimidine, a compound that exhibits three readily available polymorphs, all of which have distinct hydrogen-bonded networks.[323] Etter's study concerning carboxylic acids[88] and how they can self-assemble to form either head-to-tail chains or centrosymmetric dimers also illustrates how one can rationalize polymorphism based upon supramolecular isomers and networks.

In summary, it seems likely that use of appropriate templates or guest molecules facilitates recipes that can be used to reliably generate all supramolecular isomers that are possible for a given node. Therefore, one might assert that there are a finite number of superstructures possible for a given molecular moiety and that it will eventually be possible to determine the crystallization conditions under which each one will occur.

## B. Conformational Supramolecular Isomerism

Flexibility in ligands can lead to subtle or dramatic changes in architecture. For example, 1,2-bis(pyridyl)ethane, bipy-eta, can readily adapt *gauche-* or *anti*-conformations. In the case of $[Co(bipy-eta)_{1.5}(NO_3)_2]_n$, which contains a T-shaped node, infinite molecular ladders which contain six molecules of chloroform per cavity exist as the most commonly encountered architecture (Figure 23a).[186] In such a situation, all "spacer ligands" are necessarily *anti*. However, under certain crystallization conditions (e.g., solvent MeCN or dioxane), a bilayer architecture is obtained with two *anti-* and one *gauche*-spacer ligand per metal atom (Figure 23b).

The bilayer architecture can contain solvent molecules such as MeCN or can collapse on itself in the absence of solvent.[44] This more subtle form of supramolecular isomerism occurs if $[Co(bipy-eta)_{1.5}(NO_3)_2]_n$ is crystallized in the absence of a suitable guest or solvent.[217] Figure 24 reveals how [Co(bipy-

(a)

(b)
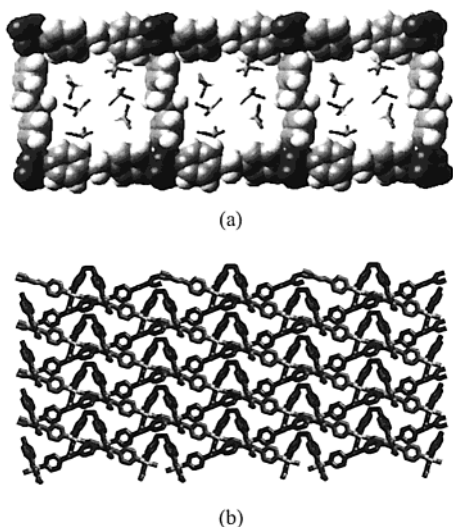
**Figure 23.** Illustrations of two structures observed for [Co-(bipy-eta)$_{1.5}$(NO$_3$)$_2$]: (a) ladder in which all bipy-eta ligands adapt an *anti*-orientation and (b) bilayer in which bipy-eta ligands adapt *anti*- and *gauche*-orientations in a 2:1 ratio.



(a)

(b)
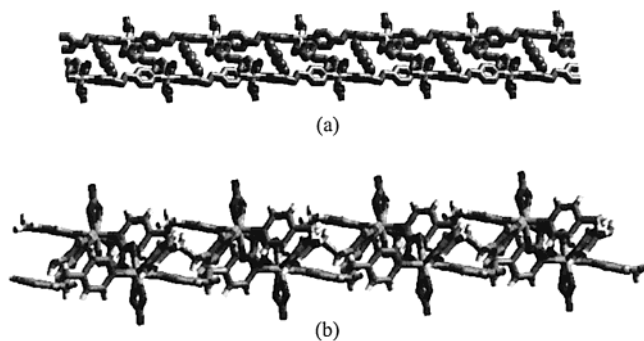
**Figure 24.** Illustrations of crystal structures of [Co(bipy-eta)$_{1.5}$(NO$_3$)$_2$] cocrystallized with (a) MeCN and (b) no solvent of crystallization. Note how the cavities collapse in the absence of the adsorbed solvent.

eta)$_{1.5}$(NO$_3$)$_2$]$_n$ collapses to close the cavity that exists when crystallized from MeCN.[44] Note the difference in torsion angles between the two compounds. A similar situation occurs in compounds based upon a longer bis-pyridyl ligand, 1,4-bis((4-pyridyl)methyl)-2,3,5,6-tetrafluorophenylene, **2**. When **2** is complexed to Cd to form compounds of formula [Cd(**2**)$_2$(NO$_3$)$_2$], three very different supramolecular isomers have been observed depending upon the nature of guests or templates: 1D chains, 2D sheets, and 3D diamondoid networks.[324]

A dramatic illustration of how conformational variability can influence crystal packing in organic compounds is illustrated by the compound 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile. This compound exists in at least six polymorphic phases. The primary difference between the six phases lies with the torsion angle between the thiophene moiety and the *o*-nitroaniline fragment, which varies from 21.7° to 104.7°.[55]
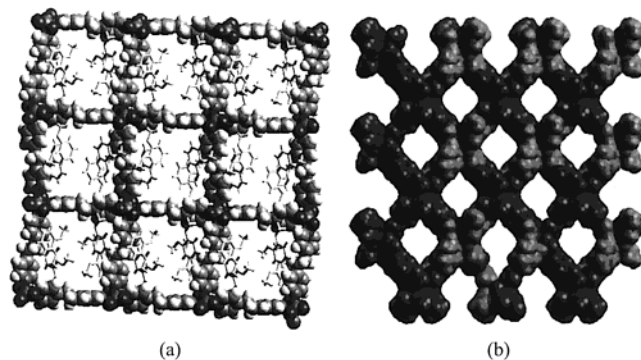
## C. Catenane Supramolecular Isomerism

The existence of independent interpenetrating networks is surprisingly common if relatively large



(a)                    (b)

**Figure 25.** Illustrations of two crystal structures of the square grid coordination polymer [Ni(bipy-eta)$_2$(NO$_3$)$_2$]: (a) with included guest molecules and (b) interpenetrated networks.

cavities are generated within a network. A thorough review of this subject in the context of coordination polymers was recently published by Batten and Robson.[58] The existence of interpenetration has been regarded as a factor that mitigates strongly against the generation of stable open framework structures. However, it is becoming clear that appropriate use of templates can afford either open framework or interpenetrated structures for the same network. This is exemplified by the prototypal diamondoid and square grid networks Cd(CN)$_2$ and M(bipy)$_2$X$_2$. Both of these compounds have been prepared as interpenetrated and noninterpenetrated forms. Furthermore, some interpenetrated structures can also be regarded as open framework since if interpenetration will not necessarily afford close-packing. Interpenetrated structures can still contain channels large enough to hold, for example, aromatic guests. Such is the case for square grid networks based upon ligands such as bipy-eta. Figure 25 reveals how either open framework square grid or interpenetrated square grid structures can be readily generated for the same square grid network.[200] Both compounds contain square grids of formula [Ni(bipy-eta)$_2$(NO$_3$)]$_n$. As would be expected, the compound illustrated in Figure 25a, [Ni(bipy-eta)$_2$(NO$_3$)]$_n$, exhibits clay-like properties and can desorb and adsorb guests. Crystallinity is lost, but the square grid architecture retains its integrity below 220 °C. The interpenetrated analogue is illustrated in Figure 25b and is effectively a 3D architecture that is built by interpenetration of square grids. This compound has a more rigid structure than its noninterpenetrated form and behaves like a zeolitic solid rather than a clay-like solid. Both compounds are stable to loss of guest, but the former loses crystallinity upon loss of guest.

Organic networks are also capable of exhibiting interpenetration, and in this context H$_3$TMA represents a prototypal example. As discussed earlier, H$_3$TMA is predisposed to generate honeycomb sheets with large cavities. Three phases of H$_3$TMA have thus far been characterized. In two of these phases, one of which is pure H$_3$TMA, 3-fold interpenetration of the individual hexagonal cavities occurs.[282] In pure H$_3$TMA, the honeycomb networks are puckered in such a manner that small cavities are generated.[280] These cavities can hold small molecules, including
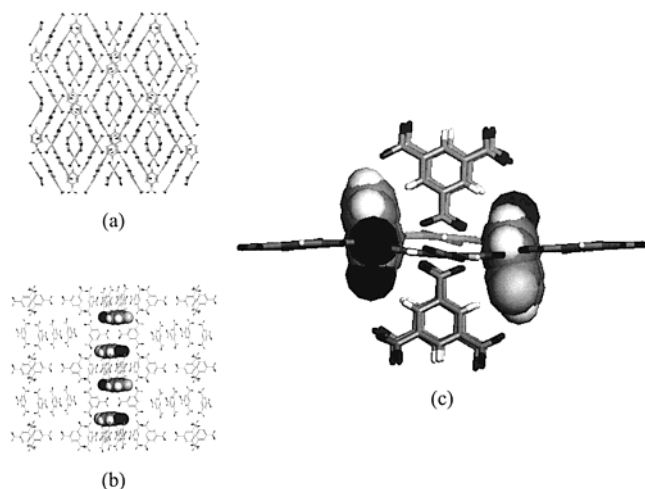
**Figure 26.** Illustration of the α-polymorph of BTC that illustrates how BTC can sustain the enclathration of *p*-nitroaniline: (a) view of the 10-fold interpenetrated puckered honeycomb networks, (b) view of a single BTC network with 3-fold interpenetration per cavity and incorporation of *p*-nitroaniline in "pockets", and (c) perspective view of two *p*-nitroanilines situated in a single cavity, surrounded by the three interpenetrating networks.

halogens[312] and *p*-nitroaniline.[325] The structure of the inclusion compound formed between $H_3TMA$ and *p*-nitroaniline is illustrated in Figure 26. The other interpenetrated phase of $H_3TMA$ contains flat sheets, and it therefore contains infinite 1D channels.[281] The noninterpenetrated phase of $H_3TMA$, illustrated in Figure 14, is formed when long-chain alkanes are used during the crystallization process.

A honeycomb network is also generated when $H_3$-TMA is cocrystallized with bipy. This structure exhibits interpenetration in 2D to form a novel carpet-like architecture.[283] However, the noninterpenetrated form remains to be isolated.

The results described above all suggest that interpenetration can be avoided if appropriate templates are used during the crystallization. It is therefore reasonable to see interpenetration as another example of supramolecular isomerism, one that can be controlled by use of guest or template molecules during crystallization.

## V. Potential Applications

A considerable amount of research into understanding the nature and predictability of supramolecular synthons remains to be conducted. An enhanced database concerning supramolecular synthons in the broad context would also assist our fundamental understanding of solution chemistry and biochemistry. Nevertheless, it is clear that there are a number of applications of crystal engineering that could be realized in the short term. Several of these are summarized below. (1) From a supramolecular perspective, binary compounds represent an illustration of how one might exploit the modular approach to design new supermolecules, especially in the solid state. It is reasonable to assert that supramolecular synthesis of new classes of cocrystal and modular solid offers potential to increase the known range of crystalline materials by two or three orders of magnitude and to facilitate combinatorial approaches to materials science. For example, if one were to only consider cocrystals that are sustained by hydrogen bonding, a wide range of compositions exists that remain to be explored. It is perhaps sobering to realize that, at least in principle, molecules that are deficient in hydrogen-bond acceptors are inherently prone to form supermolecules with molecules that contain excess hydrogen-bond acceptors. Even if one considered only simple examples such as pyridines, there are many permutations for formation of binary compounds. If one were to study, for example, 20 pyridines and 20 carboxylic acids, then one would expect 400 new binary compounds with predictable composition and structure. Such a strategy could be important in the context of supramolecular derivatives of drugs and functional materials (i.e., modification of bulk properties without changing the molecular structure of the active species) or they could serve as precursors to covalent products, including polymers. Such an approach has already been effective in formulation of polaroid film.[326] There also exists the possibility of rationalizing certain types of host−guest structures as being based upon topologically complementary networks.[241,243] Such compounds are also based upon self-assembly and might be prototypal for large numbers of related structures. (2) It is already established that solvent-free synthesis, green chemistry, offers many potential advantages, including cost and environmental benefits.[13,14] Cocrystallization of substrates and subsequently conducting reactions in the solid state offers the opportunity for very careful control over regio- and stereochemistry. It is also possible that supramolecular arrays could act as precursors to new classes of 2D and 3D covalent polymers.[327] (3) New classes of adsorbent, "organic and metal−organic clays and zeolites" represent an area in which considerable progress has already been made. Such compounds offer clear potential for the following: efficient, cost-effective alternatives to current methods of enantiomeric separations, new materials for separation of gases, liquids, and solutes, new industrial heterogeneous catalysts, new drug delivery matrixes (e.g., matrix for oral delivery of otherwise unstable drugs), a new generation of chemical sensors, and new storage matrixes for gases such as methane. Recent results indicate that synthetic metal−organic polymers can offer high levels of thermal stability and can supersede zeolites in terms of surface area and capacity for small guest molecules.[76,81] (4) The rational design of polar materials for use in materials science also represents an aspect of crystal engineering that has already provided promising developments. Unfortunately, in most organic crystals, antiparallel architectures predominate, thereby canceling dipoles of highly polarizable molecules and mitigating against optimization of bulk polarity. Fortunately, there now exists an extended range of modular, open framework organic and metal−organic solids. Many of these compounds contain architectures (e.g., square grid, honeycomb, octahedral) that favor incorporation of polar strands into channels, thereby reducing the driving force for

antiparallel alignment. Results obtained by the groups of Hollingsworth[328-332] and Hulliger et al.[333-340] suggest that such compounds, in particular channel-type inclusion compounds, hold considerable promise in the context of the design of solids that possess fine-tunable bulk polarity. Diamondoid networks also offer considerable potential in this context since tetrahedral nodes do not contain a center of inversion.[90] The recent results of Lin's group indicate that diamondoid networks can couple high thermal stability with high SHG activity.[228,229] (5) Metal−organic polymers offer considerable potential in the context of molecular magnetism, semiconductors, and conductors.[341-347] Once again, the possibility of design and fine-tuning becomes apparent when one develops structures with predictable architectures that are based upon paramagnetic metal ions. The presence of guest molecules can be a desirable feature as it would be expected to offer a degree of fine-tuning that is not inherently present in single-component compounds.

## VI. Conclusions and Future Directions

"*The peasant who wants to harvest in his lifetime cannot wait for the ab initio theory of weather*", H. G. von Schnering (1981).

The fundamental precept of crystal engineering is that all information necessary for design of extended 1D, 2D, and 3D structures is already present at the molecular level in existing chemical species. Recent advances in our understanding of supramolecular chemistry and supramolecular synthons have been aided by the advent of CCD diffractometers coupled with ever more powerful visualization and analysis tools. It should therefore be unsurprising that control over supramolecular architectures, also known as molecular tectonics,[348] has advanced rapidly in recent years. That these tools are now routinely available means that an even more concerted and systematic approach to gaining an understanding of the subtle factors that control architectures in the solid state is feasible. The rational design of supramolecular structure necessarily relies upon invoking the concepts of self-assembly, in effect supramolecular synthesis, and exploits noncovalent forces as varied as the following: (1) hydrogen bonding, including both strong hydrogen bonding (e.g., O−H- - -O) and weak hydrogen bonding (e.g., C−H- - -O and even C−H- - -$\pi$), (2) coordinate covalent bonds (e.g., metal−organic polymers), (3) electrostatic and charge-transfer attractions, and (4) aromatic $\pi$-stacking interactions.

These principles of crystal engineering and supramolecular synthesis have thus far been used to design, isolate, and characterize a number of novel network structures that are prototypal because they are based upon modular components. However, these networks are typically based upon relatively small molecular components and the number and chemical type of components is typically restricted. It is in these two areas that there appears to be almost unlimited potential for supramolecular synthesis. In the context of coordination polymer networks, a recent review indicates how wide the range of chemi-

cal components and accessible network motifs has become.[215] However, the scale of these structures is such that cavities and channels are on the order of 10 Å and, to date, each cavity is identical. Careful selection of appropriate substrates or components and ever more control over crystal packing will offer the potential for rational design of an even more extensive array of modular (i.e., binary, ternary, or even higher order) structures than those that are currently available. In particular, judicious choice of secondary building units,[84] supermolecules, or biomolecules as templates and nodes should afford composite materials with nanoscale dimensions and cavities. The same is likely to be true concerning the rational development of structures that are based upon components that are at first glance incompatible. A number of examples of pure crystalline compounds that are based upon metal−organic polymers and metal oxide clusters have been reported in recent years.[197,289,349,350] Such composite materials would represent "uncharted territory", but they are a natural outgrowth of modular approaches to chemistry and now appear to be at hand. In essence, suprasupermolecular[351] synthesis in the solid state is likely to develop considerably further and, whereas prediction of crystal structures remains an elusive goal that will continue to be addressed, it does not preclude short-term applications of crystal engineering in a number of important areas. H. G. von Schnering's comments therefore seem particularly appropriate to summarize the current opportunities for crystal engineering and design.[352]

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