

Engineering crystals by the strategy of molecular tectonics

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Detailed structures of molecular crystals cannot yet be predicted with consistent accuracy, but the strategy of molecular tectonics offers crystal engineers a powerful tool for designing molecules that are predisposed to form crystals with particular structural features and properties.

The crystallization of molecules is a commonplace phenomenon, familiar even to children, yet it remains poorly understood. Developing a full understanding of molecular crystallization is among the great unmet challenges of contemporary science.^{1–3} The knowledge that eludes us will certainly prove to be valuable, particularly because it will allow us to control crystallization rationally and thereby obtain new materials with useful properties. The rich rewards and the sheer magnitude of the problems, combined with the increasing power of methods for solving them, have drawn many researchers to the study of molecular crystallization and made it an exceptionally dynamic field of research.

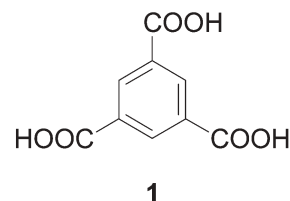
A particularly exciting subject is crystal engineering,^{4–7} which includes among its principal goals the development of a clear understanding of the relationship between individual molecules and the structures and properties of their crystals. Appropriately, the term “crystal

engineering” was coined by crystallographers,^{8,9} and crystallographers have been in the forefront of the subsequent evolution of the field. However, crystal engineering is an inherently interdisciplinary activity, and increasingly important contributions are being made by specialists in molecular synthesis, materials science, computational chemistry, and other areas. The advent of automated diffractometers, powerful and inexpensive computers, and effective software for structural analysis has begun to eliminate formal training in crystallography as a prerequisite for making significant contributions to crystal engineering.

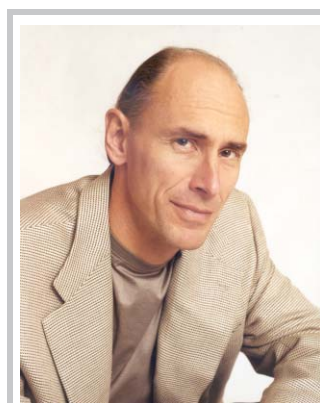
When my research group and I entered this field almost 20 years ago, we noted that much of the published work involved compounds with very simple structures, at least by the standards of chemists trained in molecular synthesis. Moreover, many early attempts to position molecules in crystals required extensive trial and error, and they frequently relied tenuously on the limited ability of very weak intermolecular interactions to control crystallization predictably. These attempts were undeniably heroic;

however, even when they were successful, they did not always offer guidance of general value to researchers trying to engineer other crystals.

The pioneering work of Etter and others began to focus attention on the ability of hydrogen bonds to help control molecular crystallization, largely because of their strength and directionality.^{10,11} Moreover, this early work revealed that reliable hydrogen-bonding motifs are formed by many elementary functional groups frequently encountered in simple molecules. Together, these observations set the stage for an important advance in crystal engineering in which structures are built from more sophisticated molecules, specifically designed to 1) incorporate multiple sites of hydrogen bonding or other directional interactions and 2) orient them in arrays favoring the assembly of networks with predictable architectures.¹² In essence, we saw the development of such molecules as an opportunity to extend and generalize the prototypic behavior of water and somewhat more complex molecules such as trimesic acid (**1**), which incorporates a periphery with three trigonally-directed carboxyl groups. As already confirmed more than 35 years ago by Duchamp and Marsh in a seminal crystallographic study,¹³ compound **1** is predisposed to form a hexagonal grid (Fig. 1), programmed by geometry and the cyclic doubly hydrogen-bonded motif favored by pairs of many carboxylic acids.



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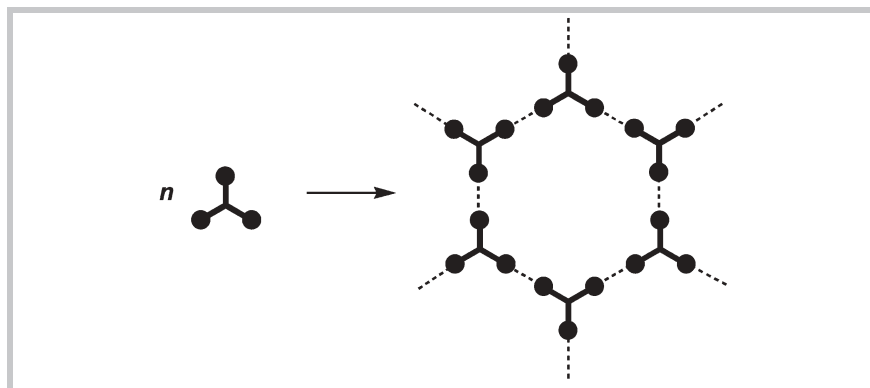


Fig. 1 Formation of a hexagonal network from a hypothetical molecule constructed by attaching sites of association (●) to a trigonal core. Broken lines represent directional intermolecular interactions.

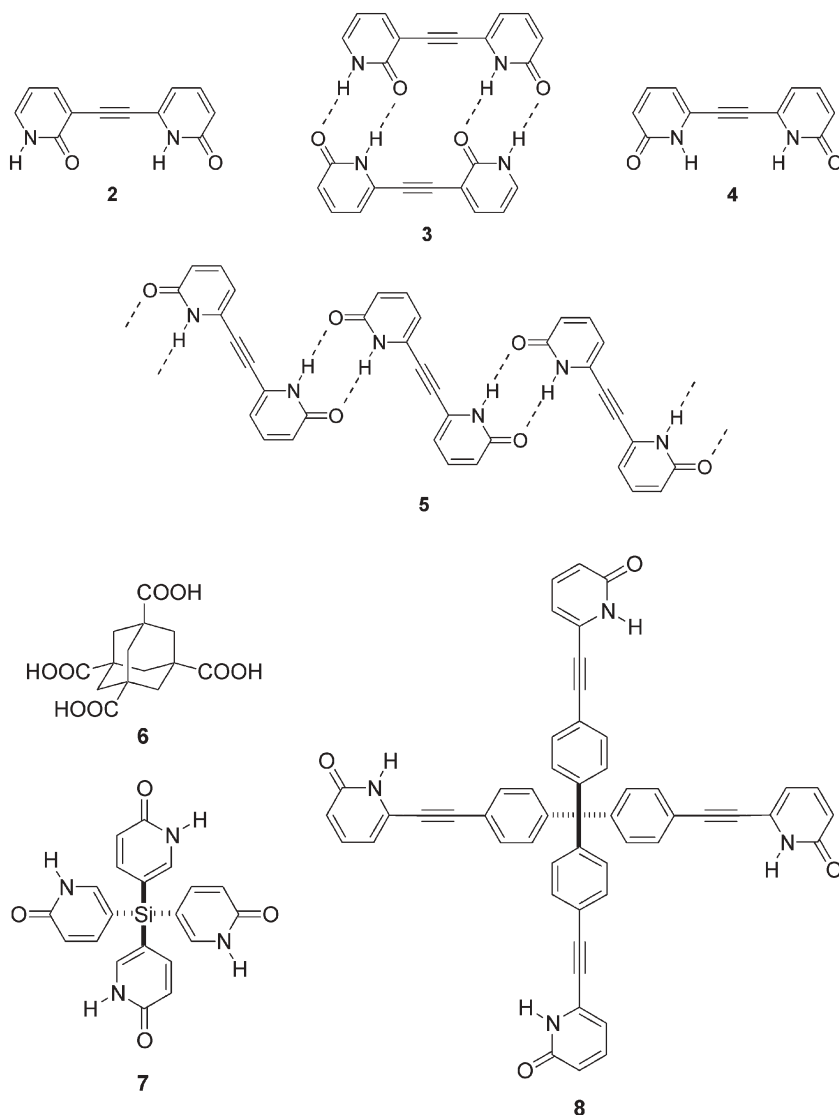
Our first paper on crystal engineering, published in 1988,¹⁴ set out a simple but broadly effective strategy for designing and synthesizing new molecules of this type. In this strategy, multiple peripheral groups that direct association according to reliable motifs, later named supramolecular synthons by Desiraju,^{15,16} are formally grafted to cores that orient the sticky peripheral groups properly. The cores may also introduce other desirable features, including chirality, charge, catalytic activity, and useful optoelectronic properties. In our initial work,¹⁴ we illustrated our approach by selecting an acetylenic core and grafting it to two 2-pyridinone groups, which are known to self-associate reliably in solution and in the solid state to form cyclic hydrogen-bonded pairs. As planned, self-complementary dipyridinone **2** crystallizes as discrete dimer **3**, whereas isomeric dipyridinone **4** forms the one-dimensional hydrogen-bonded network **5**. This work revealed how the force and specificity of association that characterize simple sticky groups can be amplified by connecting the groups to form more complex arrays. Moreover, the work confirmed the applicability of this strategy to crystal engineering by showing that it could be used to construct molecular networks with predetermined architectural features.

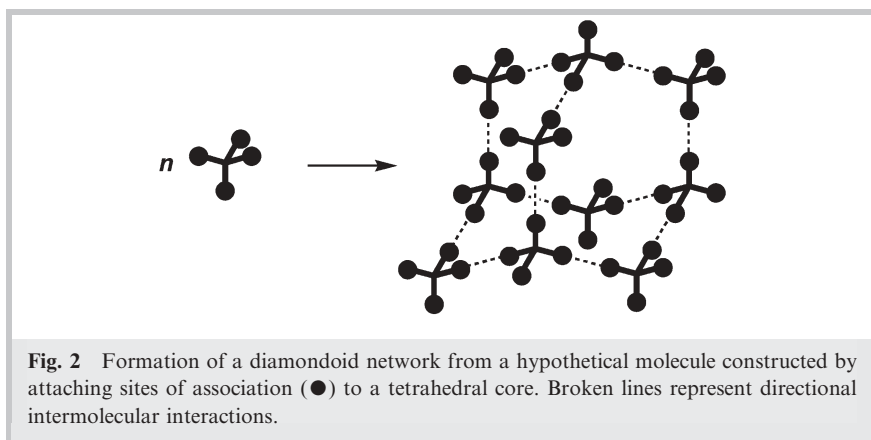
Each molecule in crystals of dipyridinones **2** and **4** uses hydrogen bonding to place certain neighboring molecules in predictable positions; however, the orientation of other neighbors is not controlled by strong directional interactions and is therefore more difficult to foresee.

Obviously, establishing the fullest possible control requires building molecules with peripheries that orient potent sticky

sites in multiple directions, thereby programming the position of the largest number of neighboring molecules. In a classic paper published in 1988,¹⁷ Ermer took an important step in this direction by showing that the crystallization of adamantane-1,3,5,7-tetracarboxylic acid (**6**) is controlled predictably by self-association of carboxyl groups to give a three-dimensional hydrogen-bonded network with diamondoid topology (Fig. 2). In the resulting crystals, four of the neighbors of each molecule have orientations predetermined by hydrogen bonding. Our group provided other early examples of similar engineering, in which diamondoid networks resulted predictably from the self-association of tetrapyridinones **7** and **8**.^{18,19}

In another influential early paper,²⁰ Hoskins and Robson demonstrated that





molecules, we gave them the name tectons,¹⁸ which is derived from the Greek word for builder. The concept of tectonic construction is already widely understood by geologists and architects, who use it to refer to interrelationships in complex forms built from multiple sub-units that retain their identity in the final structure.²⁴ Our work, as well as that of Hosseini and others,^{25–28} explicitly acknowledges that the scope of tectonics embraces chemistry as well.

Most molecules form crystals that are considered closely packed,²⁹ with no capacity to include guests and with only small residual spaces between molecules remaining unfilled. Typically, these unoccupied spaces add up to about 30% of the total volume of the crystals,³⁰ but none of the spaces would accommodate a probe sphere 2.4 Å in diameter, which corresponds roughly to the size of a molecule of water and is a common measure of porosity.³¹ In contrast, tectons cannot normally form crystals in which packing and specific directional interactions are both optimized at the same time. Strong directional interactions usually dominate, leading to the formation of open networks with a significant capacity for inclusion.^{32,33} Available space is then filled by independent interpenetrating networks^{34,35} and by included guests, typically molecules of solvent. The marked difference between tectons and normal molecules can be appreciated by noting that about 60% of the volume of crystals of tetrapyrindione **7** is accessible to guests,^{19,36} whereas no inclusion is observed in crystals of the close structural analogue **9**, which lacks the crucial ability to form strong directional intermolecular interactions.³⁷

networks with predictable architectures can also be engineered by a related strategy based on the interaction of metals with ligands containing multiple sites of coordination. Important analogies exist between networks held together by coordinative interactions and those maintained by hydrogen bonds or other weak intermolecular interactions. For the following reasons, however, it is proper to treat the resulting materials as fundamentally different:

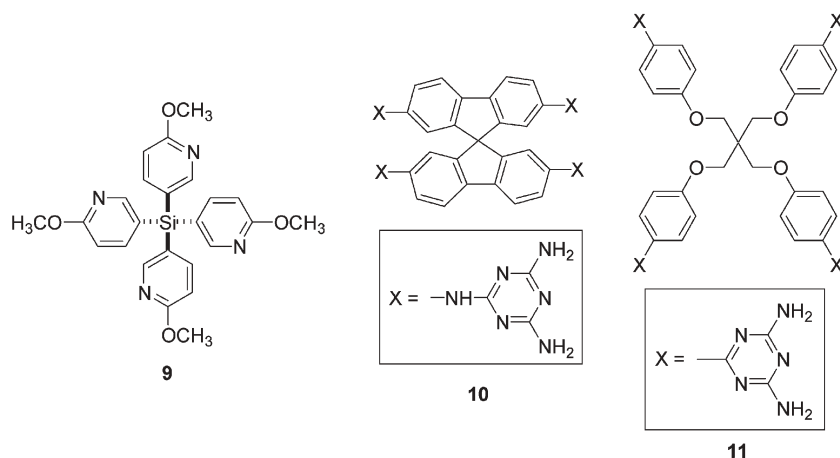
- The forces of cohesion in purely molecular crystals are much weaker than covalent bonds, so individual molecules in the resulting structure retain their identity unambiguously and can be recovered intact by simple means, such as by dissolving the crystals. In contrast, superficial examination of networks built from multidentate ligands and metals cannot reveal exactly how they were made, because the ligands displace the original sphere of coordination of the metals. Moreover, coordinative interactions between ligands and metals can be as strong as covalent bonds within the ligands themselves, so regeneration of the original components of metal-directed assembly is not always trivial.

- Individual molecules generally retain their characteristic properties in molecular crystals, but metal–ligand interactions can have profound effects on the behavior of the individual components of coordination networks.

- The dimensionality of molecular networks can be controlled with confidence by proper orientation of suitable sticky sites, whereas the geometry of coordination to metals is not always easy to foresee.

Despite these important differences, studies of crystal engineering directed by the coordination of metals and by hydrogen bonding have proceeded in tandem,^{21–23} with many fruitful exchanges of ideas. We see the development of these two types of materials as activities that are complementary, not competitive, and we expect each type of material to find applications for which it is inherently better suited than the other. For example, networks held together robustly by the coordination of metals may prove superior for the construction of ordered materials with permanent porosity, whereas molecular networks may show a balance of robustness and plasticity better suited to making materials that can adapt to guests and include them with high selectivity.

Special molecules with multiple peripheral sites of strong directional interaction define a class of compounds that are set apart from normal molecules by their properties and their inherent suitability for engineering crystals. To underscore the distinctiveness of these special



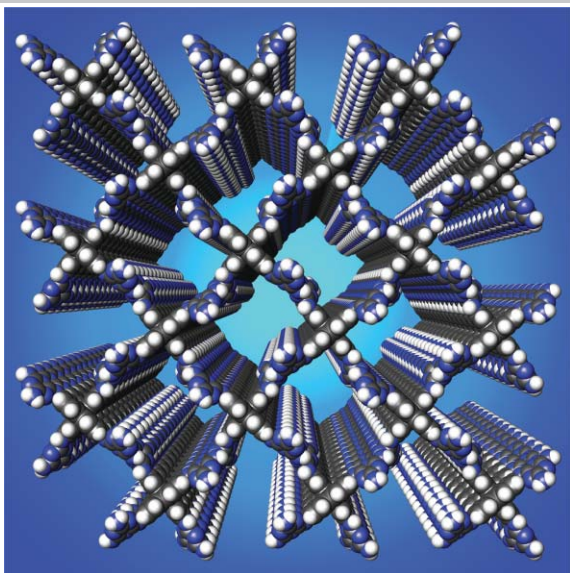


Fig. 3 Perspective view along the c axis of the porous network constructed by crystallizing tecton **10**. Guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of the channels. Atoms of hydrogen appear in white, carbon in gray, and nitrogen in blue.

Tectons with cores that are rigid, awkwardly shaped, and inherently resistant to close packing can yield networks with striking porosity. Spirobifluorene is a particularly effective core of this type. In crystals of spirobifluorene **10**,³⁸ which incorporates four sticky aminotriazine groups, 75% of the volume is accessible to guests, as estimated by PLATON (Fig. 3).³¹ So far, the hydrogen-bonded network formed by tecton **10** is the most porous ever built from small molecules. In fact, the percentage of volume available for inclusion exceeds that accessible to water and other guests in all but the most highly hydrated crystals of proteins, which have convoluted topologies far more complex than the relatively simple shape of tecton **10**. Large, rigid, and awkward molecular shapes may be necessary to set new records, but they are by no means strict prerequisites for impressive inclusion, as shown by the high porosity (66%) of networks built from flexible tecton **11**.³⁹

Structural studies of inclusion compounds have a long and rich history, starting with pioneering investigations of clathrates by Powell almost 60 years ago.⁴⁰ Most classes of compounds that tend to crystallize with guests have been discovered serendipitously. Moreover, even in the benchmark case of urea, the

volume of crystals accessible to guests does not exceed 50%. In contrast, molecular tectonics now offers a rational strategy for creating an unlimited number of new porous networks, and tectons with widely divergent molecular structures yield crystals in which guests occupy far more than 50% of the volume. By suddenly adding an essential new chapter to the well-studied field of inclusion compounds, tectons have exhibited behavior that warrants treating

them as a distinct class of compounds, qualitatively different from normal molecules.

Porous networks derived from tectons are molecular analogues of zeolites, but they are held together by hydrogen bonds and other weak interactions, making them inherently less robust. Nevertheless, the interactions that ensure molecular cohesion are numerous; for example, networks built from compounds **6–8** and **10–11** are held together by 8, 8, 8, 16, and 14 hydrogen bonds per tecton, respectively. In contrast, included guests interact weakly with the surrounding hydrogen-bonded networks, are frequently disordered, and tend to occupy channels that in principle provide easy escape from the networks. These channels can be engineered to have a remarkably wide variety of topologies and connectivities, ranging from simple parallel channels without interconnections in the case of tecton **7** to complex three-dimensional topologies with extensive interconnections in the case of tecton **12** (Fig. 4).⁴¹ Guests located in these channels can often be exchanged without loss of crystallinity, simply by exposing single crystals to new guests. As in zeolites, exchange is typically selective⁴² and appears to involve diffusion of guests within well-defined channels, rather than defects, recrystallization, or other processes requiring extensive movement of the tectons themselves.³⁶ In favorable cases, such as in crystals of tecton **13**,⁴³ multiply hydrogen-bonded networks are

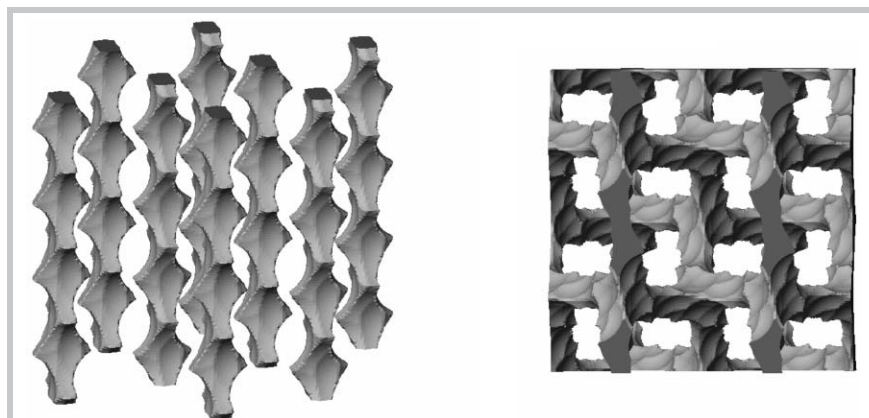
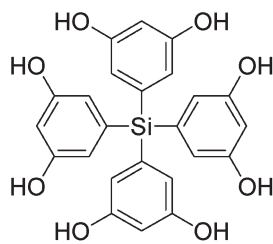
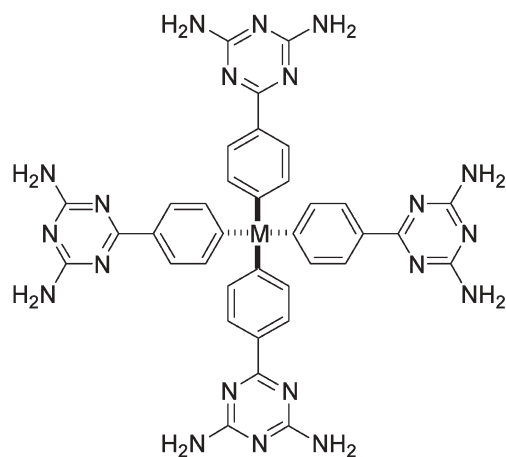


Fig. 4 Representations of channels within networks formed by crystallizing tectons **7** (left) and **12** (right). The image on the left shows the channels in a $2 \times 2 \times 4$ array of unit cells with the c axis vertical, and the image on the right corresponds to a $2 \times 2 \times 1$ array of unit cells viewed along the c axis. The surfaces of the channels are defined by the possible loci of the center of a sphere of diameter 5 Å as it rolls over the surface of the ordered network.

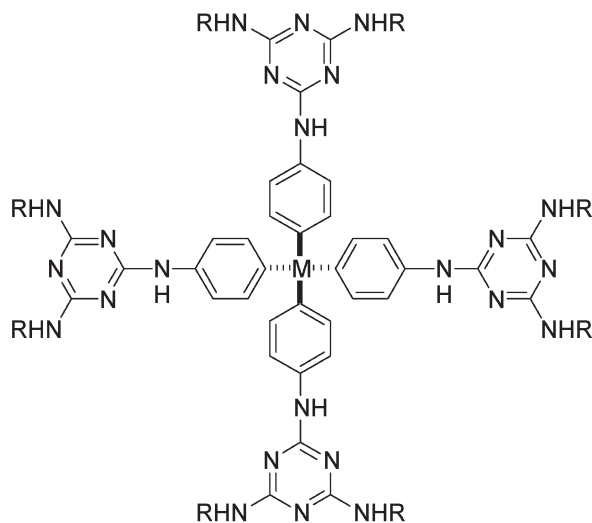


12



13 (M = C)

15 (M = B⁻)



14a (R = CH₂CH=CH₂)

14b (R = CH₂CH₂CH₂SCH₃)

even robust enough to allow significant fractions of the guests to be removed under vacuum with retention of crystallinity. These observations underscore the surprisingly high structural integrity of multiply hydrogen-bonded networks and their potential suitability for applications in separation and heterogeneous catalysis, even when temporary or permanent porosity are required.

At the same time, the inherent deformability of weak intermolecular interactions and the conformational flexibility of typical molecules allow the structures of tectonic networks to adapt to guests.³⁶ By enforcing proximity between networks and their guests, adaptive porosity may make inclusion more selective than it is in zeolites and other robust inorganic frameworks, particularly in processes requiring fine distinctions such as the resolution of enantiomers. In exceptional cases, adjustments provoked by the exchange of guests can cause crystals to undergo gross changes of geometry without loss of crystallinity.³⁶ Such dual displays of subtly balanced robustness

and plasticity suggest that crystals made by the strategy of molecular tectonics will have unique applications in materials science. Moreover, these hybrid properties hint at the possibility of using the concepts of molecular tectonics not just in the design of crystalline solids, but also in the creation of materials that are less ordered or even fluid, including liquid crystals, gels, polymers, monolayers, and glasses.^{41,44}

The interiors of crystals built by the strategy of molecular tectonics are typically accessible to external reagents, unlike those of normal close-packed crystals. We have used this accessibility to devise a powerful new way to create crystals of new compounds rationally, starting with crystals of precursors.^{45,46} Historically, such topotactic reactions are very rare because movement in normal molecular crystals is severely restricted. As a result, known topotactic reactions have typically involved intramolecular processes or have required that all necessary co-reactants be incorporated in the precursor crystals, held in

proximity, and oriented properly. These conditions have sometimes been met by laborious crystal engineering, but the limitations of this approach are obvious. We have outlined a potentially general alternative based on the use of permeable crystals constructed from tectons that incorporate specific sites of reactivity. These crystals allow external agents to enter and react at the selected sites, thereby yielding crystals of new compounds with retention of the original crystalline architecture. Proof of concept was established by studies of tecton **14a**,⁴⁵ which forms permeable hydrogen-bonded crystals in which potentially reactive –CH=CH₂ groups are exposed to guests. As planned, irradiation of single crystals of tecton **14a** in the presence of CH₃SH caused addition to the double bonds, giving isostructural single crystals of thioether **14b**.

Double addition of HS(CH₂)₂SH also occurs topotactically to crosslink molecules in crystals of tecton **14a** covalently, thereby capturing temporary supramolecular constructs as permanent crystalline

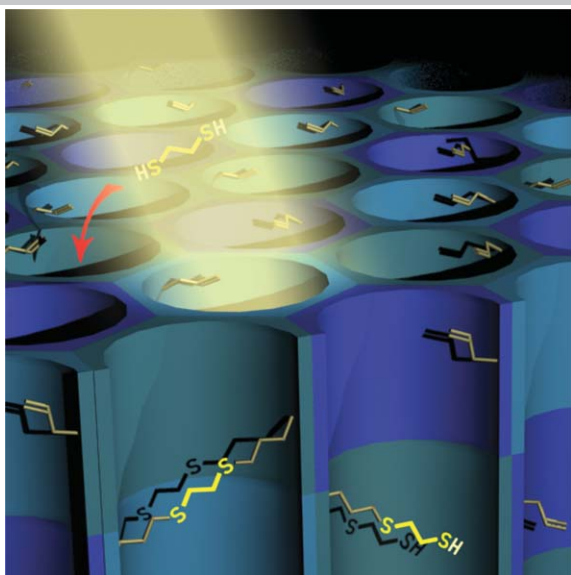


Fig. 5 Schematic representation of a permeable crystal of tecton **14a** showing how exposed allyl groups are crosslinked topotactically by the photoaddition of HS(CH₂)₂SH. This process captures a temporary supramolecular construct as a permanent crystalline macromolecular replica.

macromolecular replicas (Fig. 5). Conversely, labile groups exposed within porous networks can be cleaved topotactically and the fragments allowed to exit by diffusion, thereby yielding crystals of new compounds in which even more volume is accessible to guests.⁴⁶ Robust permeable molecular crystals made by the strategy of molecular tectonics promise to help make topotactic reactions commonplace, thereby creating a wealth of new opportunities in solid-state chemistry. In particular, such reactions can convert crystalline precursors into crystalline products with different compositions but the same structural parameters. In this way, it may be possible to create new polymorphs by design or to obtain crystals of compounds that fail to crystallize normally or are too reactive to handle in solution.

Although exciting work in crystal engineering can be done with little or no synthesis, we believe that our ability to undertake projects requiring complex molecular synthesis gives us a special advantage. Particularly valuable sources of insight in crystal engineering are structural comparisons of new tectons in which different sticky sites are attached to the same core, or in which the same sticky sites are attached to different cores. For example, synthesis of

neutral tecton **13** and its anionic analogue **15** allowed us to compare the structures of their crystals and thereby assess the effect of charge.⁴² As expected, both compounds give open hydrogen-bonded networks, but the charged network derived from borate **15** is more porous and able to undergo selective ion

exchange without loss of crystallinity, much like zeolites. Further structural studies using salts of borate **15** with widely different counterions established a consistent preference for the formation of the same hydrogen-bonded network. This observation suggests that rigid tectons are inherently resistant to crystallization in multiple polymorphic forms; instead, they are programmed by their characteristic geometry and arrays of multiple sticky sites to form one particular structure or a small number of closely related alternatives. The widespread notion that the number of polymorphic forms of a compound is limited only by the effort needed to find them may not hold true for all tectons.^{47,48}

Sophisticated molecular synthesis is also a powerful tool for engineering crystals with sub-nanometric precision.⁴⁹ For example, attachment of sticky –B(OH)₂ groups to a tetraphenylmethyl core creates tecton **16**, which crystallizes predictably as open interpenetrated diamondoid networks held together by hydrogen bonding characteristic of boronic acids.⁵⁰ Analogous tetraphenylsilane **17**, which replaces the central carbon atom in tecton **16** with silicon and thereby increases the distance from the center of the core to the peripheral sticky sites, crystallizes isostructurally as planned, giving a rationally expanded set

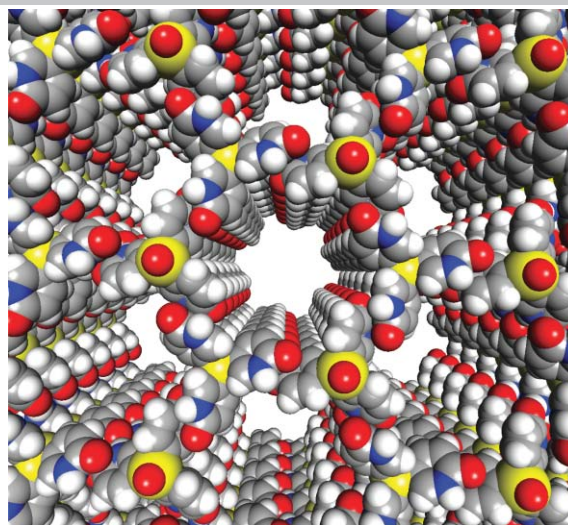
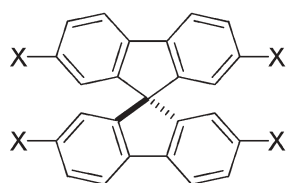
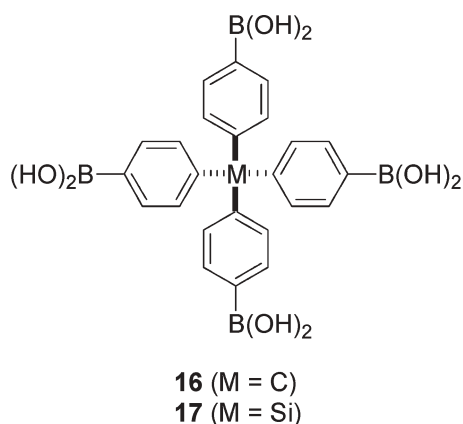
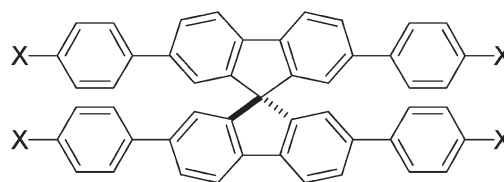
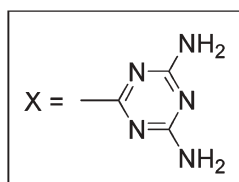


Fig. 6 Perspective view along the *c* axis of the porous network constructed by crystallizing trigonal tecton **20**. Guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of the channels. Atoms of hydrogen appear in white, carbon in gray, nitrogen in blue, oxygen in red, and phosphorus in yellow. The view is centered on a single channel and shows that adjacent P=O dipoles are opposed in hydrogen-bonded hexagonal sheets, which stack with the dipoles aligned.



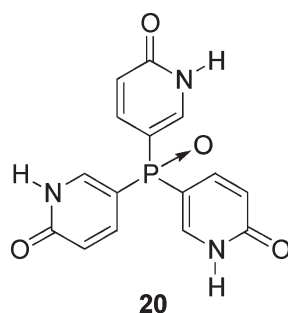
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19

of interpenetrated diamondoid networks. So far, attempts to engineer much more dramatic expansions have failed. For example, insertion of phenyl arms in spirobifluorene **18** provided markedly enlarged tecton **19**, yet its crystallization yielded a hydrogen-bonded network of lower porosity.⁵¹

Our initial explorations of molecular tectonics have targeted networks assembled from single self-associating subunits and held together uniquely by hydrogen bonds. These simplifications are by no means necessary and were made only to focus our resources on studies designed to reveal fundamental aspects of the strategy, rather than its full scope. We are now beginning to broaden our research to include networks co-assembled from two or more different tectons, as well as networks held together by strong directional interactions other than hydrogen bonds. For example, crystallization of trigonal tecton **20** is directed reliably by hydrogen bonding of pyridinone groups to form porous corrugated sheets, which then stack with the pores in registry in a process controlled predictably by the alignment of P=O dipoles (Fig. 6).⁵² The crystals can be cleaved readily in the direction perpendicular to the aligned dipoles to give nanoporous sheets of micron thickness.



These observations and others underscore the potential of molecular tectonics as a strategy for the purposeful construction of ordered materials. The principles of the strategy are simple and their roots are old. Nevertheless, molecular tectonics offers crystal engineers a very powerful tool and will continue to be a prolific source of new crystalline materials with predictable structural features and properties.

Acknowledgements

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