From Disymmetric Molecules to Chiral Polymers: A New Twist for Supramolecular Synthesis?

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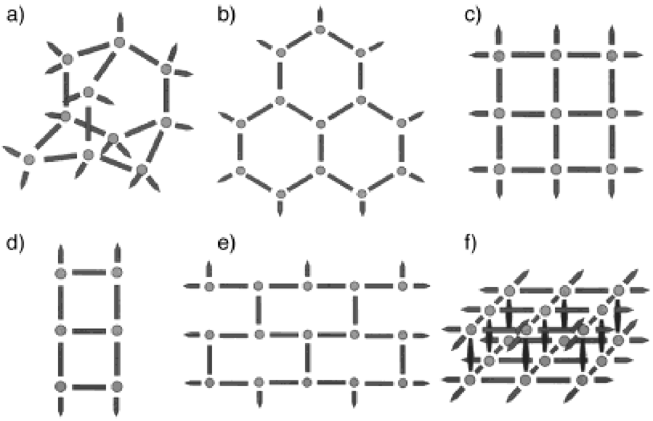
The term “crystal engineering” was first coined in 1971 in the context of photochemistry in the organic solid state, and referred specifically to topochemical control of reaction pathway and product stereochemistry.[1] However, despite the promise and challenge offered by crystal engineering (i.e. the control and prediction[2] of solid-state structure), this area did not begin to flourish until the past decade.[3, 4] Recent interest has been sparked not so much by the desire to predict crystal structures but rather the realization that supramolecular synthesis of new classes of functional solid is a natural consequence of successful crystal engineering.

Organic networks, sustained by directional noncovalent interactions,[3] and coordination polymers,[4] sustained by coordinate covalent bonds, represent the two primary classes of compound currently being investigated by crystal engineers. The two areas have thus far developed largely apart from each other, however, a paper in the previous issue of *Angewandte Chemie* suggests that this situation might soon change.[5] A synthetic strategy that potentially offers intricate control over the architecture of coordination polymers is detailed by Ranford, Vittal and Wu, namely the generation of an architecture with use of noncovalent hydrogen bonds and subsequent condensation to form a covalent polymer with the same basic architecture.

Coordination polymers offer great potential in the context of new classes of microporous[6] and/or magnetic materials.[7] The primary strategy employed is quite simple: propagate a known coordination geometry with a rigid linear bifunctional spacer ligand. This strategy has resulted in a number of obvious motifs for open-framework coordination polymers (Scheme 1), some of which are rare or even unprecedented in naturally occurring solids.[8] Furthermore, such compounds can be prepared in one-pot reactions by simply mixing the metal moiety with the bifunctional spacer ligand in the appropriate stoichiometry. Ligands that are suitable for the generation of such structures vary quite substantially in terms of length and chemical type; these include cyanide,[9a] pyrazines,[9b] and longer ligands such as 4,4′-bipyridine and derivatives.[10] However, there are two major drawbacks to this simple synthetic approach: the problems of interpenetration[11] and supramolecular isomerism/polymporphism[12] have not yet been overcome, and the number of architectures is limited.



Scheme 1. A schematic representation of several of the simpler network architectures exhibited by coordination polymers. Nodes are metal moieties, and ligands are represented by rods: a) diamondoid, b) honeycomb, c) square grid, d) ladder, e) brick, f) octahedral.

Ranford et al. describe an alternative two-step approach to the construction of networks that depends on the outer sphere of a complex and its ability to self-assemble. The complex $[\{Zn(sala)(H_2O)_2\}]\cdot 2H_2O$ (**1**, $H_2(sala)$ = *N*-(1-hydroxybenzyl)-L-alanine), exists as discrete dimers (Figure 1) which self-assemble because of complementary hydrogen bonding between hydrogen-bond donors on one of its faces (the coordinated aqua ligand and the N−H moiety of the sala ligand) and the carboxylate moiety of the sala ligand of an adjacent molecule. This supramolecular synthon sustains an unusual architecture: helical hydrogen-bonded chains (Figure 2a) which are held together by cross-linking (Figure 3a). Interestingly, there are also solvate water molecules that are hydrogen bonded in the helical channels, and the channels are aligned parallel to one another. Clearly, the structure of **1** is favorably disposed towards loss of the coordinated aqua ligands and retention of the overall architecture. Indeed, the proximity of the aqua ligands to the uncoordinated carboxylate moieties and the existence of the helical channels facilitate loss of all water molecules and generation of

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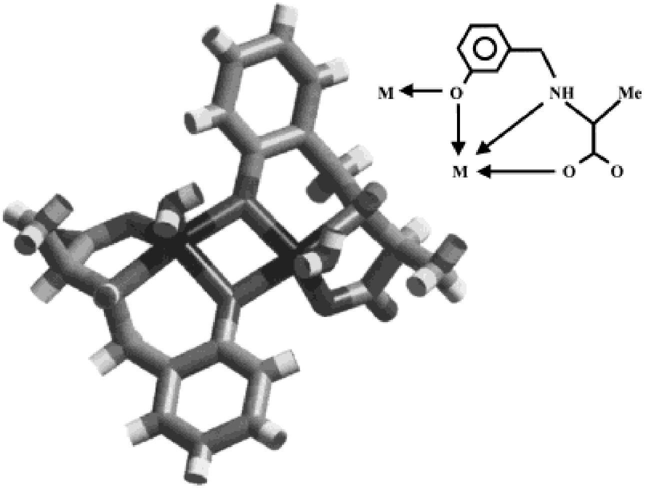

Figure 1. Stick model of compound **1** and its monomeric unit (above right). The hydrogen-bond donor groups are oriented above the plane of the molecule, whereas the acceptor groups point below the plane.

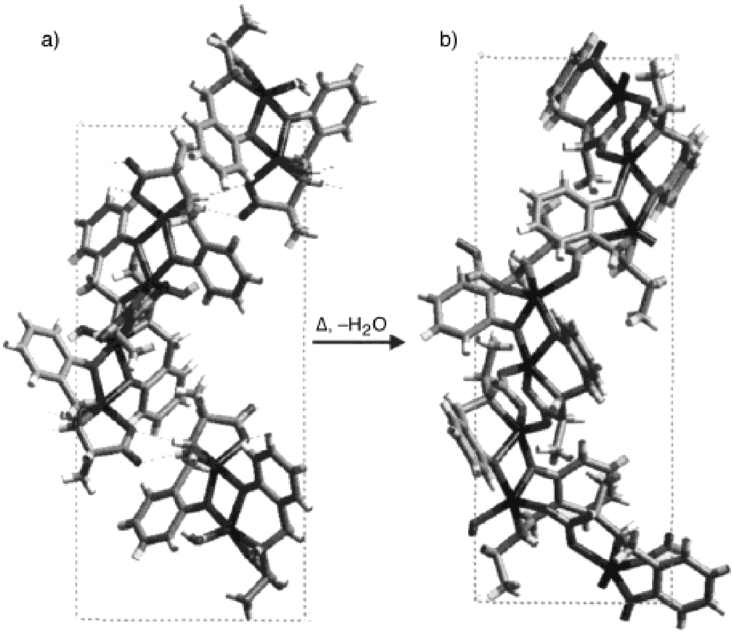

Figure 2. The helical chain architecture exhibited by compounds **1** and **2** viewed parallel to the crystallographic *c* axis.

$[\{Zn(sala)_n\}]$ (**2**). The three-dimensional coordination polymer **2** has an architecture that is very similar to that of **1** (Figures 2b and 3b) with covalent bonds between the Zn center and the oxygen atom of the carboxylate group.

Notwithstanding the novelty of the structures of **1** and **2**, the ultimate significance of the conversion of **1** into **2** probably lies in its implications beyond coordination chemistry and porosity. In principle, these compounds could represent a new synthetic paradigm: supramolecular synthesis by direct conversion of noncovalent networks into covalent polymers. Indeed, the potential for building two-dimensional and three-dimensional organic polymers with controlled architecture has already been discussed by Ermer,[13] and interest in second or outer-sphere complexation is on the rise.[14] In summary, there are several salient features of the new work:

1) A two-step approach to the construction of coordination polymers based upon manipulation of outer-sphere interactions between discrete complexes has been delineated.
2) This approach eliminates the common problems of supramolecular isomerism and interpenetration.
3) Chiral porous solids are reported.
4) The implications of the new work extend beyond the boundaries of coordination chemistry and porous solids since the same strategy should work equally well in organic and organometallic systems and could be applied to other bulk properties, especially polarity and magnetism.

In conclusion, it is worth noting that Schmidt's seminal work that defined the concept of crystal engineering remains particularly relevant and topical even after almost three decades.[1] This particular facet of crystal engineering, supramolecular synthesis of new solids, now appears ready to bear fruit.

Keywords: coordination polymers · crystal engineering · hydrogen bonds · porosity · topochemistry

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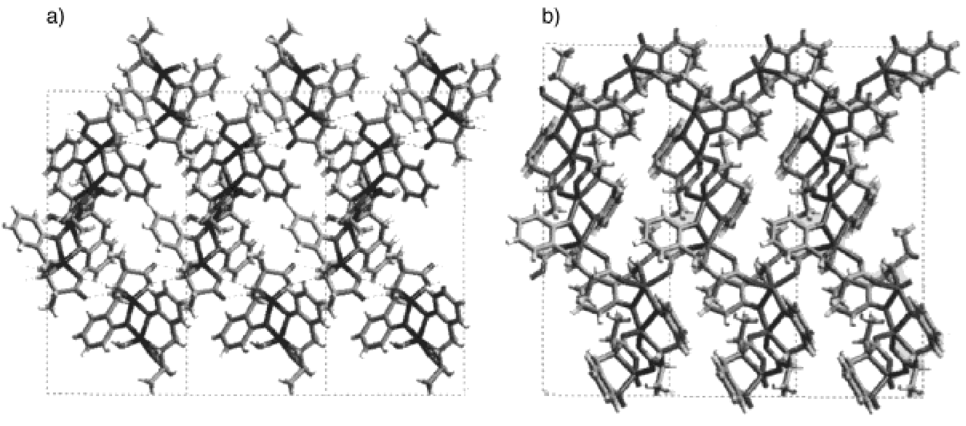

Figure 3. The structures of compounds **1** and **2** viewed along the crystallographic *ac* plane. Guest water molecules lie in the channels of compound **1**.

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Induced Chemical Defense in Plants[**]

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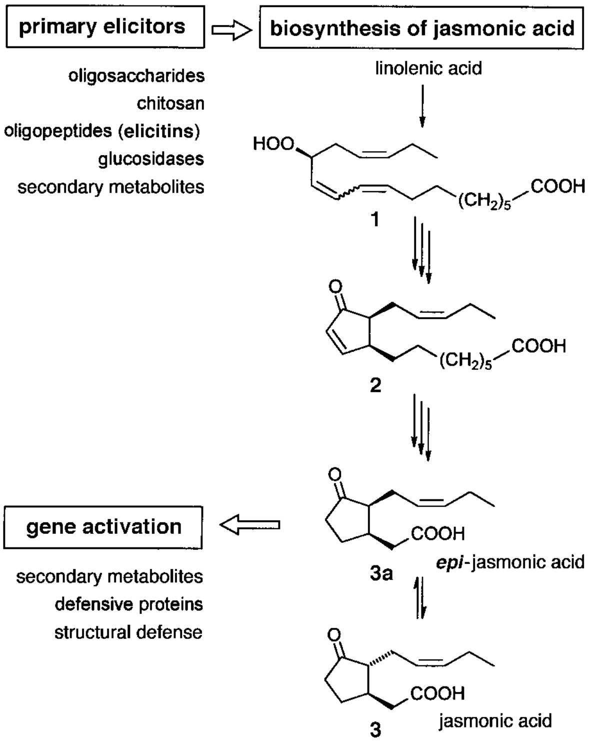
The chemical defense of plants has been a most fascinating topic of natural product chemistry since its early beginnings. To date, a large number of secondary metabolites have been identified including alkaloids, anthocyans, flavonoids, and terpenoids, which are thought to have ecological functions related to plant defense against microbial, fungal, or herbivoral attack.[1] Additionally, several plant species have been shown to produce defensive proteins such as proteinase inhibitors.[2]

While many of the defensive compounds in plants are formed constitutively, recent results show that plants have highly sophisticated regulation mechanisms that control the production of defensive secondary metabolites or proteins. A growing number of examples demonstrates that the biosynthesis of defensive compounds may be induced by damage from pathogens or herbivores.[3] These induced plant defense reactions can be local, but very often extend systemically through the plant; that is, they are not limited to the site of damage.

The induced synthesis of defensive compounds, especially when the response of the plant is systemic, must rely on highly effective signaling systems that mediate a quick response to microbial or herbivoral attack. Although the understanding of defense systems in plants is still limited, and the signaling pathways may vary among plant species, recent results suggest a general underlying pattern for plant self-defense mechanisms (Scheme 1). Depending on the nature of the attacking



Scheme 1. General pattern of signaling systems involved in induced plant defense reactions and biosynthesis of jasmonic acid (**3**).

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