

Template-Controlled Reactivity in the Organic Solid State by Principles of Coordination-Driven Self-Assembly

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In this microreview, we show how principles of coordination-driven self-assembly can be used to direct chemical reactivity in the organic solid state. We also show how products obtained from the templated solid-state reactions can be used as organic building units of metal–organic frameworks and coordination capsules. Self-assembled structures based on dinuclear Zn^{II} and Ag^I complexes are used to direct stereocontrolled [2+2] photodimerizations of vinylpyridines in the solid state in up to quantitative yield. The products are used

as bi- and polytopic ligands of self-assembled coordination capsules and metal–organic frameworks. We also describe emerging metal-based approaches to conduct mechanochemical reactions in organic solids. In addition to the field of supramolecular coordination chemistry, these observations impact the field of green chemistry.

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Introduction

Reactions that occur in the organic solid state bear widespread relevance to organic synthesis and materials science. The homogeneous, confined and surprisingly flexible nature^[1] of a molecular lattice means that molecules can react in solids with perfect control of stereochemistry and in a quantitative yield. That such reactions can occur in the absence of solvent also means that reactions in the organic solid state bear relevance to the field of green chemistry.^[2] Green chemistry has emerged owing to the accepted need to reduce and prevent pollution from the use and production of hazardous chemicals in synthetic chemistry. Thus, the development of strategies that employ reduced amounts of solvent, as well as other chemical auxiliaries, in chemical synthesis is a central goal of green chemistry.^[2]

Photoinduced reactions in the organic solid state were first discovered near the beginning of the last century. In the early 1900s, Rüber discovered that cinnamylideneacetic acid and cinnamylidene malonic acid could photoreact in the solid state to give cyclobutanes.^[3] Two decades later, Stobbe and de Jong discovered that the α - and β -forms of *trans*-cinnamic acid undergo solid-state [2+2] photodimerizations to give α -truxillic and β -truxinic acid, respectively. It was proposed that the reactions were a consequence of the packing of the monomer units;^[4] however, the mechan-

istic details of the reactions were not well understood. This was largely a result of a lack of efficient methods to characterize the structures of organic solids. Consequently, it was difficult, at the time, to foresee practical uses of reactions in organic solids. This contrasts reactivity in the liquid phase, which was being systematically studied and becoming reasonably well understood.

On the basis of X-ray crystal structure analyses of a wide range of cinnamic acids, Schmidt and coworkers identified, during the 1960s, structural requirements for two C=C bonds to undergo a [2+2] photodimerization in the solid state.^[5] The requirements, collectively known as the topochemical^[6] postulate, state that a [2+2] photodimerization can be expected to occur if the C=C bonds lie parallel to each other and with a centre-to-centre distance <4.2 Å. Thus, of the three known polymorphs of *o*-ethoxy-*trans*-cinnamic acid, namely α -, β - and γ -, the α - and β -forms are photoactive (Figure 1).^[7] In all three solids, the alkenes

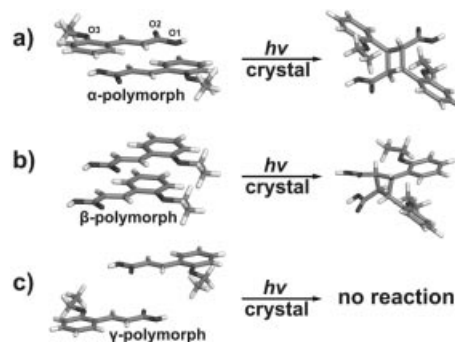


Figure 1. Solid-state reactivity of *o*-ethoxy-*trans*-cinnamic acid: (a) α -, (b) β - and (c) γ -polymorphs.

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pack parallel in one-dimensional (1D) slipped stacks. In the cases of the α - and β -forms, C=C bonds of neighbouring monomers lie parallel to each other and are separated by approximately 4 Å. Adjacent monomers of the α -poly-

morph adopt an antiparallel orientation, and they are related by a crystallographic centre of inversion. This geometry leads to the formation of the “head-to-tail” α -truxillic acid dimer upon photoreaction. Adjacent monomers of the



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β -polymorph adopt a parallel orientation, and they are related by a translation axis. Photodimerization of the β -polymorph produces a “head-to-head” β -truxinic acid. The γ -polymorph is photostable, and the C=C bonds are too far apart to react.

In recent years, we introduced a method to direct [2+2] photodimerizations in the solid state by using principles of molecular recognition and self-assembly.^[8] The method exploits the strength and directionality of hydrogen bonds to construct target molecules such as cyclophanes^[9] and ladderanes^[10] by using small molecules in the form of templates. In this microreview, we will outline how the template approach can be expanded to the principles of coordination-driven self-assembly.^[11] We will also demonstrate how molecules constructed with the use of the template method can be used as building blocks of finite and infinite coordination assemblies.^[12] We will then discuss how the area of mechanochemistry^[13] can be applied to eliminate solvents associated with reactions mediated by metal ions in organic solids.

Template-Controlled Photodimerizations by Using Organic Molecules

In 2000, we introduced a method to control chemical reactivity in the organic solid state by using small organic molecules that function as linear templates.^[8] The templates assemble olefins for [2+2] photodimerizations within multi-

component supramolecular assemblies. In particular, we demonstrated that resorcinol (res) can be used as a linear template to assemble and juxtapose *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) for photoreaction. Cocrystallization of res with 4,4'-bpe produced the four-component assembly 2(res)·2(4,4'-bpe) held together by four O–H···N hydrogen bonds. The two olefins were oriented by res in a parallel fashion and at a distance of 3.65 Å (Figure 2). This placed the C=C bonds of 4,4'-bpe in a geometry that conformed to the topochemical postulate of Schmidt for the reaction. UV irradiation of crystalline 2(res)·2(4,4'-bpe) produced the corresponding photodimer, *rect*-tetrakis(4-pyridyl)cyclobutane (4,4'-tpcb), regiospecifically and in 100% yield.^[14]

In addition to 4,4'-tpcb, we showed that the method can be used to construct relatively complex molecules such as a [2.2]paracyclophane and [*n*]ladderanes (where: *n* = 3 or 5).^[9,10] Templates based on res were used to organize di- and triolefins, similar to 2(res)·2(4,4'-bpe), within four-component hydrogen-bonded assemblies. UV irradiation of the solids produced the targeted cyclophane and ladderanes regiospecifically and in quantitative yield (Figure 3).

Template-Controlled Photodimerizations by Using Metal Ions

Inspired by work in the field of coordination-driven self-assembly,^[15] we recently addressed whether transition-metal-ion complexes can be used as linear templates to di-



Figure 2. Solid-state synthesis of 4,4'-tpcb by using resorcinol as a template.

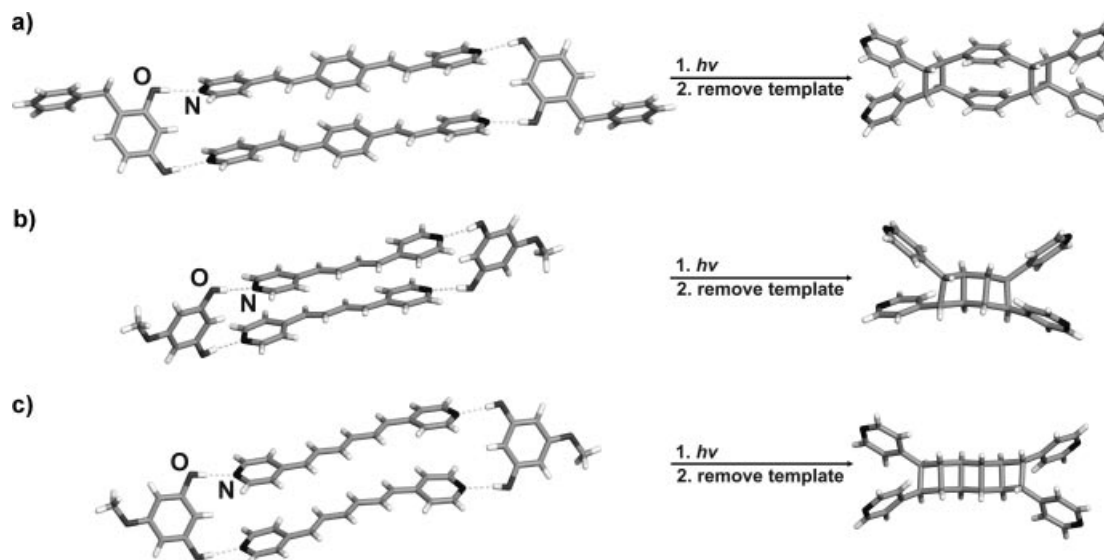


Figure 3. Solid-state synthesis of: (a) [2.2]paracyclophane, (b) [3]ladderane and (c) [5]ladderane.

rect [2+2] photodimerizations in the solid state. The field of coordination-driven self-assembly, which has experienced tremendous growth during the last decade,^[15,16] involves reactions of metal ions with bi- and polytopic ligands. The metal and organic components are used to form finite (e.g. metallomacrocyclic) and/or infinite [e.g. metal–organic framework (MOF)] self-assembled frameworks. The frameworks are designed to exhibit properties (e.g. host–guest, magnetic) typically not encountered in the individual components. We wondered whether coordination bonds could be used to effectively replace the hydrogen bonds of a resorcinol-based template. In such a design, a dinuclear metal complex would assemble and preorganize two olefins to react in a solid. The ensuing solid-state reaction could also be used to affect bulk physical properties^[11a] conferred by the metals in a solid.

Prior to our work, there were two examples in which a metal-ion complex facilitated a [2+2] photodimerization in the solid state (Figure 4).^[17–19] In particular, Praetorius and Korn reported the ability of a mononuclear complex of uranyl chloride and *trans,trans*-dibenzylideneacetone (dba) to undergo a stereospecific photodimerization to give the truxillic-type dimer *rectt*-1,3-bis(3-phenylprop-2-enoloxo)-2,4-bis(phenyl)cyclobutane (Figure 4a).^[17] X-ray crystal structures of both the unsolvated and solvated forms, $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]$ and $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2] \cdot 2\text{CH}_3\text{CO}_2\text{H}$, showed that the metal ions adopted an octahedral geometry surrounded by two chlorine atoms, two oxygen atoms of the uranyl group and two keto-oxygen atoms of the dba ligand (Figure 4a).^[18] The complexes assembled in the solid such that the distances between the alkenes of adjacent dba ligands were 4.09 and 3.51 Å in the unsolvated and solvated forms, respectively. The reactivity was, thus, largely the result of the packing of the complexes. Later, Lewis and co-workers demonstrated [2+2] photoreactivity in a series of crystalline cinnamic esters mediated by Lewis acids (e.g.

SnCl_4).^[19] The cinnamic esters formed 1:1 complexes with BF_3 and 2:1 complexes with SnCl_4 . UV irradiation of the solids produced truxillic-type dimers (Figure 4b). A structure analysis of the ethyl cinnamate– SnCl_4 complex revealed an octahedral coordination environment around the Sn^{IV} ion (Figure 4b). The photoreaction occurred between neighbouring cinnamate ligands. Adjacent ligands were stacked in a head-to-tail fashion and were separated by 4.12 Å.

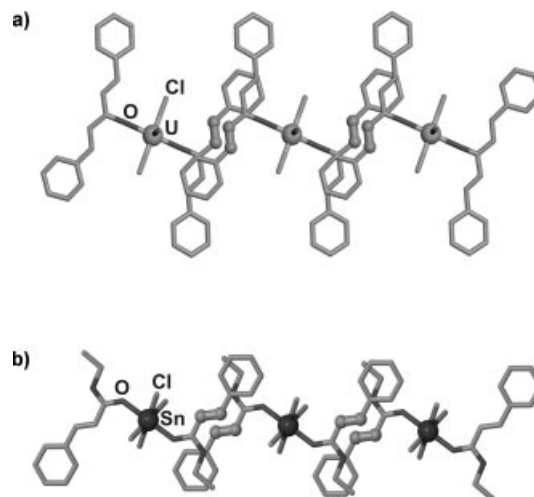


Figure 4. Crystal structures of the photoactive: (a) dba– UO_2Cl_2 complex and (b) ethyl cinnamate– SnCl_4 complex. Reactive alkene groups highlighted.

Our first study pertaining to a dinuclear complex involved the Schiff base complex $[\text{Zn}_2\text{L}(\text{OH})]^{2+}$ {where: $\text{L} = 2,6\text{-bis}[N\text{-(2-pyridylethyl)formimidoyl}]\text{-4-methylphenol}$ } as a template (Figure 5).^[11a] The Schiff base ligand was originally introduced by Robson and Okawa as a model of enzymatic processes (Figure 5a).^[20] An analysis of the Cam-

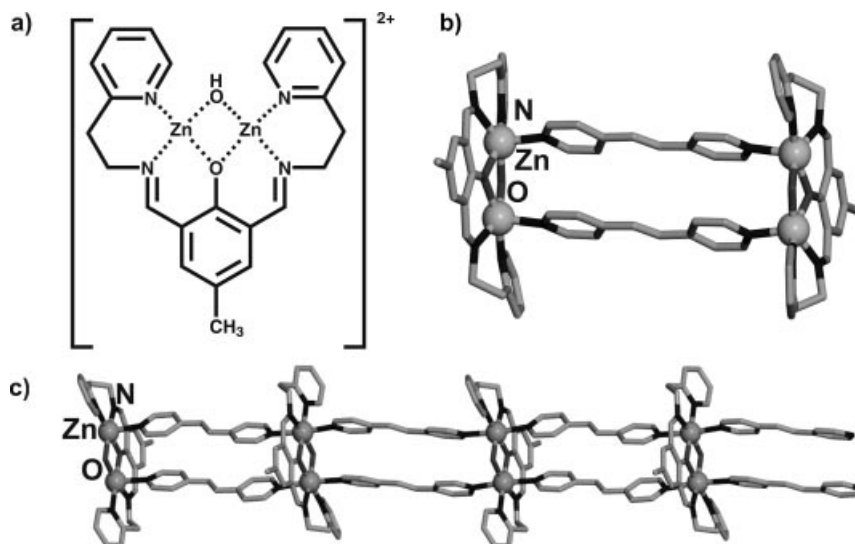


Figure 5. (a) Schematic representation of the dinuclear template first reported by Robson and Okawa and the wireframe models of (b) a discrete photoactive assembly and (c) a photoactive linear polymer.

bridge Structural Database revealed that the metal atoms of such complexes are separated on the order of 3.10 to 3.15 Å. This range was well within the distance criterion of Schmidt for photodimerization in a solid. We showed that reaction of $[\text{Zn}_2\text{L}(\text{OH})](\text{ClO}_4)_2$ with 4,4'-bpe produces the tetranuclear assembly $[\text{Zn}_4\text{L}(\text{OH})_2(4,4'\text{-bpe})_2](\text{ClO}_4)_2$ (Figure 5b). The metal atoms of the assembly adopted a square-pyramidal coordination environment and the two stacked pyridine moieties were located in the apical positions. The C=C bonds of the olefins were arranged parallel and separated by 3.64 Å. UV irradiation of the solid produced 4,4'-tpcb in quantitative yield. We later showed that stacked molecules of 4,4'-bpe could be achieved within the 1D MOF $\{[\text{Zn}_2\text{L}(\text{OH})(4,4'\text{-bpe})_2](\text{ClO}_4)_2\}_\infty$.^[11b] In this case, each metal ion adopted an octahedral coordination environment. The solid reacted to give 4,4'-tpcb in 95% yield (Figure 5c).^[21]

During the course of our studies involving tetranuclear $[\text{Zn}_4\text{L}(\text{OH})_2(4,4'\text{-bpe})_2](\text{ClO}_4)_2$, we determined that the photoreaction proceeded by a rare single-crystal-to-single-crystal (SCSC) transformation (Figure 6).^[22] We also discovered that the single crystals displayed different fluorescence emissions before and after the photoreaction.^[11a] Specifically, excitation of the crystals with 290 nm light prior to the photoreaction produced a blue emission at 464 nm, whereas the fully reacted solid produced a green emission at 520 nm. That the change in emission was a consequence of the solid-state reaction was supported by laser-scanning confocal fluorescence microscopy, which revealed a difference in the fluorescence between the unreacted and reacted solid. To the best of our knowledge, the tetranuclear assembly represented the first example of a SCSC reaction that exhibited photocontrolled fluorescence. The reaction involving the 1D framework $[\text{Zn}_2\text{L}(\text{OH})(4,4'\text{-bpe})_2](\text{ClO}_4)_2$ did not occur through a SCSC transformation.

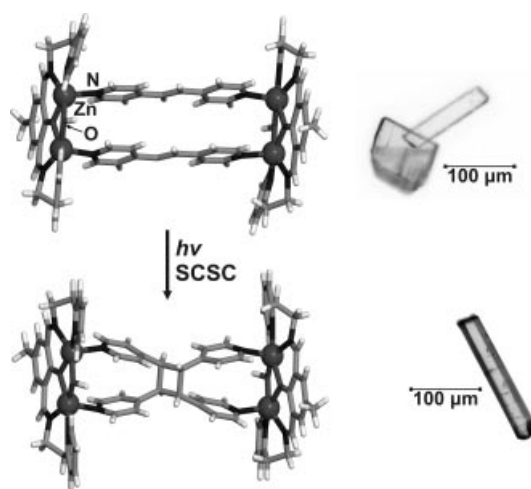


Figure 6. Photocontrolled fluorescence in single-crystalline $[\text{Zn}_4\text{L}_2(\text{OH})_2(4,4'\text{-tpcb})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$.

To expand the template method to an additional dinuclear unit, we turned to the Ag^{I} ion.^[11c] It is well established that Ag^{I} exhibits linear coordination while also participat-

ing in $\text{Ag}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ or argentophilic forces.^[23] Ag^{I} ions engaged in argentophilic forces are separated on the order of 3.40 Å, which falls within the distance criterion of Schmidt. These observations encouraged us to investigate the ability of Ag^{I} ions, in a T-shaped geometry, to steer *trans*-coordinated olefins towards a [2+2] photodimerization. In this design, the argentophilic forces would stack two pairs of olefins for reaction in a solid. We determined the ability of the Ag^{I} ions to assemble *trans*-1-(4-pyridyl)-2-(phenyl)ethylene (4-stilbz) in crystalline $[\text{Ag}_2(4\text{-stilbz})_4][\text{CO}_2\text{CF}_3]_2$ for a regiocontrolled head-to-head photodimerization to give *rcct*-1,2-bis(4-pyridyl)-3,4-bis(phenyl)cyclobutane (4-pyr-ph-cb) in quantitative yield (Figure 7). The metal ions were separated by 3.41 Å, whereas the C=C bonds of the stacked olefins exhibited a disordered criss-cross arrangement with a separation of 3.82 Å. That the photoreaction was able to proceed, despite the C=C bonds being crossed, was attributed to the olefins undergoing a pedal-like rotation.^[11c] Similar to $[\text{Zn}_4\text{L}(\text{OH})_2(4,4'\text{-bpe})_2](\text{ClO}_4)_2$, the photoreaction proceeded through a SCSC transformation.^[22]

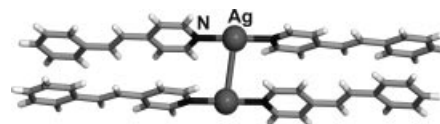


Figure 7. Alignment of 4-stilbz molecules within the dinuclear complex $[\text{Ag}_2(4\text{-stilbz})_4]^{2+}$.

The photoreaction involving $[\text{Ag}_2(4\text{-stilbz})_4][\text{CO}_2\text{CF}_3]_2$ also converted the dinuclear complex into a 1D coordination network (Figure 8). In particular, the generation of the photoproduct involved major movements of the metal and organic components. The Ag^{I} ions moved away from each other by approximately 1.16 Å ($\text{Ag}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ distance 5.73 Å), which broke the argentophilic forces. This movement was accompanied by an approximate 90° rotation of the carboxylate ions. As a result of these movements, $\text{Ag}^{\text{I}} \cdots \text{C}(\text{phenyl})$ forces ($\text{Ag}^{\text{I}} \cdots \text{C}$ distance 2.63 Å) formed between each repositioned Ag^{I} ion and the *para* carbon atom of the phenyl group of a neighbouring assembly. These new forces served,

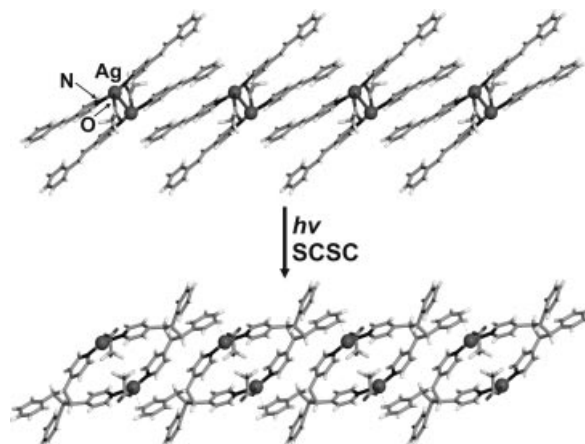


Figure 8. SCSC conversion of $[\text{Ag}_2(4\text{-stilbz})_4]^{2+}$ into 1D $[\text{Ag}_2(4\text{-pyr-ph-cb})_2]^{2+}$.

in effect, to link adjacent complexes to produce a linear coordination network. The photoconversion of $[\text{Ag}_2(4\text{-stilbz})_4]^{2+}$ into $[\text{Ag}_2(4\text{-py-ph-cb})_2]^{2+}$ was, to the best of our knowledge, the first case in which a metal complex was transformed into an infinite coordination network by a photoreaction. In related and earlier work, Foxman had revealed the ability of the Ni^{II} complex $[\text{NiBr}_2(\text{PCH}_2\text{CH}_2\text{-CN})_3]$ to undergo a highly stereocontrolled thermal polymerization in a solid that involved the formation of Ni–N coordination bonds.^[24]

Applications of the Products

The products of the [2+2] photodimerizations that we conducted in the solid state are functionalized with, in a minimal case, two pyridyl groups. The products also typically form in quantitative yield, gram amounts and in the absence of byproducts.^[8] For us, these features made the products attractive for studies in coordination-driven self-assembly. We hypothesized that the products, once removed from the template, could serve as bi- and polytopic linkers of MOFs and related materials.^[12,25–28] A cyclobutane ring could serve as a hub^[29] providing both acute and obtuse angles to propagate the coordination geometry of a metal in an assembly process. Importantly, whereas molecules synthesized in the liquid phase routinely encounter practical applications in areas ranging from pharmaceutical chemistry to materials science, the products of molecules synthesized in the solid state had experienced virtually none.^[30] This can be attributed to difficulties in engineering solid-state structures such that the molecules can undergo reactions “at will” to synthesize molecules by design.^[31]

1D MOF

In 2002, we set out to determine whether the products obtained from linear templates in the solid state could be used as ligands to form MOFs. The major driving force behind the synthesis of MOFs is a promise to generate materials with tailorable electronic,^[32] magnetic,^[33] optical^[34] and/or host–guest properties.^[35] Thus, MOFs with cavities and pores are expected to exhibit properties akin to zeolites and mesoporous materials and, thereby, have applications in areas such separations,^[36] gas storage^[37] and catalysis.^[38]

One of our first reactions involved 2,2'-tpcb with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. We generated 2,2'-tpcb by using a hydrogen-bond-mediated synthesis.^[39] In particular, we showed that the components assembled in the solid state to give a 1D MOF in which 2,2'-tpcb served as a bis-chelating ligand in $[\text{Cu}_2(\mu\text{-2-SO}_4)_2(\mu\text{-2,2'-tpcb})(\text{H}_2\text{O})_2]_\infty$ (Figure 9).^[25] Each Cu^{II} ion exhibited a square-pyramidal coordination environment with two N atoms of two 2-pyridyl groups, one O atom of a sulfate ion and one O atom of a water molecule in the basal plane. The apical site was occupied by an O atom of a second sulfate ion. The 1D polymer assembled in parallel and offset strands, with interstices occupied by solvent water molecules. In the same report, we showed that the self-assembly process was sensitive to changes to the counterion.

Specifically, reaction of 2,2'-tpcb with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ produced the dinuclear complex $[\text{Cu}_2(\text{NO}_3)_4(\mu\text{-2,2'-tpcb})]$. Similar to the 1D framework, 2,2'-tpcb served as a bis-chelating ligand. Two chelating nitrate ions completed a distorted octahedral coordination sphere.

2D MOFs

That same year, we determined that 4,4'-tpcb could be used as a 4-connected node of a porous 2D MOF. Specifically, reaction of 4,4'-tpcb with the copper paddle-wheel complex $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ produced the 2D MOF $[\text{Cu}_4(\text{O}_2\text{CCH}_3)_8(4,4'\text{-tpcb})]_\infty$ (Figure 10).^[12a] The cyclobutane and dicopper complex produced a 2D grid with identical rhombic cavities of approximate dimensions $17.2 \text{ \AA} \times 17.2 \text{ \AA}$ and corner angles 75° and 104° (Figure 10a). The 2D grids stacked to form a 3D framework with isolated 1D channels of approximate dimensions $10 \text{ \AA} \times 12 \text{ \AA}$ (Figure 10b). The channels were occupied by benzene solvent molecules, which assembled in an edge-to-face manner. We showed that the solvent molecules could be removed from the framework by a SCSC transformation.^[22] We also revealed that the methyl groups of the paddle-wheel complex were directed into the cavities. In doing so, the methyl groups segregated the space of the cavities into smaller compartments. These observations suggested that further functionalization of the cavities could be achieved by modifying the R group of the paddle-wheel complex. We termed the framework an inverted MOF (IMOF), as the metal complex acted as a linear bridge and

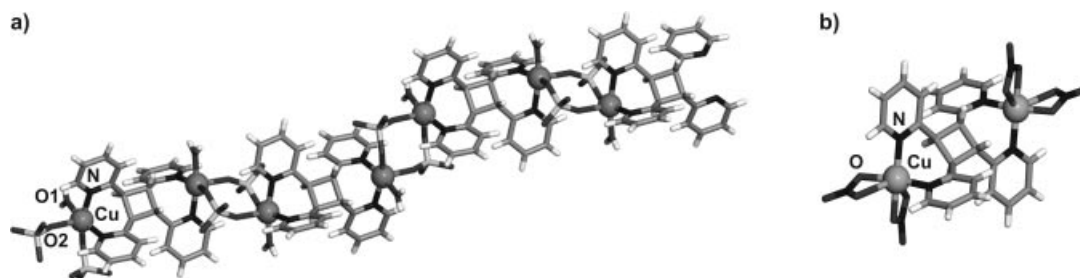


Figure 9. View of: (a) 1D polymer $[\text{Cu}_2(\mu\text{-2-SO}_4)_2(\mu\text{-2,2'-tpcb})(\text{H}_2\text{O})_2]_\infty$ and (b) dinuclear complex $[\text{Cu}_2(\text{NO}_3)_4(\mu\text{-2,2'-tpcb})]$.

the organic spacer served as a node; thus, the roles of the metal and organic components, relative to a more conventional MOF,^[15,16] were inverted or reversed. Moreover, that the metal component served as a linear bridge meant that the terminal carboxylates were available to decorate the cavities of the framework.

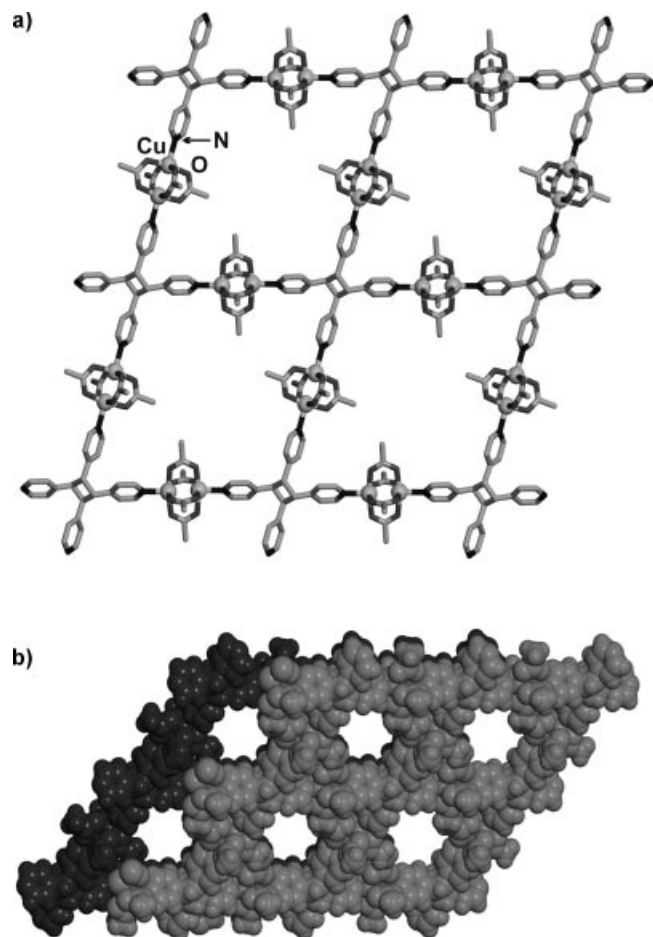


Figure 10. Perspective views of $[\text{Cu}_4(\text{O}_2\text{CCH}_3)_8(4,4'\text{-tpcb})]_\infty$: (a) ball-and-stick model and (b) space-filling model of the stacking of two layers.

In a later report, we described a 2D MOF based on 4,4'-tpcb that involved metal and cyclobutane components that served as 4-connected nodes.^[40] In particular, reaction of 4,4'-tpcb with $[\text{Co}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_4]$ produced the 2D MOF $[\text{Co}(\text{O}_2\text{CCH}_3)_2(4,4'\text{-tpcb})]_\infty$. The framework, similar to $[\text{Cu}_4(\text{O}_2\text{CCH}_3)_8(4,4'\text{-tpcb})]_\infty$, possessed rhombic cavities with edge lengths of 7.3 Å. In contrast to $[\text{Cu}_4(\text{O}_2\text{CCH}_3)_8(4,4'\text{-tpcb})]_\infty$, however, the framework was made up of two different rhombic cavities (Figure 11). That the framework possessed two different cavities was a result of the stereochemistry of the cyclobutane ring, which provided two different angles (75 and 104°) for cavities within the network. The cavities stacked in an ABAB manner producing small interstices occupied by solvent methanol molecules. We also demonstrated that the crystallinity of the solid was maintained upon removing the guests by heating.

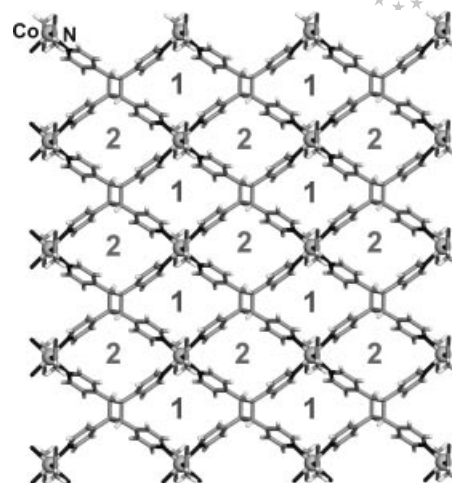


Figure 11. Perspective view of $[\text{Co}(\text{O}_2\text{CCH}_3)_2(4,4'\text{-tpcb})]_\infty$ that illustrates the different cavities of the 2D MOF.

More recently, we demonstrated that a product of a template-directed solid-state synthesis forms a 2D MOF with a topology that conforms to a nonregular net (Figure 12). Most 2D MOFs exhibit topologies of regular (i.e. tiling of regular polygons with identical nodes) or semiregular (i.e. tiling of different regular polygons with identical vertices) nets. In the minimal case, a MOF with a topology of a nonregular net will possess two different polygonal cavities and two nodes of different connectivity. It was recently argued that the self-assembly process that produces a MOF is predisposed to generate high-symmetry frameworks

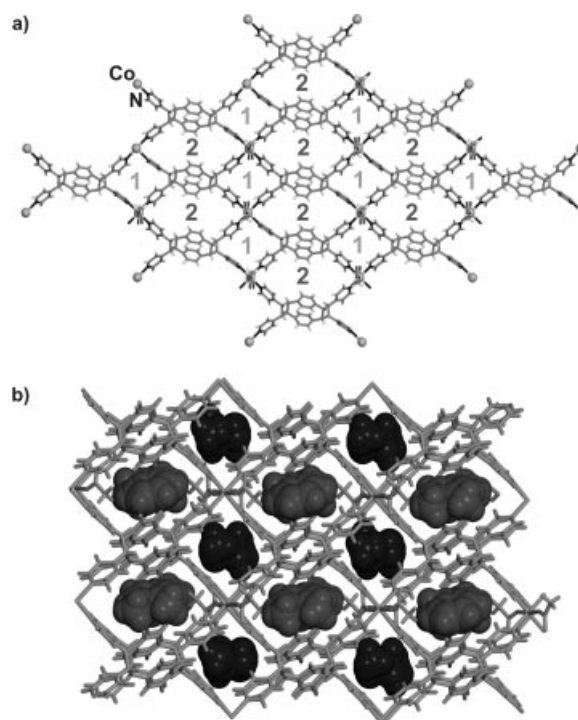


Figure 12. Perspective view of $[\text{Co}(\text{O}_2\text{CCH}_3)_2(4,4'\text{-tpcp})]_\infty$: (a) different cavities of the 2D framework and (b) space-filling model of the included solvent molecules.

based on identical nodes (i.e. regular and semiregular nets).^[41] To design a MOF that conforms to a nonregular net, we treated the [2.2]paracyclophane 4,4'-tppcp with $\text{Co}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$, which afforded the 2D MOF $[\text{Co}(\text{O}_2\text{CCH}_3)_2(4,4'\text{-tppcp})]_\infty$ (Figure 12a).^[28] The components self-assembled to give a 2D MOF with both square and hexagonal cavities in which 4,4'-tppcp and the Co^{II} ion served as 3- and 4-connected nodes, respectively. The paracyclophane effectively served as two covalently fused 3-connected nodes in which the stacked rings of the cyclophane provided the covalent connection. Moreover, that the cyclophane acted as two fused 3-connected nodes meant that the formation of higher-symmetry MOFs with structures solely based on linkages between 3- and 4-connected nodes (i.e. with no linkages between two 3-connected nodes) was prohibited. The two different cavities hosted two different solvent molecules as guests. Specifically, a methanol molecule filled hydrophilic square cavities, whereas toluene molecules filled hydrophobic hexagonal cavities (Figure 12b).

Metal–Organic Polyhedra and Polygons

In addition to MOFs, we discovered that products of linear templates in the solid state can generate metal–organic polyhedra and polygons.^[12b,26,27] The internal cavities of such self-assembled frameworks have, in recent years, gained much attention as materials with applications in areas such as logical gates,^[42] reaction vessels^[43] and catalysis.^[44]

Our first report described the self-assembly of the unsymmetrical tetrapyridine 2,4'-tpcb (Figure 13) with Cu^{II} ions to form a polyhedron. Reaction of 2,4'-tpcb with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ produced a hexanuclear polyhedron in $[\text{Cu}_6(2,4\text{-tpcb})_6(\text{H}_2\text{O})_6][\text{ClO}_4]_{12}$ with a structure that conformed to a trigonal antiprism (Figure 13).^[12b] Each metal ion adopted a square-pyramidal coordination environment and occupied a vertex of the polyhedron. The coordination environment consisted of two chelating 2-pyridyl groups and two monodentate 4-pyridyl groups that formed the base and a water molecule that formed the apex. Thus, the 4-pyridyl groups corresponded to the edges of the polyhedron whereas the 2-pyridyl groups corresponded to the corners. The coordination behaviour of the 2- and 4-pyridyl groups was consistent with the MOFs involving 4,4'- and 2,2'-tpcb.^[12] The assembly process produced a central cavity that hosted two ClO_4^- anions as guests.

Very recently, we showed that an unsymmetrical isomer of the 2,4'-tpcb ligand, namely 2,3'-tpcb, assembles with Cu^{II} ions to form a polyhedron with a structure that conforms to a tetrahedron (Figure 14).^[26] We anticipated that changing the 4-pyridyl group to a 3-pyridyl group would result in a smaller polyhedron owing to a decrease in the angle of the coordination vector (Figure 15). We employed a hydrogen-bond-directed synthesis to generate 2,3'-tpcb. As expected, 2,3'-tpcb assembled with the metal ions to form a smaller polyhedron. To our surprise, the polyhedron $[\text{Cu}_4(2,3'\text{-tpcb})_4(\text{H}_2\text{O})_4]^{8+}$ adopted a topology of a tetra-

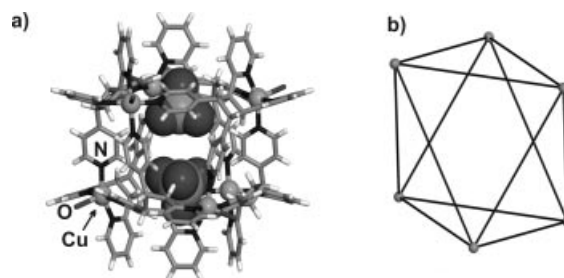


Figure 13. Perspective view of $[\text{Cu}_6(2,4\text{-tpcb})_6(\text{H}_2\text{O})_6]^{12+}$: (a) space-filling model of two encapsulated ClO_4^- ions and (b) the trigonal antiprism formed by the Cu^{II} ions.

dron and exhibited a chiral D_2 topology. The structure was a rare example of a chiral self-assembled polyhedron composed of achiral components. The chirality of the tetrahedral capsule was attributed to a geometric fit of the metal and organic components, which prohibited the formation of mirror planes in the structure. As in the case of the trigonal antiprism, the Cu^{II} ions occupied the corners of the tetrahedron and exhibited a square-pyramidal coordination environment. The tetrahedron also possessed a central cavity that hosted a NO_3^- ion as a guest.

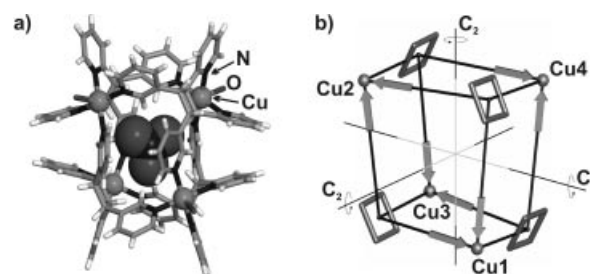


Figure 14. Perspective view of $[\text{Cu}_4(2,3'\text{-tpcb})_4(\text{H}_2\text{O})_4]^{8+}$: (a) space-filling model of the encapsulated NO_3^- ion and (b) the tetrahedron topology.

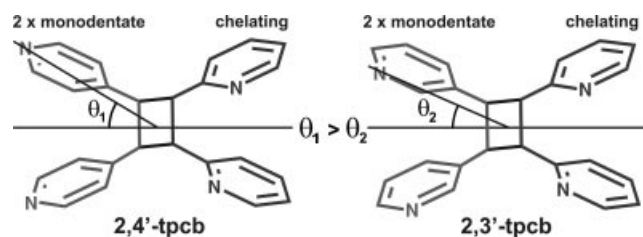


Figure 15. Polydentate 2,3'-tpcb and 2,4'-tpcb ligands (θ – angle of the coordination vector).

In addition to a polyhedron, we demonstrated that 2,4'-tpcb can form a polygon.^[27] By changing from a noncoordinating (i.e. ClO_4^-) to chelating counter anion, in the form of the hexafluoroacetylacetonate anion (hfacac), we described the formation of the tetranuclear metal–organic rhomboid $[\text{Cu}_4(2,4\text{-tpcb})_2(\text{hfacac})_8]$ (Figure 16a). In particular, two molecules of 2,4'-tpcb assembled with the Cu^{II} ions to give a dinuclear cavity of approximate dimensions $4.0 \text{ \AA} \times 4.2 \text{ \AA}$ and corner angles of 79 and 101°.

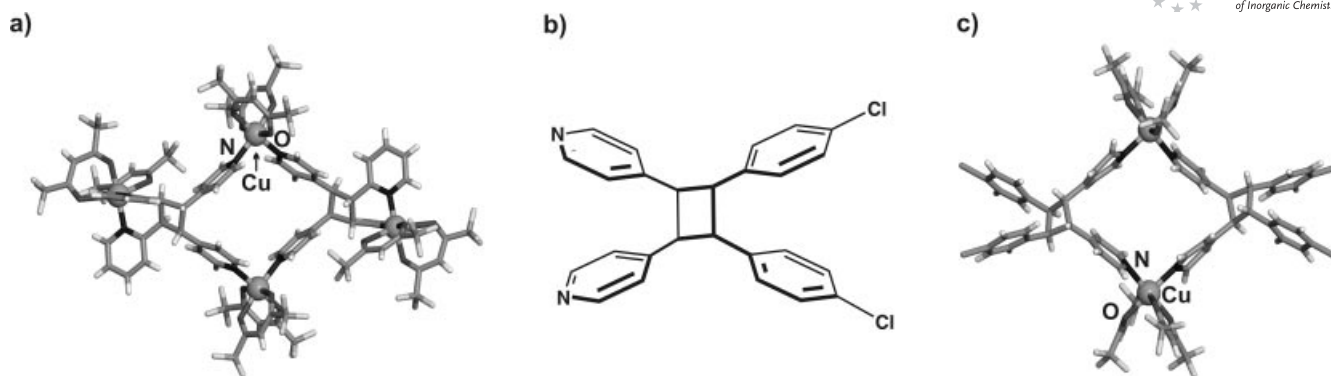


Figure 16. Perspective views of: (a) $[\text{Cu}_4(2,4\text{-tpcb})_2(\text{hfacac})_8]$, (b) schematic representation of 4-py-4-Cl-p-cb and (c) $[\text{Cu}_2(4\text{-py-4-Cl-p-cb})_2(\text{hfacac})_4]$.

dentate 4-pyridyl groups defined the edges of the polygon. Each Cu^{II} ion exhibited octahedral coordination with two 4-pyridyl units and two hfacac anions in a *cis* arrangement. Chelating 2-pyridyl groups were located along the periphery of the assembly and were being coordinated to two Cu^{II} ions. We also showed that the bifunctional cyclobutane *rectt*-1,2-bis(4-pyridyl)-3,4-bis(chlorophenyl)cyclobutane (4-py-4-Cl-p-cb; Figure 16b) supports the formation of a dinuclear polygon by, similar to $[\text{Cu}_4(2,4\text{-tpcb})_2(\text{hfacac})_8]$, the 4-pyridyl groups (Figure 16c).^[27]

Emergence of Mechanochemical Preparation of Coordination Materials

The coordination solids described above were prepared by using crystallizations that involve an organic solvent. To increase the relevance of the template approach to the field of green chemistry,^[2] it would be desirable to further reduce the organic solvents employed in the syntheses. In recent years, the field of coordination chemistry has witnessed a rapid surge of interest in the development of solvent-free, or mechanochemical, methods^[45] to synthesize self-assembled coordination materials. The approach relies on simple grinding of metal and organic components to induce the formation of metal complexes and self-assembled materials.

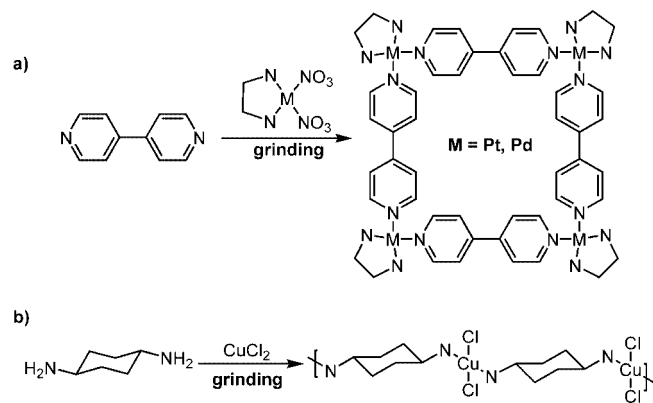


Figure 17. Coordination solids based on both (a) finite and (b) infinite self-assembled architectures constructed by mechanochemical methods.

Coordination solids based on both finite and infinite self-assembled architectures have been constructed by this approach (Figure 17).^[46,47] We are now addressing whether mechanochemical methods can be applied to construct reactive, self-assembled solids, as well as the applications of the molecules synthesized in the solid state.

Summary and Outlook

Linear templates allow chemists to organize reactive molecules within finite supramolecular assemblies constructed by coordination-driven self-assembly. In such assemblies, olefins are preorganized to conform to Schmidt's topochemical postulates for a [2+2] photodimerization in a solid. The strategy has been, thus far, used to synthesize mono- and polyfunctional pyridyls in solids. Here, we have also presented the diversity of products obtained in studies that apply the ligands in metallocsupramolecular chemistry. We have revealed that the template method provides access to molecules that can be used as organic building units of self-assembled polygons and polyhedra, as well as MOFs. We are now moving to develop this approach for the application in more mainstream synthetic chemistry and with an increasing relevance to green chemistry.

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