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Review

Supramolecular structural transformations involving coordination polymers in the solid state☆

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Contents

Abstract

Structural changes are accompanied by the movements of atoms/molecules and hence transformation of one structure to another is difficult in the solid state due to the restricted movements of molecules. While single-crystal to single-crystal conversion is more convenient way of characterizing the structures in the solid state by X-ray crystallography, the single crystalline nature of coordination polymers may not be always retained during structural transformations, since breaking and forming of coordinate and/or covalent bonds occur in more than one direction. X-ray powder diffraction techniques, thermoanalytical methods, solid-state NMR spectroscopy may be used to extract structural information in the topochemical

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reactions. This review describes a personal account of the structural transformations involving coordination polymers in the solid state along with other relevant and interesting examples from the literature.

Keywords: Self-assembly; Coordination polymers; Supramolecular interactions; Topochemical reactions; Thermal dehydration reactions; Photoreactivity; Single-crystal to single-crystal transformations

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1. Introduction

It is easier to carry out reactions involving more than one reactant in the fluid state because the molecules can move freely so that the reactive functional groups can be brought closer together in the correct orientations for the reaction to take place homogenously. On the other hand, this is not favorable in the solid state as the molecules are rigidly and orderly locked in the crystals. Although inorganic reactions can be carried out in the solid state, they are more complex and heterogeneous in nature [1–3]. Toda and others have shown that a number of organic reactions can be performed in the solid state more efficiently [4–6].

If the reactive functional groups are aligned closely in the required orientations then thermal or photochemical methods can facilitate the reaction in the solid state. Such topotactic reactions will lead to highly stereo, enantio- and regio-selective products [7–10]. When the molecules do not need to move very far and the functional groups have free space to rotate in the crystal lattice, the single crystal nature (not just morphology and transparency but also diffraction property) will be retained throughout the reaction. Such reactions will favor single-crystal to single-crystal (SCSC) transformations [11].

Conversion of *cis–trans* geometrical isomers, which can be visualized as the simplest structural transformation involving metal complexes, has been studied extensively in the solid state (see for example, Refs. [12–30]). But the transformations of structures involving coordination polymers are rare since they involve breaking and forming of coordinate and/or covalent bonds in more than one direction compared to well-studied solid-state organic photochemical reactions which mainly involve two molecules [4,7–11]. Despite the problems envisaged in studying the structural transformations involving coordination polymers in the solid state, a number of cases have been reported serendipitously. The scope of the present review is to survey these interesting solid-state conversions. We have also included other related literatures which are not strictly confined to coordination polymers.

2. Tools needed to study the solid-state structural changes

The essential tool routinely used to determine the solid-state structure is none other than X-ray crystallography which can be used unfortunately only if the single crystalline nature is maintained during the structural transformation. Not all the topochemical reactions are expected to preserve the integrity of the single crystals [11]. In those situations X-ray power diffraction (XRPD) techniques, thermogravimetry (TG), differential thermal analysis (DTA) or differential scanning calorimetry (DSC), solid-state NMR and other spectroscopic techniques are invaluable tools, but the results obtained are not conclusive without three-dimensional structural information. However, the resultant structures can be predictable. Structure determination from XRPD data collected from synchrotron radiation has now been successfully exploited to determine the structures of coordination polymers by Kitagawa and others (see for example Refs. [31–35]).

The usual analytical and spectroscopic techniques employed to characterize the molecules in solution may not be applicable to coordination polymers for two reasons. (1) The expected insolubility of these coordination polymers in common solvents. (2) If they are soluble, the solid-state structures, i.e., the molecular connectivity may not be retained in solution due to the lability of the metals ions and breaking down of polymers into oligomers due to solvation at the metal centers [36] is inevitable. Kaupp and others have used atomic force microscopy (AFM), grazing incidence X-ray diffraction (GID) and scanning near field microscopy (SNOM) to study the solid-state reactions including topologically defective and effective systems [37–39].

3. Retention of structures during the solvent and gas exchange

The removal of solvents without affecting the single crystal nature of the coordination complexes is not strictly considered as structural transformation; however, they are interesting in their own right. Such retention of single crystals due to the removal of solvents has been well documented in coordination complexes [40–42]. The SCSC transformation due to solvent removal has also been found to accompany conformational changes in the discrete coordination complexes [43–45].

A number of porous rigid coordination polymers often exhibit zeolitic behavior and retain single crystal nature during solvation and desolvation (for example, see Refs. [46–54]). Kitagawa, Yaghi, Atwood and others have demonstrated that such rigid porous coordination polymers can be used as gas storage materials [55–64]. The removal of solvents during SCSC conversion has also been found to accompany by change in magnetic properties [65], negative thermal expansion [66] and luminescent properties [67]. SCSC transformation after desolvation have also been found to be accompanied by distortion and sliding of network structures, change in conformation, coordination environment or space groups [60,68–77]. Kitagawa and Uemura have classified such behavior as flexible and dynamic motions in their review article [46].

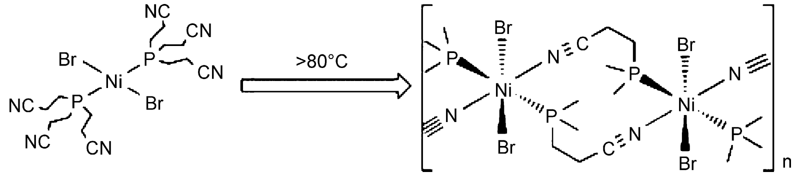

Fig. 1. A schematic diagram showing the polymerization of a Ni(II) complex due to the expansion of coordination number [81].

4. Transformation by thermal methods

The transformations of structures described below are primarily influenced by the expansion of coordination numbers, thermal dissociation, condensation, rearrangement of bonds or the removal/exchange of solvents. Although Wöhler's historic synthesis of urea from NH_4CNO has been the first recorded solid-state transformation of an organic compound by thermal means [78,79], a number of similar transformations such as $NCN{=}C(NH_2)_2$ from ammonium dicyanamide, $NH_4([N(CN)_2]$ has extensively been studied recently [80].

4.1. Tetrahedral monomer to octahedral 1D coordination polymer transformation

A red monomeric $[NiBr_2\{P(CH_2CH_2CN)_3\}_2]$ polymerizes on heating the solid at 80–130 °C or in acetone solution to form a blue linear ID coordination polymer. In the crystal lattice, one nitrogen atom of a nitrile group from each phosphine ligand mutually attacks the neighboring Ni(II) centers from axial directions and forms *trans* Ni–N bonds, thereby by expanding the coordination geometry from square-planar to octahedral. It has been shown that solid-state reaction pathway has been shown to be identical to the solution grown product forming stereo-specific all *trans*-octahedral $NiBr_2P_2N_2$ core from the square-planar $NiBr_2P_2$ core [81–83] as depicted in Fig. 1.

4.2. Hydrogen-bonded monomer to ladder-like structural transformation

Reactions of $Co(NO_3)_2$ with bpe (bpe = 4,4′-bipyridylethylene) in $MeOH/CHCl_3$ and $H_2O/EtOH$ solvents furnished $[Co(NO_3)_2(bpe)_{1.5}]\cdot 3CHCl_3$ with 1D ladder structure and a monomer, $[Co(H_2O)_4(bpe)_2](NO_3)_2\cdot(8/3)H_2O\cdot(2/3)bpe$, respectively. On heating above 150 °C the mononuclear compound is changed to ladder structure which was followed by DSC and TG analysis and the reaction is shown in Eq. (1). This is corroborated by IR spectral studies. The ladder structure on standing in humid air is slowly converted back to the mononuclear complex [84]:

$$[Co(H_2O)_4(bpe)_2](NO_3)_2\cdot(8/3)H_2O\cdot(2/3)bpe$$

$$\rightarrow [Co(NO_3)_2(bpe)_{1.5}] + (20/3)H_2O + (7/6)bpe \qquad (1)$$

4.3. 3D Hydrogen-bonded to 3D coordination polymeric structures

In the solid-state structure of $[Zn_2(Sala)_2(H_2O)_2]\cdot 2H_2O$ (H_2Sala = *N*-(2-hydroxybenzyl)-L-alanine, Fig. 2) two Zn(II) ions are bridged by two phenolato oxygen atoms of the Sala ligands to have a distorted square pyramidal geometry. The two apical coordination sites occupied by aqua ligands are on the same side of the Zn_2O_2 ring and a crystallographic two-fold rotational symmetry is present in the dimer. The dimers self-assemble in the solid to form hydrogen-bonded 3D network structures through O–H· · ·O and N–H· · ·O interactions as illustrated in Fig. 2, with chiral channels aligned along *c*-direction [85].

The two aqua ligands can be removed below 110 °C along with two lattice water molecules to form 'anhydrous $[Zn_2(Sala)_2]$'. The crystal structure of the dehydrated $[Zn_2(Sala)_2]$ revealed the formation of a 3D coordination polymeric structure. Such structural transformation from

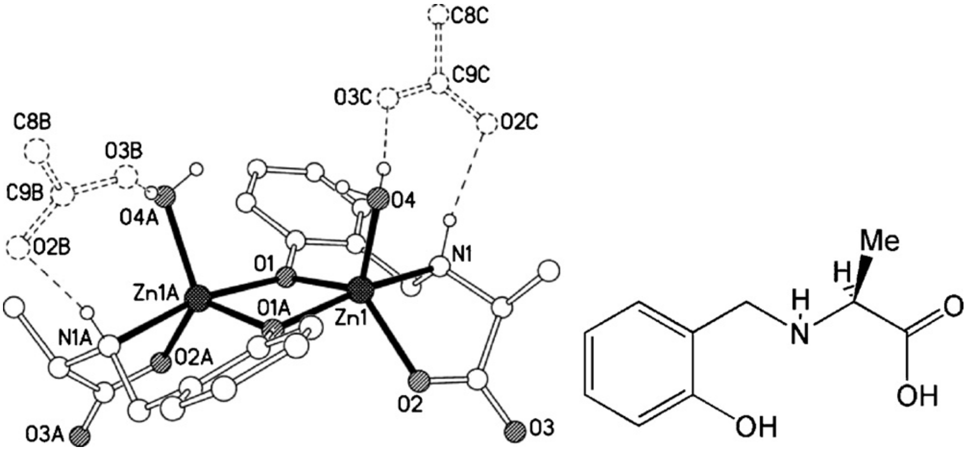

Fig. 2. (Left) A ball and stick diagram showing the intermolecular hydrogen-bonding present in $[Zn_2(Sala)_2(H_2O)_2]$. The dotted fragments are from the neighboring dimers. (Right) A schematic diagram of the ligand H_2Sala [85].

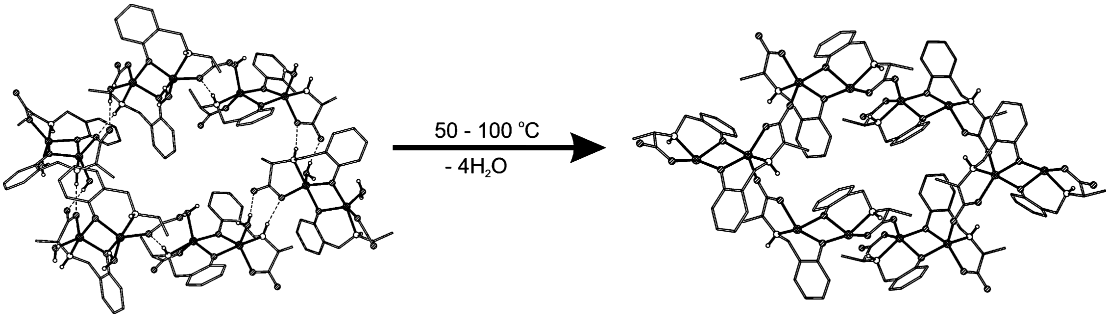

Fig. 3. The transformation of hydrogen-bonded 3D network structure to 3D coordination polymeric network structure [85]. Only a portion of the connectivity is shown for clarity for both structures.

hydrogen-bonded polymer to coordination polymer (shown in Fig. 3) is due to the breaking of Zn–OH_2 bonds and the formation new Zn–O(carboxylate) bonds aided by the N–H···O interactions in the lattice. The oxygen atoms of the neighboring carboxylate groups are already closer to the Zn(II) centers in the lattice (Zn···O distance, 3.74 Å) through a Zn–OH_2···O(carboxylate–Zn) intermolecular interactions as shown in Fig. 2. The anhydrous structure is also porous, containing chiral channels. Although both hydrated and dehydrated Zn(II)–Sala compounds crystallized in the tetragonal space group $P4_32_12$ they are not isostructural and their atomic coordinates are not superimposable [36].

The solid-state structural transformation reaction discussed above is irreversible and $[Zn_2(Sala)_2]$ cannot be rehydrated when crystallized from aqueous alcohol. But these two supramolecular structures can be interconverted when the $Sala^{2-}$ ligand has methyl or chloro groups at the *para* position of the phenolato ring. These substitutions in the $Sala^{2-}$ ligand do not alter the hydrogen-bonded 3D architecture significantly and, therefore, $[Zn_2RSala)_2(H_2O)_2]\cdot 2H_2O$ (R = Cl, Me) compounds also undergo structural transformation to 3D coordination polymeric network accompanied by thermal dehydration, but the transformation was found to be reversible. The dehydrated Zn(II)–RSala compounds readily takes back water upon crystallization from aqueous solution [86].

4.4. Transformation of 0D–2D structures

The decavanadate $(NC_7H_{14})_4[H_2V_{10}O_{28}]$ (where NC_7H_{14}: quinuclidinium cation) condenses in the solid state to form a layered compound $(NC_7H_{14})[H_2V_4O_{10}]$ on heating above 230 °C as shown in Eq. (2) and Fig. 4. The transformation was followed by VT-XRPD and TG [87]. Such condensation of zero-dimensional polyoxometallate to multidimensional structures in the solid state is expected to be prevalent in polyoxometallate chemistry, in general and nonetheless they are yet to be explored extensively:

$$2(NC_7H_{14})_4[H_2V_{10}O_{28}] \rightarrow 5(NC_7H_{14})[H_2V_4O_{10}] \qquad (2)$$

4.5. Transformation of 1D–2D structures

Ozin and co-workers reported an interesting thermal transformation of chain to layer structure of aluminophosphate in the solid state [88]. The anion in compound $[C_5H_9NH_3][Al_3P_5O_{20}H]$ having 1D chain structure is converted into $[C_5H_9NH_3][Al_2P_3O_{12}H]$ with 2D sheet-like structure on heating at 200 °C (Fig. 5). These two compounds have been synthesized under slightly different reaction conditions and crystal structures have been determined by X-ray crystallography. The thermal conversion was verified by X-ray structures, XRPD and TG measurements.

SCSC transformation from a zigzag 1D coordination polymer $[ZnCl_2(\mu\text{-bipy})]$, **1** to a 2D network structure $[Zn(\mu\text{-Cl})_2(\mu\text{-bipy})]$, **2** occurs by cooling **1** below −143 °C. Close proximity of the terminal chloride ligands to the neighboring Zn(II) centers is responsible for the structural changes accompanied by terminal to bridging chloride ligands and expansion of coordination number from four to six at Zn(II). Interestingly **1** has two polymorphs in space groups *C*2/*c* and *Pnma* and **2** has *Pban*. When **2** was heated above 87 °C it was converted to a mixture of polymorphs [89] as shown in Fig. 6. A similar lead(II) com-

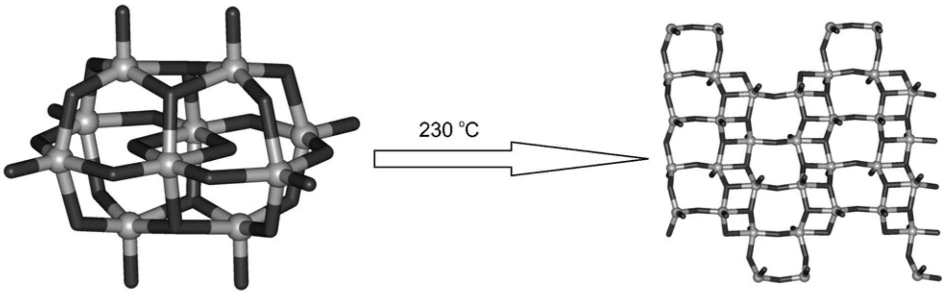

Fig. 4. A structural diagram showing the conversion of decavanate anion to 2D structure [87].

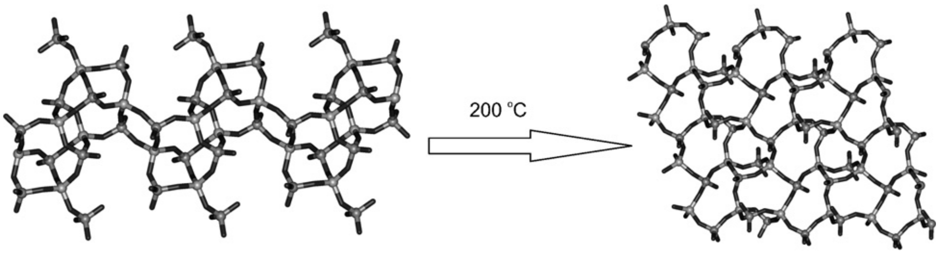

Fig. 5. Structural conversion of 1D–2D polymeric structures [88].

pound with 2D structure was found to undergo two reversible SCSC phase transformations [90].

4.6. Transformation between square grid coordination polymers

The supramolecular isomerism induced by the guest molecules has been observed in the self-assembly of $Zn(NO_3)_2$ with pyridine-3-carboxylate (nicotinate) by Zaworotko and co-workers [91]. In the products isolated, $[Zn(nicotinate)_2]\cdot MeOH\text{-}2H_2O$, possesses $4^2 \times 8^4$ network of PtS whereas $[Zn(nicotinate)_2]\cdot$naphthalene, and $[Zn(nicotinate)_2]\cdot 2PhNO_2$, exhibit square-grid, 4^4 topology. All the three coordination polymers can be converted to another square-grid structure reported by Lin et al. [92] by heating above 220 °C as monitored by XRPD and TG.

4.7. Transformation of interpenetrating to non-interpenetrating square grid structures

Another solid-state transformation involving square-grid structures has been observed by Chung and co-workers [93]. The reaction of mpe (1-methyl-1′,2-bis(4-pyridyl)ethylene) with $Co(NCS)_2$ afford non-interpenetrating square grid, two interpenetrating (4,4) nets and two mutually interpenetrating independent 3D frameworks along with an interpenetrating square-grids having the same composition $[Co(NCS)_2(mpe)_2]$ under different crystallization conditions. The interpenetrating square-grid structure on desolvation is converted into two mutually interpenetrating 3D frameworks interlocked by another (4,4) square-grid structure which on immersion in water transformed to non-interpenetrating square-grid structure. All these structural transformations of these polymers have been followed by XPRD studies and are depicted in Fig. 7.

4.8. Transformation from two- to four-fold interpenetrating (10,3) nets

Three-connected chiral interpenetrating (10,3) framework structures have been constructed by reacting M^{2+} (M = Ni and Co) ions with BTC (BTC = 1,3,5-benzenetricarboxylate) ligand. The BTC anions are bonded linearly by M^{2+} cations. The degree of interpenetration is controlled by the coordinating solvent diols. For example, ethylene glycol which coordinates to the M^{2+} cations in unidentate fashion and occupies the equatorial positions along with pyridine ligands, influence the formation of four-fold interpenetrating structure. On the other hand, 1,2-propanediol bonded to the metal centers in a bidentate fashion and occupies the equatorial positions yielded two-fold (disordered) interpenetrating structure. In both the structures solvent occupies 28 and 51% of the total volume. The micro-porous desolvated solid lost crystallinity upon complete removal of the solvents in the lattice and coordinating solvents, but the crystallinity is restored upon exposure to the vapors of the diols thereby regenerating either four- or two-fold interpenetrating (10,3) net having space groups $P4_232$ and $I4_132$, respectively. XRPD and TG have been employed extensively to follow the guest sorption/resorption studies and the framework interconversions [94,95].

4.9. Conversion of 1D–3D coordination polymer by thermal dehydration

Unlike Zn(II) complex described in Section 4.3, only one axial site is occupied by a water molecule and the other axial

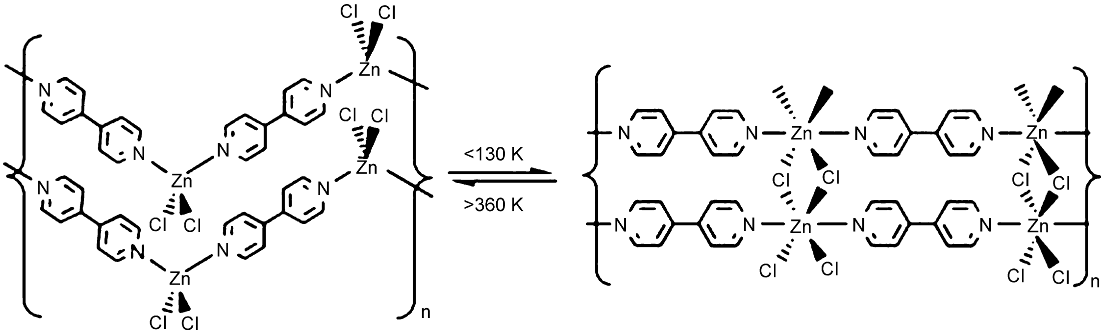

Fig. 6. Structural transformation of 1D–2D sheet structure due to the expansion of coordination number of Zn(II) [89].

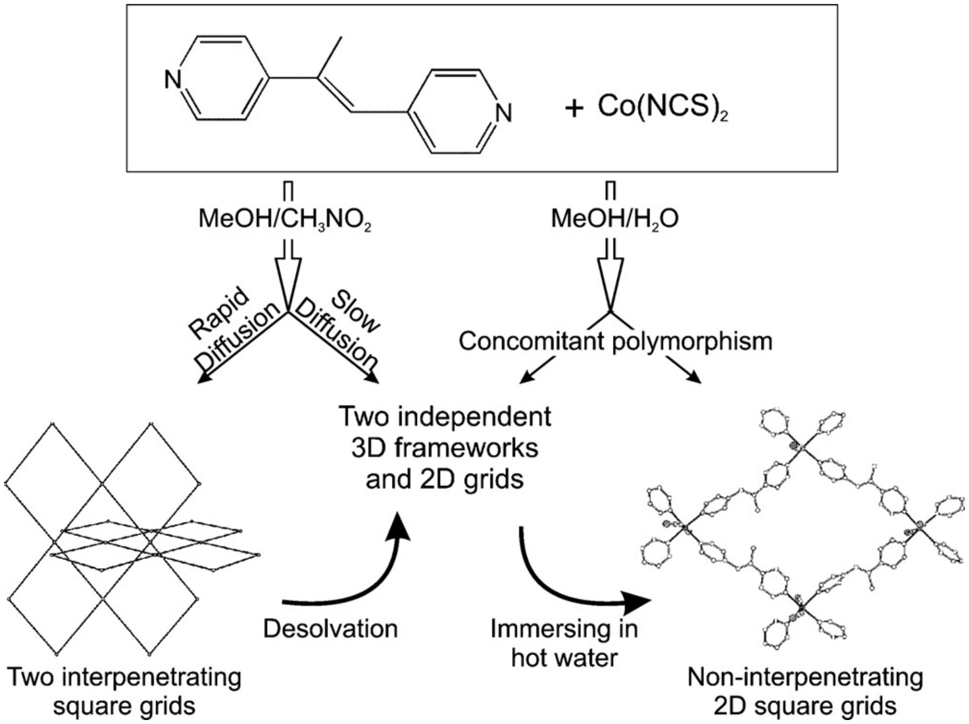

Fig. 7. A schematic diagram showing the formation and conversion of three different coordination polymeric network structures [93].

site is used to bridge an adjacent dimer through a carboxylate-*O* in the Cu(II) complex [$Cu_2(Sala)_2(H_2O)$]. As a result a helical coordination polymer is formed from apically linked dimers [96] and further sustained by O–H···O and N–H···O hydrogen-bonding as illustrated in Fig. 8. The helical strands are arranged parallel to the *a*-axis and are further hydrogen-bonded to one another in the *bc*-planes to form honeycombed hydrogen-bonded chiral network structure. The close Cu···O distance, 3.70 Å, between Cu(II) and the neighboring carboxylate-*O* atom are found to be favorable for topochemical reactions to take place. As expected, removal of the aqua ligand by thermal dehydration yielded anhydrous [$Cu_2(Sala)_2$], where the basic dimeric

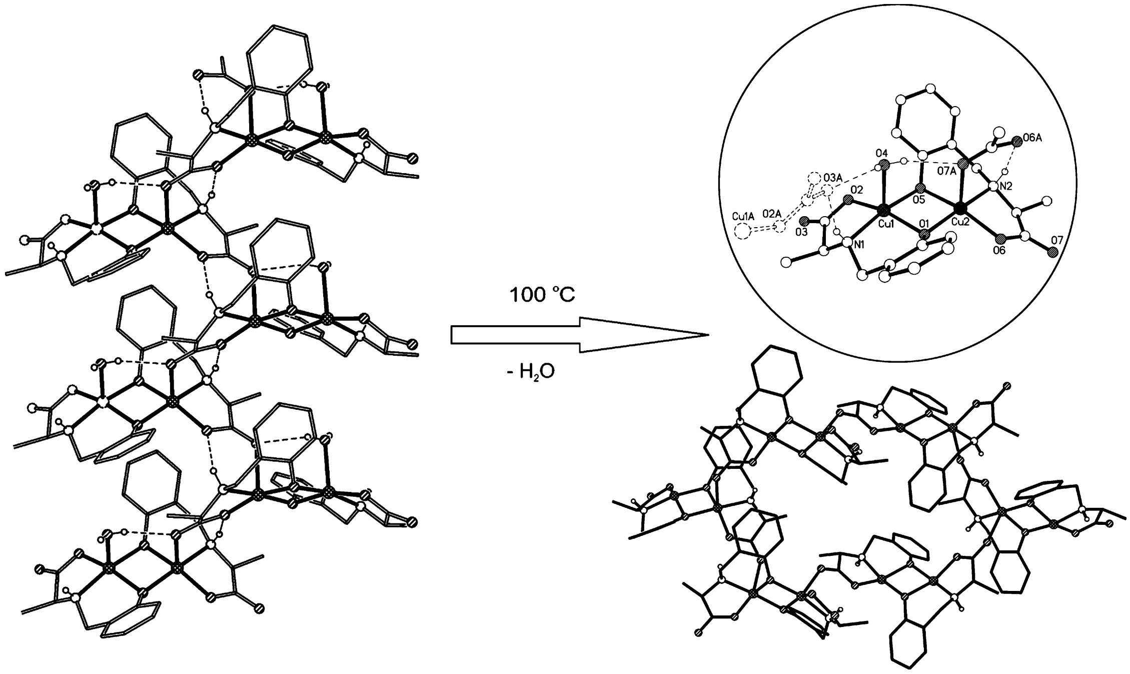

Fig. 8. A schematic diagram illustrating the structural conversion of 1D–3D coordination polymeric structures by thermal dehydration. The inset shows the intermolecular interactions around the dimeric building block shown by the dotted molecular fragments in the 1D polymer [96].

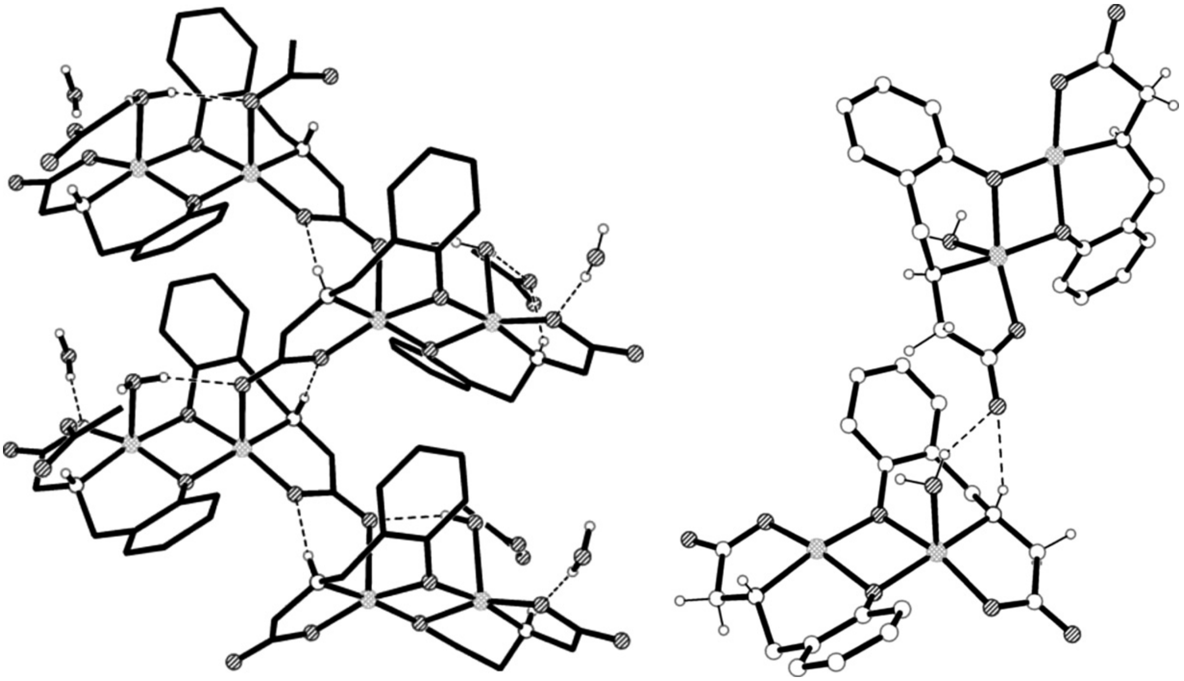

Fig. 9. The ID coordination polymeric strand in $[Cu_2(Sgly)(H_2O)]\cdot H_2O$ (left) and intermolecular interactions between the neighboring 1D strands are shown [97].

structure has remained intact but now a porous, 3D network coordination polymer has been formed similar to the Zn(II) analogue as depicted in Fig. 3.

The connectivity observed in $[Zn_2(Sala)_2(H_2O)_2]\cdot 2H_2O$ and $[M_2(Sala)_2]$ (M = Zn and Cu) resemble highly distorted diamondoid topology. The 3D coordination polymer $[M_2(Sala)_2]$ with diamondoid connectivity can be obtained by thermal dehydration of either hydrogen-bonded diamondoid structure $[Zn_2(Sala)_2(H_2O_2)_2]\cdot 2H_2O$ or hydrogen-bonded helical coordination polymer $[Cu_2(Sala)_2(H_2O)]$ with honeycomb network structure [36].

The crystal structure of $[Cu_2(Sgly)(H_2O)]\cdot H_2O$ (H_2Sgly = (*N*-(2-hydroxybenzyl)-glycine) also contains 1D coordination polymeric strands very similar to that of $[Cu_2(Sala)_2(H_2O)]$ as shown in Fig. 9. In fact the hydrogen-bonding present in $[Cu_2(Sgly)(H_2O)]\cdot H_2O$ also resembles those present in $[Cu_2(Sala)_2(H_2O)]$ which undergoes a solid-state transformation by thermal dehydration below 110 °C. But the Sgly complex fails to undergo such transformation and behaves like a normal coordination complex starts losing the coordinated water molecule only above 120 °C. The main differences between Cu(II)–Sgly and Cu(II)–Sala, are the presence of a lattice water molecule and the absence of a methyl group which is replaced by a hydrogen atom in Sgly ligand.

A detailed analysis of the intermolecular interactions present in the Cu(II)–Sgly complex showed that the presence of $C{=}O\cdots\pi$ attractive intermolecular interactions between carboxylate carbonyl and phenyl groups in the neighboring helices appear to be responsible for the weakening of the hydrogen-bonds, and thereby preventing the formation of anew Cu-O bond and the structural conversion. It is quite unexpected that the weak interaction such as $C{=}O\cdots\pi$ has major influence on the solid-state thermal dehydration behavior [97].

5. Transformation via reactions with small molecules

5.1. Oxidation of metal centers in framework structures

Suh and co-workers have reported an interesting metal–organic bilayer open framework having 3D channels obtained from a bismacrocyclic Ni(II) complex with BTC anion [70,71]. The channels of these crystals are occupied by pyridine and water guest molecules. This compound, $[Ni_2L]_3(BTC)_4\cdot 6py\cdot 36H_2O$ (L = bismacrocyclic ligand shown below in Fig. 10) exhibits sponge-like dynamic behavior in response to guest solvent molecules and may be classified as third generation porous structures [46]. Further when I_2 is reacted in DMSO/H_2O solution for 10 h, the Ni(II) ions can be oxidized to Ni(III) ions while maintaining the single crystalline nature and the channels have I_3^- and I_2 to form $[Ni_2L]_3(BTC)_4(I_3)_4\cdot nI_2\cdot 17H_2O$. The color of the single crystal changed from pale pink to dark brown during the reaction. On prolonged exposure to I_2 single crystal morphology is retained but the crystals hardly diffracted the X-ray beam. Similar reaction does not occur with Br_2 and the compound dissociated to $[Ni_2L]Br_4\cdot(Br_2)\cdot 4H_2O$. Such metal organic frameworks that are able to alter their framework charge by redox reaction are very rare [98].

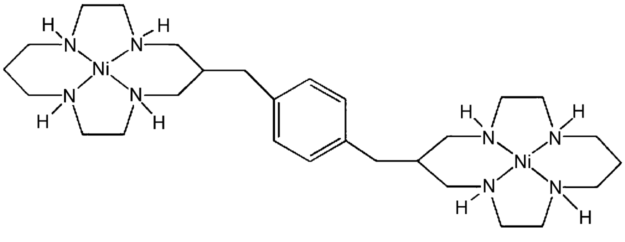

Fig. 10. Structure of the Ni_2L complex [98].

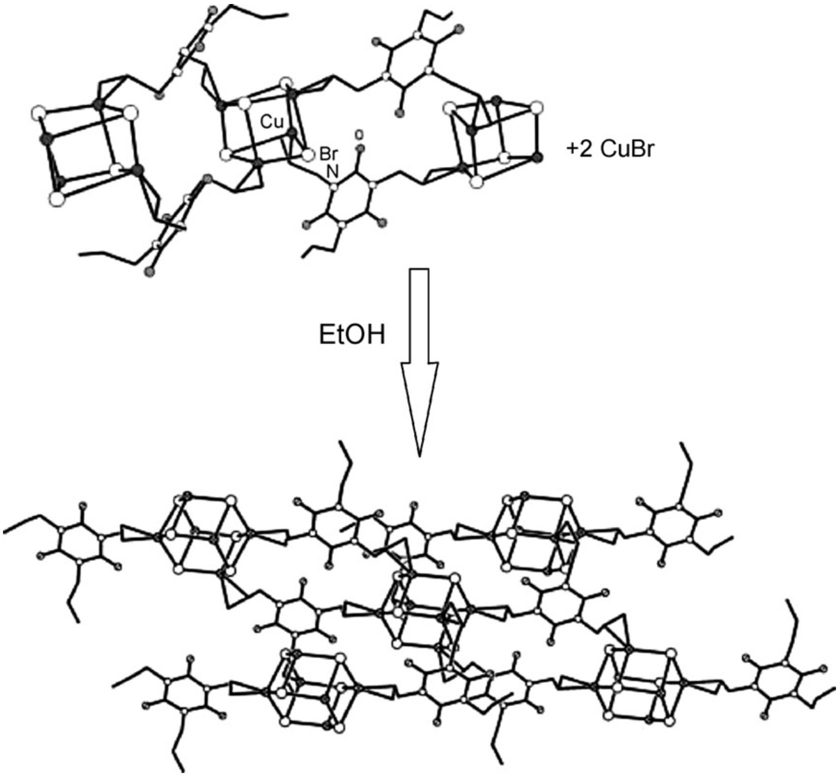

Fig. 11. Conversion of 1D–2D coordination polymeric structures [99].

5.2. *Reactions of 1D polymers leading to 2D structures*

The compound $[Cu_4Br_4(TTT)_2]$ (where TTT = triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione) was prepared by the reaction between TTT and CuBr in the 1:2 molar ratio in MeOH at 50–60 °C, where Cu_4Br_4 cubanes are linked by TTT ligands to form polymeric chain structure [99] as shown in Fig. 11. This 1D polymeric chain can be converted to $[Cu_6Br_6(TTT)_2]$ by reacting the former with CuBr in ethanol. In the new 2D network structures Cu_6Br_6 prismanes are the building blocks instead of Cu_4Br_4 cubanes.

5.3. *Redox reactions leading to multi-dimensional structural transformations*

Kanatzidis and Iordanidis have investigated redox-induced structural transformation in $M_2Bi_4Se_7$ (M = Rb and Cs) [100]. This involves oxidative coupling of entire rows of Se^{2-} to $Se_2{}^{2-}$ in the layered structure by I_2 vapors and expulsion of alkali ions to form MBi_4Se_7 with 3D network structure without affecting the integrity of the single crystals. The process can be reversed by heating MBi_4Se_7 with alkali metal. The formation of Se–Se bonds in the entire row resembles the closing action of a zipper, according to the authors.

A similar redox-induced 'zipper' action in the solid state involving SCSC conversion of 2D to 2D′ and 3D structures was noted by Kanatzidis and Iordanidis [101]. The 2D layered compound $Cs_3Bi_7Se_{12}$ has edge-sharing $BiSe_6$ octahedra which are close to each other with Se···Se contact of 3.409(2) Å. When these crystals are soaked in water and air is bubbled through the suspension overnight, it is cleanly transformed to $Cs_2Bi_7Se_{12}$ with similar 2D structure but with 50% of Se atoms are converted to Se–Se. This single crystal of $Cs_2Bi_7Se_{12}$ can be converted to 3D network compound $CsBi_7Se_{12}$ when all the Se^{2-} anions are converted to $Se_2{}^{2-}$ by treating with a concentrated solution of I_2 in CH_3CN. These two transformations are reminiscence of the *chimie douce* approach developed by Rouxel for the synthesis of a number of ternary selenides materials using the topochemical principles [102,103].

The transformation of 0D zinc phosphates, to 1D–3D structures have been obtained by reacting with $Zn(OAc)_2$, imidazole, piperazine in solution [104,105]. Although these transformations are very interesting in their own right, but they are not strictly solid-state structural transformations and hence not discussed further.

6. Transformation by photochemical reactions

Photochemical [2 + 2] cycloaddition reactions are far more attractive systems in carrying out SCSC structural transformations in the solid state [11,106–108]. The topotactic polymerization of C═C [109,110], C═C–C═C [111–114] and C≡C [115–117] bonds has also been studied extensively and in many cases SCSC transformation has been achieved.

6.1. *Photochemical polymerization of acetylene in 1D coordination polymeric complexes*

The photo polymerization of metal complexes having ligands containing acetylene functional groups has not been widely

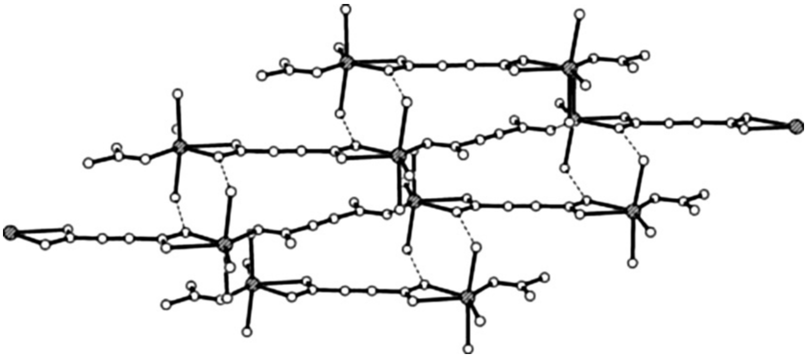

Fig. 12. Crystal packing of $[Cd(ADC)(H_2O)]\cdot H_2O$ showing the proximity of C═C bonds along *a*-axis [122].

investigated, but there are few reports on the formation of high molecular weight metal poly(alkynoates) and poly(alkenoates) by the solid-state reactions of metal alkynoates and alkenoates (for examples, see Refs. [118–121]). However, the solid-state structures of either the starting materials or the products were unknown.

The cadmium complex, $[Cd(ADC)(H_2O)]\cdot H_2O$ (where ADC acetylenedicarboxylate dianion) shown in Fig. 12 exhibits 1D coordination polymeric structure with extensive hydrogen bonding between aqua ligands and oxygen atoms of the carboxylates. This causes the C≡C bonds to align in close proximity to each other (3.27 Å). These crystals can be polymerized upon heating to form conjugated polycarboxylic chains. The polymerization process was investigated by XRPD, TG, Raman, IR and EPR spectral studies [122].

6.2. Photochemical [2 + 2] cycloaddition involving 2D coordination polymeric complexes

The extensive bridging by carboxylate ligands in the crystal structure of aquabis(3-butenoato)calcium complex leads to 2D coordination polymer as shown in Fig. 13 with bilayer arrangements prompting the reactive vinyl groups to align in parallel with close C· · ·C contacts of 3.73–3.90 Å. This compound undergoes solid-state polymerization reaction upon irradiation with ^{60}Co γ-rays [123] producing high molecular weight calcium poly(3-butenoate) with average molecular weight of 400,000 in 97% yield.

Foxman and co-workers also reported a similar solid-state polymerization reaction of the C═C bonds in 3-butenoato anions in the 2D coordination polymer, bis(3-butenoato)zinc(II) complex (shown in Fig. 14) by high energy ^{60}Co γ-rays. In this reaction the formation of 50% isotactic zinc poly(but-3-enoate) has been reported [124] despite the vinyl groups are separated by a distance of 4.21 Å.

Cadmium fumarate dihydrate forms 2D coordination polymeric network sheet structure with (4,4) grids. Short contacts between C═C bonds (3.38 Å) in the adjacent layers as shown in Fig. 15 prompted Mchaeldes and co-workers to investigate the photoreactivity of these crystals. UV-irradiation of the powder lead to the formation of highly stereospecific *trans*,*trans*,*trans*-cyclobutane-1,2,3,4-tetracarboxylate in quantitative yield. But the crystal structure of the product is not known [125] as the single crystals crumbled due to loss of water during photochemical reactions.

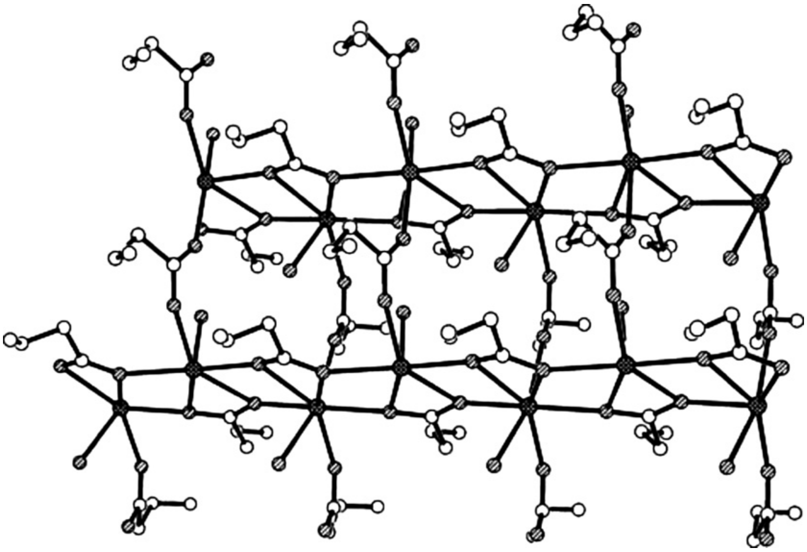

Fig. 13. A view of the crystal structure showing the alignments of C═C bonds in 3-butenoato ligands [123].

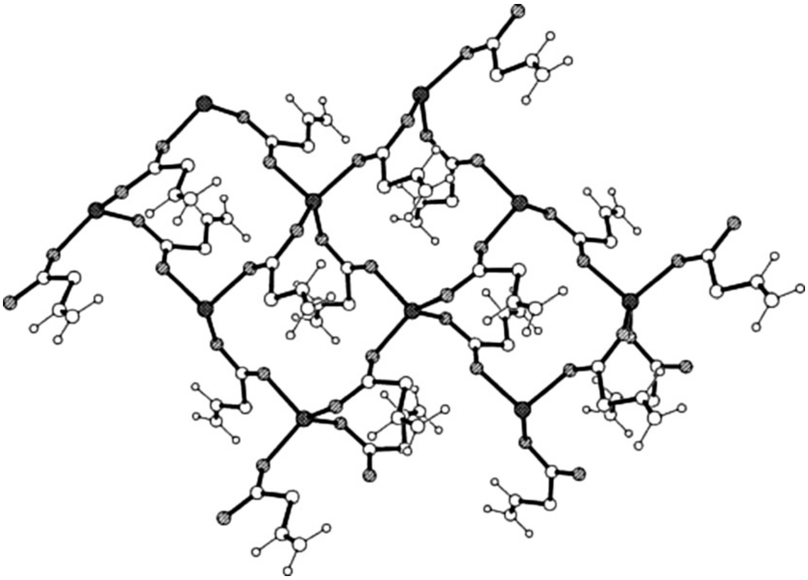

Fig. 14. A view of the 2D coordination polymeric structure showing the alignment of but-3-enoate ligands [124].

6.3. Transformation of linear 1D to ladder-like coordination polymeric structures

MacGillivray and co-workers have elegantly aligned a pair of 4,4′-bipyridylethylene (bpe) in the solid state to undergo photochemical [2 + 2] cycloaddition, using a pair of dinuclear Zn(II) coordination complexes by self-assembly [126].

This concept was then successfully extended to make 1D ladder-like coordination polymer using the same dinuclear Zn(II) complex where the pair of coordinated bpe ligands are perfectly aligned in parallel and the C=C bonds are separated by 3.19 Å as shown in Fig. 16.

Photodimerization within this polymer indeed occurs to completion in the solid state on exposure to UV light. But the loss of water from the single crystal lattice during UV irradiation does not retain the single crystal nature and hence precludes its structure determination. However, the ^{1}H NMR spectrum of the irradiated sample confirmed the formation of cyclobutane derivatives quantitatively [127].

One-dimensional metal coordination polymers with molecular ladder (or also called rail-road) structures can easily be prepared by self-assembly [128]. Hence, these structures provide an interesting possibility to align photoreactive double bonds in the solid state since the distance between the rails can be manipulated by judicious choice of the bridging ligands. Such metal coordination polymeric structures can be exploited for solid-state structural transformations. Further the distance between two metal ions can easily be controlled by the choice of the metal ions and the type of the bridging ligands. For example, the oxygen atoms of the acetate ligands can be effectively employed to maintain the distance between two transition metal ions especially Zn(II) within 4.0 Å by bridging them. Then a pair of ditopic spacer ligands with C=C bonds such as bpe can be aligned in parallel fashion by bonding to the $Zn_2(\mu\text{-OAc})_2$ units alternately to construct ladder-like 1D coordination polymers. Although such approach is very attractive for synthesizing ladder polymeric structures, the successful isolation of such compounds depend on the experimental conditions employed.

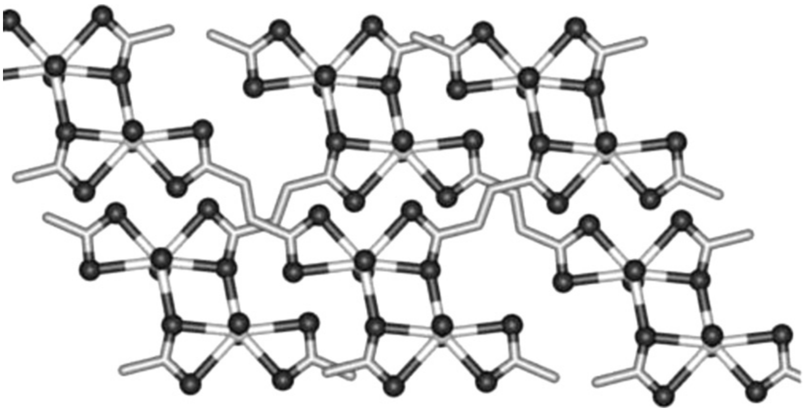

Fig. 15. An overlay of fragments of two neighboring square-grid polymeric sheets is shown highlighting the dispositions the C=C double bonds [125].

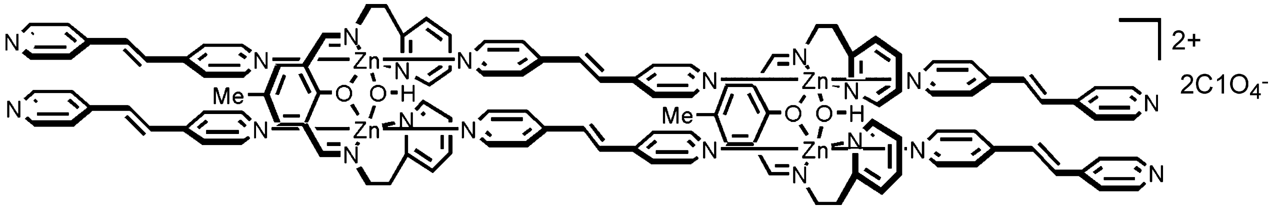

Fig. 16. A schematic diagram illustrating the ladder structure in 1D polymeric cation [127].

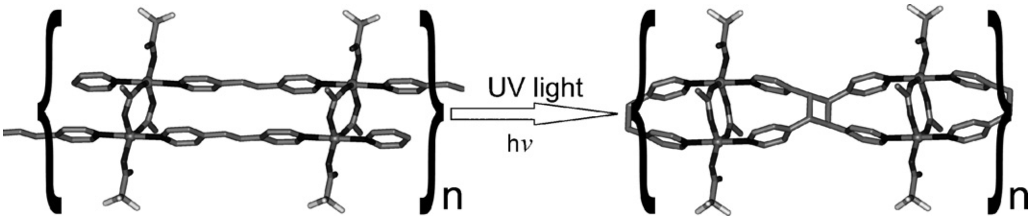

Fig. 17. Solid-state structural conversion of a 1D ladder polymer to another ladder polymer by photochemical reaction across the rails [129].

After several attempts the 1D ladder-like coordination polymer, $[\{(H_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$ was synthesized in which the bpe ligands in the adjacent chains have been aligned parallel but slightly slip stacked. The nonbonding distances between the double bonds of the two bpe ligands in the parallel chains (C···C distance, 3.63 Å and C–C···C angles, 74.0° and 106.0°) are congenial for the [2 + 2] cycloaddition to take place in the solid state [129].

The quantitative photo reactivity of this molecular ladder polymer is evident from the ^{1}H spectrum of the UV irradiated product under Xenon lamp for 14 h. The ^{1}HNMR spectrum shows complete disappearance of the olefinic protons at 7.56 ppm and the appearance of cyclobutane protons at 4.68 ppm and the shift in the bipyridyl protons from 8.61 and 7.63 ppm to 8.35 and 7.26 ppm. But the single crystal does not survive after photochemical reactions.

When half of the acetate ions are replaced by $CF_3CO_2^-$ ions, $[\{(F_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$, have been obtained. Two acetato ligands are found to bridge a pair of Zn(II) atoms in $[Zn_2(\mu\text{-bpe})_2]_n$ with a Zn···Zn distance, 3.848(1) Å to form molecular ladder polymer while a trifluoroacetate anion chelates each Zn(II) to complete distorted octahedral geometry at the metal center. As expected the two bpe ligands are disposed in parallel with the nonbonding distance, 3.747 Å between the two ethylene carbon atoms of the bpe ligands.

UV irradiation of the single crystals of this compound transformed the 1D ladder polymer to another ladder polymer, this time with the new ligand, tpcb (tetrakis(4-pyridyl)cyclobutane) produced by the photochemical [2 + 2] cycloaddition across two bpe accompanied by the preservation of single crystals as illustrated in Fig. 17.

It is evident that the solid-state supramolecular transformation of one type of coordination polymer to another accompanied by photodimerization across the rails has been accomplished using a simple strategy. Kim and co-workers [130] isolated $[Zn(H_2O)(bpe)(4\text{-tpcb})](ClO_4)_2$ by the reaction of $Zn(ClO_4)_2$ with bpe in solution. The results show that the photodimerization can indeed be achieved in solution but the nature of the products was unpredictably an interpenetrated 3D network containing bpe and its cyclo dimerized product, tpcb.

The hydrogen-bonded 2-bpe (2-bpe = *trans*-1,2-bis(2-pyridyl)ethylene) in the two supramolecular isomers of $[Mn(NCS)_2(H_2O)_4]\cdot4(2\text{-bpe})$ have been found to undergo photodimerization [131] leading to two different isomers namely *rtct* and *rctt* (shown below) (Fig. 18).

6.4. The use of argentophilic interactions in aligning double bonds in coordination polymers

MacGillivray's group has used the argentophilic interactions to stack the double bonds in the complex, $[Ag_2(4\text{-stilbz})_4](CF_3CO_2)_2$ (4-stilbz = *trans*-1(4-pyridyl)-2-(phenyl)ethylene) which lead to regiospecific [2 + 2] photodimerization. The SCSC transformation of finite metal complex to 1D coordination structure is due to the formation of Ag···C interactions, 2.63 Å between adjacent dimerized product resulted by the movement and rotation of the cations [132].

Self-assembly method has been shown to be a successful method in the construction of 1D coordination polymers [133]. Schröder, Champness and co-workers have discussed the influence of π–π, Ag-anion, Ag···π and Ag···Ag interactions on the topology, geometry and packing of 1D coordination polymers of silver(I) complexes. They have also shown that the Ag···Ag and

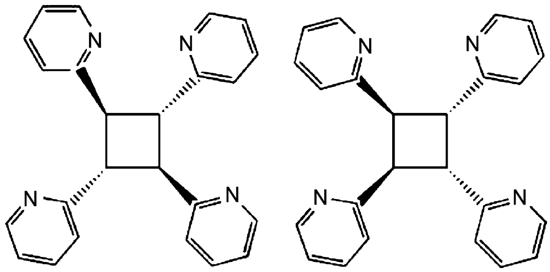

Fig. 18. The two isomers *rtct* (left) and *rctt* (right) of tetrakis(2-pyridyl)cyclobutane) [131].

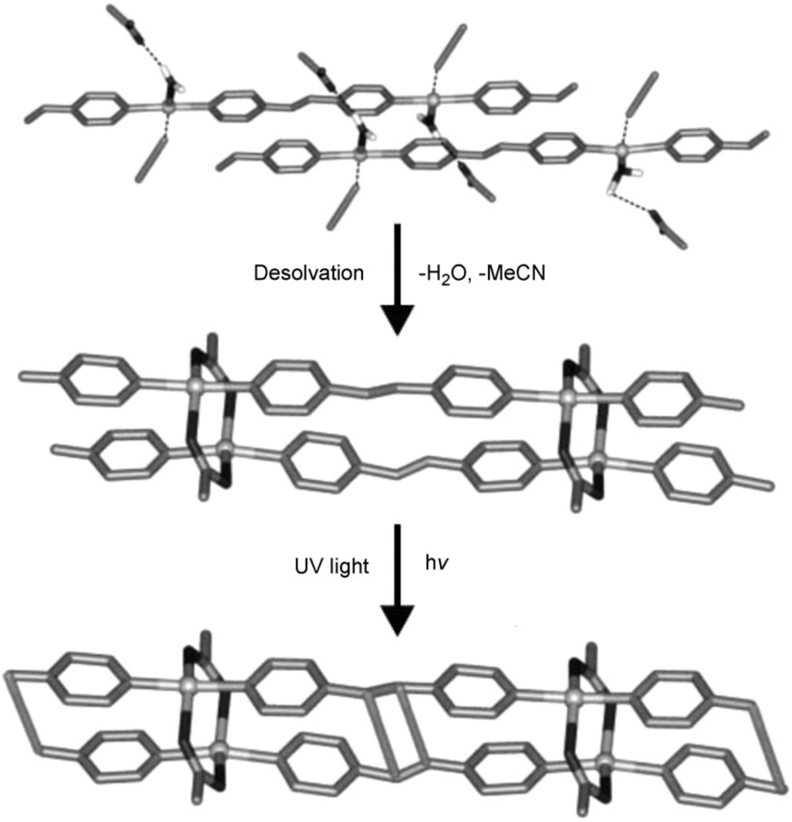

Fig. 19. A schematic diagram illustrating the formation ladder-like 1D coordination polymer from linear 1D polymer and the expected photodimerized product after [2 + 2] cycloaddition reactions [138].

π–π interactions can be used to bind two adjacent linear chains together to form infinite ladder structures [134,135]. During the crystallization process Schröder's group have found that the bpe ligand had undergone [2 + 2] cycloaddition in solution and complexed with $AgBF_4$. The product formed was a 3D coordination polymer, $[Ag(tpcb)_2](BF_4)_2$ instead of $[Ag_2(bpe)_2](BF_4)_2$ [136].

Acetate and trifluoroacetate anions can be effectively used to bridge the metal ions to make ladder-like coordination polymers [137]. This has been combined with Ag· · ·Ag interactions to align the C=C bonds in $[\{(\mu\text{-}O_2CCF_3)Ag\}_2(\mu\text{-bpe})_2]\cdot H_2O$ to form molecular ladder polymers. When the dehydrated powder is irradiated under UV light, complete conversion of the olefins to cyclobutane ring was observed as monitored by ^{1}H NMR spectroscopy. Here a ladder-like coordination polymer is converted to another coordination polymer by UV light [138].

Another linear 1D coordination polymer $[Ag(\mu\text{-bpe})(H_2O)](CF_3CO_2)\cdot CH_3CN$ with no close interactions between the bpe ligands in the crystal structure was also found to undergo [2 + 2] cycloaddition under UV light as revealed by the ^{1}H NMR spectral data of the irradiated product. The formation cyclobutane ring can occur only when the bpe ligands are preorganized during desolvation process. Hence, transformation of single stranded 1D coordination polymer to ladder-type structure has been proposed to occur during desolvation process as depicted in Fig. 19. This anisotropic cooperative molecular movements of the adjacent linear chains appears to be facilitated by Ag· · ·Ag and π–π interactions. This has been further supported by X-ray powder diffraction experiments and IR spectroscopy [138]. The movements of coordination polymers and change in the conformation of coordination polymers, sliding of layers of coordination polymers have been recorded in the literature [46,60,68–77]. However, these movements of ions did not lead to the formation of a new coordination polymer.

7. Summary and conclusions

Although all the solid-state structural transformations have been serendipitously discovered, a quick look at the packing of the reported reactive coordination polymers would enable us to rationalize the following. Crystal engineering tools including hydrogen bonding, π–π stacking, halogen–halogen and other weak interactions are mainly responsible for bringing the reactive functional groups closer together more or less in the correct orientations [139]. Absence of steric hindrance and availability of free space near these functional groups has facilitated the structural transformations by the applications of external stimuli. The nature of ligands and metal ions (especially coordination number and geometry) can also be effectively engaged as tools for crystal engineering to design the reactive coordination polymers. The isolation of the desired coordination with correct composition, connectivity and structure becomes a challenge, if the metal–ligand bonds are labile, which may lead to the formation of kinetic products. The main driving force for the structural transformation arise from the energy (thermodynamic) considerations and kinetic reasoning for the solvent trapped solid-state structures.

The field of supramolecular solid-state transformation of structures involving coordination polymers is still in its infancy. A combination of X-ray crystallography, XRPD and thermoanalytical techniques has been elegantly employed to unravel interesting transformations in coordination polymeric structures. Solid-state NMR is yet to be exploited for this purpose. The topochemical reactions along with SCSC transformation are widespread in organic chemistry [139]. However, the examples available in the literature are limited to rationalize the structural conversions (see for example Refs. [140–150]). On the other hand, this emerging field offers potential applications in materials science including synthesis of new materials, materials with switching ability due to heat, light and small molecules [151]. Braga and Grepioni have reviewed the reactions that occur in the molecular crystals by cogrinding, milling, and kneading [152]. These solvent free 'green' reactions have been used to prepare novel molecular and supramolecular solids. Such methods are waiting to be explored for structural transformations of coordination polymers. While this manuscript was under preparation a special issue on SCSC transformations edited by Barbour [153] appeared in the Australian Journal of Chemistry containing articles written by the leading researchers in this field.

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References

[1] V.V. Boldyrev (Ed.), Reactivity of Solids: Past, Present and Future, Blackwell Science, UK, 1996.
[2] Y. Ohashi, Reactivity of Molecular Solids, VCH, Tokyo, Japan, 1993.
[3] E. Boldyreva, V.V. Boldyrev, Reactivity in Molecular Solids, Wiley, Chichester, UK, 1999.
[4] F. Toda (Ed.), Organic Solid-state Reactions, Kluwer, Dordrecht, The Netherlands, 2002.
[5] K. Tanaka, F. Toda, Chem. Rev. 100 (2000) 1025.
[6] F. Toda, Acc. Chem. Res. 28 (1995) 480.
[7] G.R. Desiraju, Organic Solid State Chemistry, Elsevier, Amsterdam, 1987.
[8] G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989.
[9] V. Ramamurthy, K. Venkatesan, Chem. Rev. 87 (1987) 433.
[10] A.E. Keating, M.Z. Garcia-Garibay, in: V. Ramamurthy, K. Schanze (Eds.), Molecular and Supramolecular Photochemistry, vol. 2, Marcel Dekker, 1998, p. 195.
[11] T. Friščič, L.R. MacGillivray, Z. Kristallogr. 220 (2005) 351.
[12] M.D. Bala, C. Demetrius, N.J. Coville, J. Organomet. Chem. 69 (2006) 1919.
[13] O.G. Adeyemi, U.B. Eke, L. Cheng, L.M. Cook, D.G. Billing, B.B. Mamba, D.C. Levendis, N.J. Coville, J. Organomet. Chem. 689 (2004) 2207.
[14] V.Y. Kukushkin, Y.A. Izotova, D. Tudela, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Inorg. Synth. 34 (2004) 81.
[15] C.F. Hogan, A.M. Bond, A.K. Neufeld, N.G. Connelly, E. Llamas-Rey, J. Phys. Chem. A 107 (2003) 1274.
[16] R.S. Bogadi, D.C. Levendis, N.J. Coville, J. Am. Chem. Soc. 124 (2002) 1104.
[17] S.D. Kirik, L.A. Solovyov, A.I. Blokhin, I.S. Yakimov, Acta Crystallogr. B 56 (2000) 419.
[18] J.M. Smith, L. Cheng, N.J. Coville, J. Schulte, P.S. Dimpe, M.S. Adsetts, L.M. Cook, J.C.A. Boeyens, D.C. Levendis, Organometallics 19 (2000) 2597.
[19] V.Y. Kukushkin, D. Tudela, Y.A. Izotova, V.K. Belsky, A.I. Stash, Polyhedron 17 (1998) 2455.
[20] Y. Ihara, T. Sakino, M. Ishikawa, T. Koyata, Bull. Chem. Soc. Jpn. 70 (1997) 3025.
[21] D. Das, N.R. Chaudhuri, A. Ghosh, Polyhedron 15 (1996) 3919.
[22] S. Yamaguchi, Y. Hayashi, M. Suzuki, A. Uehara, Thermochim. Acta 208 (1992) 191.
[23] E. Itoh, K. Yamamoto, M. Funato, M. Suzuki, A. Uehara, Thermochim. Acta 195 (1992) 51.
[24] F.M. Macdonald, P.J. Sadler, Polyhedron 10 (1991) 1443.
[25] V.Y. Kukushkin, E.Y. Pan'kova, E.A. Afanas'ev, Zh. Neorg. Khim. 34 (1989) 1342.
[26] D.W. Krassowski, K. Reimer, H.E. LeMay Jr., J.H. Nelson, Inorg. Chem. 27 (1988) 4307.
[27] M. Fushimi, M. Suzuki, A. Uehara, Bull. Chem. Soc. Jpn. 61 (1988) 1809.
[28] D.A. Redfield, L.W. Cary, J.H. Nelson, Inorg. Chem. 14 (1975) 50.
[29] R. Tsuchiya, Y. Nakata, E. Kyuno, Bull. Chem. Soc. Jpn. 44 (1971) 705.
[30] G.W. Watt, D.A. Butler, Inorg. Chem. 5 (1966) 1106.
[31] R. Kitaura, R. Matsuda, Y. Kubota, S. Kitagawa, M. Takata, T.C. Kobayashi, M. Suzuki, J. Phys. Chem. B 109 (2005) 23378.
[32] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T.C. Kobayashi, Angew. Chem. Int. Ed. 44 (2005) 920.
[33] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T.C. Kobayashi, S. Horike, M. Takata, J. Am. Chem. Soc. 126 (2004) 14063.
[34] R. Kitaura, S. Kitagawa, Y. Kubota, T.C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T.C. Ozawa, M. Suzuki, M. Sakata, M. Takata, Science 298 (2002) 2358.
[35] E.V. Dikarev, B. Li, V.V. Chernyshev, R.V. Shpanchenko, M.A. Petrukhina, Chem. Commun. (2005) 3274.
[36] J.J. Vittal, in: E.R.T. Tiekink, J.J. Vittal (Eds.), Frontiers in Crystal Engineering, John Wiley & Sons, Chichester, 2006, p. 297 (Chapter 12).
[37] G. Kaupp, J. Naimi, M. Reza, Cryst. Eng. Commun. 7 (2005) 402.
[38] G. Kaupp, Top. Curr. Chem. 254 (2005) 95.
[39] G. Kaupp, in: J.E.D. Davies (Ed.), Comprehensive Supramolecular Chemistry, vol. 8, Elsevier, Oxford, 1996, p. 381.
[40] U. Englert, B. Ganter, T. Wagner, Z. Anorg. Allg. Chem. 624 (1998) 970.
[41] D.V. Soldatov, E.V. Grachev, J.A. Ripmeester, Cryst. Growth Des. 2 (2002) 401.
[42] S. Rabe, U. Müller, Z. Anorg. Allg. Chem. 625 (1999) 1367.
[43] L. Dobrzańska, G.O. Lloyd, C. Esterhuysen, L.J. Barbour, Angew Chem. Int. Ed. 45 (2006) 5856.
[44] L. Dobrzańska, G.O. Lloyd, H.G. Raubenheimer, L.J. Barbour, J. Am. Chem. Soc. 127 (2005) 13134.
[45] L. Dobrzańska, G.O. Lloyd, H.G. Raubenheimer, L.J. Barbour, J. Am. Chem. Soc. 128 (2006) 698.
[46] S. Kitagawa, K. Uemura, Chem. Soc. Rev. 34 (2005) 109, and references therein.
[47] A. Michaelides, S. Skoulika, Cryst. Growth Des. 5 (2005) 529.
[48] E.Y. Lee, M.P. Suh, Angew. Chem. Int. Ed. 43 (2004) 2798.
[49] K. Takaoka, M. Kawano, M. Tominaga, M. Fujita, Angew. Chem. Int. Ed 44 (2005) 2151.
[50] K. Takaoka, M. Kawano, T. Hozumi, S. Ohkoshi, M. Fujita, Inorg. Chem. 45 (2006) 3976.
[51] O. Ohmori, M. Kawano, M. Fujita, J. Am. Chem. Soc. 126 (2004) 16292.
[52] O. Ohmori, M. Kawano, M. Fujita, Angew. Chem. Int. Ed. 44 (2005) 1962.
[53] E. Deiters, V. Bulach, M.W. Hosseini, Chem. Commun. (2005) 3906.
[54] B. Rather, M.J. Zaworotko, Chem. Commun. (2003) 830.
[55] J.L. Atwood, L.J. Barbour, A. Jerga, B.L. Schottel, Science 298 (2002) 1000.

[56] S. Kitagawa, S. Noro, T. Nakamura, Takayoshi, Chem. Commun. (2006) 701.
[57] K. Uemura, R. Matsuda, S. Kitagawa, J. Solid State Chem. 178 (2005) 2420.
[58] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
[59] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, Angew. Chem. Int. Ed. 42 (2003) 428.
[60] T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, Angew. Chem. Int. Ed. 38 (1999) 140.
[61] O.M. Yaghi, Angew. Chem. Int. Ed. 44 (2005) 4670.
[62] J.L.C. Rowsell, O.M. Yaghi, Micropor. Mesopor. Mater. 73 (2004) 3.
[63] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705.
[64] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.
[65] M. Kurmoo, H. Kumagai, K.W. Chapman, C.J. Kepert, Chem. Commun. (2005) 3012.
[66] T. Pretsch, K.W. Chapman, G.J. Halder, C.J. Kerpert, Chem. Commun. (2006) 1587.
[67] K.-L. Wong, G.-L. Law, Y.-Y. Yang, W.-T. Wong, Adv. Mater. 18 (2006) 1051.
[68] C.-D. Wu, W. Lin, Angew. Chem. Int. Ed. 44 (2005) 1958.
[69] J.-P. Zhang, Y.-Y. Lin, W.-X. Zhang, X.-M. Chen, J. Am. Chem. Soc. 127 (2005) 14162.
[70] H.J. Choi, M.P. Suh, J. Am. Chem. Soc. 126 (2004) 15844.
[71] M.P. Suh, J.W. Ko, H.J. Choi, J. Am. Chem. Soc. 124 (2002) 10976.
[72] E.Y. Lee, S.Y. Jang, M.P. Suh, J. Am. Chem. Soc. 127 (2005) 6381.
[73] M.-H. Zeng, X.-L. Feng, X.M. Chen, Dalton Trans. (2004) 2217.
[74] K. Biradha, M. Fujita, Angew. Chem. Int. Ed. 41 (2002) 3392.
[75] K. Biradha, Y. Hongo, M. Fujita, Angew. Chem. Int. Ed. 41 (2002) 3395.
[76] T.K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, Angew. Chem. Int. Ed. 43 (2004) 3269.
[77] C.-L. Chen, A.M. Goforth, M.D. Smith, C.-Y. Su, H.-C. Zur Loye, Angew. Chem. Int. Ed. 44 (2005) 6673.
[78] F. Wöhler, Ann. Phys. (Berlin) 12 (1828) 253.
[79] J. Liebig, F. Wöhler, Ann. Phys. Leipzig. Ser. 2 (20) (1830) 369.
[80] B.C. Lotsch, J. Senker, W. Schnick, Inorg. Chem. 43 (2004) 895, and references therein.
[81] K. Cheng, B.M. Foxman, J. Am. Chem. Soc. 99 (1977) 8102.
[82] R.A. Walton, R. Whyman, J. Chem. Soc. A (1968) 1394.
[83] M.G.B. Drew, D.F. Lewis, R.A. Walton, Chem. Commun. (1969) 326.
[84] O.-S. Jung, S.H. Park, K.M. Kim, H.G. Jang, Inorg. Chem. 37 (1998) 5781.
[85] J.D. Ranford, J.J. Vittal, D. Wu, Angew. Chem. Int. Ed. 37 (1998) 1114.
[86] J.J. Vittal, X.-D. Yang, Cryst. Growth Des. 2 (2002) 259.
[87] D. Riou, O. Roubeau, G. Fèrey, Z. Anorg. Allg. Chem. 624 (1998) 1021.
[88] S. Oliver, A. Kuperman, A. Lough, G.A. Ozin, Chem. Mater. 8 (1996) 2391.
[89] C. Hu, U. Englert, Angew. Chem. Int. Ed. 44 (2005) 2281.
[90] C. Hu, U. Englert, Angew. Chem. Int. Ed. 44 (2006) 3457.
[91] B. Rather, B. Moulton, R.D.B. Walsh, M.J. Zaworotko, Chem. Commun. (2002) 694.
[92] W. Lin, O.R. Evans, R.G. Xiong, Z.Y. Wang, J. Am. Chem. Soc. 120 (1998) 13272.
[93] D.M. Shin, I.S. Lee, D. Cho, Y.K. Chung, Inorg. Chem. 42 (2003) 7722.
[94] C.J. Kepert, T.J. Prior, M.J. Rosseinsky, J. Am. Chem. Soc. 122 (2000) 5158.
[95] C.J. Kepert, M.J. Rosseinsky, Chem. Commun. (1998) 31.
[96] J.D. Ranford, J.J. Vittal, D. Wu, X. Yang, Angew. Chem. Int. Ed. 38 (1999) 3498.
[97] X.D. Yang, D. Wu, J.D. Ranford, J.J. Vittal, Cryst. Growth Des. 5 (2005) 41.
[98] M. Oh, G.B. Carpenter, D.A. Sweigart, Angew. Chem. Int. Ed. 40 (2001) 3191.
[99] X. Xue, X.-S. Wang, R.-G. Xiong, X.Z. You, B.F. Abrahams, C.-M. Che, H.-X. Ju, Angew. Chem. Int. Ed. 41 (2002) 2944.
[100] L. Iordanidis, M.G. Kanatzidis, Angew. Chem. Int. Ed. 39 (2000) 1928.
[101] L. Iordanidis, M.G. Kanatzidis, J. Am. Chem. Soc. 122 (2000) 8319.
[102] J. Rouxel, M. Tournoux, Solid State Ionics 84 (1996) 141.
[103] J. Rouxel, Chem. Eur. J. 2 (1996) 1053.
[104] A.A. Ayi, A. Choudhury, S. Natarajan, S. Neeraj, C.N.R. Rao, J. Mater. Chem. 11 (2001) 1181.
[105] A. Choudhury, S. Neeraj, S. Natarajan, C.N.R. Rao, J. Mater. Chem. 11 (2001) 1537.
[106] L.R. MacGillivray, Cryst. Eng. Commun. 4 (7) (2002) 37.
[107] C.R. Theocharis, W. Jones, Topotactic and topochemical photodimerization of benzylidenecyclopentanones, in: G.R. Desiraju (Ed.), Organic Solid State Chemistry, Elsevier, Amsterdam, 1987, p. 47 (Chapter 4).
[108] G.M.J. Schmidt, Pure Appl. Chem. 27 (1971) 647.
[109] M. Hasegawa, Chem. Rev. 83 (1983) 507.
[110] G.W. Coates, A.R. Dunn, L.M. Henling, J.W. Ziller, E.B. Lobkovsky, R.H. Grubbs, J. Am. Chem. Soc. 120 (1998) 3641.
[111] A. Matsumoto, H. Nakazawa, Macromolecular 37 (2004) 8538.
[112] S. Nagahama, T. Tanaka, A. Matsumoto, Angew. Chem. Int. Ed. 43 (2004) 3811.
[113] A. Matsumoto, K. Sada, K. Tashiro, M. Miyata, T. Tsubouchi, T. Tanaka, T. Odani, S. Nagahama, T. Tanaka, K. Inoue, S. Saragai, S. Nakamoto, Angew. Chem. Int. Ed. 41 (2002) 2502.
[114] A. Matsumoto, T. Odani, M. Chikada, K. Sada, M. Miyata, J. Am. Chem. Soc. 121 (1999) 11122.
[115] X. Yuyang, F.W. Fowler, J.W. Lauher, J. Am. Chem. Soc. 125 (2003) 12400.
[116] T. Hoang, J.W. Lauher, F.W. Fowler, J. Am. Chem. Soc. 124 (2002) 10656.
[117] J. Xiao, M. Yang, J.W. Lauher, F.W. Fowler, Angew. Chem. Int. Ed. 39 (2000) 2132.
[118] H. Morawetz, I.D. Rubin, J. Polym. Sci. 57 (1962) 669.
[119] Y. Le Page, S. Fortier, G. Donnay, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 2265.
[120] C.H.L. Kennard, G. Smith, T.M. Greaney, A.H. White, J. Chem. Soc., Perkin Trans. 2 (1976) 302.
[121] B.M. Foxman, in: R.D. Rogers, M.J. Zaworotko (Eds.), Crystal Engineering, vol. 33, ACA Transactions, Buffalo, NY, 1999.
[122] S. Skoulika, P. Dallas, M.G. Siskos, Y. Deligiannakis, A. Michaelides, Chem. Mater. 15 (2003) 4576, and reference therein.
[123] M.J. Vela, B.B. Snider, B.M. Foxman, Chem. Mater. 10 (1998) 3167, and references therein.
[124] M.J. Vela, V. Buchholz, V. Enkelmann, B.B. Snider, B.M. Foxman, Chem. Commun. (2000) 2225.
[125] A. Michaelides, S. Skoulika, M.G. Siskos, Chem. Commun. (2004) 2418.
[126] G.S. Papaefstathiou, Z. Zhong, L. Geng, L.R. MacGillivray, J. Am. Chem. Soc. 126 (2004) 9158.
[127] G.S. Papaefstathiou, I.G. Georgiev, T. Friščič, L.R. MacGillivray, Chem. Commun. (2005) 3974.
[128] A.N. Sokolov, L.R. MacGillivray, Cryst. Growth Des. 6 (2006) 2615.
[129] N.L. Toh, M. Nagarathinam, J.J. Vittal, Angew. Chem. Int. Ed. 44 (2005) 2237.
[130] J.Y. Lee, S.J. Hong, C. Kim, Y. Kim, Dalton Trans. (2005) 3716.
[131] A. Briceno, D. Leal, R. Atencio, G.D. de Delgado, Chem. Commun. (2006) 3534.
[132] Q. Chu, D.C. Swenson, L.R. MacGillivrary, Angew. Chem. Int. Ed. 44 (2005) 3569.
[133] C.-T. Chen, K.S. Suslick, Coord. Chem. Rev. 128 (1993) 293.
[134] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder, Coord. Chem. Rev. 222 (2001) 155.
[135] A.J. Blake, G. Baum, N.R. Champness, S.S.M. Chung, P.A. Cooke, D. Fenske, A.N. Khlobystov, D.A. Lemenovskii, W.-S. Li, M. Schröder, J. Chem. Soc., Dalton Trans. (2000) 4285.
[136] A.J. Blake, N.R. Champness, S.S.M. Chung, W.-S. Li, M. Schröder, Chem. Commun. (1997) 1675.
[137] T. Sampanther, J.J. Vittal, Cryst. Eng. 3 (2000) 117.
[138] M. Nagarathinam, J.J. Vittal, Angew. Chem. Int. Ed. 45 (2006) 4337.
[139] M. Nagarathinam, J.J. Vittal, Macromol. Rapid Commun. 27 (2006) 1091.
[140] T. Caronna, R. Liantonio, T.A. Logothetis, P. Metrangolo, T. Pilati, G. Reesnati, J. Am. Chem. Soc. 126 (2004) 4500.
[141] N. Shan, W. Jones, Green Chem. 5 (2003) 728.
[142] N. Shan, W. Jones, Tetrahedron Lett. 44 (2003) 3687.

[143] D.G. Amirsakis, M.A. Garcia-Garibay, S.J. Rowan, J.F. Stoddart, A.J.P. White, D.J. Williams, Angew. Chem. Int. Ed. 40 (2001) 4256.

[144] L.R. MacGillivray, Cryst. Eng. Commun. 6 (2004) 77.

[145] T.D. Hamilton, G.S. Papaefstathiou, L.R. MacGillivray, J. Solid State Chem. 178 (2005) 2409.

[146] D.B. Varshney, X. Gao, T. Friščič, L.R. MacGillivray, Angew. Chem. Int. Ed. 45 (2006) 646.

[147] L.R. MacGillivray, J.L. Reid, J.A. Ripmeester, J. Am. Chem. Soc. 122 (2000) 7817.

[148] D.B. Varshney, G.S. Papaefstathiou, L.R. MacGillivray, Chem. Commun. (2002) 1964.

[149] T. Friščič, D.M. Drab, L.R. MacGillivray, Org. Lett. 6 (2004) 4647.

[150] X. Gao, T. Friščič, L.R. MacGillivray, Angew. Chem. Int. Ed. 43 (2004) 232.

[151] L.R. MacGillivray, Data storage materials, US Patent 020,599 (2005).

[152] D. Braga, F. Grepioni, Angew. Chem. Int. Ed. 43 (2004) 4002.

[153] L.J. Barbour, Aust. J. Chem. 59 (2006) 595, and review articles therein.