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Anisotropic Movements of Coordination Polymers upon Desolvation: Solid-State Transformation of a Linear 1D Coordination Polymer to a Ladderlike Structure**

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Despite the inherent strong barriers of simultaneous bond breaking and formation in more than one direction, many interesting transformations of one coordination polymer to another in the solid state have been studied widely in recent years.[1–4] A notable success has already been achieved in positioning the ligands with olefinic double bonds in a coordination polymer, and in the isolation of their photodimerized products through single-crystal-to-single-crystal (SCSC) transformation.[5] Generally, these photochemical [2+2] cycloadditions of the olefinic double bonds are expected to occur with the minimal atomic and molecular movements when they are aligned parallel and within the range of 3.0–4.1 Å.[5–8] There are also a few interesting reports on rare phenomena, such as the anisotropic long-range molecular-movement-induced/assisted [2+2] photodimerizations of organic molecules that have been visualized in single crystals only through grazing incidence diffraction, atomic force microscopy, and near-field optical microscopy.[9] Indeed, long-range molecular movements have been demonstrated in a few coordination complexes by SCSC transformation.[10] However, the studies have not been extended to crystals that have lost their crystallinity or undergone a mild change in the crystal structure as a result of the desolvation process. To the best of our knowledge, cooperative anisotropic molecular movements resulting from desolvation in a coordination polymer have not been observed to date.

While we were investigating the photochemical activity of coordination polymers, we found that the double bonds in the desolvated crystals of the single-stranded coordination polymers $[Ag(\mu_2\text{-bpe})]_n^{n+}$ (bpe = 4,4′-bipyridylethylene) undergo [2+2] cycloaddition under UV irradiation. This polymer has neither Ag···Ag interaction nor satisfies Schmidt's topochemical criteria in the solvated structure. Such a reaction can occur only when the bpe ligands are preorganized during desolvation.[5–9] The transformation from a single-stranded to

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a ladder-type structure appears to be facilitated by Ag···Ag and π···π interactions accompanied by the anisotropic cooperative molecular movements of the adjacent linear chains upon desolvation. This notion has been further supported by X-ray powder diffraction experiments and IR spectroscopy. The details are presented herein.

Colorless thin crystals of $[Ag(\mu\text{-bpe})(H_2O)](CF_3CO_2)\cdot CH_3CN$ (**1**) were obtained by a layering method from equimolar solutions of bpe and $Ag(O_2CCF_3)\cdot H_2O$. The crystals became opaque immediately after removal from the mother liquor and disintegrated after some time. X-ray crystal structure determination at 223 K revealed the presence of linear 1D coordination polymers $[Ag(\mu\text{-bpe})]_n$ with the oxygen atom of a water molecule bonded to the Ag^I center (see Figure 1a). The nitrogen atom of the solvent CH_3CN is

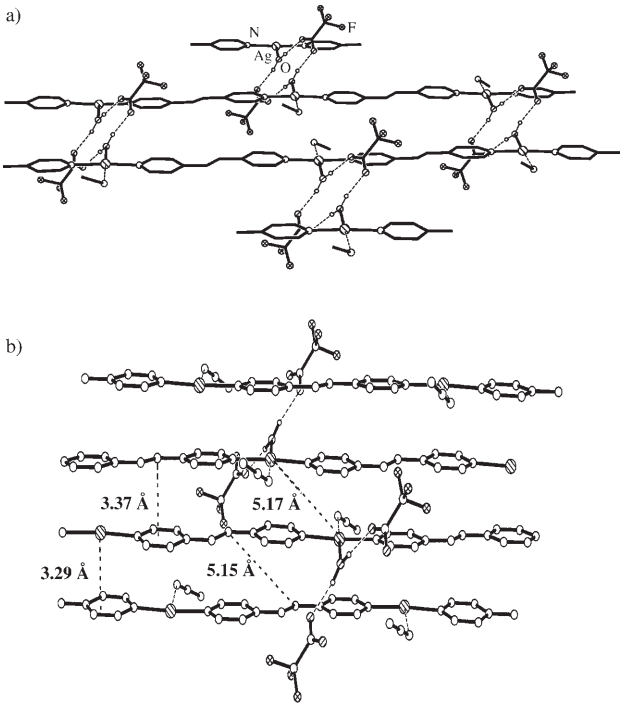


Figure 1. a) View of a portion of the hydrogen-bonded brick-wall-like structure in the crystal structure of **1**. b) View showing the non-alignment of double bonds and Ag atoms along the *b* axis in the packing. The disordered F atoms of the trifluoroacetate ions are not shown. The C–H hydrogen atoms have been omitted for clarity.

directed toward the Ag atom, and the Ag···N distance of 3.32 Å just exceeds the sum of the Van der Waals radii (3.27 Å). The hydrogen atoms of the coordinated water molecules from two neighboring polymeric strands bridge the oxygen atoms of two non-coordinated trifluoroacetate ions through hydrogen bonds (O–H···O, $d = 1.87$ Å, $D = 2.74$ Å, $\theta = 162°$) to form a 12-membered ring [notation $R_4^4(12)$],[11] similar to the analogous interactions reported in the literature.[12]

This connectivity leads to hydrogen-bonded, 2D brick-wall-like structures approximately in the *ac* plane, as a result of the *anti* dispositions of the Ag–O bonds in the polymer chains caused by crystallographic inversion at the double bonds. The closest Ag···Ag distances in this plane are 9.43 and 10.43 Å.

The adjacent polymeric strands are stacked along the *b* direction in such a way that the Ag^I atoms are close to a pyridyl ring (Ag···Py, 3.29 Å) and one carbon atom of the double bond is close to another pyridyl ring (C12···Py, 3.37 Å; see Figure 1b). The closest Ag···Ag and nonbonding interactions between the ethylenic carbon atoms of two consecutive layers are 5.17 and 5.15 Å, respectively. This finding clearly demonstrates that there is no Ag···Ag interaction, and that the silver atoms are not bridged by trifluoroacetate ligands and do not form the β-type motifs ((3.9 ± 0.2) Å), which can undergo photodimerizations with short-range molecular movements. Complex **1** satisfies the conditions for γ-type (> 5.1 Å) olefinic double bonds, which are clearly not expected to undergo photodimerizations in the solid state.[6,7]

As the crystal was desolvated and lost its crystallinity readily upon irradiation, the photoreactivity of the solvated crystal could not be studied. However, when a desolvated crystalline powder of **1** was irradiated by UV light for 8 h, complete conversion of the olefins to cyclobutane derivatives was observed. The ^{1}H NMR spectrum in $[D_6]$DMSO shows the complete disappearance of the olefinic proton signal at $\delta = 7.56$ ppm, a new signal attributable to cyclobutane protons at $\delta = 4.68$ ppm, and a shift in the bipyridyl proton signals from $\delta = 8.61$ and 7.65 ppm to $\delta = 8.35$ and 7.24 ppm, which confirms the formation of the expected photodimerized product (see Supporting Information).

Quantitative photodimerization on irradiation of desolvated **1** confirms that molecular movement occurs on removal of the solvents. The packing diagram of the crystal structure also shows clearly that there must be enough freedom for the reactive molecules to undergo the necessary lateral movements to reorganize once the solvents are removed.

The free movement of the coordination polymers, their reorganization from a linear 1D to a ladderlike structure, and the reorientation of the adjacent olefinic double bonds suitable for photodimerization in **1** on desolvation are evident from the isolation and characterization of colorless, platelike crystals of $[\{(\mu\text{-}O_2CCF_3)Ag\}_2(\mu\text{-bpe})_2]\cdot H_2O$ (**2**). Compound **2** was obtained on reaction of equimolar amounts of bpe and $Ag(O_2CCF_3)$ under different reaction conditions with the same solvents. The crystals obtained were of poor X-ray diffraction quality and readily lost lattice water to become opaque in air. Although the bpe ligands were severely disordered, which was further complicated by a crystallographic inversion center, the connectivity in the ladderlike 1D coordination polymeric structure has been proved beyond any doubt.

In **2** two linear polymers [(μ-bpe)Ag] are bridged by two trifluoroacetate ligands to form a double-stranded, molecular-ladder-like coordination polymer (Figure 2). The distances of Ag···Ag and two olefinic double bonds aligned in parallel are 3.15 and 3.62–4.06 Å, respectively. The π···π and Ag···Ag interactions provide thermodynamic stability to this ladder-type arrangement. The crystal structure of **2** signifies that we have successfully isolated a molecular-ladder-like coordina-

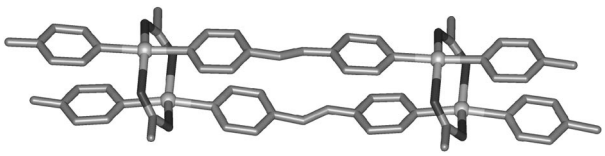


Figure 2. Perspective view of a portion of the 1D molecular ladder polymeric structure of **2**. Hydrogen atoms and disordered bpe ligands have been omitted for clarity.

tion polymer that satisfies the geometric criteria postulated by Schmidt for [2+2] photodimerizations.[6] Attempts to isolate crystals of **2** with better X-ray quality by changing the reaction conditions were in vain; they either resulted in crystals of poor X-ray quality, insoluble precipitate, or decomposition of the product to silver.

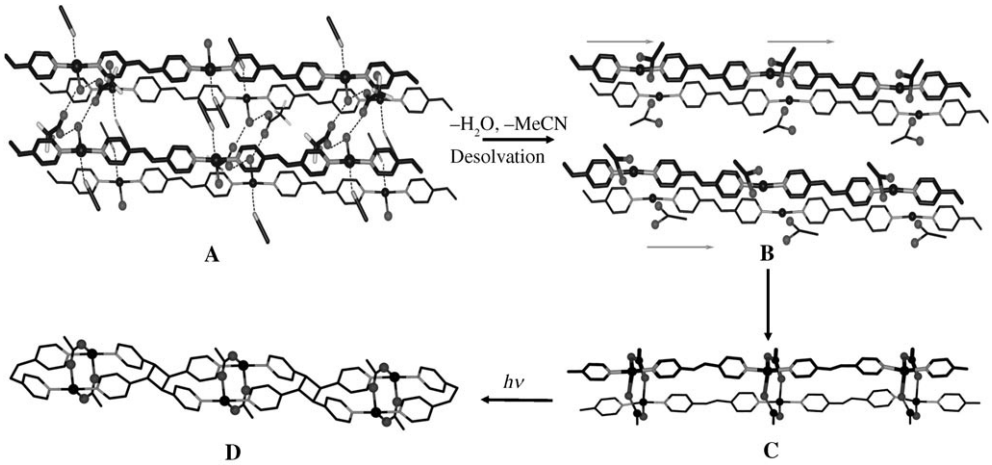
The desolvated crystalline powder of **2** was irradiated for 8 h and the ^{1}H NMR spectrum of the colorless product revealed that the product was completely photodimerized. This result supports the finding that the carboxylate-bridged silver dimer is a reliable supramolecular synthon for the alignment of bpe ligands as a silver coordination polymer. Furthermore, it confirms that the ladder structure is preserved in the desolvated **2**. But SCSC transformation was not observed because the single crystals disintegrated upon desolvation. The solvated **2** is not stable under UV irradiation similar to **1**.

The X-ray powder diffraction pattern of desolvated **1** matched reasonably well with that of desolvated **2** (see Supporting Information), which implies that the crystal structure and the orientations of the coordination polymers in the desolvated lattice of **1** are similar to those present in desolvated **2**. This XRD result helps visualizing the anisotropic molecular movements in **1**.

The transformation of a linear 1D coordination polymer to a ladder-type polymeric structure is depicted in Scheme 1. Immediately after removal of the coordinated water molecule and the lattice CH_3CN, the crystal structure starts to collapse, which is transmitted throughout the stacked layers. To balance the stress, simultaneous cooperative lateral movements of the coordination polymers and $CF_3CO_2^-$ ions occur within the crystal (**B**). During this phase-rebuilding process, the thermodynamically favored Ag···Ag interaction becomes activated between the adjacent strands along the *b* axis, rather than with the parallel strands in the *ac* plane that are nearly 10 Å away. The average Ag···O distance between the silver atom and the oxygen atom of the $CF_3CO_2^-$ ions is about 4.45 Å in **A**.

It is proposed that the trifluoroacetate ions migrate to bridge the adjacent silver atoms in the *b* direction. Such movements of the carboxylate groups that form bonds to the metal are well documented.[3c,d,5a] For example, in the topochemical conversion of a hydrogen-bonded to a covalently bonded supramolecular network, a carboxylate oxygen atom of the reduced Schiff base ligand from the neighboring molecule forms a bond to Zn^{II} guided by N–H···O hydrogen bonds on thermal dehydration.[3c,d] In this transformation, the distance between Zn^{II} and the oxygen atoms of the carboxylate group changed from 3.736(2) to 2.010(2) Å. On the other hand, molecular rotation of the trifluoroacetate group competes for coordination and forms a bridge between two Ag atoms.[5a] Completion of phase transformation leads to the formation of a ladder structure (**C**), but the bond breaking and bond making probably create high strain and the crystal disintegrates. This reveals that the influence of strain generated by desolvation of the crystal and the Ag···Ag and π···π interactions in the resultant lattice leads to the transformation and hence the molecular reactions within the crystalline solid.

The proposed mechanism is further corroborated by the solid-state FTIR spectra of desolvated **1** and **2**, which are exactly the same, and the bridging of two carboxylate oxygen atoms of the trifluoroacetate ion that is seen from the $\Delta\tilde{\nu}$(COO) value of 200 cm^{-1}, that is, the difference between the ν_{as}(COO) at 1661 cm^{-1} and ν_s(COO) at 1461 cm^{-1}.[13] The relatively higher values of ν_{as}(COO) and the $\Delta\tilde{\nu}$(COO) are a result of the asymmetric O–Ag–O arrangement in **2** (Ag···O distances of 2.71 and 2.59 Å). In a mixture of solvents, $AgBF_4$ and bpe produced a 3D network structure of the photodimerized ligand over a long period of time.[14] Clearly, the metal and ligand have rearranged in solution to give this unexpected product.



Scheme 1. Transformation of linear 1D strands in the crystal structure of **1** to a ladderlike arrangement upon desolvation. **A**: A portion of the crystal structure, **B**: proposed intermediate stage after desolvation, **C**: formation of a ladderlike structure, and **D**: photodimerized product. For clarity only one strand is shown for **C** and **D**.

A recent report by MacGillivray and co-workers on the desolvation-induced phase transition and partial loss of crystallinity of a compound that undergoes photodimerization describes that the alignment of bpe ligands through N–H···N interac-

tion was not disturbed on removal of the solvent.[8b] Although the influence of solvents on supramolecular transformation from linear 1D strands to a ladderlike coordination polymer on desolvation is not visualized through SCSC transformation, we have used Schmidt's criteria for the photodimerization[6] to investigate this phenomenon for the first time, along with X-ray powder diffraction, IR spectroscopy, and other analytical data. The detailed study of this type of cooperative, anisotropic, long-range molecular movement in a coordination polymer will not only give further insight into the solid-state reaction mechanism, but also direct inorganic coordination polymers toward materials science with great impact.

Experimental Section

1: A solution of bpe (0.018 g, 0.1 mmol) in CH_3OH (1 mL) was layered over an aqueous solution (1 mL) of $Ag(O_2CCF_3)\cdot 2H_2O$ (0.023 g, 0.1 mmol) with CH_3CN (3 mL) as a middle buffer layer. Colorless, dendrimer-shaped plates crystallized at the solvent junction. Yield: 0.07 g, 26%. IR (nujol mull): $\tilde{\nu}=1661$(m), 1604 (m), 1461(s), 1377(m), 1203(m), 1112(m), 1071(w), 829(m), 717 cm^{-1} (m). ^1H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=8.61$ (d, 4H; Py-H), 7.65 (d, 4H; Py-H), 7.56 ppm (s, 4H; CH=CH). C,H,N analysis (%) calcd for $C_{14}H_{10}F_3N_2OAg$ (desolvated **1**): C 41.71, H 2.50, N 6.95; found: C 41.67, H 2.36, N 6.78.

UV irradiation of **1**: Powdered **1** (15 mg) in between glass slides was irradiated with a Xe lamp (60 W) for approximately 8 h. IR (nujol mull): $\tilde{\nu}=1676$(m), 1604(m), 1462(s), 1377(m), 1200(m), 1112(m), 1067(w), 834 cm^{-1} (m). ^1H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=$ 8.35 (d, 4H; Py-H), 7.24 (d, 4H; Py-H), 4.68 ppm (s, 4H; CH-CH). C,H,N analysis (%) calcd for $C_{28}H_{20}F_6N_4O_4Ag_2$: C 41.71, H 2.50, N 6.95; found: C 41.67, H 2.36, N 6.92.

2: A solution of bpe (0.090 g, 0.5 mmol) in methanol (5 mL) was added to an aqueous solution (5 mL) of $Ag(O_2CCF_3)\cdot 2H_2O$ (0.115 g, 0.5 mmol), and the white precipitate formed was dissolved by further addition of CH_3CN (15 mL). The clear solution was filtered and the filtrate was slowly evaporated. Small, colorless, very thin, platelike crystals separated out after 3 days and were filtered and dried under vacuum. Yield: 0.08 g, 26%. IR (nujol mull): $\tilde{\nu}=1661$(m), 1602(m), 1461(s), 1377(m), 1203(m), 1112(m), 1071(w), 829(m), 717 cm^{-1} (m). ^1H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=8.61$ (s, 4H; Py-H), 7.65 (d, 4H; Py-H), 7.56 ppm (s, 4H; CH=CH). C,H,N analysis (%) calcd for $C_{14}H_{12}F_3N_2O_3Ag$: C 39.93, H 2.83, N 6.65; found: C 39.14, H 2.92, N 6.54; calcd for $C_{14}H_{10}F_3N_2O_2Ag$ (desolvated **2**): C 41.71, H 2.50, N, 6.95; found: C 41.67, H 2.47, N 6.78.

UV irradiation of **2**: Powdered **2** (15 mg) in between glass slides was irradiated with a Xe lamp (60 W) for approximately 8 h. IR (nujol mull): $\tilde{\nu}=1661$(m), 1602(m), 1461(s), 1377(m), 1203(m), 1112(m), 1071(w), 829(m), 717(m), 530 cm^{-1} (m). ^1H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=8.35$ (d, 4H; Py-H), 7.24 (d, 4H; Py-H), 4.68 ppm (s, 4H; CH–CH). C,H,N analysis (%) calcd for $C_{28}H_{20}F_6N_4O_4Ag_2$: C 41.71, H 2.50, N 6.95; found: C 41.67, H 2.36, N 6.92.

X-ray crystallography: Crystal data were collected on a Bruker APEX diffractometer with a CCD detector and graphite-monochromated $Mo_{K\alpha}$ radiation using a sealed tube (2.4 kW) at 223(2) K. Absorption corrections were made with the program SADABS[15] and the crystallographic package SHELXTL[16] was used for all calculations.

Crystal data for **1**: triclinic, space group $P\bar{1}$, $a=10.0330(8)$, $b=$ 10.2394(8), $c=10.9499(8)$ Å, $\alpha=104.260(2)$, $\beta=100.719(2)$, $\gamma=$ 118.696(1)°, $V=893.0(1)$ Å^3, $\rho_{calcd}=1.719$ g cm^{-1}, $Z=2$. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R1=$ 0.0364, $wR2=0.0879$, GoF = 1.056 for 2896 ($I\geq 2\sigma(I)$) reflections. Crystal data for **2**: monoclinic, space group $P2_1/m$, $a=7.349(2)$, $b=$ 17.781(5), $c=12.643(4)$ Å, $\beta=98.552(6)$°, $V=1633.6(8)$ Å^3, $Z=4$.

CCDC-295995 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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