Photochemical [2 + 2] cycloaddition as a tool to study a solid-state structural transformation†

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The solid-state structural transformation of the hydrogen-bonded 1D coordination polymer [Cd(bpe)($CH_3COO)_2$-(H_2O)]$_n$, to a ladder-type structure is evident from a photochemical [2 + 2] cycloaddition reaction forming 100% *rctt*-cyclobutane isomer.

Many interesting solid-state structural transformations of coordination polymers driven by thermal and photochemical methods have been investigated in detail in the past using single crystal X-ray crystallography.[1] The topochemical [2 + 2] photodimerization reactions can easily be monitored indirectly by NMR spectroscopy and analytical techniques.[2–8] But thorough evaluation of the thermally induced solid-state transformations reported indicates that these reactions cannot be investigated that easily using these solution methods.[1] For example, that the topochemical conversion of a hydrogen-bonded to a covalently bonded supramolecular network structure on thermal dehydration results in the coordination of a carboxylate oxygen atom of the ligand from the neighboring molecule to Zn(II) guided by N–H···O hydrogen bonds can only be confirmed by X-ray structure determination.[9] Hence, the one and only way of characterizing this type of transformation unequivocally in the solid is single crystal X-ray diffraction techniques. Due to this, topochemical reactions have been either overlooked or not amenable in systems which cannot sustain single crystalline nature during structural transformation.[10] Still there are a few reports which provide hope that the loss of single crystals suitable for X-ray studies is not the end of studying solid-state structural transformations, and also state the need for new tools to unravel the structure and packing pattern.[1,8,11]

In this communication, we demonstrate that it is possible to follow a dehydration induced structural transformation in a system which has lost its single crystalline nature, using the *photodimerization* reaction as an invaluable tool. To date, attention has been focused on (i) the alignment of photoactive molecules congenial for photochemical [2 + 2] cycloaddition reactions in the first place, either in organic or in coordination complexes, and (ii) 100% isolation of a single stereospecific photodimerized product in the solid-state.[2–8] Hence, application of a partially photodimerizable coordination polymer in a 100% photodimerizable system through dehydration is yet to be reported. This may be due to the difficulty of studying molecular movements in crystals which do not retain their single crystalline nature after the reaction.

[Cd(bpe)($CH_3COO)_2$(H_2O)]$_n$ (**1**) was isolated as colorless crystals from the slow evaporation of a solution containing equimolar amounts of 4,4′-bipyridylethylene (bpe) and Cd($CH_3COO)_2$·2H_2O in an ethanol and water mixture.‡ The cadmium atom and the oxygen of the water molecule lie on a twofold axis and there is an inversion centre at the midpoint of the ethylenic double bond of the bpe ligand. The hepta coordinated Cd(II) atom consists of two N atoms of the two bpe units, four oxygen atoms of the bidentate and the bridged acetate ions and an O atom of a water molecule. The bpe ligands bridge adjacent Cd(II) atoms to form a linear 1D coordination polymer. The bidentate acetate ions are disposed above and below the polymeric strand shown in Fig. 1a.

The coordination polymers are arranged in parallel approximately in the *ac* plane and are hydrogen-bonded to each other. The hydrogens of the coordinated water molecules form complementary hydrogen bonds to the oxygens of the chelating acetate ion in the chain above and below the plane (O–H···O, d = 1.80(1) Å, D = 2.700(4) Å, θ = 173(5)°). The nonbonding C···C distance of the ethylenic carbon atoms between the two bpe ligands in the adjacent chains is 4.33 Å and the respective torsion angle is 106° which shows that they are arranged in an anti-parallel or criss-cross fashion. This complimentary hydrogen bonding leads to 2D sheets where all the 1D coordination polymers are aligned

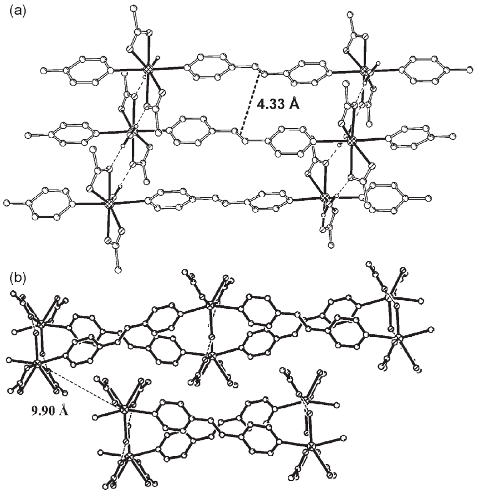

Fig. 1 (a) A view of a portion of the hydrogen-bonded 1D polymer **1** (hydrogen atoms are omitted for clarity except water). (b) Another view showing the criss-cross alignment of the ethylenic double bonds and the adjacent layer (hydrogens are not shown).

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along the *a*-axis as shown in Fig. 1. The distance between the two neighbouring Cd(II) in the hydrogen-bonded polymer chain is 5.51 Å. The closest Cd···Cd distance between the adjacent *ac* layers is 9.90 Å.

From the structure it is clear that the coordinated water molecules enforce congestion in the packing and lead to alignment of the C=C bonds in a criss-cross fashion instead of a parallel fashion. Though anti-parrallel alignment of the ethylenic double bonds does not conform to Schmidt's topochemical criteria for photochemical [2 + 2] cycloaddition in the solid-state, there exist a few reports on the isolation of either single *rctt*-tpcb [tetrakis(4-pyridyl)cyclobutane] or a mixture of *rctt*- and *rtct*-tpcb isomers.[12]

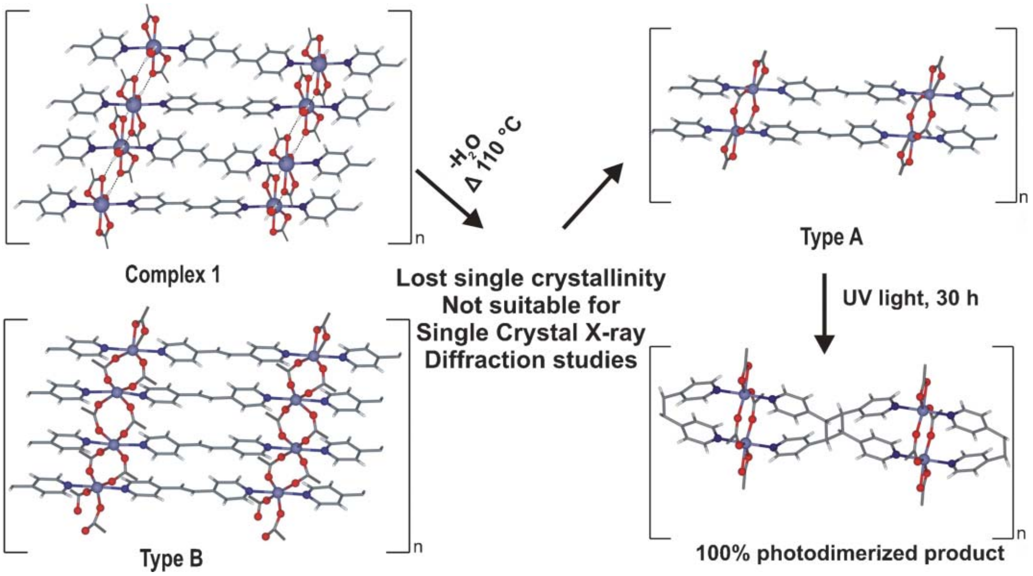
The ^1H NMR spectrum of the compound in d_6-DMSO obtained from irradiation of 30 mg of crystals of **1** in a petri dish using UVA lamps for 30 h shows peaks at 8.35, 7.24 and 4.68 ppm in addition to signals from unreacted **1**.[13] From the integration of the signals it is found that the double bonds have partially photodimerized (∼33%) to the *rctt*-tpcb derivative. Prolonged irradiation of **1** for up to 60 h did not improve the percentage of photodimerized product. The formation of the single *rctt*-tpcb isomer may be due to pedal-like motion of the bpe ligands which partially reorient in a parallel fashion before photodimerization.[12,14]

The molecular motion assisted 100% photodimerization of crystal **1** due to grinding is not observed and further the X-ray powder diffraction pattern of the crystals of **1** ground for 5 min agrees well with the simulated powder pattern of **1**. The TGA data of irradiated **1** support that the coordinated water molecule is fully intact in the crystal during grinding and on irradiation. This also raises the question of whether it is possible to realign the double bonds such that 100% photochemical [2 + 2] cycloaddition reaction can be achieved on removal of the coordinated water molecule as we have proposed in an earlier paper.[8]

The TGA data of the crystals of **1** confirm that the first weight loss of 4.3% in the range 67–106 °C is due to the loss of a coordinated water molecule. The nonbonding distance between Cd(II) and the oxygen atom of the adjacent $CH_3CO_2^-$ ion hydrogen-bonded to the water molecule is 4.44 Å. The loss of an aqua ligand at low temperature indicates the ease of formation of a new $Cd–OC\{O\}CH_3$ bond after water removal and hints that there is a possibility of topochemical structural transformation as observed in the literature.[1,9,10]

The crystal disintegrates on heating above 60 °C and the TGA data of the crystals heated at 110 °C for 3 h show complete loss of coordinated water molecules. The X-ray powder pattern of the dehydrated crystals of **1** shows that the crystallinity is lost by ∼20% and there is a phase change compared to the parent sample **1**. Due to the loss of the single crystalline nature, the solid-state structures of dehydrated **1** could not be determined by X-ray crystallography. Our attempts to grow single crystals were also not successful.

However, the ^1H NMR spectrum of the dehydrated **1** obtained after irradiation for 30 h shows 100% conversion to the *rctt*-cyclobutane ring. This implies that the bpe molecules are aligned parallel in pairs in dehydrated **1**. This result indicates that on removal of the coordinated water, migration of the acetate ion takes place in addition to the cooperative pedal-like motion of the bpe ligands. It may be proposed that the hydrogen-bonded oxygen atom of the acetato ligand now bridges the neighboring Cd(II) ion after water removal. Such migration of carboxylate groups during solid-state structural transformations have been noted previously.[8–10,15] The strain created in this process results in the cleavage of crystals and leads to the transformation of the hydrogen-bonded 1D coordination polymer into the most expected and thermodynamically favorable 1D ladder-type coordination polymer, Type A as shown in Scheme 1.[7,8] There is a possibility that this migration of acetate ions may also produce a 2D coordination polymeric structure (Type B shown in Scheme 1). A quick search of CSD[16] reveals that the Type B structure is not known so far. On the other hand, coordination polymers having ladder structures have been noted before.[7,8,17] Moreover, the formation of 100% *rctt*-cyclobutane ring can only be understood from the ladder structure.



Scheme 1 Evaluating the most favourable structure after solid-state transformation on dehydration.

The solid-state ^{113}Cd NMR spectral signal at 94.64 ppm is deshielded on dehydation of **1** from 58.26 ppm. Based on theoretical calculations, the change in the chemical shifts may be attributed to the formation of acetate bridged dimeric species.[18] Further, the change of seven coordinated cadmium(II) in **1** to six coordinated cadmium(II) during dehydration also supports this deshielding and the proposed molecular structure.[18] This deshielding of the dehydrated product in comparison to the hydrated product agrees well with the proposed bridged 1D ladder-type coordination polymer where the acetate ion bridges the two linear Cdbpe polymeric chains.

In summary, strong complementary intermolecular hydrogen bonds of the coordinated water molecule with the acetate ions in **1** did not allow cooperative molecular movements to take place completely leading to 100% photodimerization. However the closer distance between Cd(II) and the neighbouring oxygen atom of the acetate ligand, which are connected by hydrogen bonding through the aqua ligand, indicates the possibility of formation of a new Cd–OC{O}CH_3 bond upon removal of the aqua ligand at relatively low temperature. Thermal dehydration causes cooperative pedal-like motion between the adjacent bpe molecules disposed in a criss-cross fashion to form a ladder-like structure with well-aligned bpe pairs ready for 100% photodimerization reaction to furnish the *rctt*-cyclobutane ring exclusively. Although this topochemical rearrangement is closely related, it is distinctly different from the anisotropic movements of 1D coordination polymers observed before.[8] In this work, the photodimerization reaction has been used as an invaluable tool to monitor the thermally induced structural transformation resulting in samples where single crystal X-ray studies could not be used. These results also reiterate that it is possible to predict the most favorable structure after solid-state structural transformation. Exploitation of the crystal structure and its detailed packing will surely lead to productive results towards tuning photodimerization reactions and solid-state reactions, in general.

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Notes and references

‡ Complex **1**: bpe (0.09 g, 0.5 mmol) in 5 ml of ethanol was added to $Cd(CH_3CO_2)_2 \cdot 2H_2O$ (0.135 g, 0.5 mmol) in 5 ml of ethanol. A thick milky white precipitate formed immediately and was dissolved by adding 9.5 ml of H_2O dropwise to the reaction mixture. The clear solution was filtered and kept for recrystallization. Colorless cubic blocks were separated out in 2 days. The crystals were filtered, washed with acetone, ether and dried *in vacuo*. Yield: (0.15 g, 69%). Found: C, 44.54; H, 4.16; N, 6.37. $C_{16}H_{18}N_2O_5Cd$ requires C, 44.62; H, 4.21; N, 6.50%. δ_H (300 MHz; d_6-DMSO; 298 K) 8.61 (4H, d, Py–H), 7.65 (4H, d, Py–H), 7.56 ppm (4H, s, CH=CH); δ^{113}Cd CPMAS solid-state (400 MHz; 4 mm probe; 298 K; $Cd(CH_3CO_2)_2 \cdot 2H_2O$) 58.26.

Dehydrated product of **1**: Crystals of **1** were heated at 110 °C for 3 h, cooled and dried *in vacuo*. Found: C, 46.41; H, 4.01; N, 6.68; $C_{16}H_{16}N_2O_4Cd$ requires C, 46.56; H, 3.91; N, 6.79%. δ_H (300 MHz; d_6-DMSO; 298 K) 8.62 (4H, d, Py–H), 7.64 (4H, d, Py–H), 7.55 ppm (4H, s, CH=CH); δ^{113}Cd CPMAS solid-state (400 MHz; 4 mm probe; 298 K; $Cd(CH_3CO_2)_2 \cdot 2H_2O$) 94.64.

UV irradiation of **1**: The crystals were irradiated for 30 h. δ_H (300 MHz; d_6-DMSO; 298 K) 8.61 (4H, d, Py–H), 8.35 (4H, d, Py–H), 7.65 (4H, d, Py–H), 7.56 (4H, s, CH=CH), 7.24 (4H, d, Py–H), 4.68 (4H, s, CH–CH).

UV irradiation of the dehydrated product of **1**: Crystals were irradiated for 30 h. δ_H (300 MHz; d_6-DMSO; 298 K) 8.35 (4H, d, Py–H), 7.22 (4H, d, Py–H), 4.65 (4H, s, CH–CH). Found: C, 46.48; H, 4.01; N, 6.76. $C_{16}H_{16}N_2O_4Cd$ requires C, 46.56; H, 3.91; N, 6.79%.

Crystal data for $[Cd(bpe)(CH_3COO)_2(H2O)]_n$ **1**: Monoclinic, space group *C*2/*c*, *M* = 430.72, *a* = 13.2612(8), *b* = 14.7065(9), *c* = 8.6573(5) Å, β = 92.744(1), *V* = 1686.5(2) Å^3, ρcalcd = 1.696 g cm^{-1}, and *Z* = 4. In the final least-squares refinement cycles on $|F|^2$, the model converged at *R*1 = 0.0398, w*R*2 = 0.0873, GoF = 1.1791 for 1368 ($I \geqslant 2\sigma(I)$) reflections. One H atom of the aqua ligand was located in the Fourier difference map and the DFIX option was used to constrain the position in the least-squares cycles. Crystal data were collected at 223(2) K on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα radiation. CCDC 659646 for **1**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713586f

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