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Solid-State Photochemical Behavior of a Triple-Stranded Ladder Coordination Polymer

Abdul Malik Puthan Peedikakkal and Jagadese J. Vittal*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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A triple-stranded ladder coordination polymer, $[Pb_3(bpe)_3(O_2CCF_3)_4(O_2CCH_3)_2]$ [bpe = *trans*-1,2-bis(4-pyridyl)ethene] undergoes a photochemical [2 + 2] cycloaddition reaction in the solid state to furnish 100% *rctt*-tetrakis(4-pyridyl)cyclobutane (*rctt*-tpcb) in two steps via cooperative molecular movements of the partially dimerized products formed initially.

Molecular-ladder structures are of particular interest in the coordination polymers (CPs) over the past few years[1] because of their fascinating structural and novel magnetic,[2] electronic, and optical properties.[3] They have been classified as noninterpenetrated normal,[4] quasi,[5] twist,[6] undulating,[7] alternate,[8] and rope[2b,9] ladders based on their metal connectivity with ligands in rails and rungs. Although these simple ladder-like CPs are well-known, three-legged, i.e., triple-stranded, 1D ladder CP topology is still uncommon.[10–12] In all of the triple-stranded CPs reported so far, the rungs have been mainly occupied by the carboxylate groups. Gao et al. reported the first example, $[Zn_3(\mu\text{-}O_2CCH_3)_4(4,4'\text{-bpy})_3\{N(CN)_2\}_2]$, where 4,4′-bipyridine (4,4′-bpy) was used as rails in the ladder.[10] A closely similar structure is also known for the Co^{II} metal ion in which *trans*-1,2-bis(4-pyridyl)ethane was employed as rails.[11] Two more identical triple-stranded CPs, $[Zn_3(4,4'\text{-bpy})_3(\mu\text{-}O_2CCH_3)_4(H_2O)_2](X)_2\cdot H_2O$, were also reported with two different anions.[12]

Ladder CPs are some of the most suitable structures to align *trans*-1,2-bis(4-pyridyl)ethene (bpe) molecules in infinite pairs for [2 + 2] cycloaddition reactions.[13] Owing to their bridging ability, acetate and trifluoroacetate are efficiently utilized to orient the C═C bonds in bpe ligands[14] to satisfy the topochemical criteria.[15] While investigating the chemistry of Pb^{II} CPs with the bpe ligand, we isolated a triple-stranded CP, $[Pb_3(\mu\text{-bpe})_3(\mu\text{-}O_2CCH_3)_2(\mu\text{-}O_2CCF_3)_4\ \{O_2CCF_3\}_2]_n$ (**1**), where three bpe ligands are aligned parallel, suitable for [2 + 2] cycloaddition reactions. Interestingly, photodimerization reaction in a solid that has more than a pair of double bonds, satisfying Schmidt's topochemical criteria, has been rarely investigated.[16] Shan and Jones investigated a cocrystal bpe.tca (where tca = tricarballylic acid) in which three bpe molecules have been aligned in parallel fashion with the C═C distances of 3.82 Å, to yield *rctt*-tetrakis(4-pyridyl)cyclobutane (*rctt*-tpcb) up to 90% under UV light.[16a] In

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*To whom correspondence should be addressed. E-mail: chmjjv@nus.edu.sg.

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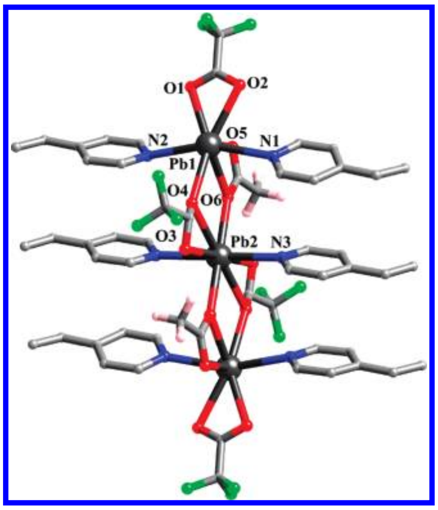

Figure 1. (a) Perspective view of the coordination geometry at the Pb^{II} centers in **1**. The C−H hydrogen atoms of pyridyl rings and disordered fluorine atoms are not shown for clarity.

this organic cocrystal where the bpe molecules are oriented by the relatively weak hydrogen bonds, we thought it would be interesting to investigate the photochemical behavior of **1** where the bpe ligands are held strongly by the coordination bonds. The results of our investigations are described in this paper.

Colorless rodlike crystals of **1** were formed by the slow evaporation of a DMF solution containing bpe, $Pb(O_2CCH_3)_2$, and trifluoroacetic acid in a molar ratio of 1:1:1.3. It may be noted that instant mixing of the reactants under similar experimental conditions yields the known 1D CP $[Pb(bpe)(O_2CCF_3)_4(OAc)]_n$ [X-ray diffraction (XRD) patterns in Figure S3 of the Supporting Information].[17] Single-crystal X-ray crystallography reveals that **1** is a linear CP comprised of three [Pb(bpe)] chains joined by $CH_3CO_2^-$ and $CF_3CO_2^-$ ligands, as shown in Figure 1. In the asymmetric unit, there are two crystallographically independent Pb^{II} centers. Of these, Pb1 present in the terminal strand has highly distorted *hemidirected* heptacoordinate geometry and Pb2 in the middle strand adopts *holodirected* hexagonal-bipyramidal geometry. Crystallographic inversion centers present at Pb2 and at the center of the C=C double bond of the middle strand generate triple-stranded ribbonlike 1D CP.

In this polymer, Pb1 and Pb2 are strongly coordinated to two pyridyl nitrogen atoms of bpe occupying the axial positions [Pb1−N1, 2.661(6) Å; Pb1−N2, 2.635(6) Å; Pb2−N3, 2.631(8) Å]. The oxygen atoms of the terminal $CF_3CO_2^-$ ligands are coordinated to Pb1 in chelating mode [Pb1−O1, 2.669(6) Å; Pb1−O2, 2.705(6) Å]. The infinite $[Pb(O_2CCF_3)(bpe)]$ chains are bridged by two trifluoroacetate ligands [Pb1−O4, 2.705(7) Å; Pb2−O4, 2.726(8) Å; Pb2−O3, 2.626(15) Å] and the two acetate ligands [Pb1−O(5, 2.340(6) Å; Pb1−O6, 2.574(6) Å; Pb2−O6, 2.629(6) Å] both in $\eta^{1,3}$ mode, as shown in Figure 1. The three bpe ligands in the adjacent strands are aligned parallel with a distance (d_1) of 3.93 Å between the center of the C=C double bonds. These alignments are reinforced by the strong $\pi\cdots\pi$ interactions between the pyridyl rings.

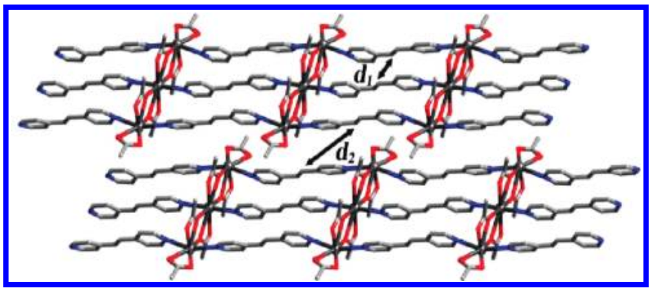

Figure 2. View of the packing of two adjacent triple strands. The hydrogen and fluorine atoms have been omitted for clarity.

The three-stranded 1D ladder CPs are running along the *b* axis as shown in Figure 2 with a minimum nonbonded Pb−Pb distance of 7.046 Å between the interstrands. This infers that the bpe ligands in the adjacent 1D ladder are aligned in parallel but slip stacked with a centroid distance (d_2) of 7.614 Å between the C=C double bonds of bpe in the adjacent 1D ladders, as shown in Figure 2, which are too far away to be photochemically reactive.

When the single crystals were subjected to UV light for a period of 40 min, the crystals of **1** undergo a photochemical reaction to produce *rctt*-tpcb in 67% yield, as monitored by ^{1}H NMR spectroscopy, and preserve the transparency of the crystals, as revealed by optical microscopy. However, single crystallinity was not maintained during the course of the reaction.[13a] In **1**, only a bpe pair is expected to undergo a [2 + 2] cycloaddition reaction and the third coordinated bpe ligand is likely to remain unreacted in the crystal lattice. Hence, the observed percentage of the *rctt*-cyclobutane derivative exactly matches the expected value based on the crystal structure. When the single crystals were ground to powder and subjected to UV irradiation for a period of 1 h, only 40% photoconversion was observed. However, when the ground powder sample was irradiated for a period of 40 h, 100% conversion was observed. The ^{1}H NMR spectrum of the irradiated product dissolved in DMSO-d_6 shows the complete disappearance of the olefinic protons at 7.53 ppm, the appearance of the cyclobutane protons at 4.65 ppm, and the corresponding shifts in the bipyridyl protons from 8.60 and 7.61 ppm to 8.32 and 7.22 ppm. Quantitative photoreactivity of the powdered sample compared to the single-crystal behavior is quite unexpected based on the crystal packing in **1**.

In order to understand the unusual reactivity of **1**, the photoreaction of single crystals and ground single crystals (manually ground for 1 min) was monitored by ^{1}H NMR spectroscopy at various time intervals. A plot of the percentage conversion versus time displayed in Figure 3 clearly reveals that the photoreaction occurs in two steps in both single-crystals and powdered samples. It is interesting to find that the single crystals react faster in the initial stage, producing 67% dimer after 1 h of UV irradiation, but with cracks appearing, they were found to disintegrate to microcrystalline particles upon further exposure to UV light. The yield of *rctt*-tpcb steadily increased and reached 100% in 60 h. The formation of *rctt*-tpcb appeared to be accompanied by the molecular movements and repacking of its lattice contents. The reorganization of adjacent strands may be necessary to reduce the strain caused by the partial formation of the cyclobutane derivative[18] in the triple-stranded polymer.

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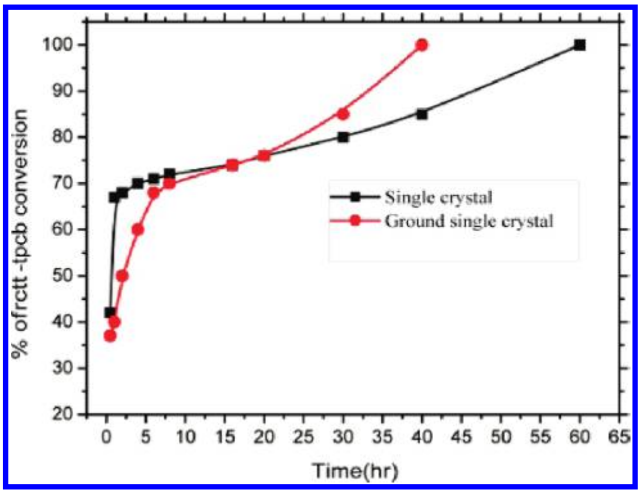


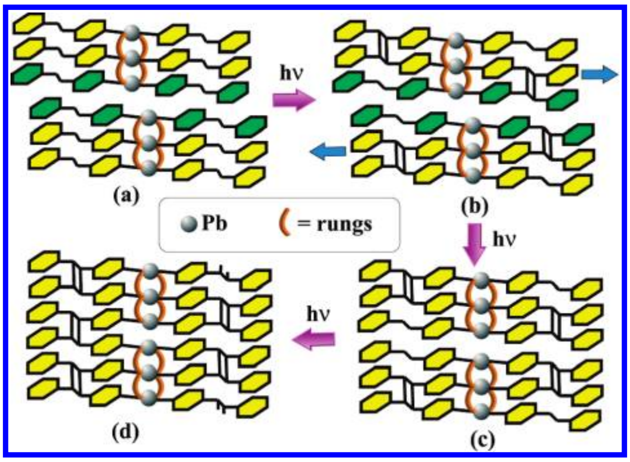
Figure 3. Plots of the product formed versus time for single crystals (black) and ground single crystals (red).

The resulting repacking appears to involve the parallel alignment of the unreacted bpe ligands. This will also promote $\pi\cdots\pi$ interactions, which may be responsible for its stability. Hence, the prolonged UV irradiation of **1** resulted in the formation of 100% of the *rtct*-tpcb derivative. Such movements of 1D CPs in the crystals have been noted before.[19]

The first step of photodimerization, which furnished 67% of the product, can occur in more than two ways. In the first mechanism, the cycloaddition takes place in a highly orderly fashion between the top two strands and all the bpe ligands in the third strand are left unreacted. This pathway requires the top strand of the next adjacent strand to contain all of the unreactive bpe ligands. In other words, only if the bottom two strands of the adjacent polymers undergo cyclization reaction completely can the remaining unreacted bpe between the adjacent triple strands undergo dimerization in the second step to give the expected 100% cyclobutane derivative.

In the second pathway, the dimerization reaction occurs between any bpe pairs in the triple strand either randomly or alternately. This will require cooperative movements of all of the 1D CPs in the lattice to establish $\pi\cdots\pi$ contacts to increase the stability of this intermediate product. Thus, the 33% unreacted bpe pairs are well aligned in parallel on the top and bottom of the adjacent strands at the end of the first step, which satisfy the Schmidt criteria and allow it to undergo photodimerization reactions. Although both of the proposed reaction pathways are equally probable, the second pathway, as shown in Scheme 1, may be preferable from a thermodynamic point of view (increase of the entropy and enthalpy).

Scheme 1. Plausible Photodimerization Pathway in **1**[a]



[a] The bpe ligands in the adjacent strands are shown in green. Parts: (a) packing in **1**, (b) random dimerization between the C=C bonds in each strand, (c) reorganization at the end of the first step (67% conversion) to realign the remaining double bonds, and (d) 100% photodimerized product.

In summary, a triple-stranded 1D CP has been synthesized and structurally characterized and its photochemical [2 + 2] cycloaddition reaction has been investigated in the solid state. This triple-stranded polymer undergoes a photodimerization reaction to yield 100% of the *rctt*-tpcb derivative, which is quite unexpected based on the crystal packing. This photochemical [2 + 2] cycloaddition reaction has been found to take place in a two-step process. Here, Schmidt's topochemical postulate has been used as a guide to rationalize the observed photoreactive behavior. The 67% photodimerization in the first step is proposed to occur between the bpe pairs of the triple-stranded CP randomly or orderly and accompanied by movements of the adjacent strands cooperatively to establish $\pi\cdots\pi$ interactions between 33% of the remaining unreacted bpe pairs in the interstrands. The formation of the 100% photodimerized product can easily be understood from this proposed intermediate structure. Although anisotropic movements of CPs have been observed before, such movements of 1D CPs induced during the photochemical reaction appear to be unique and highlight a new paradigm of cooperativity among the polymeric strands during photochemical reactions.

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Supporting Information Available: Experimental details, XRD, TGA, DSC, crystal data in CIF format, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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