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Structural Transformations

Single-Crystal-to-Single-Crystal Transformations of Two Three-Dimensional Coordination Polymers through Regioselective [2+2] Photodimerization Reactions**

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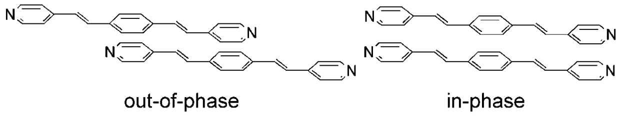
In the field of supramolecular chemistry, single-crystal-to-single-crystal (SCSC) structural transformations have received considerable attention in recent years.[1,2] In particular, reactions within crystalline coordination polymers leading to the formation of covalent bonds have been the focus of intense interest because they offer the possibility of producing regio- or stereospecific organic compounds. Such compounds may not always be accessible or easily obtained using more traditional solution-based procedures.[2,3] Unfortunately, the SCSC process often fails because crystals are unable to maintain their single-crystalline character owing to the inherent barriers to simultaneous bond formation and/or cleavage in more than one direction.[2]

Photochemical [2+2] cycloadditions are a particularly interesting type of organic solid-state reaction that can be used to create new covalent bonds not only in photoreactive organic compounds[4] but also in photoreactive coordination complexes.[5–9] To date, only a few photochemical [2+2] cycloaddition reactions accompanying SCSC transformations[4b,c] have been observed in discrete coordination complexes[5] and coordination polymers.[6]

SCSC transformations associated with photodimerization reactions involving ligands that are part of a three-dimensional coordination network are extremely rare.[6c] This is because positional and geometrical constraints placed upon bridging ligands, through their incorporation in a network structure, may not allow the reactive groups to come into the appropriate positions for the generation of new bonds. Even if the reactive centers are in a suitable position and orientation for new bond formation, once the photodimerization process begins within a network, the subsequent movement of ligands within the 3D structure may make further reactions within the crystal difficult or even impossible.

In the examples of SCSC transformations referred to above, the bridging ligand participating in the photodimerization process normally has only one olefinic bond, for example, 1,2-bis(4-pyridyl)ethane (bpe). Pairs of these bridging ligands, appropriately aligned, form similar cyclobutane derivatives.[5,6a,c] Those containing two or more olefinic bonds are seldom employed,[6b] and no photoreactive 3D coordination polymers constructed using ligands containing multiple vinyl bonds have been reported.

The ligand 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1,4-bpeb) has two C=C bonds, which thus allows pairs of ligands to link through either one or two cyclobutane units. If the alignment of the ligands within the pair is “out-of-phase”, as indicated in Scheme 1, then a single cyclcobutane unit can be formed from the two ligands. If both are “in-phase”, then it is possible to form two cyclobutane units. In some particularly elegant work, MacGillivray and co-workers have used complementary hydrogen-bonded interactions to hold a pair of 1,4-bpeb molecules in an in-phase configuration.[10] Irradiation with light leads to the formation of one or two cyclobutane units between the 1,4-bpeb molecules.



Scheme 1. In-phase and out-of-phase arrangements of 1,4-bpeb molecules.

The combination of dicarboxylate anions and dipyridyl ligands with appropriate metal ions commonly results in the formation of 3D coordination polymers.[11] With a view to generating 3D networks in which metal dicarboxylate sheets are linked by parallel, pillar-like 1,4-bpeb ligands, we combined the metal ions zinc(II) and cadmium(II) with the dicarboxylic acids 5-sulfoisophthalic acid (5-H_3sipa) and 1,3-phenylenediacetic acid (1,3-H_2pda) in the presence of 1,4-bpeb. Whilst the desired structural outcome is certainly not guaranteed, we were hopeful that within a 3D network pairs of parallel 1,4-bpeb ligands bound to neighboring metal ions would be suitably aligned for photoinduced [2+2] cycloadditions to occur.

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Hydrothermal treatment of a mixture of $Zn(NO_3)_2$, 1,4-bpeb, 5-H_3sipa, and NaOH in a 1:1:1:3 molar ratio at 160 °C for 8 h followed by slowly cooling to room temperature gives rise to yellow blocks of $\{[Zn_4(\mu_3\text{-}OH)_2(5\text{-sipa})_2(1,4\text{-bpeb})_2]\cdot 4H_2O\}_n$ (**1**) in 41 % yield. An X-ray analysis[12] of **1** revealed the formation of a two-dimensional network of the composition $\{Zn_4(\mu_3\text{-}OH)_2(5\text{-sipa})_2\}$. In the structure, $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregates are linked by six equivalent 5-sipa ligands and each 5-sipa ligand is linked to three equivalent $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregates yielding a 2D (6,3)-connected net topologically related to CdI_2. Bound to each $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregate are two pairs of 1,4-bpeb ligands that extend outwards from each side of the sheet and provide bridges to symmetry-related aggregates belonging to parallel sheets (Figure 1 a). The underlying connectivity of the 3D network is represented schematically in Figure 1 b. Details relating to the net topology are presented in the Supporting Information. Thermogravimetric analysis revealed that crystals of **1** are stable. It gradually lost two H_2O molecules per molecule in the range of 50–130 °C and did not decompose until 265 °C (see Supporting Information).

Each 1,4-bpeb ligand bridge is closely associated with two symmetry-related 1,4-bpeb ligands (Figure 1 c). Pairs of in-phase 1,4-bpeb ligands bound to a $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregate at one end are also bound to a single $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregate in the adjacent parallel sheet. Both double bonds in the ligand make relatively close contact with the double bonds in the neighboring in-phase ligand (C7···C14B 3.958 Å, C6···C15B 3.611 Å). Although the ligands, which are related by a center of inversion, appear close to parallel, the closely separated double bonds are in either criss-cross or parallel fashion. For pairs of ligands that are out-of-phase, only one of the C=C double bonds from each ligand makes close contact (C6···C7 A and C7···C6 A 3.604 Å), but unlike the in-phase ligands, the double bonds are parallel. All the contacts discussed above fall within the range of separations identified by Schmidt as being necessary for photocycloaddition reactions to proceed.[13]

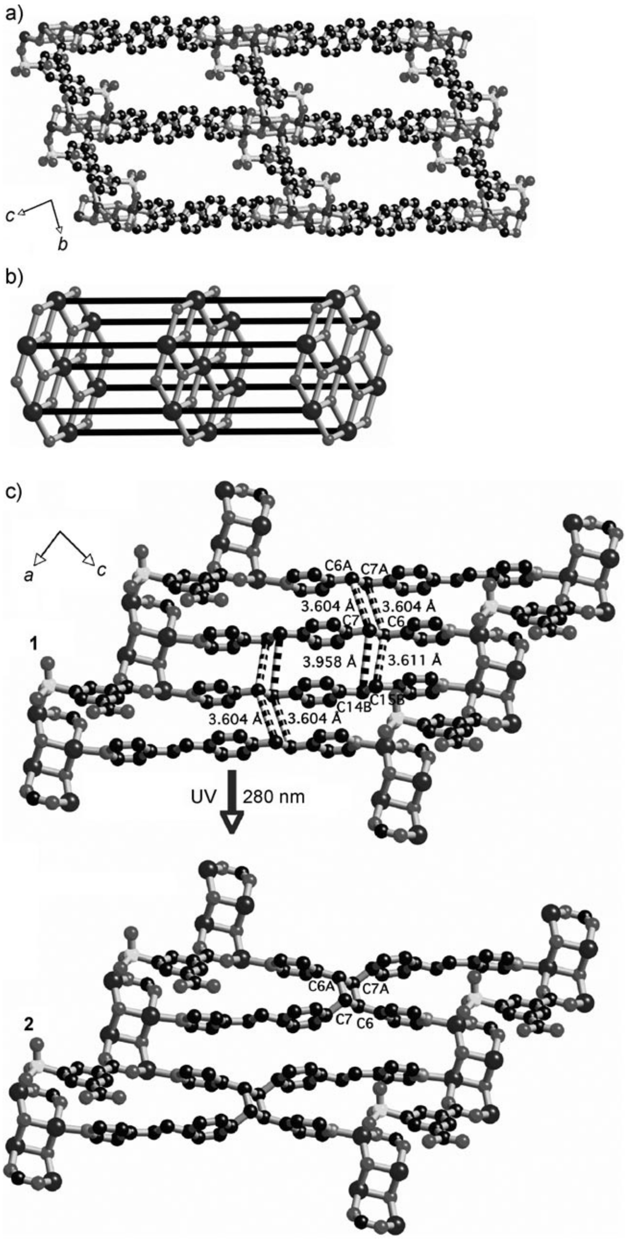

Figure 1. a) The 3D structure of **1** viewed along the *a* axis. 1,4-bpeb ligands, making close contact with each other, form stacks in a direction normal to the page. b) Representation of the underlying network connectivity of **1**. The large black and smaller gray spheres represent the 8-connecting $\{Zn_4(\mu_3\text{-}OH)_2\}$ aggregates and 3-connecting 5-sipa ligands, respectively. The long horizontal black connections represent pairs of in-phase 1,4-bpeb ligands. c) A side-on view of one of the 1,4-bpeb stacks showing close contacts between C=C units in **1** (striped connections) and the formation of bpbpvpcb ligands between out-of-phase 1,4-bpeb ligands in **2**.

UV irradiation of single crystals of **1** for 8 h using a 400W Hg lamp leads to cycloaddition occurring between the out-of-phase 1,4-bpeb ligands to produce the tetrapyridyl cyclobutane ligand, 1,3-bis(4-pyridyl)-2,4-bis[4-{2-(4-pyridyl)-vinyl}phenyl]cyclobutane (bpbpvpcb). This reaction is achieved within a SCSC process that yields crystals of $\{[Zn_4(\mu_3\text{-}OH)_2(5\text{-sipa})_2(\text{bpbpvpcb})]\cdot 2H_2O\}_n$ (**2**). Powder X-ray diffraction (PXRD) confirmed that the reaction is complete and that the bulk product of **2** is pure (see Supporting Information). The structure of the new ligand, which maintains its coordination to the zinc centers after the cycloaddition process, is shown in Figure 1 c. Single-crystal X-ray analysis reveals that the 3D framework of **2** is similar to that of **1**; however, within the distance between hydroxo-bridged Zn1 and Zn2 centers (Figure 1 c) increased from 3.428 Å to 3.503 Å (see Supporting Information). The separation between adjacent $Zn_4(\mu_3\text{-}OH)_2$ aggregates within the $\{Zn_4(\mu_3\text{-}OH)_2(5\text{-sipa})_2\}$ sheets has increased from 9.409 Å to 9.559 Å along the *b* axis but contracted along the *a* axis from 9.876 to 9.782 Å. The separation between $\{Zn_4(\mu_3\text{-}OH)_2(5\text{-sipa})_2\}$ sheets, corresponding to the *c* axis, decreases by only a small amount from 18.307 Å in **1** to 18.288 Å in **2**. Zinc centers bridged by 1,4-bpeb ligands in **1** are brought closer together following the cycloaddition (from 19.994 to 19.741 Å). To our knowledge, this is the first example of two 1,4-bpeb molecules undergoing a regiospecific dimerization reaction to produce a bpbpvpcb molecule in a SCSC transformation. However, if all the olefinic bonds were arranged in the parallel positions, the possibility may exist of polymerization of bpeb monomers in **1**, which was observed in the case of the diolefinic compound, 1,3-phenylene-3,3′-bis(2-propenoic) acid.[4d]

Encouraged by the successful SCSC transformation of **1** to **2**, another hydrothermal reaction was performed in which $Cd(NO_3)_2$ was allowed to react with 1,4-bpeb and 1,3-H_2pda in a 1:1:1 molar ratio at 160 °C over a period of 8 h. This reaction led to the isolation of yellow crystals with the formulation $\{Cd_2(1,3\text{-pda})_2(1,4\text{-bpeb})_2\}_n$ (**3**) in 83 % yield. X-ray analysis of **3** indicated the formation of $\{Cd_2(1,3\text{-pda})_2\}$ sheets (see Supporting Information). In this structure, four carboxylate groups from four separate ligands associate with a pair of closely separated cadmium centers. This $\{Cd_2(1,3\text{-pda})_4\}$ aggregate, which is approximately planar, is linked to equivalent aggregates within a 2D (4,4) network if the $\{Cd_2(1,3\text{-pda})_4\}$ aggregate is considered a single node. Almost-parallel pairs of 1,4-bpeb ligands extend out from either side of the $\{Cd_2(1,3\text{-pda})_4\}$ aggregate and link to equivalent $\{Cd_2(1,3\text{-pda})_4\}$ aggregates that are in parallel neighboring 2D $\{Cd_2(1,3\text{-pda})_2\}$ sheets, yielding a 3D network (Figure 2 a). From a topological perspective, the structure of **3** can be considered to be a simple cubic net with the $\{Cd_2(1,3\text{-pda})_4\}$ aggregates representing the nodes (Figure 2 b). According to TGA studies, the compound is relatively stable, with decomposition not occurring until 360 °C.

Although **1** and **3** share gross structural features, there are some important differences, particularly in relation to the association of the 1,4-bpeb ligands; each 1,4-bpeb ligand is only closely associated with one other 1,4-bpeb ligand. Each of the two double bonds in one 1,4-bpeb ligand is closely aligned in a parallel arrangement with a double bond in its neighbor, with separations that lie in a range appropriate for photocycloaddition to occur (C6⋯C15A and C7⋯C14A 3.886 Å and 4.023 Å, respectively; Figure 2 c).

Irradiating single crystals of **3** using a 400 W Hg lamp for about 10 h results in both double bonds in each 1,4-bpeb ligand participating in photocycloaddition reactions, leading to the generation of the dicyclobutane ligand, tetrakis(4-pyridyl)-1,2,9,10-diethano[2.2]paracyclophane (Figure 2 c). This transformation occurs in an SCSC process, which yields single crystals of $\{Cd_2(1,3\text{-pda})_2(\text{tppcp})\}_n$ (**4**). PXRD patterns indicated that the reaction was also complete and that bulk **4** was pure (see Supporting Information).

The 3D framework of **4** is closely related to that of **3** with a single tppcp ligand in **4** taking the place of the closely associated pair of 1,4-bpeb ligands in **3** (see Supporting Information). An interesting aspect of this transformation is the increase in separation between cadmium centers within the $Cd_2(1,3\text{-pda})_4$ aggregates (from 3.912 Å in **3** to 4.287 Å in **4**). The cadmium centers are thus no longer linked by a pair of oxygen atoms (Figure 2 d). As a result, the coordination number of the cadmium centers drops from seven in **3** to six in **4**. The structure of **4** is different from that of a 2D coordination polymer containing the tppcp ligand, $\{[Co(O_2CMe)_2(4,4'\text{-tppcp})]\cdot 2\,MeOH\cdot \text{toluene}\}_n$.[14]

In conclusion, the present work demonstrates that 1,4-bpeb incorporated into coordination networks can undergo photoinduced cycloaddition reactions with preservation of single-crystal character. Depending upon the alignment of the 1,4-bpeb ligands within **1** and **3**, the ligands bpbpvpcb in **2** and tppcp in **4** can be formed. It is anticipated that such a synthetic methodology may be applied to other linkers containing multiple vinyl groups to yield various known or unknown products regiospecifically. Studies along these lines are currently underway.

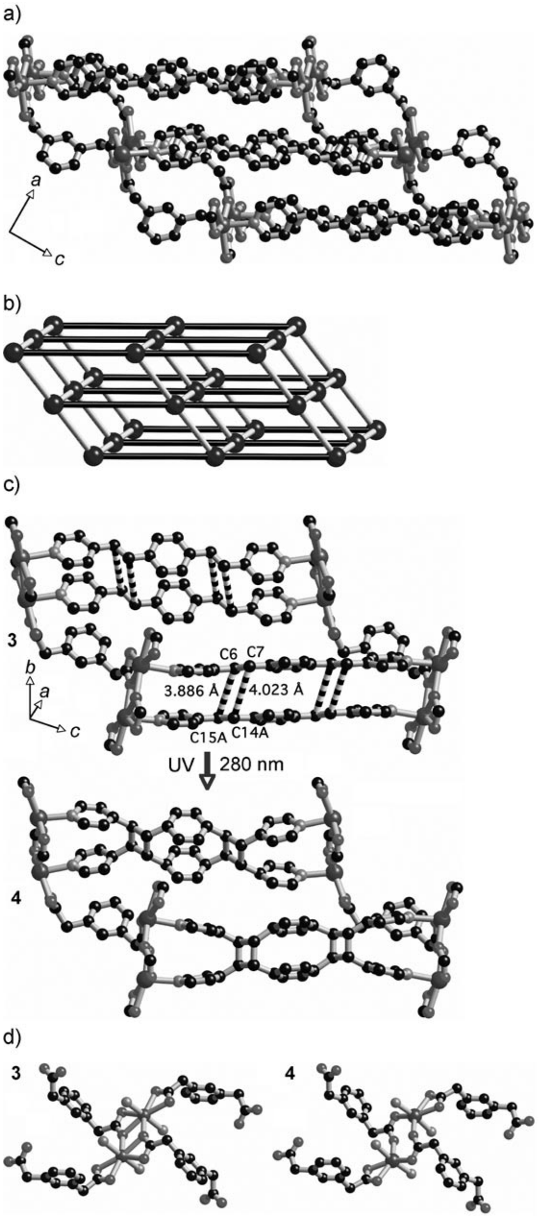

Figure 2. a) The 3D structure of **3** viewed along the *b* axis. b) The underlying network connectivity of **3**. The black spheres represent the $\{Cd_2(1,3\text{-pda})_4\}$ aggregates. The long horizontal black connections represent pairs of in-phase 1,4-bpeb ligands. c) A view of two pairs of 1,4-bpeb ligands in **3** (striped connections represent close contact between C=C units) that form tppcp ligands in **4**. d) A representation of the structural changes that occur to $\{Cd_2(1,3\text{-pda})_4\}$ aggregates following the formation of tppcp.

Experimental Section

1: $Zn(NO_3)_2\cdot 6H_2O$ (119 mg, 0.4 mmol), 5-H_3sipa (98 mg, 0.4 mmol), 1,4-bpeb (114 mg, 0.4 mmol), NaOH (48 mg, 1.2 mmol), and H_2O (15 mL) were loaded into a 25 mL Teflon-lined autoclave. The autoclave was sealed and heated in an oven to 160 °C for 8 h, and then cooled to ambient temperature at a rate of $5\,°C\,h^{-1}$, resulting in the formation of light yellow blocks of **1**. Yield: 58 mg (41 % yield based on Zn).

2: Single crystals of **1** were irradiated by a Hg lamp (400 W) for about 8 h to form crystals of **2** in 100 % yield based on **1**. As the crystals were exposed under the Hg lamp, each crystal lost two H_2O molecules per formula unit relative to that of **1**.

3: $Cd(NO_3)_2\cdot 4H_2O$ (123 mg, 0.4 mmol), 1,3-H_2pda (78 mg, 0.4 mmol), 1,4-bpeb (114 mg, 0.4 mmol), and H_2O (15 mL) were loaded into a 25 mL Teflon-lined autoclave. The autoclave was sealed and heated in an oven to 160 °C for 8 h, and then cooled to ambient temperature at a rate of $5\,°C\,h^{-1}$, leading to the formation of light yellow blocks of **3**. Yield: 195 mg (83 % yield based on Cd). The 1,3-H_2pda ligands were deprotonated in hydrothermal conditions without the presence of base, and the acidic environment was propitious to obtain single crystals in good quality.

4: Single crystals of **3** were irradiated by a Hg lamp (400 W) for about 10 h to form crystals of **4** in an almost quantitative yield based on **3**.

bpbpvpcb: A mixture of $Na_2(H_2edta)$ (298 mg), **2** (140 mg), H_2O (20 mL), and CH_2Cl_2 (25 mL) were placed in a 100 mL flask and stirred for 2 days. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phase was concentrated to dryness in vacuo. The powder was then washed thoroughly with NaOH solution and H_2O and finally dried with anhydrous Na_2SO_4 to give bpbpvpcb as yellow powder. Yield: 43 mg (76 %). ^1H NMR (400 MHz, $[D_6]$DMSO): $\delta = 8.55$ (q, 4H, Py-H), 8.29 (q, 4H, Py-H), 7.72 (d, 4H, Py-H), 7.59 (q, 4H, Py-H), 7.48 (d, 2H, CH=CH), 7.36 (d, 2H, CH=CH), 7.19 (m, 4H, Ph-H), 7.02 (d, 4H, Ph-H), 4.48 ppm (q, 4H, CH-CH).

tppcp was obtained from **4** (118 mg) as a pale yellow powder by the method used for the isolation of bpbpvpcb. Yield: 40 mg (70 %). ^1H NMR (400 MHz, $[D_6]$DMSO): $\delta = 8.35$ (d, 8H, Py-H), 7.26 (d, 8H, Py-H), 7.07 (d, 4H, Ph-H), 6.79 (d, 4H, Ph-H), 4.74 (d, 4H, CH-CH), 4.61 ppm (d, 4H, CH-CH).

The successful isolation of bpbpvpcb and tppcp also indicated that the transformations of **1** to **2** and **3** to **4** were complete.

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[12] Crystal data for **1**: triclinic, $P\bar{1}$, $a = 9.4093(19)$, $b = 9.876(2)$, $c = 18.307(4)$ Å, $\alpha = 79.35(3)$, $\beta = 87.30(3)$, $\gamma = 68.20(3)°$, $V = 1551.9(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.522\,g\,cm^{-3}$, $\mu = 1.669\,cm^{-1}$, $R_1 = 0.059$, $wR_2 = 0.162$, GOF = 1.175. **2**: triclinic, $P\bar{1}$, $a = 9.5591(19)$, $b = 9.782(2)$, $c = 18.288(4)$ Å, $\alpha = 78.75(3)$, $\beta = 86.28(3)$, $\gamma = 68.73(3)°$, $V = 1562.9(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.469\,g\,cm^{-3}$, $\mu = 1.653\,cm^{-1}$, $R_1 = 0.104$, $wR_2 = 0.196$, GOF = 1.178. **3**: monoclinic, $P2_1/c$, $a = 11.870(2)$, $b = 11.798(2)$, $c = 17.924(4)$ Å, $\beta = 95.03(3)°$, $V = 2500.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.564\,g\,cm^{-3}$, $\mu = 0.913\,cm^{-1}$, $R_1 = 0.039$, $wR_2 = 0.084$, GOF = 1.087. **4**: monoclinic, $P2_1/c$, $a = 11.804(2)$, $b = 11.912(2)$, $c = 18.226(4)$ Å, $\beta = 96.12(3)°$, $V = 2548.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.535\,g\,cm^{-3}$, $\mu = 0.896\,cm^{-1}$, $R_1 = 0.134$, $wR_2 = 0.248$, *GOF* = 1.152. CCDC 761121, 761122, 761123, and 761124 contain 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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