Photoreactive MOFs

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Single-Crystal to Single-Crystal Photochemical Structural Transformations of Interpenetrated 3D Coordination Polymers by [2+2] Cycloaddition Reactions**

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Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Solid-state structural transformations involving coordination polymers induced by light, heat, guest removal, uptake or exchange, expansion of coordination numbers, oxidation of metal centers, condensation, or reactions between the ligands are very fascinating and one of the hot topics in solid-state chemistry.[1] These structural transformations normally involve significant rearrangement of molecular components in the crystals, including rotation, bending, swinging, sliding, shrinking, or swelling. However, the single crystal has to withstand the stress during this period without the loss of single crystallinity in order to accomplish single-crystal to single-crystal (SCSC) structural transformation.[2–5] Single-crystal X-ray crystallography is the only tool currently available to characterize unequivocally the final products of these transformations in the solid state.[6] Hence understanding this SCSC phenomenon to create a stress-free structural transformation in confined coordination space is essential for further advancement in this area.

Of these structural transformations, [2+2] photodimerization of C=C bonds in various organic compounds and metal complexes has been well studied for the past few decades.[7–9] Of various organic ligands, the ditopic spacer *trans*-1,2-bis(4-pyridyl)ethene (bpe) has been one of the popular choices for studying topochemical transformations in metal complexes and coordination polymers.[7c] For a pair of double bonds to be photoreactive in solids, the topochemical criteria established by Schmidt (i.e., C=C bonds aligned parallel and separation less than 4.2 Å) should be satisfied.[10] However, only in limited cases do these dimerization reactions occur in a SCSC manner, and such SCSC transformations involving 1D or 2D coordination polymers are still rare.[11] In higher-dimensional coordination polymeric networks, the movements of the bridging bpe ligands are usually restricted, as both ends of the linear spacer are bonded to the metal ions. In such cases, although the bpe ligands have been found in parallel arrangements, the solids were not photoreactive.[12] Herein we report that bpe ligand pairs acting as pillars in the three-dimensional coordination polymers [Zn(bpe)(muco)]·DMF·H_2O (**1**), [Zn(bpe)(bdc)]·DMF (**2**), and [Zn(bpe)(fum)]·H_2O (**3**; H_2muco = *trans,trans*-muconic acid, H_2bdc = 1,4-benzene dicarboxylic acid, and H_2fum = fumaric acid) undergo 100% topochemical [2+2] cycloaddition reactions. This transformation occurs in a SCSC manner for **1** and **2**; details are given below.

Colorless block crystals of **1**–**3** were obtained in 50–70% yield by diffusing bpe and H_2muco in ethanol into a solution of aqueous $Zn(NO_3)_2 \cdot 6H_2O$ and Et_3N in DMF/MeOH. The purity of the bulk compounds was confirmed by comparing their powder X-ray diffraction patterns with those simulated from the single crystal data(see the Supporting Information). X-ray crystallographic experiments carried out at 223 K revealed that **1** and **2** crystallized in the orthorhombic space group *Pbca* with $Z = 8$, whereas **3** crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. However, **1**–**3** all exhibit 3D polymeric structures, and their connectivity exhibits α-Po topology with twofold interpenetration (Figure 1).[12a]

Figure 1. Schematic diagram of the twofold interpenetrated cubic net in **1**–**3** created by joining the center of the dimeric Zn_2 repeating units.

The asymmetric unit in **1**–**3** consists of a Zn^{II} center bonded to two bpe ligands in a *trans* manner along with chelating and bridging dicarboxylate ligands. Two such Zn^{II} centers are bridged by two dicarboxylate ligands such that the bpe pairs are aligned parallel with face-to-face π···π interactions (the distances between the centroids of the pyridyl groups are 3.82, 3.85, and 3.73 Å, respectively, in **1**–**3**) to form a ladder polymer. The distances between the centers of the adjacent C=C bonds (3.79, 3.77, and 3.99 Å, respectively, in **1**–

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3) indicate the feasibility of photochemical [2+2] cycloaddition reactions. This dimeric unit is the building block that dictates the overall topology of the framework. The connectivity of dicarboxylate ligands generates a distorted cubic (α-Po) structure (Figure 2). The overall 3D network is large enough to be interpenetrated by a second cube, and the small cavity that remains after interpenetration is occupied by solvent molecules. The three coordination polymers differ by guest solvent depending on the size of the channel. The channel in **1** hosts a DMF and a H_2O molecule, whereas **2** hosts only DMF and **3** hosts H_2O.

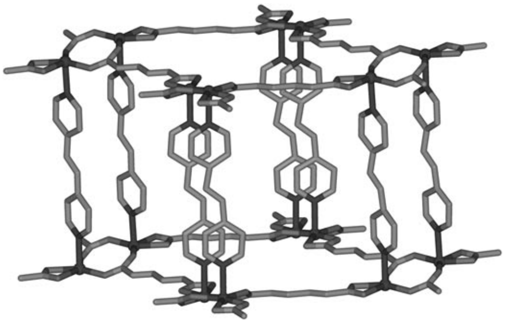


Figure 2. A perspective view of one of the interpenetrated cubic nets in **1.** The hydrogen atoms are not shown for the clarity.

As discussed above, the olefinic bonds of adjacent bpe ligands in all of the coordination polymers are positioned parallel within the distance required by the geometric criteria of Schmidt (less than 4.2 Å) for photochemical [2+2] cycloaddition reactions. This structural feature provides a rare opportunity to study the solid-state photodimerization of C=C bonds in interpenetrated 3D coordination polymers in the solid state. The single crystals and the powdered samples of **1**–**3** were subjected to UV irradiation for 30 min using a Xenon light source to test whether the olefinic C=C bonds are photoactive to give *rctt*-tetrakis(4-pyridyl)cyclobutane (*rctt*-tpcb); the quantitative photoreactivity is evident from the ^{1}H NMR spectra of the irradiated products. The ^{1}H NMR spectra show complete disappearance of the signals from olefinic protons ($\delta = 7.51$ ppm in **1**, 7.54 ppm in **2** and **3**) and appearance of the signals of the cyclobutane protons of *rctt*-tpcb ($\delta = 4.65$ ppm in **1**, **2**, and **3**) as well as a shift in the signals of bipyridine protons (from $\delta = 8.56$ and 7.68 ppm to 8.33 and 7.36 ppm in **1**, from $\delta = 8.60$ and 7.60 ppm to 8.34 and 7.21 ppm in **2** and **3**). The photodimerization was accompanied by a color change from colorless to light yellow monitored by optical microscopy.

UV irradiation of single crystals of all the compounds for half an hour revealed that the transparency and shape of the crystals remained intact during photodimerization, which gives us a first indication of a possible SCSC transformation. However, single crystals of UV-irradiated **1**–**3** showed poor diffraction patterns and were found not to be suitable for intensity data collection. Poor crystal quality could be attributed to the partial loss of solvent during irradiation. Therefore, the UV irradiation experiments were performed as follows to get better X-ray intensity data. Just after the data collection at 223 K, the single crystals were irradiated at 223 K for 30 min on the goniometer itself. After UV irradiation in this manner, the data was found to be better, and hence the data were collected at the same temperature. Among the three compounds, the single crystal of photodimerized product of **3** shows cracking. On the other hand, X-ray crystallographic analyses of photodimerized products of **1** and **2** namely, [Zn(*rctt*-tpcb)$_{1/2}$(muco)]·DMF·H_2O (**4**) and [Zn(*rctt*-tpcb)$_{1/2}$(bdc)]·DMF (**5**) revealed 100 % photodimerization reaction accompanied by SCSC transformation. This conversion is confirmed by the formation of cyclobutane rings (Figure 3). The two pyridyl rings that were previously aligned in parallel now diverge from the cyclobutane ring, and as a consequence the Zn···Zn distance increased from 3.96 Å in **1** to 4.25 Å in **4** and from 3.94 Å in **2** to 4.20 Å in **5**. In both **4** and **5**, Zn centers have the distorted octahedral coordination geometry described for **1**. In both the compounds, newly formed *rctt*-tpcb propagates along the *a* axis; the Zn−*rctt*-tpcb−Zn distance is slightly shorter than Zn−bpe−Zn distance in the initial precursors and is equal to the *a* axis in the cell (13.50 Å in **4** and 13.57 Å in **5**). Overall, the transformation is accompanied by reduction in cell volume (by 1.18 and 4.47 % in **4** and **5**, respectively). Thermogravimetric analysis before and after irradiation shows that the compounds **1** and **2** partially retain the solvents during irradiation, whereas the compound **3** does not retain any solvent at all. The loss of single-crystallinity of **3** may be due to the loss of solvent during structural transformation.

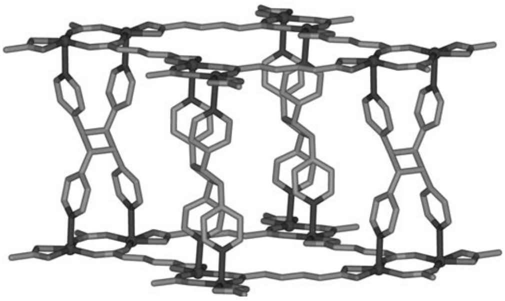
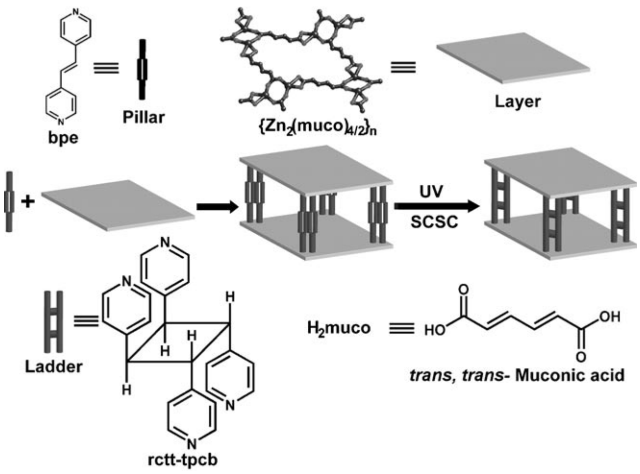


Figure 3. A perspective view of one of the two independent distorted cubic nets in **1** after UV irradiation. The hydrogen atoms are not shown for the clarity.

There are not many higher-dimensional coordination polymers in which bpe or its derivatives are oriented in pairs.[12a,13,14] For example, the Co^{II} analogue of **1**[12a] and [Ce(bpeo)$_{1.5}$(NO$_3$)$_3$] (where bpeo = *trans*-1,2-bis(4-pyridyl)-ethene-*N*,*N*′-dioxide)[14] have 3D network structures, and parallel dispositions of the bpe ligand observed in these polymers are suitable for [2+2] cycloaddition reactions. However, UV irradiation of the single crystals of these coordination polymers did not yield any cyclobutane product. In the pillar-layered coordination polymer, [Mn$_2$(HCO$_2$)$_3$-(bpe)$_2$(H$_2$O)$_2$]ClO$_4$·H$_2$O·bpe, there are two types of bridging bpe ligands.[15] In one type the bpe ligands are aligned parallel to the bpe in the lattice, and Gao et al. observed 60 % photodimerization. The hydrogen-bonded bpe in the lattice in this structure provided the flexibility needed for photodimerization. Apart from this compound, we are not aware of any other example of a photoreactive 3D coordination polymer. To our knowledge, the results described herein are the first examples of 3D→3D SCSC transformation in interpenetrated coordination polymers induced by UV light, as depicted in Scheme 1.



Scheme 1. Schematic representation of the 3D→3D structural transformation in **1**.

In summary, a novel approach to align bpe ligands in three pillar-layered interpenetrated coordination polymers has been illustrated. In these photoreactive functional porous solids, a 3D→3D topochemical structural transformation has been achieved by a photochemical [2+2] cycloaddition reaction. Furthermore, the cycloaddition reaction has been successfully accomplished in a SCSC manner by lowering the temperature to 223 K in two different structures. Finally, a photochemical method has been employed for postsynthetic modification of porous MOFs.

Experimental Section

1: A solution of bpe (0.036 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered over a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.059 g, 0.2 mmol) in H_2O (2 mL) using DMF/MeOH 1:1 (v/v, 2 mL) as a buffer; subsequently, a layer of H_2muco (0.028 g, 0.2 mmol) neutralized with Et_3N (0.021 g, 0.2 mmol) in EtOH (2 mL) was added. The colorless block crystals of [Zn(bpe)(muco)]·DMF·H_2O (**1**) were obtained after two days (0.066 g, yield 70%). ^{1}H NMR (D_2O, 300 MHz, 298 K): $\delta = 8.56$ (d, 4H, Py-H), 7.68 (d, 4H, Py-H), 7.51 (s, 2H, CH=CH), 7.04 (m, 2H, muco), 6.19 (m, 2H, muco); TG weight loss for the fresh sample calcd for one DMF and one H_2O: 19.0%; found: 18.0%.

2: Compound **2** was obtained in a similar fashion to **1**, but H_2bdc was used instead of H_2muco. Colorless blocks of [Zn(bpe)(bdc)]·DMF (**2**) were obtained after two days (0.062 g, yield 65%). ^{1}H NMR ([D_6]DMSO, 300 MHz, 298 K): $\delta = 8.60$ (d, 4H, Py-H), 8.03 (s, 4H, bdc), 7.60 (d, 4H, Py-H), 7.54 ppm (s, 2H, CH=CH); TG weight loss for the fresh sample calcd for one DMF: 15.1%; found: 14.0%.

3: When H_2fum was used in place of H_2muco for the synthesis of **3** using a similar method as described for **1**, colorless blocks of [Zn(bpe)(fum)]·0.25H_2O (**3**) crystallized after two days (0.035 g, yield 50%). ^{1}H NMR ([D_6]DMSO, 300 MHz, 298 K): $\delta = 8.60$ (d, 4H, Py-H), 7.60 (d, 4H, Py-H), 7.54 (s, 2H, CH=CH), 6.01 ppm (s, 2H, fum); TG weight loss for the fresh sample calcd for 0.25 H_2O: 1.2%; found: 2.2%.

Photodimerization reactions were carried out using fiber optics of a MAX-150 xenon light source (150 W) of 60% intensity and wavelength range 280–350 nm.

Conversion of **1** to **4:** Light yellow blocks of single crystals of [Zn(*rctt*-tpcb)$_{1/2}$(muco)]·DMF·H_2O (**4**) were obtained by UV irradiation of single crystals of **1** for 30 min. ^{1}H NMR (D_2O, 300 MHz, 298 K): $\delta = 8.33$ (d, 4H, Py-H), 7.36 (d, 4H, Py-H), 4.65 (s, 2H, CH–CH), 7.05 (m, 2H, muco), 6.19 ppm (m, 2H, muco). TG weight loss for the irradiated sample calcd for one DMF and one H_2O: 19.0%; found: 17.0% owing to partial loss of solvent during irradiation.

Conversion of **2** into **5:** Light yellow blocks of single crystals of [Zn(*rctt*-tpcb)$_{1/2}$(bdc)]·DMF (**5**) were formed by complete conversion of single crystals of **2** under similar conditions as described for **4**. ^{1}H NMR ([D_6]DMSO, 300 MHz, 298 K): $\delta = 8.34$ (d, 4H, Py-H), 8.03 (s, 4H, bdc), 7.21 (d, 4H, Py-H), 4.65 ppm (s, 2H, CH–CH). TG weight loss for the irradiated sample calcd for one DMF: 15.1%; found: 11.0% owing to partial loss of solvent during irradiation.

Conversion of **3** into **6:** Compound [Zn(*rctt*-tpcb)$_{1/2}$(fum)](**6**) was obtained in a similar fashion to **4** and **5**, but the single-crystalline nature was lost. ^{1}H NMR ([D_6]DMSO, 300 MHz, 298 K): $\delta = 8.34$ (d, 4H, Py-H), 7.21 (d, 4H, Py-H), 6.01 (s, 2H, fum), 4.65 ppm (s, 2H, CH–CH). TG weight loss for the fresh sample calcd for 0.25H_2O: 1.2%; found: 0.0% owing to complete loss of solvent during irradiation.

Crystal data: **1:** Orthorhombic space group *Pbca*, $a = 13.7372(16)$, $b = 14.7731(17)$, $c = 21.075(7)$ Å, $V = 4277.0(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.487$ g cm^{-3}, $\mu = 1.191$ mm^{-1}, $T = 223(2)$ K, $R1 = 0.0518$, $wR2 = 0.1077$, GOF = 1.066 for 3823 reflections with $I > 2\sigma(I)$.

2: Orthorhombic space group *Pbca*, $a = 13.7982(7)$, $b = 16.2380(8)$, $c = 19.0994(10)$ Å, $V = 4279.3(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu = 1.189$ mm^{-1}, $T = 223(2)$ K, $R1 = 0.0543$, $wR2 = 0.1181$, GOF = 1.116 for 4056 reflections with $I > 2\sigma(I)$.

3: Triclinic space group $P\bar{1}$, $a = 8.6690(8)$, $b = 10.0756(9)$, $c = 10.4639(10)$ Å, $\alpha = 83.766(2)$, $\beta = 66.633(2)$, $\gamma = 68.524(2)°$, $V = 780.04(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.559$ g. cm^{-3}, $\mu = 1.597$ mm^{-1}, $T = 223(2)$ K, $R1 = 0.0358$, $wR2 = 0.0888$, GOF = 1.082 for 3325 reflections with $I > 2\sigma(I)$.

4: Orthorhombic space group *Pbca*, $a = 13.500(3)$, $b = 14.702(3)$, $c = 21.245(5)$ Å, $V = 4216.7(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.508$ g cm^{-3}, $\mu = 1.208$ mm^{-1}, $T = 223(2)$ K, $R1 = 0.0870$, $wR2 = 0.1815$, GOF = 1.079 for 3202 reflections with $I > 2\sigma(I)$.

5: Orthorhombic space group *Pbca*, $a = 13.5707(15)$, $b = 15.0060(17)$, $c = 20.074(2)$ Å, $V = 4087.9(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.575$ g cm^{-3}, $\mu = 1.244$ mm^{-1}, $T = 223(2)$ K, $R1 = 0.1037$, $wR2 = 0.2352$, GOF = 1.388 for 2932 reflections with $I > 2\sigma(I)$.

Crystal data for **1–5** were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated $Mo_{K\alpha}$ radiation (λ, 0.71073 Å) using a sealed tube at 223(2) K. Absorption corrections were made with the program SADABS,[16] and the crystallographic package SHELXTL[17] was used for all calculations. CCDC 751094, 751095, 751096, 751097, 751098 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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