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Metal–Organic Frameworks

Solid-State Structural Transformations from 2D Interdigitated Layers to 3D Interpenetrated Structures**

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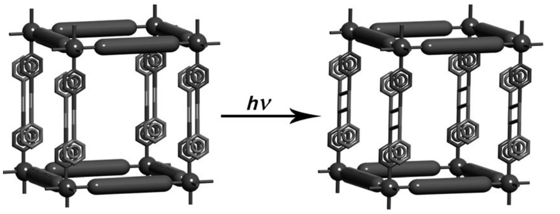
During the past two decades synthesis of coordination polymers and metal–organic frameworks (MOFs) have attracted ever increasing interest.[1] Much interest in this area is to understand how to control or fine tune the physical properties and reactivity of coordination polymers and (MOFs).[2] Of these, interdigitated two-dimensional (2D) coordination polymers have been found to show dynamic behavior, gate opening properties, provide platform for various surface conversions and selective guest trapping.[3] In addition to the expansion/shrinkage of the 2D layered structures by the guest molecules, the transformation between the 2D and 3D frameworks is expected to lead to large differences in their structural and functional behaviors.[4] Such solid-state transformations can be achieved by heat, light, guest removal, or uptake.[2f] Recently Kitagawa and co-workers have used various functional groups at the backbone of the spacer ligands in pillared layered structures to regulate the radical polymerization of methyl methacrylate in the nanochannels.[5] Herein we are interested in fine tuning the photo-reactivity of the interdigitated 2D coordination polymeric sheets.

Over the past few years, many successful attempts have been made to align the photoactive double bonds in coordination polymers.[6] So far symmetrical ditopic spacer ligands containing photoreactive double bonds such as 1,2-bis(4′-pyridyl)ethylene (bpe), have been commonly used for the solid-state photodimerization reactions.[7] The use of exodentate ligands like bpe as photoreactive pillars in pillared-layer 3D coordination polymers has been explored before.[7] In order to make such pillars in the layered 2D coordination polymeric structure, 4-styrylpyridine (4-spy) which contains a C=C bond would be an ideal terminal ligand.[8] Herein, we report the syntheses of two photoreactive interdigitated layered coordination polymers made from paddle-wheel secondary building unit (SBU) using 4-carboxycinnamic acid (H_2cca) and 2,6-naphthalenedicarboxylic acid (H_2ndc) in the presence 4-spy. The 4-spy unit in both the products undergoes photodimerization reaction under UV light. The structural transformation of one of these compounds is accompanied by single-crystal-to-single-crystal (SCSC) manner which helps to confirm the formation threefold interpenetrated 3D structure (Scheme 1).



Scheme 1. Schematic diagram shows the structural transformation of a 2D interdigitated layer into a 3D MOF.

Light yellow block-shaped crystals of $[Zn_2(cca)_2(4\text{-spy})_2]$ (**1**) were grown by the slow diffusion of 4-spy into the sodium salt of H_2cca and $Zn(NO_3)_2{\cdot}6H_2O$ in a mixture of MeOH, DMF, and water. Single crystal X-ray structure determination at 100 K revealed that **1** is a 2D coordination polymer. The asymmetric unit contains half the formula unit. The building block $[Zn_2(cca)_2(4\text{-spy})_2]$ has the well-known $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ paddle-wheel structure, where two Zn^{II} atoms are bridged by four cca ligands. In each Zn^{II} atom, the equatorial positions are coordinated by oxygen atoms of cca ligands and axial position is occupied by the N atom of 4-spy to provide a distorted square-pyramidal geometry. A crystallographic inversion center is present in the middle of the paddle-wheel structure. It may be noted that the styryl group of 4-spy ligand is disordered with occupancy ratio of approximately 65:35. The styrene fragment of the cca ligand is also disordered with the "alkene" and "aromatic" groups related by the crystallographic inversion symmetry (Figure 1).

The connectivity of the cca ligand provides a 2D coordination polymer with approximately a square-grid structure. The dimensions of the square are: side lengths, 13.27 and 13.15 Å and angles, 96.4 and 83.6°. Such a large cavity is amenable to interpenetration,[9] but in **1** this is hindered by the long 4-spy ligands present at the nodes of the square-grid structure. This results in interdigitation of 4-spy ligands to maximize the usage of the empty space as shown in Figure 2.

There are two different levels of interdigitation by the 4-spy ligands from adjacent layers of the 2D coordination

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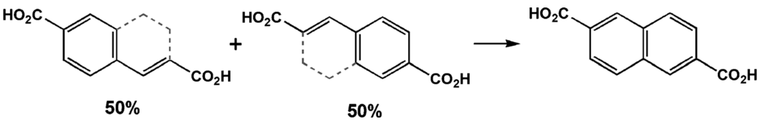

Figure 1. Disorder present in cca ligand in the crystal structure of **1** and the isostructurality between the cca and ndc ligands are shown.

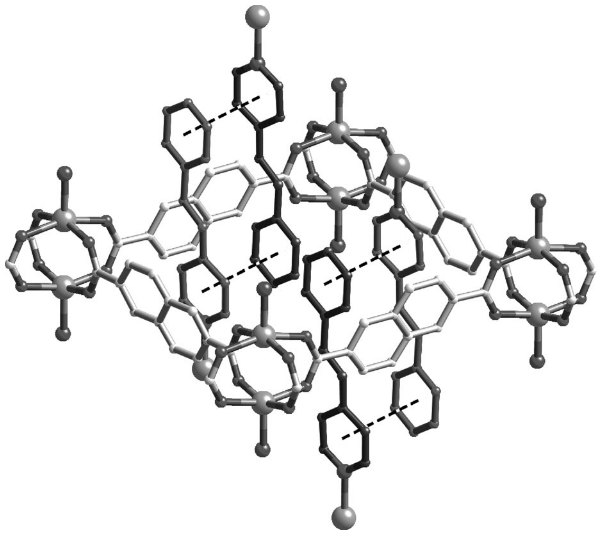

Figure 2. A perspective view showing different levels of interdigitation with respect to a single square-grid in **1** (see text for details). The cca ligand (white) resemble ndc ligands because of the disorder (see Figure 1). Only selected atoms are shown for clarity. The 4-spy groups with same shades of gray are related by crystallographic center of inversion. Zn large spheres, N small spheres.

polymer. In the first level, the centers of the pyridyl groups of two 4-spy ligands from the immediate layers (one above and one below relative to the layer concerned) roughly occupy the diagonal of each square plane. The non-bonded distance between the centers of pyridyl and phenyl rings is 8.38 Å (Figure 2).

The centers of the phenyl rings of the two 4-spy ligands from the third layers occupy the other corners inside each square plane. The 4-spy ligands of the fourth layers (one above and one below) exactly aligned parallel to the 4-spy ligand in the top and bottom of the square grids (Figure 3). Further the $C=C$ bonds in these 4-spy ligands pairs are aligned parallel with a distance of 3.85 Å. The shortest distance between the centroids of pyridyl and phenyl rings of the aligned 4-spy ligands is 3.58 Å. Due to close proximity these 4-spy ligands have close contacts (π–π) with other aromatic rings in the adjacent layers (shown as dotted lines in Figure 2).

The alignment of the olefinic bonds between the pairs of 4-spy ligands in the first and fourth layers in a head to tail fashion is of interest as this arrangement follows Schimdt's topochemical criteria (<4.2 Å) for [2+2] photochemical cycloaddition reaction in the solid state.[10] This situation provides an opportunity to conduct the structural transformation of interdigitated 2D layers into 3D interpenetrated structures. The powder X-ray diffraction pattern (PXRD) pattern of the bulk sample matches well with the simulated PXRD pattern from the single- crystal data of **1** and thus confirms the purity of the bulk.

The single crystals of **1** were subjected to UV irradiation at room temperature by Xenon source for 90 min. The ^{1}H NMR spectrum of the irradiated compound shows the disappearance of signal for the olefinic proton at $\delta = 8.25$ ppm, the shift of the signal for the pyridyl protons from 8.85 to 8.75 ppm and a signal for cyclobutane protons at $\delta = 4.99$ ppm confirms 100% conversion of 4-spy ligand into 1,3-bis(4′-pyridyl)-2,4-bis(phenyl)cyclobutane (*rctt*-4-ppcb). Note that the ^{1}H NMR spectra were recorded in [D$_6$]DMSO solution after dissolving these compounds with a drop of HNO_3 owing to their poor solubility. The single crystals were left intact even after 100% dimerization which encouraged us to study the SCSC transformation.

The single-crystal X-ray structure determination of the irradiated product [$Zn_2(cca)_2$(*rctt*-4-ppcb)] (**2**) reveals the formation of triply interpenetrated 3D pillared-layer coordination polymer with a primitive cubic topology (**pcu** nets or α-Po structure; Figure 4).[1a] Each cube in the interpenetrating network is crystallographically distinct and only related by translation symmetry along *a*-axis. Overall, the cell volume has decreased by 35.09 Å^3 (3.6%) as a result of efficient packing. The formation of cyclobutane ring restricts the dangling movement of benzene ring and hence removes the disorder in this part of the structure. However, the disorder in the cca ligand remains due to crystallographic inversion symmetry.

The disorder in cca ligand due to crystallographic inversion symmetry shown in Figure 1 resembles that of 2,6-naphthalene-dicarboxyic acid (H_2ndc). Replacing cca with ndc ligand is therefore expected to furnish a structure isostructural to **1** and also to behave similar to **1** in its photo-reactivity.

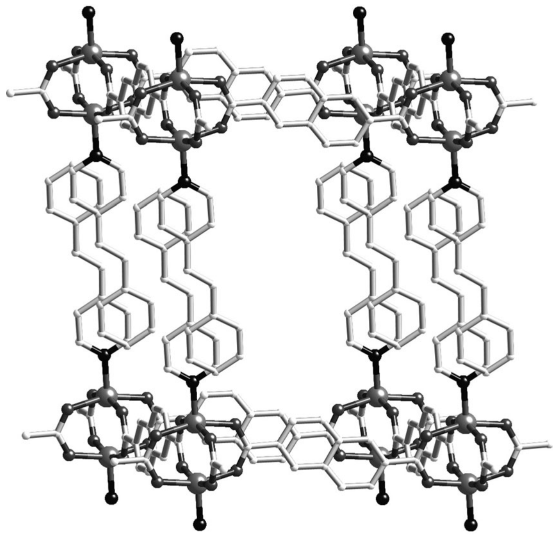

Figure 3. The alignment of 4-spy ligands between the first and fourth layers of the 2D coordination polymer in the packing of **1**. Only selected atoms are shown for the clarity.

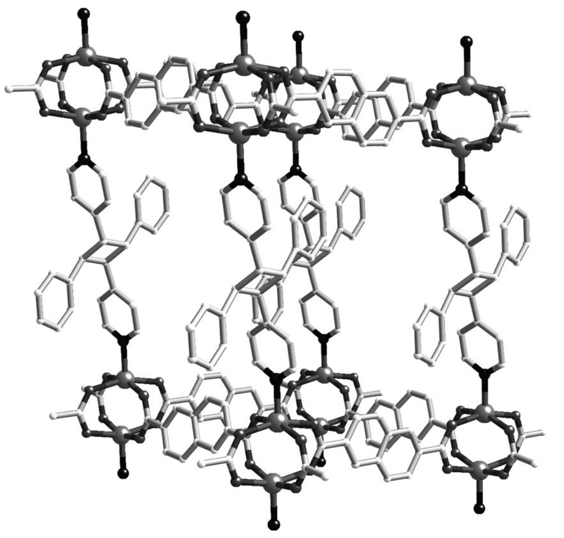

Figure 4. A portion of the **pcu** connectivity in **2**. Only relevant atoms are shown for clarity. Interpenetration is not shown.

The compound $[Zn_2(ndc)_2(4\text{-spy})_2]$ (**3**) was synthesized as light yellow block-shaped crystals by a procedure similar to **1**. The X-ray crystallographic analysis reveals that **3** is isomorphous and isostructural to **1**, except for the additional atoms in the ndc ligand. A search in the literature reveals that such hitherto unknown isostructurality between these two ligands is also present in the other 3D structures.[11] This compound is also found to be photoreactive, when the bulk was irradiated under UV light. The ^1H NMR spectrum of the irradiated sample shows the 100 % dimerization of 4-spy as observed for **2**. Unfortunately, the single crystals of **3** started breaking during UV experiment. However, the PXRD pattern of **4** matched well with that of **2** confirming that $[Zn_2(ndc)_2(\textit{rctt}\text{-4-ppcb})]$ (**4**) has a structure similar to **2**.

In summary, we presented a novel photo-induced solid-state transformation of a 2D interdigitated coordination polymer into a 3D interpenetrated structure in an SCSC manner. The utility of a photoreactive terminal ligand to perform structural transformations to a higher dimensional network structure is demonstrated. Though isostructural similarity is well documented for a few cases, such as benzene–thiophene, toluene–chlorobenzene and 1,4-dichlorobenzene–1,4-dibromobenzene,[12] the isostructural relationship between cca and ndc ligands in coordination polymers does not seem to have been realized before. This property is expected to occur in organic crystals of H_2cca and H_2ndc and their derivatives and such an investigation is currently under progress in our laboratory. Generally 3D coordination polymers (or MOFs) are prepared by self-assembly. Recently Li and Zhou reported[13] a different synthetic strategy based on the substitution of bridging ligands in soluble MOFs. Herein we report a retrosynthetic approach[14] to synthesize a 3D coordination polymer from 2D structure in the solid-state. The pillared-layer 3D coordination polymers **2** and **4** can be dissected into **1** and **3** and assembled in the solid state by photochemical method. The sterically hindered cyclobutane molecule, *rctt*-4-ppcb has been known since 1977,[15] yet this potential spacer ligand has not been exploited for making multidimensional coordination polymers. Herein we have used this pillar ligand to synthesize 3D coordination polymers.

Experimental Section

1: Careful layering of $Zn(NO_3)_2\cdot 6H_2O$ (30 mg, 0.1 mmol) in EtOH (1 mL) above the sodium salt of 4-carboxycinnamic acid (19.2 mg, 0.1 mmol) in water (1 mL) followed by DMF (1 mL) and 4-styrylpyridine (24 mg, 0.133 mmol) in MeOH (1 mL), in the order of water, DMF, MeOH, and EtOH from bottom to top, gave light yellow block shaped crystals of $[Zn_2(cca)_2(4\text{-spy})_2]$ (**1**) within a week (31 mg, 72 % yield). They were collected and washed with DMF and MeOH. ^1H NMR ($[D_6]DMSO/HNO_3$, 300 MHz, 298 K): $\delta = 8.85$ (d, 2H, pyridyl proton of 4-spy), 8.25 (d, 2H, alkene protons of 4-spy), 8.10 (d, 2H, cca), 7.40–8.00 (m, 7H of 4-spy), 7.78 (d, 2H, cca), 7.62 (d, 1H, alkene proton of cca), 6.63 ppm (d, 1H, alkene proton of cca).

1→**2**: Light yellow block single crystals of $[Zn_2(cca)_2(\textit{rctt}\text{-4-ppcb})]$ (**2**) were obtained by UV irradiation of single crystals (**1**) for 90 min. ^1H NMR ($[D_6]DMSO/HNO_3$, 300 MHz, 298 K): $\delta = 8.75$ (d, 4H, 4-ppcb), 8.10 (d, 2H, cca), 7.78 (d, 2H, cca), 7.62 (d, 1H, alkene proton of cca), 7.40–7.00 (m, aromatic 10H, pyridine 4H of 4-spy), 6.63 (d, 1H, alkene proton of cca), 4.99 ppm (dd, 4H, 4-ppcb).

3: Compound **3** was synthesized in a similar way as **1** but by using K_2ndc instead of Na_2cca in water. Light yellow blocks of $[Zn_2(ndc)_2(4\text{-spy})_2]$ (**3**) were formed within few days (60 % yield). ^1H NMR ($[D_6]DMSO/HNO_3$, 300 MHz, 298 K): $\delta = 8.85$ (d, 2H, 4-spy), 8.66 (s, 2H, ndc), 8.25 (d, 2H, alkene protons of 4-spy), 8.21 (d, 2H, ndc), 8.03 ppm (d, 2H, ndc), 7.40–8.00 (m, 7H of 4-spy),

3→**4**: After UV irradiation of block crystals of **3** for 90 min, $[Zn_2(ndc)_2(\textit{rctt}\text{-4-ppcb})]$ (**4**) were obtained. During irradiation the crystals are losing their single crystallinity. ^1H NMR ($[D_6]DMSO/HNO_3$, 300 MHz, 298 K): $\delta = 8.75$ (d, 4H, 4-ppcb), 8.66 (s, 2H, ndc), 8.21 (d, 2H, ndc), 8.03 (d, 2H, ndc), 7.91 (d 4H, 4-ppcb), 7.30–7.10 (m, Ar-5H of 4-ppcb), 4.99 ppm (dd, 4H, 4-ppcb),

Crystal data: **1**: Triclinic space group $P\bar{1}$, $a = 8.3804(9)$, $b = 9.778(1)$, $c = 12.605(1)$ Å, $\alpha = 76.871(3)$, $\beta = 75.498(2)$, $\gamma = 87.538(3)°$, $V = 973.7(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.490$ g cm^{-3}, $\mu = 1.291$ mm^{-1}, $T = 100(2)$ K, $R_1 = 0.0484$, $wR_2 = 0.1358$, GOF = 1.175 for 3559 reflections with $I > 2\sigma(I)$.

2: Triclinic space group $P\bar{1}$, $a = 7.850(5)$, $b = 10.145(6)$, $c = 13.085(8)$ Å, $\alpha = 69.954(13)$, $\beta = 73.608(12)$, $\gamma = 86.185(13)°$, $V = 938.6(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.545$ g cm^{-3}, $\mu = 1.339$ mm^{-1}, $T = 100(2)$ K, $R_1 = 0.0606$, $wR_2 = 0.1255$, GOF = 1.121 for 3252 reflections with $I > 2\sigma(I)$.

3: Triclinic space group $P\bar{1}$, $a = 8.0958(5)$, $b = 10.2640(6)$, $c = 13.0584(7)$ Å, $\alpha = 75.260(1)$, $\beta = 72.838(1)$, $\gamma = 89.416(1)°$, $V = 1000.2(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.530$ g cm^{-3}, $\mu = 1.261$ mm^{-1}, $T = 100(2)$ K, $R_1 = 0.0389$, $wR2 = 0.0928$, GOF = 1.079 for 3264 reflections with $I > 2\sigma(I)$.

Crystal data for **1**–**3** 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 100(2) K. Absorption corrections were made with the program SADABS,[16] and the crystallographic package SHELXTL[17] was used for all calculations. CCDC 829795 (**1**), 829796 (**2**), and 829797 (**3**) 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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