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From 2D to 3D: A Single-Crystal-to-Single-Crystal Photochemical Framework Transformation and Phenylmethanol Oxidation Catalytic Activity

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The solid-state structural transformation of coordination networks is a fascinating research topic because some resulting compounds can not be easily obtained by traditional synthetic routes.^[1] Of particularly interest are solid-state photochemical [2+2] cycloadditions, which can create new covalent bonds with high regio- and stereoselectivity.^[2] Over the past decade, solid-state photochemical [2+2] cycloadditions have been observed in many supramolecular complexes^[3] and metal–organic compounds.^[4–7] However, there are only a few photochemical [2+2] cycloadditions of the C=C bonds that occur in the solid state and accompany single-crystal-to-single-crystal (SCSC) transformations due to positional and geometrical constraints and the significant rearrangement of the molecular components, which can destroy the single-crystalline character.^[5–7]

Metal–organic frameworks (MOFs) are a type of material constructed from organic ligands that link metal nodes.^[8] Some photoactive olefin units in MOFs are positioned within the required distance for [2+2] photodimerization. To date, most of the SCSC transformations in metal–organic compounds have been focused on linear bipyridine-type ligands.^[6] Although many carboxylate ligands containing photoactive groups have been used for the construction of coordination networks, only one example have been used for photochemical [2+2] cycloaddition in a SCSC manner.^[7]

To avoid additional anionic effects in the synthesis of photoreactive MOFs, we have synthesized an *E*-5-(2-(pyridin-4yl)vinyl)isophthalic acid ligand (H₂L; Scheme 1). The pyridine and carboxylate groups in H₂L can bridge metal nodes to form neutral MOFs, and the C=C bond can be photoactivated for the topochemical reaction. Herein, we report a 2D coordination polymer [Mn₂L₂(H₂O)₂]·3H₂O (1) that undergoes quantitative topochemical [2+2] cycloaddition in a SCSC manner in a 2D to a 3D porous network structure transformation with interesting phenylmethanol oxidation catalytic activity.

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Scheme 1.

Brown crystals of **1** were synthesized by the reaction of H_2L and $MnCl_2 \cdot 4H_2O$ in a H_2O/DMF mixture at 80 °C for 10 d. Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the triclinic $P\bar{1}$ space group with one Mn^{II} atom, one **L**, one aqua ligand, and 1.5 lattice water molecules in the asymmetric unit.^[9] Each Mn^{II} atom is octahedrally coordinated to four carboxyl oxygen atoms of three **L**, one **L** pyridine, and one aqua ligand (Figures 1a and 2a). Two Mn centers are doubly coupled in a *syn-anti* fashion by two carboxylate groups of two **L** ligands, and are further linked by the second **L** carboxylate group in chelate fashion to propagate into a linear network. The 1D chains are further linked by the **L** pyridine groups to extend into a 2D grid framework with cavity dimensions of 7.80(2)× 8.94(4) Å².

The 2D layered lattices are further packed into a 3D supramolecular network in an \dots AA \dots -stacked fashion to give open 1D channels. PLATON calculations indicate that 1 contains 24.3 % void space that accommodates lattice water molecules.^[10] Thermogravimetric analysis (TGA) of 1 indicates that a weight loss of 12.4 % occurs between 30 and 111 °C, which corresponds to the loss of water molecules (predicted: 12.3 %). After a sample of 1 was evacuated at 90 °C for 6 h under vacuum, powder X-ray diffraction (PXRD) demonstrated that the framework structure of 1 was maintained upon the removal of all solvent molecules (Figure S11 in the Supporting Information). The N₂ sorption isotherm of 1 at 77 K has confirmed its permanent porosity, with a Brunauer–Emmett–Teller (BET) surface area of 7.54 m²g⁻¹ (Figure 3).

Note that the **L** olefinic bonds between the adjacent layers are positioned parallel in a head-to-tail fashion, and the distance between the olefinic centers (3.627 Å) meets Schmidt's geometric criteria for photochemical [2+2] cycloaddition.^[11] After crystals of **1** were subjected to Hg light ir-

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Figure 1. a) The packing diagram of the \dots AA \dots stacked-layer network in 1 viewed down the *a* axis. b) A view of the 3D framework of 2 down the *a* axis.

radiation for 24 h, a photochemical [2+2] cycloaddition compound $[Mn_2L'(H_2O)_2]$ ·3 H₂O (2; H₄L'=5,5'-(3,4-diphe-nylcyclobutane-1,2-diyl)diisophthalic acid; Scheme 1) was produced.^[9]

Single-crystal X-ray diffraction study of photodimerized product 2 revealed 100% photodimerization accompanied by an SCSC transformation. The quantitative photoreactivity is evident from the ¹H NMR spectrum (Figure S9 in the Supporting Information). The ¹H NMR spectrum shows complete disappearance of the signals from olefinic protons of L ($\delta = 7.50$ and 7.79 ppm) and appearance of the signal of the L' cyclobutane protons ($\delta = 4.93$ ppm). The purity of the bulk sample was further confirmed by elementary analysis and by comparing the simulated and experimental PXRD patterns (Figure S10 in the Supporting Information). The SCSC transformation is accompanied by an increase in the *a* and b dimensions (1.27 and 1.96%) and a reduction in the cdimension (3.28%), with a slightly increased cell volume of 1.36%. In compound 2, each Mn^{II} center has a distorted octahedral coordination geometry as described in 1 (Figure 1b). Most strikingly, the newly formed 2 presents a 3D porous framework because the four carbon atoms of the cyclobutane ring are from two original neighboring layers in 1



Figure 2. Packing diagrams of a) $\mathbf{1}$ and b) $\mathbf{2}$ as viewed slightly off the *c* axis, showing the structural differences before and after UV irradiation.



Figure 3. N₂ adsorption/desorption isotherms for the evacuated samples of 1 and 2 at 77 K; \blacktriangle : adsorption for 1; \triangle : desorption for 1; \bullet : adsorption for 2; \bigcirc : desorption for 2.

(see Figures 1b and 2b). The resulting Mn-L'-Mn distance (14.02(7) Å) is slightly longer than the Mn-L-Mn distance (12.90(7) Å) in the precursor, which subsequently results in an increased cell volume and enlarged 1D channels running along the *a* axis $(9.23(2) \times 9.35(4) Å^2)$. Calculations using PLATON showed that the effective pore volume for the inclusion of compound **2** is about 238.6 Å³ per unit cell (882.7 Å³) with slightly increased pore volume of 27.0%. Topological analysis of **2** reveals that the 3D network is an unusual (3,3,4,4)-connected tetranodal topology with a

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Schläfli symbol of $(4.6.8)_2(4.6^2.8^3)_2(6^2.8^2.10^2)(6^2.8)_2$ (Figure S14 in the Supporting Information).^[12]

The TGA plot confirmed that compound **2** retained the solvents during the irradiation. The PXRD pattern showed that the framework structure of **2** was maintained upon the removal of the solvent molecules but the diffraction is weakened (Figure S12 in the Supporting Information). The N₂ sorption measurements showed that the evacuated sample of **2** possessed permanent porosity with a BET surface area of 59.06 m²g⁻¹.

Of particular interest are the frameworks of **1** and **2**, which are comprised of the exposed Mn^{II} metal centers oriented towards the 1D channels. Because one labile water molecule occupies a coordination site of the Mn^{II} atom, we speculated that the Mn centers can be activated as a source of catalytic active sites. The development of efficient catalyst systems for the selective oxidation of phenylmethanol to form benzaldehyde has recently attracted considerable attention.^[13,14] To evaluate the catalytic properties of both compounds, we have employed our system for the selective oxidation of phenylmethanol.

After the samples of 1 and 2 were treated under vacuum at 90°C for 3 h, the dried samples were subsequently immersed in phenylmethanol for 12 h. The solid samples were separated by filtration and thoroughly washed with diethyl ether to remove the surface-adsorbed solvent molecules. The solid samples were digested with 10% aqueous NH₃ solution, which were subsequently extracted with diethyl ether. GC analysis suggests that about 0.3 or 0.5 of a phenylmethanol molecule per formula unit is found in compound 1 or 2. The catalytic experiment was performed in acetonitrile with $NaIO_4$ as the oxidant and in the presence of solid 1 under ambient light; the reaction was monitored by using GC-MS. When the reaction was performed at 60 °C for 18 h, the oxidation product was benzaldehyde in 64% yield (Table 1, entry 1). However, if 2 was used instead of 1 to prompt the catalytic reaction, the benzaldehyde yield in-

Table 1.	Selective	oxidation	of	phenylmethanol. ^[a]	
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Entry	Catalyst	Yield % ^[b]
1	1	64
2	2	97
3	-	0
4	2	95 ^[c]
5	1	70 ^[d]
6	1	98 ^[c]
7	1	28 ^[e]
8	1	34 ^[d,e]
9	1	33 ^[c,e]
10	MnCl ₂ ·4H ₂ O	80

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[a] Catalyst (0.005 mmol), phenylmethanol (0.1 mmol), and NaIO₄ (0.15 mmol) in CH₃CN (2 mL) were stirred at 60 °C for 18 h under ambient light. [b] Yields were determined by using GC on a SE-54 column. [c] The third cycle. [d] The second cycle. [e] Performed in the absence of light.

creased to 97% (Table 1, entry 2). No trace of benzaldehyde was detected in the absence of catalyst under otherwise identical reaction conditions (Table 1, entry 3). Catalyst **2** can be easily separated by filtration and was reused in a successive run without a decrease in the catalytic activity (Table 1, entry 4). The PXRD of recovered solid **2** showed that the structural integrity was maintained during the catalytic reaction (Figure S13 in the Supporting Information).

We also studied the catalytic reusability of 1 under the ambient light source. Most surprisingly, the benzaldehyde yield increased to 70% in the second run (Table 1, entry 5) and reached 98% in the third run (Table 1, entry 6), which is comparable to that of 2. The PXRD pattern of the recovered solid is similar to that of 2, which is quite different to that of freshly prepared solid 1. ¹H NMR spectroscopy suggests that L is completely transformed into L'. To gain insight into the possible transformation mechanism, the catalytic reaction was performed in the absence of light but under otherwise identical conditions. The benzaldehyde yield is only 28% for the fist run, 34% for the second run and 33% for the third run (Table 1, entries 7–9). ¹H NMR spectroscopy suggests that L remained intact during these catalytic experiments, which indicates that the transformation from 1 to 2 was induced by the ambient light source. The distinct catalytic activities of 1 and 2 can be attributed to the different cavity sizes for the diffusion of the substrate, as mentioned above. For comparison, MnCl₂·4H₂O was used as a catalyst under identical conditions. However, only an 80% yield of benzaldehyde was obtained, which is inferior to that of 2 (Table 1, entry 10). No trace of benzaldehyde was detected when phenylmethanol was treated with the hot filtrate from a mixture of 1 or 2, NaIO₄, and acetonitrile under otherwise identical conditions, which proves the nature of the heterogeneous oxidation process.

In summary, a novel approach to generate a neutral 2D MOF that has C=C centers at a reasonable distance for photochemical [2+2] cycloaddition has been demonstrated. The 2D \rightarrow 3D topochemical structural transformation represents the first example of 2D \rightarrow 3D SCSC photochemical transformation. Finally, the two MOFs present interesting catalytic activity for phenylmethanol oxidation and an associated 2D \rightarrow 3D structural transformation induced by ambient light under the catalytic conditions.

Experimental Section

Synthesis of [Mn₂L₂(H₂O)₂]·3H₂O (1): Ligand H₂L (10 mg, 0.037 mmol) and MnCl₂·4H₂O (20 mg, 0.10 mmol) were dissolved in a mixture of DMF (10 mL) and H₂O (16 mL). After the resulting yellow solution was heated at 80 °C for ten days, brown crystals were filtered, washed with DMF, H₂O, and EtOH, and dried at RT (yield: 6.0 mg; 44.2%, based on H₂L). IR (KBr pellet): $\tilde{\nu}$ =1608 s, 1560 s, 1449 s, 1424 m, 1387 s, 1293 w, 1253 w, 1224 w, 1205 w, 1015 m, 964 m, 870 w, 814 m, 781 m, 731 s, 547 cm⁻¹ m; elemental analysis calcd. (%) for 1: C 49.06, H 3.84, N 3.81; found: C 48.30, H 3.82, N 3.82.

Synthesis of $[Mn_2L'(H_2O)_2]$ - $3H_2O$ (2): A crytalline sample of 1 (15 mg) was placed between two quartz glass slides at a distance of 10 cm from a

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300 W Hg lamp, which was irradiated under the ambient atmosphere at RT for 24 h to afford yellow crystals of **2** in quantitative yield. Because **2** is insoluble in common organic solvents and water, the crystals of **2** were decomposed by using an aqueous 10% HCl solution. The resulting solid was filtered, washed with H₂O and EtOH, and dried in vacuum to obtain H₄L'. ¹H NMR ([D₆]DMSO, 500 MHz, TMS): δ = 13.30 (brs, 4H), 8.44–8.48 (m, 4H), 8.19 (s, 2H), 8.02 (s, 4H), 7.59 (s, 4H), 4.93 ppm (s, 4H); elemental analysis calcd. (%) for **2**: C 49.06, H 3.84, N 3.81; found: C 48.46, H 3.79, N 3.92.

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- [9] Crystal data for 1: $C_{30}H_{28}Mn_2N_2O_{13}$; $M_r = 734.42$; triclinic; space group $P\bar{1}$; a = 7.7506(7), b = 9.7954(7), c = 13.034(1) Å; a = 69.561(8), $\beta = 86.021(8), \gamma = 70.154(8)^{\circ}; V = 870.81(13) \text{ Å}^3; Z = 1; T = 293(2) \text{ K};$ $R_{\rm int} = 0.0319; \quad \rho_{\rm calcd} = 1.400 \text{ g cm}^{-3}; \quad \mu = 0.788 \text{ mm}^{-1}; \quad F(000) = 376;$ GOF=1.055; 6313 reflections measured; 3553 unique. The final $R_1 = 0.0773$, $wR_2 = 0.2001$ for 2271 observed reflections with $I > 2\sigma(I)$ and 211 parameters. Crystal data for 2: $C_{30}H_{28}Mn_2N_2O_{13}$; $M_r =$ 734.42; triclinic; space group $P\bar{1}$; a=7.8494(4), b=9.9876(6), c=12.6067(9) Å; $\alpha = 104.131(6)$, $\beta = 91.094(5)$, $\gamma = 111.882(6)^{\circ}$; V =882.69(9) Å³; Z=1; T=293(2) K; $R_{int}=0.0485$; $\rho_{calcd}=1.382$ g cm⁻³; $\mu = 0.788 \text{ mm}^{-1}$; F(000) = 376; GOF = 1.235; 6071 reflections measured; 3596 unique. The final $R_1 = 0.0811$, $wR_2 = 0.2057$ for 1615 observed reflections with $I > 2\sigma(I)$ and 211 parameters. CCDC-808588 (1) and 808589 (2) 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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