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A metalloporphyrin functionalized metal–organic framework for selective oxidization of styrene[†]

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A functional metal–organic framework assembled from palladiumporphyrin building blocks and cadmium(II) connecting nodes presents interesting topological network structure, high framework stability and interesting catalytic property for the selective oxidation of styrene.

Compared with traditional inorganic zeolites, the functionalities of metal–organic frameworks (MOFs) have the advantage that they can be easily modified by tailoring the organic ligands and selecting the metal nodes, which can be subsequently realized into various applications in diverse fields.^{1–3} Because metalloporphyrin molecules possess unique biological and chemical functionalities, such as structural robustness, catalysis, charge and energy transformation, the interrelated researches have attracted considerable interest in diverse fields.⁴ There are many metal–organic coordination networks assembled from porphyrin or metalloporphyrin building blocks, which present interesting topological network structures, great thermal and chemical stabilities.^{5–7} However, limited works were focused on the investigation of the catalytic properties of these interesting materials.⁷

During the course of our studies on the synthesis of functional MOFs for catalytic applications, we think that incorporating metalloporphyrin building blocks in porous MOFs might generate some interesting properties for heterogeneously catalytic applications. Because the active metal sites are fixed in the rigid porphyrin cores, the catalytic active sites on the channel walls of MOFs should be accessible to the included substrates. Most interestingly, the catalytic functionalities can be simply tailored by adjusting the active metal sites and the peripheral environments of the porphyrin cores. Inspired by the relevant functionalities, we have recently synthesized a series of robust functional porous MOFs based on 5,10,15,20-tetra(carboxyphenyl)metal-porphyrin (M-H₄TCPP) ligand. Herein, we report the synthesis and characterizations of a novel Pd^{II}-porphyrin-based solid

of $[Cd_{1.25}(Pd-H_{1.5}TCPP)(H_2O)] \cdot 2DMF$ (1), which showed significant catalytic activity for styrene oxidation.

Dark brown crystals of 1 were synthesized by heating a mixture of Pd-H₄TCPP and Cd(NO₃)₂·4H₂O in a mixed solvent of DMF, MeOH and acetic acid at 80 °C for ten days.[‡] Single crystal X-ray structural analysis has revealed that there are two crystallographically independent cadmium(II) atoms, one partially protonized ligand, one agua ligand and two DMF guest molecules in the asymmetric unit.§ The first Cd atom coordinates to eight carboxyl oxygen atoms of four Pd-TCPP carboxylate groups, while the second partially occupied Cd atom is surrounded by four carboxyl groups of four Pd-TCPP ligands and two water molecules. Because the second Cd atom is only quarterly occupied, the Cd atoms are bridged by the carboxylate groups to extend into a pseudo linear network. Alternatively, each Pd-TCPP ligand acts as an octadentate ligand to coordinate eight Cd atoms of four neighboring Cd chains to propagate into a 3D framework structure (Fig. 1). The solid-state framework contains two kinds of channels with dimensions of 4.61 \times 12.55 Å² and 8.27×9.32 Å² (considering the van der Waals diameters) along the *a* axis. The channels are filled with DMF solvent molecules.



Fig. 1 (a) A view of the 3D framework of **1** down the 1 1 0 direction, showing the arrangement of the palladium-porphyrins. (b) The 3D framework of **1** as viewed down the *a* axis, showing the 1D opening channels and the accessible Pd^{II} sites. (c) Side view of the 1D channel in the porous framework of **1**.

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Table 1Selective oxidation of styrene catalyzed by solid 1^a

$ \begin{array}{c} & & & \\ & $				
			Select. $(\%)^c$	
Entry	Acid^b	Conv. (%) ^{<i>c</i>}	Ι	II
1	1	100	91	9
2	0	0	0	0
3	0.5	75	82	18
4	1.5	100	88	12
5	1 (HOAc)	0	0	0
6	1 (HCl)	5	52	47
7	$1 (HNO_3)$	80	86	14
8	$1 (H_2 SO_4)$	90	95	5
9	1	90	78	22^{d}
10	1	0	0	0^e
11	1	35	49	51 ^f
12	1	100	57	7^g
13	1	100	89	11^{h}

^{*a*} Solid **1** (0.01 mmol), styrene (0.2 mmol), HClO₄ (70%, 0.01 mmol) and H₂O₂ (30%, 0.6 mmol) in CH₃CN (6 mL) were stirred at 55 °C for 12 h. ^{*b*} Acid/catalyst ratio (the acids other than perchloric acid are shown in the parentheses). ^{*c*} Conversion% and selectivity% were determined by GC on a *SE-54* column. ^{*d*} Catalyzed by Pd–H₄TCPP. ^{*e*} Catalyzed by PdCl₂. ^{*f*} Catalyzed by Pd/Cl₂. ^{*f*} Catalyzed by Pd/Cl₂. ^{*f*} The sixth cycle.

It is worth noting that the porphyrin unit in **1** adopts a coplane conformation with the mean deviation of 0.0275 Å, while the palladium atom is fully coplane with four pyrrole nitrogen atoms. In the crystal structure, all of the porphyrin units are packed along two orientations with the dihedral angle of 95.3°. PLATON calculations indicate that **1** contains 38.9% (2218.5 Å³ per unit cell) void space which is accessible to the solvent molecules.⁸ Thermogravimetric analysis showed a weight loss of 13.8% occurred between 25 and 310 °C, corresponding to the loss of DMF molecules and aqua ligands (expected 13.7%).

Whereas the catalytic application of MOFs requires that the framework structures need to be maintained without solvent guests or exchanged with other molecules, we therefore examined the framework stability of 1 during solvent removal and inclusion processes. After a sample of 1 was treated under vacuum at 90 °C for 12 h, a PXRD of the resultant crystalline solid showed a sharp diffraction pattern that is similar to that of the pristine sample (supporting information Fig. S5[†]). This result indicates that the porous framework was maintained after the removal of the solvent molecules. Furthermore, the crystals of the evacuated sample did not change in the morphology, size and transparency that were observed under a microscope. Single crystal X-ray analysis of 1a in a sealed capillary showed that the robust solvent free framework presents almost identical structural features as the original.⁶ Interestingly, upon exposure of the solvent free framework 1a to the vapor of water for one day or in air for one week, 1a can adsorb water molecules as guests enclosed in the channels to form hydrated solid 1b, which was characterized by single crystal X-ray analysis. The framework of 1b is essentially identical to that of 1. The only difference between 1 and 1b lies in the inclusion of different solvent molecules. PXRD of the bulk sample of 1b showed that the sharp diffraction

patterns are similar to that of the freshly prepared sample. To eliminate the ambiguity of the solvent identities from X-ray diffraction studies, we have monitored the solvent exclusion processes by ¹H NMR spectroscopy (supporting information Fig. S6[†]). With a benzene internal standard and CDCl₃ as the solvent, we determined that a freshly prepared sample of 1 contains two DMF molecules per formular unit. After a sample of 1 was treated under vacuum at 90 °C for 12 h, ¹H NMR spectroscopy has showed that the DMF molecules are almost fully evaporated, which confirmed the solvent free framework of 1a. The above experiments indicate that the porous frameworks were maintained after the removal or absorption of the solvent molecules, which led to the solids with permanent porosity and framework integrity. These results suggest that the framework structure of 1 can be maintained during potential heterogeneous catalytic reactions.

We are aware that the porous network of 1 comprises the palladium sites in the channel walls along with the tailored functional zeolitic periphery. Recent studies have shown that such kind of metal sites within porous MOFs present interesting catalytic activities.^{7,9} Since the oxidation of styrene has attracted considerable interest for the academic research and utilization in the industry,^{10,11} we have evaluated the accessibility of the open channels in 1 to styrene molecules by submerging the crystals of the evacuated sample of 1a in styrene for 12 h. The resultant crystals of 1c can tolerate such treatment without losing the crystallinity as confirmed by PXRD. The single crystal X-ray analysis showed that the unitcell dimensions of the resultant crystals are not significantly changed, and the styrene molecules are enclosed in the channels of 1c.§ ¹H NMR spectroscopy showed that the formular unit of **1c** contains two styrene molecules, as determined by ¹H NMR integrations with a methanol internal standard and CDCl₃ as the solvent.

Recently, the palladium-catalyzed selective oxidation of styrene to acetophenone has attracted considerable interest because the practical importance of acetophenone and the high selectivity of the palladium-catalysts.¹¹ The styrene oxidation by solid 1 was conveniently performed in CH₃CN using H₂O₂ as oxidant in the present of HClO₄ with GC-MS monitored through out the reaction. When the reaction was performed at 55 °C for 12 h, styrene was completely oxidized into a mixture of 91% acetophenone and 9% benzaldehyde (Table 1, entry 1). The catalytic results are very sensitive to the quantity and acidity of the additive acids (Table 1, entries 2-8). Addition of solid 1 alone, there is no detectable product (Table 1, entry 2). When the additive quantity of HClO₄ was increased, the styrene conversion increases gradually. However, the acetophenone selectivity is depressed concomitantly (Table 1, entries 3 and 4). To understand the different acid additive effect on the catalytic transformation, we have attempted the reactions using a variety of acids instead of perchloric acid (Table 1, entries 5-8). HOAc did not give any help for the catalytic transformation, while HCl prompted the transformation less efficiently. Despite the acetophenone selectivities of HNO₃ and H₂SO₄ which are comparable to that of HClO₄, the styrene substrate cannot be oxidized completely. These results indicate that the acids and their acidities play critical roles for the styrene oxidation.

To make a comparison, a series of control catalysts were used to conduct the catalytic experiments. $Pd-H_4TCPP$ is less efficient to prompt the catalytic transformation, while $PdCl_2$ cannot prompt the catalytic transformation (Table 1, entries 9 and 10). Moreover, when Pd/C was used as catalyst, only a small amount of styrene was oxidized with very low acetophenone selectivity (Table 1, entry 11). Despite $Pd(OAc)_2$ can prompt styrene to be fully oxidized, the acetophenone selectivity is highly decreased (Table 1, entry 12). These results suggest that the catalytic activity of **1** is superior to its corresponding components.

After a mixture of solid 1 and CH₃CN in the presence of HClO₄ was heated at 55 °C for 12 h under stirring, H₂O₂ and styrene were subsequently added into the hot filtrate, which was heated at 55 °C for another 12 h. GC result indicates that the mixture is unreactive. Additionally, ¹H NMR spectroscopy indicates that no detectable Pd-TCPP ligand was released into the solution. Catalyst 1 can be simply recovered by filtration, which was subsequently used in the successive runs without deteriorating the catalytic activity (Table 1, entry 13). A PXRD pattern of the recovered solid suggests that the structural integrity of the catalyst was maintained after the catalytic experiment (supporting information Fig. S5[†]). All these experiments proved that the present catalyst system is heterogeneous in nature, and especially the catalytic activity was highly depressed when homogeneous components were used instead of solid 1.

In summary, we have synthesized a new porous MOF 1, which incorporates the functional bridging ligand with Pd^{II} active sites in the porous solid 1 for the catalytic oxidation reaction. Compound 1 undergoes interesting transformations from the solvent inclusion to solvent free to solvent inclusion frameworks. The framework-immobilized solid 1 not only conferred the advantage of higher stability, but also showed significant styrene oxidation activity, easier separation and recyclability for the catalytic application.

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Notes and references

‡ Yield: 38 mg (37.8%, based on Pd–H₄TCPP). IR (KBr): $\nu = 1605$ (m), 1586 (m), 1541 (m), 1401 (s), 1351 (w), 1177 (w), 1102 (w), 1014 (s), 871 (w), 853 (w), 795 (w), 777 (w), 715 (w), 495 (w) cm⁻¹.

§ Crystal data for 1: $C_{54}H_{41.5}Cd_{1.25}N_6O_{11}Pd$, $M_r = 1197.33$, monoclinic, space group C2/c, a = 7.2953(1) Å, b = 25.5761(7) Å, c = 30.7597(6) Å, $\beta = 96.361(2)^\circ$, V = 5704.0(2) Å³, Z = 4, T = 293(2), $R_{int} = 0.0332$, $D_c = 1.394$ g cm⁻³, $\mu = 6.756$ mm⁻¹, F(000) = 2406, GOF = 1.024, 15512 reflections measured, 4054 unique. The final $R_1 = 0.0776$, $wR_2 = 0.1837$ for 3395 observed reflections with $I > 2\sigma(I)$ with 284 parameters. Crystal data for 1a: $C_{48}H_{25.5}Cd_{1.25}N_4O_8Pd$, $M_r = 1033.12$, monoclinic, space group C2/c, a = 7.217(2) Å, b = 25.613(5) Å, c = 30.660(3) Å, $\beta = 96.39(1)^\circ$, V = 5632.5(17) Å³, Z = 4, T = 293(2), $R_{int} = 0.0585$, $D_c = 1.218$ gcm⁻³, $\mu = 6.713$ mm⁻¹, F(000) = 2046, GOF = 0.908, 7339 reflections measured, 3942 unique. The final $R_1 = 0.0886$, $wR_2 = 0.1752$ for 1498 observed reflections with

 $I > 2\sigma(I)$ with 275 parameters. *Crystal data for* 1b: C₄₈H_{47.5}Cd_{1.25}N₄O₁₉Pd, $M_r = 1231.30$, monoclinic, space group C2/c, a = 7.1564(9) Å, b = 25.080(4) Å, c = 31.192(3) Å, $\beta = 96.29(1)^{\circ}$, V = 5564.7(12) Å³, Z = 4, T = 293(2), $R_{int} = 0.0783$, $D_c = 1.470$ g cm⁻³, $\mu = 7.036$ mm⁻¹, F(000) = 2486, GOF = 0.788, 8511 reflections measured, 3941 unique. The final $R_1 = 0.0938$, $wR_2 = 0.2092$ for 1638 observed reflections with $I > 2\sigma(I)$ with 284 parameters. *Crystal data for* 1c: C₆₄H₄₁Cd_{1.25}N₄O_{8.5}Pd, $M_r = 1248.91$, monoclinic, space group C2/c, a = 7.2751(3) Å, b = 25.591(2) Å, c = 30.775(1) Å, $\beta = 96.478(4)^{\circ}$, V = 5692.9(5) Å³, Z = 4, T = 293(2), $R_{int} = 0.0417$, $D_c = 1.457$ g cm⁻³, $\mu = 6.754$ mm⁻¹, F(000) = 2508, GOF = 1.070, 9346 reflections measured, 4037 unique. The final $R_1 = 0.0969$, w $R_2 = 0.2234$ for 2852 observed reflections with $I > 2\sigma(I)$ with 280 parameters.

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