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A Sn^{IV}–Porphyrin-Based Metal–Organic Framework for the Selective Photo-Oxygenation of Phenol and Sulfides

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Supporting Information

ABSTRACT: A functional tin(IV)–porphyrin derivative was used as a building block to construct a novel 3D porous metal–organic framework (MOF). The MOF is built up from tin(IV)–porphyrin struts linking up Zn atoms and formates joining Sn^{IV} centers. The immobilization of the photoactive Sn–porphyrins in the channel walls lets the MOF present remarkable photocatalytic activities for the oxygenation of phenol and sulfides, resulting in excellent yields and remarkable selectivity in heterogeneous phases.

Metal–organic frameworks (MOFs) have gained extensive attention in the past decade due to their interesting properties for potential applications in various fields such as nonlinear optics,[1] gas storage,[2] catalysis,[3] chemical sensoring,[4] and biomedical imaging.[5] Because of the remarkable functionalities of structural robustness, catalysis, charge ,and energy transformations derived from metalloporphyrin molecules,[6] using metalloporphyrins as building blocks for the construction of functional MOFs has gained particular favor.[7] Despite the fact that many metalloporphyrins present distinct photocatalytic activity in the homogeneous phase,[8] an investigation of the photocatalytic properties of metalloporphyrin-based MOFs has not been initialized yet.

Sensitizers are conjugated organic molecules with good photochemical characteristics for light activation. However, such structural features allow the sensitizers to be easily deactivated by reaction with the singlet oxygen in the homogeneous phase. Therefore, an efficient way to overcome the quenching process was developed involving immobilization of the sensitizers on suitable solids.[9] During our study of the synthesis of functional MOFs for photochemical catalytic applications, we have synthesized a series of metalloporphyrin-based porous MOFs. Herein, we report a 3D porous MOF of $[Zn_2(H_2O)_4Sn^{IV}(TPyP)(HCOO)_2]\cdot 4NO_3\cdot DMF\cdot 4H_2O$ (**1**), which is constructed from 5,10,15,20-tetra(4-pyridyl)-tin(IV)-porphyrin (Sn^{IV}TPyP) and formate linking up zinc atoms, and it presents excellent photocatalytic activities for phenol and sulfide oxygenations.

Dark purple crystals of **1** were synthesized by heating a mixture of $Sn^{IV}(OH)_2$TPyP and $Zn(NO_3)_2\cdot 6H_2O$ in a mixed solvent of DMF and CH_2Cl_2 at 50 °C for five days. Single crystal X-ray diffraction analysis has revealed that compound **1** crystallizes in the tetragonal *P*4/*mbm* space group with two zinc(II) atoms, one Sn^{IV}TPyP ligand, four aqua ligands, and two formates in the formular unit.[10] The anionic formate should be a thermal decomposition product of DMF.[11] The Zn atom coordinates to two pyridines of two Sn^{IV}TPyP ligands and two water molecules in a distorted tetrahedral geometry. Each Sn^{IV}TPyP ligand acts as a tetradentate ligand to bridge four Zn atoms, which further propagates into a 2D framework structure lying in the *ab* plane (Figure 1). The porphyrin unit and tin atom adopt a coplanar conformation in **1**. In the crystal structure, two porphyrin units are coupled together by a formate strut to coordinate two tin atoms. Consequently, the lamellae are linked by the formates to extend into a 3D porous network (Figures 2 and 3). The solid-state framework contains two kinds channels with dimensions of 6.32(1) × 32.39(1) Å^2 along the *a* and *b* axes and 5.97(1) × 26.92(1) Å^2 along the *c* axis. The channels are filled with DMF and water solvent molecules and nitrate anions. PLATON calculations indicate that **1** contains 54.8% void space, which is accessible to the guest molecules.[12] TG showed that a weight loss of 15.2% occurred between 25 and 239 °C, corresponding to the loss of DMF and water molecules (expected 15.3%).

Due to the widespread use of pesticides, herbicides, and insecticides, pollution from phenolic compounds has increased quickly.[13] Most importantly, phenolic compounds are highly toxic and are very difficult to degrade. To evaluate the photocatalytic activity, we have employed a system of the selective photo-oxygenation of 1,5-dihydroxynaphthalene in the presence of **1**.

When a mixture of 1,5-dihydroxynaphthalene and **1** in solvent MeOH, THF, CH_3CN, H_2O, or CH_2Cl_2 was subjected to a 350 W Xe lamp irradiation in an oxygen atmosphere for 3.5 h, only a small amount or no product was detected as monitored by GC-MS (Supporting Information, Table S2). When the reaction was performed in the optimized solvent of CH_2Cl_2/MeOH (4:1, v/v), the substrate could be fully oxidized into 5-hydroxynaphthalene-1,4-dione (Table 1, entry 1). This should be attributed to CH_2Cl_2 being able to prolong the lifetime of the singlet oxygen ($^1O_2$), but it is not a good solvent for the substrate, while MeOH is, on the contrary.[14] Remarkably, the mixed solvents can merge their merits to prompt photo-oxygenation smoothly. When the reaction was performed in the dark, no product could be detected (Table 1, entry 2). Detailed experiments showed that the catalytic activity of **1** is very sensitive to various factors such as the oxidant, light source, catalyst loading, and reaction time (Supporting Information, Table S2).

To make a comparison, a series of control catalysts was used to conduct the catalytic experiment. When $Sn^{IV}(OH)_2$TPyP was used as a catalyst under identical conditions, the product yield was 98%, while TPyP and $Zn(NO_3)_2\cdot 6H_2O$ only generated trace amounts of the product (Table 1, entries 3–5).

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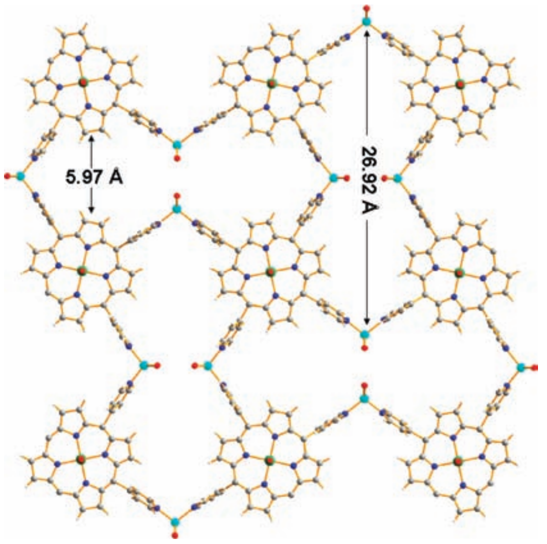


Figure 1. The lamellar network of Zn^{II} atoms linking up Sn^{IV}−porphyrins in **1** as viewed down the *c* axis.

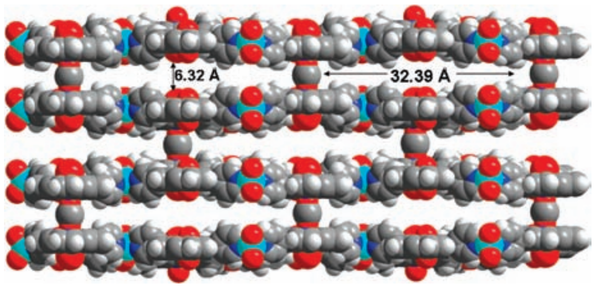


Figure 2. A side view of the 3D network of the lamellae linked by the formate struts in **1** down the *b* axis.

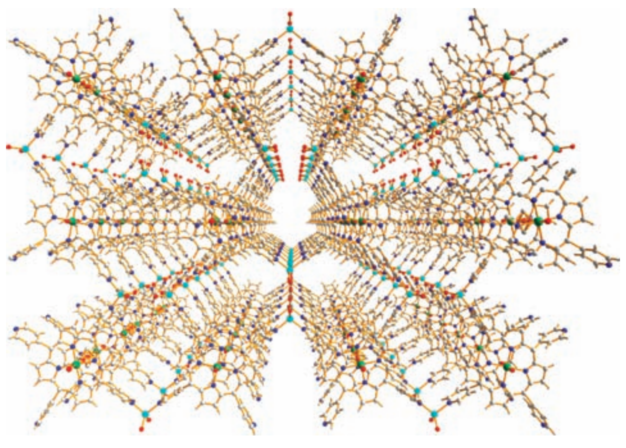
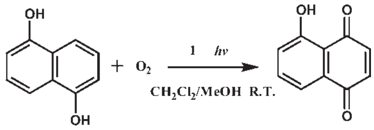


Figure 3. A perspective view of the 3D framework of **1** down the *c* axis.

Table 1. Photo-Oxygenation of 1,5-Dihydroxynaphthalene Catalyzed by 1[a]



entry	cat.	light source	yield%[b]
1	**1**	Xe	>99.9
2	**1**	dark	0
3	$Sn^{IV}(OH)_2TPyP$	Xe	98
4	TPyP	Xe	<1
5	$Zn(NO_3)_2 \cdot 6H_2O$	Xe	<1
6	**1**	Xe	>99.9[c]
7	$Sn^{IV}(OH)_2TPyP$	Xe	17[c]

[a] Solid **1** (0.005 mmol) and 1,5-dihydroxynaphthalene (0.05 mmol) in a mixed solvent of CH_2Cl_2/MeOH were stirred at room temperature under the irradiation of a 350 W Xe lamp for 3.5 h in the presence of O_2. [b] Based on GC-MS analysis. [c] The fourth cycle.

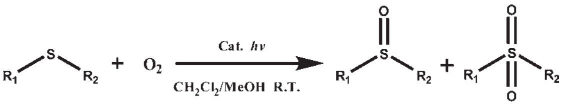
Catalyst **1** can be simply recovered by filtration, which was subsequently used in the successive run without deterring the catalytic activity (Table 1, entry 6). No trace product was detected when the filtrate from a mixture of 1,5-dihydroxynaphthalene and solid **1** in CH_2Cl_2/MeOH was used instead of **1** under otherwise identical conditions, which proved that the present catalyst platform is heterogeneous in nature. However, the catalytic activity of the recovered $Sn^{IV}(OH)_2TPyP$ decreases gradually to a minimum of 17% for the fourth run (Table 1, entry 7). These results suggest that the homogeneous catalyst is easily deactivated compared with solid **1**.

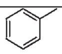
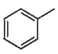
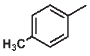
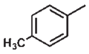
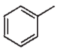
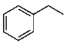
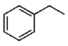
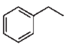
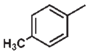
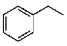
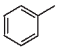
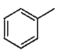
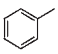
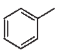
Sulfoxides are important complexes which have been extensively used as auxiliary ligands and synthetic intermediates.[15] One of the important methods for the synthesis of sulfoxides is via photo-oxygenation of sulfides.[16] To further evaluate the photocatalytic activity of **1**, photo-oxygenation of methyl(phenyl) thioether catalyzed by **1** was performed in various solvents at room temperature under irradiation with a light source. Detailed experiments showed that the catalytic activity is very sensitive to various factors such as the oxidant, solvents, catalyst loading, and reaction time (Supporting Information, Table S3). When the reaction was performed in the optimized solvent CH_2Cl_2/MeOH, the substrate was completely converted into the corresponding sulfoxide at room temperature under irradiation with a 350 W Xe lamp using O_2 as an oxidant (Table 2, entry 1). Under catalytic conditions, compound **1** can also prompt the transformation of various sulfides into sulfoxides (Table 2, entries 2−7). The product yields of sulfoxides range from 93 to >99.9%. Catalyst **1** can be simply recovered by filtration, which was subsequently used in the successive run without deterring the catalytic activity (Table 2, entry 8).

When $Sn^{IV}(OH)_2TPyP$ was used as a catalyst under identical conditions, the sulfide could be fully oxidized into a mixture of 94% sulfoxide and 6% sulphone (Table 2, entry 9), while TPyP let the substrate be partially oxidized into a mixture of 68% sulfoxide and 12% sulphone. $Zn(NO_3)_2 \cdot 6H_2O$ is less efficient at prompting the catalytic process (Table 2, entries 10 and 11). These results suggest that the catalytic activity of **1** is superior to those of its corresponding components.

In summary, we have synthesized a robust 3D porous MOF constructed from photoactive Sn^{IV}TPyP building blocks. The photo-oxygenation of 1,4-dihydroxybenzene and sulfides catalyzed by **1** under Xe lamp irradiation gave excellent product yields, which are superior to those of its corresponding

Table 2. Photo-Oxygenation of Sulfides Catalyzed by 1[a]



Entry	R_1	R_2	sulfoxide Yield%[b]	sulphone yield%[b]
1		$-CH_3$	>99.9	0
2		$-CH_2CH_3$	>99.9	0
3		$-CH_3$	>99.9	0
4		$-CH_2CH_3$	>99.9	0
5			93	0
6			>99.9	0
7			97	0
8		$-CH_3$	99	0[c]
9		$-CH_3$	94	6[d]
10		$-CH_3$	68	12[e]
11		$-CH_3$	12	0[f]

[a] Sulfide (0.05 mmol) and solid **1** (0.005 mmol) in a mixed solvent of CH_2Cl_2/MeOH (4 mL/1 mL) were stirred at room temperature for 12 h under the irradiation of a 350 W Xe lamp in an O_2 atmosphere. [b] Based on GC-MS analysis. [c] The sixth cycle. [d] Catalyzed by $Sn^{IV}(OH)_2TPyP$. [e] Catalyzed by TPyP. [f] Catalyzed by $Zn(NO_3)_2 \cdot 6H_2O$.

components. This work showed that the photoactive sites can be immobilized in the channel walls of porous MOFs to subsequently realize the outstanding photocatalytic performances in heterogeneous phases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, additional figures, catalytic results, and crystallographic data (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for **1**: $C_{45}H_{49}N_{13}O_{25}SnZn_2$, M_r = 1421.40, tetragonal, space group $P4/mbm$, a = 22.8951(3) Å, c = 9.3454(5) Å, V = 4898.7(3) Å^3, and Z = 2, D_c = 0.964 g·cm^{-3}, μ = 0.794 mm^{-1}, F(000) = 1440, R1 = 0.0899, wR2 = 0.2271, and S = 1.018.

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