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A metal–metalloporphyrin framework based on an octatopic porphyrin ligand for chemical fixation of CO_2 with aziridines†

Xun Wang,‡[ab] Wen-Yang Gao,‡[b] Zheng Niu,[b] Lukasz Wojtas,[b] Jason A. Perman, [ID] *[b] Yu-Sheng Chen,[c] Zhong Li,*[a] Briana Aguila[b] and Shengqian Ma [ID] *[b]

A new porous metal–metalloporphyrin framework, MMPF-10, has been constructed from an octatopic porphyrin ligand, which links copper paddlewheel units to form a framework with fmj topology. *In situ* metallation of the porphyrin ligands provides MMPF-10 with two unique accessible Cu(II) centers. This allows it to behave as an efficient Lewis acid catalyst in the first reported reaction of CO_2 with aziridines to synthesize oxazolidinones catalyzed by an MMPF.

Given the competitive nature to outperform traditional porous materials, such as zeolites and carbonaceous materials for their porous properties, an increase in the use of metal–organic frameworks (MOFs) is prevalent in the scientific literature.[1] These materials are designed and synthesized from metal ions/clusters and organic molecules (participating as nodes and spacers),[1,2] which have shown higher tunability than their strictly inorganic or carbonaceous counterparts – in part due to the large assortment of reagents. Desired structures are obtainable by the judicious selection of reagents, followed by appropriate reaction conditions.[3] Once synthesized, the organic ligands or metal ions can be modified *via* post-synthetic procedures to impart new physical or chemical properties in the materials.[4]

As an important subclass of MOFs, metal–metalloporphyrin frameworks (MMPFs)[5] have attracted an increasing amount of attention because they have been shown to perform well in applications such as gas storage/separation,[6,7] catalysis,[8,9] photochemistry,[10,11] and additional areas of research.[12,13]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China. E-mail: cezhli@scut.edu.cn

[b] Department of Chemistry, University of South Florida, 4202 East Flower Avenue, Tampa, Florida 33620, USA. E-mail: sqma@usf.edu; Fax: +1-813-974 3203; Tel: +1-813-974 5217

[c] ChemMatCARS, Center for Advanced Radiation Sources, The University of Chicago, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

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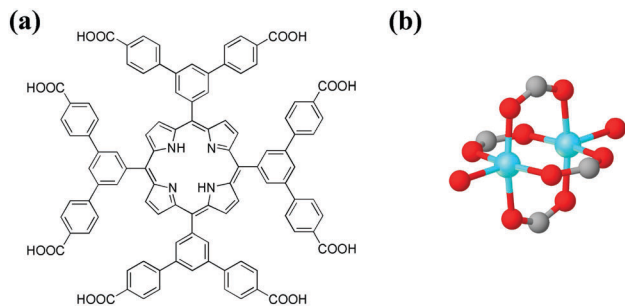
‡ These authors contributed equally to this work.

MMPFs can possess mono-, bi- or multi-metallic systems because the porphyrin molecule can be metallated before, or *in situ*, or after the syntheses of these materials.[14,15] Porphyrin ligands allow extra accessible metal sites (if not coordinated from other ligands) which will allow them to participate as catalytic sites similarly to naturally occurring systems.[16,17] In addition, porphyrin molecules are chemically modifiable and their dimensions or chemical functionality can be altered at the *meso*-positions. The resulting MMPF synthesized from larger porphyrin molecules could possess bigger pores that would help facilitate both faster diffusion of substrates and larger substrates to reach the many reactive centers within a porous framework to enhance its catalytic activity.[17,18]

Many MOFs, particularly MMPFs, have been used as heterogeneous Lewis-acid catalysts for CO_2 chemical transformation reactions with epoxides to form cyclic carbonates.[16,19,20] A class of heterocyclic chemicals similar to epoxides, aziridines,[21] allows the cycloaddition reactions with CO_2 to form oxazolidinones.[22–24] This class of compounds is particularly important for use in antimicrobial agents such as tedizolid,[25,26] linezolid,[27,28] and radezolid.[29,30] Previously, homogenous catalysts have shown good abilities to convert CO_2 and aziridines into oxazolidinones.[31–33] However, these catalysts cannot be easily recycled, thus bringing about a need for new heterogeneous catalysts to perform as well or better than homogeneous catalysts. Comparably, only a few heterogeneous catalysts have been reported for this reaction.[34–36] To the best of our knowledge, MMPFs have not been used as a catalyst for CO_2 cycloaddition reactions with aziridines.

In this work, we report a porous metal–metalloporphyrin framework, MMPF-10, which is constructed from an octatopic ligand, tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (H_{10}TBCPPP, Fig. 1a) and copper paddlewheel building blocks (Fig. 1b). With the inclusion of Cu(II) as a Lewis acid catalytic site, we explored this material's performance in the cycloaddition reactions between aziridines and CO_2.

Dark red block-shaped crystals of MMPF-10 were obtained *via* the solvothermal reaction of H_{10}TBCPPP and Cu(NO$_3$)$_2$·2.5H$_2$O

Fig. 1 (a) Tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (H$_{10}$TBCPPP) and (b) copper paddlewheel SBU (turquoise, copper; red, oxygen; grey, carbon).

in *N,N*-dimethylacetamide (DMA) at 65 °C (ESI†). Single crystal X-ray diffraction analysis revealed that MMPF-10 [Cu$_4$(CuTB-CPPP)(H$_2$O)$_4$] crystallized in the orthorhombic *Immm* space group with a = 26.294(4) Å and c = 34.046(6) Å. Each copper paddlewheel is connected with four porphyrin ligands, which in turn connect to eight copper paddlewheels producing a 3D non-interpenetrated structure. When assuming the copper paddle-wheel to be a 4-connected node and the porphyrin ligand to be one 4-connected node (porphyrin ring) and four 3-connected nodes (terphenyl arm), MMPF-10 displays a (3,4,4)-connected network with the topology of **fmj** (Fig. 3a), which differs from the **fjh** topology of UNLFPF-1[6] constructed from the same porphyrin ligand joined with the zinc paddlewheel. The differences between these two materials can be attributed to the torsion angle between the porphyrin ring and its *meso*-substituent phenyl rings. The torsion angles are 92.92° for MMPF-10 and 117.06° for UNLFPF-1 (Fig. S4 and S5, ESI†). This difference in torsion angle results in a different pore structure of MMPF-10 (Fig. 2). The primary elongated hexagonal channels are observed along the *c*-axis and shown from the side view (Fig. 2a and c). This channel is generated from a ring of four metallated porphyrin ligands and four copper paddlewheels, which form a channel with cross-sectional dimensions of 25.6 × 15.6 Å, measured between pyrrole carbon atoms and two *meso*-substituent phenyl rings. The secondary cavity is enclosed by a porphyrin's *meso* side arm coordinating with four copper pad-dlewheels and a porphyrin base, exhibiting a pentagonal-like window and a cavity suitable to fit a sphere with a diameter of 11 Å. (Fig. 2b). The free space in the fully desolvated MMPF-10 calculated using PLATON is 79.6% of the total crystal volume, which is comparable with 79.4% of PCN-222, a typical porphyrin-based MOF, and is slightly higher than the 78.0% free space of UNLFPF-1.[6]

Phase purity of MMPF-10 was confirmed by powder X-ray diffraction (PXRD) studies, which show good agreement with the calculated diffraction pattern (Fig. S6, ESI†). Its permanent porosity was evaluated through N$_2$ isotherm measurements at 77 K after samples were activated using supercritical CO$_2$ (ESI†). A type I adsorption isotherm was observed for MMPF-10 that confirmed its microporous nature, with an uptake of ∼120 cm^3 g^{-1} at the saturated pressure (Fig. 3b). Derived from the N$_2$ adsorption isotherm, MMPF-10 possesses a
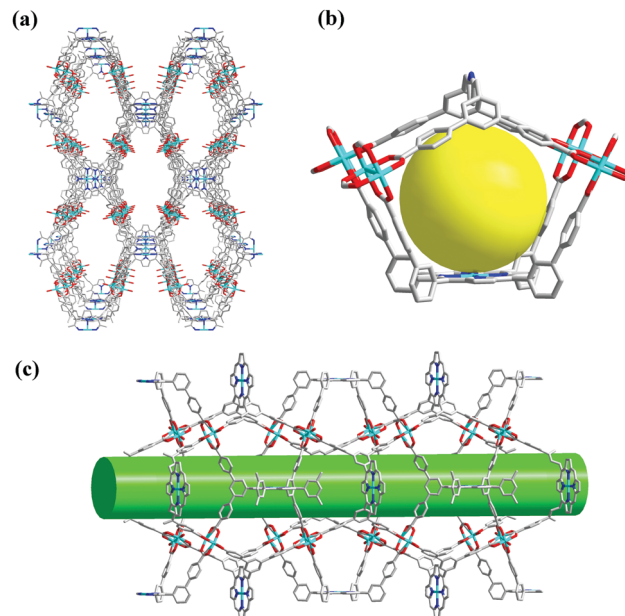

Fig. 2 (a) Hexagonal channel of MMPF-10 viewed along the *c*-axis; (b) pentagonal cavity of MMPF-10; and (c) a side view of the hexagonal channel (turquoise, copper; red, oxygen; grey, carbon; blue, nitrogen).
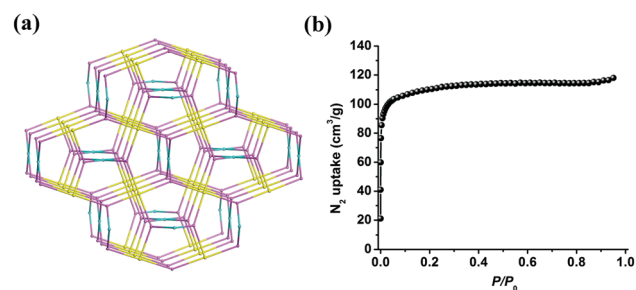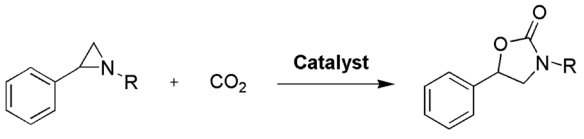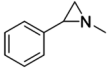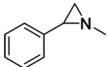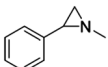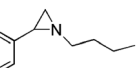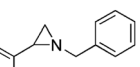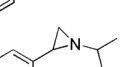

Fig. 3 (a) (3,4,4)-Connected network of MMPF-10 (blue points, porphyrins; yellow points, paddlewheels; pink points, terphenyl arms). (b) N$_2$ adsorption isotherm of MMPF-10 at 77 K.

Brunauer–Emmett–Teller (BET) surface area of ∼419 m^2 g^{-1} (corresponding to a Langmuir surface area of ∼478 m^2 g^{-1}).

Albeit MMPFs have shown high catalytic activity in cycload-dition reactions between CO$_2$ and epoxides, they have not been explored to catalyze the reaction between aziridines and CO$_2$. Table 1 (entries 1–3) shows the catalytic results from the aziridine cycloaddition under 1 bar of CO$_2$ at room tempera-ture. MMPF-10 displayed a moderate catalytic activity for the cycloaddition of 1-methyl-2-phenylaziridine to form 3-methyl-5-phenyl-2-oxazolidinone with a yield of 63% (Table 1, entry 1), which was higher than 47% for HKUST-1 under similar reaction conditions (Table 1, entry 2). The higher catalytic activity for MMPF-10 compared with HKUST-1 could be presumably ascribed to the higher propensity for aziridines situated near the easier accessible Lewis-acid Cu(II) sites in the metallated porphyrin ring, which are activated, followed by attack of Br$^-$ from *n*Bu$_4$NBr and reaction with CO$_2$ molecules.[18,36,37]

Table 1 Cycloaddition reactions of different substituted aziridines with CO_2 catalyzed by MOFs

Entry	Substrate	CO_2 pressure (MPa)	Yield (%)
1[a]		0.1	63
2[b]		0.1	47
3[c]		2	>99
4[c]		2	99
5[c]		2	96
6[c]		2	71

[a] Reaction conditions: aziridine (1 mmol), MMPF-10 (0.625 mol% based on copper paddlewheel units), TBAB (0.05 mmol), 25 °C, 3 days. [b] Same reaction conditions catalyzed by HKUST-1 (0.625 mol%). [c] Same amounts of aziridines and catalysts, 100 °C, 10 h.

To further enhance the yield of the reaction, we conducted the experiment under high pressure (2 MPa CO_2) and elevated temperature conditions [Table 1, entries 3–6]. The yield of the corresponding oxazolidinone from 1-methyl-2-phenylaziridine increased to over 99%, implying that the catalytic activity was significantly improved under higher pressure and higher temperature. This increased activity is ascribed to the faster conversion rate of CO_2 cycloaddition with aziridines after the concentration of CO_2 was increased, compared to that of self-polymerization of aziridines to form a dimer product.[38–40] We also investigated the cycloaddition reaction activity of MMPF-10 in CO_2 cycloaddition with different substituted aziridines under similar reaction conditions. The results showed that all the corresponding oxazolidinones were obtained in high yields even after increasing the molecular sizes of the substrates. Interestingly, only 71% yield was achieved for 1-isopropyl-2-phenylaziridine (entry 6), which was reasonable due to a larger steric hindrance from the isopropyl group attached to the nitrogen atom.

In summary, a porous metal–metalloporphyrin framework, MMPF-10, was synthesized using an octatopic porphyrin, tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine and copper paddle-wheel building blocks. MMPF-10 showed a different topology from that of UNLFPF-1 because of the differences in the torsion angle of the porphyrin's *meso*-substituents, resulting in a network of **fmj** topology. Both the copper paddlewheel building blocks and the copper metallated porphyrin ligand played important roles for

showing catalytic activity on the chemical fixation of CO_2 with aziridines to form oxazolidinones. Additional research is being explored in our group to find methods to maintain the high yields while working at 1 bar of CO_2 pressure.

Conflicts of interest

There are no conflicts to declare.

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