View Article Online View Journal

# ChemComm

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Wang, W. Gao, Z. Niu, L. Wojtas, J. A. Perman, Y. Chen, Z. Li, B. Aguila and S. Ma, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC08844B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

# ChemComm



Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 08 December 2017. Downloaded by University of Newcastle on 08/12/2017 12:28:12.

A Metal-Metalloporphyrin Framework based on an Octatopic Porphyrin Ligand for Chemical Fixation of CO<sub>2</sub> with Aziridines

Xun Wang,<sup>a,b,‡</sup> Wen-Yang Gao,<sup>b,‡</sup> Zheng Niu,<sup>b</sup> Lukasz Wojtas,<sup>b</sup> Jason A. Perman,<sup>\*b</sup> Yu-Sheng Chen,<sup>c</sup> Zhong Li,<sup>\*a</sup> Briana Aguila<sup>a</sup> and Shengqian Ma<sup>\*b</sup>

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 renders 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 a MMPF.

Given the competitive nature to outperform traditional porous materials, such as zeolites and carbonaceous materials for their porous properties, a rise in the use of metal-organic frameworks (MOFs) are prevalent in the scientific literature.<sup>1</sup> These materials are designed and synthesized from metal ions/clusters and organic molecules (participating as nodes and spacers),<sup>1-2</sup> that 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.<sup>3</sup> Once synthesized, the organic ligands or metal ions can be modified by post-synthetic procedures to impart new physical or chemical properties in the materials.<sup>4</sup>

As an important subclass of MOFs, metal-metalloporphyrin frameworks (MMPFs)<sup>5</sup> have attracted an increasing amount of attention because they have shown to perform well in applications of gas storage/separation,<sup>6-7</sup> catalysis,<sup>8-9</sup> photochemistry,<sup>10-11</sup> and additional areas of research.<sup>12-13</sup> MMPFs can possess mono-, bi- or multi-metallic systems because the porphyrin molecule can be metallated before, or in-

XXXX/XXXXXX

situ, or after the syntheses of these materials.<sup>14-15</sup> 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.<sup>16,17</sup> 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.<sup>17,18</sup>

Many MOFs, particularly MMPFs, have been used as heterogeneous Lewis-acid catalysts for CO<sub>2</sub> chemical transformation reactions with epoxides to form cyclic carbonates.<sup>16, 19-20</sup> A class of heterocyclic chemicals, similar to epoxides, aziridines,<sup>21</sup> allows the cycloaddition reactions with CO<sub>2</sub> to form oxazolidinones.<sup>22-24</sup> This class of compound is particularly important for use in antimicrobial agents such as tedizolid,<sup>25-26</sup> linezolid,<sup>27-28</sup> and radezolid.<sup>29-30</sup> Previously, homogenous catalysts have shown good abilities to convert CO<sub>2</sub> and aziridines into oxazolidinones.<sup>31-33</sup> However, these catalysts can't be easily recycled, thus bringing about a need for new



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

This journal is © The Royal Society of Chemistry 20xx

<sup>&</sup>lt;sup>a</sup> School of Chemistry and Chemical Engineering, South China University of

Technology, Guangzhou 510640, P.R. China. E-mail address: <u>cezhli@scut.edu.cn</u> b.Department of Chemistry, University of South Florida, 4202 East Flower Avenue, Tampa, Florida 33620, USA. E-mail: <u>sqma@usf.edu</u>; Fax: +1-813-974 3203;

<sup>&</sup>lt;sup>c</sup> ChemMatCARS, Center for Advanced Radiation Sources, The University of

Chicago, 9700 South Cass Avenue, Argonne, Illinois 60439, United States † Electronic supplementary information (ESI) available: Experimental details, torsion angles figures, XRD patterns and single-crystal data. CCDC 1580770. For ESI and crystallographic data in CIF or other electronic format see DOI:

<sup>1</sup> These authors contributed equally to this work

### COMMUNICATION





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

heterogeneous catalysts to perform as well or better than homogeneous catalysts. Comparably, only a few heterogeneous catalysts have been reported for this reaction.<sup>34-36</sup> To the best of our knowledge, MMPFs have not been used as a catalyst for CO<sub>2</sub> 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<sub>10</sub>TBCPPP, Fig. 1a) and the copper paddlewheel building block (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 aziridine and CO<sub>2</sub>.

Dark red block-shaped crystals of MMPF-10 were obtained by solvothermal reaction of H10TBCPPP and Cu(NO3)2·2.5H2O in N,N-Dimethylacetamide (DMA) at 65 °C (ESI<sup>+</sup>). Single crystal diffraction analysis revealed that MMPF-10 X-rav [Cu<sub>4</sub>(CuTBCPPP)(H<sub>2</sub>O)<sub>4</sub>] 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 paddlewheel 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 topology of fmj (Fig. 3a), which differs from the **fjh** topology of UNLFPF-1<sup>6</sup> 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~S5, ESI<sup>+</sup>).



**Fig. 3** (a) (3, 4, 4)-connected network of MMPF-10 (blue points, porphyrins; yellow points, paddlewheels; pink points, terphenyl arms). (b) N<sub>2</sub> adsorption isotherm of MMPF-10 at 77 K.

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 2c). This channel is generated from a ring of four metellated 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 porphryin's meso side arm coordinating with four copper paddlewheels and a porphyrin base, exhibiting a pentagonal-like windows 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 by PLATON is 79.6% of the total crystal volume, which is comparable with 79.4% of PCN-222, a typical porphyrin-based MOFs, 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). Its permanent porosity was evaluated through N<sub>2</sub> isotherm measurement at 77 K after samples were activated using supercritical CO<sub>2</sub> (ESI<sup>+</sup>). A type I adsorption isotherm was observed for MMPF-10 that confirmed its microporous nature, with an uptake of ~120 cm<sup>3</sup>g<sup>-1</sup> at the saturated pressure (Fig. 3b). Derived from the N<sub>2</sub> adsorption isotherm, MMPF-10 possesses a Brunauer-Emmett-Teller (BET) surface area of ~419 m<sup>2</sup>g<sup>-1</sup> (corresponding to a Langmuir surface area of ~478 m<sup>2</sup>g<sup>-1</sup>).

Albeit MMPFs have shown high catalytic activity in cycloaddition 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 aziridines cycloaddition under 1 bar of  $CO_2$  at room temperature. MMPF-10 displayed a moderate catalytic activity for 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 then followed by attack of Br<sup>-</sup> from *n*Bu4NBr and reaction with  $CO_2$  molecules.<sup>18, 36, 37</sup>

Journal Name

4<sup>c</sup>

54

60

$( N_R + CO_2 $ Catalyst $( N_R + CO_2 $			
Entry	Substrate	CO₂ Pressure(MPa)	Yield(%)
1 <sup><i>a</i></sup>	N_	0.1	63
2 <sup>b</sup>	N_	0.1	47
3 <sup>c</sup>	N_	2	>99

2

2

99

96

71

 Table 1. Cycloaddition Reactions of different substituted

 aziridines with CO2 catalyzed by MOFs

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

To further enhance the yield of the reaction, we conducted the experiment under high pressure (2 MPa CO<sub>2</sub>) 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 CO2 cycloaddition with aziridines after the concentration of CO2 was increased, compared to that of selfpolymerization of aziridines to form a dimer product.<sup>38-40</sup> We also investigated the cycloaddition reaction activity of MMPF-10 in CO<sub>2</sub> cycloaddition with different substituted aziridines under similar reaction conditions. These results showed that all corresponding oxazolidinones were obtained in high yields even after increasing the molecular sizes of the substrates. Interestingly, only a 71% yield was achieved for 1-isopropyl-2phenylaziridine (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

paddlewheel building blocks. MMPF-10 showed Adifferent topology from UNLFPF-1 because of the differences 484 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<sub>2</sub> 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<sub>2</sub> pressure.

The authors acknowledge the China Scholarship Council (CSC), Key Program of National Natural Science Foundation of China (No. 21436005), National Natural Science Foundation of China (No. U1662136) and the United States National Science Foundation (DMR-1352065) and the University of South Florida (USF) for financial support of this work.

## Notes and references

- 1 H.-C. Zhou and S. Kitagawa, Chem. Soc. Rev., 2014, 2014, 5415.
- 2 M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675.
- 3 J. Jiang, Y. Zhao and O. M. Yaghi, J. Am. Chem. Soc., 2016, **138**, 3255.
- 4 B. Li, M. Chrzanowski, Y. Zhang and S. Ma, *Coord. Chem. Rev.* 2016, **307**, 106.
- 5 W. Y. Gao, M. Chrzanowski and S. Ma, *Chem. Soc. Rev.*, 2014, **43**, 5841.
- 6 J. A. Johnson, Q. Lin, L. C. Wu, N. Obaidi, Z. L. Olson, T. C. Reeson, Y. S. Chen and J. Zhang, *Chem. Commun.*, 2013, **49**, 2828.
- 7 W.-Y. Gao, Z. Zhang, L. Cash, L. Wojtas, Y.-S. Chen and S. Ma, *CrystEngComm*, 2013, **15**, 9320.
- 8 a) M. Zhao, S. Ou and C.-D. Wu, Acc. Chem. Res., 2014, 47, 1199. b)
   Y. Chen and S. Ma, Dalton Trans., 2016, 45, 9744.
- 9 a) H. He, J. A. Perman, G. Zhu and S. Ma, *Small.* 2016, **12**, 6309. b) J.
   W. Maina, C. P-Gonzalo, L.-X Kong, J. Schütz, M. Hill and L. F. Dume'e, *Mater. Horiz.*, 2017, **4**, 345.
- 10 a) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angew. Chem. Int. Ed.*, 2012, **51**, 7440. b) W.-Y. Gao, Z. Zhang, L. Cash, L. Wojtas, Y.-S. Chen and S. Ma, *CrystEngComm*, 2013, **15**, 9320. c) O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 5652. d) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C. D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 87.
- 11 H. Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S. H. Yu and H. L. Jiang, J. Am. Chem. Soc., 2015, 137, 13440.
- 12 R. R. Salunkhe, Y. V. Kaneti, and Y. Yamauchi, *ACS Nano*, 2017, **11**, 5293
- 13 Y. Wang, L. Wang, H. Chen, X. Hu and S. Ma, ACS Appl. Mater. Interfaces, 2016, 8, 18173.
- 14 W. Morris, B. Volosskiy, S. Demir, F. Gandara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443.
- 15 D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10307.
- 16 W. Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. Cai, Y. S. Chen and S. Ma, *Angew. Chem. Int. Ed.*, 2014, 53, 2615.
- 17 W. Y. Gao, C. Y. Tsai, L. Wojtas, T. Thiounn, C. C. Lin and S. Ma, *Inorg. Chem.*, 2016, **55**, 7291.

### COMMUNICATION

Published on 08 December 2017. Downloaded by University of Newcastle on 08/12/2017 12:28:12.

- 18 W. Y. Gao, L. Wojtas and S. Ma, Chem. Commun., 2014, 50, 5316.
- 19 M. Ding, S. Chen, X. -Q. Liu, L. -B. Sun, J. Lu, and H. -L Jiang, *ChemSusChem*, 2017, **10**, 1898.
- 20 L. Liu, S. -M. Wang, Z. -B. Han, M. Ding, D. -Q. Yuan, and H. -L. Jiang, *Inorg. Chem.*, 2016, **55**, 3558.
- 21 S. Stankovic, M. D'Hooghe, S. Catak, H. Eum, M. Waroquier, V. Van Speybroeck, N. De Kimpe and H. J. Ha, *Chem. Soc. Rev.*, 2012, 41, 643.
- 22 T. A. Mukhtar and G. D. Wright., Chem. Rev., 2005, 105, 529
- 23 N. Pandit, R. K. Singla and B. Shrivastava, *Int. J. Med. Chem.*, 2012, 2012, 159285.
- 24 K. J. Shaw and M. R. Barbachyn, *Ann. N. Y. Academy. Sci.*, 2011, **1241**, 48.
- 25 J. B. Locke, G. E. Zurenko, K. J. Shaw and K. Bartizal, *Clin. Infect. Dis.*, 2014, **58 Suppl 1**, 35.
- 26 G. G. Zhanel, R. Love, H. Adam, A. Golden, S. Zelenitsky, F. Schweizer, B. Gorityala, P. R. Lagace-Wiens, E. Rubinstein, A. Walkty, A. S. Gin, M. Gilmour, D. J. Hoban, J. P. Lynch, 3rd and J. A. Karlowsky, *Drugs.*, 2015, **75**, 253.
- 27 M. A. Hedaya, V. Thomas, M. E. Abdel-Hamid, E. O. Kehinde and O. A. Phillips, J. Chromatogr. B, 2017, 1040, 89.
- 28 S. M. Swaney, H Aoki, M. C. Ganoza, and D. L. Shinabarg, Antimicrob. Agents. Chemother., 1998, 42, 3251.
- 29 S. Lemaire, P. M. Tulkens and F. Van Bambeke, *Antimicrob. Agents. Chemother.*, 2010, **54**, 2540.
- 30 K. Michalska, E. Bednarek, E. Gruba, K. Lewandowska, M. Mizera and J. Cielecka-Piontek, *Chem. Cent. J.*, 2017, **11**. 1
- 31 P. Tascedda and E. Duñach, Chem. Commun., 2000, 449.
- 32 A. Sudo, Y. Morioka, E. Koizumi, F. Sanda and T. Endo, *Tetrahedron Lett.*, 2003, 44, 7889.
- 33 Y. Wu and G. Liu, Tetrahedron Lett., 2011, 52, 6450.
- 34 A. C. Kathalikkattil, J. Tharun, R. Roshan, H.-G. Soek and D.-W. Park, *Appl. Catal.*, *A*, 2012, **447-448**, 107.
- 35 X.-Z. Lin, Z.-Z. Yang, L.-N. He and Z.-Y. Yuan, *Green Chem.*, 2015, 17, 795.
- 36 H. Xu, X. F. Liu, C. S. Cao, B. Zhao, P. Cheng and L. N. He, Adv. Sci., 2016, 3, 1600048.
- 37 J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031.
- 38 L. C. Stewart , C. C. Lee, R. G. Bergman and F. D. Toste, J. Am. *Chem. Soc.*, 2005, **127**, 17616.
- 39 C. O. Kim, S. J. Cho and J. W. Park, *J. Colloid Interface Sci.*, 2003, **260**, 374.
- 40 A. Harpe, H. Petersen, Y. X. Li, T. Kissel, *J. Control Release.*, 2000, **69**, 309.



A new porous metal-metalloporphyrin framework, MMPF-10, was synthesized for CO2 cycloaddition with aziridines.

Page 4 of 4

View Article Online DOI: 10.1039/C7CC08844B