

Two rare indium-based porous metal–metalloporphyrin frameworks exhibiting interesting CO₂ uptake†

Wen-Yang Gao,^{‡,a} Zhuxiu Zhang,^{‡,a} Lindsay Cash,^a Lukasz Wojtas,^a Yu-Sheng Chen^b and Shengqian Ma^{*a}

Cite this: *CrystEngComm*, 2013, 15, 9320

Received 10th June 2013,
Accepted 10th July 2013

DOI: 10.1039/c3ce41090k

www.rsc.org/crystengcomm

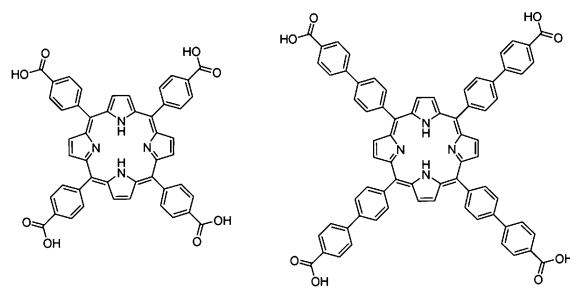
Two rare indium-based porous metal–metalloporphyrin frameworks (MMPFs), MMPF-7 and MMPF-8, were constructed by self-assembly of In(III) and two custom-designed porphyrin–tetracarboxylate ligands. MMPF-7 and MMPF-8 possess the pts topology and exhibit interesting CO₂ adsorption properties.

Metal–organic frameworks (MOFs)¹ have been intensively developed as a promising new type of functional porous materials over the past two decades. The features of their designability of structures, tunability of pore sizes and modularity of properties,² by virtue of crystal engineering strategies³ as well as their unprecedented permanent porosity afford them great potential for applications in gas storage,⁴ gas separation,⁵ heterocatalysis,⁶ sensors⁷ and other areas.⁸ In addition, under the concept of “reticular synthesis”,⁹ the properties of prototypal MOF platforms could be targeted *via* versatile functionalization or the custom-design of organic linkers, *e.g.* metallosalen ligands,¹⁰ metalloporphyrin-based ligands.^{11,12}

Metal–metalloporphyrin frameworks (MMPFs), as one expanding branch of MOFs recently demonstrated by our group¹¹ and several other groups,¹² have been explored as candidates for a promising platform for the aforementioned applications, particularly towards biomimetic catalysis,^{11e,13} light harvesting¹⁴ and gas storage.¹⁵ Among the various metalloporphyrins, In–metallated porphyrins are known as

anion carriers for ion-selective electrodes based on polymeric membranes.¹⁶ However, it occurred to us that indium-based MMPFs still remain underexplored. In this contribution, we report two rare indium-based porous MMPFs, dubbed MMPF-7 and MMPF-8, which are based upon 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (tcpp) and 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (tcbpp), respectively (Scheme 1).

Dark red block crystals of MMPF-7 and MMPF-8 were harvested by reacting In(NO₃)₂·xH₂O with the tcpp ligand and tcbpp ligand, respectively, in *N,N*-dimethylformamide (DMF) under solvothermal conditions for 48 hours (see ESI†). Single-crystal X-ray crystallographic analysis revealed that MMPF-7 crystallizes in the space group of *C2/c*.§ The asymmetric unit (Fig. 1a) of MMPF-7 contains one tcpp ligand and two In(III) cations, one of which resides in the porphyrin ring center of the tcpp ligand. The other In(III) ion is eight-coordinate *via* chelation in a bidentate manner with four carboxylate groups from four different tcpp ligands. Every indium–metallated tcpp ligand connects with four In(III) ions to form an overall three-dimensional (3D) structure for MMPF-7 (Fig. 1b and c). Due to the strong π – π interactions among the porphyrin macrocycles (the distance between every two porphyrin rings is ~ 4.2 Å), three-fold



Scheme 1 Drawings of the 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin ligand (tcpp, left) and 5,10,15,20-tetrakis(4-carboxybiphenyl)porphyrin (tcbpp, right) ligand.

^a Department of Chemistry, University of South Florida, 4202 East Flower Avenue, Tampa, Florida 33620, United States. E-mail: sqma@usf.edu; Fax: +1-813-974 3203; Tel: +1-813-974 5217

^b ChemMatCARS, Center for Advanced Radiation Sources, The University of Chicago, 9700 S. Cass Avenue, Argonne, IL 60439, USA

† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis of the crystals, powder X-ray diffraction patterns, TGA plots, heats of adsorption of CO₂, crystal data of MMPF-7 and MMPF-8. CCDC reference number 943643 for MMPF-7 and 943644 for MMPF-8. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41090k

‡ These authors contributed equally.

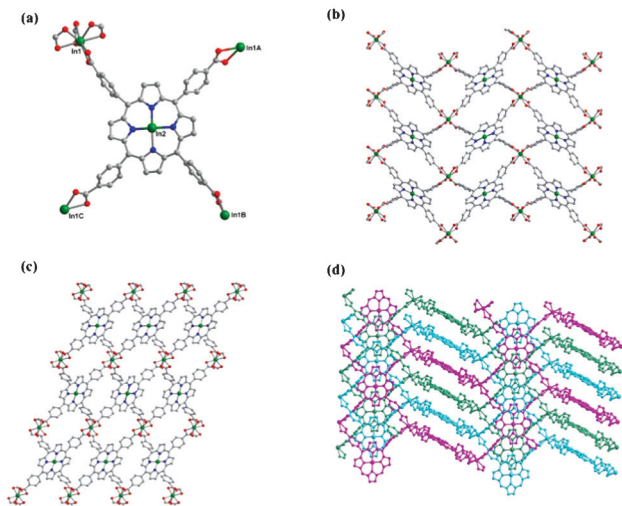


Fig. 1 (a) The asymmetric unit in MMPF-7; (b) the non-interpenetrating structure from the *a* direction; (c) the non-interpenetrating structure from the *b* direction; (d) the three-fold interpenetrating structure of MMPF-7.

interpenetration is observed in the structure of MMPF-7 (Fig. 1d). Single-crystal X-ray crystallographic studies conducted using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory, revealed that MMPF-8 crystallizes in the space group Cc . \ddagger With regard to MMPF-8, the asymmetric unit is comprised of four tcbpp ligands and eight In(III) ions, four of which are located in the porphyrin macrocycles (Fig. 2a). Similar to the coordination mode in MMPF-7, each of the remaining four In(III) ions is eight-coordinate with eight oxygen atoms of four carboxyl groups from four different tcbpp ligands *via* a bidentate chelation manner (Fig. 2b,c). In contrast, the extension from tcpp to tcbpp *via* the phenyl ring leads to a four-fold interpenetrating 3D structure in MMPF-8 (Fig. 2d).

Topologically, both MMPF-7 and MMPF-8 can be described as 4,4-connected pts networks, in which each In(III) ion, serving as the 4-connected node, is bridged by four

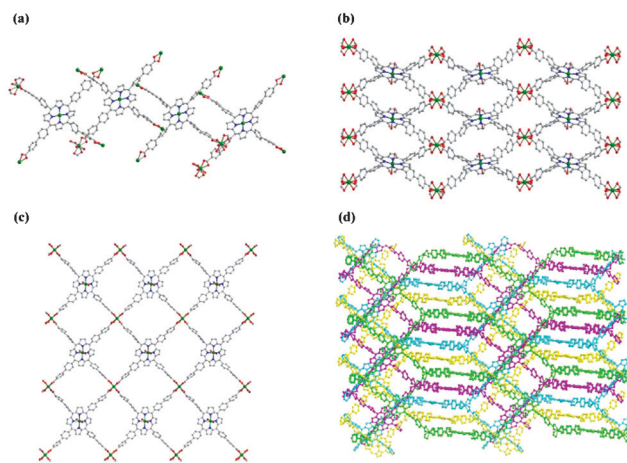


Fig. 2 (a) The asymmetric unit in MMPF-8; (b) the non-interpenetrating structure from the *a* direction; (c) the non-interpenetrating structure from the *b* direction; (d) the four-fold interpenetrating structure of MMPF-8.

In(III)-metallated porphyrin ligands (tcpp or tcbpp) serving as the 4-connected linkers through the carboxylate groups.^{17a} Both MMPF-7 and MMPF-8 are porous and have a solvent accessible volume of 40.2% and 52.1%, respectively, calculated using PLATON.^{17b}

The phase purity of MMPF-7 and MMPF-8 was verified by powder X-ray diffraction studies, which revealed that the diffraction patterns of the fresh samples are consistent with the calculated ones (Fig. S1 and S2, ESI \dagger). Thermogravimetric analysis (TGA) studies were conducted on fresh MMPF-7 and MMPF-8 samples. MMPF-7 exhibits a continuous weight loss of ~17% from 30 °C to ~200 °C, corresponding to the loss of guest solvent molecules trapped in the channels and coordinated water molecules of the In ions within the porphyrin rings. The plot is followed by a relatively steady plateau from 200 to 400 °C before complete decomposition of the framework (Fig. S3, ESI \dagger). MMPF-8 demonstrates a weight loss of ~38% from 30 °C to ~180 °C, corresponding to the loss of guest molecules. The plot is followed by a steady plateau from 180 to 400 °C before complete decomposition of the framework (Fig. S3, ESI \dagger). On the basis of the thermogravimetric plots of these two samples, both of them share the same decomposition temperature of around 400 °C. The thermal behavior characterized by the TGA indicates the robustness of these frameworks.

To evaluate the permanent porosity of MMPF-7 and MMPF-8, gas adsorption studies were performed on the activated samples. As shown in Fig. S4, ESI \dagger , the N₂ adsorption isotherm collected at 77 K reveals that MMPF-8 exhibits an uptake capacity of ~150 cm³ g⁻¹ at one atmosphere pressure with typical type-I adsorption behaviour, as expected for microporous materials. Derived from the N₂ adsorption data at 77 K, MMPF-8 possesses a Brunauer–Emmett–Teller (BET) surface area of ~440 m² g⁻¹ ($P/P_0 = 0.01$ – 0.10), corresponding to a Langmuir surface area of ~510 m² g⁻¹ ($P/P_0 = 0.9$). However, the activated MMPF-7 did not show a significant uptake of N₂ at 77 K, which can be presumably due to the relatively small pore size precluding the access of N₂ molecules.

We evaluated the CO₂ uptake performances of MMPF-7 and MMPF-8. As shown in Fig. 3a, MMPF-7 can adsorb substantial amounts of CO₂ with an uptake capacity of 10.7 wt% (55 cm³ g⁻¹) at 273 K and 6.6 wt% (34 cm³ g⁻¹) at 298 K under 1 atm pressure. These values are moderate compared to some porous MOFs with open metal sites or amine functional groups. In comparison, MMPF-8, with a higher number of interpenetration folds, demonstrated an enhanced CO₂ uptake capacity with 16.2 wt% (82 cm³ g⁻¹) at 273 K and 9.3 wt% (47 cm³ g⁻¹) at 298 K under 1 atm pressure. Different from other reports of enhancing CO₂ uptake *via* interpenetration,¹⁸ we speculate that the higher CO₂ uptake capacity of MMPF-8 should be mainly due to its larger surface area compared to MMPF-7 (910 m² g⁻¹ vs. 600 m² g⁻¹ calculated by non-local density functional theory¹⁹ on the basis of the CO₂ adsorption isotherm at 273 K), since the calculated heat of adsorption of CO₂ of MMPF-8 is lower than that of MMPF-7 (~28 kJ mol⁻¹ vs. ~32 kJ mol⁻¹) (Fig. 3b).

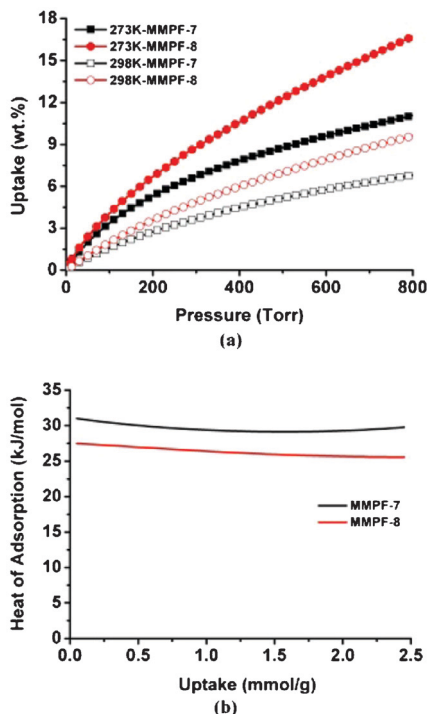


Fig. 3 (a) CO₂ adsorption isotherms of MMPF-7 and MMPF-8 at 273 K and 298 K; (b) Q_{st} of CO₂ for MMPF-7 and MMPF-8.

In summary, two rare examples of indium-based porous metal-metalloporphyrin frameworks with pts topology, MMPF-7 and MMPF-8, have been constructed based upon custom-designed porphyrin ligands featuring tetracarboxylate groups. MMPF-7 and MMPF-8 exhibit permanent porosity and demonstrate interesting CO₂ adsorption performances. Ongoing work in our laboratories includes the custom-design of new variants of porphyrin-based ligands for the construction of functional MMPF materials and exploring them for applications in sensors, catalysis and photoreaction systems.

The authors acknowledge the University of South Florida for financial support of this work. The crystal data of MMPF-8 was collected at the Advanced Photon Source on a beamline 15ID-B of ChemMatCARS Sector 15, which is principally supported by the National Science Foundation/Department of Energy under grant number NSF/CHE-0822838. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Notes and references

§ X-ray crystal data for MMPF-7: C₄₈H₂₄N₄O_{8.57}In_{1.29}, FW = 941.38, monoclinic, C2/c, $a = 7.6333(3)$ Å, $b = 24.1332(11)$ Å, $c = 30.5291(14)$ Å, $V = 5613.4(4)$ Å³, $Z = 4$, $T = 228$ K, $\rho_{\text{calcd}} = 1.114$ g cm⁻³, R_1 ($I > 2\sigma(I)$) = 0.0535, ωR_2 (all data) = 0.1367. X-ray crystal data for MMPF-8: C₇₂H₄₀N₄O₁₀In₂, FW = 1350.72, monoclinic, Cc, $a = 41.982(2)$ Å, $b = 21.5588(12)$ Å, $c = 43.755(2)$ Å, $V = 39560(4)$ Å³, $Z = 16$, $T = 100$ K, $\rho_{\text{calcd}} = 0.907$ g cm⁻³, R_1 ($I > 2\sigma(I)$) = 0.0699, ωR_2 (all data) = 0.1891.

- (a) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, 43, 2334; (b) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, 112, 673.
- (a) J. J. Perry, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, 38, 1400; (b) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, 112, 675.
- (a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, 101, 1629.
- (a) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, 38, 1294; (b) S. Ma and H.-C. Zhou, *Chem. Commun.*, 2010, 46, 44; (c) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, 112, 782; (d) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, 112, 836.
- (a) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, 38, 1477; (b) S. Ma, *Pure Appl. Chem.*, 2009, 81, 2235; (c) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, 112, 869.
- (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, 38, 1450; (b) A. Corma, H. Garcia and F. X. Llabres i Xamena, *Chem. Rev.*, 2010, 110, 4606; (c) V. Lykourinou, Y. Chen, X.-S. Wang, L. Meng, T. Hoang, L.-J. Ming, R. L. Musselman and S. Ma, *J. Am. Chem. Soc.*, 2011, 133, 10382; (d) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, 112, 1196.
- (a) B. Chen, S. C. Xiang and G. D. Qian, *Acc. Chem. Res.*, 2010, 43, 1115; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.*, 2012, 112, 1105; (c) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, 112, 1126.
- (a) S. Ma and L. Meng, *Pure Appl. Chem.*, 2011, 83, 167; (b) C. Wang, T. Zhang and W. Lin, *Chem. Rev.*, 2012, 112, 1084; (c) W. Zhang and R. Xiong, *Chem. Rev.*, 2012, 112, 1163; (d) S. M. Cohen, *Chem. Rev.*, 2012, 112, 970; (e) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, 112, 1232; (f) A. Betard and R. A. Fischer, *Chem. Rev.*, 2012, 112, 1055; (g) Y. Chen, V. Lykourinou, T. Hoang, L.-J. Ming and S. Ma, *Inorg. Chem.*, 2012, 51, 9156; (h) Y. Chen, V. Lykourinou, C. Vetromile, T. Hoang, L.-J. Ming, R. Larsen and S. Ma, *J. Am. Chem. Soc.*, 2012, 134, 13188.
- O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, 423, 705.
- (a) F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.*, 2010, 132, 15390; (b) A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, 133, 13252; (c) J. M. Falkowski, C. Wang, S. Liu and W. Lin, *Angew. Chem., Int. Ed.*, 2011, 50, 8674; (d) C. Zhu, G. Yuan, X. Chen, Z. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2012, 134, 8058.
- (a) X.-S. Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y.-S. Chen, X. P. Zhang and S. Ma, *J. Am. Chem. Soc.*, 2011, 133, 16322; (b) X.-S. Wang, M. Chrzanowski, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, X. P. Zhang and S. Ma, *Chem. Commun.*, 2012, 48, 7173; (c) X.-S. Wang, M. Chrzanowski, W.-Y. Gao, L. Wojtas,

- Y.-S. Chen, M. J. Zaworotko and S. Ma, *Chem. Sci.*, 2012, 3, 2823; (d) L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Cheng, M. J. Zaworotko, X. P. Zhang and S. Ma, *Angew. Chem., Int. Ed.*, 2012, 51, 10082; (e) Y. Chen, T. Hoang and S. Ma, *Inorg. Chem.*, 2012, 51, 12600; (f) X.-S. Wang, M. Chrzanowski, L. Wojtas, Y.-S. Chen and S. Ma, *Chem.-Eur. J.*, 2013, 19, 3297.
- 12 (a) M. E. Kosal, J. H. Chou, S. R. Wilson and K. S. Suslick, *Nat. Mater.*, 2002, 1, 118; (b) K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry and S. R. Wilson, *Acc. Chem. Res.*, 2005, 38, 283; (c) B. J. Burnett, P. M. Barron, C. Hu and W. Choe, *J. Am. Chem. Soc.*, 2011, 133, 9984; (d) C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. B. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, 133, 15858; (e) X.-L. Yang, M.-H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, 134, 10638; (f) 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.
- 13 (a) J. T. Hupp, *Nat. Chem.*, 2010, 2, 432; (b) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, 51, 10307.
- 14 (a) H.-J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, 135, 862; (b) S. Jin, H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, 135, 955.
- 15 W. Morris, B. Voloskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, 51, 6443.
- 16 (a) S. B. Park, W. Matuszewski, M. E. Meyerhoff, Y. H. Liu and K. M. Kadish, *Electroanalysis*, 1991, 3, 909; (b) K. L. Gemene and M. E. Meyerhoff, *Electroanalysis*, 2012, 24, 643.
- 17 (a) A. Fateeva, S. Devautour-Vinot, N. Heymans, T. Devic, J.-M. Grenèche, S. Wuttke, S. Miller, A. Lago, C. Serre, G. D. Weireld, G. Maurin, A. Vimont and G. Férey, *Chem. Mater.*, 2011, 23, 4641; (b) A. L. Spek, *J. Appl. Crystallogr.*, 2003, 36, 7.
- 18 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, K. Forrest, S. Ma, B. Space, L. Wojtas, R. Luebke, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, 495, 80.
- 19 J. Weber, J. Schmidt, A. Thomas and W. Bohlmann, *Langmuir*, 2010, 26, 15650.