

# Formation of a Metalloporphyrin-Based Nanoreactor by Postsynthetic Metal–Ion Exchange of a Polyhedral-Cage Containing a Metal–Metalloporphyrin Framework

Xi-Sen Wang,<sup>[a]</sup> Matthew Chrzanowski,<sup>[a]</sup> Lukasz Wojtas,<sup>[a]</sup> Yu-Sheng Chen,<sup>[b]</sup> and Shengqian Ma\*<sup>[a]</sup>

Metal–organic frameworks (MOFs),<sup>[1]</sup> which are typically comprised of metal ions or metal clusters (also known as secondary building units, SBUs) that are linked by multitopic organic ligands into two- or three-dimensional networks,<sup>[2]</sup> have been a significant topic of research in recent decade. A major driving force behind their rapid development lies in their amenability to design: a desired structure can thus be targeted by judicious selection of the organic linker and the SBU.<sup>[3]</sup> Furthermore, their modular nature means that the properties (for example, pore size and surface area) of prototypical MOFs can be tuned by custom-designing the functional organic ligands under the concept of “reticular synthesis”.<sup>[4]</sup> Such features not only make them stand out over traditional porous materials in terms of potential applications for gas storage/separation,<sup>[5]</sup> but also offer them an opportunity to be developed as a new type of heterogeneous catalysts.<sup>[6]</sup>

In the context of developing MOFs for catalysis application, current efforts have been mainly dedicated to three aspects, namely the utilization of their pore systems to encapsulate catalytically active guest species,<sup>[6a,7]</sup> post-synthetic modification to graft catalytically active moieties,<sup>[8]</sup> and direct incorporation of active centers into the frameworks.<sup>[6,9]</sup> An appealing approach to achieve highly efficient MOF-based catalytic systems is decorating vertexes, and/or edges, and/or faces of polyhedral cages in MOFs<sup>[10]</sup> with catalytically active centers to afford MOF-based nanoreactors. This kind of nanoreactor features a high density of active sites within the confined nanospace, which could lead to cooperative interactions between the active sites and substrates, thus resulting in high catalytic activities.<sup>[11]</sup> To create polyhedral cage-containing MOFs as nanoreactors, catalyti-

cally active metallo-ligands<sup>[12]</sup> can be employed as linkers that could reside on the vertexes, or edges or faces of the polyhedron. In this regard, metalloporphyrin ligands<sup>[13]</sup> which can be readily custom-designed to meet the geometry requirements for the formation of polyhedral cages,<sup>[14]</sup> are most promising. The porphyrin macrocycles of custom-designed porphyrin ligands could be pre-metalated<sup>[15]</sup> or metalated in situ<sup>[11,16]</sup> with active metal centers to afford metalloporphyrin-based nanoreactors. However, the premetalation approach usually requires tedious synthetic procedures, whereas the approach of metalation in situ inevitably leads to the same metal centers in both the porphyrin rings and SBUs, thus making the systems complicated for study. Herein, we report a facile route to create a metalloporphyrin-based nanoreactor by post-synthetic metal-ion exchange with active metal cations of a catalytically inactive metal-metalloporphyrin framework (MMPF) that consists of nanoscopic polyhedral cages. The local coordination environment of the active metal center within the porphyrin macrocycle after metal-ion exchange was crystallographically identified, and the resulted metalloporphyrin-based nanoreactor was proved to be catalytically active and demonstrated interesting performance in catalytic epoxidation of *trans*-stilbene.

Using a crystal engineering strategy of vertex-directed self-assembly, we recently constructed a porphyrin-based MOF, MMPF-5, that is based upon small cuboctahedral cages.<sup>[17]</sup> Each small cuboctahedral cage is composed of the faces of six Cd<sup>II</sup>-metalated tetrakis(3,5-dicarboxyphenyl)porphine (tdcpp(Cd)) moieties that are linked by eight triangular Cd(CO<sub>2</sub>)<sub>3</sub> moieties and that exhibits window dimensions of 8.004 Å × 8.574 Å and internal cage diameter of 22.521 Å (atom to atom distance) (Figure 1a). In the crystal structure of MMPF-5, it is observed that the Cd<sup>II</sup> cation residing within the porphyrin ring of the tdcpp ligand lies far out of the porphyrin plane: ΔC<sub>β</sub>, the average deviation of β-carbon atoms from the porphyrin plane, is 0.86 Å, and the Cd–N bond distances are 2.327(3) Å (Figure 1b). This indicates weak bonding of Cd<sup>II</sup> cation within the porphyrin macrocycle and prompted us to exchange the large Cd<sup>II</sup> cation with smaller divalent metal cations.<sup>[18]</sup>

Immersing the crystals of MMPF-5 in the DMSO solution of Co(NO<sub>3</sub>)<sub>2</sub> at 85 °C for two days afforded the Co<sup>II</sup>-exchanged MMPF-5 (hereafter denoted MMPF-5(Co)). UV/

[a] Dr. X.-S. Wang, M. Chrzanowski, Dr. L. Wojtas, Prof. Dr. S. Ma  
Department of Chemistry, University of South Florida  
4202 E. Fowler Avenue, Tampa, FL 33620 (USA)  
Fax: (+1) 813-974-3203  
E-mail: sqma@usf.edu

[b] Dr. Y.-S. Chen  
ChemMatCARS, Center for Advanced Radiation Sources  
The University of Chicago, 9700 S. Cass Avenue  
Argonne, IL 60439 (USA)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201204358>.

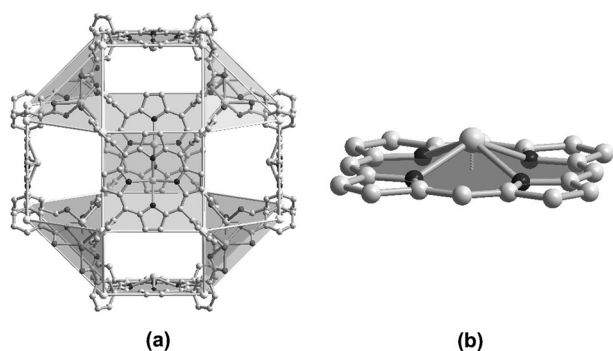


Figure 1. a) Representation of the crystal structure of the small cubicuboctahedron in MMPF-5 formed by 6 square tdcpp(Cd) moieties and 8 triangular  $\text{Cd}(\text{CO}_2)_3$  moieties. Internal diameter 22.521 Å, window dimensions 8.004 Å × 8.574 Å. b) The metalloporphyrin macrocycle in MMPF-5, showing that the  $\text{Cd}^{\text{II}}$  cation lies far out of the porphyrin plane with  $\Delta C_\beta = 0.86$  Å.

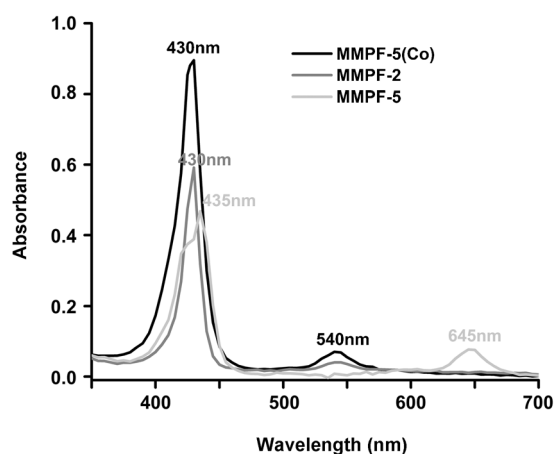


Figure 2. Solution-state UV/Vis spectra of MMPF-5(Co), MMPF-5, and MMPF-2<sup>[16c]</sup> digested by hydrochloric acid in water.

Vis spectroscopy studies (Figure 2) on the hydrochloric acid digested samples in water revealed that the Soret band at 435 nm and Q band<sup>[19]</sup> at 645 nm for MMPF-5 shifted to 430 nm and 540 nm, respectively, for MMPF-5(Co), which is consistent with the Soret band and Q band for MMPF-2 that is based upon tdcpp(Co<sup>II</sup>).<sup>[16c]</sup> These results therefore indicated the successful and complete exchange of  $\text{Cd}^{\text{II}}$  cations with  $\text{Co}^{\text{II}}$  cations within the porphyrin rings of tdcpp ligands.

MMPF-5 retained its single-crystalline nature after metal-ion exchange with  $\text{Co}^{\text{II}}$ . Single-crystal X-ray crystallographic studies conducted using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory revealed that MMPF-5(Co) also crystallized in the space group  $Pm\bar{3}m$  with  $a = 22.260(11)$  Å, which is in good agreement with the unit cell parameters of MMPF-5 (Table 1). In the crystal structure of MMPF-5(Co), all of the  $\text{Cd}^{\text{II}}$  cations within the porphyrin macrocycles of tdcpp ligands are replaced by  $\text{Co}^{\text{II}}$  cations, and the  $\text{Co}^{\text{II}}$  cations are located within the porphyrin plane with  $\Delta C_\beta = 0$  and  $\text{Co-N} = 2.028(3)$  Å (Figure 3 a). Interestingly, the  $\text{Cd}^{\text{II}}$  cations serving

Table 1. Crystal data and structure refinements of MMPF-5 and MMPF-5(Co).

	MMPF-5 <sup>[b]</sup>	MMPF-5(Co) <sup>[c]</sup>
formula	$\text{C}_{156}\text{H}_{60}\text{Cd}_{11}\text{N}_{12}\text{O}_{51}$	$\text{C}_{156}\text{H}_{60}\text{Cd}_8\text{Co}_3\text{N}_{12}\text{O}_{54}$
<i>F</i> <sub>w</sub>	4154.56	4042.15
$\lambda$ [Å]	1.54178	0.41328
crystal system	cubic	cubic
space group	$Pm\bar{3}m$	$Pm\bar{3}m$
<i>a</i> [Å]	22.521(15)	22.260(11)
<i>b</i> [Å]	22.521(15)	22.260(11)
<i>c</i> [Å]	22.521(15)	22.260(11)
$\alpha$ [°]	90.00	90.00
$\beta$ [°]	90.00	90.00
$\gamma$ [°]	90.00	90.00
<i>V</i> [Å <sup>3</sup> ]	11423(13)	11029(9)
<i>Z</i>	1	1
crystal size [mm]	0.10 × 0.10 × 0.10	0.11 × 0.11 × 0.11
GOF	1.037	1.006
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>[a]</sup>	0.0816, 0.2483	0.1087, 0.2524

[a]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $wR_2 = \{[\sum_w (F_o^2 - F_c^2)^2] / [\sum_w (F_o^2)^2]\}^{1/2}$ .  
[b] CCDC 862932. [c] CCDC 895641.

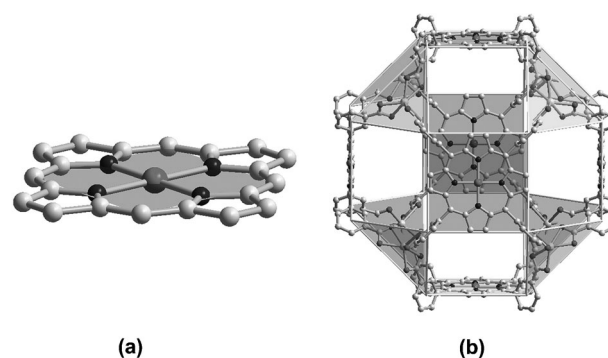


Figure 3. a) The metalloporphyrin macrocycle in MMPF-5(Co), showing that  $\text{Co}^{\text{II}}$  cation is located within the plane of the porphyrin with  $\Delta C_\beta = 0$ . b) The small cubicuboctahedron in MMPF-5(Co) formed by 6 square tdcpp(Co) moieties and 8 triangular  $\text{Cd}(\text{CO}_2)_3$  moieties. Internal diameter 22.260 Å, window dimensions 7.929 Å × 8.440 Å.

as the nodes in the framework remain intact, which is possibly due to their strong chelation with six oxygen atoms from three carboxylate groups. Therefore the small cubicuboctahedral cage in MMPF-5(Co) features the faces of six  $\text{Co}^{\text{II}}$ -metalated tdcpp moieties that are linked by eight triangular  $\text{Cd}(\text{CO}_2)_3$  moieties with an internal diameter of 22.260 Å and window dimensions of 7.929 Å × 8.440 Å (atom-to-atom distance) (Figure 3 b). The exclusive substitution of  $\text{Cd}^{\text{II}}$  cations within the porphyrin rings of tdcpp ligands by  $\text{Co}^{\text{II}}$  cations was further confirmed by inductively coupled plasma mass spectrometry (ICP-MS) studies, which revealed a Cd/Co ratio of 2.69:1 consistent with the stoichiometric ratio of 2.67:1 derived from crystal data. These results thus distinguished MMPF-5(Co) from other post-synthetic metal-ion exchange behavior in MOFs in which the metal cations in the SBUs<sup>[20]</sup> or in both metalloligands and SBUs<sup>[21]</sup> are involved in the exchange processes. MMPF-5(Co) is also a rare example of a structure of metal-ion exchanged crystal that has been determined by single crystal X-ray diffraction

analysis.<sup>[20a,21b]</sup> The retention of framework integrity and phase purity for bulk MMPF-5(Co) was confirmed by powder X-ray diffraction studies (Supporting Information, Figure S1). MMPF-5(Co) also preserved its permanent porosity, as seen by CO<sub>2</sub> adsorption isotherms at 273 K, which revealed a NLDFT (non-local density functional theory)<sup>[22]</sup> surface area of about 600 m<sup>2</sup>g<sup>-1</sup>. (Supporting Information, Figure S2). The decrease in surface area compared to pristine MMPF-5 (ca. 740 m<sup>2</sup>g<sup>-1</sup>) could be presumably be due to partial decomposition during either metal-ion exchange process or activation procedure.

To show that MMPF-5(Co) is catalytically active, we evaluated the performance of MMPF-5(Co) as metalloporphyrin-based nanoreactor in the context of epoxidation of *trans*-stilbene.<sup>[23]</sup> Catalytic assays for the epoxidation of *trans*-stilbene were carried out using *tert*-butyl hydroperoxide as oxidant in acetonitrile at 60°C. Control experiments were conducted for MMPF-5, homogeneous cobalt(II) metalated tetrakis(3,5-dicarboxymethylesterphenyl)porphine (tdcmpp(Co)), and a blank under the same conditions. As revealed in Figure 4 and Table 1, MMPF-5(Co) showed much more efficient catalytic activity for epoxidation of *trans*-stilbene in

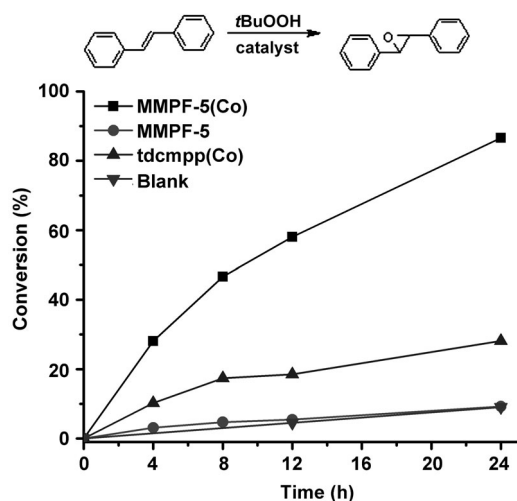


Figure 4. Kinetic traces of *trans*-stilbene epoxidation catalyzed by MMPF-5(Co) and MMPF-5 (mol ratio of *trans*-stilbene/*t*BuOOH/catalyst = 1000:3000:1 was used for the catalytic assays), tdcmp(Co) (ratio *trans*-stilbene/*t*BuOOH/catalyst = 1000:3000:1), and the blank.

terms of both yield (87.0% over 24 h) and selectivity (81.5% epoxide product) compared to MMPF-5 (9.2% yield, 55.1% epoxide), which is basically as inactive as the blank (9.0% yield, 55.8% epoxide). The low activity (28.1% yield, 64.4% epoxide; Table 2) observed for homogeneous tdcmp(Co) could be attributed to catalyst deactivation as a result of the oxo-bridged dimer formation,<sup>[24]</sup> which on the other hand indicates the stabilization of active Co<sup>II</sup> center within porphyrin ring through the MOF framework. MMPF-5(Co) also outperformed 3D channeled MMPF-2<sup>[16c]</sup> (67.2% yield, 58.0% epoxide) and 2D layered PPF-1Co<sup>[16c]</sup> (23.7% yield, 30.1% epoxide) in epoxidation of

Table 2. Summary of catalytic data for epoxidation of *trans*-stilbene catalyzed by MMPF-5(Co) and related catalysts.<sup>[a]</sup>

Catalyst	Conversion [%]	Epoxide [%]
MMPF-5(Co)	87.0	81.5
tdcmpp(Co) <sup>[b]</sup>	28.1	64.4
MMPF-5	9.2	55.1
blank	9.0	55.8
filtrate <sup>[c]</sup>	9.1	55.9
MMPF-5(Co) <sup>[d]</sup>	80.1	80.2

[a] *trans*-Stilbene (1 mmol), *t*BuOOH (3.0 mmol), catalyst (0.001 mmol), acetonitrile (5.0 mL) were stirred at 60°C for 24 h. [b] 0.003 mmol catalyst. [c] After catalytic assay for MMPF-5(Co). [d] The fifth cycle.

*trans*-stilbene under similar conditions,<sup>[11]</sup> thus highlighting the high efficiency of metalloporphyrin-based nanoreactor in MMPF-5(Co). No detectable leaching of the active site or cobalt metal in the reaction solution was observed after removal of MMPF-5(Co) by filtration, as shown by the fact that the filtrate exhibited virtually the same activity (9.1% yield, 55.9% epoxide) as the blank (Table 2). MMPF-5(Co) could be reused for five cycles without significant drop in its catalytic activity (Table 2; Supporting Information, Figure S3), and its structure remained intact after catalysis as evidenced by PXRD studies (Supporting Information, Figure S1).

It should be noted that several factors, such as amount of catalyst, oxidant, solvent, reaction temperature, and time, can profoundly influence performance (for example, conversion, epoxide selectivity) in catalytic epoxidation of *trans*-stilbene.<sup>[25]</sup> We are currently studying these factors in the context of MMPF-5(Co) and are also investigating epoxidation of different olefin substrates of various molecular sizes and shapes to assess whether or not size- and shape-selectivity can be effected. Additionally, we noticed that Co<sup>II</sup>-based metalloporphyrins have recently been widely investigated as homogeneous catalysts<sup>[26]</sup> for reactions of cyclopropanation,<sup>[27]</sup> C–H amination,<sup>[28]</sup> and aziridination of alkenes.<sup>[29]</sup> The exploration MMPF-5(Co) as metalloporphyrin-based nanoreactor for these types of reactions is underway as well. These studies will be reported separately in the near future.

Apart from post-synthetic metal-ion exchange with Co<sup>II</sup> for MMPF-5, our preliminary results indicated that MMPF-5 can also be exchanged with Cu<sup>II</sup>, Mn<sup>III</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup> (Supporting Information, Figure S4). Results along this line will be reported as a full article in due course.

In summary, a metalloporphyrin-based nanoreactor was created in MMPF-5(Co) by post-synthetic metal-ion exchange with Co<sup>II</sup> cations for the catalytically inactive Cd<sup>II</sup>-based MMPF-5 that consists of small cubicuboctahedral cages. The structure of MMPF-5(Co) was determined by single-crystal X-ray diffraction analysis, which together with UV/Vis and ICP-MS studies confirmed the successful and complete replacement of Cd<sup>II</sup> by Co<sup>II</sup> occurring exclusively within the porphyrin macrocycles. MMPF-5(Co) preserved permanent microporosity and demonstrated interesting performances in catalytic epoxidation of *trans*-stilbene. The facile and exclusively exchange of metal ions within por-

phyrin rings without losing single crystallinity and permanent porosity for the framework as illustrated here suggests an easy and versatile route to create porphyrin-based MOFs of different active centers with the same framework structure for heterogeneous catalysis.

## Experimental Section

**Preparation of MMPF-5(Co):** MMPF-5(Co) was obtained by placing crystals of MMPF-5, which were synthesized according to the procedures in Ref. [17], into a dimethylsulfoxide (DMSO) solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (20 mg mL<sup>-1</sup>), followed by heating at 85 °C for 48 h. The crystals were washed with DMSO and methanol several times to afford pure MMPF-5(Co).

Full experimental details, PXRD patterns, gas sorption isotherms, and UV/Vis spectra are presented in the Supporting Information.

CCDC 862932 (MMPF-5) and CCDC 895641 (MMPF-5(Co)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgements

S. Ma acknowledges the University of South Florida for financial support of this work. The crystal diffraction of MMPF-5(Co) was carried out at the Advanced Photon Source on 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.

**Keywords:** catalysis • ion exchange • metal–organic frameworks • metalloporphyrins • nanoreactors

- [1] H.-C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 673–674.
- [2] a) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) S. Ma, L. Meng, *Pure Appl. Chem.* **2011**, *83*, 167–188.
- [3] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; b) M. O’Keeffe, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 675–702.
- [4] a) O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; b) M. O’Keeffe, *Chem. Soc. Rev.* **2009**, *38*, 1215–1217.
- [5] a) B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115–1124; b) M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* **2012**, *112*, 782–835; c) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869–932; d) H. Wu, Q. Gong, D. H. Olson, J. Li, *Chem. Rev.* **2012**, *112*, 836–868.
- [6] a) A. Corma, H. Garcia, F. X. Llabres i Xamena, *Chem. Rev.* **2010**, *110*, 4606–4655; b) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196–1231; c) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459; d) L. Q. Ma, C. Abney, W. B. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1256.
- [7] a) J. Juan-Alcañiz, J. Gascon, F. Kapteijn, *J. Mater. Chem.* **2012**, *22*, 10102–10118; b) A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama, Q. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 13926–13929; c) C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren, Z. M. Su, *J. Am. Chem. Soc.* **2009**, *131*, 1883–1888; d) R. W. Larsen, L. Wojtas, J. Perman, R. L. Musselman, M. J. Zaworotko, C. M. Vetromile, *J. Am. Chem. Soc.* **2011**, *133*, 10356–10359; e) V. Lykourinou, Y. Chen, X.-S. Wang, L. Meng, T. Hoang, L.-J. Ming, R. L. Musselman, S. Ma, *J. Am. Chem. Soc.* **2011**, *133*, 10382–10385; f) Y. Chen, V. Lykourinou, C. Vetromile, T. Hoang, L.-J. Ming, R. Larsen, S. Ma, *J. Am. Chem. Soc.* **2012**, *134*, 13188–13191; g) Y. Chen, V. Lykourinou, T. Hoang, L.-J. Ming, S. Ma, *Inorg. Chem.* **2012**, *51*, 9156–9158.
- [8] a) S. M. Cohen, *Chem. Rev.* **2012**, *112*, 970–1000; b) D. J. Lun, G. I. N. Waterhouse, S. G. Telfer, *J. Am. Chem. Soc.* **2011**, *133*, 5806–5809; c) Y. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 4212–4216; *Angew. Chem. Int. Ed.* **2008**, *47*, 4144–4148; d) M. Banerjee, S. Das, M. Yoon, H. Jung Choi, M. H. Hyun, S. M. Park, G. Seo, K. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 7524–7525.
- [9] a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152; b) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607–2614; c) L. Ma, J. M. Falkowski, C. Abney, W. Lin, *Nat. Chem.* **2010**, *2*, 838–846.
- [10] a) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417; b) Y. Inokuma, T. Arai, M. Fujita, *Nat. Chem.* **2010**, *2*, 780–783; c) S.-T. Zheng, T. Wu, B. Irfanoglu, F. Zuo, P. Feng, X. Bu, *Angew. Chem.* **2011**, *123*, 8184–8187; *Angew. Chem. Int. Ed.* **2011**, *50*, 8034–8037.
- [11] L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Cheng, M. J. Zaworotko, X. P. Zhang, S. Ma, *Angew. Chem.* **2012**, *124*, 10229–10232; *Angew. Chem. Int. Ed.* **2012**, *51*, 10082–10085.
- [12] a) M. C. Das, S. Xiang, Z. Zhang, B. Chen, *Angew. Chem.* **2011**, *123*, 10696–10707; *Angew. Chem. Int. Ed.* **2011**, *50*, 10510–10520; b) S. A. Kumalah Robinson, M.-V. L. Mepin, A. J. Cairns, K. Travis Holman, *J. Am. Chem. Soc.* **2011**, *133*, 1634–1637; c) S. H. Cho, B. Q. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563–2565; d) F. Song, C. Wang, J. M. Falkowski, L. Ma, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 15390–15398; e) C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* **2012**, *134*, 8058–8063.
- [13] a) *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000–2003**; b) I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guilard, C. Stern, *Chem. Rev.* **2009**, *109*, 1659–1713; c) C. M. Drain, A. Varotto, I. Radiojevic, *Chem. Rev.* **2009**, *109*, 1630–1658; d) B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, *369*, 727–729; e) I. Goldberg, *Chem. Commun.* **2005**, 1243–1254; f) L. D. DeVries, P. M. Barron, E. P. Hurley, C. Hu, W. Choe, *J. Am. Chem. Soc.* **2011**, *133*, 14848–14851; g) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent, M. J. Rosseinsky, *Angew. Chem.* **2012**, *124*, 7558–7562; *Angew. Chem. Int. Ed.* **2012**, *51*, 7440–7444.
- [14] X.-S. Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y.-S. Chen, X. P. Zhang, S. Ma, *J. Am. Chem. Soc.* **2011**, *133*, 16322–16325.
- [15] a) O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2011**, *133*, 5652–5655; b) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu, *J. Am. Chem. Soc.* **2011**, *133*, 87–90; c) X.-L. Yang, M.-H. Xie, C. Zou, Y. He, B. Chen, M. O’Keeffe, C.-D. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 10638–10645; d) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem.* **2012**, *124*, 10453–10456; *Angew. Chem. Int. Ed.* **2012**, *51*, 10307–10310; e) Y. Chen, T. Hoang, S. Ma, *Inorg. Chem.* **2012**, *51*, 12600–12602; f) W. Morris, B. Voloskiy, S. Demir, F. Gandara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart, O. M. Yaghi, *Inorg. Chem.* **2012**, *51*, 6443–6445.
- [16] a) M. E. Kosal, J. H. Chou, S. R. Wilson, K. S. Suslick, *Nat. Mater.* **2002**, *1*, 118–121; b) K. S. Suslick, P. Bhyrappa, J.-H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry, S. R. Wilson, *Acc. Chem. Res.* **2005**, *38*, 283–291; c) E.-Y. Choi, C. A. Wray, C. Hu, W. Choe, *CrytEngComm* **2009**, *11*, 553–555; d) A. M. Shultz, O. K. Farha, J. T.

- Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2009**, *131*, 4204–4205; e) X.-S. Wang, M. Chrzanowski, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, X. P. Zhang, S. Ma, *Chem. Commun.* **2012**, *48*, 7173–7175.
- [17] X.-S. Wang, M. Chrzanowski, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko, S. Ma, *Chem. Sci.* **2012**, *3*, 2823–2827.
- [18] J. S. Lindsey, in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, R. Guilard, Eds.; Academic Press: San Diego, **2000**; Vol. 1; p129.
- [19] A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, E. W. Baker, *J. Am. Chem. Soc.* **1968**, *90*, 6577–6583.
- [20] a) S. Das, H. Kim, K. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 3814–3815; b) T. K. Prasad, D. H. Hong, M. P. Suh, *Chem. Eur. J.* **2010**, *16*, 14043–14050; c) J. Zhao, L. Mi, J. Hu, H. Hou, Y. Fan, *J. Am. Chem. Soc.* **2008**, *130*, 15222–15223; d) J. A. Botas, G. Calleja, M. Sánchez-Sánchez, M. G. Orcajo, *Langmuir* **2010**, *26*, 5300–5303; e) D. Denysenko, T. Werner, M. Grzywa, A. Puls, V. Hagen, G. Eickerling, J. Jelic, K. Reuter, D. Volkmer, *Chem. Commun.* **2012**, *48*, 1236–1238; f) C. K. Brozek, M. Dincă, *Chem. Sci.* **2012**, *3*, 2110–2113; g) J. Tian, L. V. Saraf, B. Schwenzler, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno, P. K. Thallapally, *J. Am. Chem. Soc.* **2012**, *134*, 9581–9584; h) M. Kim, J. F. Cahill, H. Fei, K. A. Prather, S. M. Cohen, *J. Am. Chem. Soc.* **2012**, *134*, 18082–18088; i) X. J. Wang, P. Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li, Y. Zhao, *Chem. Commun.* **2012**, *48*, 10286–10288; j) X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon, M. S. Lah, *Chem. Mater.* **2012**, *24*, 3065–3073.
- [21] a) A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2011**, *133*, 13252–13255; b) Z. Zhang, L. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi, M. J. Zaworotko, *J. Am. Chem. Soc.* **2012**, *134*, 924–927.
- [22] J. Weber, J. Schmidt, A. Thomas, W. Bohlmann, *Langmuir* **2010**, *26*, 15650–15656.
- [23] R. A. Sheldon, *Metalloporphyrins in catalytic oxidations*, Marcel Dekker, Inc. New York, **1994**.
- [24] T. C. Bruice, *Acc. Chem. Res.* **1991**, *24*, 243–249.
- [25] C.-M. Che, J.-S. Huang, *Chem. Commun.* **2009**, 3996–4015.
- [26] H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899–1909.
- [27] S. Zhu, X. Xu, J. A. Perman, X. P. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799.
- [28] H. Lu, H. Jiang, L. Wojta, X. P. Zhang, *Angew. Chem.* **2010**, *122*, 10390–10394; *Angew. Chem. Int. Ed.* **2010**, *49*, 10192–10196.
- [29] V. Lyaskovskyy, A. I. Olivos Suarez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264–12273.

Received: December 7, 2012  
Published online: February 5, 2013