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Mn(III)-Porphyrin Containing Heterogeneous Catalyst based on Microporous Polymeric Constituents as a New Class of Catalyst Support

Jigyoung Yi,[a] Ha Young Jeong,[b] Dae Yong Shin,[a] Cheal Kim*[b] and Suk Joong Lee*[a]

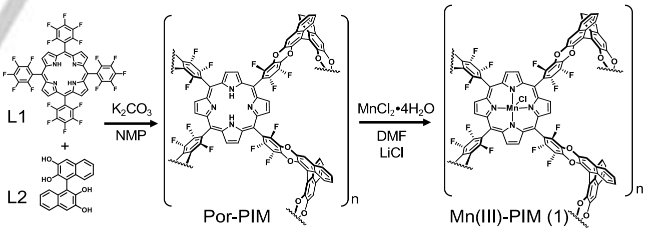
Dedication ((optional))

Abstract: A new class of heterogeneous catalyst, **Mn(III)-PIM (1)**, using polymer with intrinsic microporosity (PIM) as a support was developed. It shows efficient catalytic activity for olefin epoxidation with good reusability. Remarkably, recycling enabled one batch of **1** to be continuously used for all substrates. It was proposed that Mn(V)=O and Mn(IV)=O are key active oxidants.

Owing to their large internal surface area, porous materials often provide a tremendous catalytic advantage over their non-porous analogs. Recently, tremendous research effort has been focused on developing a variety of porous materials, such as metal-organic frameworks (MOFs).[1] Intensive studies have been conducted on a wide range of applications of porous materials including catalysis,[2] gas storage,[3] chemical sensing,[4] and chemical separations.[5] However, they are often reported to suffer from relatively low chemical stability,[6] which limits their practical potential.[7] Recently, a new class of porous materials called porous organic polymers (POPs)[8] has received considerable attention because of their high chemical stability; this arises because their preparation involves the generation of strong and irreversible covalent bonds such as C–C, C–N, and/or C–O bonds[9] that are the foundation of the hyper-crosslinked polymeric materials. POPs are constructed through the incorporation of multi-topic monomers into step-growth and chain-growth polymerization reactions to generate cross-links that yield three-dimensional (3D)–network materials.[10]

Recently, a new type of porous polymeric material has received considerable attention because of its fascinating structural features including high porosity and surface area.[11] Polymers are not generally porous because they have high intermolecular attraction and sufficient structural flexibility to eliminate any void space.[12] However, a new class of porous polymeric materials has emerged: Polymers with intrinsic microporosity (PIMs) are extremely rigid and distorted macromolecules with high porosity and surface area because of ineffective packing. Their rotational flexibility is restricted along the polymer backbone because the building blocks contain constrained sites, such as a binaphthalene or spirocenter unit, which results in a significant number of pores and large surface area.[13] The synthesis of a new class of PIMs with highly accessible inherent surface areas and pores has recently received significant attention. These PIMs have the potential for several practical applications upon the incorporation of moieties with a wide range of chemical functionalities.[14] In particular, the incorporation of a molecular catalyst that exploits their intrinsic porosity may generate a highly tunable platform for a variety of single-site catalytic reactions.[15] Well-controlled catalytic platforms are critical for the development of practical heterogeneous catalysts. Accordingly, the synthesis of materials with well-defined pores has recently been considered to be one of the most promising techniques to maximize the full catalytic potential.[16]

Herein, we report the preparation of a new class of catalytic PIM containing an immobilized Mn(III)-porphyrin as a new recyclable heterogeneous catalyst for the oxidation of various olefins.[17] Although porphyrinic complexes of Mn(III) are well-known catalysts for the effective oxidation of a variety of olefins, they often degrade during the reaction through ligand oxidation or μ-oxo dimer formation.[18] We envisage that immobilization of the catalyst in a PIM framework may prevent this disadvantage, resulting in an efficient catalyst system.



Scheme 1. Preparation of **Por-PIM** and Mn(III)-PIM (**1**).

Main Text Paragraph. A new porphyrin-embedded PIM, **Por-PIM**, was prepared by following a modified literature procedure[19] that involves the formation of rigid dibenzodioxane units *via* aromatic nucleophilic substitution. A solution of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**L1**) and 1,1'-binaphthalene-2,2',3,3'-tetraol (**L2**) in anhydrous *N*-methyl-2-pyrrolidinone (NMP) with K_2CO_3 as a base was heated at 80 °C for 24 h under a nitrogen atmosphere (**Scheme 1**). After washing intensively with water, acetone, DMF and MeOH, Por-PIM was obtained as a dark brown solid (86% yield; see the Supporting Information section for detailed syntheses and characterizations). The nitrogen adsorption isotherm of **Por-PIM** at 77 K revealed a relatively high surface area of 1028 m^2g^{-1} with a mean pore diameter of 5.14 nm (**Fig. 1**). Subsequent metalation with $MnCl_2{\cdot}4H_2O$ in NMP afforded Mn(III)-PIM (**1**) in a

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Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) high yield (98%) with a surface area of 823 m^2g^{-1} and mean pore diameter of 2.49 nm (**Fig. 1**). The small decrease observed in the surface area and pore diameter upon metalation was attributed to the addition of mass (**Table S1**).

Infrared (IR) and solid-state nuclear magnetic resonance (NMR) spectroscopic analyses of Por-PIM clearly show evidence of the formation of a polymer.[20] In the IR spectra of **Por-PIM** and **1** (**Fig. S1**), the stretches of the hydroxyl groups at ~3490 cm^{-1} are much less intense than those of the parent 1,1'-binaphthalene-2,2',3,3'-tetraol (**L2**) material, suggesting the formation of dibenzodioxane units. In the ^{13}C cross-polarization–magic angle spinning (CP-MAS) NMR spectrum of **Por-PIM**, the peaks that occur around 30 and 225 ppm (from the spinning side bands) and several overlapping peaks between 120 and 150 ppm (from the aromatic carbon atoms) clearly support the formation of dibenzodioxane units containing binaphthalene and porphyrin groups (**Fig. S2**).[21] Additionally, the solid-state ^{19}F MAS NMR spectrum of Por-PIM shows distinctive isotopic peaks at −128, −148, and −175 ppm, which also supports the formation of dibenzodioxane units (**Fig. S3**).[22]

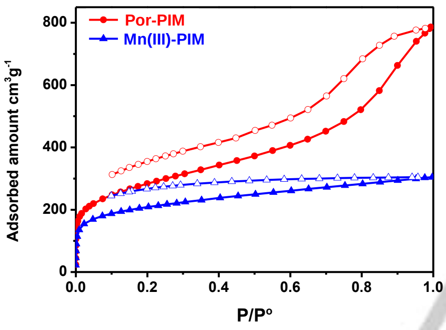

Figure 1. N_2 adsorption (filled markers) and desorption (empty markers) isotherms of **Por-PIM** (red) and **1** (blue).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of digested **1** indicates a Mn content of 6.43 wt.%, while energy dispersive X-ray spectroscopy (EDX) analysis showed a Mn content of 5.82 wt.% (**Fig. S4**), as summarized in **Table S1**. As a control, **Por-PIM** was also analyzed via ICP-AES; no Mn was evident. To assess the thermal stability of the polymers, thermal gravimetric analysis (TGA) was conducted. As shown in **Figure S5**, both **Por-PIM** and **1** are thermally stable up to 400 °C with a small continuous weight loss at low temperatures due to the removal of free solvent molecules. Degradation of the irregular and/or relatively short polymeric structures slightly broadens the thermal decomposition range within which the polymer networks collapse.[23]

To examine the catalytic ability of **1**, it was tested for the epoxidation of styrene using 1-(*tert*-butylsulfonyl)-2-iodosylbenzene (SPhIO) as an oxidant with various solvent systems (**Table S2**). The highest yield of styrene oxide (51.8%) was observed in CH_2Cl_2 with a reaction time of 2 h at 20 °C. We also verified that direct oxidation of the substrate by the oxidant was insignificant without a catalyst. The recyclability of the catalyst during the epoxidation of styrene was also studied (**Table S3**): The catalyst was successfully used for several cycles, suggesting that it is very stable and robust. We also performed an additional control reaction to assess the potential catalytic contribution of Mn(III) species that leach from **1**: First, we filtered the reaction solution after the epoxidation reaction of styrene and then analyzed the filtrate using ICP. The results showed no evidence of any Mn(III) species, which suggests that the catalytic reactive species is **1** and not leached Mn(III).

Next, we performed catalytic epoxidation of a wide variety of olefins by SPhIO using **1** in CH_2Cl_2 at 20 °C. By recovering the catalyst, we successfully used one batch of **1** for all the substrates and the results of epoxidation reactions are displayed in **Table 1**. Further reusability study of the catalyst was verified in **Table S3**. Cyclic olefins, including cyclopentene, cycloheptene, and cyclooctene, were converted to their corresponding epoxides with moderate to high yields (48.4% to 90.9%, entries 1–3). In contrast, cyclohexene gave cyclohexene oxide (68.1%) as the major product with small amounts of 2-cyclohexen-1-ol (4.5%) and 2-cyclohexen-1-one (3.0%) as by-products (entry 4). This result indicates that free-radical-type oxidation was only a minor contributor to the epoxidation reaction.[24] Terminal alkenes, 1-hexene and 1-octene, which are usually the least reactive olefins towards metal-catalyzed epoxidation,[25] were moderately oxidized to their corresponding epoxides (38.7 and 38.5%, entries 5 and 6). *cis*-2-Octene and *cis*-2-hexene were used as substrates to examine the stereochemistry of the epoxidation reaction; the results showed that *cis*-2-octene oxide and *cis*-2-hexene oxide were exclusively produced in yields of 66.4% and 69.8% (entries 7 and 9), respectively. Reactions using *trans*-2-octene and *trans*-2-hexene resulted in the production of only trans-2-octene oxide and trans-2-hexene oxide, respectively (21.1% and 80.4%, entries 8 and 10).

Styrene was primarily oxidized to styrene epoxide (51.8%, entry 11) along with small amounts of phenylacetaldehyde (14.3%). While *cis*-stilbene was converted to a mixture of *cis*-stilbene oxide (25.0%, entry 12), 2-phenylacetophenone (4.4%), and *trans*-stilbene oxide (4.6%), *trans*-stilbene was oxidized to *trans*-stilbene oxide (30.2%, entry 13) as a major product with minor amounts of 2-phenylacetophenone (5.1%). The product distributions of olefins with aromatic moieties suggest that either the peroxyl radical or Mn(IV)=O species was partially involved as the epoxidizing reactive oxidants. This is because these species are expected to produce non-stereospecific or radical-type rearranged products during the epoxidation reactions of aromatic olefins.[26] These results led us to assume that two different reactive species, Mn(V)=O (**3**) and Mn(IV)=O (**4**), might be generated in these catalytic systems with **4** resulting in non-stereoretentive epoxidation (**Scheme S1**).

To elucidate the nature of the reactive intermediates responsible for this epoxidation reaction, we investigated the substituent electronic effects on the epoxidation rate using styrene and four *para*-substituted styrenes. Assay of a Hammett plot gave a ρ value of −0.42 (**Fig. 2**), which suggests that the active oxidants have an electrophilic character. This ρ value is greater than those reported for the epoxidation of styrene with Mn(III) salen (ρ = −0.3)[26] and Mn(III) tetraphenylporphyrin (ρ = −0.41),[27] and somewhat lower than those of Re_4 cluster–

supported Mn(^{H,Me}PyTACN)(CF_3SO_3)$_2$ (ρ = −0.67; ^{H,Me}PyTACN= 1-methyl-4-methyl(2-pyridyl)-1,4,7-triazacyclononane)[28] and Mn(III) saloph (ρ = −0.66; saloph = *N,N'-o*-phenylenebis(Salicylidenaminato)).[29]

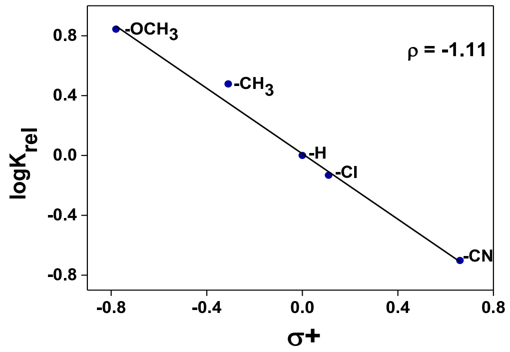

Figure 2. Hammett plot for selective epoxidation of styrene to *para*-substituted styrenes by **Mn(III)-PIM** (**1**) with SPhIO.

Competition experiments were performed to obtain more information about the selectivity of *cis*- and *trans*-2-octene toward the active intermediates. The results are displayed in **Table S4**. The ratios of *cis*- to *trans*-2-octene oxides increased with increasing substrate concentration from 10 to 80 mM (1.4 to 2.2, entries 1–4), which indicates that the Mn(III)-OIR species (**2**) might be involved in the epoxidations. This is evident from the preference of **2** for *cis*-olefins over *trans*-olefins because of the steric hindrance between the *trans* substrate and **2**.[30]

Based on our reactivity studies, the most possible mechanism for the formation of the reactive intermediates responsible for olefin epoxidation is that shown in **Scheme S1**: First, SPhIO reacts with **1** to produce **2**, which then undergoes either heterolysis or homolysis to afford Mn(V)=O (**3**) or Mn(IV)=O (**4**) intermediates. The Mn(V)=O species generated from heterolysis (pathway (a) of **Scheme S1**) might be responsible for the high epoxide yields and stereochemical retention. In contrast, the Mn(IV)=O species generated from homolysis (pathway (b) of **Scheme S1**) might promote radical-type oxidation through the formation of allylic oxidation products, which generates a loss of stereospecificity. With increasing concentration of olefin, **2** might be a possible reactive intermediate for epoxidation (pathway (c)). Therefore, **3** and **4** might act simultaneously as key active oxidants, while the Mn(III)-OIR species contributes to the epoxidation reaction at high olefin concentrations.[31]

For a control, molecular catalyst Mn(III)-porphyrin (**Mn(III)-L1**) was prepared and its catalytic performance in cyclohexene

Table 1. Olefin epoxidation by Mn(III)-PIM (**1**) with SPhIO in CH_2Cl_2 at 20 ºC.[a],[b]

Entry	Substrate	Product	Mn(III) catalyst **1**[c]	
			Conversion (%)	Yield (%)
1	cyclopentene	epoxide	79.2 ± 4.3	48.4 ± 3.0
2	cycloheptene	epoxide	96.5 ± 4.0	90.9 ± 0.7
3	cyclooctene	epoxide	59.1 ± 7.7	55.5 ± 2.6
4	cyclohexene	epoxide	68.0 ± 3.7	68.1 ± 2.4
		2-cyclohexene-1-one		3.0 ± 0.1
		2-cyclohexene-1-ol		4.5 ± 0.1
5	1-hexene	epoxide	38.7 ± 0.7	38.7 ± 0.3
6	1-octene	epoxide	39.5 ± 4.0	38.5 ± 0
7	cis-2-hexene	cis-oxide	66.2 ± 6.4	69.8 ± 5.9
		trans-oxide		trace
8	trans-2-hexene	trans-oxide	79.8 ± 5.0	80.4 ± 5.5
9	cis-2-octene	cis-oxide	66.4 ± 2.0	66.4 ± 0.3
		trans-oxide		trace
10	trans-2-octene	trans-oxide	32.6 ± 0	21.1 ± 0.7
11	styrene	epoxide	68.9 ± 5.7	51.8 ± 3.0
		benzaldehyde		trace
		phenylacetaldehyde		14.3 ± 0
12	cis-stilbene	cis-stilbene oxide	75.7 ± 2.9	25.0 ± 4.1
		trans-stilbene oxide		4.6 ± 0.4
		benzaldehyde		trace
		2-phenylacetophenone		4.4 ± 0.2
13	trans-stilbene	trans-stilbene oxide	66.9 ± 1.5	30.2 ± 1.8
		benzaldehyde		trace
		2-phenylacetophenone		5.1 ± 0.2

[a]Reaction conditions: olefin (2.2 × 10^{-2} mmol), catalyst (2.2× 10^{-3} mmol), SPhIO (2.2× 10^{-2} mmol), and a reaction time of 2 h. [b]One batch of **1** was used for all substrates by recycling. [b]Based on substrate

oxidation was compared with **1**. As shown in **Figure S7**, the initial catalytic activity of **Mn(III)-L1** was greater than that of **1**, but it was slowly reduced and no further reaction took place after 10 min of reaction time. Presumably, the degradation of **Mn(III)-L1** by the formation of less active dimer and/or aggregated species and oxidation of ligand is responsible for this observation.[32] The site isolation strategy is effective to reduce the potential of catalyst deactivation and thus increase catalytic activity and stability.

In summary, we designed and synthesized a new class of PIM as a platform for molecular catalyst. Mn(III)-PIM (**1**) showed efficient catalytic activity towards olefin epoxidation and good reusability using SPhIO as an oxidant. Remarkably, recycling enabled one batch of **1** to be continuously used for all substrates. Mechanistic studies, including product analysis, Hammett plot, and competitive reactivity, revealed that Mn(V)=O and Mn(IV)=O might act simultaneously as key reactive oxidants while the Mn(III)-OIR intermediate contributes partially to the epoxidation reaction under the high olefin concentrations.

Experimental Section

Catalytic olefin epoxidations by SPhIO in the presence of Mn(III)-PIM (1): SPhIO (0.0218 mmol) was added to a mixture of substrate ($2.2x10^{-2}$ mmol), **Mn(III)-PIM (1)** ($2.2x10^{-3}$ mmol), and solvent (CH_2Cl_2, 1 mL). The mixture was stirred for 2 h at room temperature. Each reaction was monitored by GC/mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. Dodecane as an internal standard was used to quantify the yields of products and conversions of substrates. All reactions were run at least in triplicate, and the average conversions and product yields are presented. Conversions and product yields were based on substrate.

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Keywords: PIM • microporous • heterogeneous • epoxidation • olefin

[1] (a) H.-C. Zhoua, S. Kitagawa, *Chem. Soc. Rev.* **2014**, *43*, 5415-5418; (b) F. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.

[2] (a) D. Yang, S. O. Odoh, T. C. Wang, O. K. Farha, J. T. Hupp, C. J. Cramer, L. Gagliardi, B. C. Gates, *J. Am. Chem. Soc*. **2015**, *137*, 7391-7396; (b) A. N. Mlinar, B. K. Keitz, D. Gygi, E. D. Bloch, J. R. Long, A. T. Bell, *ACS Catal*. **2014**, *4*, 717.

[3] L.-B. Sun, X.-Q. Liu, H.-C. Zhou, *Chem. Soc. Rev*. **2015**, *44*, 5092.

[4] H. G. T. Nguyen, M. H. Weston, A. A. Sarjeant, D. M. Gardner, Z. An, R. Carmieli, M. R. Wasielewski, O. K. Farha, J. T. Hupp, S. T. Nguyen, *Cryst. Growth Des*. **2013**, *13*, 3528.

[5] (a) M. Stalzer, M. Delferro, T. Marks, *Catal. Lett*. **2015**, *145*, 3; (b) H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer, S. M. Cohen, *J. Am. Chem. Soc*. **2014**, *136*, 4965.

[6] (a) D. Saha, S. Deng, *J. Phys. Chem. Lett*. **2009**, *1*, 73; (b) W. Zhou, H. Wu, T. Yildirim, *Chem. Phys. Lett*. **2010**, *499*, 103.

[7] K. K. Tanabe, C. A. Allen, S. M. Cohen, *Angew. Chem., Int. Ed*. **2010**, *49*, 9730.

[8] M. J. Kim, S. Ahn, J. Yi, J. T. Hupp, J. M. Notestein, O. K. Farha, S. J. Lee, *Catal. Sci. Technol.* **2017**, *7*, 4351.

[9] J. Weber, J. Schmidt, A. Thomas, W. Bohlmann, *Langmuir* **2010**, *26*, 15650.

[10] Q. Sun, Z. Dai, X. Meng, F. S. Xiao, *Chem. Soc. Rev*. **2015**, *44*, 6018-6034.

[11] P. Kaur, J. T. Hupp, S. T. Nguyen, *ACS Catal*. **2011**, *1*, 819.

[12] J. D. Dunitz, G. Filippini, A. Gavezzotti, *Helv. Chim. Acta.* **2000**, *83*, 2317.

[13] N. B. McKeown, P. M. Budd, *Macromolecules* **2010**, *43*, 5163.

[14] S. Das, P. Heasman, T. Ben, S. Qiu, *Chem. Rev*. **2017**, *117*, 1515.

[15] H. G. T. Nguyen, N. M. Schweitzer, C.-Y. Chang, T. L. Drake, M. C. So, P. C. Stair, O. K. Farha, J. T. Hupp, S. T. Nguyen, *ACS Catal*. **2014**, *4*, 2496.

[16] H. G. T. Nguyen, M. H. Weston, A. A. Sarjeant, D. M. Gardner, Z. An, R. Carmieli, M. R. Wasielewski, O. K. Farha, J. T. Hupp, S. T. Nguyen, *Cryst. Growth Des.* **2013**, *13*, 3528.

[17] A. Mavrogiorgou, M. Baikousi, V. Costas, E. Mouzourakis, Y. Deligiannakis, M. A. Karakassides, M. Louloudi, *J. Mol. Catal. A*. **2016**, *413*, 40.

[18] K. Y. Lee, Y. S. Lee, S. Kim, H. M. Ha, S.-E. Bae, S. Huh, H. G. Jang, S. J. Lee, *CrystEngComm* **2013**, *15,* 9360.

[19] N. B. McKeown, S. Hanif, K. Msayib, C. E. Tattershall, P. M. Budd, *Chem. Commun.* **2002**, 2782.

[20] K. K. Tanabe, N. A. Siladke, E. M. Broderick, T. Kobayashi, J. F. Goldston, M. H. Weston, O. K. Farha, J. T. Hupp, M. Pruski, E. A. Mader, M. J. A. Johnson, S. T. Nguyen, *Chem. Sci.* **2013**, *4*, 2483.

[21] M. H. Weston, O. K. Farha, B. G. Hauser, J. T. Hupp, S. T. Nguyen, *Chem. Mater.,* **2012**, *24*, 1292.

[22] R. G. Hill, D. G. Gillam, X. Chen, *Mater. Lett*. **2015**, *156*, 69.

[23] A. Dani, V. Crocellà, C. Magistris, V. Santoro, J. Y. Yuhan, S. Bordiga, *J. Mater. Chem. A*. **2017**, *5*, 372.

[24] (a) J. T. Groves, T. E. Nemo, *J. Am. Chem. Soc.* **1983**, *105*, 5786; (b) S. H. Lee, J. H. Han, H. Kwak, S. J. Lee, E. Y. Lee, H. J. Kim, J. H. Lee, C. Bae, S. N. Lee, Y. Kim, C. Kim, *Chem. Eur. J.,* **2007**, *13*, 9393.

[25] (a) C. Choe, Z. Lv, Y. Wu, Z. Chen, T. Sun, H. Wang, G. Li, G. Yin, *Molecular Catalysis* **2017**, *438*, 230; (b) R. Ottenbacher, E. Talsi, K. Bryliakov, *Chem. Rec*. **2018**, *18*, 78.

[26] (a) T. Taguchi, K. L. Stone, R. Gupta, K.-L. Benedikt, J. Yama, M. P. Hendrich, A. S. Borovik, *Chemical Science* **2014**, *5*, 3064; (b) H. M. Ahn, J. M. Bae, M. J. Kim, K. H. Bok, H. Y. Jeong, S. J. Lee, C. Kim, *Chem. Eur. J*. **2017**, *23*, 11969.

[27] O. Bortolini, B. Meunier, *J. Chem. Soc*. **1984**, *Perkin Transaction 2*, 1967.

[28] I. Garcia-Bosch, A. Company, X. Fontrodona, X. Ribas, M. Costas, *Org. Lett.* **2008**, *10*, 2095.

[29] J. M. Bae, M. M. Lee, S. A. Lee, S. Y. Lee, K. H. Bok, J. Kim, C. Kim, *Inorg. Chim. Acta.* **2016**, *451*, 8.

[30] (a) B. Wang, Y.-M. Lee, M. Clemancey, M. S. Seo, R. Sarangi, J.-M. Latour, W. Nam, *J. Am. Chem. Soc.* **2016**, *138*, 2426; (b) R. Zhao, J. Wang, D. Zhang, Y. Sun, B. Han, N. Wang and K. Li, *Applied Catalysis A: General* **2017**, *532*, 26.

[31] K. H. Bok, M. M. Lee, G. R. You, H. M. Ahn, K. Y. Ryu, S.-J. Kim, Y. Kim, C. Kim, *Chem. Eur. J.* **2017**, *23*, 3117.

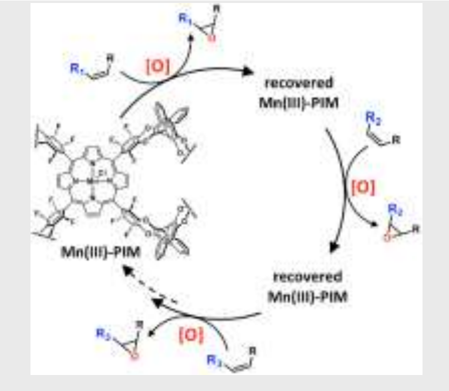
[32] (a) A. Schiller, R. Scopelliti, K. Severin, *Dalton Trans.*, **2006**, 3858. (b) S. Kim, K. Y. Lee, Y. S. Lee, H. G. Jang, J. K. Lee, S. J. Lee, *J. Porphyrins Phthalocyanines,* 2014, ***18***, 579.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A new class of heterogeneous catalyst, **Mn(III)-PIM (1)**, using polymer with intrinsic microporosity (PIM) as a support was developed. It shows efficient catalytic activity for olefin epoxidation with good reusability. Remarkably, recycling enabled one batch of **1** to be continuously used for all substrates without losing activity.



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