ChemPubSoc Europe
DOI: 10.1002/chem.201601151
CHEMISTRY
A European Journal
Communication

Heterogeneous Catalysis

Metalloporphyrin-Based Hypercrosslinked Polymers Catalyze Hetero-Diels–Alder Reactions of Unactivated Aldehydes with Simple Dienes: A Fascinating Strategy for the Construction of Heterogeneous Catalysts

Zhiyu Dou,*[b] Li Xu,[a, b] Yongfeng Zhi,[a] Yuwei Zhang,[a] Hong Xia,[c] Ying Mu,[a] and Xiaoming Liu*[a]

Abstract: We describe a novel and intriguing strategy for the construction of efficient heterogeneous catalysts by hypercrosslinking catalyst molecules in a one-pot Friedel–Crafts alkylation reaction. The new hypercrosslinked polymers (HCPs) as porous solid catalysts exhibit the combined advantages of homogeneous and heterogeneous catalysis, owing to their high surface area, good stability, and tailoring of catalytic centers on the frameworks. Indeed, a new class of metalloporphyrin-based HCPs were successfully synthesized using modified iron(III) porphyrin complexes as building blocks, and the resulting networks were found to be excellent recyclable heterogeneous catalysts for the hetero-Diels–Alder reaction of unactivated aldehydes with 1,3-dienes. Moreover, this new strategy showed wide adaptability, and many kinds of homogeneous-like solid-based catalysts with high catalytic performance and excellent recyclability were also constructed.

Over the last few years, intensive efforts have been devoted to immobilizing homogeneous catalysts by introducing them on or into nanoporous materials[1] such as crystalline metal organic frameworks (MOFs),[2] covalent organic frameworks (COFs),[3] conjugated microporous polymers (CMPs),[4] polymers of intrinsic microporosity (PIMs),[5] and hypercrosslinked polymers (HCPs),[6] which leads to the formation of porous solid catalysts. Heterogeneous catalysts are desirable for practical application due to their convenience of recovery and recycling. In general, however, the heterogeneous process causes a significant decrease in catalytic activity and selectivity, attributed to the complexity of multi-step syntheses and difficulty of tailoring the active centers. Thus, the development of a new judiciously chosen strategy for the construction of porous solid catalytic systems, that combine the advantages of homogeneous and heterogeneous catalysis, is a crucial and emerging task for advancing the research progress of porous polymer materials and catalysis.

Our strategy is to employ homogeneous catalysts with excellent catalytic properties as monomers for the construction of novel heterogeneous catalysts by a hypercrosslinking method, which exhibits a wide applicability to homogeneous catalytic molecules. Thus, a series of homogeneous-like solid-based catalysts, which demonstrate well the combination of advantages of both homogeneous and heterogeneous catalysts, can be obtained. Here, we first utilized iron(III) porphyrin complexes as building blocks and constructed a series of metalloporphyrin-based HCPs with inherently hierarchical porosities and single-site catalytic centers through a one-pot Friedel–Crafts alkylation reaction promoted by anhydrous $FeCl_3$ (Scheme 1, FeP-HCPs). In particular, this synthetic strategy has a wide applicability to many metalloporphyrin molecules with different substitutions, including at the adjustable position and electronic properties, and the obtained FeP-HCPs have flexible active centers similar to homogeneous analogues. Interestingly, we demonstrated that FeP-HCPs can efficiently catalyze the hetero-Diels–Alder reaction between simple dienes and unactivated aldehydes, with high activity, wide substrate scope, and excellent catalyst recyclability, leading to the formation of pyran structural units as products in high yields.

Metalloporphyrin complexes possess unique chemical, material, biological, and catalytic functionalities, and they represent an excellent class of molecule-based solids.[7] More importantly, metalloporphyrin-based porous materials can effectively limit the deactivation of the catalyst framework in the catalytic reaction. We designed and successfully synthesized the FeP-HCPs with a facile Friedel–Crafts alkylation method. Typically, a substituted iron(III) porphyrin monomer was crosslinked using formaldehyde dimethylacetal as a crosslinking agent promoted by anhydrous $FeCl_3$ under solvated thermal conditions (1,2-di-

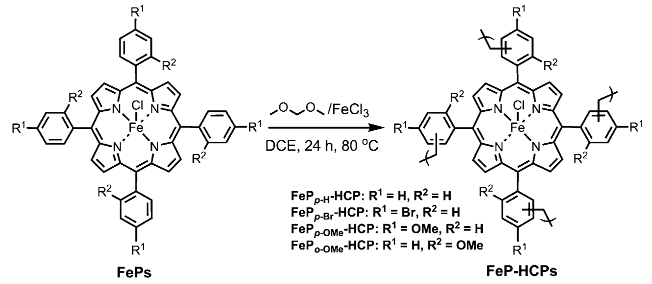
---

[a] L. Xu, Y. Zhi, Dr. Y. Zhang, Prof. Y. Mu, Prof. X. Liu
State Key Laboratory for Supramolecular Structure and Materials
College of Chemistry, Jilin University
Changchun, 130012 (P. R. China)
E-mail: xm_liu@jlu.edu.cn

[b] Dr. Z. Dou, L. Xu
Department of Chemistry and Chemical Engineering
Changchun University of Science and Technology
Changchun, 130022 (P. R. China)
E-mail: douzhiyu79@sina.cn

[c] Prof. H. Xia
State Key Laboratory on Integrated Optoelectronics
College of Electronic Science and Technology
Jilin University, Changchun 130012 (P. R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201601151.



Scheme 1. Synthesis of metalloporphyrin-based porous hypercrosslinked polymers.

chloroethane (DCE), 80 °C, 24 h). The resulting solids were washed with various solvents to afford a series of FeP-HCPs in excellent yields. No changes were observed in these materials upon exposure to air, humidity, and organic solvents. FeP-HCPs were unambiguously characterized by Fourier transform infrared spectroscopy, electronic adsorption spectroscopy, thermogravimetric analysis, and elemental analysis (see Figures S1–S4 in the Supporting Information). Powder X-ray diffraction measurements (PXRD) reveal that FeP-HCPs are amorphous, with no definite signals evident (see Figure S5). Field-emission scanning electron microscopy (FE-SEM) was performed to investigate the morphology of the polymer networks (see Figure S6). The SEM image of FeP$_{p\text{-H}}$-HCP samples displayed rather rough surfaces and the particles were on the order of micrometer in size (Figure 1 a). The size distribution of the FeP$_{p\text{-H}}$-HCP samples at room temperature in a methanol suspension was 615.1 ± 140 nm (Figure 1 b). High-resolution transmission electron microscopy (HR-TEM) images proved the existence of hierarchical porosities (Figure 1 c). The elemental mapping by energy-dispersive X-ray specroscopy (EDS) analysis displayed a homogeneous distribution of iron (see Figure S7). X-ray photoelectron spectroscopy (XPS) was conducted for the FeP-HCPs to determine the their chemical composition (see Figure S8).

The permanent porosity of the polymers was revealed by nitrogen sorption measurements at 77 K (see Figure S9). The curve resulting from FeP$_{p\text{-H}}$-HCP exhibits a steep adsorption and hysteresis loop at high relative pressure, suggesting the co-existence of both micro- and mesopores in the network (Figure 2 a). Based upon the calculations of the Saito–Flory method, the pore sizes are distributed around 0.51, 1.06, 2.04, and 2.41 nm, respectively. The Brunauer–Emmett–Teller (BET) surface area of FeP$_{p\text{-H}}$-HCP is estimated at 735 m^2 g^{-1} with a pore volume of 0.678 cm^3 g^{-1} (Figure 2 b).

Owing to the high concentration of iron porphyrin-based catalytic sites in new HCP networks, their heterogeneous catalytic characters are highly desired. It is well known that the hetero-Diels–Alder reaction is one of the most powerful synthetic methods to construct the pyran structural units that has been widely applied in the synthesis of natural products.[8] Recently, an important breakthrough in this field (i.e., that a cationic iron(III) porphyrin can efficiently catalyze the hetero-Diels–Alder reaction of unactivated aldehydes and simple dienes)[9] motivated us to explore the catalytic activity of new FeP-HCPs as recyclable solid catalysts for this reaction. The influences of solvent and reaction temperature on the yield in the cycloaddition reaction were first investigated. Heating a mixture of benzaldehyde with 2,3-dimethyl-1,3-butadiene and AgBF$_4$ in benzene at 80 °C for 12 h in the presence of FeP$_{p\text{-H}}$-HCP led to the formation of pyran **3 aa** in 95 % yield (see the Supporting Information, Table S1, entry 4). In sharp contrast, low and moderate yields were obtained in THF, dioxane, and toluene, respectively. Control experiments were also performed in the absence of FeP$_{p\text{-H}}$-HCP or AgBF$_4$, in both cases providing no detected target product. Besides catalytic activity, reusability is also crucial for an outstanding heterogeneous catalyst performance. As shown in Figure S12, the catalyst was easily isolated by centrifugation and reused at least five times without any significant loss of the catalytic activity and original shape, all of which is attributed to the built-in character of the covalently linked catalytic sites on the metalloporphyrin-based porous skeleton. In addition, we filtered the FeP$_{p\text{-H}}$-HCP from the hot solution at 60 % conversion, the isolated solution did not exhibit any further reactivity, which clearly is an indication of the heterogeneous catalytic nature of this new porous solid catalyst. In relation to this, we were curious if the catalyst would be applicable a larger scale synthesis. As shown in

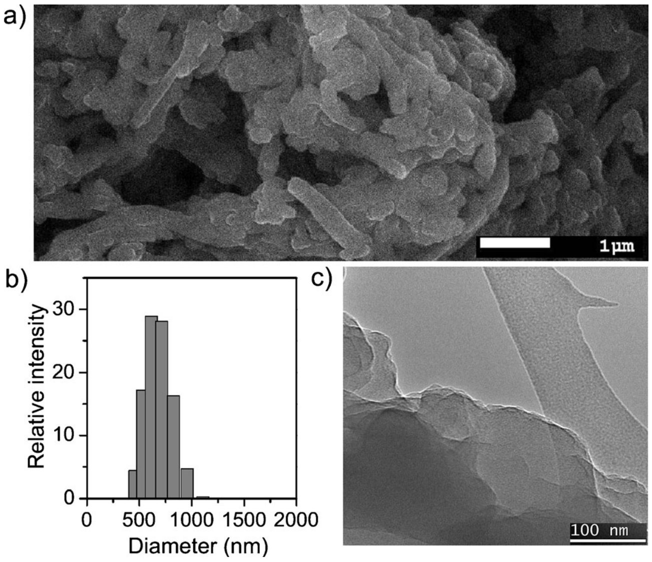


Figure 1. a) FE-SEM image of a typical FeP$_{p\text{-H}}$-HCP sample on mica; b) DLS profile of the FeP$_{p\text{-H}}$-HCP; c) TEM image of the FeP$_{p\text{-H}}$-HCP.

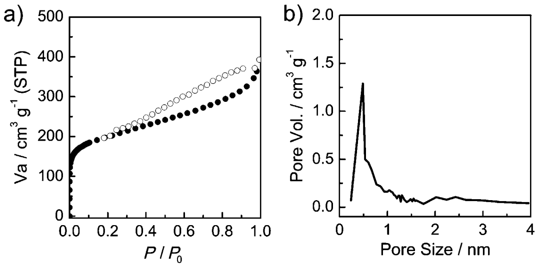


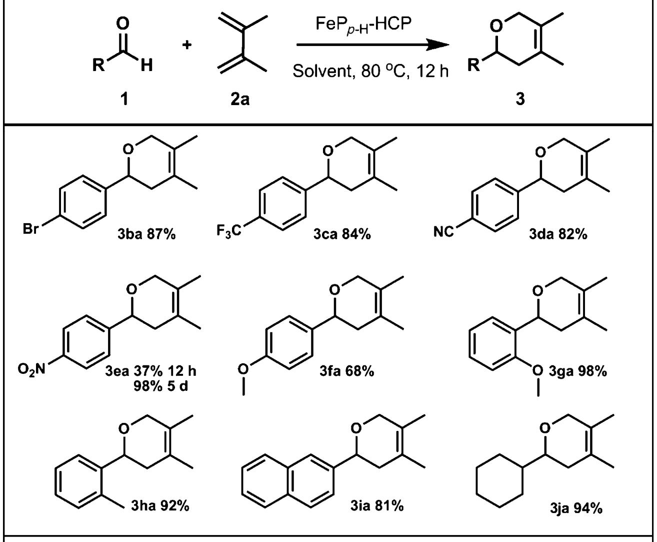
Figure 2. a) Nitrogen adsorption (●) and desorption (○) isotherm profiles of FeP$_{p\text{-H}}$-HCP at 77 K; b) pore size distribution of FeP$_{p\text{-H}}$-HCP on the N$_2$ adsorption isotherms.

Scheme S1 in the Supporting Information, we examined this possibility using **1 a** (1.06 g, 10 mmol) as a substrate in 40 mL of solvent at 80 °C. A good yield (87.2 %) was also afforded in the scaled-up reaction. Notably in this case, the turnover number (TON) reaches 4359 with a turnover frequency (TOF) of 91 h^{-1} after 48 h without loss of catalytic activity in the following runs (see Figure S13).

The excellent catalytic activity of the cationic iron(III) porphyrin-based HCP encouraged us to further explore the generality of the catalytic system; several benzaldehydes with different steric and electronic characters were tested (Table 1). Benzaldehydes with electron-withdrawing substituents including bromide, trifluoromethyl, and nitrile afforded pyrans in good yields. In particular, a nitro substituent group on benzaldehyde was tolerated under the present reaction conditions, and the corresponding product **3 ea** was obtained in excellent yield upon a considerable elongation of reaction time (five days). Benzaldehydes **1 f**, **1 g**, and **1 h**, all of which have electron-donating substituents such as methoxy or methyl groups, can efficiently react with **2 a** to produce the desired cycloaddition compounds. In addition, naphthaldehyde **1 i** also worked well and the reaction afforded the corresponding substituted pyran in 81 % yield. Furthermore, the cationic iron(III) porphyrin-based porous network was also found to be effective for the cycloaddition of aliphatic aldehydes with **2 a**. For example, cyclohexanecarbaldehyde (**1 j**) reacted with **2 a** to give pyran **3 ja** in 94 % yield.

Indeed, the catalytic activity of the $FeP_{p\text{-}H}$-HCP network in the hetero-Diels–Alder reaction was similar to that of the homogeneous small complex.[9] More importantly, this new synthetic strategy was also used to construct a series of other Fe^{III} porphyrin-based polymer networks by tailoring the active center. The $FeP_{p\text{-}Br}$-HCP, $FeP_{p\text{-}OMe}$-HCP, and $FeP_{o\text{-}OMe}$-HCP all have large BET surface areas of 419, 902, and 977 $m^2 g^{-1}$, respectively. For the cycloaddition of benzaldehyde with 2,3-dimethyl-1,3-butadiene, these FeP-HCPs exhibited excellent catalytic performances, and corresponding yields were 91 % for $FeP_{p\text{-}Br}$-HCP, 96 % for $FeP_{p\text{-}OMe}$-HCP, and 97 % for $FeP_{o\text{-}OMe}$-HCP. To further investigate the scope of the process, we tested the reaction between benzaldehyde and simple isoprene (Table 2). The $FeP_{p\text{-}H}$-HCP catalyst achieved only 30 % conversion under the optimized reaction conditions, which is lower than that of the cycloaddition reaction with **2 a**. The reaction in the presence of $FeP_{p\text{-}OMe}$-HCP gave the corresponding pyran in moderate yield (55 %). It outperforms that of $FeP_{p\text{-}H}$-HCP, which may be attributed to the higher BET surface area of $FeP_{p\text{-}OMe}$-HCP. $FeP_{p\text{-}Br}$-HCP, however, exhibits higher conversion (65 %) than that of both $FeP_{p\text{-}H}$-HCP and $FeP_{p\text{-}OMe}$-HCP for the same cycloaddition reaction, although the *p*-H and *p*-OMe variants have larger surface areas. This could be attributed to the fact that the Br in the porphyrin network of $FeP_{p\text{-}Br}$-HCP is an electron-withdrawing group, which could decrease the electron density on the iron center and increase the catalytic activity. It is noteworthy to mention here the fascinating strategy can construct new kinds of porous heterogeneous catalysts, which combine the advantages of both homogeneous and heterogeneous catalysts.

Table 1. $FeP_{p\text{-}H}$-HCP-catalyzed cycloaddition of various aldehydes with 2,3-dimethyl-1,3-butadiene.[a]

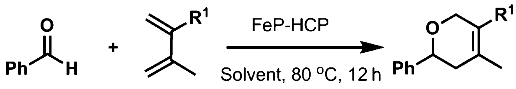


[a] $FeP_{p\text{-}H}$-HCP (5.0 mmol of aldehyde), $AgBF_4$ (7.5 mmol of aldehyde), aldehyde **1** (1.0 mmol), and diene **2 a** (2.0 mmol); yields determined by GC using undecane as the internal standard.

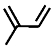
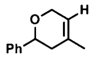
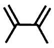
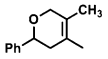
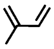
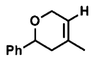
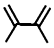
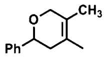
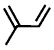
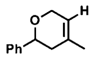
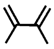
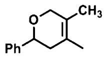
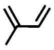
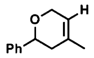
Furthermore, this hypercrosslinking homogeneous catalytic molecule strategy can be useful for the construction of various heterogeneous catalysts with excellent catalytic performances, including heterogeneous organocatalysts, asymmetric heterogeneous organocatalysts, metal-free heterogeneous photocatalysts, etc. (see Schemes S2 and S3). For instance, a series of chiral porous HCPs based on 3,3′substituted-1,1′-binaphthalen-2,2′-diyl-phosphoric acid have also been synthesized using this strategy. Similar to the homogeneous small molecule analogue, these HCPs possess an adjustable chiral Brønsted acid center, and exhibit good asymmetric benzoxazine reduction in the presence of a Hantzsch ester (see Table S2). This new construction strategy for porous heterogeneous catalysts is superior to the previously reported immobilizing methods, which usually need specific polymerizable groups in monomers and an expensive metal catalyst for the synthesis process.

In summary, we have dedicated the judiciously chosen strategy of hypercrosslinking homogeneous catalytic molecules to the construction of porous catalytic HCPs, which have been demonstrated as highly efficient heterogeneous catalysts once synthesized using the one-pot Friedel–Crafts alkylation reaction. Owing to high surface area, good stability, and specially tailored catalytic centers, new HCP architectures as porous solid catalysts exhibit the combined advantages of both homogeneous and heterogeneous catalysis, which can be difficult to achieve with previously reported synthetic methods. Specifically, a new class of metalloporphyrin-based HCPs with specially designed built-in catalytic centers were constructed using modified iron(III) porphyrin complexes as building blocks, and the resulting FeP-HCPs were found to be excellent recyclable heterogeneous catalysts for the hetero-Diels–Alder reaction of unactivated aldehydes with 1,3-dienes. Considering the huge amount of homogeneous catalytic molecules and the broad applicability of the Friedel–Crafts alkylation reaction, our strat-

Table 2. FeP-HCP-catalyzed cycloaddition of benzaldehyde and dienes.[a]



1a 2 3

Catalyst	Diene	Product	Yield [%][b]
FeP$_{p\text{-H}}$-HCP			30
FeP$_{p\text{-Br}}$-HCP			91
FeP$_{p\text{-Br}}$-HCP			65
FeP$_{p\text{-OMe}}$-HCP			96
FeP$_{p\text{-OMe}}$-HCP			55
FeP$_{o\text{-OMe}}$-HCP			97
FeP$_{o\text{-OMe}}$-HCP			73

[a] FeP-HCP (5.0 mmol of aldehyde), AgBF$_4$ (7.5 mmol of aldehyde), aldehyde **1** (1.0 mmol), and diene **2a** (2.0 mmol). [b] Determined by GC using undecane as the internal standard.

egy may facilitate the design and construction of porous HCPs with excellent catalytic performances, including heterogeneous organocatalysis, metal-free photocatalysis, and asymmetric catalysis. Moreover, this research expands the known scope of HCPs, and opens up new opportunities for the design and construction of excellent heterogeneous catalysts.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51473064, 61435005, and 21274050). X.L. is also grateful for support by the Frontiers of Science and Interdisciplinary Innovation Project of Jilin University (No. 450060481015).

Keywords: hetero-Diels–Alder reaction · heterogeneous catalysis · hypercrosslinked polymers · metalloporphyrin-based networks · polymers

[1] a) A. Thomas, *Angew. Chem. Int. Ed.* **2010**, *49*, 8328–8344; *Angew. Chem.* **2010**, *122*, 8506–8523; b) Z. Wang, G. Chen, K. Ding, *Chem. Rev.* **2009**, *109*, 322–359; c) Y. Liu, W. Xuan, Y. Cui, *Adv. Mater.* **2010**, *22*, 4112–4135; d) P. Kaur, J. Hupp, S. Nguyen, *ACS Catal.* **2011**, *1*, 819–835; e) Y. Zhang, S. Nurhanna, *Chem. Soc. Rev.* **2012**, *41*, 2083–2094; f) Q. Sun, Z. Dai, X. Meng, F. Xiao, *Chem. Soc. Rev.* **2015**, *44*, 6018–6034.

[2] a) J. Lee, O. Farha, J. Roberts, K. Scheidt, K. Scheidt, S. Nguyen, J. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459; b) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.

[3] a) S. Ding, J. Gao, Q. Wang, Y. Zhang, W. Song, C. Su, W. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 19816–19822; b) C. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas, L. Prati, *Nano Lett.* **2010**, *10*, 537–541; c) C. Chan-Thaw, A. Villa, L. Prati, A. Thomas, *Chem. Eur. J.* **2011**, *17*, 1052–1057; d) Q. Fang, S. Gu, J. Zheng, Z. Zhuang, S. Qiu, Y. Yan, *Angew. Chem. Int. Ed.* **2014**, *53*, 2878–2882; *Angew. Chem.* **2014**, *126*, 2922–2926; e) H. Xu, J. Gao, D. Jiang, *Nat. Chem.* **2015**, *7*, 905–912; f) S. Lin, C. S. Diercks, Y. Zhang, N. Kornienko, E. M. Nichols, Y. B. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science* **2015**, *349*, 1208–1213.

[4] a) L. Chen, Y. Yang, D. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 9138–9143; b) Z. Xie, C. Wang, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 2056–2059; c) J. X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. L. Xiao, S. J. Higgins, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* **2011**, *50*, 1072–1075; *Angew. Chem.* **2011**, *123*, 1104–1107; d) R. S. Sprick, J. Jiang, B. Bonillo, S. J. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2015**, *137*, 3265–3270; e) H. Li, B. Xu, X. Liu, S. A, C. He, H. Xia, Y. Mu, *J. Mater. Chem. A* **2013**, *1*, 14108–14114; f) Y. Zhang, S. A, Y. Zou, X. Luo, Z. Li, H. Xia, X. Liu, Y. Mu, *J. Mater. Chem. A* **2014**, *2*, 13422–13430; g) X. Ding, B. Han, *Angew. Chem. Int. Ed.* **2015**, *54*, 6536–6539; *Angew. Chem.* **2015**, *127*, 6636–6639.

[5] a) H. J. Mackintosh, P. M. Budd, N. B. McKeown, *J. Mater. Chem.* **2008**, *18*, 573–578; b) P. M. Budd, B. Ghanem, K. Msayib, N. B. Mckeown, C. Tattershall, *J. Mater. Chem.* **2003**, *13*, 2721–2726; c) N. B. McKeown, P. M. Budd, *Macromolecules* **2010**, *43*, 5163–5176.

[6] a) B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, *Adv. Mater.* **2012**, *24*, 3390–3395; b) S. Bhunia, B. Banerjee, A, Bhaumik, *Chem. Commun.* **2015**, *51*, 5020–5023; c) Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F. Xiao, *J. Am. Chem. Soc.* **2015**, *137*, 5204–5209; d) Q. Sun, M. Jiang, Z. Shen, Y. Jin, S. Pan, L. Wang, X. Meng, W. Chen, J. Li, F. Xiao, *Chem. Commun.* **2014**, *50*, 11844–11847; e) Y. Huangfu, Q. Sun, S. Pan, X. Meng, F. Xiao, *ACS Catal.* **2015**, *5*, 1556–1559.

[7] a) M. Zhao, S. Ou, C. Wu, *Acc. Chem. Res.* **2014**, *47*, 1199–1207; b) G. Simonneaux, P. Le Maux, Y. Ferrand, J. Rault-Berthelot, *Coord. Chem. Rev.* **2006**, *250*, 2212–2221; c) S. Lee, J. Hupp, *Coord. Chem. Rev.* **2006**, *250*, 1710–1723; d) C. Li, X. Wang, X. Sun, Y. Tang, J. Zheng, Z. Xu, Y. Zhou, L. Dai, *J. Am. Chem. Soc.* **2007**, *129*, 1494–1495; e) S. Lee, S. Cho, K. Mulfort, D. Tiede, J. Hupp, S. Nguyen, *J. Am. Chem. Soc.* **2008**, *130*, 16828–16829; f) J. Hupp, *Nat. Chem.* **2010**, *2*, 432–433; g) B. Abrahams, B. Hoskins, D. Michall, R. Robson, *Nature* **1994**, *369*, 727–729; h) E. Deiters, V. Bulach, M. W. Hosseini, *Chem. Commun.* **2005**, 3906–3908; i) R. Totten, Y. Kim, M. Weston, M. Farha, J. Hupp, S. Nguyen, *J. Am. Chem. Soc.* **2013**, *135*, 11720–11723; j) A. Shultz, O. Farha, J. Hupp, S. Nguyen, *Chem. Sci.* **2011**, *2*, 686–689; k) X. Liu, Y. Xu, Z. Guo, A. Nagai, D. Jiang, *Chem. Commun.* **2013**, *49*, 3233–3235; l) X. Liu, H. Li, Y. Zhang, B. Xu, S. A, H. Xia, Y. Mu, *Polym. Chem.* **2013**, *4*, 2445–2448; m) B. Saha, D. Gupta, M. Abu-Omar, A. Modak, A. Bhaumik, *J. Catal.* **2013**, *299*, 316–320; n) D. Feng, Z. Gu, Y. Chen, J. Park, Z. Wei, Y. Sun, M. Bosch, S. Yuan, H. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 17714–17717; o) X. Yang, M. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe, C. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 10638–10645.

[8] a) L. Tietze, G. Kettschau, *Top. Curr. Chem.* **1997**, *189*, 1–107; b) S. Danishefsky, M. DeNinno, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 15–23; *Angew. Chem.* **1987**, *99*, 15–23; c) R. Schmidt, *Acc. Chem. Res.* **1986**, *19*, 250–259; d) V. K. Aggarwal, G. P. Vennall, P. N. Davey, C. Newman, *Tetrahedron Lett.* **1997**, *38*, 2569–2572; e) S. Oi, K. Kashiwagi, E. Terada, K. Ohuchi, Y. Inoue, *Tetrahedron Lett.* **1996**, *37*, 6351–6354; f) Y. Huang, V. H. Rawal, *J. Am. Chem. Soc.* **2002**, *124*, 9662–9663; g) M. El Remaily, V. Naidu, S. Ni, J. Franzén, *Eur. J. Org. Chem.* **2015**, 6610–6614; h) B. Gole, A. K. Bar, A. Mallick, R. Banerjee, P. S. Mukherjee, *Chem. Commun.* **2013**, *49*, 7439–7441; i) D. Samanta, S. Mukherjee, Y. P. Patil, P. S. Mukherjee, *Chem. Eur. J.* **2012**, *18*, 12322–12329; j) B. Mondal, K. Acharyya, P. Howlader, P. S. Mukherjee, *J. Am. Chem. Soc.* **2016**, *138*, 1709–1716.

[9] K. Fujiwara, T. Kurahashi, S. Matsubara, *J. Am. Chem. Soc.* **2012**, *134*, 5512–5517.

Received: March 10, 2016

COMMUNICATION

Holey HCPs: Porous solid catalysts were constructed from hypercrosslinking polymers (HCPs), and exhibited the combined advantages of homogeneous and heterogeneous catalysis. New metalloporphyrin-based polymers were found to be excellent recyclable heterogeneous catalysts for the hetero-Diels–Alder reaction of unactivated aldehydes with 1,3-dienes. This strategy demonstrated a wide applicability, and many kinds of homogeneous-like solid catalysts were constructed.

Heterogeneous Catalysis

Z. Dou, L. Xu, Y. Zhi, Y. Zhang, H. Xia, Y. Mu, X. Liu**

■■–■■

Metalloporphyrin-Based Hypercrosslinked Polymers Catalyze Hetero-Diels–Alder Reactions of Unactivated Aldehydes with Simple Dienes: A Fascinating Strategy for the Construction of Heterogeneous Catalysts