JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Chiral Nanoporous Metal–Metallosalen Frameworks for Hydrolytic Kinetic Resolution of Epoxides

Chengfeng Zhu, Guozan Yuan, Xu Chen, Zhiwei Yang, and Yong Cui*

School of Chemistry and Chemical Technology and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

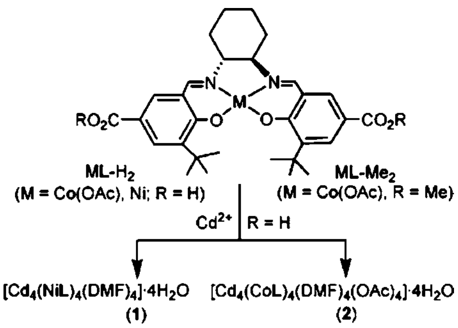
Supporting Information

ABSTRACT: Chiral nanoporous metal–organic frameworks are constructed by using dicarboxyl-functionalized chiral Ni(salen) and Co(salen) ligands. The Co(salen)-based framework is shown to be an efficient and recyclable heterogeneous catalyst for hydrolytic kinetic resolution (HKR) of racemic epoxides with up to 99.5% ee. The MOF structure brings Co(salen) units into a highly dense arrangement and close proximity that enhances bimetallic cooperative interactions, leading to improved catalytic activity and enantioselectivity in HKR compared with its homogeneous analogues, especially at low catalyst/substrate ratios.

Metal–organic frameworks (MOFs) made from metal ions linked by organic ligands have emerged as one of the most fascinating porous crystalline materials for diverse applications.[1,2] In particular, MOFs offer great potential in heterogeneous catalysis because of their many catalysis-friendly features, such as large surface areas, extensive porosity, well-defined cavities and portals, and chemical and composition tunability.[3,4] The modular de novo construction of MOFs under mild synthetic conditions is ideal for the integration of catalytically active (chiral) functions by using functionalizing molecular catalysts as bridging linkers. In comparison with other immobilized systems, MOFs can have highly ordered crystalline structures, high catalyst loadings, more uniform and accessible catalytic sites, and enhanced catalytic activity in some cases by providing confined spaces for reactants and eliminating multimolecular catalyst deactivation pathways.[5] In addition, the cavities of MOFs contain multiple isolated active centers that may facilitate synergistic interactions with substrates, as exemplified in some supramolecular catalysts,[6,7] even though examples of catalytic MOFs, especially chiral species built of molecular catalysts, are still limited and framework confinement effect on catalysts has not yet been well explored.[8,9]

Chiral salen ligands such as (*R*,*R*)-1,2-cyclohexanediamino-*N*,*N*′-bis(3-*tert*-butyl-salicylidene) have been established as one of the best known privileged ligands in the field of asymmetric synthesis.[10] Given their rigidity and excellent asymmetric catalytic behavior, metallosalens are expected to be ideal functional struts in chiral functional MOFs. Nevertheless, only a few chiral metal–metallosalen frameworks have thus far been reported.[9,11] For example, Hupp and Lin constructed chiral MOFs based on Mn-/Ru-Salen-derived bipyridine or bicarboxylate ligands and demonstrated their asymmetric catalytic activity in alkene epoxidation and cyclopropanation reactions.[9] Chiral Co(salen) complexes have been demonstrated to be highly effective in catalyzing hydrolytic kinetic resolution (HKR) of racemic epoxides.[12] HKR follows a cooperative bimetallic catalysis where epoxide and H_2O are activated simultaneously by two Co(salen) catalysts.[12b] To enhance such cooperativity, different types of supported catalysts using organic and inorganic supports have been developed.[13,14] We report here the synthesis of dicarboxyl-functionalized chiral salen complexes of Ni and Co to make porous MOFs and show that the Co(salen)-based MOF is an efficient heterogeneous catalyst for HKR of epoxides, suppressing the performance of its homogeneous analogues owing to enhanced cooperation activation.

Scheme 1. Synthesis of 1, 2, and Their Precursors



Metalation of enantiopure 1,2-cyclohexanediamine-*N*,*N*′-bis-(3-*tert*-butyl-5-(carboxyl)salicylide (**L**-H_4) with Ni(OAc)·$4H_2O$ and Co$(OAc)_2\cdot 4H_2O$ afforded [Co(**L**-H_2)(OAc)] and [Ni(**L**-H_2)] (Scheme 1), respectively. The Co analogue [Co(**L**-Me_2)(OAc)] was prepared similarly from the ester **L**-H_2Me_2 of **L**-H_4. Heating a mixture of $Cd(NO_3)_2\cdot 6H_2O$ and [Co(**L**-H_2)(OAc)] or [Ni(**L**-H_2)] (a 2:1 molar ratio) in DMF and H_2O afforded single crystals of $[Cd_4(Ni\mathbf{L})_4(DMF)_4]\cdot 4H_2O$ (**1**) or $[Cd_4(Co\mathbf{L})_4(DMF)_4\text{-}(OAc)_4]\cdot 4H_2O$ (**2**) in good yields. The products were stable in air and insoluble in water and common organic solvents and were formulated on the basis of elemental analysis, IR spectroscopy, and thermogravimetric analysis (TGA). Phase purity of the bulk sample was established by comparison of their observed and simulated powder X-ray diffraction (PXRD) patterns.

Received: March 9, 2012
Published: April 30, 2012

© 2012 American Chemical Society

dx.doi.org/10.1021/ja302340b | *J. Am. Chem. Soc.* 2012, 134, 8058–8061

A single-crystal X-ray diffraction study revealed that **1** adopts a 3D chiral nanoporous framework and crystallizes in the chiral space group C_2, with one whole formula unit in the asymmetric unit. The basic building block is a square-planar tetrameric $[Cd_4(O_2C)_8]$ unit, with a C_2 axis passing through one metal center, clustered by six bidentate and two tridentate carboxylate groups of eight Ni**L** units (Figure 1). Of the three independent Cd ions, Cd1 is coordinated by six oxygen atoms from four bidentate and two tridentate carboxylate groups, Cd2 is coordinated by one DMF molecule and four oxygen atoms from two bidentate and two tridentate carboxylate groups, and Cd3 is coordinated by two DMF molecules and four oxygen atoms from two bidentate and two tridentate carboxylate groups. The Cd1 and Cd3 ions adopt a distorted octahedral geometry, with Cd−O bond lengths ranging from 2.133(15) to 2.391(17) Å, whereas the Cd2 adopts a square pyramidal geometry with Cd−O bond lengths ranging from 2.080(15) to 2.35(2) Å. All Ni**L** units exhibit an *exo*-pentadentate coordination mode including one bridging bidentate and one chelating-bridging tridentate carboxylate groups. Each Ni ion is coordinated in a distorted square-planar geometry with two nitrogen atoms and two oxygen atoms from the **L** ligand. Each tetranuclear Cd_4 cluster in **1** is thus linked by eight Ni**L** ligands, and each Ni**L** ligand is linked to three cadmium ions to generate a chiral porous 3D framework with channel cross sections of ~1.2 × 0.8 nm along the *a*-axis, which are filled with DMF and water molecules. Thus, the channel surfaces are uniformly lined with chiral Ni**L** units with coordinatively unsaturated Ni^{2+} ions that are accessible to guest molecules and available for chemical modification as well.

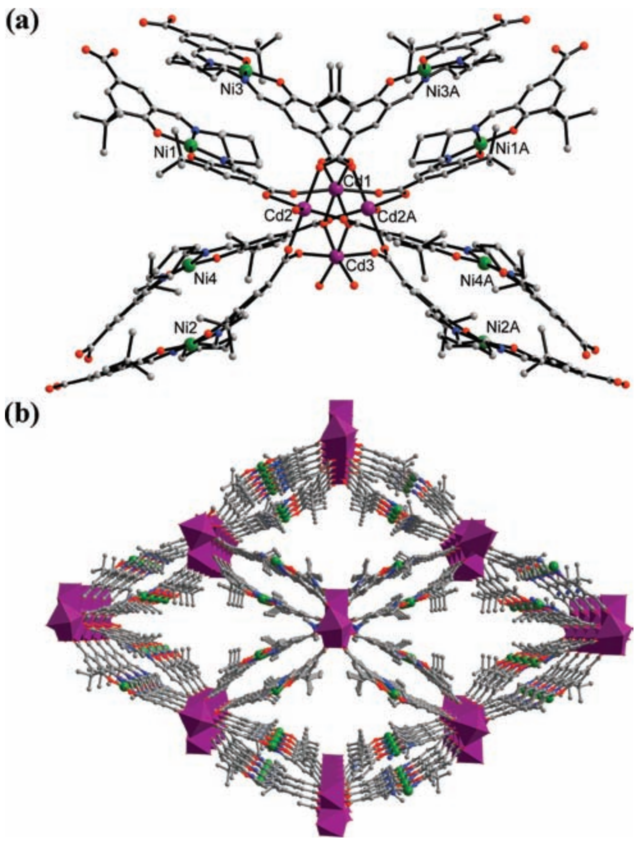
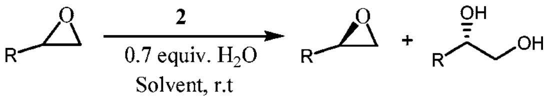


Figure 1. (a) Building block in **1** (only the O atoms of DMF molecules are shown for clarity) and (b) view of 3D porous structure of **1** along the *a*-axis (the Cd atoms are shown in polyhedron). Symmetry code: A, $-x+1$, y, $-z$.

2 is isostructural to **1** and adopts a similar porous 3D network structure that is built from Cd_4 clusters and Co**L** linkers with open channels of ~1.2 × 0.8 nm along the *a*-axis. Calculations using PLATON show that both **1** and **2** have about ~44% of the total volume available for guest inclusion.[15] Circular dichroism spectra of **1** made from *R* and *S* enantiomers of the **L**-H_4 ligand are mirror images of each other, indicative of their enantiomeric nature. In the X-ray photoelectron spectroscopy (XPS) spectra of **2** and its precursors, the Co $2p_{3/2}$ lines all appeared at ~781 eV, suggesting the cobalt ions are in +3 oxidation state,[16] which is also evidenced by their UV visible spectra that show the characteristic absorption band of Co^{III}(salen) at ~380 nm.[17] TGA revealed that the guest molecules could be readily removed in the temperature range 100−220 °C, and the frameworks are stable up to ~350 °C. PXRD experiments indicate that the frameworks and crystallinity of **1** and **2** remain intact upon complete removal of guest molecules. The N_2 sorption measurements of their

Table 1. HKR of Terminal Epoxides[a]



entry	R	cat. load. (mol %)[b]	reaction time (h)	ee_{ep} (%)[c]	conv (%)[d]	K_{rel}[e]
1	CH_2OPh	0.5	48	95	56	25
2	CH_2O(*o*-$NO_2C_6H_4$)	0.5	48	92	54	27
3	CH_2O(*p*-MeC_6H_4)	0.5	48	87	57	13
4	CH_2O(*p*-$OMeC_6H_4$)	0.5	48	94	55	27
5	CH_2O(*o*-MeC_6H_4)	0.5	48	97	54	43
6	CH_2O(*m*-$ClCgH_4$)	0.5	48	98	55	41
7	CH_2O(1-naphthyl)	0.7	48/60	95/99	53/57	43/40
8	CH_2O(2-naphthyl)	0.7	48/60	94/99	56/62	23/20
9	CH_2O(triphenylethane)	0.7	72	n.d.	<5[f]	n.d

[a] For reaction details see Supporting Information. Solvents: THF for entries 2, 3, and 7; CH_2Cl_2/CH_3CN for other entries. [b] Catalyst loading based on racemic epoxide. [c] ee values determined by HPLC. [d] Isolated yield based on racemic epoxide. [e] $K_{rel} = \ln[1 - c(1 + ee)]/\ln[1 - c(1 - ee)]$, where ee is the enantiomeric excess of the epoxide, and *c* is the conversion of the epoxide. [f] Estimated by ^1H NMR.

apohost samples at 77 K showed only surface adsorption, although the theoretical values are expected to be 1231.9 m^2/g.

The good stability and metric attributes of the Co(salen)-containing MOF **2** prompted us to explore its utilization as a solid catalyst for HKR of epoxides. Phenoxy epoxides are particularly attractive substrates for HKR because the racemates are available inexpensively and the chiral three-carbon building blocks derived from them are versatile synthetic intermediates. The resolved reactions were carried out with a 0.7:1 molar ratio of water to the substrate in THF or a mixed solvent of CH_3CN and CH_2Cl_2 at 23 °C. A 0.5 mol % loading of **2** with regard to the racemic substrates afforded the resolved target epoxides in 87−98% ee and 54−57% conversions within 48 h. As shown in Table 1 (entries 1−6), HKR reactions proceeded in good conversions and good to excellent enantioselectivity with a range of benzyloxy epoxide derivatives bearing both electron-donating and electron-withdrawing substituents. The resolutions of 1- and 2-naphthyl glycidyl ethers required a little higher catalyst loading (0.7 mol % **2**) to produce, within 48 h, 95 and 94% ee and 53 and 56% conversions of the epoxides, respectively. Increasing the reaction time to 60 h led to 99.5 and 99% ee and 57 and 62% conversions, respectively (Table 1, entries 7 and 8). Note that the examined epoxides exhibited good to excellent kinetic resolution selectivities (K_{rel} = 13−43, the ratio of relative rates of the two substrate enantiomers).[12,18]

To probe whether activation of the epoxide species occurs inside the pores or on the surface of the solid catalyst, a sterically more demanding substrate triphenyl glycidyl ether was synthesized and subjected to HKR conditions. Less than 5% conversion was observed after 72 h, much lower than the >53% conversions obtained by using [Co(**L**-H_2)(OAc)] and [Co(**L**-Me_2)(OAc)] (0.7 mol % loading). This result suggests that this bulky substrate cannot access the catalytic sites in the porous structure due to its large diameter. Therefore, catalytic HKR is indeed occurring within the MOF. This point is also suggested by the fact that ground and unground particles of **2** exhibited similar catalytic performance in resolution of phenyl glycidyl ether (25 vs 24% and 57 vs 56% conversions after 18 and 48 h, respectively).[19] In addition, control experiments showed that the Ni analogue **1** could not resolve 1,2-epoxy-3-phenoxypropane, indicating that both Cd and Ni sites could not function as active centers for HKR and activation of the substrate occurs on the Co sites within **2**.

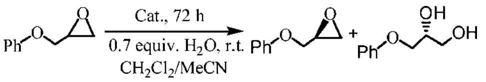
We also examined the heterogeneity of the MOF catalyst. The supernatant from HKR of phenyl glycidyl ether after filtration through a regular filter did not afford any additional diol product. To evaluate the stability of the solid catalysts, we investigated recycled and reused **2** in the resolution of 2-naphthyl glycidyl ethers. Upon completion of the reaction with 48 h, the catalyst **2** could be recovered in quantitative yield and used repeatedly without significant loss of catalytic activity for the following four runs (conversions ~53% and 94, 96, 92, 94, and 92% ee for runs 1−5, respectively). PXRD indicated that catalyst **2** remained highly crystalline after five cycles. The XPS spectrum showed that the recovered cobalt complex retained +3 oxidation state. Inductively coupled plasma atomic mass spectrometry (ICP-AMS) analysis of the product solution indicated little loss of the metal ions (~0.012% for both Co and Cd from the structure per cycle, either as molecular species or as particles too small to be removed by filtration through Celite).

To study the confinement effect of a MOF on the catalyst, the activities of Co(salen) monomers were studied. With 2% loading of the catalysts (the same loading of Co(salen) as the heterogeneous reaction), HKR of phenyl glycidyl ether after 24 h afforded 53% conversion with 83% ee of the epoxide for [Co(**L**-H_2)(OAc)] (K_{rel} = 17) and 57% conversion with 87% ee of the epoxide for [(Co(**L**-Me_2)(OAc)] (K_{rel} = 13). The framework-confined catalyst (56% conversion, 95% ee, and K_{rel} = 25 of phenyl glycidyl ether) thus gave higher enantioselectivities and K_{rel} values and comparable conversion with respect to its homogeneous analogues, although the heterogeneous reactions required longer time, due to slow mass diffusion in the porous media.

To further understand the confinement effect, we compared the catalytic activities of MOF **2** and Co(salen) monomers for HKR at low catalyst/substrate (C/S) ratios [the molar ratio of racemic epoxide to Co(salen)] in 48 h. At a C/S of 1:1000, [Co(**L**-H_2)(OAc)] and [(Co(**L**-Me_2)(OAc)] afforded 16 and 25% conversions of the epoxide, respectively, and **2** gave 37% conversion. When the C/S ratio decreased from 1:1000 to 1:5000 and 1:10000, the conversion sharply decreased from 16 to 6 and 2% for [Co(**L**-H_2)(OAc)], and from 25 to 10 and 2% for [(Co(**L**-Me_2)(OAc)], respectively, whereas **2** could still produce 23 and 16% conversions under similar conditions. So, the difference in catalytic activity became larger as the C/S ratio decreased, and the [Co(salen)] catalyst confined in the MOF displays much higher activity than the homogeneous counterparts, especially at low C/S ratios.

The concentration of [Co(salen)] units in the reaction system greatly affects HKR of epoxides because the reaction involves at least two [Co(salen)] complexes to generate the cooperative activation.[7] In homogeneous solutions at lower C/S ratios, the possibility for [Co(salen)] species to meet each other decreases, making it difficult for the bimetallic interaction to occur. The catalytic activity thus drops greatly (Table 2). Careful examination of the crystal structure of **2** reveals that the channel surfaces are lined by twisted Co(salen) planes with Co sites pointing to the open channels, and the shortest Co−Co

Table 2. HKR of Racemic Phenyl Glycidyl Ether on Homogeneous Co(salen) Catalysts and 2[a]



catalyst	C/S[b]	conv (%)[c]	ee_{ep} (%)[d]	ee_{diol} (%)[d]
Co(**L**-H_2)(OAc)	1:50[e]	53	83	73
	1:1000	16	15	78
	1:5000	6	4	69
	1:10000	2	2	n.d.
Co(**L**-Me_2)(OAc)	1:50[e]	57	87	65
	1:10000	25	27	82
	1:5000	10	8	76
	1:10000	2	2	n.d.
2	1:50[f]	56	95	73
	1:1000	37	44	76
	1:5000	23	22	74
	1:10000	16	13	70

[a] For reaction details see Supporting Information. [b] Molar ratio of [Co(salen)] to racemic epoxide. [c] Conversion is calculated from the equation, conversion = $(ee_{epoxide}/ee_{diol})/(1 + ee_{epoxide}/ee_{diol}) \times 100\%$, according to ref 13b. [d] Determined by HPLC. [e] Reaction time, 24 h. [f] Reaction time, 48 h.

distance of adjacent surfaces in a channel is 6.277(3) Å. This close proximity and appropriate spatial orientation of Co(salen) units thus offer the possibility that H_2O activated by one Co(salen) could attack the epoxide activated by another Co(salen) (Figure S11), affording the product with impressive activity even at a low C/S ratio. Generation of cooperative activation in a solid catalyst is important since lots of catalytic transformations proceed through a dual activation pathway, but it remains a challenge because of its inability to elaborately control the proper proximity and the conformation of active centers.[20] This work highlights the potential of making heterogeneous dual-active catalysts by using MOFs as support structures.

In summary, we have constructed two chiral, robust, porous MOFs based on dicarboxylate-functionalized Ni(salen) and Co(salen)(OAc) ligands. The Co(salen) units accessible via the open MOF channels were utilized to generate an efficient heterogeneous asymmetric catalyst for HKR of epoxides to afford the product at up to 99.5% ee. The MOF catalyst features a high local density of coorperative bis[Co(salen)] motifs, exhibiting improved catalytic performance relative to the monomeric catalysts at low C/S ratios. The solid catalyst can be easily recycled and reused without any apparent loss of catalytic activity and enantioselectivity. The ready tunability of such a modular approach based on metallosalens promises to lead to a number of chiral solid catalysts with unique and practically useful enantioselective functions.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

yongcui@sjtu.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by NSFC-21025103 and 20971085, "973" Programs (2009CB930403), and Shanghai Science and Technology Committee (10DJ1400100).

■ REFERENCES

(1) (a) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 657. (b) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (d) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, *112*, 836. (e) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Duyne, R. P. V.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105.

(2) (a) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330. (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (c) Li, J.; Kuppler, R. J.; Zhou, H. *Chem. Soc. Rev.* **2009**, *38*, 1477. (d) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (e) Cohen, S. M. *Chem. Rev.* **2011**, *112*, 970. (f) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem. Rev.* **2012**, *112*, 1126.

(3) (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (b) Lee, J.-Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (c) Liu, Y.; Xuan, W.; Cui, Y. *Adv. Mater.* **2010**, *22*, 4112.

(4) (a) Corma, A.; Garcia, H.; Xamena, F. X. L.. *Chem. Rev.* **2010**, *110*, 4606. (b) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196.

(5) Roberts, J. M.; Fini, B. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. *J. Am. Chem. Soc.* **2012**, *134*, 3334.

(6) (a) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. *Chem. Rev.* **2009**, *109*, 1659. (b) Haak, R. M.; Wezenberga, S. J.; Kleij, A. W. *Chem. Commun.* **2010**, *46*, 2713.

(7) (a) Gianneschi, N. C.; Bertin, P. A.; Nguyen, S. T.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10508. (b) Ready, J. M.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2002**, *41*, 1374.

(8) (a) Wang, X.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.; Zhang, X. P.; Ma, S. *J. Am. Chem. Soc.* **2011**, *133*, 16322. (b) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 4204. (c) Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684.

(9) (a) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563. (b) Song, F.; Wang, C. J.; Falkowski, M.; Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 15390. (c) Falkowski, J. M.; Wang, C.; Liu, S.; Lin, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 8674. (d) Shultz, A. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2011**, *133*, 13251. (e) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. *Nat. Chem.* **2010**, *2*, 838. (f) Tanaka, K.; Odaa, S.; Shirob, M. *Chem. Commun.* **2008**, 820. (g) Tanaka, K.; Otani, K.-i. *New J. Chem.* **2010**, *34*, 2389. (h) Ingleson, M. J.; Barrio, J. P.; Bacsa, J.; Dickinson, C.; Park, H.; Rosseinsky, M. J. *Chem. Commun.* **2008**, *11*, 1287. (i) Banerjee, M.; Das, S.; Yoon, M.; Chois, H. J.; Hyun, M. H.; Park, S. M.; Seo, G.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 7524.

(10) (a) Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691. (b) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410.

(11) (a) Yuan, G.; Zhu, C.; Xuan, W.; Cui, Y. *Chem.—Eur. J.* **2009**, *15*, 6428. (b) Xiang, S.; Zhang, Z.; Zhao, C.; Hong, K.; Zhao, X.; Ding, D.; Xie, M.; Wu, C.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. *Nat. Commun.* **2011**, *2*, 204. (c) Jeon, Y. M.; Heo, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 7480. (d) Yuan, G.; Zhu, C.; Liu, Y.; Cui, Y. *Chem. Commun.* **2010**, *47*, 3180.

(12) (a) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307. (b) Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 1360.

(13) (a) Breinbauer, R.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 3604. (b) Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 4147. (c) Blackmond, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 545. (d) Ready, M. J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 2687.

(14) (a) Yang, H.; Zhang, L.; Zhong, L.; Yang, Q.; Li, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6861. (b) Ma, J.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566. (c) Gill, C. S.; Long, W.; Jones, C. W. *Catal. Lett.* **2009**, *131*, 425.

(15) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(16) Oh, C. R.; Choo, D. J.; Shim, W. H.; Lee, D. H.; Roh, E. J.; Lee, S.; Song, C. E. *Chem. Commun.* **2003**, 1100.

(17) Thakur, S. S.; Li, W.; Shin, C.; Kim, G. *Catal. Lett.* **2005**, *104*, 151.

(18) We also performed HKR reactions using (*R*)- and (*S*)-phenyl glycidyl ether as substrate, and their conversions were found to be 53 and 15%, respectively, in 36 h. This means the (*R*) enantiomer reacts with H_2O about 3.5 times faster than the (*S*) enantiomer in the presence of (*R*)-**2**.

(19) Because most MOFs, including **2**, are mechanically unstable, they tend to fracture into smaller particles by magnetic stirring (Figure S19). It is thus hard to obtain quantitative kinetic parameters since the reaction rate depends on the catalyst sizes and the stirring rate.

(20) (a) Thomas, J. M.; Raja, R. *Acc. Chem. Res.* **2008**, *41*, 708. (b) Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187.