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A Homochiral Metal–Organic Framework as an Effective Asymmetric Catalyst for Cyanohydrin Synthesis

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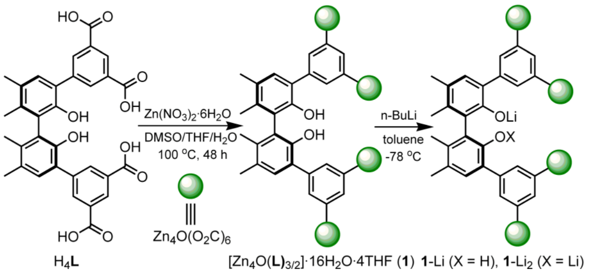
Ⓢ *Supporting Information*

ABSTRACT: A homochiral metal–organic framework (MOF) of an enantiopure 2,2′-dihydroxy-1,1′-biphenyl ligand was constructed. After exchanging one proton of the dihydroxyl group for Li(I) ions, the framework is shown to be a highly efficient and recyclable heterogeneous catalyst for asymmetric cyanation of aldehydes with up to >99% ee. Compared with the homogeneous counterpart, the MOF catalyst exhibits significantly enhanced catalytic activity and enantioselectivity, especially at a low catalyst/substrate ratio, due to that the rigid framework could stabilize the catalytically active monolithium salt of biphenol against its free transformation to catalytically inactive and/or less active assemblies in reactions. The synthetic utility of the cyanation was demonstrated in the synthesis of (*S*)-bufuralol (a nonselective *β*-adrenoceptor blocking agent) with 98% ee.

Metal–organic frameworks (MOFs) are crystalline hybrid solids composed of organic struts and inorganic nodes and have emerged as a novel class of porous materials.[1,2] Thanks to their catalysis friendly features such as large surface areas and porosity, tunable and functionalizable pore walls, MOFs have more advantages to be a kind of heterogeneous catalyst, especially for asymmetric catalysis than traditional organic and inorganic porous materials.[3−5] Although lots of chiral MOFs have been described,[6] versions featuring accessible catalytic active sites that induced high enantioselectivity remain scarce.[7] An appealing strategy for making chiral MOF catalysts involves using homogeneous asymmetric catalysts (or precatalysts) such as Ti-binolate and metallosalen complexes as organic linkers. Even though, the heterogenized catalysts are typically less effective, with limited substrate scope, than their homogeneous analogs.[8,9] Remarkably, in several instances it is also possible to generate MOFs with enhanced catalytic performance, e.g., by providing confined spaces for reactants and eliminating multimolecular catalyst deactivation pathways[5e,f] or by bringing active sites into a high local density arrangement and close proximity to facilitate synergistic interactions with substrates.[8e] It is therefore highly desirable to control the assembly of a chiral molecular catalyst into a MOF to improve its catalytic performance, so that predictive structure–property relationships can be established.[4]

Chiral diols such as 1,1′-biphenol and 1,1′-binaphthol (binol) are privileged catalyst structures utilized in a wide range of reactions that continue to expand.[10] Li(I) complexes of binol, e.g., could catalyze a variety of organic reactions, such as cyanosilylation of aldehydes to generate chiral cyanohydrins.[14] The real active species was shown to be a monomeric lithium binolate aqua complex, but there exists a dynamic mixture of binolate/Li species [(binolate)$_x$-Li, where *x* refers to the molar ratio of binol-to-Li] in solution, which is detrimental to the catalyst activity and selectivity.[14] Similar catalytic behavior was also observed in the biphenolate/Li system (Scheme S1). We report here the synthesis of an enantiopure tetracarboxylate ligand of biphenol (H_4**L**) to build a chiral MOF and show that incorporation of biphenol into a porous network, after partially exchanging its hydroxyl protons for Li ions, effectively enhanced reaction rates and enantioselectivity of cyanation of aldehydes, owing to the framework prohibited the free transformation of the catalytically active assemble to inactive and/or less active species (Scheme 1).

Scheme 1. Synthesis of MOF 1 and Its Post-Synthetic Modification



The ligand H_4**L** was prepared in an overall 76% yield by the suzuki cross-coupling of dimethyl-5-(pinacolboryl)isophthalate and (*R*)- or (*S*)-5,5′,6,6′-tetramethyl-3,3′-dibromo-biphenyl-2,2′-diol[12] and followed by hydrolysis with NaOH. Heating a mixture of H_4**L** and $Zn(NO_3)_2{\cdot}6H_2O$ (a 1:2 molar ratio) in DMSO, THF, and water at 100 °C afforded single crystals of $[Zn_4\mathbf{O}(\mathbf{L})_{3/2}]{\cdot}16H_2O{\cdot}4THF$ (**1**) in good yield. The product was stable in air and insoluble in water and common organic solvents and was formulated based on elemental analysis, IR spectroscopy, and thermogravimetric analysis (TGA). The phase purity of the bulk sample was established by comparison of its observed and simulated powder X-ray diffraction (PXRD) patterns.

(*S*)-**1** exhibits a 3D chiral nanoporous framework and crystallizes in the cubic chiral space group $I2_13$, with the asymmetric unit containing one-third of the formula. The basic

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building unit in **1** is a $[Zn_4(\mu_4\text{-}O)(\mathbf{L})_{3/2}]$ cluster with one crystallographic C_3 axis running through one Zn atom and the central oxygen atom. Four zinc atoms are each tetrahedrally coordinated to one μ_4-O atom and three carboxylate oxygen atoms from three **L** lignds. The **L** ligand exhibits an *exo*-octadentate coordination fashion, binding to four Zn_4O clusters via four bidentate carboxylate groups. The two phenyl rings are twisted along the pivotal 1,1′-bond with a dihedral angle of 74.0(1)°.

As show in Figure 1a, three pairs of 12 Zn_4O clusters that are related by C_3 symmetry and bridged by carboxylate groups merge at two more Zn_4O cores to generate a D_3-symmetric cage. The cage can also be viewed as a triply stranded structure with two Zn_4O cores located at opposite positions surrounded by three metallomacrocycles, each of which is built of ten Zn_4O clusters bridged by isophthalate linkers. The cage has an irregular open cavity with a maximum inner width of ~1.8 nm (considering van der Waals radii). The hexahedral aperture on each face has a diagonal distance of ~1.6 × 1.6 nm. Sharing the hexahedral windows with neighboring cages leads to multidirectional zigzag channels in the framework. The cage cavities are periodically decorated with the dihydroxy groups of biphenyl backbones that are accessible to guest molecules.

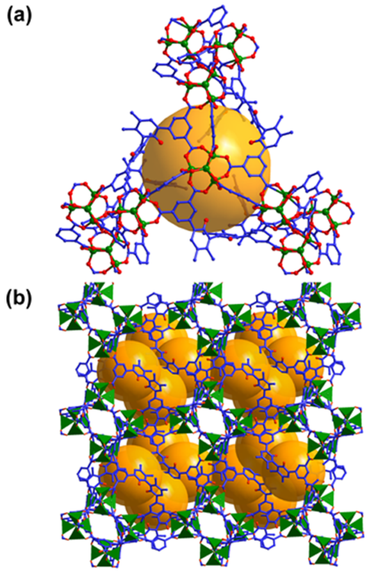


Figure 1. (a) A triply stranded cage in **1** encapsulated by 10 Zn_4O clusters (the cavity is highlighted by a colored sphere). (b) 3D structure of **1** viewed along the *a*-axis (the Zn atoms are shown in polyhedron).

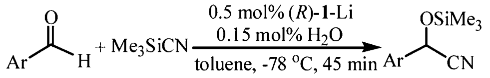
Calculations using the PLATON program indicate that 71.9% of the total volume of **1** is occupied by solvent molecules.[13] Circular dichroism (CD) spectra of **1** made from *R* and *S* enantiomers of the $H_4\mathbf{L}$ ligand are mirror images of each other, indicative of their enantiomeric nature. TGA revealed that the guest molecules could be readily removed in the temperature range from 80 to 150 °C and the decomposition of the framework starts at ~400 °C. The crystallinity of the framework remains intact upon removal of guest molecules. After soaking **1** in water for 2 days, PXRD indicated the sample retained its crystallinity. The CO_2 sorption measurement of the apohost **1** at 273 K gave a BET surface area of 172 m^2/g. **1** could adsorb ~2.0 methyl orange (MO, ~1.47 × 0.53 × 0.53 nm in size) per formula unit in solution, causing the initially colorless crystals becoming dark orange, and the inclusion solid exhibited the same PXRD pattern as the pristine sample. This result indicates that the structural integrity and open channels of **1** are maintained in solution.

Exchange of hydroxyl protons of **1** was achieved by replacing (via soaking) the initially present guest molecules with more volatile THF molecules and then stirring the evacuated MOF in a solution of *n*-BuLi in toluene containing a small amount of water.[15] Note that lithiated MOF catalysts of this type have been used before, but only with lithiation, no catalysis was reported.[15] Mono- and dilithium salts of $\mathbf{1}\text{-Li}(H_2O)_2$ (**1**-Li) and $\mathbf{1}\text{-Li}_2(H_2O)_4$ ($\mathbf{1}\text{-Li}_2$) were prepared from 1:2 and 1:4 molar ratios of **1** (per formular unit) and *n*-BuLi, respectively. The formation of the lithium salts was suggested by inductively coupled plasma optical emission spectrometer (ICP-OES). PXRD showed the post-modified MOF remained crystallinity. **1**-Li gave a decreased BET surface area (124 m^2/g) compared with **1**.

After optimization of reaction conditions, **1**-Li was found to be an active catalyst for cyanation of aldehydes with Me_3SiCN in the presence of a catalytic amount of water in toluene at −78 °C. The co-existence of water as coactivator is significant to the enantioselectivity of this cyanation, which is similar to the homogeneous reactions.[14a] Specifically, 0.5 mol % loading of (*R*)-**1**-Li with 0.15 mol % water catalyzes cyanation of benzylaldehyde to give 97% conversion with 98% enantiomeric excess (ee) of the desired product in 45 min. If the dilithium salt $\mathbf{1}\text{-Li}_2$ was used as catalyst, 90% conversion with 79% ee of the product was obtained, indicating that **1**-Li was more active and enantioselective than $\mathbf{1}\text{-Li}_2$, consistent with the observed higher activity of $Me_4\mathbf{L}$-Li in the homogeneous system. The chiral nature of the product is determined by the handedness of the catalyst, as evidenced by that cyanation of benzylaldehyde by (*S*)-**1**-Li gave the *R* enantiomer over the *S* enantiomer (96% ee, Table 1, entry 2).

Aromatic aldehydes with an electron-withdrawing group gave the desired product almost quantitatively with enantioselectivities up to >99% ee (Table 1, entries 3−5). Introduction of an

Table 1. Cyanation of Aldehydes Catalyzed by (*R*)-1-Li[a]



entry	Ar	conv (%)[b]	ee (%)[c]
1	C_6H_5	97	98 (*S*)
2	C_6H_5	97	96 (*R*)[d]
3	C_6H_5	90	79 (*S*)[e]
4	*p*-ClC_6H_4	99	>99 (*S*)
5	*p*-BrC_6H_4	99	92 (*S*)
6	*p*-$NO_2C_6H_4$	99	>99 (*S*)
7	*m*-$MeOC_6H_4$	99	81 (*S*)
8	3-pyridyl	97	>99 (*S*)
9	2-fural	95	99 (*S*)
10	$C_6H_5CH{=}CH$	98	98 (*S*)
11	1-naphthyl	99	94 (*S*)
12	2-naphthyl	99	>99 (*S*)
13	9-anthral	67	67 (*S*)
14	coronenyl	<5[f]	nd
15	coronenyl	60[g]	nd

[a] For reaction details see Experimental section in SI, catalyst and water loading based on aldehyde (30 mol % water loading based on the catalyst). [b] Calculated by ^1H NMR. [c] Determined by HPLC. [d] Catalyzed by 0.5 mol % (*S*)-**1**-Li. [e] Catalyzed by 0.5 mol % (*R*)-$\mathbf{1}\text{-Li}_2$. [f] Reaction time: 3 h. [g] Catalyzed by 1 mol % (*R*)-$Me_4\mathbf{L}$-Li.

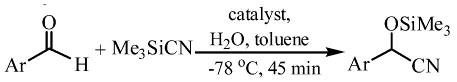
electron-donating −OMe group into the phenyl ring of the substrate led to decreased stereoselectivity (81% ee, entry 7). 3-Pyridylaldehyde and 2-furylaldehyde bearing a heterocycle gave excellent results up to >99% ee (entries 8 and 9). High enantioselectivity was also attained with the vinyl-type aromatic aldehyde cinnamaldehyde, affording 98% conversion and 98% ee. 1- and 2-naphthaldehydes were readily converted to the products with 94% and >99% ee, respectively. For the bulky substrate, 9-anthralaldehyde, moderate conversion (67%) and ee (67%) were obtained.

To determine whether catalysis by **1**-Li occurs predominantly within the cavities or instead on the external surface, competitive size selectivity studies were performed. A sterically more demanding substrate coronenyl aldehyde was synthesized and subjected to conditions of cyanation reaction. Less than 5% conversion was observed after 3 h, much lower than the 60% conversion obtained by using Me_4**L**-Li in 45 min. This result may suggest that this bulky substrate cannot access the catalytic sites in the framework due to its large diameter. It is thus likely that the catalytic reactions are heterogeneous and may occur within the MOF. This point is further indicated by the fact that ground and unground particles of **1**-Li (∼180 nm in size) exhibited almost the same reactivity (97% vs 96% conversions in 45 min) in cyanation of benzaldehyde.

We examined the heterogeneity and recyclability of the MOF catalyst. The supernatant from cyanation of benzlaldehyde after filtration through a regular filter did not afford any additional product. To evaluate the stability of the solid catalyst, we investigated recycled and reused **1**-Li in cyanantion of benzaldehyde. Upon completion of the reaction, the catalyst could be recovered in nearly quantitative yield and used repeatedly without significant loss of activity for the following four runs (>96% conversions and 98, 98, 97, and 97% ee for 1−4 runs, respectively). The conversions versus reaction time of the fresh and recycled catalysts are given in Figure S9. The two lines are almost coincide with each other, further confirming the recyclability of the catalyst. After five cycles, the MOF catalyst remained highly crystalline and still could adsorb ∼1.9 MO per formula unit in solution, indicating maintenance of its porous structure. ICP-OES analysis of the product solution indicated little loss of the metal ions (∼0.001%) 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 the MOF on the molecular catalyst, we compared the activities of Me_4**L**-Li and **1**-Li at different C/S ratios (the molar ratio of biphenol-Li to aldehyde). With a C/S ratio of 1:100, Me_4**L**-Li catalyzed cyanations of benzaldehyde, *p*-Br-benzaldehyde and 1-naphthylaldehyde in 45 min affording 83% conversion with 92% ee of the product, 91% conversion with 90% ee, and 90% conversion with 90% ee, respectively (Table 2). It appears that the MOF catalyst gave improved reactivity and enantioselectivity related to its homogeneous counterpart under similar conditions, although it required mass diffusion in the porous material. The difference in the reactivity was clearly manifested in the reaction kinetics. The conversion versus reaction time of the hetero- and homogeneous catalysts suggested that the former is more active than the latter, especially in the beginning 20 min (Figure S9). For example, the conversion of benzaldehyde (76%) with **1**-Li is about twice of that (39%) with Me_4**L**-Li in 10 min. Notably, the difference in catalytic performances became larger at a low C/S ratio. For instance, when the C/S ratio was decreased from 1:100 to 1:1000, **1**-Li still could catalyze cyanation of benzaldehyde giving 84% conversion with 96% ee of the product in 45 min, whereas Me_4**L**-Li (0.1 mol % loading) only gave 60% conversion with 86% ee. Cyanations of *p*-Br-benzaldehyde and 1-naphthylaldehyde followed the same trend with the heterogeneous catalyst giving higher levels of activity and enantioselectivity than the molecular catalyst at a low C/S ratio (Table 2).

Table 2. Cyanation of Aldehydes Catalyzed by 1-Li and Me_4L-Li at Different Catalyst/Substrate Ratios[a]



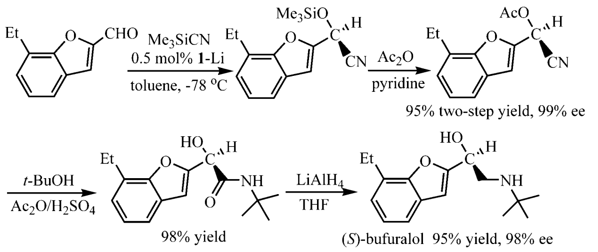
		heterogeneous		homogeneous	
C/S[b]	Ar	conv (%)[c]	ee (%)[d]	conv (%)[c]	ee (%)[d]
1:100	C_6H_5	97	98	83	92
	p-BrC_6H_4	99	92	91	90
	1-naphthyl	99	94	90	90
1:1000	C_6H_5	84	96	60	86
	p-BrC_6H_4	88	92	65	82
	1-naphthyl	86	92	63	87

[a] For reaction details see Experimental section in SI. Thirty mol % water loading based on the catalyst. [b] Molar ratio of biphenol-Li to aldehyde. [c] Calculated by ^1H NMR. [d] Determined by HPLC.

The catalyticaly active monomer of biphenolate/Li is subtle changes in reaction conditions that have a big influence on the catalytic performance. This is due to the coexistence of different kinds of species during the catalytic process as a result of a dynamic mixture of biphenolate/Li species equilibrating with each other in solution.[14] This makes the usage of catalyst inefficient, thus reducing the catalyst activity, especially at low catalyst loading. In contrast, immobilization of the catalyst on MOF **1** may help to keep the monomer in its active form by fixing one **L** ligand and one Li ion in a proper position, prohibiting the free transformation of different assemblies of biphenolate/Li. This would favor the usage efficiency of the catalysts, which may contribute to its high activity. On the other hand, geometrical constrains imposed by the chiral amphiphilic cages of **1** may exert steric influence on the binding substrate of biphenol-Li active centers and so impart enantioselectivity. In solution, many metal catalysts would convert themselves among active, less active, and/or unactive forms because of their labile coordination bonds, but it remains difficult to control the composition of equilibrium mixtures to optimize catalyst activities.[16] This work highlights the potential of modifying catalytic performances of metal catalysts with structural dynamism in solution by using MOFs as support structures. An in-depth investigation of the mechanistic aspect of this catalytic system is still underway.

Chiral cyanohydrins are well-known natural products and versatile synthetic intermediates for pharmaceuticals and agrochemicals.[17] Although great efforts have been made to heterogenize molecular catalysts for asymmetric cyanation, the heterogeneous catalysts usually resulted in a significant lowering of their enantioselectivity, which, with a few exceptions, did not exceed 90%.[3b,18] To demonstrate the synthetic utility of our cyanation approach, we examined the preparation of an optically enriched (*S*)-bufuralol (a potent *β*-adrenergic blocker with peripheral vasodilating activity) on a gram scale.[19] As shown in Scheme 2, 7-ethylbenzofuran-2-carbaldehyde (1 g) could be transformed into a chiral (*S*)-benzofuryl eyanohydrin in 95% yield with 99% ee. The addition of *tert*-butyl alcohol to the O-protected derivative of (*S*)-benzofuryl cyanohydrin afforded an

Scheme 2. Synthesis of (*S*)-bufuralol from the cyanation product



amide intermediate, which could be reduced to give (*S*)-bufuralol in 95% yield with 98% ee.

In summary, we have presented a homochiral biphenol-based MOF decorated with chiral dihydroxyl auxiliaries. Such dihydroxyl groups accessible via the open MOF channels could be partially exchanged by Li ions to generate a highly efficient and recyclable heterogeneous catalyst for asymmetric cyanation of aldehydes with up to >99% ee. The direct assembly of biphenol into the MOF may stabilize the catalytically active monolithium salt of biphenol against deactivation to catalytically inactive or less active assemblies of biphenolates/Li in reactions, enhancing the catalyst activity and enantioselectivity, especially at a low C/S ratio. This cyanation approach is suitable for process chemistry to ensure the practical gram-scale cyanohydrin synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Duyne, R. P. V.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105. (b) Stock, N.; Biswas, S. *Chem. Rev.* **2012**, *112*, 933.

(2) (a) Li, J.; Kuppler, R. J.; Zhou, H. *Chem. Soc. Rev.* **2009**, *38*, 1477. (b) Cohen, S. M. *Chem. Rev.* **2011**, *112*, 970. (c) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem. Rev.* **2012**, *112*, 1126. (d) Morris, R. E.; Bu, X. *Nat. Chem* **2010**, *2*, 356. (e) Xuan, W.; Zhu, C.; Liu, Y.; Cui, Y. *Chem. Soc. Rev.* **2012**, *41*, 1677.

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

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

(5) (a) Wang, X.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.; Zhang, X.; 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) Feng, D.; Gu, Z.; Li, J.; Jiang, H.; Wei, Z.; Zhou, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307. (d) Zhang, Z.; Gao, W.; Wojtas, L.; Ma, S.; Eddaoudi, M.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 9330. (e) 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. (f) Wang, C.; Zheng, M.; Lin, W. *J. Phys. Chem. Lett.* **2011**, *2*, 1701.

(6) (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) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106. (d) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495. (e) Xiong, R.-G.; You, X.-Z.; Abrahams, B. F.; Xue, Z.; Che, C.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4422. (f) Liu, B.; Shekhah, O.; Arslan, H. K.; Liu, J. X.; Woll, C.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 807. (g) Padmanaban, M.; Müller, P.; Lieder, C.; Gedrich, K.; Grünker, R.; Bon, V.; Senkovska, I.; Baumgärtner, S.; Opelt, S.; Paasch, S.; Brunner, E.; Glorius, F.; Klemm, E.; Kaskel, S. *Chem. Commun.* **2011**, *47*, 12089. (h) Suh, K.; Yutkin, M. P.; Dybtsev, D. N.; Fedin, V. P.; Kim, K. *Chem. Commun.* **2012**, *48*, 513. (i) Jeon, Y. M.; Heo, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 7480.

(7) (a) Ingleson, M. J.; Barrio, J. P.; Bacsa, J.; Dickinson, C.; Park, H.; Rosseinsky, M. J. *Chem. Commun.* **2008**, *11*, 1287. (b) 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. (c) Dang, D.; Wu, P.; He, C.; Xie, Z.; Duan, C. *J. Am. Chem. Soc.* **2010**, *132*, 14321. (d) Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. *J. Am. Chem. Soc.* **2011**, *133*, 5806. (e) Jeong, K. S.; Go, Y. B.; Shin, S. M.; Lee, S. J.; Kim, J.; Yaghi, O. M.; Jeong, N. *Chem. Sci.* **2011**, *2*, 877. (f) Gedrich, K.; Heitbaum, M.; Notzon, A.; Senkovska, I.; Fröhlich, R.; Getzschmann, J.; Mueller, U.; Glorius, F.; Kaskel, S. *Chem.—Eur. J.* **2011**, *17*, 2099. (g) Wu, P.; He, C.; Wang, J.; Peng, X.; Li, X.; An, Y.; Duan, C. *J. Am. Chem. Soc.* **2012**, *134*, 14991.

(8) (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.; Falkowski, J. M.; Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 15390. (c) Shultz, A. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2011**, *133*, 10352. (d) Falkowski, J. M.; Wang, C.; Liu, S.; Lin, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 8674. (e) Zhu, C.; Yuan, G.; Chen, X.; Yang, Z.; Cui, Y. *J. Am. Chem. Soc.* **2012**, *134*, 8058. (f) Zhang, T.; Song, F.; Lin, W. *Chem. Commun.* **2012**, 8766.

(9) (a) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. *Nat. Chem.* **2010**, *2*, 838. (b) Tanaka, K.; Oda, S.; Shiro, M. *Chem. Commun.* **2008**, 820. (c) Tanaka, K.; Otani, K.-i. *New J. Chem.* **2010**, *34*, 2389. (d) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (e) Wu, C.; Lin, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1075. (f) Ma, L.; Wu, C.; Wanderley, M. M.; Lin, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 8244. (g) Zhang, Z.; Ji, R.-Y.; Wojtas, L.; Gao, W.-Y.; Ma, S.; Zaworotko, M. J.; Antilla, J. C. *Chem. Commun.* **2013**, *49*, 7693.

(10) Brunel, M. J. *Chem. Rev.* **2007**, *107*, 1.

(11) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155.

(12) Yuan, G.; Zhu, C.; Liu, Y.; Xuan, W.; Cui, Y. *J. Am. Chem. Soc.* **2009**, *131*, 10452.

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

(14) (a) Hatano, M.; Ikeno, T.; Miyamoto, T.; Ishihara, K. *J. Am. Chem. Soc.* **2005**, *127*, 10776. (b) Hatano, M.; Horibe, T.; Ishihara, K. *J. Am. Chem. Soc.* **2010**, *132*, 56.

(15) Mulfort, K. L.; Farha, O. K.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 3866.

(16) (a) Balsells, J.; Davis, T. J.; Carroll, P.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 10336. (b) Liu, X.; Bai, S.; Yang, Y.; Li, B.; Xiao, B.; Li, C.; Yang, Q. *Chem. Commun.* **2012**, *48*, 3191. (c) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155.

(17) Brunel, J. M.; Holmes, I. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2752.

(18) Khan, N. H.; Kureshy, R. I.; Abdi, S. H. R.; Agrawal, S.; Jasra, R. V. *Coord. Chem. Rev.* **2008**, *252*, 593.

(19) Marek, Z.; Agnieszka, T.-K.; Andrzej, P.-K. *Tetrahedron: Asymmetry* **2005**, *16*, 3205.