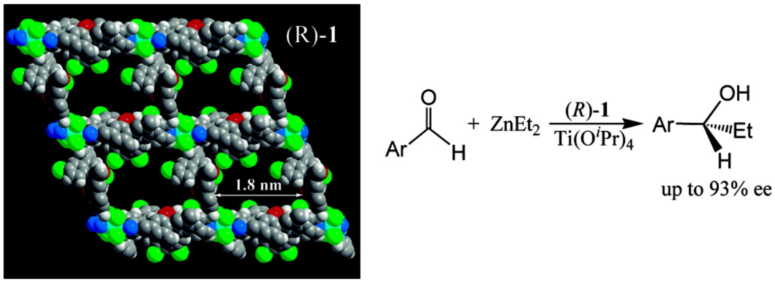
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

A Homochiral Porous Metal–Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis

Chuan-De Wu, Aiguo Hu, Lin Zhang, and Wenbin Lin

J. Am. Chem. Soc., **2005**, 127 (25), 8940-8941• DOI: 10.1021/ja052431t • Publication Date (Web): 04 June 2005



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 148 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Homochiral Porous Metal−Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis

Chuan-De Wu, Aiguo Hu, Lin Zhang, and Wenbin Lin*

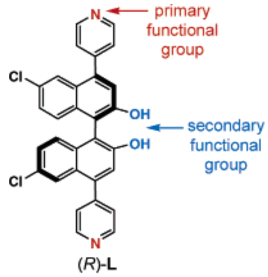
Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599

Received April 14, 2005; E-mail: wlin@unc.edu

Zeolites are used for the production of numerous chemical intermediates and household products.[1] The importance of chirality in biological processes has prompted significant efforts on developing chiral zeolites for applications in stereoselective processes. Few enantiopure zeolites have been obtained to date, and none have found applications in stereoselective processes.[2] Porous metal−organic frameworks (MOFs) are zeolite analogues with permanent porosity and absorption capacity.[3] The mild conditions typically used to synthesize MOFs allow the rational design of novel functional materials.[3,4] Judicious choices of building blocks can lead to chiral porous MOFs that can be used for heterogeneous asymmetric catalysis.[5] Herein we wish to report the synthesis of a highly porous homochiral MOF and its application in heterogeneous asymmetric catalysis with activity and stereoselectivity rivaling its homogeneous counterparts.

Our strategy for creating catalytically active chiral porous MOFs utilizes chiral bridging ligands containing orthogonal functional groups. The primary functional groups can be linked by metal-connecting units to form extended networks, whereas the orthogonal secondary chiral groups can then be used to generate asymmetric catalytic sites (Chart 1). This synthetic strategy leads to ideal heterogeneous asymmetric catalysts in which both the catalytic sites and the secondary environments around them are identical throughout the solid. Compared to other immobilization approaches,[6] the present strategy allows the synthesis of heterogeneous asymmetric catalysts with higher catalyst loading and more accessible catalytic centers.

Chart 1



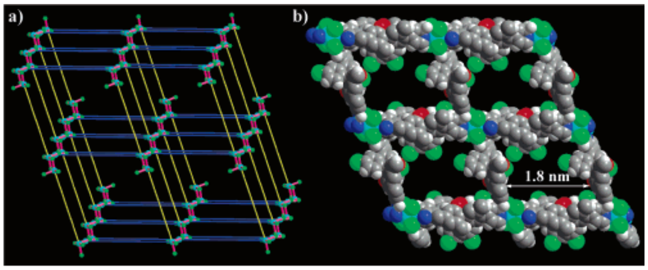


Figure 1. Crystal structure of **1**. Cyan, green, red, blue, gray, and white represent Cd, Cl, O, N, C, and H atoms, respectively. (a) Schematic representation of the 3D framework of **1** as viewed slightly off the *a*-axis. The 3D network is formed by linking the $[Cd(\mu\text{-}Cl)_2]_n$ SBUs (zigzag chains shown in purple) with the **L** ligands shown in yellow sticks and pairs of blue sticks. (b) Space-filling model of **1** as viewed down the *a*-axis showing the large chiral 1D channels (~1.6 × 1.8 nm).

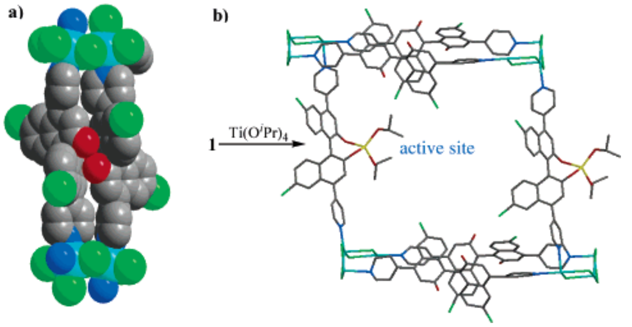
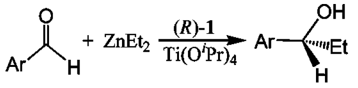


Figure 2. (a) Space-filling presentation of the tightly paired **L** ligands via strong hydrogen bonding and $\pi\cdots\pi$ interactions. (b) Schematic representation of the active (BINOLate)Ti(O^{i}Pr)$_2$ catalytic sites in the open channels of **1**. Cyan, green, red, blue, gray, and yellow represent Cd, Cl, O, N, C, and Ti atoms, respectively.

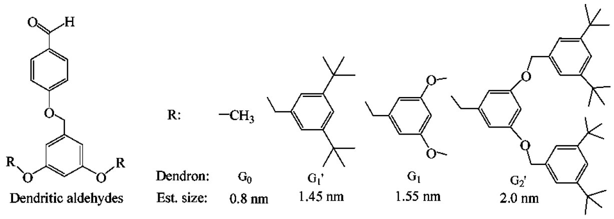
Axially chiral bridging ligand (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine, **L**, which contains the bipyridyl primary functionality and orthogonal chiral 2,2′-dihydroxy secondary functionality,[7] was used to construct homochiral porous MOFs. Colorless crystals of $[Cd_3Cl_6L_3]\cdot 4DMF\cdot 6MeOH\cdot 3H_2O$, **1**, were obtained in high yield by slow diffusion of diethyl ether into a mixture of **L** ligand and $CdCl_2$ in MeOH/DMF for 3 days.[8] **1** crystallizes in the triclinic $P1$ space group with three Cd atoms, six chloride atoms, and three **L** ligands in each unit cell. Octahedrally coordinated Cd(II) centers in **1** are doubly bridged by the chlorides to form 1D zigzag $[Cd(\mu\text{-}Cl)_2]_n$ chains that serve as secondary building units (SBUs) (Figure 1). Each Cd(II) center in the 1D zigzag chain further coordinates to two pyridyl groups of the **L** ligands and connects adjacent 1D $[Cd(\mu\text{-}Cl)_2]_n$ SBUs to form a noninterpenetrating 3D network with very large chiral channels of ~1.6 × 1.8 nm cross-section along the *a*-axis (measured from van der Waals surfaces). Interestingly, two of the three **L** ligands in each unit cell pair up via strong hydrogen bonding between neighboring hydroxy groups (O···O distance of 2.78 Å) and $\pi\cdots\pi$ interactions between pyridyl and naphthyl rings (the nearest C···C distance of 3.27 Å) and between the naphthyl rings (the nearest C···C distance of 3.32 Å). The dihydroxy groups for these two **L** ligands are shielded from the open channels by the naphthyl rings (Figure 2a). The third **L** ligand of **1** is not involved in supramolecular interactions, and the dihydroxy group points to the open channel. PLATON calculations indicate that **1** contains 54.4% void space that is accessible to the solvent molecules.[9] TGA analysis showed that **1** lost 18.8% of its mass in the 20−250 °C range, corresponding to the loss of all solvent molecules (expected 18.7%). X-ray powder diffraction demonstrated that the framework structure of **1** was maintained upon the removal of all the solvent molecules.

10.1021/ja052431t CCC: $30.25 © 2005 American Chemical Society

Table 1. Ti(IV)-Catalyzed $ZnEt_2$ Additions to Aromatic Aldehydes[a]



	BINOL/Ti(O^iPr)$_4$		1·Ti	
Ar	conv %	ee %	conv %	ee %
1-Naph	>99	94	>99	93
Ph	>99	88	>99	83
4-Cl−Ph	>99	86	>99	80
3-Br−Ph	>99	84	>99	80
4′-G_0OPh	>99	80	>99	88
4′-G_1′OPh	>99	75	73	77
4′-G_1OPh	>99	78	63	81
4′-G_2′OPh	95[b]	67[b]	0	−



[a] All the reactions were conducted with 13 mol % of **1** or 20 mol % BINOL and excess amounts of Ti(O^iPr)$_4$ at room temperature for 12 h. Conv % were determined by GC or NMR, while ee % values were determined on chiral GC or HPLC for all the secondary alcohols except for 4′-G_2′OPh whose ee % was determined by NMR spectrum of its Mosher's ester. [b] With 40 mol % BINOL.

CO_2 adsorption isotherms measured at 273 K indicated that the evacuated sample of **1** possesses permanent porosity with a specific surface area of 601 m^2/g and a pore volume of 0.26 mL/g.

We have used **1** for heterogeneous asymmetric catalysis by taking advantage of the readily accessible chiral dihydroxy groups. Ti(O^iPr)$_4$ can react with the chiral dihydroxy groups in BINOL or its analogues to afford Lewis acidic (BINOLate)Ti(O^iPr)$_2$ compounds which are active catalysts for the addition of $ZnEt_2$ to aromatic aldehydes to afford chiral secondary alcohols.[10] Treatment of **1** with excess Ti(O^iPr)$_4$ indeed led to an active catalyst (designated as **1**·Ti) for the $ZnEt_2$ addition reactions (Figure 2b). Specifically, **1**·Ti catalyzes the addition of $ZnEt_2$ to 1-naphthaldehyde to afford (*R*)-1-(1-naphthyl)propanol with complete conversion and 93% enantiomeric excess (ee) (Table 1). This level of ee rivals that of the homogeneous analogue under similar conditions (94% ee). **1**·Ti also catalyzes the addition of $ZnEt_2$ to a range of other aromatic aldehydes with complete conversion and ee values comparable to those of the homogeneous analogue. **1**·Ti represents a unique highly enantioselective asymmetric catalyst derived from a homochiral MOF. The only prior literature report gave a modest ee of 8% for a transesterification process catalyzed by a homochiral MOF.[5]

No secondary alcohol product was obtained when 1-naphthaldehyde was treated with $ZnEt_2$ in the presence of the supernatant from a mixture of **1** and Ti(O^iPr)$_4$, indicating heterogeneous nature of the present catalyst system. To ascertain that $ZnEt_2$ and aromatic aldehydes are accessing the internal (BINOLate)Ti(O^iPr)$_2$ sites via the open channels, we have designed a series of aromatic aldehydes of varying sizes. Molecular mechanics simulations indicated that these aromatic aldehydes containing Fréchet-type dendrons have an estimated size ranging from ~0.8 to ~2.0 nm. As expected, the efficiency for homogeneously catalyzed $ZnEt_2$ additions is not affected by the dendron size (Table 1). In contrast, the yields of $ZnEt_2$ addition products catalyzed by **1**·Ti greatly depend on the dendron size: as the size of the dendritic aldehyde increases, the yield of the $ZnEt_2$ addition product steadily decreases (>99, 73, 64, and 0%). No $ZnEt_2$ addition product was observed for the largest aldehyde 4′-G_2′-PhCHO, presumably because it cannot access the catalytic sites as a result of its large diameter. This set of experiments unambiguously demonstrates that **1**·Ti is a true heterogeneous asymmetric catalyst with both $ZnEt_2$ and aromatic aldehyde accessing the catalytic sites via the open channels.

As illustrated in Figure 2, we believe that only one-third of all **L** ligands in **1** react with Ti(O^iPr)$_4$ to generate the active catalyst because the other two **L** ligands are tightly paired via strong hydrogen-bonding and $\pi\cdots\pi$ stacking interactions.[11] Heterogeneous asymmetric diethylzinc addition reactions with **1**·Ti were therefore carried out with catalyst loading lower (13 mol %) than that of the homogeneous control experiments (20 mol %). The fact that complete conversions were observed for all the small aromatic aldehydes in these heterogeneous reactions demonstrates the high catalytic activity of **1**·Ti. The **1**·Ti system is also more enantioselective in diethylzinc addition reactions (by >20% ee) than analogous heterogeneous catalysts derived from structurally ill-defined zirconium phosphonates.[12]

Taken together, we have designed a highly active and enantioselective asymmetric catalyst **1**·Ti via creating readily accessible uniform catalytic sites inside a porous MOF. The modular nature of the present synthetic strategy should allow the incorporation of chiral bridging ligands with a diverse range of primary and secondary functionalities to lead to new chiral porous MOFs for practically useful heterogeneous asymmetric catalysis.

Acknowledgment. We acknowledge financial support from NSF. W.L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, a Cottrell Scholar of Research Corp, and a Camille Dreyfus Teacher-Scholar.

Supporting Information Available: Experimental procedures, analytical data, 13 figures, 1 table, and crystallographic data (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.
(2) (a) Anderson, M. W.; Terasaki, O.; Ohsuna, T.; Philippou, A.; MacKay, S. P.; Ferreira, A.; Rocha, J.; Lidin, S. *Nature* **1994**, *367*, 347. (b) Newsam, J. M.; Treacy, M. M. J.; Koetsier, W. T.; de Gruyter, C. B. *Proc. R. Soc. London, Ser. A* **1988**, *420*, 375.
(3) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (c) Suslick, K. S.; Bhyrappa, P.; Chou, J.-H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. *Acc. Chem. Res.* **2005**, *38*, 283. (d) Lee, S.; Mallik, A. B.; Xu, Z.; Lobkovsky, E. B.; Tran, L. *Acc. Chem. Res.* **2005**, *38*, 251. (e) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542.
(4) (a) Zheng, N.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2002**, *124*, 9688. (b) Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-G. *Angew. Chem., Int. Ed.* **2002**, *41*, 583. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (d) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511.
(5) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.
(6) Fan, Q. H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385.
(7) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554.
(8) Crystallographic data for **1**: triclinic, space group *P*1, $a = 10.234(1)$, $b = 19.118(1)$, $c = 20.929(1)$ Å, $\alpha = 67.553(3)$, $\beta = 86.753(3)$, $\gamma = 83.630(3)°$, $V = 3760.8(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.102$ gcm^{-3}, μ(Mo Kα) = 0.684 mm^{-1}. Least-squares refinements based on 16 121 reflections with $I > 2\sigma(I)$ and 865 parameters led to convergence, with a final R1 = 0.083, wR2 = 0.222, Flack parameter = 0.01(5), and GOF = 1.08.
(9) Spek, A. L. *PLATON*, a multipurpose crystallographic tool; Utrecht University: Utrecht, The Netherlands, 2001.
(10) (a) Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757. (b) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948.
(11) The inability of tightly paired BINOL units to react with Ti(O^iPr)$_4$ to generate active catalysts was demonstrated in a related supramolecular system. See: Jiang, H.; Lin, W. *Org. Lett.* **2004**, *6*, 861.
(12) Ngo, H. L.; Hu, A.; Lin, W. *J. Mol. Catal. A: Chem.* **2004**, *215*, 177.

JA052431T