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Postsynthetic Modification Switches an Achiral Framework to Catalytically Active Homochiral Metal−Organic Porous Materials

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Metal-organic porous materials (MOPMs) are a newly emerging, important class of materials comprising metal "nodes" linked with "rod" shaped organic linkers, which have attracted considerable attention because of their profound range of applications such as in catalysis, separation, and gas storage.[1] In particular, chiral MOPMs are potentially useful in heterogeneous asymmetric catalysis[2] because of the presence of microporous, readily accessible cavities with imbedded, regularly ordered chiral functionalities that can impose high enantioselectivity.[2c−e] Homochiral MOPMs studied to date are typically synthesized by sensibly choosing metal ions and chiral organic linkers and linking them together under solvothermal conditions. This strategy however requires extensive efforts to synthesize every single framework, which often leads to interpenetrated frameworks limiting their applications as chiral catalysts.[3]

In an alternative approach, the introduction of chiral auxiliary units inside preassembled achiral frameworks may be possible by postmodification. A significant advantage of this approach is that a chemically and thermally robust single framework can be converted to numerous catalytically active chiral MOPMs for a variety of asymmetric transformations by attaching suitable chiral catalytic units. Although this general strategy[4] has been applied to the generation of achiral MOPMs by attaching achiral units either at their organic linkers[5] or unsaturated metal centers,[6] there is no report of chiral MOPMs produced by postmodification and their applications in catalytic asymmetric organic transformations. Herein, we report the synthesis of chiral MOPMs from a preassambled achiral framework by postsynthetic modification with chiral catalytic units, which show remarkable catalytic activity in asymmetric aldol reactions.

For the synthesis of chiral MOPMs by postsynthetic modification we first chose MIL-101[7] as a parent framework because (1) it has a chemically and thermally robust structure with large pores (2.9−3.4 nm) and windows (1.2−1.4 nm), (2) it has open metal coordination sites to which a chiral organic ligand can be attached, and (3) it is insoluble in most organic solvents and water. We also chose L-proline as a chiral catalytic unit to be incorporated into the pores of the MOPM because L-proline and its derivatives are well-known asymmetric organocatalysts accelerating a variety of enantioselective organic reactions, including C−C bond forming aldol and Michael reactions under homogeneous reaction conditions.[8] To incorporate the L-proline unit into MIL-101, we designed chiral organic ligands $\mathbf{L_1}$ [(*S*)-*N*-(pyridin-3-yl)-pyrrolidine-2-carboxamide][9] and $\mathbf{L_2}$ [(*S*)-*N*-(pyridin-4-yl)-pyrrolidine-2-carboxamide] where the 3- or 4-pyridyl unit will be coordinated to the open metal coordination sites of the framework.

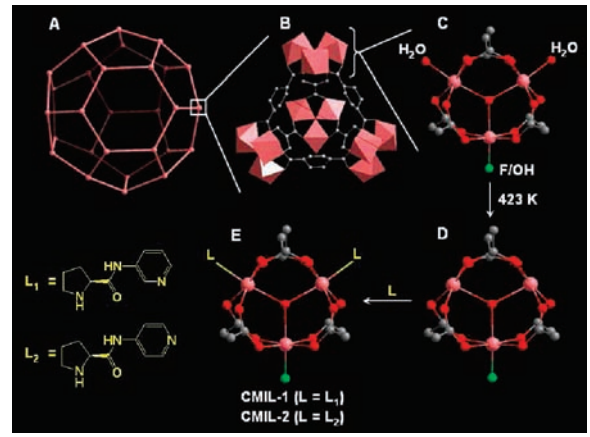

Figure 1. Schematic representation of (A) the large cage of MIL-101 delimited by the vertex sharing of the super tetrahedron (the vertices represent the center of each ST); (B) the ST cage drawn in polyhedron mode; (C) the μ_3-O bridged trimeric SBU chelated by six carboxylate; (D,E) postmodification of the dehydrated chromium(III) centers with L-proline-derived auxiliary ligands.

Postmodification of MIL-101 was achieved by treating it with chiral ligand $\mathbf{L_1}$ or $\mathbf{L_2}$ in a 1:3 ratio in refluxing chloroform for 1 d (Figure 1). The new chiral MOPMs, CMIL-1, $[Cr_3O(\mathbf{L_1})_{1.8}(H_2O)_{0.2}F(bdc)_3]\cdot 0.15(H_2bdc)\cdot H_2O$ and CMIL-2, $[Cr_3O(\mathbf{L_2})_{1.75}(H_2O)_{0.25}F(bdc)_3]\cdot 0.15(H_2bdc)\cdot H_2O$, were characterized by various techniques including powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), nitrogen adsorption measurements, IR spectroscopy, and microanalysis (see Supporting Information (SI) for details). Elemental analysis data indicated that ∼1.8 ligands per formula are incorporated for both CMILs. Both CMILs have PXRD patterns similar to that of MIL-101 supporting the retention of the parent framework structure. IR spectroscopy showed amide C═O bands at 1558 and 1695 cm^{-1}, and N−H stretching bands at 3189 and 3220 cm^{-1} for CMIL-1, and a similar pattern for CMIL-2, supporting the successful incorporation of the organic lignads in the postmodified MOPMs.[10] Nitrogen adsorption measurements indicated that both chiral MOPMs are highly porous even after postmodification (BET surface area, 1420 m^2/g for CMIL-1 and 1375 m^2/g for CMIL-2).

The catalytic activities of CMILs in asymmetric aldol reactions between various aromatic aldehydes and ketones were assessed (Table 1, see SI for additional information). The reactions catalyzed by CMILs produced aldol products in good to excellent yields (60−90%) and with fair to good enantioselectivity for *R*-isomers (ee 55−80%). For example, CMIL-1 efficiently catalyzed the aldol reaction between *p*-nitrobenzaldehyde and acetone at room temp in the absence of any added solvents with a decent yield (66%) and a fairly high enantioselectivity (69% ee) (Table 1, entry 1). A control experiment with

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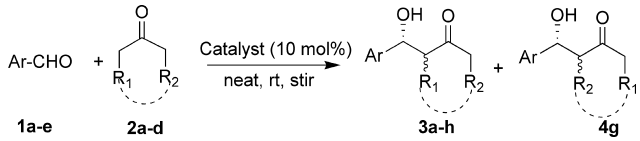
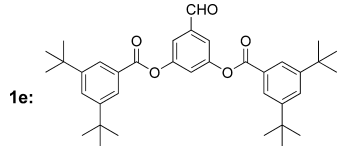
Table 1. Aldol Reactions between Different Aldehydes and Ketones



entry	Ar	substituents at ketone	catalyst	time (h)	yield[b] (%)	ee[c,d] (%) (dr)[e]
1.	**1a:** 4-NO_2Ph	**2a**: $R_1 = R_2 = H$	CMIL-1	24	66	69
			L_1	24	58	29
			CMIL-2	24	59	63
			L_2	24	64	21
2.	**1b:** 4-py	**2a**	CMIL-1	16	91	76
			L_1	12	91	66
			CMIL-2	16	87	58
			L_2	16	89	37
3.	**1c:** 4-ClPh	**2a**	CMIL-1	40	74	70
			L_1	40	78	25
			CMIL-2	48	69	52
			L_2	48	75	23
4.	**1d:** 2-naph	**2a**	CMIL-1	60	80	63
			L_1	72	77	36
5.	**1a**	**2b**: $R_1, R_2 = -(CH_2)_3-$	CMIL-1	24	81	66[f] [4:1]
			L_1	24	76	49[f] [4:1]
6.	**1a**	**2c**: $R_1, R_2 = -CH_2-CH(t\text{-Bu})-CH_2-$	CMIL-1	36	86[g]	68[f] [5:1]
			L_1	24	81[g]	62[f] [5:1]
7.	**1a**	**2d**: $R_1 = H, R_2 = CH_3$	CMIL-1	36	**3g**: 49 **4g**: 27	81 69
8.	**1e**	**2a**	CMIL-1	36	5[h]	n. d.
			L_1	36	58	n. d.

[a] Reactions were carried out under neat condition using 0.15 mmol of aldehyde and 1.50 mmol of ketone. [b] Isolated yields based on aldehydes. [c] The ee values were determined by chiral HPLC on a Chiralpak-AS or Chiralpak AD-H columns. [d] The absolute conuration (*R*) was assigned by comparison of the optical rotation of the isolated compound, with the values reported in literature. [e] The dr values were determined from NMR of the crude reaction mixtures. [f] Value represents the major isomer. [g] Reaction was carried out in 100 μL of DMf. [h] A total of 92% of starting material recovered; n. d. = not determined.

unmodified MIL-101 showed only 10% conversion (0% ee) after 5 d (presumably catalyzed by the mild Lewis acidic chromium centers). Most importantly, the same reaction when performed under homogeneous conditions with **L_1** acting as a catalyst resulted in much lower ee (29% ee) (Table 1, entry 1). In fact, these heterogeneous catalysts always produced the aldol products with much higher enantiomeric excess than the corresponding homogeneous catalysts (Table 1, entry 1−6). The better enantioselection in the case of the heterogeneous catalysts may originate form the restricted movement of the substrates in the confined microporous systems in combination with multiple chiral inductions. Both CMIL-1 and CMIL-2 showed comparable catalytic efficiency in terms of yield and reaction time; however, CMIL-1 imposed better enantioselectivity in each case (Table 1, entry 1−3). Although the origin of the observed difference in ee values between CMIL-1 and CMIL-2 is not clear, one possibility is that CMIL-1 having a bent ligand **L_1**, may impose additional steric hindrance to the approaching aldehyde from β-face of the reaction site than CMIL-2 with a straight ligand **L_2**, resulting in higher enantioselectivity.



The smooth reaction between *tert*-butylcyclohexanone and *para*-nitrobenzaldehyde suggested that the window size of these catalysts is large enough to allow such large substrates to pass through (Table 1, entry 6). To make sure that the aldol reactions occur mostly in the cavities of the catalyst, not on the external surface, a size selectivity study was performed (see SI). While the reaction between bulky aldehyde **1e**, which is larger than the window size of CMIL-1, and *para*-nitrobenzaldehyde in the presence of **L_1** was completed within 36 h, only 5% of the aldol product was observed in the presence of CMIL-1 after the same period of time (Table 1, entry 8). Finally, CMIL-1 can be reused for the asymmetric aldol reaction between *para*-nitrobenzaldehyde and acetone up to three times without much change in yield and enantioselectivity (see SI).

In summary, we have demonstrated a simple and efficient route to chiral MOPMs by postsynthetic modification of a preassembled achiral metal−organic framework. In this study, L-proline-based chiral ligands were attached to the open metal coordination sites of MIL-101, and the resulting chiral MOPMs showed remarkable catalytic activities in asymmetric aldol reactions, including much higher enantioselectivity than the chiral ligands themselves. Although in several cases, ee values were not highly satisfactory, we believe that proper modification of the chiral catalytic unit will lead to much better enantioselection. A variety of chiral catalytic units can be incorporated into chemically robust MOPMs with large pores by postmodification and the resulting chiral MOPMs may find useful applications in catalytic asymmetric transformations. Further work along this line is in progress.

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Supporting Information Available: Experimental details for synthesis of chiral linkers and CMILs, general procedure of catalysis reactions, tables of reaction condition and recycling studies, and IR, PXRD, TGA, and N_2 adsorption isotherms of CMILs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Recent reviews. (a) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (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) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (d) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.

(2) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y.; Kim, K. *Nature* **2000**, *404*, 982. (b) Lin, W. *MRS Bull.* **2007**, *32*, 544. (c) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (d) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563. (e) Wu, C. D.; Lin, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1075.

(3) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72.

(4) Wang, Z.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315.

(5) (a) Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 12368. (b) Tanabe, K. K.; Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2008**, *130*, 8508. (c) Burrows, A. D.; Frost, C. G.; Mahon, M. F.; Richardson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 8482.

(6) Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Jhung, S. H.; Seo, Y.-K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Férey, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 4144.

(7) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.

(8) (a) Yang, J. W.; Chandler, C.; Stadler, M.; Kampen, D.; List, B. *Nature* **2008**, *452*, 453. (b) List, B.; Lerner, R. A.; Barbas III, C. F. *J. Am. Chem. Soc.* **2000**, *122*, 2395. (c) Wolfgang, N.; Fujie, T.; Barbas III, C. F. *Acc. Chem. Res.* **2004**, *37*, 580. (d) D'Elia, V.; Zwicknagl, H.; Reiser, O. *J. Org. Chem.* **2008**, *73*, 3262.

(9) Xu, X.-Y.; Tang, Z.; Wang, Y.-Z.; Luo, S.-W.; Cun, L.-F.; Gong, L.-Z. *J. Org. Chem.* **2007**, *72*, 9905.

(10) The bands at 1435 (sh) and 1487 cm^{-1} in the IR spectrum of CMIL-1 (Figure S9) have been tentatively assigned as the pyridine group of **L_1** bound to the metal center of the framework (see SI for details).

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