Inorganic Chemistry

Chiral Cu(salen)-Based Metal–Organic Framework for Heterogeneously Catalyzed Aziridination and Amination of Olefins

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S Supporting Information

ABSTRACT: A homochiral 3D porous metal–organic framework was assembled from a chiral dicarboxylic acid-functionalized Cu(salen)-based catalyst and could serve as an efficient heterogeneous catalyst for aziridination and allylic amination of olefins. Besides easy separation and reuse of the catalyst, the chiral framework confinement could impart substrate size selectivity, enhance catalyst activity, and induce product enantioselectivity.

H eterogenization of homogeneous catalysts is of great interest because of the ease of separation from the product stream and reusability and has been attempted using polymeric matrixes and porous inorganic oxides via ion exchange or impregnation.¹ Such hybrid catalysts afforded by these methods are normally less effective than their homogeneous counterparts. The isolation and uniformity of the catalysts were insufficient, and the environment surrounding the catalysts could not be well understood.² If a molecular catalyst can be directly incorporated onto the channel surface of a crystalline solid, a completely isolated and uniform arrangement may be realized. In this context, it is ideal for the integration of catalytically active functions into metal–organic frameworks (MOFs) by using functionalizing molecular catalysts as bridging linkers.³

MOFs have good stability, high void volumes, and well-defined tailorable cavities of uniform size.⁴ Such networks have shown potential in stabilizing catalytic centers by isolating the sites in a manner similar to that of the peptide architecture of enzymes in biological systems and induce selectivity, regioselectivity, or shape/size selectivity by creating an appropriate environment around the metal center in the restricted space.^{5–7} Metallosalen complexes have diverse applications in homogeneous catalysis.⁸ Chiral MOFs based on M(salen) have been explored as catalysts for asymmetric transformations.^{7,9} However, the direct incorporation of chiral Cu(salen) into MOFs as heterogeneous catalysts has not been reported. Herein we report the synthesis, structure, and heterogeneous catalysis characteristics of a chiral Cu(salen)based MOF. For aziridination and allylic amination of olefins, the immobilized Cu(salen) catalyst exhibits a much better catalytic performance than its homogeneous counterparts as a result of the framework confinement effect.

The reaction of N,N'-bis(3-tert-butyl-5-(carboxyl)salicylide (L-H₄) and Cu(NO₃)₂·4H₂O in methanol at room temperature results in Cu(L-H₂). [Cu(L-Me₂)] was obtained in a way similar to that for the ester L-H₂Me₂ of L-H₄. Heating a mixture of CdI and Cu(L-H₂) (2:1 molar ratio) in N,N-dimethylformamide

(DMF) and water (H₂O) at 80 $^{\circ}$ C afforded single crystals of [Cd₄(CuL)₄(DMF)₄]·DMF·4H₂O (1) in good yield (Figure 1).



Figure 1. Synthesis of **1** from tetrameric $[Cd_4(O_2C)_8(DMF)_4]$ units and $Cu(L-H_2)$, and a view of the 3D structure of **1** along the *a* axis (Cd, blue; Cu, green; O, red; N, turquoise; C, gray; Cd₄ units are shown as polyhedra; only the O atoms of DMF are shown for clarity).

Single-crystal X-ray analysis revealed that 1 crystallizes in the chiral space group C2. Four Cd atoms are bridged by four bidentate and four tridentate carboxylate groups of eight CuL units and four DMF to form a square-planar tetrameric $[Cd_4(O_2C)_8(DMF)_4]$ secondary building unit, with a C_2 axis passing through one metal center. There are three crystallographically independent Cd ions in 1, all of which adopt distorted octahedral geometries by coordinating to six carboxylate O atoms for Cd1, five carboxylate O atoms and one DMF for Cd2, and four carboxylate O atoms and two DMF for Cd3. All of the CuL ligands exhibit an exo-pentadentate coordination mode, and each Cu adopts a distorted square-planar geometry (Figures S1 and S2). Each CuL ligand is thus linked to two Cd₄ cores and each Cd₄ unit is linked by eight CuL ligands, forming a unique 3D framework with 1D channels of $\sim 1.2 \times 0.8$ nm² along the *a* axis, which are filled with guest molecules DMF and H₂O. The

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topology of 1 can be described as a 2,8-c net with the point (Schläfli) symbol $\{4^4.12^{24}\}\{4\}_4$ when the tetrameric Cd₄ unit and CuL ligand are treated as 8- and 2-connected nodes, respectively (Figure S3).

The solvent-accessible void space of 1 was about ~44%, calculated using *PLATON*.¹⁰ The phase purity of the bulk sample was established by a comparison of the observed and simulated powder X-ray diffraction (PXRD) patterns. Thermogravimetric analysis revealed that the guest molecules could be readily removed in the temperature range from 100 to 220 °C and the framework is stable up to 350 °C (Figure S4). Variable-temperature PXRD experiments suggested that the network is stable at least up to 280 °C (Figure S5). The enantiomeric nature of 1 made from *R* and *S* enantiomers of Cu(L-H₂) was demonstrated by the mirror images in solid-state circular dichroism spectra (Figure S6). The N₂ adsorption measurement provided a Brunauer–Emmett–Teller (BET) surface area of 195.6 m²/g (Figure S7).

Given that copper complexes are promising oxidation catalysts in many important organic transformations,¹¹ the catalytic activity of 1 toward olefin aziridination was examined. Aziridines are important intermediates in organic synthesis for many nitrogen-containing pharmaceuticals and biologically active compounds.¹² The reaction was carried out with a 4:1 molar ratio of styrene and [N-(p-tolylsulfonyl)imino]phenyliodinane (PhI=NTs) in CH₃CN at room temperature. A 2.3 mol % loading of 1 led to 81% conversion of PhI=NTs after 12 h. We found that 1 was an efficient catalyst for the reactions of a variety of olefins including derivatives with electron-withdrawing or -donating substituents (Table 1, entries 1-5). Despite good transformation, we only observe fairly and specific asymmetric induction. An aziridination product of styrene gave 8.6% ee, while products of substituted styrenes were essentially racemic (<2% ee). Notably, when α -methylstyrene or 4-chloro- α -

Table 1. Catalyzed Aziridination and Amination of Styrene and Its Derivatives by $PhI=NTs^{a}$

	$\frac{R_2 = Me}{2.3 \text{ mol}\% 1}$ $\frac{R_2 = Me}{2.3 \text{ mol}\% 1}$ $\frac{R_2 = Me}{1}$ $\frac{R_2 = Me}{1}$ $\frac{R_2 = Me}{1}$	R_1	$R_2 = H$ $2.3 \text{ mol}\% 1$ $CH_3CN,$ r.t., 12 h R_1 B
Entry	R_1	Product	Yield[%] ^b
1 ^c	Н	А	$81^{d}/45^{e}/52^{f}$
2	$4-CH_3$	Α	$63^{\rm d}/45^{\rm e}/48^{\rm f}$
3	4-Cl	А	$84^{d}/34^{e}/45^{f}$
4	4-Br	Α	$85^{\rm d}/48^{\rm e}/79^{\rm f}$
5	3-CH ₃ O	А	$74^{\rm d}/50^{\rm e}/40^{\rm f}$
6	3-BnO	Α	66 ^d
7	3-R ₀ O	А	0^{d}
8	Н	В	$57^{\rm d}/47^{\rm e}/52^{\rm f}$
9	4-Cl	В	$71^{\rm d}/60^{\rm e}/62^{\rm f}$
$\begin{array}{c} & & \\ & & \\ & & \\ R_{0:} \end{array}$			

^{*a*}For reaction details, see the Supporting Information. ^{*b*}Isolated yield after column chromatography. ^{*c*}The ee values (determined by HPLC) were 8.6% for entry 1 and <2% for entries 2-5. ^{*d*}2.3 mol % loading of 1. ^{*e*}9.2 mol % loading of Cu(**L**-H₂). ^{*f*}9.2 mol % loading of Cu(**L**-Me₂).

methylstyrene was employed, **1** showed a remarkable selectivity for the allylic amine rather than aziridine production (Table 1, entries 8 and 9), probably because of the fact that these substrates readily undergo nitrene insertion into allylic C–H bonds at secondary C atoms.^{12c} The allylic amines were obtained in 57 and 71% isolated yields, respectively, and no aziridination product was detected. The starting PhI=NTs is recovered as sulfonamide after column chromatography.

After completion of the reaction, simple filtration of the mixture allowed separation of the solid-state catalyst in almost quantitative yield (>98%), and the recovered solids could be used for at least five cycles in the amination of styrene without significant loss of catalytic activity (isolated yields 81, 81, 80, 78, and 76%, respectively). PXRD showed that 1 remained highly crystalline after five cycles. The BET surface area of the recycled sample was found to be $137 \text{ m}^2/\text{g}$. Moreover, a hot filtration test showed no indication of catalysis by leached homogeneous species, suggesting the heterogeneous nature of our catalyst system. The leaching percentages of metal ions in each cycle during recycling of the catalyst were ~2.1% and 0.9% for Cu and Cd, respectively, as determined by inductively coupled plasma optical emission spectrometry analysis.

To ascertain whether the substrates are accessing the internal active sites via open channels, we synthesized a series of styrene derivatives of varying sizes. An obvious size-selectivity effect consistent with the channel dimensions was observed (Table 1, entries 5–7). The molecular dimensions of 3-methoxystyrene allow it to diffuse swiftly through the pores, such that its conversion to the aziridine derivative reaches 74%, while the conversion yields for 3-benzyloxystyrene decreased to 66% under similar conditions. In contrast, no aziridine product was observed for the largest olefin 3-R₀O-styrene, presumably because it cannot access the catalytic sites as a result of its large diameter. Such shape and size selectivity implied that catalysis primarily occurs in the channels.

To identify the catalytically active sites, the isostructural Ni(salen)-MOF^{7d} to 1 was prepared and employed as the catalyst. When styrene or α -methylstyrene and PhI=NTs were treated with the Ni(salen) analogue, no desired product was detected, thus indicating that the unsaturated Cu sites within 1 are active centers for the oxidation process indeed. A transient Cu=NTs group is hypothesized to form on the open coordination sites of the Cu(salen) core upon reaction with PhI=NTs.¹³ Further research on the nature of the intermediate is needed in order to investigate the mechanism of nitrogentransfer reactions.

To compare the catalytic activities of the immobilized Cu catalyst and homogeneous analogues, olefin aziridination and amination catalyzed by $Cu(L-H_2)$ and its ester $Cu(L-Me_2)$ were carried out. Under identical conditions, 9.2 mol % loading of $Cu(L-H_2)$ or $Cu(L-Me_2)$ could also catalyze aziridination of styrene or 4-bromostyrene and amination of α -methylstyrene or 4-chloro- α -methylstyrene, but the yields of ~10% were much lower than those by 1 and, moreover, no enantioselectivity was observed for the aziridination product (Table 1, entries 1, 4, 8, and 9). Obvious enhancement in the activity was observed for the Cu(salen) units in 1 compared with homogeneous counterparts. Such activity enhancement could presumably be attributed to the site isolation of Cu(salen) units, thus avoiding the deactivation caused by dimerization and/or oligomerization.¹⁴ Moreover, because of the geometrical constraints imposed by chiral channels around the Cu^{II} centers, 1 demonstrated specific enantioselectivity in the aziridination reactions, which, however,

was not observed for the homogeneous counterparts. The positive confinement effect of immobilization on the catalytic performances has been observed in hosts based on mesoporous and layered inorganic solids¹⁵ and has also received attention in MOFs.^{3,7}

In summary, we have constructed a chiral robust MOF by using a chiral dicarboxylic acid-functionalized Cu(salen) ligand and demonstrated that the MOF could catalyze aziridination and allylic amination of olefins. Besides easy separation and reuse of the catalyst, the chiral framework confinement could impart substrate size selectivity, enhance catalyst activity, and induce product enantioselectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02151.

Experimental details and spectral data (PDF) Crystallographic file in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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