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Enhanced Activity and Enantioselectivity of Henry Reaction by the Postsynthetic Reduction Modification for a Chiral Cu(salen)-Based Metal−Organic Framework

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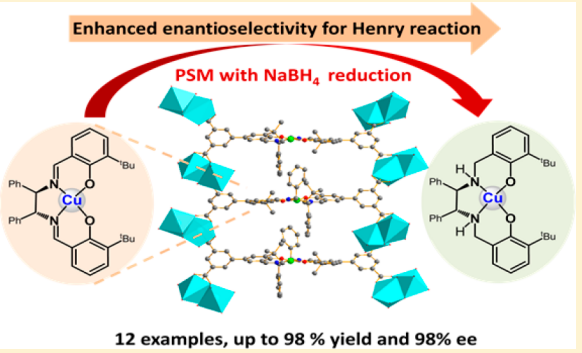
Supporting Information

ABSTRACT: Metal−organic frameworks (MOFs) imbedded privileged molecular catalysts are of particular interest due to their higher catalytic activities derived from the MOFs pore/channel confinement effect, improved lifetime through eliminating intermolecular deactivation pathway, and the recyclability based on their heterogeneity. In this work, a 3D chiral metallosalen-based MOF $[Cd_2(Cu(salen))(DMF)_3]\cdot DMF\cdot 3H_2O$ (**1**) with a 1D open channel was synthesized and characterized by single-crystal X-ray diffraction and other physicochemical methods. Upon postsynthetic reduction modification with $NaBH_4$, the conversion from imino to amino group on salen cores of **1** generates the reduction product **2** with a more flexible chiral group and more alkaline backbone, meanwhile still maintaining the original porous framework. **2** can be used as an efficient heterogeneous catalyst for the asymmetric Henry reaction with broad substrate applicability and exhibits higher activity and enantioselectivity (ee up to 98%) compared with the unreduced **1**. Note that **2** can accelerate the Henry reaction of pyridine-2-carboxaldehyde possessing a potential coordination atom with excellent ee value; however, the homogeneous counterpart does not. In addition, the bulky aldehydes show a decrease in activity but almost the same enantioselectivity with an increase in the molecular size of substrates as a result of the chiral confinement effect of **2**, indicating the size-dependent selectivity. To the best of our knowledge, this is the highest enantioselectivity for asymmetric Henry reaction catalyzed by MOF-based catalysts.



INTRODUCTION

Henry (nitroaldol) reaction is an excellent tool for the stereoselective carbon−carbon bond forming reaction from the viewpoint of green chemistry, and the product β-nitroalcohols are significant chemical intermediates of natural compounds, insecticides, fungicides, antibiotics, etc. To date, diversified homogeneous molecular catalysts, including BINOL,[1] aminoalcohol,[2] salen,[3] and Schiff bases[4] complexes, have been developed to promote the asymmetric Henry reaction. Prominent among these are a series of Cu complexes with the reduced salen ligands that can vary the steric and electronic properties about the metal centers, and enhance the alkalinity and flexibility of ligand frame.[3c] However, most homogeneous molecular catalysts commonly encounter recovery difficulty and facile intermolecular dimerization of metal complexes, which then reduce catalyst stability and lifetime. A promising approach for the utilization of elaborated ligands is isolation of catalytic centers within a robust solid-state matrix. The synthetic designability of metal−organic frameworks (MOFs) allows for this strategy that metal active sites can be incorporated and separated within a porous framework.

Recently, MOFs, also known as porous coordination polymers, have drawn considerable attention as very prominent materials for heterogeneous catalysis owing to their high surface areas, adjustable pore volume and shape, tunable composition (organic linkers or metal clusters), and amenability to bottom-up assembly methodology.[5] MOFs having imbedded, well-defined privileged molecular catalysts are of particular interest due to their higher catalytic activities derived from MOFs pore/channel confinement effect, improved lifetime through eliminating the multimolecular deactivation pathways, and recyclability based on their heterogeneity.[5c,d] Following this synthetic strategy and motivated by the excellent asymmetric catalytic activities of metallosalen compounds,[3,6] a number of MOFs constructed by chiral M(salen)-derived ligands (M: Cu/Ni/Co/Fe/Mn/Cr/VO/Ru) were synthesized over the past decade.[7] These M(salen)-based MOFs were extensively used in various asymmetric catalytic reactions, such as epoxidation of olefins,[8] hydrolytic kinetic resolution,[9] olefin aziridination,[10] cyclopropanation,[11] cyanosilylation,[12] aminolysis of epoxides,[13] and

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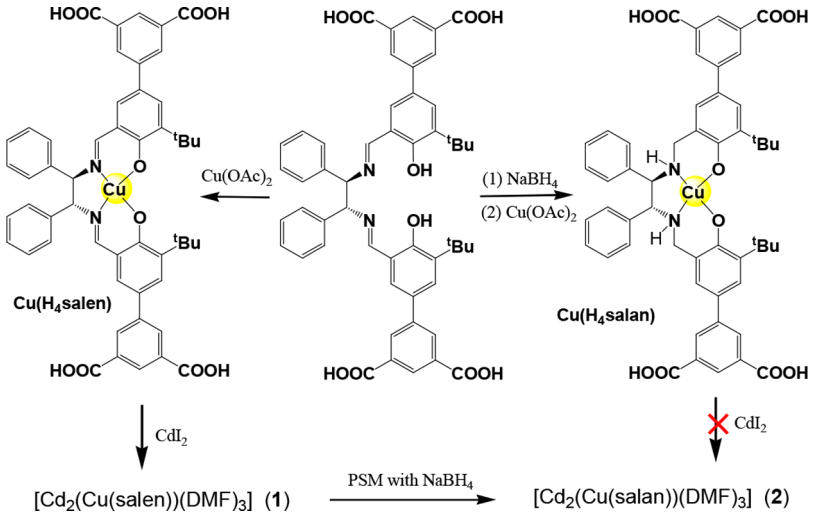
Scheme 1. Synthesis of 1 and 2



cycloaddition reaction of CO_2 with epoxides.[14] In this field, a pioneering work is that in 2006, Hupp and co-workers successfully introduced a chiral Mn(salen) catalyst into a porous MOF for heterogeneous catalysis of asymmetric olefin epoxidation with good yield and enantioselectivity, which can compare with that of its homogeneous counterpart.[8a] In addition to the directly solvothermal synthesis, some metallosalen-based chiral MOFs with high catalytic activity could be constructed by the postsynthetic modification (PSM). For example, Lin and co-workers developed a pair of Ru^{III}(salen)-based chiral MOFs that could undergo reversible single-crystal to single-crystal reduction/reoxidation.[11a] The reduction sample, Ru^{II}(salen)-based MOF, was highly active for the asymmetric cyclopropanation of alkenes with very high diastereoselectivity and enantioselectivity. Moreover, Cui and co-workers reported several chiral VO(salen)-based MOFs and the oxidation of V^{IV} to V^{V}, producing efficient and recyclable heterogeneous catalysts for the cyanosilylation of aldehydes with improved enantioselectivity.[12a] These works illustrate that chiral M(salen)-based MOFs synthesized by direct immobilization or PSM strategies have potential application for various organic transformations.

Although many chiral MOFs based on M(salen) have been explored as catalysts for asymmetric transformations, Cu(salen)-based chiral MOFs for heterogeneous catalysis are less constructed.[10,12b] Moreover, only a few examples of MOF-based heterogeneous catalysts for the Henry reaction have been reported to date.[15] In continuation of our works on the M(salen)-based MOFs for heterogeneous catalysis,[12d,14,16] herein, a new three-dimensional (3D) Cu(salen)-based MOF(**1**) was constructed by tetracarboxyl-functionalized chiral salen ligand H_6salen (Scheme 1). Notably, upon PSM reduction with $NaBH_4$, the conversion from imino to amino on salen cores in **1** generates a reduction product **2** with a more flexible chiral group and more alkaline backbone, which not only maintains the original porous framework but also exhibits much higher activity and enantioselectivity (ee up to 98%) for the asymmetric Henry reaction compared with the unreduced **1**. Furthermore, **2** could be reused five times without losing its structural integrity and catalytic activity. To the best of our knowledge, this is the first example of reduction PSM of salen cores within M(salen)-based MOFs, achieving exceptional enantioselectivity in MOFs-catalyzed asymmetric Henry reaction.

EXPERIMENTAL SECTION

Materials and Instrumentation. All of the reagents were commercially available and were used without further purification. Elemental analyses (EA) for C, H, and N were carried out with a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu Kα radiation (λ = 1.5406 Å). Thermogravimetric analyses (TGA) were performed on a Q600SDT instrument under a flow of N_2 at a heating rate of 10 °C min^{-1}. Solid-state circular dichroism (CD) spectra were recorded on a J-800 spectropolarimeter. Infrared (IR) spectra were measured by using KBr pellets on a Nicolet Model Nexus 470 FT-IR spectrometer in the range of 4000−400 cm^{-1}. The gas adsorption measurements were performed by using a Micro Active ASAP2460 system under N_2 (77 K) and CO_2 (273 K), respectively. HPLC was recorded on an Agilent 1200 series system with an analytical CHIRALCEL chiral column for enantiomeric excess (ee) determination. Mass spectrum (MS) measurement was conducted using an Agilent 7700 equipment. The X-ray photoelectron spectroscopy (XPS) experiment was performed using a spectrometer with an Al Kα radiation source.

Synthesis of Cu(H_4salen). The enantiopure tetracarboxyl-functionalized salen ligand (H_6salen) was synthesized according to our reported procedure.[16b] A solution of $Cu(OAc)_2{\cdot}H_2O$ (0.12 g, 0.58 mmol) in MeOH (30 mL) was added dropwise to a solution of H_6salen (0.5 g, 0.58 mmol) in MeOH (20 mL). The reaction mixture was stirred at room temperature for 4 h. The blue powder precipitated off, which was collected by centrifugation, washed with MeOH, and dried under reduced pressure (0.48 g, 91%). IR data (υ/cm^{-1}): 2951.4, 2517.5, 1705.7, 1603.9, 1534.6, 1402.8, 1263.6, 1088.9, 1004.7, 907.2, 766.3, 685.1, 557.8. ESI-MS: m/z = 944.2350 for $[Cu(H_4salen) + Na]^+$.

Synthesis of $[Cd_2(Cu(salen))(DMF)_3]{\cdot}DMF{\cdot}3H_2O$ (1). A mixture of CdI_2 (9.6 mg, 0.02 mmol) and Cu(H_4salen) (10 mg, 0.01 mmol) was dissolved in a mixed solvent of *N*,*N*-dimethylformamide and water (DMF/H_2O, 2.0 mL/0.5 mL) with 60 μL of 3 M HCl in a capped vial and heated at 80 °C for 3 days. After cooling to room temperature, red block crystals were filtered, washed with DMF and THF, and dried at room temperature. IR data (υ/cm^{-1}): 2943.7, 1650.0, 1539.2, 1387.4, 1255.2, 1163.4, 1093.9, 992.3, 921.8, 855.9, 779.5, 716.8, 657.3, 560.9. EA, calcd. for $C_{64}H_{76}Cd_2N_6CuO_{17}$: C, 51.60; H, 5.14; N, 5.64; found: C, 51.02; H, 5.36; N, 5.37.

Postsynthetic Reduction Modification of 1. **1** (15 mg, 0.01 mmol) and $NaBH_4$ (2 mg, 0.04 mmol) were dissolved in anhydrous methanol (2 mL) at 0 °C, and the mixture was stirred at room

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temperature for 12 h. After that, methanol was removed by centrifugation and the reduction product **2** (where the salen ligand could be reduced to hydrogenated salen, that is salan, as shown in Scheme 1) was washed with DMF and MeOH for several times. IR data (υ/cm^{-1}): 3407.0, 2950.5, 2872.6, 2195.4, 1618.1, 1533.7, 152.2, 1401.6, 1266.8, 1165.4, 1089.9, 1044.5, 921.6, 885.2, 853.4, 776.4, 725.3, 655.7, 565.8.

Crystal Structure Determination. Single-crystal X-ray diffraction data collection and structure determination of **1** was performed at 100 K with an Xcalibur Onyx Nova four-circle diffractometer with a CCD system utilizing graphite-monochromatic Cu Kα radiation (λ = 1.54184 Å). The empirical absorption correction was performed using the Crystal Clear program. The structure was solved using a direct method, and refined by full-matrix least-squares on F^2 employed in the program SHELXL-2016/6 program package.[17] We employed the PLATON software/SQUEEZE subroutine to compute the diffraction contribution of the solvent molecules and to generate a group of solvent-free diffraction intensities. The resulting new HKL file was used to further refine the structure. The crystallographic data and structure refinement parameters are summarized in Table S1. CCDC 1814252 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Typical Experimental Procedure for Henry Reaction. 1 (or **2**) (60 mg, 1 mol %) was added to a solution of anhydrous MeOH (2 mL) in 5 mL screw-capped vial. Then nitromethane (12.6 mL, 20 mmol) and aldehyde (2 mmol) were added to the above solution. After stirring for 48 h, the volatile components were removed under reduced pressure, and the crude product was purified by flash column chromatography.

Recycling of 2. After catalytic reaction, the solid phase was collected by centrifugation, rinsed with THF, dried for 2 h in vacuum, and then used as recovered catalyst for recycling experiments.

RESULTS AND DISCUSSION

Characterization of Catalysts. Single-crystal X-ray diffraction analyses revealed that **1** adopts a 3D porous framework and crystallizes in the chiral space group $P2_12_12_1$. The asymmetric unit is composed of a Cu(salen) unit (Figure 1a), two Cd^{2+} ions, and three DMF molecules. In the Cu(salen) ligand, each Cu atom adopts a square-planar geometry with the equatorial plane occupied by the N_2O_2 donors from salen (Cu−O_{avg} = 1.8964 Å, Cu−N_{avg} = 1.9179 Å). The two Cd ions are coordinated by one bis-tridentate chelating-bridging, two bidentate-bridging, and one bidentate carboxylate groups from four Cu(salen) ligands and three DMF, forming a $[Cd_2(O_2C)_4(DMF)_3]$ secondary building unit (SBU, Figure 1b). Thus, the 3D framework (Figure 1c) with 1D channel of about 8.0 × 9.0 Å^2 along the *a* axis is constructed by the linkage of SBU by four isophthalate groups on Cu(salen) ligands. Overall, **1** has the same network topology as the Ni(salen)-based MOF[16b] with the same salen ligand, except for the different catalytic metal center. It is worth noting that the empty coordination sites of Cu^{2+} and chiral diphenyl groups orient to the 1D channel, which are available for Lewis acid activation and chiral induction for the trapped substrates or intermediate transition state. The PLATON calculation shows that **1** has about 36.8% of the total volume available for guest inclusion that can be removed by thermal activation in vacuum. The solvent content was established by a combination of EA and TGA, and was lower than that calculated by the electron count from SQUEEZE.

The phase purity of the bulk sample was established by a comparison of the observed and simulated PXRD pattern from crystal data (Figure 2a). The solid-state CD spectra in the wavelength range 400−800 nm of **1** made from *R*- and *S*-

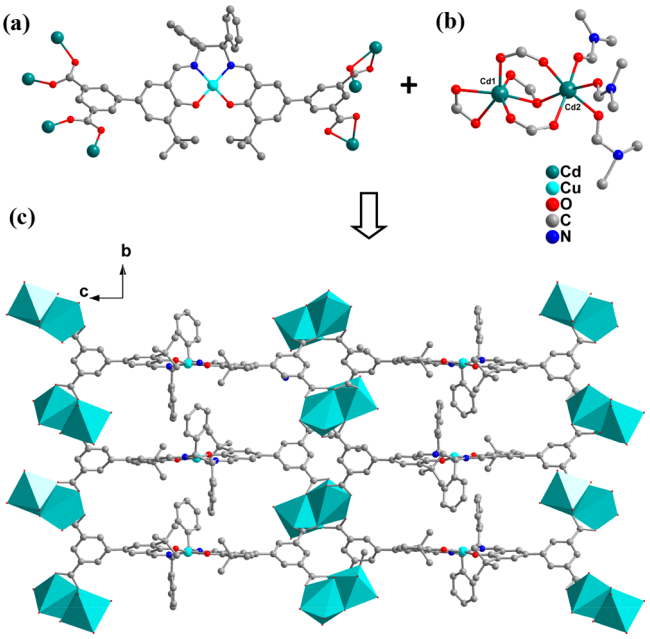

Figure 1. (a) View of coordination mode of Cu(salen) ligand. (b) The coordination environment of dinuclear Cd_2 cluster. (c) 3D network along the crystallographic *a* axis (dinuclear Cd_2 clusters are presented by polyhedron).

enantiomers of the salen ligand are mirror images of each other, showing their enantiomeric nature (Figure 2b). TGA of **1** shows a weight loss in the range of 25−260 °C amounting to 8.20% (Figure S1), which corresponds to the loss of three water and one DMF molecules from the channels (calc. 8.53%). When the temperature increased to above 300 °C, a steep weight loss revealed the structure has decomposed. In order to verify the porosity of **1**, the sorption isotherms of N_2 and CO_2 were measured at different temperatures. The sample was exchanged with methanol overnight and then activated under vacuum at 120 °C for 10 h, affording the desolvated **1.** As can be seen in Figure 2c, the N_2 adsorption of desolvated **1** at 77 K revealed Type I behavior, indicative of a microporous material, and the apparent Brunauer−Emmett−Teller (BET) surface area is 421 m^2 g^{-1}. The pore size distribution calculated from nonlocal density functional theory method resulted in a pore size of 9.8 Å, which is in good agreement with the crystal structure analysis. Moreover, the CO_2 uptake of **1** is 36.3 m^2 g^{-1} at 273 K and 1 atm, higher than that of a Ni(salen)-based MOF[16b] constructed by the same ligand, highlighting that Cu(salen) has stronger affinity than Ni(salen) for CO_2 (Figure 2d).

Catalytic Activity for Asymmetric Henry Reaction. As mentioned above, Cu(II) complexes were proved to be one of the most efficient catalysts for Henry reaction. Thus, **1** might serve as a superior catalyst for symmetric Henry reaction due to the ordered Cu(salen) units and inherent chiral groups inside the 1D channel. Before the catalytic reaction, **1** was activated at 120 °C under vacuum for 10 h to remove guest molecules. Initially, we performed the reaction by using benzaldehyde as the model substrate with nitromethane and activated catalyst. As summarized in Table 1, the activity of **1** was first tested at 25 °C and in a solvent-free system with 1 mol % catalyst loading. However, no desired product was detected after 2 h, and the yield of 12% for β-nitroalcohols with a 17% ee value was achieved when prolonging the

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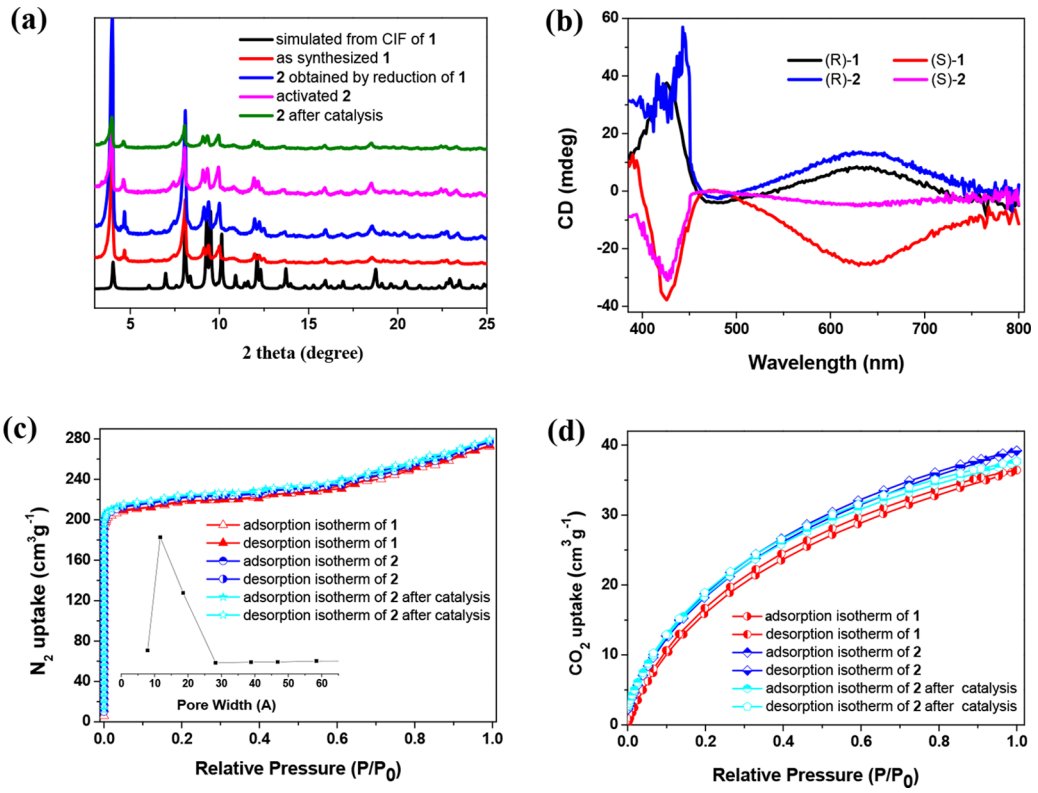

Figure 2. (a) PXRD patterns of **1**, **2**, activated **2**, and recovered **2** after fifth catalysis. (b) Solid-state CD spectra of **1** and **2**. (c) N_2 adsorption and desorption isotherms of **1** and **2** at 77 K and the pore size distribution of **1** (inset). (d) CO_2 sorption isotherms of **1** and **2** at 273 K.

reaction time to 48 h (Table 1, entry 4). The lower yield may stem from the poor interaction between the catalyst and substrate in the solvent-free system. After that, the influences of solvent on the activity were investigated. It can be seen from Table 1, MeOH and EtOH as solvent afforded relative good yield and ee value, while other aprotic solvents, such as tetrahydrofuran, toluene, acetonitrile, and dichloromethane, gave very poor yields and enantioselectivities. On the basis of solvent screening, MeOH was selected as optimal reaction solvent. Because the deprotonation of nitromethane to form nitronate ion is a rate-determining step in the Henry reaction,[18] several bases as additive were investigated. An inorganic base, like K_2CO_3, offered high yield (51%) but low enantioselectivity (21%), which may be interpreted that it had an excellent effect on the products both of the two conformations (*R* and *S*). The screening results demonstrated that DIPEA (*N*,*N*-diisopropylethylamine), TEA (tris(2-hydroxyethyl)amine), TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as additives afforded higher enantioselectivity (Table 1, entries 12−15). However, other organic bases, such as PPh_3, 2,6-lutidine, and DABCO (1,4-diazabicyclo[2.2.2]octane), gave low yields or trace enantioselectivity (Table 1, entries 16−18). In view of the above results, DIPEA was selected as an additive to accelerate this reaction. Besides, owing to the racemization at higher temperature, we lowered the reaction temperature to 10 °C (or 0 °C); a significant increase for the ee values from 51% to 78% (or 89%) was achieved, but accompanied by the very obviously decreased yield (Table 1, entries 19 and 20). To our surprise, elevating the reaction temperature to 45 °C led to moderate yield with a 84% ee value (Table 1, entry 21). Further elevating the reaction temperature to 50 °C afforded a slight increase in yield and significant decrease in enantioselectivity (Table 1, entry 22). Consequently, the optimal reaction temperature is set to 45 °C. Under the optimal reaction conditions, the use of (*S*)-**1** in the Henry reaction of benzaldehyde gave the *S*-enantiomer over its *R*-enantiomer with 87% ee, which unveiled that the enantioselectivity of the product is controlled by the intrinsic chiral nature of the catalyst (Table 1, entry 23).

In contrast, a control experiment was conducted by employing the isostructural MOF with Ni(salen) linker under otherwise identical conditions. The yield of the corresponding product dramatically decreased from 49% to trace, demonstrating the catalytic performance of Cu(salen) sites in **1** for the Henry reaction. Moreover, homogeneous control experiment was also performed using the Cu(H_4salen) ligand (the molar amount of Cu(salen) was the same as in **1**) under optimal conditions, and an almost same yield of *β*-nitroalcohol was obtained, but with significant decrease in enantioselectivity (Table 1, entry 26). These results demonstrate the chiral framework confinement and/or synergistic effects work together during the catalytic process when **1** was used as the catalyst.

It was reported that the reduction of Schiff base-type ligands to hydrogenated analogues can enhance the asymmetric induction ability for some organic transformations owing to their stronger alkaline N and more flexible backbone.[3c,19,20] Therefore, **1** was reduced to **2** by the reduction with $NaBH_4$ through PSM, generating a more flexible chiral induction environment and stronger alkaline sites in the channel. Surprisingly, the reaction proceeded very smoothly, giving the expected product with enhanced yield (71%) and excellent enantioselectivity (95%) when **2** was used as catalyst under the

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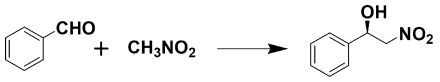
Table 1. Optimization of Henry Reaction Conditions[a]



entry	catalyst[b]	temp (°C)	solvent	additive	time (h)	yield[c] (%)	ee[d] (%)
1	**1**	25			2	n.d.	n.d.
2	**1**	25			8	trace	3
3	**1**	25			24	5	9
4	**1**	25			48	12	17
5	**1**	25	MeOH		48	31	41
6	**1**	25	EtOH		48	24	29
7	**1**	25	THF		48	17	7
8	**1**	25	$PhCH_3$		48	13	5
9	**1**	25	CH_3CN		48	10	4
10	**1**	25	DCM		48	20	9
11	**1**	25	MeOH	K_2CO_3	48	51	21
12	**1**	25	MeOH	DIPEA	48	39	51
13	**1**	25	MeOH	TEA	48	30	37
14	**1**	25	MeOH	TMEDA	48	31	32
15	**1**	25	MeOH	DBU	48	23	29
16	**1**	25	MeOH	PPh_3	48	<5	n.d.
17	**1**	25	MeOH	2,6-lutidine	48	20	3
18	**1**	25	MeOH	DABCO	48	11	7
19	**1**	0	MeOH	DIPEA	48	3	89
20	**1**	10	MeOH	DIPEA	48	17	78
21	**1**	45	MeOH	DIPEA	48	49	84
22	**1**	50	MeOH	DIPEA	48	51	56
23	(*S*)-**1**	45	MeOH	DIPEA	48	47	87(s)
24	**2**	45	MeOH	DIPEA	48	71	95
25	(*S*)-**2**	45	MeOH	DIPEA	48	70	95(s)
26	Cu(H_4salen)	45	MeOH	DIPEA	48	45	37
27	Cu(H_4salan)	45	MeOH	DIPEA	48	52	64

[a]Reaction conditions: benzaldehyde (2 mmol) and nitromethane (20 mmol). [b]The loading of catalyst is 1 mol %. [c]Isolated yield. [d]Determined by chiral HPLC analysis.

optimal conditions (Table 1, entry 24). The utilization of (*S*)-**2** as catalyst gave the corresponding *S*-enantiomer with 95% ee value, confirming the reduction process could not influence the intrinsic chiral nature (Table 1, entry 25). In addition, the catalytic performance of **2** for asymmetric Henry reaction is higher than that of homogeneous Cu(salan) catalyst (Table 1, entry 27), and can compare that of the monomeric macrocyclic copper-[H_4]salen-based homogeneous catalytic system,[3c] but the latter needs higher catalyst loading (10 mol %).

Our initial attempt to characterize the reduction process through single-crystal to single-crystal transformation was unsuccessful, because this PSM reduction causes the deterioration of single crystals quality, which led to poor diffraction data. Nevertheless, the conversion from imino to amino group on salen units of **1** was confirmed by the following experimental results. First, the comparative analysis of the IR (Figure S2) spectra of **1** and **2** shows that the characteristic peak at 1650 cm^{-1}, attributed to υ(C═N) stretching vibration, disappears in **2**, while accompanying the occurrence of a new peak at 3407 cm^{-1}, which indicates the reduction from C═N to C-N group.[20] Second, this PSM reduction is also unambiguously demonstrated by the ICP-AMS analysis of **2** that displayed a molecular ion peak at m/z of 865.4, corresponding to $[(H_8salan) + H]^+$ (Figure S5). Lastly, to confirm whether the oxidation state of copper ion changed during the reduction process, the XPS of **2** was measured (Figure S6). The peaks of Cu $2p_{3/2}$ at 932.7 eV and Cu $2p_{1/2}$ at 952.5 eV, together with two satellite peaks at 940 and 945 eV, indicate that the oxidation state of the copper species remains +2.[21,22] In addition, upon reduction with $NaBH_4$, the 3D framework, thermal stability, porosity, and enantiomeric nature still retain, illustrating that this PSM process has no effect on the stability of MOF (Figures 2 and S1).

On the other hand, we prepared the hydrogenated metallosalen ligand (designated as Cu(salan)) (Scheme 1) through the reduction of the salen ligand with $NaBH_4$, and then metalation with $Cu(OAc)_2{\cdot}H_2O$. However, it was found that many efforts for de novo synthesis of **2** from the Cu(salan) ligand using a hydrothermal method all failed. We speculate the possible reason is that the metallosalen ligand after reduction is more flexible and is not conducive to the synthesis of MOF. These results further demonstrate that the PSM of MOF sometimes is the only method by which certain moieties can be incorporated into the MOF without affecting the underlying structure, and will ultimately play a key role in accessing next-generation materials.

The turnover number (TON, defined as moles of product per mole of catalyst used) and turnover frequency (TOF, defined as moles of product per mole of catalyst used per unit of time) of the model reaction under optimized conditions are 134.9 and 2.8 h^{-1}, respectively. An important issue for heterogeneous catalysts is the possibility that some of the active species can leak from the solid support into the liquid

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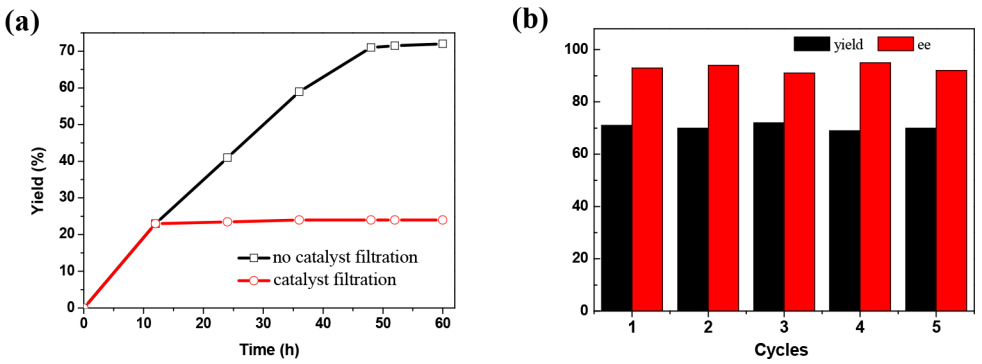
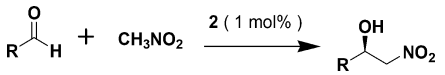


Figure 3. (a) Reaction time examination (black line) and leaching test (red line) and (b) catalytic cycles for asymmetric Henry reaction of benzaldehyde and nitromethane catalyzed by **2** (1 mol %). Reaction conditions: benzaldehyde (2 mmol), nitromethane (20 mmol), DIPEA (1 mmol) in 2 mL of MeOH at 45 °C.

phase during the reaction. With this in mind, we conducted the leaching tests to determine whether Cu^{2+} ion in **2** could leach into the liquid phase during the course of the reaction. To be specific, the liquid phase of the reaction mixture was divided into two parts after 12 h, in which one fraction had the MOF catalyst while the other one was without the MOF catalyst that was removed by centrifugation. After an additional 36 h, it was found that the yield of the reaction system without catalyst still remained at about 23%, almost unchanged, whereas the yield of the other was up to 71% (Figure 3a). These results revealed that the reaction did not proceed further without catalyst, which ruled out the existence of active catalytic species in solution. The saturation of the yield around 50 h of reaction may be due to the inactivation of this MOF catalyst as its channels are occupied by some small molecules (solvent, substrate, and product) after a long time of reaction. A control experiment that an extra fresh catalyst was added to the above reaction system showed the yield can increase to 80% after 6 h. Furthermore, ICP-AMS analysis of the filtered reaction demonstrated that there was no obvious metal ion leakage into the catalytic system (ca. 0.00017% for Cu^{2+} and ca. 0.0013% for Cd^{2+}). Therefore, all the above results undoubtedly indicate the heterogeneous behavior of **2** as a catalyst for the symmetric Henry reaction. In addition, the recyclability of **2** was also examined. Pleasingly, recycled **2** could be reused up to 5 times without any discernible reduction in its catalytic activity and enantioselectivity (Figure 3b). The PXRD pattern of recovered **2** showed that the structural integrity of the MOF remained almost unchanged after the catalytic reaction (Figure 2a). Besides, N_2 and CO_2 adsorption curves matched well with the as-synthesized **2** and **1** (Figure 2c,d), which strongly supported the stability of the MOF structure, despite the presence of organic base DIPEA in this catalytic reaction process.

With the optimal reaction conditions in hand, we next turned our attention to examine the applicability of this catalytic reaction by employing **2** as catalyst, and the results are presented in Table 2. To our delight, aromatic, heteroaromatic, and aliphatic aldehydes underwent smooth transformation to generate the desired *β*-nitroalcohols in high yields and excellent enantioselectivities, and in all the cases, *β*-nitroalcohols (R) were obtained using (*R*)-**2** catalyst. It was found that the reaction displayed good tolerance toward a wide range of functional groups, involving different electron-donating groups (OMe and Me) and electron-withdrawing substituents (Br and NO_2). Comparing the results obtained, it is clear that

Table 2. Asymmetric Henry Reaction Catalyzed by 2[a]



entry	R	yield[b] (%)	ee[c] (%)	TON[d]
1	Ph	71	95	135
2	2-$MeOC_6H_4$	88	98	172
3	3-$MeOC_6H_4$	84	92	155
4	4-$MeOC_6H_4$	78	91	142
5	2-MeC_6H_4	83	93	154
6	2-BrC_6H_4	75	93	140
7	2-$NO_2C_6H_4$	73	91	133
8	4-$NO_2C_6H_4$	61	67	82
9	*n*Bu	98	91	198
10	cyclohexyl	84	92	155
11	2-fural	86	93	160
12	2-pyridyl	98	93	182
13	1-naphthyl	31	81	50
14	9-anthracyl	11	45	10
15	1-pyrenyl	trace		

[a]Reaction conditions: aldehyde (2 mmol), DIPEA (1 mmol), and nitromethane (20 mmol) in 2 mL of MeOH at 45 °C for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]The number of moles of *β*-nitroalkanol per mole of the catalyst.

electron-donating aromatic aldehydes gave higher yield than electron-withdrawing ones, and the closer the substituents to the formyl group on aldehydes, the higher the yield and enantioselectivity. It is worthy of note that very high yield and enantioselectivity were achieved when aliphatic aldehydes were used, such as butyraldehyde and cyclohexanecarboxaldehyde. Heteroaromatic aldehydes, especially pyridine-2-carboxaldehyde, usually gave very low enantioselectivity in a homogeneous Cu-catalyzed system,[3c,22] possibly because the presence of the coordinating nitrogen of pyridine-2-carboxaldehyde changed the transition state responsible for product formation. However, in our catalytic system, excellent enantioselectivity was realized when pyridine-2-carboxaldehyde was employed, further evidencing the superiority of the MOF catalyst (Table 2, entry 12). Under identical conditions, a homogeneous control experiment was also carried out using the Cu(H_4salen) ligand as catalyst for this substrate, and only about 10% ee value was obtained.

Besides, the reaction was sensitive to steric factor. 1-Naphthaldehyde (10.2 × 8.4 $Å^2$) and 9-anthraldehyde (11.8 × 9.0 $Å^2$) with bulky molecular size (Table S2) showed very low

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Table 3. Comparison of Activities and Enantioselectivities of MOFs (or COFs) as Catalyst for the Asymmetric Henry Reaction with Aromatic Aldehyde and Nitromethane

entry	catalyst	solvent/additive/temp/time	aldehyde	yield (%)	ee (%)	ref
1	**2**	MeOH/DIPEA/45 °C/48 h	benzaldehyde	71	95	this work
2	**2**	MeOH/DIPEA/45 °C/48 h	4-nitrobenzaldehyde	61	67	this work
3	CPs S-3b	DCM-THF/NaOAc/25 °C/24 h	benzaldehyde	85	70	15i
4	[Cu(cpna)(phen)]	CH_3NO_2/30 °C/48 h	4-nitrobenzaldehyde	55	47	15g
5	[Cu(Tzmp)]	EtOH/−25 °C/24 h	4-nitrobenzaldehyde	96	69	15e
6	Pd@CCOF-MPC	EtOH/K_2CO_3/25 °C/8 h	benzaldehyde	97	95	23
7	CCOF-TpTab-Cu	mesitylene/DIEA/−10 °C/2 d	4-bromobenzaldehyde	85	35	24

reactivity, which afforded the corresponding products with 31% and 11% yield, while with good ee values of 81% and 45%, respectively. The sterically more hindered 1-pyrenecarboxaldehyde (12.5 × 9.6 Å^2) gave trace yield (Table 2, entry 15), very likely because the bulky substrate cannot access into the catalytic sites in the channel (8.0 × 9.0 Å^2). On the contrary, the homogeneous catalyst Cu(H_4salen) ligand still afforded the desired product with 35% yield. These results indicated the size selectivity of **2** and the catalytic reaction occurred inside the 1D channel.

The efficiency of **2** in comparison with various MOFs and covalent organic frameworks (COFs) that have been used as catalysts in the asymmetric Henry reaction with aldehydes and nitromethane is shown in Table 3. Although our catalyst shows relatively lower activity, it has the highest enantioselectivity in MOF-based catalysts to date, and the enantioselectivity can compare with that of chiral COF-supported palladium nanoparticles reported recently.[23] Thus, **2** can be a valuable complement for MOF-based asymmetric catalysts for the Henry reaction.

On the basis of our experimental results and the reported works previously,[15b,f,25] a plausible mechanism for the Henry reaction catalyzed by **2** involves the activation of aldehydes trapped in the 1D channel by the Cu^{2+} ions from salen cores, and the deprotonation of nitromethane to form the corresponding nitronate by DIPEA. The nitronate ion enters into the MOF channel and then nucleophilically attacks the activated aldehyde carbonyl group with the help of the polar and protic characters of solvent (CH_3OH), leading to β-nitroalkanols. Besides, the generated amino groups in **2** through PSM reduction might also facilitate the abstraction of a proton from nitroalkane to produce a nitronate ion. Compared to unreduced catalyst **1**, **2** exhibits enhanced enantioselectivity, likely attributing to the more labile chiral diphenyl groups around the catalytic copper center, which offer a more energetically favorable transition state where the chiral induction groups remain in close proximity to the electrophile during the enantioselectivity-determining step of the catalytic cycle. Moreover, pyridine-2-carboxaldehyde as substrate is able to perform Henry reaction smoothly with excellent enantioselectivity, partly because, in the MOF channel, the pyridine nitrogen atom cannot disturb the activation ability of Cu^{2+} to aldehydes due to the steric hindrance of the 1D channel. Meanwhile, the synergistic induction in the 1D channel of **2** is beneficial to the enhancement of enantioselectivity. In the homogeneous case, the pyridine nitrogen of pyridine-2-carboxaldehyde might alter the transition state responsible for product formation through the possibly preemptive coordination to Cu^{2+}, hence resulting in lower activity and enantioselectivity.

CONCLUSIONS

In summary, we have reported the synthesis and structural characterization of a chiral 3D porous Cu(salen)-based MOF, and its isostructural sample obtained by $NaBH_4$ reduction. The postsynthetic reduction from imino to amino group on salen cores of this MOF can provide a more flexible chiral group and more alkaline backbone, which resulted in significantly enhanced activity for asymmetric Henry reaction with excellent enantioselectivity. The enantioselectivity of this MOF is higher than that of the corresponding homogeneous counterpart, demonstrating the combination of the chiral framework confinement and synergistic effects in MOFs catalyst. Remarkably, this catalyst achieved very high enantioselectivity for the substrate with a coordination atom (pyridine-2-carboxaldehyde), while the homogeneous catalyst does not, further elucidating the unique advantage of MOF catalysts. The retention of MOFs structure and the absence of catalytic centers leakage during the reaction procedure evidence the heterogeneity of this catalyst. Furthermore, this MOF can be easily separated and reused for five successive runs without obvious loss of activity. The present work highlights that structurally PSM for MOF catalysts can enhance the catalytic activity and enantioselectivity for organic transformations, and even endows the specific activity compared to the homogeneous counterpart.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01551.

Crystallographic data of **1**; TG curves, ^{1}H NMR, and ^{13}C NMR of H_6salen; IR spectra, ICP-AMS, and BET area of **1** and **2**; XPS of **2**; chiral HPLC spectra of β-nitroalcohols; calculated molecular size of aldehydes (PDF)

Accession Codes

CCDC 1814252 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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