JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 08 Jun 2017

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Chiral Covalent Organic Frameworks with High Chemical Stability for Heterogeneous Asymmetric Catalysis

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Supporting Information

ABSTRACT: Covalent organic frameworks (COFs) featuring chirality, stability and function are of both fundamental and practical interest, but are yet challenging to achieve. Here we reported the metal-directed synthesis of two chiral COFs (CCOFs) by imine-condensations of enantiopure 1,2-diaminocyclohexane with C_3-symmetric tri-salicylaldehydes having one or zero 3-*tert*-butyl group. Powder X-ray diffraction and modeling studies, together with pore size distribution analysis demonstrate that the Zn(salen)-based CCOFs possess a two-dimensional hexagonal grid network with AA stacking. Dramatic enhancement in the chemical stability toward acidic (1 M HCl) and basic (9 M NaOH) conditions was observed for the COF incorporated with *tert*-butyl groups on the pore walls compared to the non-alkylated analog. The Zn(salen) modules in the CCOFs allow for installing multivariate metals into the frameworks by post-synthetic metal exchange. The exchanged CCOFs maintain high crystallinity and porosity and can serve as efficient and recyclable heterogeneous catalysts for asymmetric cyanation of aldehydes, Diels-Alder reaction, alkene epoxidation, epoxide ring-opening and related sequential reactions with up to 97% ee.

INTRODUCTION

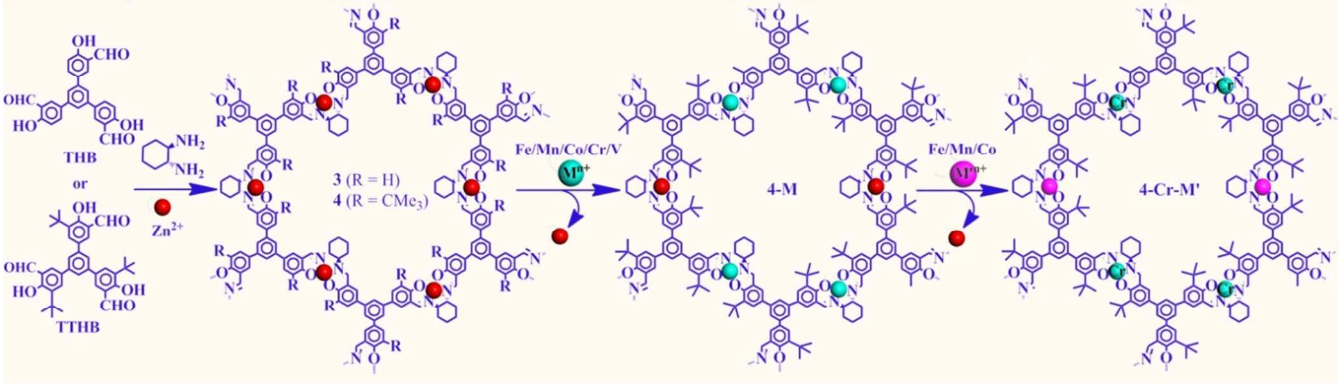
Covalent–organic frameworks (COFs), covalently formed from organic building units,[1-3] are a structurally and compositionally varied class of crystalline porous materials of which the host–guest behavior has been explored for diverse applications that include gas storage,[4] separations,[5] catalysis,[6,7] sensors,[8] optoelectronics[9] and energy storage.[10] In particular, COFs hold great potential as heterogeneous catalysts because of the large channels that make the catalytic sites readily accessible to substrates, and the capability of precisely controlling the environment around these sites. Although many COFs have been examined as solid catalysts,[6,7] examples of stereoselective COF catalysts are very scarce.[7] In fact, it is still challenging to construct chiral COFs (CCOFs) because of the discrepancy between asymmetry and crystallinity. Another challenge facing COFs is their generally low stability under harsh conditions, thus limiting their use in practical processes.[7c,11] In this work, we demonstrated how to address such issue by using chiral metallosalen catalysts with bulky hydrophobic groups as building blocks for CCOF construction.

Chiral salen ligands such as (*R*,*R*)-1,2-cyclohexanediamino-*N*,*N*′-bis(3-*tert*-butyl-salicylidene) are well-known privileged ligands for asymmetric catalysis.[12] Some examples of salen-based asymmetric catalysis include epoxidation of olefins catalyzed by Mn(salen) and Fe(salen) complexes,[13a,13b] ring-opening of epoxides catalyzed by Co(salen) and Cr(salen) complexes,[13c,13d] and cyanation of aldehydes by VO(salen) complexes.[13e] To allow their recyclable uses, M(salen) catalysts have been immobilized on diverse porous solid supports such as silica and metal-organic frameworks (MOFs).[14,15] Very recently, one report has used salen-type linkers to build achiral COFs.[16] Nonetheless, the synthesis of CCOFs from M(salen) complexes has not yet been explored. Here we report the synthesis of two Zn(salen)-based 2D CCOFs by co-condensation of chiral 1,2-diaminocyclohexane and tri-salicylaldehydes. By introducing bulky hydrophobic groups into the pore walls to protect hydrolytically susceptible backbones through kinetic blocking, drastic boost of chemical stability for the CCOF in acidic and alkaline solutions has been achieved. After exchanging Zn^{2+} ions for other metal ions, the CCOFs are shown to be efficient and recyclable heterogeneous catalysts for the archetypical M(salen)-catalyzed asymmetric reactions and related sequential reactions, with stereoselectivities comparable to the homogeneous analogs.

RESULTS AND DISCUSSION

Synthesis and characterization. CCOFs **3** and **4** were synthesized by solvothermal reactions of THB or TTHB (0.067 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.15 mmol) and chiral 1,2-diaminocyclohexane (0.1 mmol) in 1.5 mL of mesitylene/EtOH (1:1 v/v) or DMF/EtOH (2:1 v/v) at 120 °C for three days, which afforded yellow crystalline solids in ~70% yields (Scheme 1). Both CCOFs are stable in common organic solvents. In the FT-IR spectra of **3** and **4**, the characteristic C=O stretching bands (1658 and 1648 cm^{-1}, respectively) disappeared, indicative of the consumption of the aldehydes (Figure S1). Strong stretching vibration bands attributed to the new generation of C=N linkages were observed at 1624 and 1612 cm^{-1}, respectively. In the ^{13}C CP-MAS NMR spectra of **3** and **4,** the characteristic signals due to C=N bonds were observed at 167 and 170 ppm, respectively (Figure S2). The aldehyde carbon peaks were no longer present. The chemical shifts of other fragments are consistent with those of the monomers. Circular dichroism (CD) spectra of **3** and **4** made from the opposite enantiomers of 1, 2-diaminocyclohexane were mirror images of each other, suggesting their enantiomeric nature (Figure S3). The CD spectra were consistent with their corresponding UV-vis spectra (Figure S4). Thermal gravimetric analysis (TGA) showed that both CCOFs were stable up to around 350 °C (Figure S5).

Scheme 1. Synthesis of the CCOFs



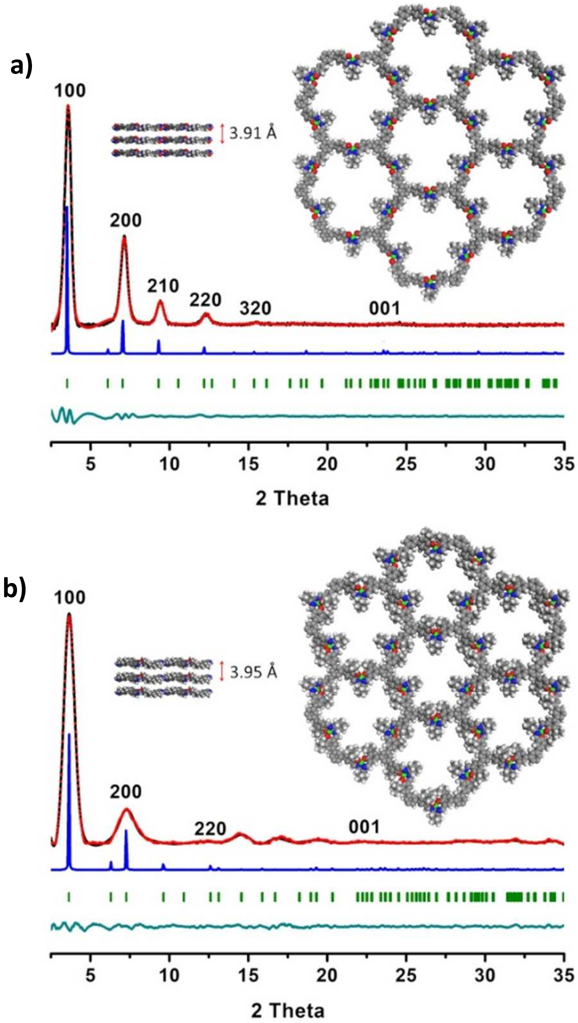


Figure 1. PXRD patterns of CCOFs **3** (a) and **4** (b) with the experimental profiles in black, Pawley-refined profiles in red, calculated profiles in blue, and the differences between the experimental and refined PXRD patterns in dark cyan (Insert: Views of space-filling models along the c-axis with the layer distances).

The crystalline structures of the CCOFs were determined by powder X-ray diffraction (PXRD) analysis with Cu Kα radiation (Figure 2). Two types of possible 2D structures were generated for them, that is, eclipsed stacking (AA) and staggered stacking (AB). After a geometrical energy minimization based on the AA stacking mode for CCOFs **3** and **4**, the unit cell parameters were obtained (a = b = 27.47 Å, c = 3.97 Å, $\alpha = \beta = 90°$, $\gamma = 120°$ for **3**; a = b = 27.21 Å, c = 4.05 Å, $\alpha = \beta = 90°$, $\gamma = 120°$ for **4**). CCOF **3** exhibited strong PXRD peaks at at 3.51°, 7.02°, 9.29°, 12.18°, 15.34° and 22.72°, which were assigned to the (100), (200), (210), (220), (320) and (001) facets of *P*321 space group, respectively (Figure 1a, black curve). This PXRD pattern agreed well with the simulated pattern generated from the AA stacking of the 2D layers. Lattice modeling and Pawley refinement (Materials Studio, version 7.0) gave optimized parameters of a = b = 29.05 Å, c = 3.91 Å, $\alpha = \beta = 90°$, $\gamma = 120°$) for the unit cell with space group *P*321, which provided good agreement factors (R_p = 2.96% and R_{wp} = 3.75%).

CCOF **4** (Figure 1b, black curve) gave strong PXRD peaks at 3.63°, 7.26°, 9.61°, 14.55°, and 22.48°, corresponding to the (100), (200), (210), (400) and (001) facets of space group *P*321, respectively (Figure 1b, black curve). This experimental pattern matched well with the simulated pattern based on the AA stacking structure. The refinement results yielded unit cell parameters nearly equivalent to the predictions (a = b = 28.09 Å, c = 3.95 Å, $\alpha = \beta = 90°$, $\gamma = 120°$ for the unit cell with the space group of *P*321) with acceptably low residuals (R_p = 3.14% and R_{wp} = 4.12%). PXRD patterns were also calculated for the two CCOFs on the other structures, but the calculated patterns did not match the experimental patterns well (Figure S12). In the PXRD patterns, peaks at 22.72° for **3** and 22.48° for **4** correlating to the values of the interlayer distances were observed; the d spacing for them was calculated to be 3.91 Å and 3.95 Å, respectively.

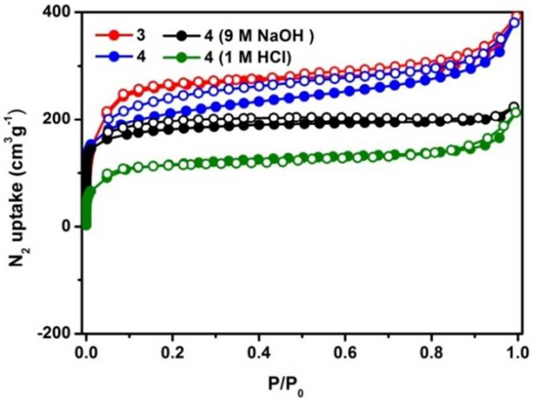


Figure 2. N_2 adsorption-desorption isotherms (77 K) and pore size distribution profiles (insert) of CCOFs **3** (red) and **4** (blue), as well as **4** after 7 days treatment in 1 M HCl (green) and 9 M NaOH (black).

The porosity of the CCOFs was examined by measuring N_2 sorption isotherms at 77 K on the activated samples. The adsorption curves of the CCOFs exhibited the type-I isotherm (Figure 2), a characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface areas of **3** and **4** were estimated to be 826 and 683 m^2g^{-1}, respectively. Their total pore volumes were calculated to be 0.61 and 0.45 cm^3g^{-1} at P/P_0 = 0.99, respectively. The nonlocal density functional theory (NLDFT) gave rise to a narrow pore size distribution with an average pore width 1.84 nm for **3**, and 1.65 nm for **4**, in good agreement with the related simulated values (2.0 nm and 1.6 nm, respectively).

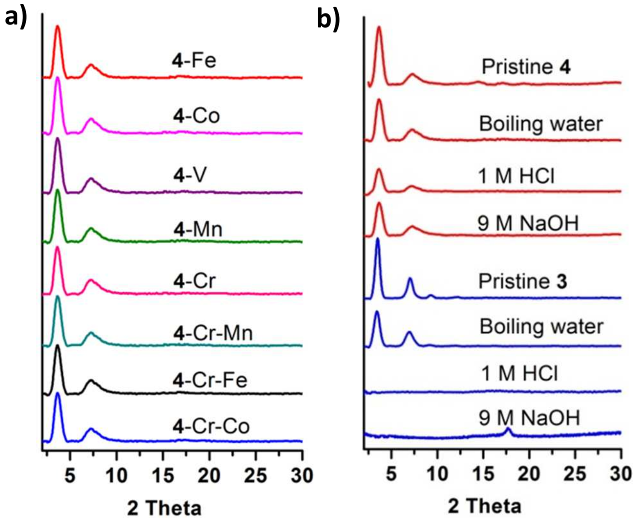


Figure 3. (a) PXRD patterns of CCOFs **3** and **4** after 7 days treatment in boiling water, 1M HCl (aq.) and 9 M NaOH (aq.). (b) PXRD patterns of **4** after post-synthetic metal exchange.

The chemical stability of the materials was examined by PXRD and N_2 sorption after 7 days treatment in boiling water, 1 M HCl (aq) and 9 M NaOH (aq) (Figure 3a). Both CCOFs are stable in boiling water, but CCOF **3** gave a decreased crystallinity. The difference between the stabilities of **3** and **4** is most striking under acidic and alkaline conditions. At 1 M HCl (aq) and 9 M NaOH, the alkyated CCOF **4** retained good crystallinity whereas the nonalkylated CCOF **3** was nearly or completely dissolved and the remaining material was rendered amorphous. The as-treated samples of **4** have a BET surface area of 373 and 569 m^2g^{-1}, respectively (Figure 2). A small decrease in signal-to-noise ratio and an obvious decrease in the surface area of **4** (683 m^2g^{-1}) indicate just partial structural collapse upon treatment. It is worth noting that **3** can retained its crystalline structure after 7 days treatment in 3 M NaOH, as indicated by PXRD (Figure S10). In **4**, the bulky *tert*-butyl groups were positioned near phenoxo oxygens that can protect hydrolytically susceptible Zn(salen) cores through kinetic blocking, which led to high chemical stability.[17]

The relative liability of Zn-O/N bonds and the readily accessible channels of **4** prompted us to explore the metal-exchange capacity of the framework. Indeed, when crystals of **4** were immersed in saturated solutions containing M^{n+} salts (M^{n+} = Cr^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, V^{4+}) at r.t. for 1-2 days with refreshment of the solutions three times, they were transformed into new CCOFs **4-M**. While **4-Cr-M′** were obtained through a dual strategy, involving sequential exchanges of Zn^{2+} ions in **4** with Cr^{2+} ions and **M′**$^{2+}$ ions (**M′** = Mn, Fe and Co) in solutions. The ion exchanges were clearly indicated by dramatic changes in the color of the crystals that were consistent with the colors reported for the molecular metallosalen analogs. ICP-OES (inductively coupled plasma optical emission spectrometry) indicated molar *ratios* of Zn/M ranging from *1:*12 to 1:54 (Zn/Mn = 1:17, Zn/Fe = 1:29, Zn/V = 1:12, Zn/Cr = 1:54 and Zn/Co = 1:15) and Zn/Cr/M′ ranging from 1:16:10 *to 1*:46:45 (Zn/Cr/Mn = 1:16:10, Zn/Cr/Fe = 1:46:45, and Zn/Cr/Co = 1:36:20). X-ray photoelectron spectroscopy (XPS) spectra suggested Fe, Cr, Mn and Co in the +3 oxidation state and V in the +4 oxidation state (Figures S9). In the bimetallic substituted samples, the reason for the third metal ions did not substitute Cr^{3+} ions can be ascribed to the kinetic inertness of their coordination bonds. Scanning electron microscope-energy-dispersive X-ray spectra (SEM-EDS) analysis demonstrated the homogeneous distribution of metal ions in the crystal structures (Figures S6 and S7). PXRD showed that the exchanged CCOFs **4-M** and **4-Cr-M′** retained high crystallinity and the original crystal structure (Figure 3b). The porosity (BET surface area = 547-628 m^2g^{-1}) of them is close to that of CCOF **4** (Figure S11).

Heterogeneous Asymmetric catalysis. **4-M** demonstrated excellent activity and selectivity for several catalytic reactions. We first studied the catalytic activity of **4-V.** After oxidation of V(IV) to V(V) with *m*-CPBA, 5 mol% loading of **4-V** catalyzed cyanation of aldehydes with TMSCN in the presence of Ph_3PO in THF at 0 °C, which gave 89-94% ee of cyanohydrin silyl ethers (Figure 4a), which are versatile synthetic intermediates for pharmaceuticals.[18a] **4-Co** can catalyze asymmetric Diels-Alder (DA) reaction of 1-aminosubstituted butadienes and *α*-substituted acroleins, which provides one of the m*ost powe*rful methods for the preparation of cyclic molecules.[18b] The DA reactions was performed in $CHCl_3$ at r.t in the presence of $AgNO_3$, 4 Å molecular sieves and 5.0 mol% **4-Co**, providing the cycloadducts with 86-96% ee (Figure 4b). Both **4-Mn** and **4-Fe** are active in the synthetically important reactions of epoxidation of alkenes. At 1.0 mol% loading, **4-Mn** catalyzed oxidation of 2,2-dimethyl-2*H*-chromene and its substrates with 2-(tertbutylsulfonyl)iodosylbenzene (*s*PhIO) as oxidant in $CHCl_3$ at 0 °C, affording 77-97% ee of the targeted epoxides (Figure 4c). However, when the NaClO was used as oxidant, no product were detected. (Table S6). In the presence of iodosylbenzene (PhIO), **4-Fe** promoted the above oxidation reactions to yield the products with up to 92% ee. **4-Cr** could serve as a catalyst for the aminolysis of *trans*-stilbene oxide with different anilines, which constitutes a useful method to synthesize biologically important enantioenriched anti-*β*-amino alcohols.[18c] 5 mol% loading of **4-Cr** promoted the aminolysis reactions in $CHCl_3$ at r.t, affording 82-96% ee of the amino alcohols (Figure 4d).

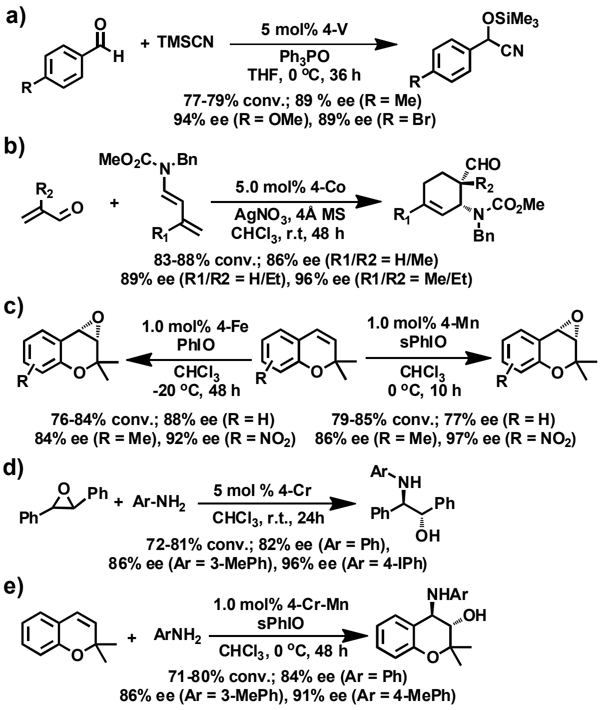


Figure 4. Asymmetric reactions catalyzed by the CCOFs.

Given that that **4-Mn** can promote epoxidation of alkenes and **4-Cr** promote ring opening of epoxides, we studied the catalytic performance of **4-Cr-Mn** bearing two different active metal centers in the sequential reactions initiated by epoxidation of alkene followed by ring opening *of epoxide* to afford the amino alcohol. In the presence of 1.0 mol% **4-Cr-Mn**, epoxidation of 2, 2-dimethyl benzopyran with PhIO as oxidant and subsequent ring-opening reactions with different anilines were performed in $CHCl_3$ at r.t.. The reactions proceeded smoothly to give the amino alcohols with up to 91% ee (Figure 4e). COF-mediated sequential reactions should prove highly valuable for the synthesis of complex molecules with excellent stereo-controls.

The present CCOF catalysts displayed enantioselectivities comparable to those of the corresponding homogeneous controls and other M(salen)-based hybrid solid catalysts for the examined reactions and substrates (Tables S11-14).[14,15] All CCOF catalysts can be readily recycled and reused for at least five times without obvious loss of activity and enantioselectivity (Tables S15-S19). For instance, the conversions/ee's for **4-V**-catalyzed cynation of 4-methoxybenzaldehyde are 77/94%, 77/94%, 76/93%, 76/93% and 75/92% for 1-5 runs, respectively. ICP-OES analysis of the filtrate after the reaction revealed almost no leaching of Zn and V ions. PXRD showed that the recovered solid after five recycles remained crystalline and structurally intact (Figure S13)

CONCLUSIONS

We have synthesized two isostructral 2D metallosalen-based CCOFs and demonstrated that the chemical stability of the framework can be improved by incorporating bulky alkyl groups. The structure assignment is supported by PXRD analysis, modeling studies, and the pore size distribution experimental data. The framework constituting Zn(II) ions can undergo exchange with a variety of metal ions in solutions without alternation of structural integrity and loss in crystallinity. The exchanged materials can serve as efficient and recyclable heterogeneous catalysts for several asymmetric transformations. This work provides a new approach to achieve high chemical stability, catalytic activity and enantioselectivity in COFs and will promote the design of CCOFs from privileged chiral ligands/catalysts that will display interesting chirality properties.

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.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation of China (Grants 21371119, 21431004, 21401128, 21522104 and 21620102001), the National Key Basic Research Program of China (Grants 2014CB932102 and 2016YFA 0203400), and the Shanghai "Eastern Scholar" Program.

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