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COMMUNICATION

Chiral metal–organic frameworks with tunable open channels as single-site asymmetric cyclopropanation catalysts†‡

Joseph M. Falkowski, Sophie Liu, Cheng Wang and Wenbin Lin*

Received 5th January 2012, Accepted 8th May 2012
DOI: 10.1039/c2cc32232c

A pair of interpenetrated and non-interpenetrated chiral metal–organic frameworks with the same catalytic sites but different open channel sizes catalysed asymmetric cyclopropanation of substituted terminal alkenes with excellent diastereoselectivities (up to 9.6) and enantioselectivities (up to >99%).

Metal–organic frameworks (MOFs) represent an interesting class of hybrid materials composed of organic bridging ligands and metal ion or metal cluster connecting points.[1] In the past 15 years, MOFs have been explored for a wide range of applications, including nonlinear optics,[2] gas storage,[3] chemical separations,[4] molecular sensing,[5] and drug delivery.[6] Since MOFs are typically constructed from molecular building blocks under mild conditions, they provide a great opportunity to immobilize homogeneous catalysts[7] in a modular and tunable fashion leading to truly single-site solid catalysts, which offer several advantages over their solution counterparts, including recyclability and reusability as well as facile removal of the toxic catalyst components from the organic products. Additionally, the highly ordered nature of MOFs allows for the precise characterization of their catalytic sites through X-ray diffraction studies, which is not possible in other heterogenized catalysts.[8] The detailed structural characterization of MOF catalytic sites can in turn allow for the elucidation of the structure–function relationships in this unique class of single-site solid catalysts.

Although many MOFs have been examined as potential heterogeneous catalysts,[7,9] examples of stereoselective MOF catalysts are still scarce.[10] Highly efficient asymmetric MOF catalysts have been generated either *via* a post-synthesis modification strategy[11] or by direct incorporation of catalytically competent bridging ligands into MOFs.[12] In this work, we report the synthesis of a pair of interpenetrated and non-interpenetrated chiral MOFs with the same catalytic sites but different open channel sizes by direct incorporation of an elongated dicarboxylate ligand, [Ru(**L**)(Py)$_2$]Cl [**L** is deprotonated (*R*,*R*)-(−)-*N*,*N*′-bis(3-acrylate-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, Fig. 1a], into the Zn-carboxylate MOF of the primitive cubic unit (pcu) topology. The different open channel sizes of this pair of chiral MOFs exert a significant influence on the conversions and stereoselectivities of asymmetric cyclopropanation reactions.

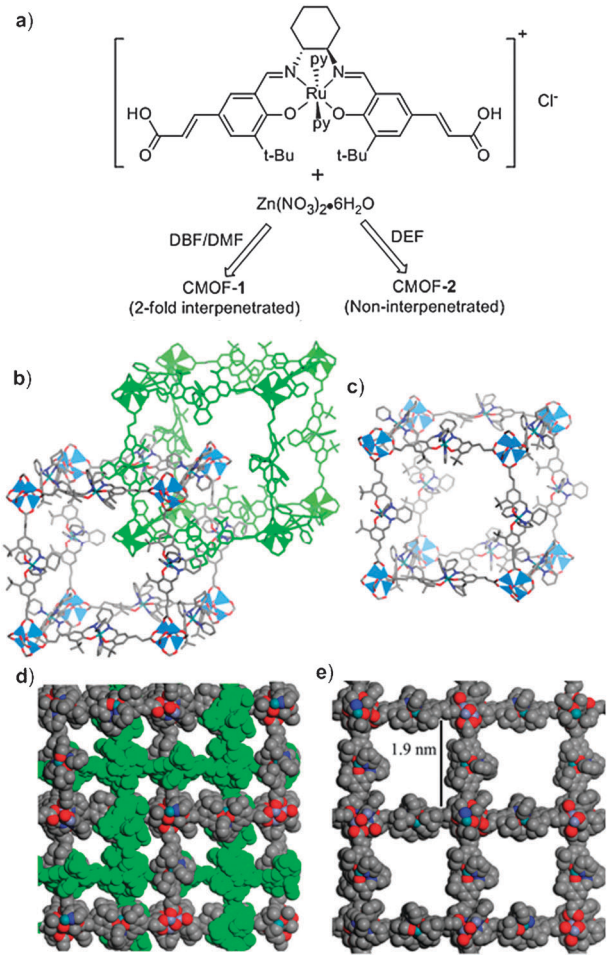


Fig. 1 (a) Synthesis of CMOF-**1** and **2** from the [Ru(**L**-Me$_2$)(Py)$_2$]Cl ligand. Stick and polyhedron structure model of 2-fold interpenetrated **1** (b) and non-interpenetrated **2** (c): blue tetrahedron = ZnO_4, grey node = C, red node = O, blue node = N, dark green node = Ru, green network = the second set of the network. Space-filling model of **1** (d) and **2** (e) as viewed along the [10−2] direction.

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, NC 27599, USA. E-mail: wlin@unc.edu; Web: http://www.chem.unc.edu/people/faculty/linw/wlindex.html

† This article is part of the *ChemComm* 'Chirality' web themed issue.

‡ Electronic supplementary information (ESI) available: Experimental details and characterization data including TGA, NMR, GC, PXRD, and X-ray structures. CCDC 860688. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc32232c

The enantiopure Ru^{II} complex $Ru(\mathbf{L}\text{-}Me_2)(Py)_2$ was synthesized by a metathesis reaction between the potassium salt of $\mathbf{L}\text{-}Me_2$ and $[RuCl_2(p\text{-cymene})]_2$, which was hydrolyzed by saponification followed by acidification with dilute hydrochloric acid. The resulting mixture was further oxidized with nitric acid in air followed by ion exchange with chloride to afford the pure Ru^{III}-Salen derived dicarboxylic acid, $[Ru(\mathbf{L}\text{-}H_2)(Py)_2]Cl$. The diamagnetic complex $[Ru(\mathbf{L}\text{-}Me_2)(Py)_2]$ was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy whereas the paramagnetic $[Ru(\mathbf{L}\text{-}H_2)(Py)_2]Cl$ was characterized by electrospray ionization-mass spectrometry.

Solvothermal reactions of $Zn(NO_3)_2{\cdot}6H_2O$ with $[Ru(\mathbf{L}\text{-}H_2)(Py)_2]Cl$ in *N*,*N*-dibutylformamide (DBF)/dimethylformamide (DMF) or diethylformamide (DEF) with added ethanol resulted in single crystals of $[Zn_4(\mu_4\text{-}O)\{[Ru\mathbf{L}(Py)_2]Cl\}_3]_2{\cdot}10DBF{\cdot}7DMF$ (CMOF-**1**) and $[Zn_4(\mu_4\text{-}O)\{[Ru\mathbf{L}(Py)_2]Cl\}_3]{\cdot}51DEF$ (CMOF-**2**), respectively.§ Both **1** and **2** were constructed from the octahedral $Zn_4(\mu_4\text{-}O)(carboxylate)_6$ secondary building blocks (SBUs), which are interconnected by the linear dicarboxylate ligand $[Ru\mathbf{L}(Py)_2]Cl$ to give 3D frameworks of the pcu topology. **1** and **2** adopt two-fold interpenetrated and non-interpenetrated structures, respectively (Fig. 1b and c), presumably as a result of the different solubility of $\mathbf{L}\text{-}H_2$ in different formamides. **1** crystallizes in the *R*32 space group, with the asymmetric unit containing two $[Ru\mathbf{L}(Py)_2]Cl$ ligands and two-thirds of the $Zn_4(\mu_4\text{-}O)$ cluster. The two sets of interpenetrated nets in **1** are related to each other by a two-fold axis. CMOF-**1** possesses 3-D inter-connected zigzag channels (Fig. 1d), with the largest channel dimensions of $0.7 \times 0.7\ nm^2$ and a PLATON-calculated void space of 74.0%.

Although large crystals of **2** could be synthesized, their crystallinity is quite poor. Repeated attempts led to one single-crystal diffraction dataset of 2.1 Å resolution. **2** has the same asymmetric unit as **1** but crystallizes in the *R*3 space group. The absence of the 2-fold axis in the *R*3 space group (as compared to the *R*32 space group for **1**) leads to the non-interpenetrated structure for **2** (ESI‡). Based on the structural model, **2** possesses 3-D inter-connected channels of $1.9 \times 1.9\ nm^2$ dimensions (Fig. 1e) with an 87.5% void space as calculated by PLATON.

The catenation assignments of **1** and **2** were supported by several additional evidences. First, the powder X-ray diffraction (PXRD) pattern of **2** is very similar to that of a 2-fold interpenetrated CMOF based on the $[Mn\mathbf{L}(OAc)]$ bridging ligands and $Zn_4(\mu_4\text{-}O)(carboxylate)_6$ SBUs (ESI‡),[12b] indicating their isostructural nature. Although **1** and **2** have the same systematic absence, the relative peak intensities are quite different, consistent with their different structures (Fig. 2c). Second, **1** and **2** exhibit very different solvent weight loss in the 25 to 250 °C temperature range of 45% and 75%, respectively (Fig. 2a). Third, **1** and **2** exhibit very different Brilliant Blue R-250 (BBR-250) dye uptake of 14% and 39%, respectively (Fig. 2b).

N_2 adsorption studies do not necessarily provide meaningful information on the porosity of CMOFs with large open channels, presumably due to framework distortion upon removal of the solvent molecules. Instead, the uptake of bulky dye molecules by MOFs has recently been used by us to qualitatively assess their substrate-accessible pore volumes.[14] Both **1** and **2** allow the inclusion of BBR-250, indicating the presence of large open channels in them, but the non-interpenetrated **2** (39 wt%) had much higher BBR-250 uptake capacity than the 2-fold interpenetrated **1** (14 wt%).

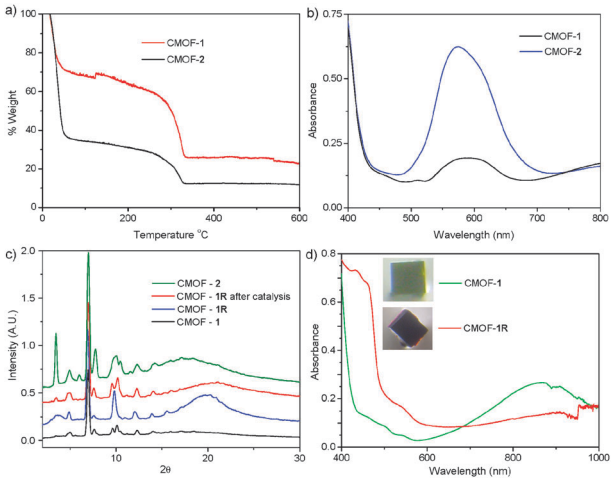
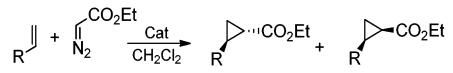


Fig. 2 (a) TGA traces for **1** and **2**. The solvent weight loss for **1** and **2** is 45 and 75%, respectively. **1** and **2** were soaked in DMF prior to TGA analyses. (b) UV-Vis spectra of BBR-250 released from **1** and **2**. (c) PXRD patterns of **1**, **1R**, **1R** after catalysis, and **2**. (d) Vis-NIR spectra of the oxidized (**1**) and reduced (**1R**) forms of CMOF-**1** after dissolution in MeOH/Na_2EDTA.

The new pair of CMOFs was screened for their catalytic activities in the asymmetric cyclopropanation of substituted olefins. Like the previously reported Ru-salen derived CMOFs,[13] **1** and **2**, in their Ru^{III} oxidation states, are not active catalysts for the cyclopropanation reactions (Table 1, entry 3). However, **1** and **2** can be readily reduced to their Ru^{II} counterparts **1R** and **2R**, respectively, upon treatment with $LiBEt_3H$ or $NaB(OMe)_3H$, leading to active catalysts for asymmetric cyclopropanation of substituted olefins. The reduction of **1** and **2** to afford **1R** and **2R** was indicated by their colour change from dark green to dark red. The characteristic Ru^{III}-salen LMCT bands at 867 nm disappeared in the solution Vis-NIR spectra of **1R** and **2R** upon dissolution in MeOH/Na_2EDTA (Fig. 2d). This result was further

Table 1 Cyclopropanation of terminal olefins catalysed by **1R** and **2R**[a]



Entry	Cat	R	Yield (%)	*trans* ee (%)	*cis* ee (%)	dr
1	**1R**	Ph	39	93	80	7.1
2	**2R**	Ph	55	94	92	9.6
3	**2**	Ph	<2	0	35	2.3
4	$Ru(\mathbf{L}\text{-}Me_2)(py)_2$	Ph	56	92	93	11.7
5	**1R**	OEt	22	79	95	2.6
6	**2R**	OEt	22	76	>99	2.6
7	$Ru(\mathbf{L}\text{-}Me_2)(py)_2$	OEt	18	80	89	20
8	**1R**	$CH_3(CH)_2$	11	40	49	1.7
9	**2R**	$CH_3(CH)_2$	19	19	21	1.8
10	$Ru(\mathbf{L}\text{-}Me_2)(py)_2$	$CH_3(CH)_2$	8	80	85	1.5

[a] Reactions were carried out at room temperature with 2 mol% catalyst loading (based on **L**) and 15 equiv. of olefin. The yields and selectivities were determined by GC on a β-Dex 120 or a 225 chiral column.

supported by the diffuse reflectance Vis-NIR spectra of **1R** and **2R** solids (ESI‡).

As shown in Table 1, both **1R** and **2R** are competent cyclopropanation catalysts for substituted alkenes. In the case of styrene, the non-interpenetrated **2R** gave higher isolated yields of cyclopropanation products than the 2-fold interpenetrated **1R**, presumably as a result of the larger open channels in **2R** that facilitate the substrate and product diffusion through the CMOFs. This trend was not observed for ethyl vinyl ether, possibly due to the limited steric demand for this substrate. The isolated yields of cyclopropanation products afforded by **2R** rival those of the homogeneous control catalyst Ru(**L**-Me_2)$(py)_2$. For styrene and ethyl vinyl ether substrates, **1R** and **2R** gave diastereoselectivities (dr's) and enantioselectivities (ee's) comparable to those of Ru(**L**-Me_2)$(py)_2$. Comparison of the present results to our earlier asymmetric cyclopropanation reactions catalysed by CMOFs built from shorter Ru-salen-derived dicarboxylic acid [Ru(**L**′)$(py)_2$] (**L**′ is the deprotonated form of (*R*,*R*)-(−)-*N*,*N*′-(3-carboxyl-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine; the 2-fold interpenetrated and non-interpenetrated MOFs are herein denoted **3** and **4**, respectively) reveals several interesting insights. First, while **1R** is catalytically competent, the 2-fold interpenetrated **3** is totally inactive. This result supports the heterogeneous nature of all these CMOF catalysts (**3** would have been active if it had dissolved under catalytic conditions) and reinforces the importance of open channels in MOF catalysis. Second, while **2R** only provided slight enhancements in isolated yields for the cyclopropanation products compared to **4**, significant increases in both dr's and ee's were observed for **2R**. For the cyclopropanation of styrene, **2R** gave an 8% increase in the *cis* ee and a 3% increase in the *trans* ee compared to those of **4**. For the cyclopropanation of ethyl vinyl ether, **2R** gave a 16% increase in the *cis* ee and a 2% increase in *trans* ee compared to those of **4**.

We have also carried out experiments to demonstrate that the present MOF catalysts are heterogeneous and recyclable. First, the supernatant of the MOF catalyst showed no cyclopropanation activity. Second, the MOF recovered from the catalytic reactions remained active for cyclopropanation reactions, albeit with lower yields and selectivities (Fig. S30, ESI‡). The deterioration in the catalytic performance is likely a result of catalyst deactivation caused by the loss of the axial pyridine ligands.[15]

In summary, we have synthesized a new pair of porous chiral MOFs that were constructed from the same catalytically active bridging ligand but possessed different open channel sizes as a result of the different catenation modes. Upon reduction, this pair of chiral MOFs became active catalysts for highly diastereo- and enantio-selective cyclopropanation reactions of substituted alkenes. Both the yields and selectivities of the cyclopropanation reactions are markedly dependent on the MOF open channel sizes. Chiral MOFs thus provide a tunable platform for the design of highly efficient and stereoselective single-site solid catalysts.

We thank the NSF (CHE-1111490) for financial support and Kathryn deKrafft and Rachel Huxford-Phillips for experimental help. J.M.F. is supported by a DOE Office of Science graduate fellowship under the DOE contract number DE-AC05-06OR23100. C.W. acknowledges the UNC Department of Chemistry for an Ernest L. Eliel Fellowship. S.L. was supported by a UNC William W. and Ida W. Taylor Fellowship.

Notes and references

§ Crystal data for **1**: trigonal, *R*32, $a = b = 35.140(2)$ Å, $c = 92.240(8)$ Å, $V = 98640(11)$ Å^3, $\rho_{calc} = 0.530$ g cm^{-3}. $R_1 = 0.132$, w$R_2 = 0.318$. CCDC 860688.

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