

Two homochiral organocatalytic metal organic materials with nanoscopic channels†

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Zhuxiu Zhang,[‡] Young Ran Ji,[‡] Lukasz Wojtas, Wen-Yang Gao, Shengqian Ma, Michael J. Zaworotko* and Jon C. Antilla*

Two homochiral organocatalytic MOMs were prepared using tetra- and octa-carboxylate ligands, respectively. The nanoscopic channels in these MOMs are lined by organocatalytic chiral phosphoric acid derivatives of binol and ocMOM-1 exhibited improved enantioselectivity over the parent ligand in the context of transfer hydrogenation of a series of benzoxazines.

Metal-organic materials (MOMs)¹ constructed from metals or metal clusters (nodes) and multi-topic ligands (linkers or nodes) have gained considerable attention at least in part because of their amenability to crystal engineering.² MOMs can be diverse in composition, structure and properties because of the extensive range of suitable molecular building blocks (MBBs),³ in particular those that are capable of serving as 3-connected (3-c, e.g. triangle), 4-connected (4-c, e.g. square, tetrahedron⁹) or 6-connected (6-c, e.g. trigonal prism,⁴ octahedron) nodes. Uninodal networks from such MBBs are exemplified by **dia**,^{3a} kagomé (**kag**),^{3b} **acs**^{3c} and **pcu**^{3d} networks, respectively. That MOMs can possess unparalleled permanent porosity affords them with potential for utility in gas adsorption,⁵ catalysis⁶ and separations.⁷ Whereas catalysis is now well established in MOMs thanks to the pioneering work of Fujita^{6a} and Kim,^{6b} homochiral MOMs that exhibit enantioselective organocatalysis, ocMOMs, remain relatively underexplored.⁸

ocMOMs based upon chiral catalytically active MBBs are attractive targets because in principle they would exhibit the following features: chemical and thermal stability; facile recyclability; size selectivity; confined space in channels or cages.^{6e} Recently, Lin and co-workers reported an ocMOM (CMOF-1)^{8e} formed from Cu²⁺ “paddlewheel” MBBs and a tetra-carboxylic acid derivative of a binol based chiral phosphoric acid, **L**₁. Activation of CMOF-1 afforded a MOM with 0.8 × 2.6 nm

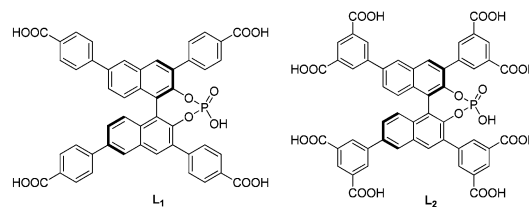


Fig. 1 Homochiral phosphoric acid ligands decorated by four (**L**₁) and eight (**L**₂) carboxylic acid moieties.

channels that catalyzed Friedel–Crafts reactions between indole and imines with ee values from 29–44%. It occurred to us that **L**₁ and related ligands such as the octacarboxylic acid **L**₂ (Fig. 1) can serve as 4-c or 8-c nodes, respectively, and generally form MOMs with organocatalytic properties. Herein we address this matter by investigating **L**₁ and **L**₂ for their ability to form permanently porous MOMs that facilitate enantioselective transformations.¹⁰

Solvothermal reaction of In(NO₃)₃·xH₂O and **L**₁ in DMF–EtOH afforded pale yellow crystals of [(In₃O)₆(NO₃)₆(**L**₁)₉][EtOH₃₂₀], ocMOM-1, that crystallize in the chiral space group R3 with *a* = *b* = 31.1023(19), *c* = 45.205(3) (Table S1, ESI†). The bulk purity of ocMOM-1 was verified by comparing the calculated and experimental X-ray powder diffraction patterns (Fig. S1, ESI†). The crystal structure of ocMOM-1 is illustrated in Fig. 2. The naphthalene rings of **L**₁ exhibit a dihedral angle of 57.86° with respect to the C1–C1′ bond (Fig. S7, ESI†). Each of the four 4-benzoate moieties of **L**₁ link to trigonal prismatic [In₃(μ₃-O)(CO₂)₆] MBBs^{4b–d} through their vertices (Fig. 2a). The (*R*)-configuration of **L**₁ and the 6-c trigonal prismatic MBBs facilitate the formation of a [4,6] network that exhibits the simple but rare **hea** (heazlewoodite) topology (Fig. 2c) as opposed to the **stp**⁸¹² topology that is known to form between trigonal prismatic and square MBBs (Fig. S7, ESI†). The **hea** net is sustained by four-membered rings that are composed of 2 trigonal prisms and 2 ligands (Fig. 2b) that generate 1.5 nm channels parallel to [001] (Fig. 2d). With axial ligands and solvent molecules removed, ocMOM-1 exhibits 65% void space as calculated by PLATON. To the best of our knowledge,

Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE 205, Tampa, Florida 33620, USA. E-mail: xtal@usf.edu, jantilla@usf.edu

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‡ These authors contributed equally.

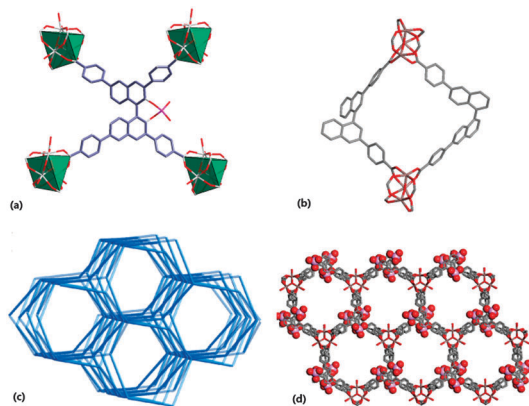


Fig. 2 The structure of ocMOM-1: (a) L_1 connects four trigonal prismatic $[\text{In}_3(\mu_3\text{-O})(\text{CO}_2)_6]$ MBBs; (b) 4-connected rings are formed from two molecules of L_1 and two $[\text{In}_3(\mu_3\text{-O})(\text{CO}_2)_6]$ MBBs; (c) schematic representation of the hea net; (d) 1.5 nm channels parallel to [001] are comprised of alternating trigonal prismatic MBBs and L_1 .

ocMOM-1 represents the first **hea** net in the field of MOMs. Alternatively, if L_1 is treated as two triangular MBBs it is the first 3,3,6-c net with stoichiometry $(3\text{-c})_3(3\text{-c})_3(6\text{-c})_2$.

Solvothermal reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and L_2 in DMF afforded pale brown leaf-like crystals $[\text{Cd}_2((\text{CH}_3)_2\text{NH}_2)_4(L_2)] \cdot [55\text{DMF}]$, ocMOM-2 (Table S2, ESI[†]) which crystallize in chiral space group $P2_12_12_1$ with $a = 17.4396(10)$, $b = 22.4040(15)$, $c = 29.2728(19)$. The bulk purity of ocMOM-2 was confirmed by comparing the calculated and experimental X-ray powder diffraction patterns (Fig. S4, ESI[†]). The structure of ocMOM-2 reveals that the four 1,3-benzenedicarboxylate, 1,3-bdc, moieties of L_2 orient in almost perpendicular fashion with respect to the naphthalene rings. Each carboxylate group is linked to $[\text{Cd}(\text{O}_2\text{C})_4]$ MBBs,^{9a,b} which thereby serve as 4-c pseudotetrahedral nodes (Fig. 3a). 4-c “paddlewheels” linked at their vertices by 1,3-bdc moieties are known to be capable of forming triangular or square nanoscale secondary building units (nSBUs),^{3b,11} that generate **kag** or square grid nets, respectively. In ocMOM-2 we observe triangular and pentagonal^{11b} nSBUs from 4-c Cd nodes and 1,3-bdc moieties. These nSBUs exhibit a

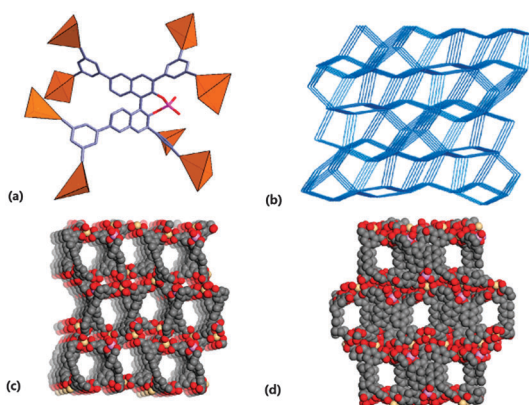


Fig. 3 The structure of ocMOM-2: (a) 8 pseudotetrahedra are connected to each L_2 ; (b) schematic representation of the 4,8-c nets in ocMOM-2 (c) 1.2 nm channels parallel to [100]; (d) 0.8 nm channels parallel to [010].

new type of tessellation consisting of triangles and pentagons (Fig. S14, ESI[†]). Ligand-to-ligand cross-linking of these sheets between the 5 positions of the 1,3-bdc moieties affords a 3-D net in which L_2 serves as the pillar between each layer. The resulting net is a new 4,8 connected network with topological point symbol of $\{4^{10} \cdot 6^{16} \cdot 8^2\}\{4^5 \cdot 6\}_2$ (Fig. 3b). There are two types of channels (Fig. 3c and d): 1.2 nm channels formed by 4-membered rings along [100]; 0.8 nm channels formed by different 4-membered rings along [010] (Fig. S8 and S9, ESI[†]). With solvent molecules removed ocMOM-2 exhibits 65% void space as calculated by PLATON.

Thermogravimetric analysis (Fig. S3 and S6, ESI[†]) revealed that ocMOM-1 and ocMOM-2 exhibit similar thermal stability with 62.5% and 44.6% weight loss, respectively, below 100 °C and no further weight loss up to 410 and 390 °C, respectively. To evaluate the gas adsorption properties of ocMOM-1 and ocMOM-2, N_2 and CO_2 gas adsorption studies were conducted. ocMOM-1 was degassed at 60 °C for 24 h under vacuum and N_2 adsorption isotherms at 77 K revealed type-I adsorption behaviour and a Brunauer–Emmett–Teller (BET) surface area of $1298 \text{ m}^2 \text{ g}^{-1}$ (Langmuir surface area of $1636 \text{ m}^2 \text{ g}^{-1}$), which represents a relatively large surface area in the context of ocMOMs (Fig. S12, ESI[†]).⁸ ocMOM-2 after supercritical CO_2 drying activation was found to exhibit CO_2 uptake of $23 \text{ cm}^3 \text{ g}^{-1}$ at 273 K/760 Torr and there was no observable N_2 uptake at 77 K (Fig. S13, ESI[†]). Pore size distribution analysis of ocMOM-1 revealed a distribution of micropores from 12–18 Å, (Fig. S11, ESI[†]) consistent with the SCXRD data.

To examine the catalytic ability of ocMOM-1, transfer hydrogenation of benzoxazine, a classic reaction that is relevant to the synthesis of pharmaceuticals, was studied.¹² Crystals of ocMOM-1 were activated using the same procedure used for gas adsorption studies and then immersed in CHCl_3 together with benzoxazine and Hantzsch ester (HEH). After stirring for 3 days, formation of dihydro-2H-benzoxazine was detected with 78% conversion. The enantioselectivity of the product was found to be 31% as determined by chiral HPLC analysis (Table 1, entry 2).

Table 1 Survey of catalysts for the transfer hydrogenation of benzoxazine^a

Entry	Catalyst	Solvent	Yield ^b (%)	ee ^c (%)
1	Null	CHCl_3	0	0
2	ocMOM-1	CHCl_3	78	31
3	L_1	CHCl_3	95	11
4	1a	CHCl_3	97	Racemic

^a Reaction conditions: benzoxazine (1.0 equiv.), Hantzsch ester (1.25 equiv.) and catalyst (5 mol%) in 1.5 mL solvent at rt. ^b Yield of isolated product after column chromatography. ^c ee determined by HPLC analysis using a Chiralcel OD-H column.

Table 2 Substrate scope of the enantioselectively catalyzed hydrogenation of benzoxazines by ocMOM-1

Entry	Benzoxazine	Yield (%)	ee (%)
1		78	31
2		56	62
3		90	84
4		91	35
5		18	57

A series of control experiments revealed no conversion of the substrate without catalyst (Table 1, entry 1) whereas **L**₁ afforded 95% conversion but only 11% ee (Table 1, entry 3). (*R*)-3,3'-diphenyl-1,1'-binaphthyl phosphoric acid (**1a**) was also evaluated as a catalyst and after 3 days 97% conversion had occurred but the product was found to be racemic (Table 1, entry 4). A possible explanation for the low ee values is the relatively open nature of the chiral environment (steric crowding is known to enhance ee in related reactions¹³). These results prompted us to explore the effect of the size of the substrate. A series of 3-aryl substituted benzoxazines studied with either electron donating or electron-withdrawing groups were found to convert with ee from 31–84% and yields from 56–90% (Table 2). It is of note that all bulky substrates afforded higher ee than that obtained for benzoxazine. The superior performance observed for the largest substrate suggests that steric effects promote stereo differentiation, perhaps through π - π stacking¹⁴ between the substrate and the framework.

We also studied the recyclability of ocMOM-1 by recovering ocMOM-1 *via* centrifugation and washing with anhydrous chloroform 3 times (Fig. S10, ESI†). The PXRD pattern of ocMOM-1 after catalysis matched that of freshly prepared crystals. However, the ee of the recovered catalyst decreased from 31% to 17% after applying the same reaction conditions in Table 1.

In summary, two new MOMs with organocatalytic functionality and novel topologies were prepared *via* binding of the chiral phosphoric acid ligands **L**₁ and **L**₂ by trigonal prismatic MBBs and pseudotetrahedral MBBs, respectively. ocMOM-1 exhibits permanent porosity and serves as a fairly efficient and selective catalyst for reduction chemistry. Further studies concerning catalytic enantioselective synthesis utilizing ocMOMs will focus upon new variants of ligands with organocatalytic functionality.

Single crystal diffraction studies on ocMOM-1 were conducted at the Advanced Photon Source on beamline 15ID-B of ChemMatCARS Sector 15, which is principally supported by the National Science Foundation/Department of Energy under grant number NSF/CHE-0822838. Use of the advanced photon source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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