

Post-Synthesis Modification of a Metal–Organic Framework To Form Metallosalen-Containing MOF Materials

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S Supporting Information

ABSTRACT: A series of metallosalen-based metal–organic frameworks (MOFs) have been prepared by the post-synthesis modification of $\text{Mn}^{\text{III}}\text{SO-MOF}$, a $\text{Mn}^{3+}(\text{salen})$ -based MOF. Treatment of $\text{Mn}^{\text{III}}\text{SO-MOF}$ with H_2O_2 effects the removal of the Mn^{3+} ions from the salen struts, which can then be remetallated with a variety of metal precursors to form isostructural **MSO-MOF** materials. The presence of the new metallosalen struts in **MSO-MOF** was fully confirmed by ICP-OES, MALDI–TOF MS, PXRD, and TGA. Furthermore, the remetallated $\text{Mn}^{\text{III}}\text{SO-MOF}$ material displays similar catalytic activity and porosity to the parent MOF.

Metal–organic frameworks (MOFs) have attracted substantial attention because of their unique properties as highly tailorable microporous materials.¹ The ability to incorporate a wide range of chemical functionalities via the organic struts has motivated the synthesis of MOFs for a plethora of potential applications including gas storage,² gas separations,³ chemical sensing,⁴ ion exchange,⁵ drug delivery,⁶ and catalysis.⁷ A particularly attractive material entry to many of these applications is the incorporation of metal complexes that can be fine-tuned for specific purposes. Most of the advances in this approach have taken place in the context of MOF-based catalysis by incorporating, as struts, molecules that have proven to be effective homogeneous catalysts, particularly metallosalens,⁸ metalloporphyrins,⁹ and Ti–binolate complexes,¹⁰ among others. While this method has been generally successful, a major challenge has been the lack of general synthetic strategies that are compatible with struts possessing *coordinatively unsaturated* metal centers. Unfortunately, typical MOF synthesis procedures tend to form *coordinatively saturated* metal centers because of the high concentration of ligating functionalities present. In addition, while the intrinsic modularity of MOF designs has been a primary motivation in the development of isostructural materials with varying cavity environments, very few examples exist for isostructural MOFs that possess tunable, coordinatively unsaturated metal complexes. To the best of our knowledge, to date there has been only one report of the preparation of a homologous series of MOFs possessing different combinations of unsaturated metal complexes.^{9b} In this paper, we report a general post-synthesis technique for preparing metallosalen-based MOFs containing a wide variety of metal centers.

Along with the well-known use of $\text{Mn}(\text{salen})$ complexes as catalysts for the asymmetric epoxidation of olefins, many metallosalen complexes have been shown to be catalytically active,¹¹ making them attractive components for incorporation into MOF

materials. Some examples of metallosalen-based catalysis include the asymmetric ring-opening reactions of epoxides and aziridines catalyzed by $\text{Co}(\text{salen})$ and $\text{Cr}(\text{salen})$ complexes,¹² the enantioselective addition of alkynes to ketones catalyzed by $\text{Zn}(\text{salen})$ complexes,¹³ and the asymmetric oxidation of sulfides to sulfides catalyzed by both $\text{Ti}(\text{salen})$ ¹⁴ and $\text{V}(\text{salen})$ ¹⁵ complexes. In view of the widely demonstrated versatility of these complexes, a general synthetic strategy that can yield a modular series of metallosalen-based MOFs is highly desirable.

We have recently shown that a porous, noncatenated MOF based on Zn paddlewheel nodes ($\text{Mn}^{\text{III}}\text{SO-MOF}$, Scheme 1) can be readily synthesized from a tetracarboxylic acid (**1**) and a dipyrindyl $\text{Mn}(\text{salen})$ strut (**2-MnCl**). In theory, analogues of $\text{Mn}^{\text{III}}\text{SO-MOF}$ could be synthesized in a conventional direct fashion from the appropriate metallosalen starting materials. However, changing the identity of the metal center in this building block can have strikingly adverse effects on our ability to synthesize isostructural MOFs. For example, we have been uniformly unsuccessful in efforts to synthesize the Co^{III} analogue of $\text{Mn}^{\text{III}}\text{SO-MOF}$ from the corresponding dipyrindyl $\text{Co}(\text{salen})$ starting material using the same conditions and coreactants as in the synthesis of $\text{Mn}^{\text{III}}\text{SO-MOF}$. This is not surprising in view of the well-established observation that complexes of Co^{III} tend to display particularly high affinities for nitrogenous ligands.¹⁶ As such, the dipyrindyl $\text{Co}(\text{salen})$ often self-aggregates during MOF synthesis and becomes unavailable for MOF formation.

Post-synthesis modification has recently emerged as a useful strategy for preparing a variety of MOFs that would be difficult to produce otherwise,¹⁷ including MOFs with long hydrophobic chains,¹⁸ MOFs with free carboxylic acids,¹⁹ and MOFs with nonstructural metal centers.²⁰ We subsequently showed that post-synthesis removal of the Mn ions from the salen struts of $\text{Mn}^{\text{III}}\text{SO-MOF}$ with aqueous H_2O_2 can be used to modify its surface selectively and induce size-selective pore-based catalysis.^{8b} Herein, we report that when $\text{Mn}^{\text{III}}\text{SO-MOF}$ is completely “de-manganated”, the resulting **dSO-MOF** can be further modified by remetallating the salen struts with a wide variety of metal ions, resulting in facile incorporation of different *unsaturated* metal centers as part of a chiral salen complex (Scheme 2).

The “de-manganation” of $\text{Mn}^{\text{III}}\text{SO-MOF}$ crystals was carried out by soaking them in methanol and then treating them with aqueous H_2O_2 overnight. As observed by inductively coupled plasma-optical emission spectroscopy (ICP-OES), the Zn:Mn ratio went from $\sim 2:1$ in the as-synthesized material to $\sim 20:1$

Received: May 25, 2011

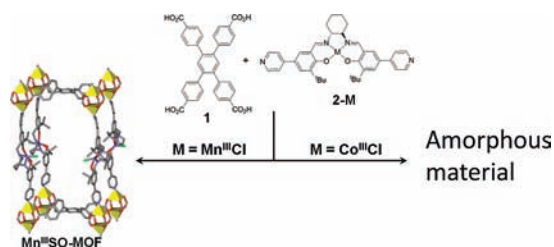
Published: July 19, 2011

(90% depletion) in the Mn-depleted material (dSO-MOF). Following evacuation of dSO-MOF, samples of the material were placed under nitrogen and exposed to solutions containing M^{II} salts ($M = \text{Cr}, \text{Co}, \text{Mn}, \text{Ni}, \text{Cu}, \text{Zn}$) for 24 h (~ 1.5 equiv of M^{II} in most cases). Qualitatively, the remetalation of the MOF materials was immediately indicated by dramatic changes in the color of the crystals (Figure 1) that were consistent with the colors reported for the homogeneous metallosalen analogues, including the clear difference in the colors of the $\text{Mn}^{II}\text{SO-MOF}$ product and the $\text{Mn}^{III}\text{SO-MOF}$ starting material.²¹ Each MOF sample was extensively rinsed on a Soxhlet extractor and then sonicated in pyridine to partially dissolve the crystals, after which the dissolved portion was analyzed by MALDI–TOF MS to confirm the presence of the metallosalen species (Figure 2).

The extent of remetalation in each MSO-MOF was quantified by ICP-OES, with five of the six remetalated MOFs exhibiting metal concentrations close or equal to 100% of the available salen sites (Table 1). Notably, CuSO-MOF displayed a Cu mass equivalence much higher than that expected for remetalation of only the salen sites. This is not surprising in view of previous observations that the metal ions in the structural nodes of some MOFs can undergo exchange upon exposure to external metal ions in solution.²² Indeed, this phenomenon has been observed for pillared-paddlewheel MOFs wherein the Zn nodes readily exchange with Cu ions to form Cu paddlewheel nodes.²³ In a similar vein, the slightly higher than expected metal contents in the cases of Co^{II} and Cr^{II} are likely due to some limited metal exchange at the nodes of the MOF.

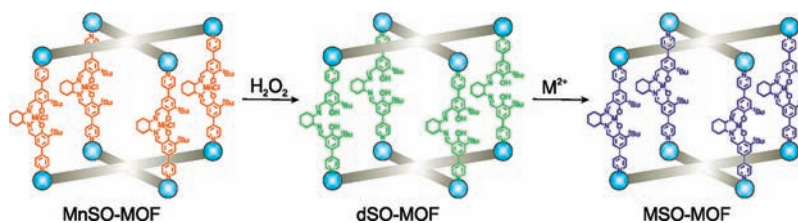
The specific surface areas of the pristine $\text{Mn}^{III}\text{SO-MOF}$ starting material and the remetalated $\text{Mn}^{II}\text{SO-MOF}$ product,

Scheme 1. Synthesis of $\text{Mn}^{III}\text{SO-MOF}^a$ and Attempted Synthesis of the Co^{III} Analogue



^aThe synthesis of $\text{Mn}^{III}\text{SO-MOF}$ was carried out in the presence of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 80 °C in *N,N*-dimethylformamide (DMF). The unit cell of $\text{Mn}^{III}\text{SO-MOF}$ is shown as a stick representation (yellow polyhedra = Zn, red = O, green = Cl, blue = N, gray = C, purple = Mn). Solvent molecules, H atoms, and disordered atoms have been omitted for clarity. To maintain consistency with previously employed nomenclature,^{8b} the term SO-MOF is used to describe a MOF comprising Zn paddlewheel corners, dipyriddy Mn(salen) struts, and 1,2,4,5-tetrakis(4-carboxyphenyl)benzene struts containing eight O atoms.

Scheme 2. Demetalation of $\text{Mn}^{III}\text{SO-MOF}$ and Its Subsequent Remetalation



as measured by Brunauer–Emmett–Teller analysis of the N_2 adsorption isotherms at 77 K (Figure 3A), were fairly close (478 and 385 m^2/g , respectively; both samples were activated with supercritical CO_2),²⁴ suggesting that they have similar porosities. Intriguingly, thermogravimetric analysis (TGA) of solvated dSO-MOF showed this material to have a significantly smaller solvent capacity than the pristine material ($\sim 20\%$ solvent by weight vs $\sim 45\%$; Figure 3B). We interpret this behavior in light of previous observations that unmetalated salens are significantly more flexible than their metalated analogues.²⁵ Such increased flexibility inside the dSO-MOF crystal could cause partial shrinkage of the pore volume, resulting in decreased solvent uptake. Consistent with this hypothesis, remetalation of dSO-MOF resulted in recovery of the high solvent capacity observed for the original $\text{Mn}^{III}\text{SO-MOF}$ (Figure 3B). Notably, all of the SO-MOF materials showed decomposition temperatures of ~ 425 °C, except for CuSO-MOF [~ 350 °C; Figure S1 in the Supporting Information (SI)]. This corresponds well with previous observations of lower thermal stability for Cu pillared-paddlewheel MOFs relative to their Zn congeners.²⁶

Unfortunately, we were unable to obtain single-crystal X-ray structures for the remetalated MSO-MOF materials and had to



Figure 1. Digital photographs of vials containing solvated crystals of (right to left, as labeled) the $\text{Mn}^{III}\text{SO-MOF}$ parent, dSO-MOF, and MSO-MOFs after remetalation. There is a clear difference in color between the parent $\text{Mn}^{III}\text{SO-MOF}$ and the remetalated $\text{Mn}^{II}\text{SO-MOF}$ (third from the right).

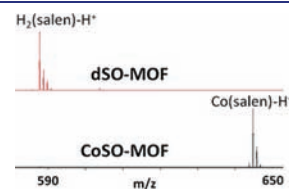


Figure 2. MALDI–TOF mass spectra of (top) dSO-MOF and (bottom) CoSO-MOF after sonication of the MOFs in pyridine. Peaks for the other SO-MOFs are listed in the SI.

rely on powder X-ray diffraction (PXRD) to confirm that these various SO-MOFs were indeed isostructural. However, conventional techniques for measuring PXRD patterns of MOFs have presented particular problems for this series of materials, which tend to crystallize as thin, rectangular plates. In fact, this high-aspect-ratio morphology is quite common for pillared paddle-wheel MOFs based on tetracarboxylate **1** and its derivatives.²⁷

Table 1. Extents of Remetalation of dSO-MOF

entry	M	M:2Zn ratio ^a
1	Cr	1.16
2	Co	1.10
3	Mn	1.00
4	Ni	0.86
5	Cu	7.67 (86% ^b)
6	Zn	N/A (67% ^c)

^a Quantitative metalation of the available salen sites would give a theoretical ratio of one salen-sited M²⁺ ion for every two node-based Zn²⁺ ions. ^b Percentage of all metal sites (including both the salen and structural nodes) composed of Cu, as measured by the wt % of Cu in the sample. ^c Percentage of available salen sites complexed with Zn, as measured by the wt % of Zn in the sample.

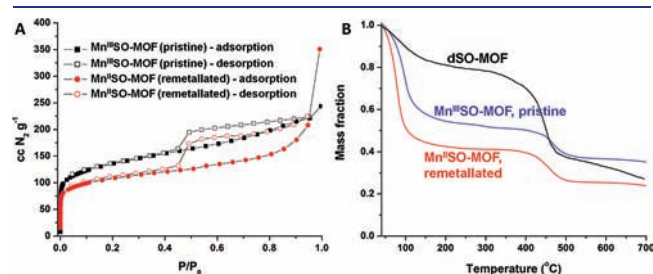


Figure 3. (A) N₂ isotherms obtained at 77 K for as-synthesized Mn^{III}SO-MOF (black) and remetalated Mn^{II}SO-MOF (red). (B) TGA profiles of selected SO-MOF derivatives. TGA profiles for all of the SO-MOF derivatives are shown in Figure S1 in the SI.

Such flat plates tend to adopt a preferred orientation on the PXRD sample holder when these MOFs are prepared for measurement, leading to highly uneven sampling of the various crystal planes during measurement (Figure 4A). To address this problem, as-synthesized Mn^{III}SO-MOF, dSO-MOF, and the remetalated derivatives were analyzed by placing the respective crystals in capillary tubes, which were then spun during the measurements to prevent (albeit not completely) the selective enhancement of diffraction peaks from the preferred orientation.^{9b} When the SO-MOF samples were analyzed by this method, their closely related PXRD patterns clearly revealed them to be crystalline and isostructural (Figure 4B).

We showed previously that Mn^{III}SO-MOF can enantioselectively epoxidize 2,2-dimethylchromene with 80% ee.^{8b} As expected, dSO-MOF shows no activity for epoxidation, indicating that no catalytically active Mn sites remain in this material. However, once it is remetalated with Mn^{II} and exposed to a mixture of oxidant and olefin, both the catalytic activity and enantioselectivity are restored, although at lower values (~750 turnovers, 37% ee). There is a long induction period at the beginning of the epoxidation catalyzed by remetalated Mn^{II}SO-MOF that is much longer than the one attributed to diffusion of reagents and products in the Mn^{III}SO-MOF-catalyzed epoxidation^{8b} (Figure S2 in the SI). We attribute this to the need for the remetalated Mn^{II} center to be oxidized to Mn^{III} before catalysis can take place.²¹ That the enantioselectivity remains at ~37% over an 8 h period when the oxidant is added over 2 h further supports the hypothesis that the catalysis is probably due to Mn^{III} centers and not a combination of Mn^{II} and Mn^{III}.

The aforementioned catalysis data strongly suggest that the Mn(salen) struts are reformed as in the original material, albeit not completely. One potential explanation for the lower rate and enantioselectivity is the imperfect reformation of the Mn(salen) struts in the remetalation process, which might be due to the mechanical stress caused by the aforementioned partial shrinkage of the pore in dSO-MOF. Such stress may result in partially coordinated (i.e., half-salen-type) complexes that are also active for epoxidation but accomplish it more slowly and less

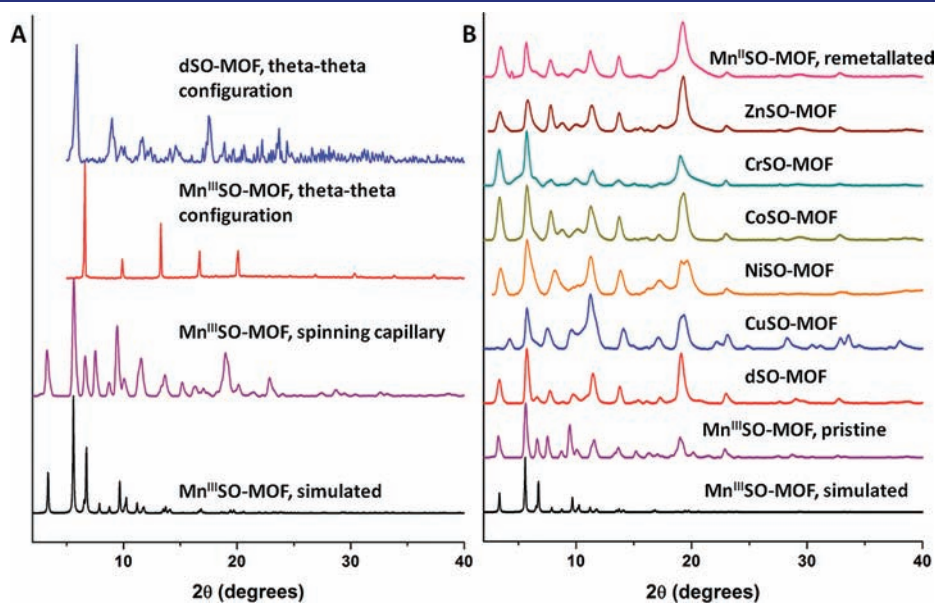


Figure 4. (A) Comparison of PXRD patterns obtained with a spinning capillary and a conventional theta–theta configuration. (B) Simulated PXRD pattern of Mn^{III}SO-MOF and spinning-capillary experimental PXRD patterns of Mn^{III}SO-MOF, dSO-MOF, and remetalated MSO-MOFs.

enantioselectively than the full salen complex.²⁸ Additionally, this mechanical stress may cause the remetalated Mn(salen) struts in **Mn^{II}SO-MOF** to remain in a less enantioselective conformation than the Mn^{III}(salen) struts in the parent **Mn^{III}SO-MOF** and the homogeneous catalyst **2-MnCl** (Figure S2 in the SI).

In conclusion, a general and selective demetalation–remetalation strategy has been demonstrated for the facile post-synthesis creation of a homologous series of metallosalen-based MOFs containing a wide variety of coordinatively unsaturated metal centers. Notably, these include metallosalens that, because of competitive self-association, cannot be directly incorporated into MOF structures readily (or at all). While we have emphasized the potential of these newly accessible MOFs to enable the heterogeneous utilization of a broad range of salen-based catalysts, other applications such as selective chemical sensing or separations may also prove significant. We note, for example, the recent report by Chen, Thomas, and co-workers on the ability of a Cu^{II}(salen)-containing MOF to separate ethylene and acetylene.²⁹ Our ongoing work is focused chiefly on developing metallosalen-based catalytic chemistry that appears to be difficult or impossible to implement with molecular catalysts.

■ ASSOCIATED CONTENT

S Supporting Information. Full characterization data and description of reaction conditions, including catalysis, and complete ref 6b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We thank Ms. Anastasiya Vinokur for assistance with the PXRD measurements. We gratefully acknowledge the Northwestern Institute for Catalysis in Energy Processes (U.S. Department of Energy, Grant DE-FG02-03ER15457), the Northwestern NSEC, DTRA (Grant HDTRA1-09-01-0007), and AFOSR (Grant FA-9550-07-1-0534) for financial support of this work.

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