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Post-synthesis modification of a metal-organic framework to form metallosalen-containing MOF materials

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I. Materials. MnSO-MOF,^{S1} 2,2-dimethyl-2H-chromene^{S2} was synthesized according to a published procedure. 2-(*Tert*-butylsulfonyl)iodobenzene was synthesized according to a modified version^{S1} of a published procedure.^{S3} H₂O₂ (30 wt% in H₂O, Sigma-Aldrich), manganese(II) acetate tetrahydrate (Alfa Aesar), zinc acetate (Sigma-Aldrich), copper(II) chloride anhydrous (Alfa Aesar), chromium(II) chloride anhydrous (Alfa Aesar), cobalt(II) acetate anhydrous (Alfa Aesar), and nickel(II) acetate tetrahydrate (Sigma-Aldrich) were obtained from commercial sources and used as received.

Anhydrous solvents were obtained from a two-column Dow-Grubbs purification system installed by Glass Contours (now SG Water USA, Nashua, NH). The collected anhydrous solvent was degassed with 3 freeze-pump-thaw cycles and stored in a Strauss flask before use. Other solvents were obtained from Sigma-Aldrich and used as received.

II. General procedures and instrumentation.

Gas chromatography was performed using a Hewlett-Packard 5890 instrument equipped with an HP-5 capillary column (30 m × 0.320 mm × 0.25 μm film thickness) and an FID detector. Product concentration was calculated from calibration curves, relative to an internal standard. For the epoxidation of 2,2-dimethylchromene, the product yield was calculated by combining peaks corresponding to both the epoxide and the ketone (approximately 30% of the epoxide isomerizes to the ketone under GC conditions). The following method was used for analysis of TOF: initial temperature = 70 °C, initial time = 5 minutes, ramp = 10 °C/min, final temperature = 180 °C, final time = 4 minute. For the determination of enantiomeric excess, a Supelco β-DEX 120 column was used on an HP 6890 gas chromatograph equipped with an FID detector and ChemStation software. Column head pressure was 23 psi. The column temperature was ramped from 140 to 175 °C at a rate of 1 °C/min and held at 175 °C for 20 min.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on a Varian ICP-OES spectrometer that is equipped to cover the 175-785 nm spectral range. Samples (1-2 mg) were digested in 3:1 v/v conc. H₂SO₄:H₂O₂ (30 wt% in H₂O) and heated at 120 °C until the solution became clear and colorless and no further vapor was produced. An aliquot of this acidic solution was diluted to 5 vol% with ultrapure deionized H₂O (resistivity >18 MΩ-cm, collected from a Mili-Q Biocel system) and analyzed for Zn (202.548 and 206.200 nm), Mn (257.610 and 294.921 nm), Cu (213.598 and 324.754 nm), Co (230.786 and 238.892 nm), Cr (283.563 and 284.325 nm), or Ni (230.299 and 231.604 nm) content as compared to standard solutions.

Matrix-assisted laser-desorption-ionization time-of-flight (MALDI-ToF) mass spectra were obtained on a Bruker Autoflex III Smartbeam MALDI-ToF mass spectrometer in positive ionization mode with 2-hydroxy-1-naphthoic acid as a matrix. MALDI-ToF samples were prepared by sonicating a small sample of MOF (< 1 mg) in pyridine (0.5 mL) for 20 minutes, then spotting the resulting suspension on the sample holder along with an acetone solution of the matrix. Samples were allowed to sit for at least 20 minutes to allow the solvent to evaporate.

Supercritical CO₂ activation was performed with a Tousimis™ Samdri® PVT-30 critical point dryer. Prior to drying, the MOF samples were soaked in absolute ethanol (EtOH), replacing the soaking solution every 24 h over a 72-h period, to exchange the occluded solvent for EtOH. After the 72-h exchange process was complete, the ethanol-containing samples were placed inside the dryer and the adsorbed ethanol was exchanged with CO₂ (l) over a period of 8 h. During this time, the liquid CO₂ was vented under positive pressure for five minutes every 2 h. The rate of venting of CO₂ (l) was always kept below the rate of filling so as to maintain a full drying chamber. After 8 h of venting and soaking with CO₂ (l), the chamber was sealed and the temperature was raised to 40 °C, bringing the chamber pressure to ~1300 psi, above the critical point of CO₂. The chamber was held above the critical point for 1 hour, at which point the chamber was slowly vented over the course of 15-18 h.

Adsorption measurements were performed using a Autosorb 1-MP from Quantachrome Instruments. Ultra-high purity grade N₂ was used for adsorption measurements. Isotherms were measured at 77 K; a liquid nitrogen bath was used to maintain the temperature. Samples were activated by processing with supercritical CO₂ prior to gas adsorption analysis.

Powder X-ray diffraction patterns for capillary-encapsulated samples were obtained at room temperature with a Bruker MX IμS microsource (CuKα radiation) and ApexII CCD detector. Samples were mounted in capillaries with supernatant liquid; capillaries were sealed with wax and placed on goniometer heads for mounting on the diffractometer. The PXRD data were collected with an area detector as rotation frames over 180° in φ at 2θ values of 12°, 24°, and 36° and exposed for 10 minutes for each frame. At a distance of 150 mm, the detector area covers 24° in 2θ. Overlapping sections of data were matched and the resulting pattern integrated using the Bruker APEX2 Phase ID program. Powder-pattern data were treated for amorphous background scatter and unit cell indexing was performed with the Bruker Topas program. The experimentally obtained powder patterns were compared to simulated patterns calculated from the refined structural models using Mercury software.

III. Synthesis

dSO-MOF. A sample of as-synthesized **Mn^{III}SO-MOF** (~5 mg, 0.0035 mmol Mn(salen)) was placed in a 4-mL screw-cap vial. To these crystals were added 1 mL of a 1:1 v/v solution of H₂O₂ (30 wt% solution in H₂O) and methanol. This resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 18 h. After decantation and rinsing with methanol (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction. The solvent was then exchanged with ethanol and the crystals were dried with supercritical CO₂, as detailed above. MALDI-ToF MS: *m/z* 589.41 (Calculated 589.35 for **2-H₂-H⁺**).

CrSO-MOF. A stock solution of anhydrous chromium chloride (19 mg, 0.15 mmol) was prepared in dry, degassed THF (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed a sample of **dSO-MOF** (5 mg, ~0.003 mmol salen) that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed THF (1 mL) and CrCl₃ (0.3 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with THF (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF MS: *m/z* 638.94 (Calculated 639.28 for **2-Cr^{III}-H⁺**).

Mn^{II}SO-MOF (remetallated). A stock solution of manganese acetate tetrahydrate (37 mg, 0.15 mmol) was prepared in dry, degassed methanol (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed **dSO-MOF** (5 mg, ~0.003 mmol salen), that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed methanol (1 mL) and Mn(OAc)₂·4H₂O (0.3 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with methanol (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF-MS: *m/z* 640.98 (Calculated 641.27 for **2-Mn^{III}**).

CoSO-MOF. A stock solution of anhydrous cobalt acetate (27 mg, 0.15 mmol) was prepared in dry, degassed methanol (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed **dSO-MOF** (5 mg, ~0.003 mmol salen), that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed methanol (1 mL) and Co(OAc)₂ (0.25 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with methanol (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF-MS: *m/z* 646.26 (Calculated 646.27 for **2-Co^{II}-H⁺**).

NiSO-MOF. A stock solution of nickel acetate hexahydrate (43 mg, 0.15 mmol) was prepared in dry, degassed methanol (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed **dSO-MOF** (5 mg, ~0.003 mmol salen), that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed methanol (1 mL) and Ni(OAc)₂·6H₂O (0.3 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with methanol (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF-MS: *m/z* 645.23 (Calculated 645.27 for **2-Ni^{II}-H⁺**).

CuSO-MOF. A stock solution of anhydrous copper chloride (100 mg, 0.74 mmol) was prepared in dry, degassed THF (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed **dSO-MOF** (5 mg, ~0.003 mmol salen), that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed THF (1 mL) and CuCl₂ (0.3 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with THF (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF-MS: *m/z* 650.29 (Calculated 650.27 for **2-Cu^{II}-H⁺**).

ZnSO-MOF. A stock solution of anhydrous zinc acetate (28 mg, 0.15 mmol) was prepared in dry, degassed methanol (10 mL). In a crimp-cap vial equipped with a Teflon-lined septum was placed **dSO-MOF** (5 mg, ~0.003 mmol salen), that had been pre-activated *via* heating to 80 °C under continuous vacuum overnight. Under N₂, dry, degassed methanol (1 mL) and Zn(OAc)₂ (0.3 mL of the aforementioned stock solution) were added to the **dSO-MOF** crystals. The resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) for 24 h. After decantation and rinsing with methanol (10 mL), the left-over crystals were then washed with methanol (30 mL) for 24 h *via* Soxhlet extraction and stored under DMF. MALDI-ToF-MS: *m/z* 650.93 (Calculated 651.27 for **2-Zn^{II}-H⁺**).

As reported above, our demetallation-remetallation strategy (Scheme 2 in the main text) takes advantage of the well-known fact that “empty” salen ligands readily undergo metalation. Evidence supporting this approach is provided by the mass spectrometric data shown in Figure 2 in the main text: when the ‘de-manganated’ material, **dSO-MOF** is dissolved and examined by mass spectrometry, we only observe the primary peak observed corresponds to the *unmetallated* dipyriddy salen strut; when the Co-remetallated material, **CoSO-MOF**, is subjected to the same analysis, we only see the Co-metallated dipyriddy salen strut and not the unmetallated one. Furthermore, while we observed a decrease in the Mn content of **dSO-MOF**, no decrease of the Zn content is observed via ICP-OES analysis,^{S1} implying that the overall

structure and corner-to-strut composition of the SO-MOF materials remains constant throughout the demetallation; this is also consistent with the PXRD data. Similarly, when the material is remetallated, mass spectrometric (Figure 2) and ICP-OES (Table 1) data are consistent with formation of the expected metallosalen complexes. It is unlikely that the observed MS peaks would be present if the proposed metallosalen complexes were not being formed.

IV. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC 1 interfaced with a PC using Star software. Samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. TGA curves for all materials are shown in Figure S1. The intermediate solvent content of **ZnSO-MOF** (between that for **dSO-MOF** and those for the metallated SO-MOFs) is consistent with the relatively low extent of remetallation (67%) observed for Zn (Table 1).

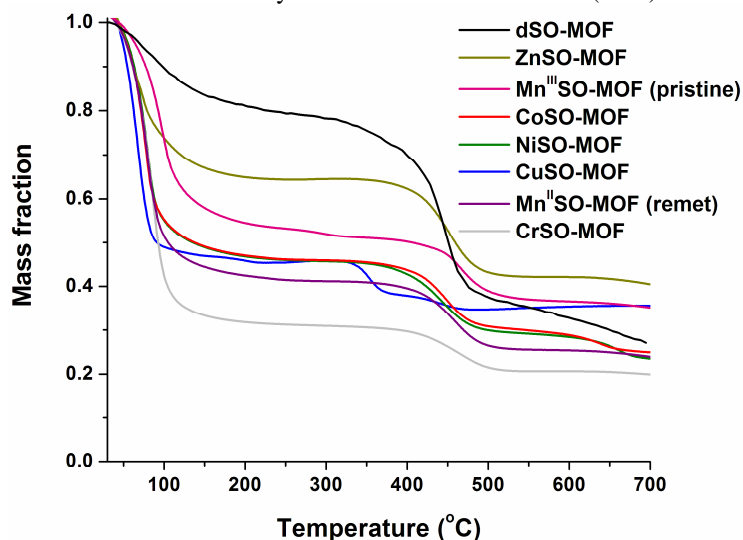


Figure S1. TGA data of the various SO-MOF materials.

V. Catalytic reactions

General procedure for the asymmetric epoxidation catalyzed by MnSO-MOF. To a 4-mL screw-thread vial equipped with a Teflon-lined cap were added a dichloromethane solution (1 mL of a 2.5 mM solution of substrate) containing 2,2-dimethyl-chromene (2.5×10^{-3} mol) and biphenyl (30.7 mg) as an internal standard. Crystals of either **Mn^{III}SO-MOF** (pristine) or **Mn^{II}SO-MOF** (remetallated) (2.5×10^{-7} mol, based on Mn(salen) strut) were placed in the vial, and the resulting mixture was placed on an orbital shaker (Thermolyne Maxi-Mix III) to mix the reaction. The oxidant, 2-(*tert*-butylsulfonyl)iodosylbenzene (45 mg, 1.3×10^{-4} mol), was added to the solution to start the reaction. This same quantity of oxidant was added 14 more times at 10-min intervals (total amount added = 680 mg, 2.0×10^{-3} mol). Aliquots (20 μ L) of the reaction mixture were taken periodically, filtered through a silica plug (0.5 cm \times 3 cm) and washed with dichloromethane (5 mL). The combined filtrate was analyzed by GC for yield and chiral GC for enantioselectivity.

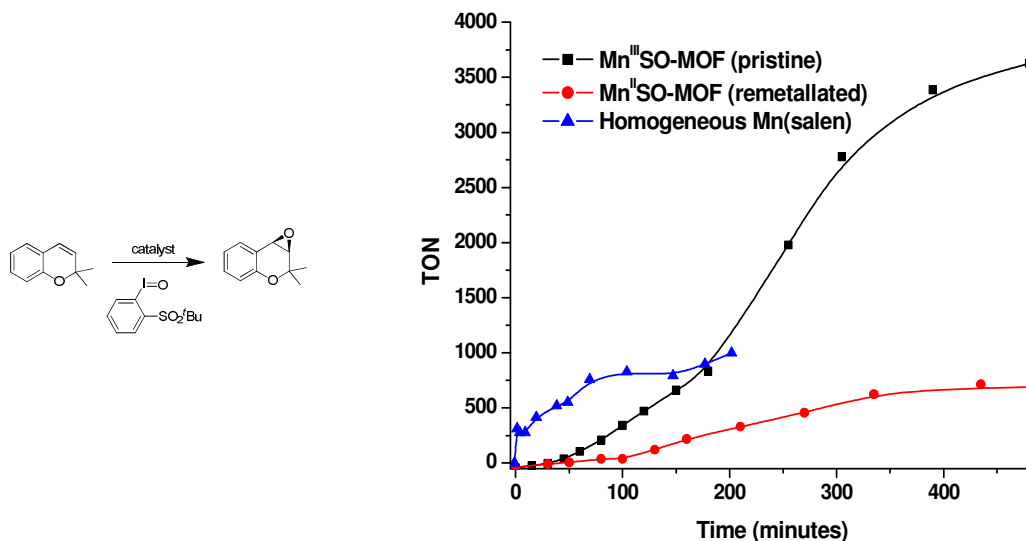


Figure S2. The epoxidation of 2,2-dimethylchromene by **Mn^{III}SO-MOF** (pristine) (data obtained from reference 8b in the main text), **Mn^{II}SO-MOF** (remetallated), and the homogeneous Mn(salen) complex **2-MnCl** (data obtained from reference 8a in the main text). All three datasets were obtained under identical conditions.

As should be clear in the synthesis described above in section III, we remetallated the **dSO-MOF** with Mn^{II} under anaerobic conditions, so we expect the remetallated **Mn^{II}SO-MOF** material to contain Mn^{II} (salen) as compared to the original Mn^{III} (salen)-containing **Mn^{III}SO-MOF** material. As discussed in the main text, Mn^{II} (salen) was classified by Kochi and coworkers as an inferior catalyst for olefin epoxidation compared to Mn^{III} (salen) (reference 21 in the main text) and that serves to partly explain the relatively poor catalytic activity we observed for **Mn^{II}SO-MOF** (Figure S2).

VI. Complete reference 6b in the main text

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VII. References

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