

Synthesis and Characterization of Metal–Organic Framework-74 Containing 2, 4, 6, 8, and 10 Different Metals

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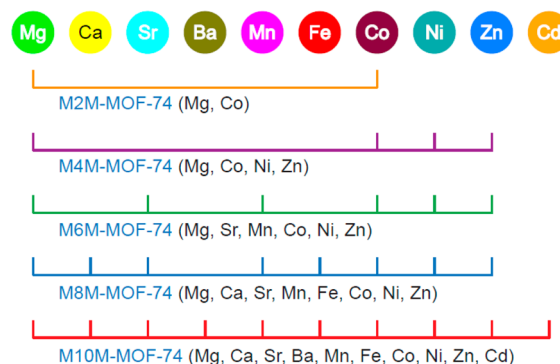
Supporting Information

ABSTRACT: Metal–organic frameworks (MOFs) containing more than two kinds of metal ions mixed in one secondary building unit are rare because the synthesis often yields mixed MOF phases rather than a pure phase of a mixed-metal MOF (MM-MOF). In this study, we use a one-pot reaction to make microcrystalline MOF-74 [M₂(DOT); DOT = dioxidoterephthalate] with 2 (Mg and Co), 4 (Mg, Co, Ni, and Zn), 6 (Mg, Sr, Mn, Co, Ni, and Zn), 8 (Mg, Ca, Sr, Mn, Fe, Co, Ni, and Zn), and 10 (Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, and Cd) different kinds of divalent metals. The powder X-ray diffraction patterns of MM-MOF-74 were identical with those of single-metal MOF-74, and no amorphous phases were found by scanning electron microscopy. The successful preparation of guest-free MM-MOF-74 samples was confirmed by N₂ adsorption measurements. Elemental analysis data also support the fact that all metal ions used in the MOF synthesis are incorporated within the same MOF-74 structure. Energy-dispersive X-ray spectroscopies indicate that metal ions are heterogeneously distributed within each of the crystalline particles. This approach is also employed to incorporate metal ions (i.e., Ca, Sr, Ba, and Cd) from which the parent MOF structure could not be made as a single-metal-containing MOF.

Metal–organic frameworks (MOFs) are well-known for the diversity in their chemical composition and connectivity of their underlying constituent organic and inorganic secondary building units (SBUs).¹ Progress in the field over the past decade has led to reports of >6000 unique MOF structures. The MOFs' interior can also be tailored by both pre- and postsynthetic functionalization of organic linkers, further expanding the scope of this chemistry.² Recently, we have reported the synthesis and characterization of a multivariate (MTV) MOF, where a MOF-5 framework was made with multiple organic functionalities.³ In this structure, up to eight organic functionalities are incorporated into MOF-5 without phase separation. Interestingly, these MOFs showed higher hydrogen and carbon dioxide uptake capacities compared with the unfunctionalized MOF-5.³ After the discovery of this unique phenomenon, we sought to extend the concept of MTV-MOFs to include the incorporation of several metal ions within one structure to make mixed-metal MOFs (MM-MOFs).⁴ Herein, we report the synthesis

and characterization of five isostructural, single-phase MOF-74 structures having 2 (Mg and Co), 4 (Mg, Co, Ni, and Zn), 6 (Mg, Sr, Mn, Co, Ni, and Zn), 8 (Mg, Ca, Sr, Mn, Fe, Co, Ni, and Zn), and 10 (Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, and Cd) divalent metals, respectively (Scheme 1). These materials

Scheme 1. Combination of Metal Ions Used To Synthesize MM-MOF-74



were characterized by powder X-ray diffraction (PXRD), inductively coupled plasma optical emission and energy-dispersive X-ray spectroscopies (ICP-OES and EDS), scanning electron microscopy (SEM), and N₂ adsorption measurements. The results demonstrate that MM-MOF-74, of varying metal composition containing up to 10 different metal ions, is obtained through a one-pot solvothermal reaction with good reproducibility and that this approach can be employed to incorporate metal ions (i.e., Ca, Sr, Ba, and Cd) from which the parent MOF structure remains unknown.

It is known that the equivalent Zn-MOF-74 [Zn₂(DOT); DOT = 2,5-dioxidoterephthalate]^{5,6} structure can be made using many different (but unmixed) divalent metal ions (M^{II} = Mg,^{7a} Ni,^{7b} Co,^{7c} Fe,^{7d} Mn,^{7e} and Cu^{7f}). The MOF-74 structure is composed of infinite rods M₃O₃(CO₂)₃ and DOT linkers, where each metal ion is coordinated to three carboxyl, two hydroxyl groups, and a coordinated ligand [*N,N*-dimethylformamide (DMF) or water].⁵ These characteristics provide evidence that MOF-74 is a logical system to expand the MTV concept of incorporating

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multiple metals, with a wide range of ionic radii sizes, within a single SBU of a pure phase of MOF-74.

Crystalline samples of the entire series of MM-MOF-74 (M2M-, M4M-, M6M-, M8M-, M10M-MOF-74, where the number indicates the number of metal ions incorporated into the respective MM-MOFs) were obtained through a solvothermal reaction. H_4DOT and selected metal salts (nitrate salts of Mg, Ca, Sr, Ba, Mn, Co, Ni, and Zn and acetate salts of Fe and Cd) were dissolved in a solvent mixture of DMF, ethanol, and water [10:0.6:0.6 (v/v/v)]. The solvent mixture was placed in a vial and heated at 120 °C for 20–24 h.^{8–10} M2M-, M4M-, and M6M-MOF-74 samples were obtained in the form of prismatic crystals, whose size ranged from 5 to 50 μm . M8M- and M10M-MOF-74 appeared in the form of submicrometer-sized particles.

Guest-free materials were prepared prior to the detailed characterization because any contamination by unreacted metal salts (residing in the pores) can affect the results of metal analysis. Therefore, the as-synthesized MM-MOF-74 materials were washed five times with 15 mL of DMF, exchanged 12 times with 15 mL of anhydrous methanol, and then evacuated at room temperature. Dried samples were then heated at 250 °C to remove coordinated methanol.¹¹ As discussed below, the porosity of these phases indicates the absence of any metal complexes in the pores.

The crystallinity of the MM-MOF-74 series was confirmed by PXRD analysis (Figure 1). All PXRD patterns of the MM-MOF-74

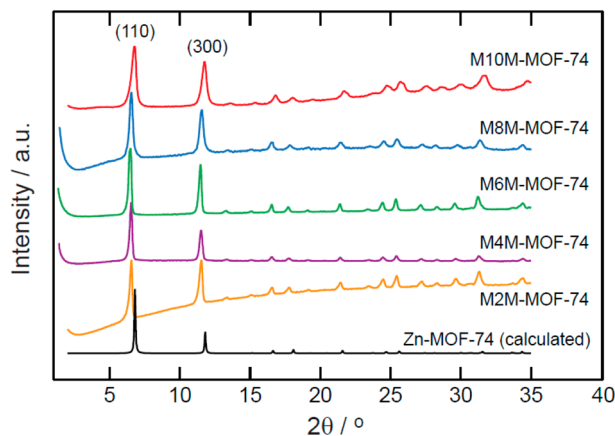


Figure 1. PXRD patterns of the series MM-MOF-74. As a reference, the calculated pattern of Zn-MOF-74 is overlaid.

series coincide with the calculated PXRD pattern of the parent MOF-74 structure, indicating that the topology is retained and thus all members are isostructural. To exclude the possibility of contamination by an amorphous phase in this sample, SEM observation was performed (Figures S1–S5 in the Supporting Information, SI). The SEM images of the MM-MOF-74 samples display homogeneous nanocrystallites aggregated in clusters with no other morphology present.¹²

The presence of guest molecules within the pores was also excluded by gas adsorption measurements. The porosity of the MM-MOF-74 materials was evaluated by N_2 adsorption at 77 K (Figure S11 in the SI). The profile of the N_2 isotherm for all activated MM-MOF-74 materials was classified as a typical Type-I isotherm, in which the Langmuir (Brunauer–Emmett–Teller) surface areas of M2M-, M4M-, M6M-, M8M-, and M10M-MOF-74 were calculated to be 1310 (1200), 1040 (900), 1240 (1100), 1210 (1070), and 1280 (1140) m^2/g , respectively. The surface area values for MM-MOF-74 are slightly lower than those for Mg-MOF-74 [1490 (1350) m^2/g] because it is 20–30% lighter

than MM-MOF-74. Nevertheless, the porosity measurement data clearly supports the fact that the MOF pores were successfully activated and guest molecules, including free metal ions, were removed.

The amounts of metals in the activated MM-MOF-74 materials were analyzed using ICP-OES.¹⁰ When the results were normalized to 1.00 for Mg, the average normalized metal ratio and corresponding standard deviations for M10M-MOF-74 were calculated to be the following: Mg, 1.00; Ca, 0.08 ± 0.02 ; Sr, 0.11 ± 0.01 ; Ba, 0.28 ± 0.04 ; Mn, 0.87 ± 0.06 ; Fe, 1.57 ± 0.34 ; Co, 1.01 ± 0.11 ; Ni, 1.05 ± 0.04 ; Zn, 0.74 ± 0.04 ; Cd, 0.73 ± 0.09 . The small standard deviations indicate that the synthesis of the MM-MOFs is reproducible. From the ICP-OES data, an empirical formula of the M10M-MOF-74 is described as $\text{Mg}_{0.269}\text{Ca}_{0.022}\text{Sr}_{0.030}\text{Ba}_{0.075}\text{Mn}_{0.234}\text{Fe}_{0.422}\text{Co}_{0.272}\text{Ni}_{0.282}\text{Zn}_{0.199}\text{Cd}_{0.196}(\text{DOT}) \cdot (\text{H}_2\text{O})_{7.8}$.¹³ As expected, ICP-OES data also demonstrate that M2M-, M4M-, M6M-, and M8M-MOF-74 samples contain all metal ions added to the reaction mixture (Table S1 in the SI). There is a trend that the observed amounts of Ca, Sr, and Ba ions are less than the other metal ions (Mg, Mn, Fe, Co, Ni, Zn, and Cd), although the starting molar ratio of the metal ions remained the same. This is most likely a result of Ca, Sr, and Ba ions being capable of easily taking the coordination number of eight rather than six. However, it is to be noted that the final molar ratio of the metal ions is affected by many factors, such as the reactivity, solubility, and coordination sphere of the metal ions and the pH of the reaction mixture.

The data presented above indicate that mixing different kinds of metal ions in a one-pot MOF synthesis can form MM-MOF-74. Considering that each metal ion should have different crystal growth rates, there is a possibility that metal ions are heterogeneously distributed in a microcrystalline sample, resulting in

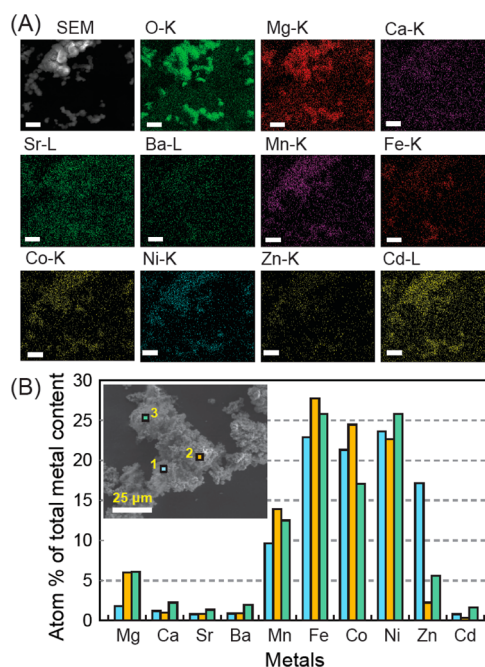


Figure 2. EDS analysis of M10M-MOF-74. (A) SEM image and EDS mapping of the same sample area, demonstrating the presence of oxygen and each of the 10 metals. Scale bar, 10 μm . (B) Ratio of metals found in three distinct regions of a different M10M-MOF-74 sample (indicated by different colors: blue, orange, and green). Inset: SEM image indicating the specific region in which EDS was collected to quantify the ratio of metals present.

deviation of the metal ratio in the microenvironment. To investigate the distribution of metal ions in micrometer resolution, SEM and EDS analyses were carried out using the M2M-, M4M-, M6M-, and M10M-MOF-74 samples.¹⁰ As an illustrative example, the mapping data for M10M-MOF-74 are shown in Figure 2A. EDS mapping of each element in a sample of M10M-MOF-74 shows that all metals are spread out within the area of the crystalline particles. This clearly demonstrates the presence of all 10 metals in the M10M-MOF-74 microcrystalline sample. The SEM image and EDS mapping of micrometer-sized crystal particles for M2M-, M4M-, and M6M-MOF-74 also show the presence of all expected metal ions,¹⁰ indicating that the samples are not a physical mixture of several different kinds of metal MOF-74 compounds.

To assess the metal distribution at the micrometer scale, EDS analysis of M10M-MOF-74 was performed on three distinct regions of the same sample (Figure 2B). The data show the presence of all 10 metals, and a nonnegligible degree of deviation was observed. Similar deviations were observed for other MM-MOF-74 samples.¹⁰ If each MM-MOF-74 crystal has the same homogeneous distribution of metals, then the EDS data would show similar metal values for several different regions or crystals of the materials. However, the EDS results implied a different scenario; it is highly likely that each MM-MOF-74 crystal contains all of the metals expected but with each crystal having a different distribution of the metals.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed synthetic procedures and characterization, SEM images, thermogravimetric curves, N₂ adsorption isotherms, EDS mapping data, and complete refs 6 and 9. 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.

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- (8) For example, M10M-MOF-74 was prepared by the following procedure: Equimolar amounts (ca. 4.5×10^{-5} mol) of 10 different divalent metal salts [Mg(NO₃)₂·6H₂O (11.6 mg), Ca(NO₃)₂·4H₂O (10.6 mg), Sr(NO₃)₂ (9.6 mg), Ba(NO₃)₂ (11.8 mg), Mn(NO₃)₂·4H₂O (11.3 mg), Fe(CO₂CH₃)₂ (7.9 mg), Co(NO₃)₂·6H₂O (13.2 mg), Ni(NO₃)₂·6H₂O (13.2 mg), Zn(NO₃)₂·6H₂O (13.4 mg), and Cd(CO₂CH₃)₂·6H₂O (12.0 mg)] were dissolved with H₄DOT (30 mg, 1.5×10^{-4} mol) in a 20-mL scintillation vial containing a solvent mixture of 10 mL of DMF, 0.6 mL of ethanol, and 0.6 mL of water. The vial was capped tightly and placed in an oven at 120 °C for 24 h to yield black microcrystalline powder.
- (9) Although all metals used in the synthesis were in the 2+ oxidation state, we cannot rule out the possibility that several metals were oxidized during the synthesis and have been incorporated into the structure with a higher oxidation state. Bloch, E. D.; et al. *J. Am. Chem. Soc.* **2011**, *133*, 14814–14822.
- (10) See the SI for descriptions of the synthesis, SEM images, thermogravimetric analysis, N₂ isotherms, and EDS mapping.
- (11) Methanol-exchanged M10M-MOF-74 was evacuated (100–200 mTorr) at room temperature for 12 h and then heated at a constant rate of 4 °C/min to 250 °C for 10 h in a stepwise fashion (100 °C for 1 h, 150 °C for 1 h, and 200 °C for 1 h) under a vacuum (30 mTorr).
- (12) SEM observations indicate that the particle sizes of M6M-, M8M-, and M10M-MOF-74 are smaller than those of M2M- and M4M-MOF-74. M6M-, M8M-, and M10M-MOF-74 contain metal ions that can have a coordination number of eight, which may hinder these metal ions' ability to react readily during formation of the MM-MOF-74 structure. This is in sharp contrast to M4M-MOF-74, where such metals are not included in the synthesis. It is thus implied that the lowered crystallinity is caused by the presence of these metal ions rather than by the simple incorporation of many different types of metal ions into the MOF structure.
- (13) Elem anal. Calcd: C, 20.93; H, 3.86; N, 0.00. Found: C, 21.41; H, 3.67; N, <0.1.