

Isolation and Studies of Oxo-heme Complexes in Metal-Organic Frameworks

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Postsynthetic metal exchange has become a powerful tool to construct metal-organic frameworks (MOFs) that are not amenable to direct synthesis. MOFs synthesized via postsynthetic metal exchange have shown exotic coordination geometries for activating small gas molecules.

However, one frequently-observed limitation is their slow reaction kinetics. Some of the metal exchange reactions require several weeks to a year to reach thermodynamic

equilibrium, and only a fraction of the native metal was replaced in many cases. Therefore, developing methods to

accelerate metal-exchange and boost completeness are highly-desirable.

We developed a method that can accelerate metal exchange by over 2000-fold through harnessing the structural dynamics of a 2D manganese-benzoquinoid MOF.¹ This represents the most effective method to accelerate metal exchange to date.

We first investigated the metal exchange using fully-solvated crystals of $(\text{Et}_4\text{N})_2[\text{Mn}_2(\text{L})_3]$ (**1**), which was prepared using solvothermal method (Fig 1a). Soaking **1** in a DMF solution of Co^{2+} or Zn^{2+} leads to complete (for Co) or partial (57% for Zn) metal-exchanged MOFs featuring $[\text{M}^{\text{II}}(\text{DMF})_6]^{2+}$ ($\text{M} = \text{Co}, \text{Zn}$) as oppose to $(\text{Et}_4\text{N})^+$ counterion to balance the charge (Figure 1b). To achieve 50% metal exchange, the reaction takes 98 (for Co) and 79 (for Zn) hours. This $[\text{M}^{\text{II}}(\text{DMF})_6]^{2+}$ counterion can be readily exchanged with $(\text{Et}_4\text{N})^+$ by soaking in its chloride salt solution.

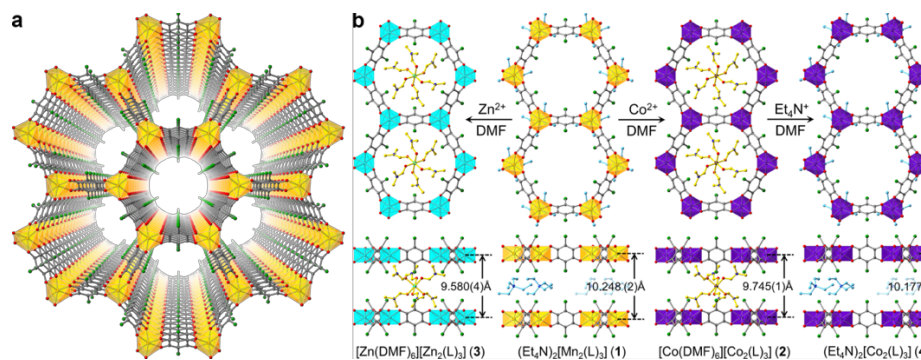


Figure 1. (a) Crystal structure of **1** highlighting the hexagonal channels along c direction. $(\text{Et}_4\text{N})^+$ Counterion is omitted for clarity. (b) A scheme showing the single-crystal-to-single-crystal conversions between **1–4** via metal and counterion exchanges. Views shown on top depicts structures in ab planes; views shown on bottom depicts stacked two layers of honeycombs.

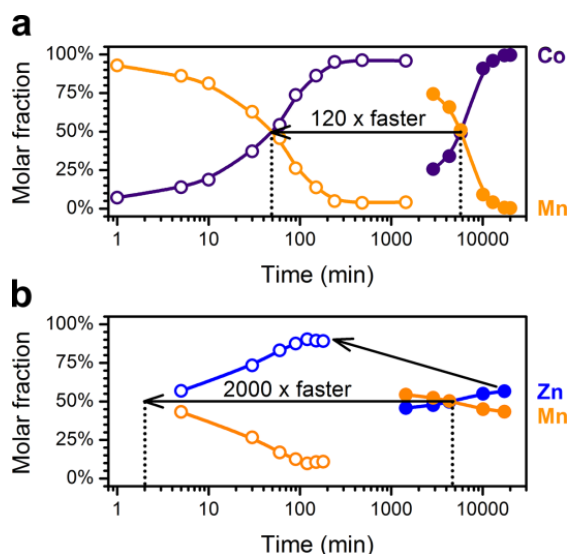


Figure 2. Metal exchange monitored by *ex situ* ICP-OES.

According to the single-crystal structures, the bulkiness of the $[M^{II}(\text{DMF})_6]^{2+}$ relative to the diameter of the 1D channel within the MOFs suggests the metal exchange might be kinetically hindered caused by the diffusion barrier along this channel. To verify this hypothesis, we prepared a partially metal-exchanged MOF for EDS analysis. A fully solvated sample of **1** was soaked Co^{2+} solution for 120 hours followed by counterion exchange with $(\text{Et}_4\text{N})^+$. This MOF has a formula of $(\text{Et}_4\text{N})_2[\text{Mn}_{1.38}\text{Co}_{0.62}(\text{L})_3]$. Both EDS mapping and a line scan along c direction indicate gradual radial distributions of the two metals to form a sandwich-like structure. A line scan within ab plane suggests a homogenous distribution of the two metals. These findings unequivocally confirmed our hypothesis.

We discovered that **1**, upon desolvation or resolvation, undergoes a fully-reversible phase change. A 20% volume change is associated with this structure dynamics. Since the volume expansion upon resolvation must incur rapid adsorption of solvent molecules towards the interior, we sought to utilize this dynamic structural behavior to accelerate metal exchange.

Indeed, when we soak partially-desolvated crystals of **1** directly to a metal solution, we observed a drastic acceleration by 120 times and over 2000 times for Co and Zn, respectively (**Fig 2**). Moreover, it boosted the degree of metal exchange for zinc from 57% to 89%. In addition, this method produced the phase-pure $[\text{Co}(\text{DMF})_6][\text{Co}_2\text{L}_3]$, which is otherwise produced with an impurity from fully-solvated **1**.

Support from the PRF has had a profound impact on my career and the careers of my students. This was one of the very first grants I received as an assistant professor, and this funding allowed my group to carry out work that we otherwise would not have been able to do. In addition to resulting in publications, which have helped my students graduate and obtain jobs, we have leveraged work stemming from this grant to obtain additional external and renewable grants. My students and I are very grateful for the investment the donors of the ACS PRF has made on our careers.

ⁱ Liu, L.; Li, L.; DeGayner, J. A.; Winegar, P. H.; Fang, Y.; Harris, T. D. "Harnessing Structural Dynamics in a 2D Manganese-Benzoquinoid Framework to Dramatically Accelerate Metal Transport in Diffusion-Limited Metal Exchange Reactions" *J. Am. Chem. Soc.* **2018**, *140*, 11444-11453.