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# A Nanoporous Ag−Fe Mixed-Metal−Organic Framework Exhibiting Single-Crystal-to-Single-Crystal Transformations upon Guest Exchange

**Yixun Zhang, Banglin Chen,[†] Frank R. Fronczek, and Andrew W. Maverick***

*Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803*

The reaction of solutions of $Fe(Pyac)_3$ [PyacH = 3-(4-pyridyl)-2,4-pentanedione] and $AgNO_3$ produces two types of porous mixed-metal−organic frameworks (M′MOFs). With lower $AgNO_3$ concentrations, the product (**M′MOF1**) has a 2D honeycomb structure with Ag:Fe = 1:1 and pores of ca. 12 × 16 Å. When a higher concentration of $AgNO_3$ is employed, however, the product (**M′MOF2**) has Ag:Fe = 3:2 and a porous 1D ladder structure. A variety of nonpolar solvents serve as guests in **M′MOF2**: with 1,2-$C_6H_4Cl_2$, $[AgNO_3]_3[Fe(Pyac)_3]_2(1,2-C_6H_4Cl_2)_{5.5}$ (**M′MOF2a**); with $C_6H_5Br$, $[AgNO_3]_3[Fe(Pyac)_3]_2(C_6H_5Br)_6$ (**M′MOF2b**). M′MOFs **2a** and **2b** can be interconverted by treatment with the appropriate solvent, in *single-crystal-to-single-crystal transformations.*

Porous metal−organic frameworks (MOFs) that are stable upon guest removal and exchange are being studied for a variety of applications.[1] The most stable of such frameworks retain their crystallinity upon guest exchange, as demonstrated by single-crystal X-ray analysis.[2,3] The majority of these robust MOFs are three-dimensional (3D) networks linked by coordination bonds; only a few are based on one-dimensional (1D) frameworks.[3]

Recently, we have applied the emerging preconstructed building block approach[4] to the syntheses of porous mixed-metal−organic frameworks (M′MOFs).[5,6] For example, we have successfully incorporated $Cu(Pyac)_2$ {bis-[3-(4-pyridyl)pentane-2,4-dionato]copper(II)} into porous Cd−Cu M′MOFs that contain unsaturated metal sites in their pores.[5b] However, their 1D and two-dimensional (2D) networks are not stable under guest/solvent exchange. Herein we report the syntheses and crystal structures of two different M′MOFs by the reaction of the tridentate preconstructed building block $Fe(Pyac)_3$ with $AgNO_3$.[7] The new M′MOFs have Ag:Fe ratios of 1:1 (**M′MOF1**, $[AgNO_3][Fe(Pyac)_3](G)_m$, with a 2D trigonal grid structure) and 3:2 (**M′MOF2**, $[AgNO_3]_3[Fe(Pyac)_3]_2(G)_n$, with a 1D ladder structure). Surprisingly, the 1D **M′MOF2**, reinforced by weak Ag···Ag and Ag−nitrate−Ag interactions, is robust and exhibits reversible single-crystal-to-single-crystal transformations upon guest exchange. Also, although M′MOFs **2a** and **2b** contain the same framework, they have slightly different crystal symmetry and their channels have different shapes. This indicates that the framework is not only sufficiently robust to withstand guest exchange but also flexible enough to accommodate variations in guest size and packing.

Domasevitch et al. found that $Fe(Pyac)_3$ shows a substantial deviation from regular trigonal symmetry in the solid state (N···Fe···N 71.7, 135.3, 152.9°). In coordination assemblies of $Fe(Pyac)_3$ with metal ions such as $Cd^{2+}$, they found a similarly wide range of N···Fe···N angles.[6b] We were interested in M′MOFs constructed from $Fe(Pyac)_3$ because of this compatibility with a variety of site symmetries.

* To whom correspondence should be addressed. E-mail: maverick@lsu.edu.
† Present address: Department of Chemistry, The University of Texas-Pan American, Edinburg, TX 78541.

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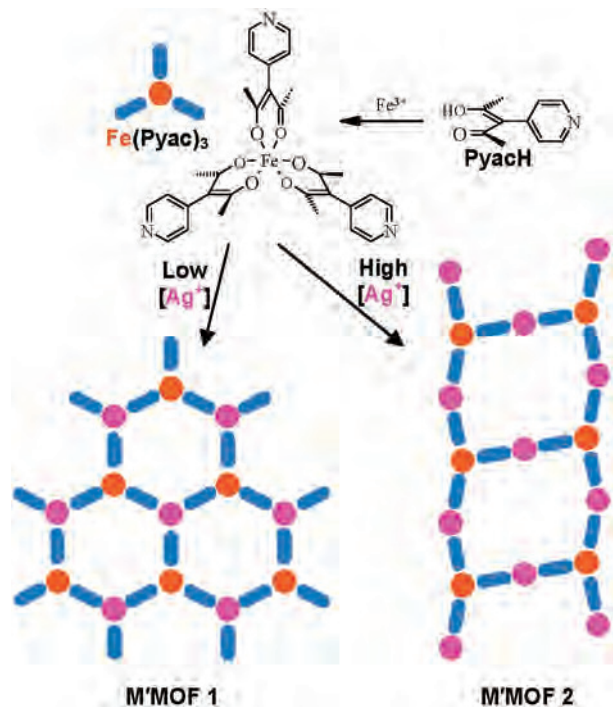
**Figure 1.** Reaction of the trigonal building block Fe(Pyac)$_3$ with Ag$^+$ produces two frameworks: 2D honeycomb **M′MOF1** and 1D ladder **M′MOF2**.



**Figure 2.** Portion of one 2D layer in the crystal structure of **M′MOF1**, [AgNO$_3$][Fe(Pyac)$_3$](CH$_3$CN)$_2$(1,2-C$_6$H$_4$Cl$_2$)$_2$. H atoms are omitted for clarity.
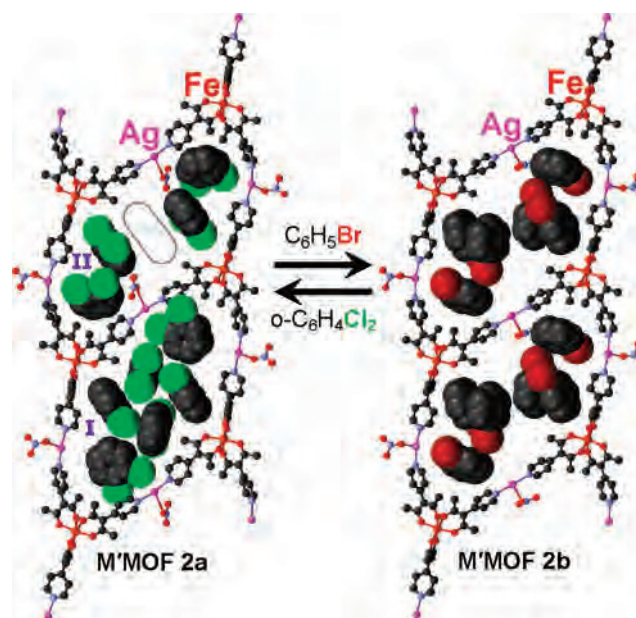


**Figure 3.** Crystal structures of **M′MOF2a**, [AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$(1,2-C$_6$H$_4$Cl$_2$)$_{5.5}$, and **M′MOF2b**, [AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$(C$_6$H$_5$Br)$_6$, and reactions representing their single-crystal-to-single-crystal transformation. H atoms and minor components of disordered guest molecules are omitted for clarity. The gray oval in **M′MOF2a** shows the location of the disordered fifth guest molecule in pore **II**.

We prepared the two new M′MOFs[8] by the reaction of solutions of Fe(Pyac)$_3$ (in nonpolar organic solvents) and AgNO$_3$ (in a small amount of CH$_3$CN), as shown schematically in Figure 1.

Figure 2 shows a portion of one 2D layer from the crystal structure of **M′MOF1**. The pores in this structure are approximately hexagonal in shape, ca. 11.7 × 16.0 Å.

Crystals of **M′MOF1** become opaque within a few minutes when they are immersed in other solvents. This indicates that the lattice is not stable under solvent (guest) exchange. However, the second type of framework is much more robust: **M′MOF2** ([AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$(G)$_n$), with Ag:Fe = 3:2, forms when a higher concentration of Ag$^+$ is used. It crystallizes with a variety of guest molecules; the products with 1,2-dichlorobenzene (**M′MOF2a**) and bromobenzene (**M′MOF2b**) are discussed in detail here.

In the **M′MOF2** structure (see Figures 1 and 3), AgNO$_3$ nodes are bridged by tridentate Fe(Pyac)$_3$ building blocks to form a 1D porous ladder with Fe···Fe distances of ca. 19 Å.

When the Fe(Pyac)$_3$ reactant is dissolved in 1,2-C$_6$H$_4$Cl$_2$, the product is **M′MOF2a**, [AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$(1,2-C$_6$H$_4$-

(8) Crystal data for **M′MOF1**: [AgNO$_3$][C$_{30}$H$_{30}$FeN$_3$O$_6$](C$_6$H$_4$Cl$_2$)$_2$(CH$_3$CN)$_2$, $M$ = 1130.39, $T$ = 100 K, triclinic, $P\bar{1}$, $a$ = 10.474(2) Å, $b$ = 15.215(3) Å, $c$ = 17.051(4) Å, $\alpha$ = 109.691(10)°, $\beta$ = 98.453(10)°, $\gamma$ = 90.388(12)°, $V$ = 2526.0(9) Å$^3$, $Z$ = 2, $D_c$ = 1.486 g cm$^{-3}$, $\mu$ = 0.944 mm$^{-1}$, $R1$ [$I >$ 2$\sigma(I)$] = 0.068, $wR2$ (all data) = 0.196. Crystal data for **M′MOF2a**: [AgNO$_3$]$_3$[C$_{30}$H$_{30}$FeN$_3$O$_6$]$_2$(C$_6$H$_4$Cl$_2$)$_{5.5}$, $M$ = 2487.00, $T$ = 100 K, triclinic, $P\bar{1}$, $a$ = 7.606(2) Å, $b$ = 22.397(6) Å, $c$ = 31.296(11) Å, $\alpha$ = 83.892(10)°, $\beta$ = 85.753(11)°, $\gamma$ = 82.90(2)°, $V$ = 5250(3) Å$^3$, $Z$ = 2, $D_c$ = 1.583 g cm$^{-3}$, $\mu$ = 1.171 mm$^{-1}$, $R1$ [$I >$ 2$\sigma(I)$] = 0.111, $wR2$ (all data) = 0.346. Crystal data for **M′MOF2b**: [AgNO$_3$]$_3$[C$_{30}$H$_{30}$FeN$_3$O$_6$]$_2$(C$_6$H$_5$Br)$_6$, $M$ = 2620.54, $T$ = 110 K, triclinic, $P\bar{1}$, $a$ = 7.788(4) Å, $b$ = 15.728(9) Å, $c$ = 22.439(15) Å, $\alpha$ = 94.37(3)°, $\beta$ = 95.32(3)°, $\gamma$ = 100.51(2)°, $V$ = 2679(3) Å$^3$, $Z$ = 1, $D_c$ = 1.625 g cm$^{-3}$, $\mu$ = 3.109 mm$^{-1}$, $R1$ [$I >$ 2$\sigma(I)$] = 0.139, $wR2$ (all data) = 0.382.

Cl$_2$)$_{5.5}$. In this structure, the Fe···Fe distances are 19.50 Å (across the "rungs" of the ladder) and 18.35 and 19.01 Å (along the "uprights"). This framework encloses two crystallographically independent, centrosymmetric pores, labeled **I** and **II** in Figure 3, with cross-sectional areas of ca. 189 and 154 Å$^2$, respectively.[9] The larger pores (**I**) accommodate six guest molecules, and the smaller pores (**II**) five, for a total of 5.5 guest molecules per [AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$ formula unit. These 1D ladders are further interconnected

(9) The areas of the pores in these structures were estimated by using graphical space-filling models generated by the program *Mercury* (version 1.4.1, Cambridge Crystallographic Data Centre, Cambridge, U.K., 2005; http://www.ccdc.cam.ac.uk/mercury/), with the view perpendicular to the least-squares plane of the 1D ladder framework. The "slice" feature of this program was also used to estimate the perpendicular distances between adjacent layers.
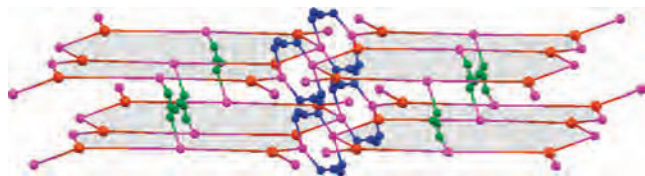
**Figure 4.** Schematic illustration of the structure of **M′MOF2a**, showing only Ag, Fe, and nitrates. Pores within the 1D ladders are shaded for clarity. Nitrate ions joining one 1D ladder to the next one in the same layer are shown in blue, and those joining one layer to the next in green.

by weak Ag···Ag interactions (3.29 Å) and accompanying bridging nitrate anions (Ag−O 2.61 and 2.72 Å) to form infinite 2D sheets that are separated by ca. 5.9 Å; see Figure 4. Also, the "rung" Ag atoms in adjacent 2D layers are linked by nitrate ions (Ag···O−N−O···Ag 7.61 Å; also shown in Figure 4) to produce an overall 3D network. In this nanoporous Ag−Fe M′MOF (**2a**), 43.1% of the volume is "solvent-accessible".[10]

When the Fe(Pyac)$_3$ reactant is dissolved in bromobenzene instead, the product is [AgNO$_3$]$_3$[Fe(Pyac)$_3$]$_2$(C$_6$H$_5$Br)$_6$, **M′MOF2b** (Figure 3). The structure of **2b** is similar to that of **2a**, with Fe···Fe distances of 19.53 Å (rung) and 18.78 Å (edge), except that all pores in **2b** have the same dimensions and contain six bromobenzene guest molecules. Contacts between the 1D ladders are Ag···Ag (3.25 Å) and Ag−O (2.57 and 2.77 Å). In **2b**, the interlayer separation is ca. 5.7 Å (with Ag···O−N−O···Ag 7.79 Å) and 43.6% of the volume is "solvent-accessible".

M′MOFs **2a** and **2b** can also be prepared when methanol is used as the solvent for AgNO$_3$ (rather than CH$_3$CN), though in lower yield. Details of this preparation are available as Supporting Information.

The ladder-type M′MOFs **2a** and **2b** are soluble in CH$_3$CN, *N,N*-dimethylformamide, and dimethyl sulfoxide, and cannot be recovered from their solutions easily; this indicates that the framework dissociates in these coordinating solvents. This was surprising at first because CH$_3$CN is used as a solvent in the synthesis of **2a** and **2b**. However, it is only a minor fraction of the synthesis solvent mixture; see the Supporting Information for details. In contrast, crystals of **2a** and **2b** are insoluble and remain transparent in noncoordinating solvents such as diethyl ether, C$_6$H$_6$, chlorobenzene, and 1,2-dichlorobenzene. This observation led us to examine the

possibility of guest exchange reactions in these solvents by single-crystal diffraction studies. We find that **2a** and **2b** can be interconverted in single-crystal-to-single-crystal transformations, as illustrated in Figure 3.

As an example of these interconversions, we prepared crystalline **M′MOF2a** directly from Fe(Pyac)$_3$ in a 1,2-dichlorobenzene solution. We chose one single crystal of **2a** from this batch, converted it into **2b** by immersion in bromobenzene, and then converted it back to **2a** by immersion in 1,2-dichlorobenzene again. The transformations were essentially complete in 24 h in both directions, as judged by the successful solution of structures **2a**, **2b**, and **2a** again (after both exchange processes) on the same single crystal, including resolved solvent/guest molecules. This experiment clearly establishes that the nanoporous Ag−Fe **M′MOF2** is robust upon solvent exchange. In other words, **M′MOF2** retains its framework connectivity despite the fact that the different guests lead to noticeable changes in the pore geometry and symmetry, Fe···Fe and Ag···Ag distances, and interlayer separations.

Compounds **2a** and **2b** are unusual examples in which shorter- and longer-range Ag···Ag interactions[11] serve to connect 1D units in the second and third dimensions. These interactions may contribute to the stability of the lattice under guest exchange. Taking advantage of the richness of the preconstructed building block approach and interactions such as Ag···Ag, we expect that a variety of porous M′MOFs will be possible. We are now studying the range of guest molecules that can be accommodated within the framework of **M′MOF2** and exploring the potential applications of these M′MOFs in sensors, gas storage, and catalysis.

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