

Communication

An Exceptionally Stable Metal-Organic Framework Constructed from Chelate-based Metal-Organic Polyhedra

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Supporting Information Placeholder

ABSTRACT: We report the rational design and synthesis of a water-stable metal-organic framework (MOF), Fe-HAF-1, constructed from supramolecular, Fe3+-hydroxamate-based polyhedra with mononuclear metal nodes. Owing to its chelatebased construction, Fe-HAF-1 displays exceptional chemical stability in organic and aqueous solvents over a wide pH range (pH 1-14), including in the presence of 5 M NaOH. Despite the charge-neutrality of the Fe3+-tris(hydroxamate) centers, Fe-HAF-1 crystals are negatively charged above pH 4. This unexpected property is attributed to the formation of defects during crystallization that results in uncoordinated hydroxamate ligands or hydroxide-coordinated Fe centers. The anionic nature of Fe-HAF-1 crystals enables selective adsorption of positively charged ions in aqueous solution, resulting in efficient separation of organic dyes and other charged species in a size-selective fashion. Fe-HAF-1 presents a new addition to a small group of chelatebased MOFs and provides a rare framework whose 3D connectivity is exclusively formed by metal-hydroxamate coordination.

Metal-organic frameworks (MOFs) are a class of porous, crystalline materials¹⁻³ with many potential applications in catalysis,⁴⁻⁹ gas storage,¹⁰⁻¹¹ drug delivery,¹²⁻¹³ molecular separation,¹⁴⁻¹⁷ and molecular sensing.¹⁸⁻¹⁹ MOFs are comprised of metal nodes and bridging organic ligands that form highly ordered structures.²⁰⁻²¹ Each node is comprised commonly of polynuclear clusters of metal atoms, also known as secondary building units (SBUs). The introduction of the SBU concept has allowed access to diverse node geometries, ultimately leading to MOFs with greater structural complexity.²² Early SBUs were primarily composed of divalent transition metals (Zn²⁺ or Cu²⁺) and carboxylate groups.²³⁻²⁴ The metal-ligand bonds in these nodes are relatively weak and prone to hydrolysis in aqueous conditions.¹ Infiltration of water molecules into the SBUs of these MOFs undermines the structural integrity of the materials, eventually leading to collapse of the crystalline framework. One successful approach to improve the aqueous stability of the framework is to selectively design nodes with stronger metalligand bonds.25

> Chelating ligands, such as catecholates and hydroxamates, are well known for their ability to form strong bonds with a wide

range of metals.²⁶ These functional groups are found in siderophores, which are small organic molecules produced by bacteria to scavenge metal ions, most notably Fe^{3+} , with remarkable affinities.²⁷⁻²⁸ Hydroxamates are an attractive chelating group for the synthesis of extended structures since they are rotationally flexible and sterically unencumbered with a coordination footprint similar to commonly used carboxylates.

A previous example of a hydroxamate-containing MOF was reported by Farha and Hupp, whereby 1,4-benzenedihydroxamic acid (p-H₂bdh) was incorporated into a Zr-based MOF (UiO-66) via postsynthetic exchange,²⁹ with the resulting framework stable under alkaline conditions. Recently, Martí-Gastaldo reported a Tip-H₂bdh-based MOF, MUV-11, prepared by direct synthesis.³⁰ However, the hydroxamate-mediated connectivity of this framework only extended in two dimensions. Indeed, most MOFs containing chelating motifs, such as those based on catechol groups, form either 2D sheets connected by noncovalent interactions (π - π stacking or H-bonding) or employ monodentate ligands to facilitate connectivity in the third dimension.³¹⁻³⁴ A rare exception was provided by protein-MOFs in which p-H₂bdh linkers were employed to link spherical ferritin molecules into porous, crystalline 3D lattices.³⁵⁻³⁶ In comparison to extended 3D frameworks, chelate-based ligands are more prevalent in metalorganic polyhedra (MOPs).³⁷⁻³⁹ In fact, MOPs have been previously used as building blocks (or SBUs) for construction of MOFs with diverse structures and properties.⁴⁰ In this work, we employed this strategy to generate the first example of a 3D Fehydroxamate framework, namely Fe-HAF-1. Inspiration for the chelate-based SBU was derived from a tetrahedral M4L6 coordination cluster reported by Raymond.³⁹ This cluster was based on the isophthal-di-N-(4-methylphenyl)hydroxamic acid as the linker and Fe³⁺/Ga³⁺ as the metal node, with four dimethylformamide (DMF) molecules partially filling the rigid cavity. This design successfully demonstrated that a combination of a three-fold symmetry at a pseudo-octahedral metal center with a rigid linker containing two-fold symmetry can create a symmetry-driven tetrahedral cluster.39

We prepared a nearly identical cluster by combining *m*benzenedihydroxamic acid (m-H₂bdh) and FeCl₃ in DMF at room temperature (Figure 1). *m*-H₂bdh lacks the *N*-toluyl groups used in the previously reported ligand,³⁹ forming the desired cluster with reduced steric bulk. Fe₄(*m*-bdh)₆ clusters crystallized readily into a lattice with *P*2₁3 symmetry. As expected, each Fe-

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tris(hydroxamate) center formed a C₃ vertex of the discrete cluster. Because each metal center is chiral, each discrete cluster can have T ($\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda$), C_3 ($\Delta\Delta\Delta\Lambda$ or $\Lambda\Lambda\Lambda\Delta$), or S₄ ($\Delta\Delta\Lambda\Lambda$) symmetry in solution. Each unit cell is comprised of eight clusters with T symmetry (four $\Delta\Delta\Delta\Delta$ and four $\Lambda\Lambda\Lambda\Lambda$). On average, the Fe-carbonyl and Fe-hydroxyl bond lengths are 2.05 Å and 1.98 Å, respectively. The clusters in this crystal lattice are held together by a series of H-bonding and π - π stacking interactions (Figure S3). Each cluster has an interior cavity that is ca. 7.5 Å in diameter (Figure 1).



Figure 1. Ball-and-stick representation of a single discrete cluster of Δ -Fe₄(*m*-bdh)₆. The blue sphere highlights the central cavity of the cluster. Gray, red, blue, white, and orange spheres represent C, O, N, H, and Fe atoms, respectively.

To connect $Fe_4(m-bdh)_6$ clusters into an extended 3D framework (Fe-HAF-1), we synthesized a linear dimer of m-H₂bdh, biphenyl tetrahydroxamic acid (H₄BPTH) (Figure 2a). Reaction of the H₄BPTH linker with FeCl₃ in a solution of N,Ndiethylformamide (DEF) and 1,4-dioxane at 70 °C for 24 h vielded a dark-red microcrystalline powder of Fe-HAF-1, which consisted of 4-6 µm cube-shaped particles (Figure S4). Powder Xray diffraction (PXRD) measurements indicated a face-centered cubic lattice with a = 34.566 Å (Figure 2b). Through slow temperature-ramping and -cooling steps during synthesis, we obtained ca. 100-µm-sized crystals that were suitable for singlecrystal X-ray diffraction (sc-XRD). Much like the microcrystalline powder, these crystals all exhibit a cubic morphology (Figure S5) with a chiral lattice (F432), in which each tetrahedral, hydroxamate-based SBU is connected to six adjacent SBUs through the bridging ligand. The pores that form between individual clusters are approximately 16 Å in diameter (Figure 2c), with 8 Å apertures. Each cluster maintains a cavity with a 7.5 Å diameter. The topology of Fe-HAF-1 is twisted boracite (tbo), with the underlying net consisting of C_3 vertices at each metal and C_4 vertices at each ligand, yielding a similar lattice architecture as the canonical Cu-based MOF, HKUST-1.41 The phenyl-phenyl dihedral angle is 20.4°, which is similar to other MOFs (such as UiO-67) containing biphenyl bridging ligands.⁴² Unlike the discrete $Fe_4(m-bdh)_6$ cluster, which possesses T, C₃, or S_4 symmetry in solution and exists as a racemic mixture of Δ and Λ in the crystal lattice, the linker connectivity in Fe-HAF-1 leads to enantiopure (either Δ or Λ) crystals. Because there is no preference for either Δ or Λ during MOF synthesis, the bulk sample exists as a racemic mixture.

The thermal stability of Fe-HAF-1 was evaluated by thermogravimetric analysis (TGA). The TGA curves displayed no significant weight loss up to 120 °C (Figure S6). Despite the

calculated accessible surface area of 2160 m²/g, the N₂ adsorption isotherm at 77 K for the Fe-HAF-1 revealed no significant gas uptake (BET <10 m² g⁻¹); similar results were reported with a 3D Fe-catecholate framework (Fe-CAT-5).³⁴ We ascribe the low N₂ adsorption uptake to DEF molecules retained in the pores as well as within the individual tetrahedral SBUs (Figure S12). Conventional activation protocols led to the structural collapse of Fe-HAF-1 upon evacuation of solvent molecules (SI Methods).

The ability of MOFs to resist degradation under harsh chemical conditions is directly linked to the strength of the metal-ligand bonds at their nodes.²⁵ In particular, hard, carboxylate-based linkers are known to give rise to a wide variety of stable frameworks43 with hard, high-valent metal ions, including MIL-53 (Cr3+), MIL-100 (Fe3+), and UiO-66 (Zr4+).44-46 Accordingly, we expected that Fe-HAF-1 would also exhibit high chemical stability, which could be further bolstered by the chelating nature of the hydroxamate ligands. As shown in Figure 3a, Fe-HAF-1 retained its crystallinity under both highly acidic (pH 1) and highly basic conditions (5 M NaOH), which compares favorably to the very stable carboxylate-based MOFs, such as UiO-66 (Figure S10)⁴⁷ and the highly alkaline-stable frameworks, ZIF-8, PCN-601, and ZrPP-1.48 In addition to providing excellent aqueous stability, the strong bonds of the chelate-based node also resist decomposition across a range of coordinating solvents, such as carboxylic acids and amines as well as other common organic solvents (Figure 3b). To further confirm the structural integrity of the frameworks, we analyzed the samples by scanning electron microscopy (SEM) after incubation under different conditions. SEM images indicated that Fe-HAF-1 maintained its cubic morphology in all cases (Figure S11). Our findings illustrate that it is possible to attain very high chemical stability in a porous framework even with mononuclear metal nodes.



Figure 2. (a) The chemical structure of H_4BPTH . (b) PXRD pattern for Fe-HAF-1 is consistent with a face-centered cubic lattice. (c) The unit cell of the Fe-HAF-1. The internal pore is highlighted by a yellow sphere (16 Å), and the cavity of the cluster is highlighted with a blue sphere (7.5 Å). (d) A representation of the 3D network of Fe-HAF-1.

Interestingly, despite an expected neutral charge based on its composition, we observed that Fe-HAF-1 behaved as an ionic MOF. Zeta potential measurements (Figure S7) indicated that Fe-HAF-1 was highly negatively charged above a pH of 4. We attribute this property to the formation of defects⁴⁹ during

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synthesis (owing to the highly chelating nature of the BPTH linker), which likely results in free hydroxamate groups or Fe³⁺ centers with hydroxide ligands.⁵⁰ Notably, although the pK_a of the free hydroxamic acid is >8.5, polyhydroxamic acid polymers were previously shown to display negative zeta potentials above pH

 $3.8.^{51}$ Further implicating the formation of defects, FTIR spectra of Fe-HAF-1 displayed O–H stretching vibrations as a broad peak at 3180 cm⁻¹ similar to the



Figure 3. PXRD patterns of Fe-HAF-1 after exposure to (a) aqueous solutions at different pH and (b) different organic solvents for one week. All organic solvents were neat except for ammonium hydroxide (50% v/v). The simulated pattern was calculated using Λ -Fe-HAF-1.

H₄BPTH linker (Figure S8), consistent with the presence of free hydroxamic acid groups.⁵² The possibility of mixed-valence Feclusters (i.e., the presence of Fe²⁺ species), which could also give rise to an overall negative charge, was ruled out by X-ray photoelectron spectroscopy (XPS) measurements (Figure S9).⁵³

Ionic MOFs have been explored as platforms for selective uptake of organic dyes.54-63 To evaluate the accessibility of charged molecules to the pores of Fe-HAF-1, we chose four cationic organic dyes (Methylene Blue (MLB⁺), Lauth's Violet (LV^{+}) , Rhodamine B (RB⁺), and Alcian Blue (AB⁴⁺)), a cationic metal complex (Ru(bpy) $_{3}^{2+}$), and two anionic organic dyes, (Orange G (OG²⁻) and Rose Bengal (RB²⁻)) as potential guest molecules. The size of all dyes except (AB⁴⁺) is suitable for pore permeation (Figure S13). A typical sample used in uptake measurements contained 5 mg of Fe-HAF-1 and initial dye concentrations of 10 ppm, and the change in UV-vis absorbance was monitored over time. As shown in Figures 4 and S14-19, the cationic species (MLB⁺, LV⁺, RB⁺ and Ru(bpy)₃²⁺) were efficiently taken up by Fe-HAF-1 over the course of 2-6 h, while both anionic dyes (OG2- and RB2-) and the large cationic dye AB4+ remained in solution. These results confirmed the anionand size-selectivity of Fe-HAF-1 for dye uptake. The selective cation uptake by Fe-HAF-1 was further corroborated by competition experiments using an equimolar (0.025 mmol) mixture of the similarly sized by oppositely charged MLB⁺ and OG²⁻ dyes (Figure 4c), which showed that 97% of the former but none of the latter was sequestered from solution over the course of 2 h. Similar competitive selectivity between cationic dye and anionic dye was also observed with mixture of MLB⁺ and RB²⁻ (Figure S20).

PXRD measurements indicated that Fe-HAF-1 remained crystalline after dye uptake (Figure S21), which prompted us to

test the recyclability of the MOF. In these experiments, LV^+ was first fully adsorbed into Fe-HAF-1 powders to obtain a colorless solution, followed by a treatment with DEF or saturated NaNO₃ to induce the release of LV^+ from the MOF. The results showed that the uptake and release of the cationic dye were quantitative and fully reversible over at least three cycles (Figure S22), whereby the crystallinity of Fe-HAF-1 was largely preserved (Figure S21).

In summary, we have rationally designed a new MOF, Fe-HAF-1, which was constructed from tetrahedral, Fe³⁺hydroxamate-based clusters. This chelate-based, cubic MOF was found to be not only stable in different organic solvents, but also in water over a wide pH range (pH = 1 to 5 M NaOH), making it one of the most alkaline-stable MOFs. High crystallinity could be achieved despite the chelating nature of the tetra-hydroxamate ligand H₄BPTH, which led to the formation of defects during crystallization and an attendant anionic character for Fe-HAF-1 MOFs. Consequently, Fe-HAF-1 crystals were highly selective for the reversible uptake of positively charged dye molecules. Our results, along with previous reports on protein-35-36 and Ti-based MOFs,³⁰ further establish hydroxamate functionalities as a valuable addition to the synthetic toolkit for MOFs. In addition, the large number of symmetry-driven coordination cages described in the literature⁶⁴⁻⁶⁷ open up many opportunities for new MOFs based on these supramolecular SBUs.



Figure 4. UV-vis spectra of MOF uptake experiments with dyes: (a) 10 ppm of MLB⁺, (b) 10 ppm of OG²⁻, and (c) mix of MLB⁺ and OG²⁻inwaterinthepresenceofFe-HAF-1overtime.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and full characterization for ligands, Fe₄:*m*-bdh₆ cluster and Fe-HAF-1, single crystal X-ray analysis data for Fe₄:*m*-bdh₆ Cluster and Fe-HAF-1, SEM, TGA, zeta potential, IR, XPS, chemical stability and dye uptake properties of Fe-HAF-1 (PDF)

Fe₄:*m*-bdh₆ cluster (CIF) Fe-HAF-1 (CIF)

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