

Fluorous Metal–Organic Frameworks for High-Density Gas Adsorption

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The search for new crystalline porous materials, either with an inorganic¹ or a metal–organic framework (MOF),² is very topical as fueled by the use of such materials in a range of applications. These include catalysis,³ separations,⁴ gas storage,⁵ ion-exchange,⁶ sensors, and optoelectronics.⁷ In particular, stable MOFs with permanent channels or cavities may become effective, convenient, safe, and cost-effective gas-storage materials for fuel-cell-driven automobiles in the near future.⁸ Extensive efforts have been devoted to the rational design and construction of new MOFs with zeolite-like, well-defined, stable micro- or mesopore-size channels exhibiting higher, more reversible, or more selective gas affinity.⁹ Pioneered by Yaghi et al., a vast number of organic ligands with a variety of donor groups and over 40 metal cations have been explored in MOF construction.^{2,10}

Inspired by the unusual stability, extraordinary functional properties, and numerous applications of fluorinated molecules,¹¹ we have ignited an effort to explore the synthesis and functional properties of fluorinated metal–organic frameworks (FMOFs), wherein hydrogen atoms are substituted by fluorine atoms in all ligands. Compared to their non-fluorinated counterparts, FMOFs with fluoro-lined or fluoro-coated channels or cavities are expected to possess enhanced thermal stability and catalytic activity, higher gas affinity and selectivity, and higher stability to oxidation and light.^{11,12} In addition, fluorination may impart a variety of new functional properties to FMOFs, such as superacidity, enhanced hydrophobicity, low surface energy and surface tension, low refractive index, exceptional chemical and biological inertness, and excellent optical and electrical properties.¹³ Many nanoscale fluorinated environments have been created mainly via self-assembly processes, including nanoballs, channels, micelles, vesicles, microbubbles, tubules, and hollow fibers.^{11,14} However, porous FMOFs providing a perfluorinated pore surface are yet unknown among reported MOFs.

This work is in the context of ongoing efforts that we have recently launched to study the structure, optoelectronic properties and acid–base chemistry of coinage-metal triazoles.¹⁵ The work herein demonstrates an expansion of the potential of such materials to include FMOFs. A few reports on MOFs utilizing non-fluorinated metal triazoles have recently appeared.¹⁶ One of our strategies to obtain porous FMOFs with fluoro-lined channels exploits robust, perfluorinated metal–triazole clusters as building blocks, which bear unsaturated metal sites and *exo*-N donor atoms. Such building blocks, therefore, can readily assemble into coordination polymers with 1-, 2-, or 3D framework structures.¹⁷

The sodium salt of the perfluorinated ligand 3,5-bis(trifluoromethyl)-1,2,4-triazole (NaTz),¹⁸ reacts with silver nitrate in methanol to afford colorless crystals upon evaporation and recrystallization from acetonitrile/toluene. The crystallinity remains intact after evacuating the crystals by heating at 100 °C under vacuum overnight. Analysis of the evacuated crystals by single-crystal X-ray diffraction reveals a neutral FMOF with the formula $\{\text{Ag}_2[\text{Ag}_4\text{Tz}_6]\}_n$, **FMOF-1**.¹⁹ The crystal structure of **FMOF-1** shows extended 3D nanotubular open frameworks consisting of six-

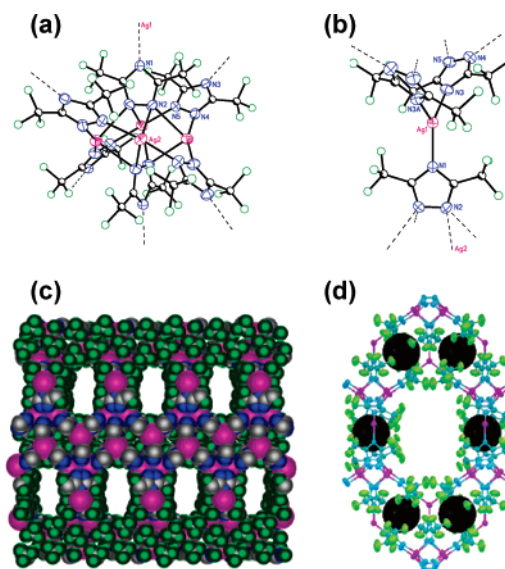


Figure 1. Structure of **FMOF-1** showing 50% thermal ellipsoidal plots of the building blocks consisting of a tetranuclear $[\text{Ag}_4\text{Tz}_6]$ cluster (a) and three-coordinate $\text{Ag}(\text{I})$ centers (b), a space-filling representation of the large fluoro-lined channels (c), and a perspective view of the small cavities, denoted by black spheres, surrounding the large channels (d).

connected tetranuclear $[\text{Ag}_4\text{Tz}_6]$ clusters linked by three-coordinate $\text{Ag}(\text{I})$ centers (Figure 1). The six triazolate ligands utilize their 1- and 2-positioned N-atoms to link four four-coordinate $\text{Ag}(\text{II})$ atoms into tetranuclear $[\text{Ag}_4\text{Tz}_6]$ clusters with adjacent $\text{Ag}(\text{II})$ – $\text{Ag}(\text{II})$ distance of 3.469(1) Å. The equatorial $\text{Ag}(\text{II})$ – $\text{N}(4)$ and $\text{Ag}(\text{II})$ – $\text{N}(5)$ distances are 2.18(1) and 2.18(1) Å, respectively, and the axial $\text{Ag}(\text{II})$ – $\text{N}(2)$ distance is 2.62(1) Å. The $[\text{Ag}_4\text{Tz}_6]$ clusters are interconnected via three-coordinate $\text{Ag}(\text{I})$ atoms through the 4-positioned N atoms of the triazolate ligands, with $\text{Ag}(\text{I})$ – $\text{N}(1)$ = 2.21(1), $\text{Ag}(\text{I})$ – $\text{N}(3)$ = 2.272(9) Å, and $\text{N}(1)$ – $\text{Ag}(\text{I})$ – $\text{N}(3)$ = 128.1(2)°, generating a 3D framework of $(4^2 \cdot 6)(4^4 \cdot 6^2 \cdot 8^8 \cdot 10)$ topology (see Figure S1 in the Supporting Information). The framework consists of interconnected large open-ended, hollow tubes extending along both the *a*- and *b*-axes, and the hollow tubes intersect at crystallographically imposed special positions with an S_4 point-group symmetry. The cylindrical channels of the tubular framework possess hydrophobic internal cavities, as the CF_3 groups of the perfluorinated ligands point into the channels. A cross section of each fluoro-lined channel in the space-filling representation entails a semirectangular shape with $\sim 12.2 \text{ Å} \times 7.3 \text{ Å}$ dimensions. The walls of the channels consist of diamond-shaped small cavities with $\sim 6.6 \text{ Å} \times 4.9 \text{ Å}$ dimensions (Figure 1d). Each cavity is formed by two adjacent $[\text{Ag}_4\text{Tz}_6]$ clusters interconnected by two $\text{Ag}(\text{I})$ atoms. Two pairs of channel-surface CF_3 groups located on top of the cavity function as a gate for the small cavity to communicate with the large channel. The fluoro-lined channels account for 40.8% of the unit cell volume as calculated by PLATON,²⁰ which is the

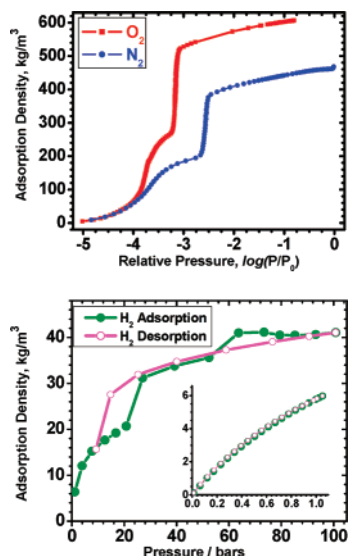


Figure 2. Volumetric uptake of N_2 and O_2 gases (top), and H_2 gas (bottom) within **FMOF-1** at 77 K. (Inset) Isotherms of a low-pressure run of H_2 adsorption/desorption cycle.

highest in metal–triazolate frameworks¹⁶ and comparable to the best high-porosity MOFs.^{2–6}

The architectural stability and porosity of **FMOF-1** is confirmed by the gas adsorption results at 77 K (Figure 2). The adsorption isotherms of O_2 and N_2 within **FMOF-1** at low pressure show two pore-filling steps at $\log(P/P_0)$ of -4.0 and -3.2 for O_2 and -4.0 and -2.7 for N_2 . It is reasonable to assign the first uptake to micropore filling of gas molecules into the large channels, whereas the second steep uptake is assigned to the small pores since the size of the latter (vide supra) can accommodate the dynamic size of the gas molecules studied herein (largest is N_2 , $4.1 \text{ \AA} \times 3.0 \text{ \AA}$).²¹ Fitting the BET equation to the N_2 isotherm gives an apparent surface area of $810.5 \text{ m}^2/\text{g}$ and a pore volume of $0.324 \text{ cm}^3/\text{g}$ at $P/P_0 = 0.978$. These values surpass those of the most porous zeolites and are similar to those of the best-performing activated carbons and MOFs.

The hydrogen-adsorption isotherm also shows a two-step filling profile similar to that of O_2 and N_2 at low pressure. Interestingly, the desorption isotherm does not retrace the adsorption isotherm and shows an abrupt drop at ~ 14 bar. This remarkable hysteretic adsorption/desorption of H_2 within **FMOF-1**, which has been reproduced three times, would allow H_2 to be adsorbed at high pressures but stored at lower pressures.²² To the best of our knowledge, this is the first example of a hysteretic sorption behavior of supercritical H_2 at a high-pressure range. The volumetric capacity of hydrogen within **FMOF-1** at 77 K and 64 bar is 41 kg/m^3 , which is close to the DOE 2010 target of 45 kg/m^3 . Similar capacities have recently been reported at 77 K for Mn(II) –tetrazolate (43 kg/m^3 at 90 bar)²³ and Cu(II) –terphenyl-tetracarboxylate (39.4 kg/m^3 at 78 K and 20 bar).²⁴

Given that the densities of liquid O_2 , N_2 , and H_2 are 1142, 804, and 70.8 kg/m^3 , respectively,²¹ the adsorption densities for O_2 and N_2 even at very low pressure (e.g., 592 and 427 kg/m^3 , respectively, at 0.03 bar) and for H_2 at high pressure (e.g., 41 kg/m^3 at 64 bar) suggest that the gas is highly compressed within the pores of **FMOF-1**. The volumetric gas uptake of **FMOF-1** is the highest yet reported for O_2 and among the best for H_2 .

In conclusion, **FMOF-1** represents a new class of porous materials with superior volumetric gas uptake. The unique hysteretic sorption of H_2 into **FMOF-1** paves a promising way for H_2 to be filled at high pressures but stored at lower pressures. We expect

that fluororous coordination polymers of this type will find applications in gas storage and separation, catalysis, sensors, switches, actuators, and n -type field-effect transistors.

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Supporting Information Available: Crystallographic data and additional experimental details and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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