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Fluorous Metal–Organic Frameworks with Superior Adsorption and Hydrophobic Properties toward Oil Spill Cleanup and Hydrocarbon Storage

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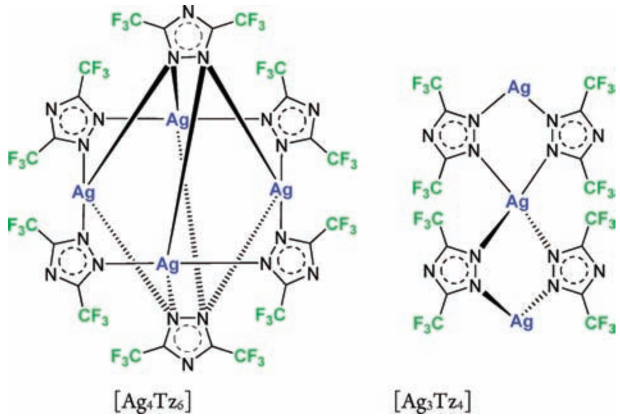
Supporting Information

ABSTRACT: We demonstrate that fluorous metal–organic frameworks (FMOFs) are highly hydrophobic porous materials with a high capacity and affinity to C_6–C_8 hydrocarbons of oil components. **FMOF-1** exhibits reversible adsorption with a high capacity for *n*-hexane, cyclohexane, benzene, toluene, and *p*-xylene, with no detectable water adsorption even at near 100% relative humidity, drastically outperforming activated carbon and zeolite porous materials. **FMOF-2**, obtained from annealing **FMOF-1**, shows enlarged cages and channels with double toluene adsorption vs **FMOF-1** based on crystal structures. The results suggest great promise for FMOFs in applications such as removal of organic pollutants from oil spills or ambient humid air, hydrocarbon storage and transportation, water purification, etc. under practical working conditions.

Chart 1. Building Blocks of FMOF-1 (left) and FMOF-2 (right)



Oil and petroleum hydrocarbon products are some of the most important energy sources in the world. As long as oil is prospected, transported, stored, and used, there will be a risk of spillages that may result in significant environmental damage and vast economic loss. Oil spill cleanup costs worldwide amount to over $10 billion dollars annually.[1] The adverse impact to ecosystems and the long-term effects of environmental pollution by these and other releases call for an urgent need to develop new materials for cleaning up oil from impacted areas, especially because the effectiveness of oil treatment varies with time, type of oil and spill, location, and weather conditions.[2] There are many adsorbents in use for oil spill cleanup, including sand, organoclays, and cotton fibers. These adsorbents, however, have a strong affinity to water, limiting their effectiveness in cleanup operations. Therefore, the development of waterproof sorbents that are effective even at a very low concentration of oil residue remains an urgent challenge. The recent Deepwater Horizon oil spill devastation raised awareness and underscored the urgent need for water-stable/-proof sorbents that can effectively remove oil residue in water, land, and air.

Metal–organic frameworks (MOFs) are promising adsorbents for many guest molecules, although reports concerning adsorption of hydrocarbon vapor in MOFs remain scarce compared to their H_2, CO_2, and inert gas adsorption.[3] The high affinity and reactivity of many common MOFs toward water and humid air largely limit their open-air applications.[4] Thus, the search for water-stable and hydrophobic MOFs combining good thermal stability, high selectivity, and excellent recyclability is a major challenge of great technological importance for oil spill cleanup, hydrocarbon storage in a solid matrix to allow transportation in smaller and safer vehicles, catalysis, water purification, component/isomer separation from gasoline mixtures, greenhouse gas remediation, etc. Fluorous metal–organic frameworks (FMOFs) are a new class of advanced porous material that we reported recently, whose pore surface is fluorine-lined and hydrogen-free that endows greater stability and more favorable adsorption properties vs nonfluorinated or partially fluorinated MOFs.[5,6] The hydrophobic character of the perfluorinated inner surface of FMOFs offers unprecedented potential for enhancing and fine-tuning the affinity for oil adsorbates in the presence of water or moist air. **FMOF-1** was the first example of FMOFs, constructed from silver(I) 3,5-bis(trifluoromethyl)-1,2,4-triazolate (AgTz).[5] Here we show that **FMOF-1** and **FMOF-2** (Chart 1) are highly hydrophobic and efficient for adsorption of typical aromatic and aliphatic oil components. This is a significant finding given that the confinement and interaction of water in hydrophobic space

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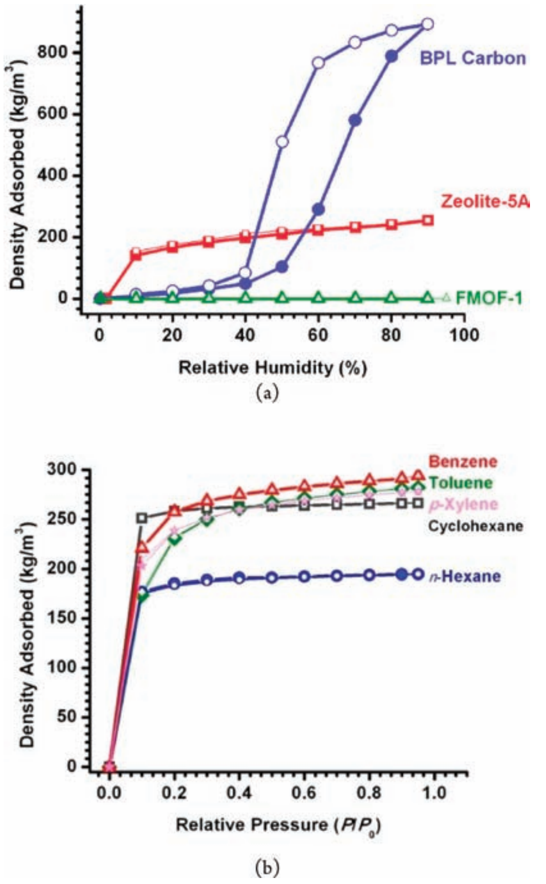

Figure 1. (a) Water adsorption isotherms for **FMOF-1**, zeolite-5A, and BPL carbon. (b) Oil components adsorption in **FMOF-1** using vapors of cyclohexane, *n*-hexane, benzene, toluene, and *p*-xylene. Open symbols indicate desorption.

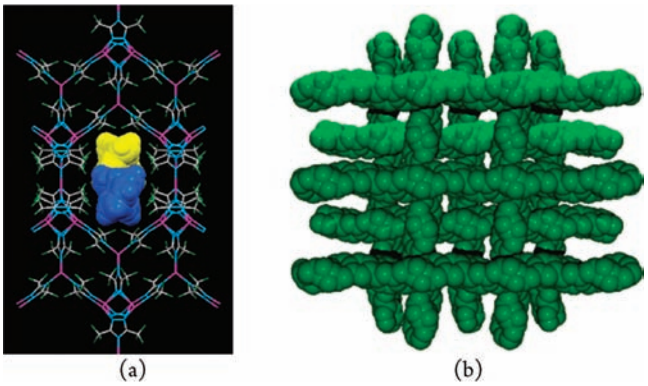

Figure 2. (a) Crystal structure of **FMOF-1**·2Toluene showing toluene molecules in one large channel repeat unit. (b) Packing of toluene guest molecules in **FMOF-1**·2Toluene cavities.

represent an important issue in science and technology[7] that has attracted increasing interest in the past decade, including water adsorption in activated carbons and all-silica zeolites,[8] functionalized or coated mesoporous materials,[9] and biological channels.[10]

Water adsorption isotherms reveal that **FMOF-1** is highly hydrophobic and significantly superior to BPL carbon and zeolite-5A (Figure 1a). Zeolite-5A, which is hydrophilic, adsorbs water at very low P/P_0 (<0.1). BPL carbon, which is hydrophobic, has a water adsorption isotherm that shows little uptake up to $P/P_0 = 0.4$, followed by a steep rise and attainment of a saturation capacity exceeding 800 kg/m^3 at $P/P_0 = 0.8$ with a hysteresis loop (type V). In contrast, **FMOF-1** shows negligible water adsorption even at P/P_0 up to 0.9 (Figure 1a). These results indicate that the large channels (1.2 × 0.8 nm) in **FMOF-1** are "closed" to water, rendering superior hydrophobic behavior. To confirm the water stability and high hydrophobicity of **FMOF-1**, we have carried out single crystal X-ray diffraction analysis using a water-soaked single crystal of **FMOF-1**. The *evacuated* single crystal of **FMOF-1** was soaked in distilled water for several days before X-ray data collection. The XRD pattern of water-soaked **FMOF-1** is identical to that of the water untreated sample, indicating that the porous crystal structure of **FMOF-1** holds after water treatment and that no water molecules are included in the channels (Figures S4–S5; Tables S7–S10). The unit cell volume of the water-soaked **FMOF-1** crystal is comparable to that of the evacuated **FMOF-1** crystal. The cell volumes are 6999(2) Å^3 water-treated and 7063.0(8) Å^3 for **FMOF-1** under vacuum. Both crystal structures were collected at the same temperature (100 K), indicating no solvent molecules were found ordered in the cavities, even in the large channels. While this is an unusual result for MOFs, which almost invariably include solvent molecules before activation, we note that single crystal X-ray measurements cannot completely rule out the existence of solvent molecules in the crystal structure. IR can be used to ascertain whether water molecules indeed are adsorbed in the channels, because one would see O–H stretches if there is any distribution of H_2O molecules in the inner core. A representative large single crystal of water-treated **FMOF-1** that had been evacuated and soaked in water for several days before being sliced carefully to remove the outside shell was selected for the IR measurement. The IR spectrum of this water-treated sample is the same as that of the evacuated **FMOF-1** sample (Figure S6), showing no O–H stretches at all. This further confirms that water molecules cannot enter into the channels of **FMOF-1**. Only a few water adsorption isotherms are available for nonfluorous MOFs, perhaps due to reactivity or lack of stability of common MOFs such as MOF-5 and HKUST-1 upon water exposure.[4] Although nature has shown us marvelous examples of superhydrophobic surfaces, such as lotus leaves and water strider legs,[11] and a number of synthetic superhydrophobic surfaces have been reported,[12] **FMOF-1** seems scarce as a highly hydrophobic 3-D porous crystal with a uniform micropore size that is "closed" to water. The water adsorption behavior of **FMOF-1** and its superior hydrophobic pore surfaces suggest very weak guest–host interactions between **FMOF-1** walls and water molecules as a consequence of the presence of a fluorine lining in the channel walls. The reason why water molecules cannot enter the internal microchannels of **FMOF-1** may relate to the superhydrophobic phenomenon, where water molecules tend to form thin films via strong H-bonding interactions between water molecules outside the superhydrophobic surface,[11,12] which prevents water molecules from entering into channels. However, contact angle and other surface measurements are needed before we can affirm that **FMOF-1** is, indeed, "superhydrophobic".

The high porosity of **FMOF-1** allows potential access by a variety of organic vapor molecules, particularly the most common oil components embodied by C_6–C_8 hydrocarbons. The sorption behavior of *n*-hexane, cyclohexane, benzene, toluene, and *p*-xylene at 298 K are shown in Figure 1b, featuring typical type-I isotherms. At $P/P_0 = 0.10$, the adsorptions of *n*-hexane and cyclohexane reach saturation, whereas benzene, toluene, and

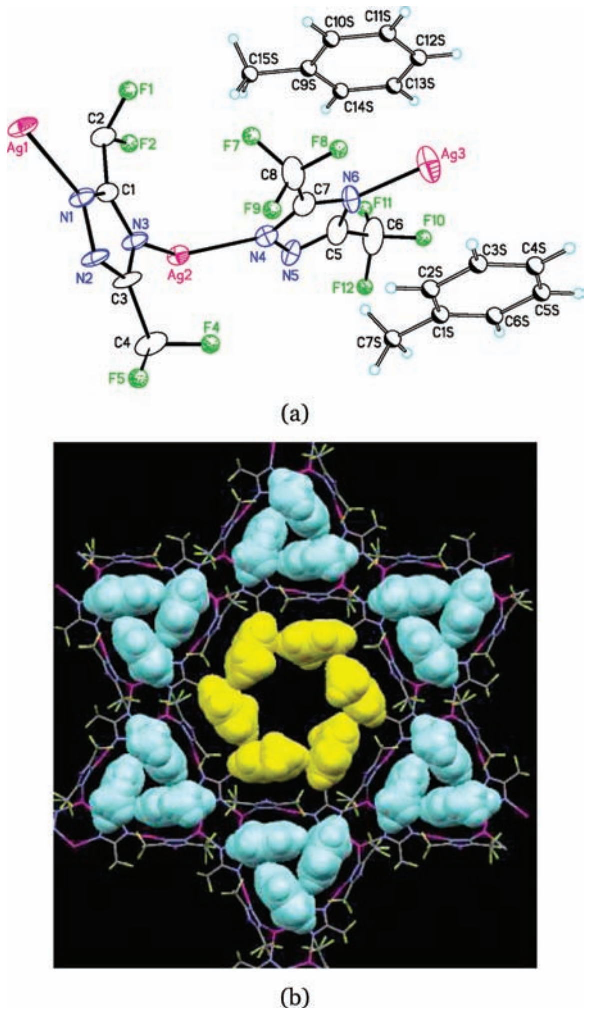

Figure 3. Crystal structure of **FMOF-2**·4Toluene: (a) Asymmetric unit showing atomic numbering scheme. (b) Packing of toluene molecules in the small cage (light blue sphere) and the channel (yellow sphere).

p-xylene reach saturation at $P/P_0 = 0.20$. The strong uptake at low pressure indicates the presence of strong host−guest interactions through confinement effects for aromatic adsorbates. The amounts adsorbed for *n*-hexane, cyclohexane, benzene, toluene, and *p*-xylene are 190, 300, 290, 270, and 265 kg/m^3, respectively. The toluene and benzene capacities of **FMOF-1** are close to that of the best performing MOF known to date (MOF-199)[13] and superior to that of other MOF materials.[14] The C_6-C_8 adsorption/desorption isotherms in **FMOF-1** are found to be fully reversible, indicating that incoming guests can move freely into and out of the channels. This can be attributed to the fact that the dimensions of guest molecules (2.6 × 6.8, 4.3 × 4.3, 3.3 × 6.6, and 4.0 × 6.6 Å^2 for *n*-hexane, cyclohexane, benzene, and toluene, respectively)[15] could be accommodated by the larger cavity size in **FMOF-1** (vide supra; also see Figure 2 illustrating toluene inclusion). The toluene adsorption level in **FMOF-1** amounts to 8 molecules per unit cell (7478.4(6) Å^3 at 298 K) according to Figure 1b data, indicative of commensurate adsorption.[16] Figure 2 shows the toluene solvate of **FMOF-1**, $Ag_2[Ag_4Tz_6]$•2Toluene (**FMOF-1**·2Toluene), whose crystal structure reveals an adsorption limit of 8 molecules per unit cell,[5] or 1/3 toluene solvent molecule per AgTz unit. The toluene content based on the crystal structure is in agreement with the adsorption isotherm. Toluene molecules are disordered in two symmetric positions (yellow and blue spheres in Figure 2a) and adopt a *zig-zag* packing within **FMOF-1**·2Toluene channels (Figure 2b).

The small cages around the main channels in **FMOF-1** are large enough to accommodate gas molecules such as N_2, O_2, and H_2, with one molecule per cage,[5,6] but are too small to include oil components like toluene and hexanes. Enlarging the cage size around the channels, therefore, could potentially boost the oil capacity of such hydrophobic frameworks. It has been reported that phase transition *via* annealing is a good strategy to obtain new thermally stable porous crystals.[17] We have successfully isolated such a framework, $[Ag(Ag_3Tz_4)]_{3/2}$•4Toluene (**FMOF-2**•4Toluene; Figure 3), by annealing **FMOF-1** at ca. 300 °C overnight and then reassembling the framework from toluene/acetonitrile, effectively doubling the toluene solvate content per AgTz unit. The structure of **FMOF-2**[18] consists of a sub-building unit $[Ag_3Tz_4]$ with two$[Ag_2Tz_2]$ plane moieties (Chart 1 and Figure 3a) that are perpendicular to each other and interconnected via sharing the four-coordinate Ag(1). The Ag(2) atom in each of the plane moieties is three-coordinate and connects to the adjacent $[Ag_3Tz_4]$ units to form 2D grid sheets (porous layers) parallel to the *ab* plane. These layers are then interconnected vertically via the two-coordinate Ag(3) atoms (Ag(3)−N(6), 2.118(8) Å) along the *c*-axis to form a 3-D porous network with $\{Ag[Ag_3Tz_4]\}_{3/2}$ repeat units in *P*6/*m* space group symmetry. Two types of voids are observed for the 3-D porous network along the *c*-axis: microporous hexagonal channels, about 1.8 nm in width, and triangular-shaped nanocages with pores about 1.0 nm in diameter surrounding the channels (Figure 3b). The defining features of the cages are their two-gate openings exposed to adjacent cages along the *c*-axis, each consisting of three flexible CF_3 groups that provide communication between the cages. Both the large channels and small cages are filled by toluene molecules, with 3 and 6 molecules per cage and channel in each layer, respectively. Toluene molecules whose planes are parallel to the *c*-axis are arranged as propeller blades around the *c*-axis to give idealized C_3- and C_6-symmetries in the cage and channel, respectively. The toluene solvate of **FMOF-2** can be formulated accordingly as $[Ag(Ag_3Tz_4)]_{3/2}$•4Toluene. The toluene content in **FMOF-2** is *doubled* as compared to **FMOF-1**, giving an adsorption limit of 12 toluene molecules within the unit cell of 5799.8 Å^3.

In summary, we have demonstrated superhigh hydrophobic FMOFs exhibiting remarkable air and water stability and a high capacity with high affinity to C_6-C_8 hydrocarbons of oil components. These FMOFs can selectively adsorb C_6-C_8 hydrocarbons in preference to water, through a combination of hydrophobicity and capillary action. Our results suggest that the FMOFs represent a promising class of porous materials that should find practical applications in the removal of organics, particularly in the field of oil spill cleanup and hydrocarbon storage. While available FMOFs are stable when exposed to water and air and can be readily recycled many times, the practicality of their use and mass production considerations will increase upon expansion to include abundant metals such as Cu and Zn instead of Ag.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Crystal data for **FMOF-2·**4Toluene: $C_{26}H_{16}Ag_3F_{18}N_9$, FW = 1120.09, Hexagonal, $P6/m$, a = 23.4261(14) Å, c = 12.2033(15) Å, V = 5799.79(9) Å^3, Z = 6, T = 100 K, D_c = 1.924 g/cm^3; R_1 = 0.0640, wR_2 = 0.1639, GOF = 1.459.