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Hydrogen Storage in a Highly Interpenetrated and Partially Fluorinated Metal−Organic Framework

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A partially fluorinated metal−organic framework, Zn(bpe)(tftpa)·cyclohexanone [bpe = 1,2-bis(4-pyridyl)ethane; tftpa = tetrafluoroterephthalate], has been synthesized, and its H_2 storage properties are reported. The structure is highly interpenetrated yet contains templating cyclohexanone molecules, which can be easily removed to give a porous material with fluorine atoms exposed to the pore surface. The material adsorbs 1.04 wt % H_2 at 77 K and 1 atm with an adsorption enthalpy (Q_{st}) of 6.2 kJ/mol, which represents a slight enhancement in the binding strength due to the presence of fluorine atoms over comparable metal−organic frameworks, which bind through purely physisorptive methods.

Recent activity in the field of metal−organic frameworks (MOFs) has been dominated by reports of porous structures that adsorb hydrogen and other gases.[1] The physisorptive binding of H_2 to the surfaces of these materials is weak, and therefore increasing the strength of this interaction has become important. The incorporation of coordinatively unsaturated metal sites within the structure has been one successful method of achieving this, as has the engineering of materials with smaller pore sizes that approach the kinetic diameter of the H_2 molecule (2.89 Å).[2−4] We and other groups have reported interesting H_2 adsorption properties in materials containing fluorinated ligands.[5−8] Our previous example, $Zn_5(trz)_6(tftpa)_2(H_2O)_2$ (trz = triazolate; tftpa = tetrafluoroterephthalate), displays a H_2 adsorption enthalpy (Q_{st}) of 8.0 kJ/mol at low coverages,[7] a significant enhancement over materials such as MOF-5, which contain large pores and adsorb through purely physisorptive methods (typically 4−5 kJ/mol). This enhancement was attributed to a combination of the fluorine atoms exposed to the pore surface and the small size of the pore (3.7 Å × 6.7 Å). The only other fluorinated hybrid structure for which a Q_{st} value has been reported is $Zn(SiF_6)(pyrazine)_2$, which displays a similar value of 8.2 kJ/mol and a comparably sized pore (4.5 Å × 4.5 Å).[8] It is therefore unclear to what degree this enhancement can be attributed to the fluorine atoms, if at all. Herein we present another partially fluorinated material that contains a much larger pore than these previous examples. The gas storage results for this structure suggest that the enhancement seen in these previous cases is more attributable to the small pore size than to the presence of fluorine atoms.

We have previously shown that perfluorinated dicarboxylates are easily incorporated into hybrid structures when a second nitrogen-donor ligand is present.[9−13] For this work, 1,2-bis(4-pyridyl)ethane (bpe) was chosen in combination with tftpa. The hydrothermal reaction of zinc acetate, bpe, and H_2tftpa at 100 °C for 24 h yields colorless crystals of Zn(bpe)(tftpa) (**1**),[12] a three-dimensional coordination polymer comprising two interpenetrating sublattices. The sublattice contains trimerlike units, composed of a ZnO_4N_2 octahedron and two identical ZnO_3N_2 trigonal bipyramids. These trimerlike units are then connected in one direction through bpe ligands and in the other two directions through bridging tftpa ligands. The large pore present in the sublattice is of the correct size to accommodate the second sublattice with no empty space (see the Supporting Information).

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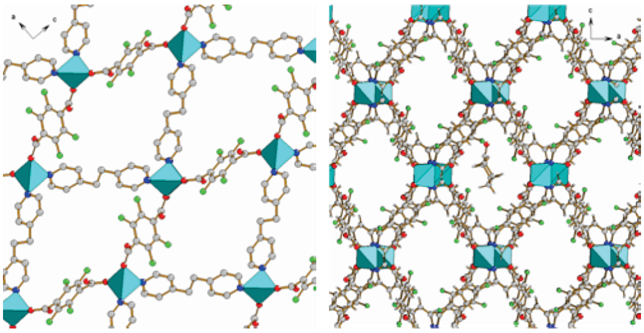

Figure 1. Structure of **2**. Left: View of one sublattice down the *b* axis. Right: View of all four sublattices down the channel axis (*b* direction), with one templating cyclohexanone molecule shown in the center (others omitted).

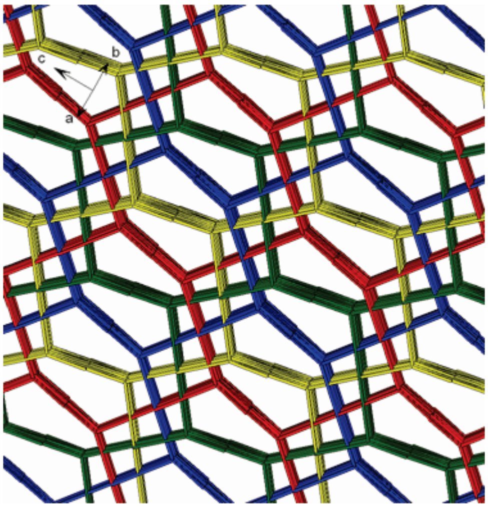

Figure 2. Simplified view of the 4-fold interpenetration of **2** with the different sublattices shown in red, yellow, green, and blue.

We attempted to synthesize the noninterpenetrated version of **1** by a variety of methods, one of which was the use of templating organic molecules to effectively block the interpenetration. Surprisingly, this strategy was both successful and unsuccessful when a slight excess of cyclohexanone was added to the reaction under the same conditions.[14] The resulting structure, Zn(bpe)(tftpa)·cyclohexanone (**2**),[15] incorporates cyclohexanone molecules as a templating agent but is simultaneously 4-fold-interpenetrated. The structure contains diamond-like sublattices built up from ZnO_2N_2 tetrahedra bound to two bpe ligands and two tftpa ligands (Figure 1). Remarkably, the cyclohexanone molecules cause an alignment of the four sublattices such that they occupy a large one-dimensional channel down the *b* axis with a diameter of approximately 6.5 Å (Figure 2). The cyclohexanone molecules are effectively close-packed down this channel with a closest intermolecular H−H distance of 2.32 Å.

A number of MOFs have been reported that contain high degrees of interpenetration and permanent porosity.[16−20] The use of small organic molecules as templates in the synthesis of MOFs has been a successful method of reducing interpenetration, incorporating porosity, and introducing chirality into structures.[16,17,21−23] However, this is the first time, to our knowledge, that cyclohexanone has been used for this purpose and the first example of a material for which organic templating simultaneously increases interpenetration and porosity. The permanent porosity of **2** was confirmed by thermogravimetric analysis data, which indicate that the cyclohexanone molecules are completely removed in one step between 125 and 170 °C and that the resulting structure (**2a**) is stable to 230 °C (see the Supporting Information). The structure of **2** can be completely desolvated by heating the material in a vacuum oven at 150 °C for 16 h. Crystals of **2a** degrade slowly when exposed to the atmosphere; however, we successfully obtained unit cell information from single-crystal X-ray diffraction data for the desolvated structure (though structure solution attempts were unsuccessful).[24] The unit cell volume of **2a** indicates a 5.6% increase over that of **2**, which indicates that the framework structure is fairly flexible upon removal of the cyclohexanone molecules.

Because of the permanent porosity of **2a**, gas sorption experiments were performed. A Brunauer−Emmett−Teller surface area for **2a** of 512 m^2/g and a pore volume of 0.203 mL/g were determined based on the Ar adsorption isotherm at 77 K. H_2 adsorption isotherms were carried out on **2a** at both 77 and 87 K from 0 to 1.0 atm (Figure 3). The isotherm at 77 K displays a maximum uptake of 1.04 wt % H_2 at 1.0 atm, which is comparable to other hybrid frameworks under similar conditions with similar pore sizes. In accordance with previous reports of H_2 adsorption in fluorinated hybrids, the desorption curve displays a slight hysteresis.[6,8] The Q_{st} value, obtained by applying the Clausius−Clayperon equation to the isotherms obtained at 77 and 87 K, is approximately 6.2 kJ/mol at low coverages.[25] This value can only be viewed as a slight enhancement over any physisorptive binding to nonfluorinated structures and does not approach the two previous fluorinated examples mentioned above, which achieved Q_{st} values of around 8 kJ/mol. Because the pore in **2a** is large enough to discount any additional binding enhancement due to confinement effects, it is apparent that the fluorine atoms in this structure are only slightly enhancing the Q_{st} value.

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(14) A mixture of $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.022 g, 1.00 mmol), bpe (0.018 g, 0.10 mmol), H_2tftpa (0.024 g, 0.10 mmol), and cyclohexanone (0.028 g, 0.30 mmol) was added to 3 mL of water and heated at 100 °C for 18 h in a 23-mL Teflon-lined stainless steel autoclave. Colorless block-shaped crystals of **2** were isolated by filtration and washed with water and acetone. Elem anal. Calcd for **2** ($ZnC_{26}H_{22}F_4N_2O_5$): C, 53.5; H, 3.80; N, 4.80. Found: C, 53.3; H, 3.82; N, 4.92.

(15) Crystal data for **2** at 150 K: monoclinic, $P2_1/n$, $a = 11.7527(13)$ Å, $b = 12.4829(13)$ Å, $c = 16.6089(18)$ Å, $\beta = 90.477(3)°$, $V = 2436.6(5)$ Å^3, $Z = 4$, $\rho = 1.592$ g/cm^3, $\mu = 1.080$ mm^{-1}, R1 = 0.0656, wR2 = 0.1184.

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(24) Unit cell data for **2a** at 150 K: monoclinic, $P2_1/n$, $a = 12.908(4)$ Å, $b = 12.219(4)$ Å, $c = 16.313(5)$ Å, $\beta = 90.080(8)°$, $V = 2572.9(13)$ Å^3.

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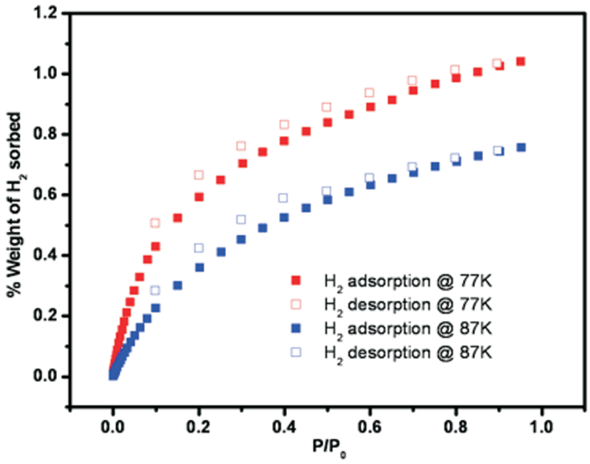

Figure 3. H_2 adsorption and desorption curves for **2a** at 77 K (red) and 87 K (blue).

These results underscore some key problems in quantifying the extent to which fluorination affects the H_2 binding strength. First, perfluorinated ligands show significant conformational differences relative to their nonfluorinated analogues, so that the synthesis of analogous structures is not possible.[12] Our recent work with perfluorinated benzenedicarboxylates has illustrated that the extent to which the carboxylate group is twisted out of the plane of the benzene ring when fluorine atoms are present is so significant that the manner in which metals bind to these ligands is altered. The inability to synthesize analogous structures obviously makes direct comparisons between fluorinated and nonfluorinated structures difficult. A second issue is that both **2a** and the previous examples mentioned above do not contain completely fluorinated pores; rather, they contain fluorine atoms in one of the two ligands exposed to the pore surface. There has yet to be a Q_{st} value reported for a MOF with totally perfluorinated pores, and it is therefore still unclear what effect this would have on H_2 binding interactions. It is likely that multiple structure characteristics, such as pore surface alteration, pore size effects, and coordinatively unsaturated metal sites, may need to be combined in one material to provide the substantial increase in H_2 binding strengths that are needed to meet the U.S. Department of Energy targets.

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Supporting Information Available: Description of the synthesis and structure of **1**, thermogravimetric analysis data and powder X-ray diffraction patterns for **2**, description of the structure solution, and crystallographic data in CIF format for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.