Communication

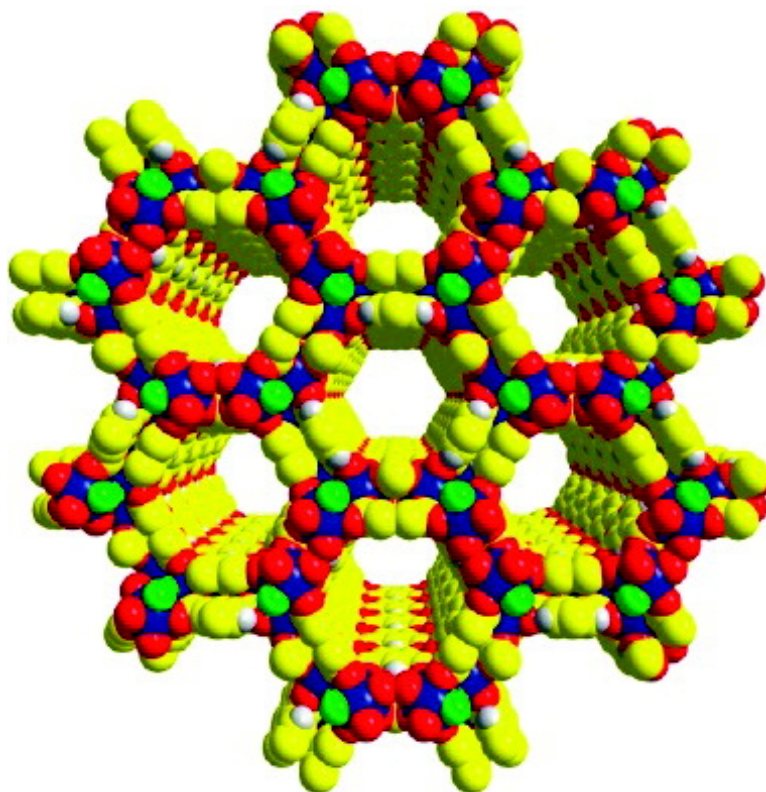# TOF-2: A Large 1D Channel Thorium Organic Framework

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TOF-2: A Large 1D Channel Thorium Organic Framework

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Metal organic framework materials have been attracting great attention due to their crucial applications in absorption, separation, ion-exchange, sensing, catalysis, and gas storage.[1] Metal organic framework materials not only have been showing interesting features in common with inorganic zeolites but also have been demonstrating a wide variety of geometries and framework flexibilities by the suitable choice of metal and ligand combinations.[2] For example, numerous framework topologies that demonstrate large porosities have been isolated by combinations of transition metals and carboxylate linkers.[3] In contrast, actinide organic framework materials adopting diverse topologies and coordination environments have been rarely observed. A few actinide-based nanotubular inorganic framework materials with possible applications to nuclear waste storage and nanotechnology have been reported.[4] We have been interested in preparing porous actinide-organic frameworks. In 2003, we were able to structurally characterize the first thorium organic framework.[5] We now report the first 1D hexagonal nanotubular thorium organic framework, $Th[C_6H_3(CO_2)_3F]\cdot0.3H_2O$, which we denote TOF-2 (thorium organic framework-2), and its phase-pure synthesis, crystal structure, and characterizations.

TOF-2 was synthesized hydrothermally by combining $N(CH_3)_4$-Cl, $Th(NO_3)_4\cdot6H_2O$, 1,3,5-benzenetricarboxylic acid (BTC), HF, $HCON(CH_3)_2$, and H_2O in a Teflon-lined autoclave at 140 °C for 1 d.[6] Although the synthesis requires the addition of either an ammonium halide such as $(C_nH_{2n+1})_4NX$ ($n = 1-6$; X = Cl or Br) or an amine such as $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (TMEDA), none of these compounds are incorporated into the structure. TOF-2 crystallizes as light yellow needle-shaped crystals.[7] The structure is composed of hexagonal channels consisting of eight-coordinate ThO_6F_2 polyhedra and BTC groups that are connected through oxygen and fluorine atoms (see Figure 1(a)). Each Th^{4+} cation is bonded to two fluorine and six oxygen atoms. The single unique $Th^{4+}-F$ bond length is 2.3449(15) Å, and the $Th^{4+}-O$ bond lengths range from 2.352(4) to 2.424(4) Å. These values are consistent with those of previously reported thorium compounds.[5] Each ThO_6F_2 group is connected through F atoms resulting in infinite unidimensional chains along the [001] direction. As can be seen in Figure 1(b), these chains are further interconnected along the [010] direction by the BTC groups, which create an unprecedented neutral hexagonal framework structure. An interesting structural feature of TOF-2 is that the BTC groups are aligned parallel to each other along the c-axis, forming perfectly eclipsed "double walled" pore sides; we believe this double wall arrangement has not been previously observed. This nonslipped parallel $\pi-\pi$ stacking arrangement is not normally observed for aromatic hydrocarbons as this arrangement is significantly repulsive. The separation between benzene rings of the BTC groups is 3.58 Å which is similar to the ring—ring separation of 3.57 Å typically found in the arene-perfluoroarene complexes. Bond valence calculations[8] on TOF-2
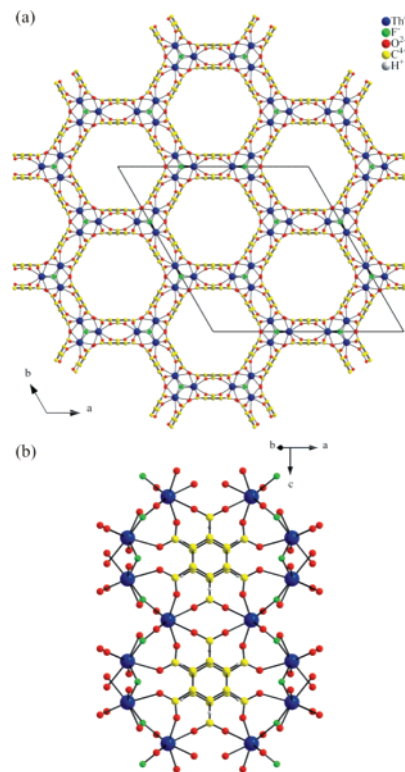
Figure 1. (a) Ball-and-stick representation of TOF-2 revealing hexagonal channels along the c-axis. Occluded water molecules have been removed for clarity. (b) ThO_6F_2 groups form infinite one-dimensional chains along the c-axis and the interconnected BTC groups are in perfectly eclipsed pairs which form the walls of the tunnels.

resulted in a value of 4.27 for Th^{4+} cation. The dimensions of the hexagonal channels running down the c-axis are approximately 13.7 Å (face to face) × 14.7 Å (corner to corner). Using the van der Waals radii of the constituent atoms the diameter of the largest sphere that will fit into the channels is ca. 11 Å.[9] We believe there are some disordered water molecules residing within the hexagonal pores, but these are very poorly resolved by the X-ray diffraction experiment.

The amount of void space can be calculated by removing all the occluded water molecules and using the CALC SOLV command in PLATON.[10] For TOF-2, the amount of void space is 41%, whereas the value for the zeolite cloverite is 60%. The powder X-ray diffraction pattern of the polycrystalline bulk sample of TOF-2 is in excellent agreement with the generated pattern based upon the single-crystal model (see the Supporting Information).

Thermal analysis of TOF-2 indicates a weight loss of 1.2% between room temperature and 400 °C, which is attributed to the loss of 0.3 equiv of occluded water. The framework starts decomposing after 410 °C, and the material completely collapses to $ThOF_2$[11] by 800 °C.
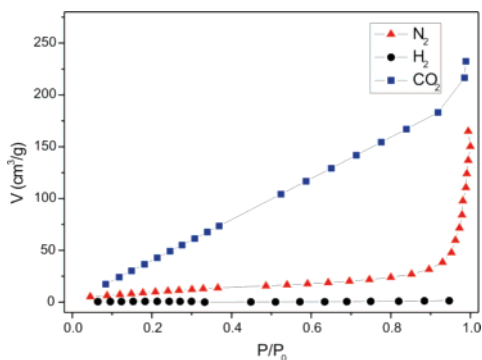
Figure 2. Adsorption isotherms of H_2 ($\bullet$, 77 K), N_2 ($\blacktriangle$ (red), 77 K), and CO_2 ($\blacksquare$ (blue), 196 K) on TOF-2.

The room temperature ^{13}C magic angle spinning (MAS) solid-state NMR spectra of TOF-2 only exhibits the four resonances which we assign to the four crystallographically unique carbons which make up the core benzene ring of BTC ligand; we did not observe the other two crystallographically unique carbonyl carbons of the BTC ligand presumably due to relaxation effects. No other resonances were observed that could be assigned to either occluded DMF or the amine-based directing agents. The ^{19}F MAS solid-state NMR contains a single fluorine resonance which is in agreement with the structural model.[12]

Despite the stable framework and a large effective pore diameter, to our surprise no nitrogen diffusion into micropores is observed at 77 K. The N_2 adsorption isotherm for TOF-2 at 77 K exhibits features resulting from multilayer adsorption (Figure 2). However, the adsorption capacity of TOF-2 for CO_2 is significantly greater. Differential gas adsorption in a channel framework has recently been reported.[13] The authors ascribed this behavior to strong interaction of the N_2 molecules with the pore windows which could be due to the considerable quadrupole interactions of N_2 with the electrostatic field gradients near the surface,[14] which subsequently block other molecules from passing into the pore, as the framework has no additional open channels along the a- and b-axes. In the case of CO_2 at 196 K, such interactions are overcome by thermal energy. Analysis of the experimental data based on the CO_2 adsorption yields 293 m^2/g for the specific surface area and approximate pore diameters of 1.7−2.7 nm. Details of the fit of the N_2 adsorption isotherm data are deposited in the Supporting Information.

Time-resolved, in situ energy-dispersive X-ray powder diffraction (EDXRD) experiments indicate that the crystallization of TOF-2 is fast (see the Supporting Information). A signal corresponding to the (312) Bragg reflection ($d = 3.76$ Å) for TOF-2 was first observed about 15 min after the reaction has reached temperature; this signal then increased in intensity over the next 10 min, at which point its intensity remained constant during the remainder of the experiment.

In summary, we have successfully synthesized and characterized a new large channel thorium organic framework material. We are in the process of extending the organic linkers and some intercalation experiments using a variety of guest molecules.

Supporting Information Available: Experimental and calculated powder XRD pattern, ^{13}C and ^{19}F magic angle spinning (MAS) solid-state NMR spectra, time-resolved in situ energy-dispersive powder X-ray diffraction (EDXRD) data, and N_2 gas adsorption isotherm fits for $Th[C_6H_3(CO_2)_3F]\cdot0.3H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) $Th[C_6H_3(CO_2)_3F]\cdot0.3H_2O$ was synthesized by combining $N(CH_3)_4Cl$ (0.219 g, 2.00×10^{-3} mol), $Th(NO_3)_4\cdot6H_2O$ (0.588 g, 1.00×10^{-3} mol), 1,3,5-$C_6H_3(CO_2H)_3$ (0.078 g, 3.71×10^{-4} mol), $HCON(CH_3)_2$ (0.25 mL), water (5 mL), and HF(aq) (40%, 0.14 g) in a Teflon lined stainless steel autoclave and heating to 140 °C for 24 h, before being cooled to room temperature at a rate of 3 °C h^{-1}. The mother liquor was decanted from the products, which were then sonicated and washed with water. Light yellow needle crystals were recovered by filtration. A yield of 78% (based on thorium) was observed. IR data (cm^{-1}): 3586, 2867, 1612, 1529, 1438, 1367, 1228, 1112, 936, 761, 624, 608, 544, 519. Elemental analysis. Calcd: C, 23.30; H, 0.78; Th, 50.07. Exptl: C, 23.66; H, 0.68; Th, 50.02.
(7) Crystal data: crystal size $0.02 \times 0.02 \times 0.50$ mm^3, hexagonal, space group R-$3m$ (no. 166) with $a = b = 29.401(4)$ Å, $c = 8.8526(18)$ Å, $V = 6627.2(19)$ Å^3, $Z = 18$, $\rho_{calc} = 2.091$ g cm^{-1}, $2\theta_{max} = 54.94°$, $\lambda = 0.71073$ Å, $T = 298$ K, total data 5988, unique data 1782, observed data ($I > 3\sigma(I)$) 1782, $\mu = 10.148$ mm^{-1}, 86 parameters, $R(F)/R_w(F) = 0.0323/0.0674$ on $|F^2|$.
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(12) Analysis of ^{19}F MAS NMR spinning sideband manifold gave a single chemical shift at 75.5 ppm. In ^{13}C MAS NMR gave four resonances at 172.9 ppm, 172.1 ppm, 135.0 ppm, and 133.7 ppm which are assigned to the carbon atoms on the benzene ring. The carbonyl carbons were not observed, presumably due to its slow relaxation time.
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