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Single-Crystalline UiO-67-Type Porous Network Stable to Boiling Water, Solvent Loss, and Oxidation

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Supporting Information

ABSTRACT: With methylthio groups flanking the carboxyl groups, the 3,3′,5,5′-tetrakis(methylthio)biphenyl dicarboxylate (TMBPD) linker forms a zirconium(IV) carboxylate porous framework featuring the topology of the UiO-67 prototype, i.e., with a face-centered-cubic array of the $Zr_6O_4(OH)_4$ clusters. Thioether functionalization proves valuable because the ZrTMBPD crystal is found to be exceptionally stable not only upon long-term exposure to air but also in boiling water and a broad range of pH conditions. The hydrophobicity of the metal−organic framework can also be tuned by simple H_2O_2 oxidation, as illustrated in the water contact-angle measurement of the pristine and H_2O_2-treated ZrTMBPD solid.

The issue of stability occupies a central position in the study and application of metal−organic frameworks (MOFs) as a growing class of porous materials.[1−7] Unlike the inorganic zeolites that are built on robust covalent Si−O and Al−O bonds, MOFs build on generally more labile coordination bonds between organic linkers and metal ions and are prone to degradation, e.g., upon exposure to water or other reagents. In this context, zirconium(IV)-based MOFs (e.g., the UiO series and analogues)[8−13] attract great attention because of its noted stability to water, H_2S, and other acids, stability that apparently arises from the robust zirconium(IV) carboxyl interaction and broadens the latitude of functionalization and applications.

One outstanding issue that besets the prominent UiO-type networks, however, is their tendency to collapse upon solvent removal. Even though the smallest member UiO-66 (based on terephthalic acid) is stable in the activated, solvent-free state,[14,15] the expanded versions (e.g., UiO-67, based on 4,4′-biphenyldicarboxylic acid) become quite sensitive to solvent loss: when taken out of solvents (*N*,*N*-dimethylformamide, acetonitrile, or water), the crystallinity can largely degrade within just a few hours.[16−18] Certain solvent-exchange treatments (e.g., with acetone) mitigate the problem,[17] but better stability remains highly pertinent, as is illustrated by Lillerud's recent reports on a binaphthyl analogue of UiO-67 that sustains direct drying from water[19] and on a bipy-functionalized UiO-67.[20]

Building on the long-standing studies on the sulfur chemistry of open frameworks,[21−26] we here report the dramatic stability improvement imparted by symmetrically attaching thioether groups onto the zirconium-based network of UiO-67 [see the 3,3′,5,5′-tetrakis(methylthio)biphenyl dicarboxylic acid (H_2TMBPD) molecule in Figure 1]. Besides remaining highly crystalline even after being stored in air for years in the activated, solvent-free state, the ZrTMBPD framework can also withstand the harsh conditions of wide-ranging pH conditions and boiling water. We will also describe the oxidation of thioether groups of ZrTMBPD for tuning the hydrophilicity properties of this robust porous solid.

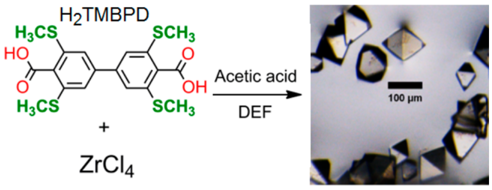

Figure 1. Synthetic scheme for the ZrTMBPD crystals (photograph shown in the right).

The linker molecule H_2TMBPD was synthesized in a reliable and economical protocol. Specifically, the tetrakis(fluoro)-biphenyl precursor (molecule **S3**, Scheme S1) was obtained in 74% yield by a nickel-mediated homocoupling reaction at 50 °C. Facile substitution on **S3** with sodium thiomethoxide produced a tetrakis(methylthio)biphenyl diester compound (**S4**) in excellent yield (90%), which was then hydrolyzed to afford H_2TMBPD. Notably, the synthetic route involves no palladium or other noble-metal catalysts and only requires earth-abundant metal elements such as nickel and zinc for the coupling reaction.

Hydrothermally reacting H_2TMBPD with $ZrCl_4$ reliably produced colorless, octahedral single crystals of UiO-67-4MS (0.1−0.3 mm; Figure 2; see also the Supporting Information for details), which readily yields to X-ray crystallographic analysis. The crystal structure of UiO-67-4MS adopts the space group $Fm\bar{3}m$ (No. 225), consisting of a face-centered-cubic array of $Zr_6O_4(OH)_4$ clusters bridged by the carboxylate units of the TMBPD linker to give the fcu topology of the prototype UiO-67 (based on 4,4′-biphenyl dicarboxylate)[10] and related struc-

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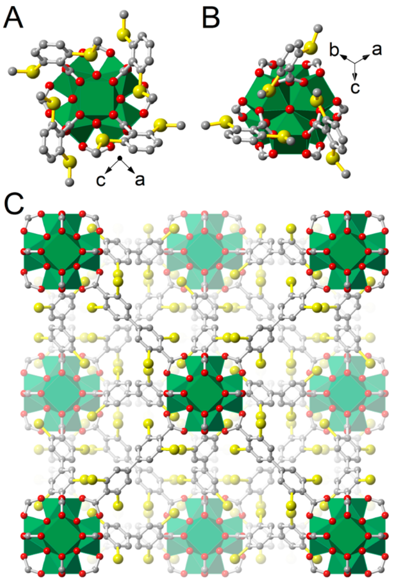

Figure 2. Single-crystal structures of ZrTMBPD: local bonding environment of the Zr6-oxo cluster along the (a) [1 0 0] and (b) [1 1 1] directions. (c) Unit cell of the cubic framework. Disorder of the biphenyl and methyl units is omitted for clarity. Zirconium coordination polyhedra are displayed in green. Atom colors: red, O; yellow, S; gray, C.

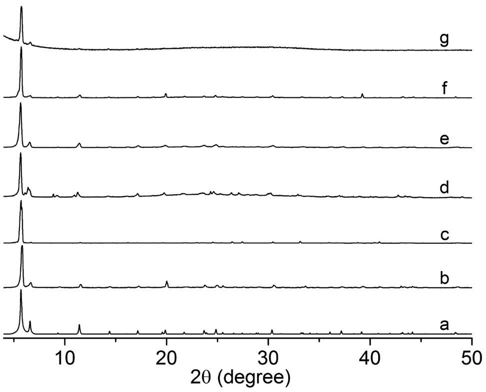

Figure 3. PXRD patterns (Cu Kα, $\lambda = 1.5418$ Å) of (a) a simulation from the single-crystal structure of ZrTMBPD, (b) an as-made sample of ZrTMBPD, (c) an activated sample of ZrTMBPD, (d) an activated sample of ZrTMBPD after storage in air over 2 years, (e) an as-made sample of ZrTMBPD after stirring in boiling water for 24 h, (f) an as-made sample of ZrTMBPD after soaking in 1.62 M HCl (pH = 0) at room temperature (rt) for 24 h, and (g) an as-made sample of ZrTMBPD after soaking in 0.01 M NaOH (aq, pH = 12.6) at rt for 24 h.

tures.[19] The flanking MeS− groups are densely disposed around the zirconium oxo cluster to create significant steric shielding. The biphenyl units are disordered over 2 times five sets of positions around the linker axes. The extensive disorder makes it difficult to pinpoint the ligand geometry. One possibility compatible with chemically allowed interatomic distances points to dihedral angles of 77° for the biphenyl units and 52.5° for benzoic unit, with the intermolecular S−S distance among the thioether units being 4.0 Å.

As per N_2 sorption studies at 77 K, the activated sample of ZrTMBPD displayed type I gas adsorption isotherms (Figure S4) with a Brunauer−Emmett−Teller surface area of 1153 m^2 g^{-1}. Elemental analyses on an as-made sample of ZrTMBPD found 36.21% carbon, 5.12% hydrogen, and 1.58% nitrogen. A fitting formula can be determined to be $Zr_6O_4(OH)_4\cdot(C_{18}H_{16}O_4S_4)_6\cdot(DEF)_5\cdot(H_2O)_{37}$ (formula mass = 4399), which gives a calculated profile of 36.31% carbon, 5.25% hydrogen, and 1.59% nitrogen. The water and *N*,*N*-diethylformamide (DEF) content of (1172/4399) × 100% = 26.6% calculated based on elemental analyses is slightly greater than that observed in the first step of weight loss in the thermogravimetric analysis (TGA) plot (100% − 76% = 24%; see Figure S2). The ZrO_2 (formula mass = 123) content from $Zr_6O_4(OH)_4\cdot(C_{18}H_{16}O_4S_4)_6$ (formula mass = 3227) equals [(6 × 123)/3227] × 100% = 22.9%, matching the residual weight percentage found in TGA: (18%/76%) × 100% = 23.7%.

To demonstrate the water stability of the host framework, the as-made crystals were first boiled in water for 24 h, filtered out, and then air-dried. Powder X-ray diffraction (PXRD) indicates retention of the host network (Figure 3, pattern e), and the N_2 sorption isotherm remains largely unchanged (e.g., <15% variation in the surface area; Figure S5). In addition, the PXRD pattern also remains consistent (Figure S8, pattern c) after being heated at 200 °C in air for 4 h, even though the crystals changed from colorless to reddish brown. The long-term stability of the activated crystals is also excellent; for example, a sample stored in air for over 2 years shows a PXRD pattern identical with that of the fresh sample (Figure 3, pattern d).

The stability to acids and bases is also substantial. For example, after being immersed in 1.62 M HCl (pH = 0) for 24 h, the PXRD pattern remained unchanged, with the individual crystals retaining their pristine, transparent appearance. Upon immersion in 0.01 M NaOH (measured pH = 12.6) for 24 h, a translucent whiteness developed in the crystals, even though PXRD indicative of the original crystalline lattice can still be obtained. In higher basicity, e.g., at 0.1 M NaOH (measured pH = 13.8), substantial dissolution of the crystal solid was observed, with the remaining solid exhibiting no well-defined PXRD peaks, indicating its amorphous nature. Such stability to varying pH is similar to that of other robust zirconium(IV)-based MOF solids.[19,27,28] A comparison with the prototypal, unsubstituted UiO-67 is also informative. As reported,[17] acetone exchange enhances the stability of UiO-67 in the activated (solvent-free) state (e.g., for 1 week; see Figure S8, patterns e and f), but treatment with boiling water or 0.1% NaF solutions readily degrades its crystallinity (Figure S8, patterns g and h). By comparison, the ZrTMBPD solid remains highly crystalline under similar conditions (Figure 3, pattern e, and Figure S8, pattern i).

The water stability of the ZrTMBPD crystals led us to explore oxidization of the thioether groups by H_2O_2 solution.[25] After treatment with 5% H_2O_2 (in acetic acid and water) at rt for 24 h, the PXRD pattern was consistent with that of the fresh sample (Figure S8). Moreover, thioethers inside the resulting network were all oxidized, giving sulfoxide and sulfone units in an approximately 10:3 ratio, as determined by solution ^1H NMR of the resulting solid dissolved in 4% NaF in D_2O. More interestingly, the hydrophobicity of the crystals was found to be significantly reduced after H_2O_2 treatment, with the contact angle changed from 81.65° of an activated sample to 68.17° of the H_2O_2-treated sample (Figure 4). The reduced hydrophobicity is consistent with the more polar sulfoxide and sulfone units, which readily hydrogen bonds with water guests. The tuning of the hydrophobicity of MOF solids[29−37] is of relevance for gas adsorption and other guest exchange properties; for example, the polar sulfoxide/sulfone units attract more strongly

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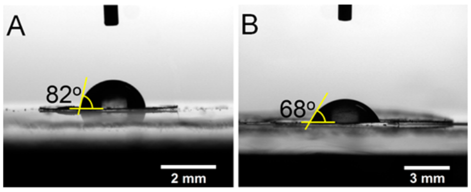

Figure 4. Photographs for the water contact-angle measurement of a pressed pellet of (a) an activated sample of ZrTMBPD (contact angle: 81.65°) and (b) a H_2O_2-treated sample of ZrTMBPD (contact angle: 68.17°).

the quadrupole of CO_2 and dipoles of SO_2 and H_2S molecules, which may facilitate their separation from natural gas.

In summary, thioether groups symmetrically installed at both ortho positions of the carboxyl unit have resulted in better stability of the UiO-67-type network of ZrTMBPD. The dense array of thioether groups not only sterically shields the Zr−O cluster node from boiling water and other encroaching species (e.g., the F^- ions) but also improves the framework rigidity to prevent collapse in the activated state. In the context of making stable MOF solids, the use of steric shielding may help to circumvent the dilemma between the reversible reaction for crystallization and strong (and less reversible) coordination for stability. Further studies, however, are needed to better account for the stability improvement observed here; for instance, one may install only one thioether group next to the carboxyl unit, as a comparison with the present case. One may also compare the water adsorption isotherms for ZrTMBPD and its sulfone/sulfoxide derivatives, in order to highlight the tunability of this stable, sulfur-equipped MOF solid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00404.

> Experimental procedures, additional photographic images, solution ^{1}H and ^{13}C NMR spectra, elemental analysis data, and TGA plots (PDF)

Accession Codes

CCDC 1823105 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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