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Enhancing Water Stability of Metal–Organic Frameworks via Phosphonate Monoester Linkers

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Supporting Information

ABSTRACT: A new porous metal–organic framework (MOF), barium tetraethyl-1,3,6,8-pyrenetetraphosphonate (CALF-25), which contains a new phosphonate monoester ligand, was synthesized through a hydrothermal method. The MOF is a three-dimensional structure containing 4.6 Å × 3.9 Å rectangular one-dimensional pores lined with the ethyl ester groups from the ligand. The presence of the ethyl ester groups makes the pores hydrophobic in nature, as determined by the low heats of adsorption of CH_4, CO_2, and H_2O (14.5, 23.9, and 45 kJ mol^{-1}, respectively) despite the polar and acidic barium phosphonate ester backbone. The ethyl ester groups within the pores also protect CALF-25 from decomposition by water vapor, with crystallinity and porosity being retained after exposure to harsh humid conditions (90% relative humidity at 353 K). The use of phosphonate esters as linkers for the construction of MOFs provides a method to protect hydrolytically susceptible coordination backbones through kinetic blocking.

Metal–organic frameworks (MOFs) are a class of highly porous crystalline materials that have highly tunable structures because of the range of accessible components and their modular assembly.[1] Potential applications for MOFs include gas storage, gas separation, catalysis, ion conduction, and use as sensors.[2] For practical applications, stability of the MOF material is important, as high turnover numbers result in reduced costs. One current issue with implementing many types of MOFs into practical applications is instability toward water, both in the liquid and vapor phase. Water has been reported to attack the metal connectors within MOFs, displacing ligands and causing phase changes, loss in crystallinity, and/or decomposition to reduce or destroy the porosity of the materials.[3] Acid–base reactions may also occur at basic metal clusters. For example, the $[Zn_4O]^{6+}$ clusters present in MOF-5 are easily hydrolyzed by water vapor, forming a nonporous product containing zinc(II) hydroxide chains (MOF-69c).[4] As moisture is omnipresent in target applications such as postcombustion CO_2 capture, if MOFs are to find use in these processes, their instability toward water needs to be overcome.

Our approach to enhancing the water stability of MOFs is the use of phosphonate monoesters as linkers. Phosphonate monoesters (RPO_2OR') have the potential to offer carboxylate-like coordination modes (they are monoanionic with bidentate O donor ligation) but with the added variable of the organic tether on the ester group. Phosphonate monoesters are an underexplored class of ligands, with earlier reports concerning only structural studies using clodronate esters as ligands and two materials for NLO applications.[5] Recently our group has used phosphonate monoesters to form porous MOFs, where the porosity was sustained through van der Waals (vdW) interactions of the alkyl esters and the pore size was tuned by varying the alkyl ester.[6] The premise of this approach was that the monoanionic charge of a phosphonate monoester would moderate the self-assembly and allow for stable yet crystalline products while the ester tether could sterically shield the most hydrolytically vulnerable M–O bonds and augment the hydrolytic stability of MOFs. Here we report the synthesis of a porous and hydrophobic phosphonate monoester MOF, barium tetraethyl-1,3,6,8-pyrenetetraphosphonate, BaH_2L (CALF-25, where CALF stands for Calgary Framework), with high water vapor stability arising from the protective ethyl groups lining the pores.

Crystallization of CALF-25 was performed solvothermally, with partial hydrolysis of octaethyl-1,3,6,8-pyrenetetraphosphonate occurring in situ through the use of an ethanolic solvent system. The crystal structure of **1** (Figure 1) is a three-dimensional polymeric framework consisting of one-dimensional (1D) barium phosphonate chains cross-linked to four other chains through the pyrene ligands, leaving 1D pores parallel to the chains. The 1D barium phosphonate chains contain nine-coordinate barium centers that are saturated by phosphonate monoester O atoms; a similar 1D chain has been reported in a barium carboxylate MOF. Each pyrene unit bridges two chains, with two phosphonate groups connecting three barium centers within a chain. The pores formed from the cross-linking pyrene units are rectangular in shape (4.59 Å × 3.89 Å including vdW radii), with the ethyl ester groups lining the corners of the pores and the pyrene ligand cores defining their walls. Overall the formula has 1:1 barium to ligand ratio, which means that the MOF is acidic since it has two phosphonic acid monoethyl esters per ligand.

Activation of CALF-25 was performed at 100 °C under vacuum (10^{-5} Torr) with no subsequent loss in crystallinity. The material is permanently porous, with nitrogen adsorption at 77 K showing a type-I isotherm (BET surface area = 385 m^2 g^{-1}). Further gas sorption analysis was performed with CO_2 (Figure 2) and CH_4. To characterize the surface properties, isosteric heats of adsorption were calculated using CO_2 at 263 and 273 K and CH_4 at 268 and 278 K (Figure S4 in the

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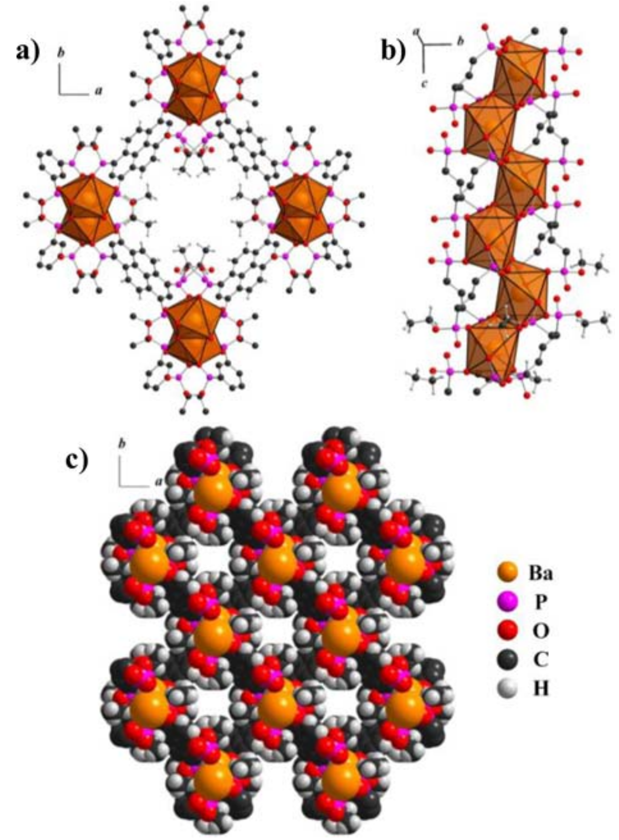

Figure 1. (a) Crystal structure of CALF-25 viewed along the *c* axis in a ball-and-stick representation, showing ethyl groups lining the barium phosphonate chains. (b) Structure of the edge-sharing barium phosphonate polyhedra within a 1D chain, with ethyl groups removed from the top half of the chain and disorder removed for clarity. (c) Space-filling representation of CALF-25 showing the ethyl-lined pores along the *c* axis.

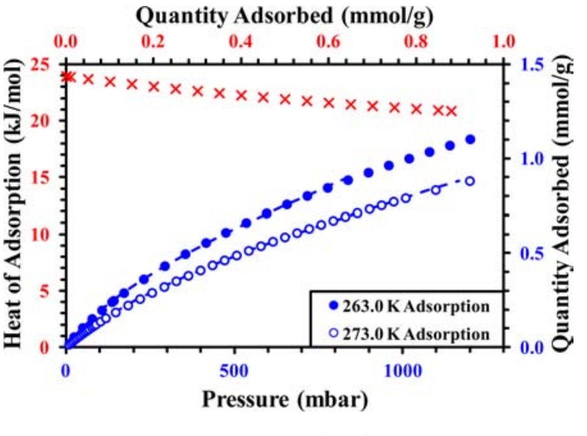

Figure 2. CO_2 adsorption isotherms (blue) and the isosteric heat of adsorption of CO_2 (red) for CALF-25. Fits to virial models are shown by dashed lines.

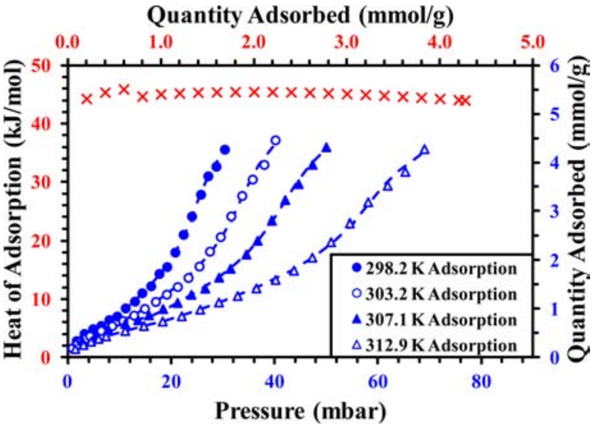

Figure 3. H_2O adsorption isotherms (blue) and the isosteric heat of adsorption of H_2O (red) for CALF-25. Fits to virial models are shown by dashed lines.

Supporting Information). The zero-loading heats of adsorption were found to be 23.9 kJ mol^{-1} for CO_2 and 14.5 kJ mol^{-1} for CH_4, both of which are low values comparable to those of some hydrophobic MOF materials, suggesting a weakly polarizing pore surface despite the acidic nature of the material.[7]

To assess the hydrophobic nature of CALF-25, water vapor sorption was performed at 5 K intervals between 298 and 313 K (Figure 3). These isotherms showed type-III behavior indicative of low affinity between the adsorbate molecules and the surface. The heat of adsorption was calculated to be ~45 kJ mol^{-1} across all loadings of water; a zero-loading value was not calculated because of inadequate low-pressure data. This very low heat of adsorption for water suggests that the pore surface is hydrophobic. The value is comparable to those of graphite and other hydrophobic MOF materials and is only marginally higher than the heat of vaporization of water at room temperature (43.98 kJ/mol).[8] Since CALF-25 is composed of metal cations and oxo anions and is an acidic material, such a low value for the heat of adsorption for water is remarkable. This suggests that the ester groups lining the pore surfaces effectively shield the polar, acidic barium phosphonate chains behind the less polar ethyl groups, making the pores hydrophobic.

The stability of CALF-25 toward water was further studied by powder X-ray diffraction (PXRD) and gas sorption on samples exposed to harsh humid conditions. CALF-25 used for water vapor sorption analysis was exposed to maximum conditions of 95% relative humidity at 312.9 K, corresponding to a water vapor partial pressure of 69.2 mbar. Following water vapor sorption, there was no change in the PXRD pattern (Figure S8) and only a 2% reduction in N_2 uptake at 77 K (Figure S1). For comparison, Walton and co-workers exposed numerous MOFs to 90% relative humidity through water vapor sorption under ambient conditions (22.4 mbar H_2O assuming a temperature of 294.2 K) followed by reactivation and nitrogen sorption at 77 K.[9] Under these conditions, only two of the studied MOFs were reported to have comparable water vapor stability, both from the UiO-66 family. That study did not include members of the ZIF family,[10] which show stability toward boiling water, nor "superhydrophobic" MOFs post-synthetically modified with alkyl groups.[11] There has also been one report of kinetic stabilization of MOF-5 through the introduction of trifluoromethoxy groups onto the ligand cores for steric protection, although an 81% loss in surface area was observed after exposure to steam for 1 week.[12] A highly porous barium carboxylate MOF, barium benzene-1,3,5-trisbenzoic acid, which has an edge-sharing barium chain structure similar to that of CALF-25 as well as 1D pores through the material, has also been reported.[13] This barium carboxylate MOF does not have ethyl groups protecting the barium carboxylate chains and was reported to lose crystallinity upon exposure to moist air.

To test the stability further, higher temperatures were employed. CALF-25 was exposed for 24 h to 90% relative humidity at 353 K, corresponding to a water partial pressure of 426.7 mbar. This treatment also gave no changes in the PXRD pattern. CO_2 gas sorption at 273 K (maximum CO_2 partial pressure of $P/P_0 = 0.03$) also showed no decrease in uptake relative to the pristine sample (Figure S3). Interestingly, the same sample run at 195 K showed a 17% loss in CO_2 uptake (Figure S2). Furthermore, N_2 sorption at 77 K showed a 40% reduction in uptake, still with no change in the postsorption PXRD pattern (Figures S1 and S8). The retention of crystallinity and porosity of CALF-25 at 273 K after exposure to humid conditions suggests that the material is stable toward water vapor. The reduction in uptake *observed only at lower temperatures* may be a kinetic phenomenon arising from surface defects due to water exposure. The sizable pyrenyl ligand could yield partial pore blockages that can be overcome by adsorbate molecules with more thermal energy. This may explain why the reduction in gas uptake is more pronounced as the temperature decreases. This is also supported by the appearance of a slight hysteresis in the desorption loop of the N_2 sorption at 77 K after water treatment (Figure S1). While CALF-25 is stable toward water vapor at 353 K, boiling the MOF in water caused a significant loss in crystallinity (Figure S9), a partial phase change, and partial solubilization of the material, suggesting that the water vapor stability is due to a kinetic protective effect of the ethyl groups within the pores.

Phosphonate monoesters are uncommon ligands for MOFs, but they offer potential benefits for making more moisture-stable materials, a key challenge for MOF chemistry. CALF-25 is a permanently porous MOF with a highly hydrophobic pore surface resulting from the use of phosphonate monoester linkers. *CALF-25, despite being a material composed of metal cations and acidic oxo anions, is of comparable hydrophobicity to porous carbons*. Moreover, retention of crystallinity and porosity upon exposure to high humidity at elevated temperatures was confirmed by PXRD and a reproducible CO_2 sorption isotherm. The stability arises from the steric protection offered by ethyl ester groups shielding the inorganic backbone of CALF-25 and defining the nature of the pore. Appending organic tethers has been established as a means of enhancing the water stability of MOFs.[11,12] The ease of tuning the pore surface in phosphonate monoester MOFs is potentially a major benefit in addition to standard means of regulating structure in a MOF.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, analytical data, Figures S1−S10, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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