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Phosphonate Monoesters as Carboxylate-like Linkers for Metal Organic Frameworks

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S Supporting Information

ABSTRACT: Bidentate phosphonate monoesters are analogues of popular dicarboxylate linkers in MOFs, but with an alkoxy tether close to the coordinating site. Herein, we report 3-D MOF materials based upon phosphonate monoester linkers. Cu(1,4-benzenediphosphonate bis(monoalkyl ester), CuBDPR, with an ethyl tether is nonporous; however, the methyl tether generates an isomorphous framework that is porous and captures CO_2 with a high isosteric heat of adsorption of 45 kJ mol^{-1}. Computational modeling reveals that the CO_2 uptake is extremely sensitive both to the flexing of the structure and to the orientation of the alkyl tether.

Metal Organic Frameworks (MOFs)/Porous Coordination Polymers (PCPs) offer systematic and tunable routes to the generation of new porous solids.[1] This fact has led to these materials being extensively pursued as new sorbents for gas separation and storage.[2] The role of the organic linkers is foremost to delineate the primary pore structure but these groups also define the chemical potential of the pore surfaces[3] and can possibly kinetically gate sorption phenomena.[4] The fact that these solids can also demonstrate flexible architectures further extends their scientific interest and offers potential for new applications tied to their dynamic behavior.[5]

Many MOF/PCP materials reported incorporate carboxylate anions as, in appropriate rigid and polyvalent forms,[6] these linkers provide sufficient thermodynamic stability to enable permanent porosity but also sufficient kinetic lability that crystalline products are typically obtained. Phosphonate monoesters (RP(=O)(−OH)(−OR) are a largely unexplored ligating functionality in coordination polymer science.[7,8] We recently reported Zn 1,4-benzenediphosphonate bis(monoethyl ester), Zn(BDPEt),[9] a van der Waals compound with permanent porosity despite having only two-dimensional connectivity. In this compound, the monoanionic and bidentate coordination mode of the phosphonate monoesters was reminiscent of the ligation displayed by dicarboxylate linkers in MOFs. A fundamental difference between a phosphonate monoester and a carboxylate is obviously the presence of the alkoxy tether on the P atom. Herein, we report two new 3-D MOFs, Cu(1,4-benzenediphosphonate bis(monoalkyl ester), CuBDPR, R = ethyl, **1**; R = methyl, **2**. Through a joint experimental and computational study, we demonstrate that the alkoxy tether can play a crucial role in mediating gas sorption. More generally, we show that phosphonate monoesters, like carboxylates, can strike a balance between robustness and crystallinity to form porous 3-D architectures. Compound **2** shows preferential adsorption of CO_2 over other gases and an exceptionally high ΔH_{ads} (45 kJ/mol) for CO_2.

The ligands, 1,4-benzenediphosphonate bis(mono ethyl and methyl esters), BDPEt and BDPMe, respectively, were synthesized from 1,4-dibromobenzene and the appropriate trialkylphosphite via a Michaelis−Arbuzov reaction followed by controlled hydrolysis to the bis(monoalkyl ester) as described previously for the ethyl analogue.[9] Compounds **1** and **2** were synthesized (single crystal and bulk) by ethanol diffusion into an aqueous solution of $CuCl_2 \cdot 2H_2O$ and the disodium salt of the ligand.

The crystal structure of **1**, depicted in Figure 1c, showed the formation of a 3-D network with channels, in contrast to the Zn structure. In **1**, one-dimensional Cu(R−PO_3Et) chains are formed down the *c*-axis (Figure 1b shows Me analogue), with the chains being linked by fully deprotonated BDPEt dianions forming a rhombohedral grid of 14.565(4) × 7.790(2) Å (P−P distance and metal−metal distances as depicted by the arrows in Figure 1c). The ethyl groups of the phosphonate esters protrude into the pores restricting the aperture to ∼4.5 Å. The channel walls are decorated with the ethyl groups of the ligand and the CuO_4 metal cores. The coordination geometry of Cu is 4-coordinate and best described as heavily distorted tetrahedral tending to square planar. Ligation is exclusively by O atoms excluding the alkylated oxygen of the phosphorus. From the crystal structure, porosity was not evident as the channels appeared largely filled by the pendant ethyl groups. No solvent accessible pore space was able to be calculated. The lack of porosity was corroborated by thermogravimetry on solvated samples, which showed no mass loss from RT to decomposition, and the fact that **1** showed no significant adsorption of any gas, including CO_2 at 298 K. The methyl ester analogue, **2**, was prepared with the intent that the BDPMe ligand would form a framework of comparable dimensions but with accessible pores owing to the smaller alkyl group. On the other hand, the framework could also flex[10] in response to the smaller R group, thereby closing the pores.

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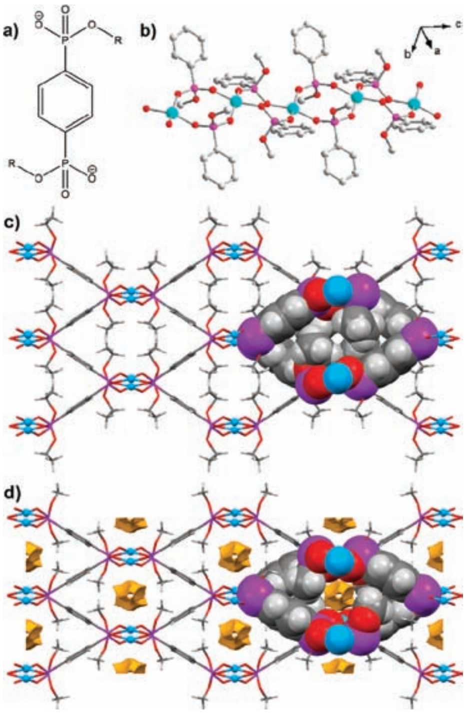

Figure 1. (a) The dianionic ligand, BDPR, where R = Et or Me. (b) Single crystal structure of one column of CuBDPMe, **2** (**1** is similar), showing the bidentate coordination of the phosphonate monomethylester and the 4-coordinate geometry of Cu. (c and d) Views down the *c*-axis, of the frameworks showing (c) solvent inaccessible 1-D channels in **1**, and (d) 1-D pores in **2** with solvent accessible voids (1.2 Å probe in gold). In c and d, one channel is shown in a space filling representation.

The single crystal X-ray analysis of **2** (Figure 1b,d) showed a framework that could almost be superimposed (Figure S1) on that of **1**, excepting the position of the ester alkyl groups. One-dimensional Cu(R$-$PO$_3$Me) chains and BDPMe linkers framed one-dimensional channels (14.933(2) × 7.024(2) Å, P$-$P distance and metal$-$metal) comprising ~17% of the structure. The methyl groups of the phosphonate esters still protrude into the pores but leave an aperture of ~6 Å. There is disordered water in the pores located above the "axial" site of the 4-coordinate Cu ion at 3.65(6) Å, a weak interaction at best (Σ vdW 2.92 Å).

This solvent inclusion was demonstrated in bulk samples as TGA/DSC analysis (Figure S6) indicated a mass loss of ca. 5.0 wt% to 100 °C (calculated 5.2 wt% for 1 H_2O). Between 100 and 350 °C, no significant mass loss was observed and the sample decomposed at 350 °C. This stability was confirmed by PXRD after heating the sample in air to 200 °C for 24 h (Figure S2). During the desolvation process, the PXRD indicated a small structural contraction. To elucidate the nature of this contraction, an in situ PXRD measurement was conducted on a desolvated sample under a nonadsorbing gas (helium). Refinement of the resulting pattern (Figure S4) indicated a 1.8% reduction in the cell volume in comparison to the as made crystal structure (Table S1). This contraction did not collapse the pores and the permanent porosity of **2** was confirmed by gas sorption analysis. As with many small pore MOFs, the material showed no significant adsorption of N_2, H_2, or CH_4 at any temperature (Figure S8). A modest uptake of CO_2 at ambient temperatures was observed (Figure 2), 30.9 cm^3(STP)/g, 1.38 mmol/g, 6.06 wt% at 273 K and 1200 mbar. This equates to a loading of 0.45 CO_2 per Cu center. The enthalpy of adsorption (ΔH_{ads}) for CO_2 was determined as a function of loading (Figures S13$-$S16). At zero loading, indicative of the highest energy sites, the ΔH_{ads} was calculated as 45 kJ/mol, a very high value for a physisorptive process.[11]

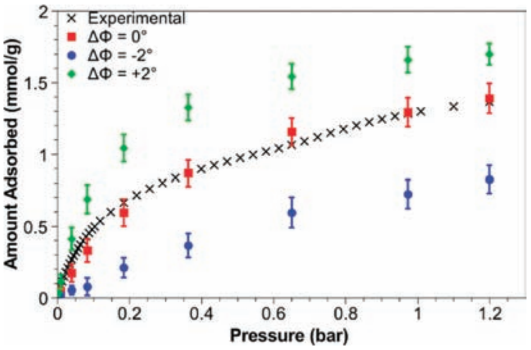

Figure 2. Comparison of experimental and simulated CO_2 adsorption isotherms at 273 K, where the geometry of the methoxy groups have been altered from the X-ray structure in silico.

The experimental determination of this ΔH_{ads} value merits comment as the total CO_2 uptake by **2** is modest and so relative errors in extracting the ΔH_{ads} from experimental isotherms are magnified. Using isotherms at 263 and 273 K, a zero-loading ΔH_{ads} for CO_2 of 52 kJ/mol was initially calculated for **2**. Recognizing the uncertainty in this value, new samples tubes were prepared that decreased the dead volume of the analysis by ~70% (see Supporting Information). Isotherms were also measured at four temperatures (263, 268, 273, 278 K) and the linearity of all the van't Hoff fits gave a high degree of confidence in the reassessed value of 45 kJ/mol. This value was sustained over the entire loading. Recent reports have shown a strong correlation between high ΔH_{ads} and high selectivities for low pressure CO_2 capture.[12] Often, high ΔH_{ads} can be connected to the presence of coordinatively unsaturated metal centers (e.g., HKUST-1, 35 kJ/mol;[13] MIL-101, 44 kJ/mol;[14] Mg-MOF-74/CPO-27-Mg, 47 kJ/mol;[15] MIL-100, 63 kJ/mol.[14] Considering three pieces of data (high value for ΔH_{ads}; stoichiometry of 0.45 CO_2/Cu; transannular Cu···Cu distance of 7.02 Å between pseudosquare planar Cu centers), it is tempting to hypothesize that the CO_2 molecules in this system are in a dual end-on bridging mode between Cu centers. ΔH_{ads} values can also be augmented by the presence of polar functional groups such as amines lining the pores,[16] although higher amination is not always necessarily beneficial for CO_2 uptake.[17]

Given the relevance to capture methodologies, molecular insights to the nature of CO_2 interactions with a porous sorbent are valuable,[18] especially one with a ΔH_{ads} of 45 kJ/mol as with **2**. To investigate the nature of the CO_2 binding and sorption properties of **2**, dispersion corrected periodic DFT and classical grand canonical Monte Carlo (GCMC) simulations were employed.[19] The dual end-on bridging interaction of CO_2 with two Cu centers was first examined with DFT as such a binding mode might involve weak orbital interactions. All attempts to locate a minimum energy structure corresponding to this mode of CO_2 failed even when the framework and cell vectors were allowed to fully relax. Instead, all structures optimized to geometries in which the CO_2 molecules were oriented roughly perpendicular to the hypothesized end-on bridging mode in the direction of the channels.

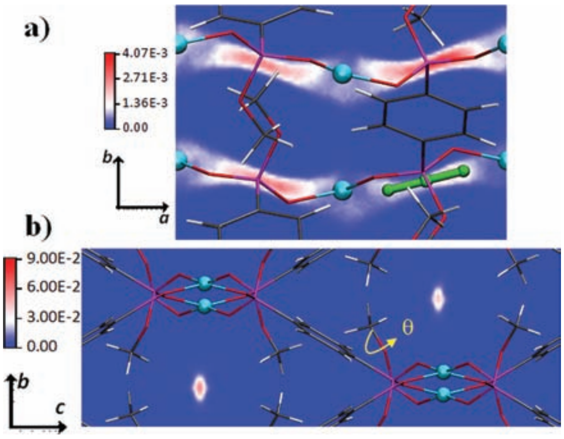

Figure 3. Probability density plots of the CO_2 oxygen atom in a unit cell of **2** at 1 bar, 273 K from simulation. In panel a, probabilities along the *c*-axis are projected onto the *a*−*b* plane, while in panel b, probabilities along the *b*-axis are projected onto the *b*−*c* plane. A green CO_2 molecule is shown in panel) for reference.

To further investigate the CO_2 sorption in **2**, GCMC simulations were performed using the UFF parameters[20] and REPEAT[21] charges that were able to successfully reproduce the experimental CO_2 binding sites and isotherms of a Zn amino-triazole-oxalate MOF.[22] Figure 3 shows the CO_2 oxygen atom probability distribution resulting from a GCMC simulation of **2** at 1 atm CO_2 and 273 K. The plots show that there are four symmetrically equivalent binding sites in the unit cell. The guest molecules align along the channels with either the carbon or oxygen of the CO_2 at the midpoint between the methyl groups. Consistent with the DFT calculations, no dual end-on bridging was seen with the GCMC simulations. One key experimental observation supporting the lack of direct interaction of CO_2 with the Cu sites is that, in the crystal structure, although the Cu centers are 4-coordinate, there is no ligated water. Typically, an open metal site requires activation[13−15] which is not the case with **2**.

CO_2 adsorption isotherms were also determined from the GCMC simulations. The CO_2 adsorption behavior of **2** was found to be highly sensitive to the structure of the framework. For example, when the solvent included X-ray structure of **2** is used in the simulation, the CO_2 uptake is found to be 15−20% lower than that determined experimentally throughout the pressure range (Figure S19). However, if this structure is adjusted to the lattice parameters determined in situ with 1.2 bar CO_2, the simulated isotherm (Figure 2, red) reproduces the experimental uptake well throughout the pressure range examined. Additionally, we found a strong CO_2 uptake dependence on the methoxy group orientation, which can be defined by the C_{me}−O−P−O dihedral angle, ϕ, as highlighted in Figure 3b. Shown in Figure 2 are the simulated adsorption isotherms with the ϕ angle of all methoxy groups in the framework changed by $\Delta\phi = -2$ and +2 degrees from that in the original structure. Negative $\Delta\phi$'s correspond to the channel closing, while positive values open the channel. A 2° change in ϕ, which corresponds to a ∼0.08 Å change in pore width, results in a dramatic increase or decrease in the simulated gas adsorption. Therefore, the slight inflection in the experimental isotherm of **2** at ∼0.6 bar can be attributed to a subtle change in the framework geometry upon CO_2 uptake. While not explicitly demonstrated in this work, in general, the high sensitivity of the uptake to the methoxy group orientation in **2** suggests the potential of the alkoxy tethers in the phosphonate monoester based MOFs to modulate the adsorption behavior. The dynamic nature of the alkyl tether may also permit optimal arrangement between CO_2 molecules to maximize cooperative interactions.[23]

A fundamental difference between a carboxylate and a phosphonate monoester is the presence of the alkoxy tether. Clearly, between **1** and **2**, the alteration from ethyl to methyl ester groups greatly affects CO_2 uptake but the orientation of the alkyl group is also critical. Phosphonate monoesters as linkers in coordination polymer/MOF materials have not been nearly as studied as carboxylate or phosphonate linkers. Some compounds were formed from partial hydrolysis of phosphonate diesters in the generation of target metal phosphonates.[7] With respect to targeted studies of phosphonate monoesters, it has been recognized, by Kontturi et al., on studies of monoester derivatives of clodronic acid,[8] that the alkoxy tether is a structural variable that can regulate dimensionality of the inorganic backbone in coordination polymers (larger groups favoring lower dimensional assemblies) but no gas sorption data on this family have been reported. The present study shows that phosphonate monoesters can balance crystallinity and permanent porosity giving a structure (**2**) accessible to CO_2 with a heat of adsorption measured as 45 kJ/mol. Moreover, the alkoxy group represents a mechanism for regulating porosity by both modifying the size/shape of the pore but also by potentially acting in a dynamic manner as a gate for guest diffusion. A final point of note is that the alkyl tether must be in proximity to the M−O bonds and may kinetically enhance the hydrolytic stability of MOF materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** CIF files, detailed physical characterization of **1** and **2**, and details of computational methods including simulated HOA calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) See Supporting Information for a full description of the computational methods used and a more detailed analysis.

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