

# Zn<sub>7</sub>O<sub>2</sub>(RCOO)<sub>10</sub> Clusters and Nitro Aromatic Linkers in a Porous Metal–Organic Framework

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## S Supporting Information

**ABSTRACT:** A new metal–organic framework, CALF-22 comprising Zn<sub>7</sub>O<sub>2</sub>(COO)<sub>10</sub> secondary building units and 2-nitro-1,4-benzenedicarboxylate, is reported. The porosity and gas adsorption of N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> are studied, and CALF-22 has a surface area in excess of 1000 m<sup>2</sup>/g. The stability of the larger zinc cluster and the effect of the nitro group on gas sorption are also studied.

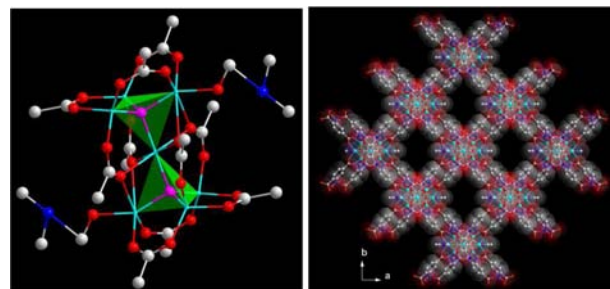
The growth of research in metal–organic frameworks (MOFs) reflects both their potential application and modular options to tune the material.<sup>1</sup> While seemingly infinite options for an organic linker are available, the other component, the metal center or secondary building unit (SBU), is more limited because SBUs must be stable enough to allow the isolation of materials. The most common SBUs are the carboxylate aggregates Zn<sub>4</sub>O(COO)<sub>6</sub>, Cu<sub>2</sub>(COO)<sub>4</sub> paddle-wheel, and M<sub>3</sub>O(COO)<sub>6</sub> (MIL-101 cluster).<sup>2,3</sup> Beyond the role of the SBU as a simple connection unit, many SBUs have coordinated solvents that can often be removed to generate a bare metal site to act as a high-energy adsorption site for gas molecules.<sup>4,5</sup> Polar organic functional groups can also act as high-energy adsorption sites.<sup>6</sup> The most widely studied system is the Lewis basic amine group that interacts with CO<sub>2</sub> molecules.<sup>6e</sup> High surface areas and large pore volumes are also key attributes to maximizing absolute storage capacities. A larger SBU could increase pore size or raise the connectivity to augment framework robustness. With these ideas in mind, we investigated the use of nitro groups on the adsorption properties of MOFs.

The –NO<sub>2</sub> group is highly polar and polarizing with significant charge density on the O centers. The NO<sub>2</sub> group is also very electron-withdrawing, and it was anticipated that this could perturb the typical benzenedicarboxylate (BDC) coordination. Despite being commercially available, there are only a handful of known structures with the 2-nitro-1,4-benzenedicarboxylate (BDC-NO<sub>2</sub>) ligand.<sup>7</sup> Here we report a new highly porous MOF, [(Zn<sub>7</sub>(μ<sub>4</sub>-O)<sub>2</sub>(BDC-NO<sub>2</sub>)<sub>5</sub>(DMF)]·H<sub>2</sub>O, CALF-22 (CALF = Calgary framework; DMF = *N,N*-dimethylformamide), containing BDC-NO<sub>2</sub> linkers and that features an uncommon<sup>8–10</sup> Zn<sub>7</sub>(μ<sub>4</sub>-O)<sub>2</sub>(COO)<sub>10</sub> SBU. The MOF also features large 3D pores and a high surface-accessible volume. The porosity is investigated by probing with N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, with the latter two also being described by the enthalpy of the

adsorption data. To our knowledge, no other reports of enthalpy adsorption data in nitro derivatives of MOFs exist.

CALF-22 was prepared solvothermally with Zn(OAc)<sub>2</sub> and H<sub>2</sub>BDC-NO<sub>2</sub> in 1:1 dry DMF/ethanol (EtOH) at 120 °C for 2 days. These conditions gave single crystals in 15% yield with respect to H<sub>2</sub>BDC-NO<sub>2</sub>. It was found that using Zn(NO<sub>3</sub>)<sub>2</sub> gave impurities, as did increasing the temperature. The synthesis was also sensitive to the ratio and dryness of the solvent because altering the ratio reduced the yield and using wet solvent reduced the stability of the end product.

The structure of CALF-22 contains a Zn<sub>7</sub>(μ<sub>4</sub>-O)<sub>2</sub>(COO)<sub>10</sub> cluster unit that links 10 BDC-NO<sub>2</sub> groups. The cluster, including two ligated DMF molecules, is shown in Figure 1.



**Figure 1.** Structure of CALF-22: (a) view of the Zn<sub>7</sub>(μ<sub>4</sub>-O)<sub>2</sub>(COO)<sub>10</sub> cluster where the apical BDC-NO<sub>2</sub> COO<sup>−</sup> groups are pointing to the left and right; (b) view along the *c* axis with free solvent graphically removed from the pores.

The cluster can be viewed as composed of two vertex-sharing Zn<sub>4</sub>O tetrahedra. The Zn ion shared between these two tetrahedra is octahedral. Of the other three Zn atoms in each tetrahedron, two are tetrahedral and the third (DMF-ligated) is distorted octahedral. For the central octahedral Zn atom, equatorial coordination is from four different μ<sup>3</sup>-bridging BDC-NO<sub>2</sub> carboxylate groups, and apical coordination is by the two O<sup>2−</sup> anions in the center of the Zn<sub>4</sub>O tetrahedra. For the tetrahedral Zn centers, the ligands are from the carboxylate groups of three monodentate BDC-NO<sub>2</sub> groups and the oxide anion. The Zn atom with the distorted octahedral geometry is coordinated by four different carboxylate moieties, an oxide anion, and a DMF solvent molecule. Each cluster links to six other clusters. In the *ab* plane, four pairs of BDC-NO<sub>2</sub> groups

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bridge the clusters. These BDC-NO<sub>2</sub> units are parallel and offset with C2...C7 distances of 3.556(1) Å. Perpendicular to this plane, single BDC-NO<sub>2</sub> molecules link to two other clusters. The nitro groups are positioned above and below the *ab* plane, as are the coordinated DMF molecules. Interestingly, no appreciable electron density is observed off of the aryl rings of the apical terephthalate groups in the single-crystal structure. With reproducible healthy yields of single crystals, a loss of NO<sub>2</sub> groups from 20% of the BDC-NO<sub>2</sub> groups seemed unlikely and elemental analysis supported retention of all NO<sub>2</sub> groups (some uncertainty remained with the potential for strongly bound DMF molecules). <sup>1</sup>H NMR on dissolved crystals definitively showed only the presence of BDC-NO<sub>2</sub> linkers (see Figure S2 in the Supporting Information, SI).

The efficient packing of the layers and the regular parallel orientation of the pillaring units running along the *c* axis create a regular 3D structure with channels along each of the *b* and *c* axes and the [110] direction. Considering the cluster as a 6-connecting node, one can visualize the structure being a tilted cubic network. The largest channels, along the *c* axis, have dimensions of 12.25 × 11.03 Å [8.83 × 7.71 Å accounting for van der Waals (vdW) radii]. The channels along the *b* axis are lined by the nitro groups with dimensions of 10.97 × 10.08 Å (7.65 × 6.76 Å including vdW radii). Channels along the [110] direction are also lined by nitro groups and have dimensions of 6.74 × 9.57 Å (3.42 × 6.25 Å including vdW radii). Analysis of the structure reveals significant potential void space, calculated at 55% (*SQUEEZE*) with coordinated DMF remaining and 65% upon DMF removal (these values are elevated because of the absence of NO<sub>2</sub> groups on the apical BDC groups in the crystal structure). Thermogravimetric analysis (TGA) showed a 30.5% mass loss to 200 °C followed by a second step, decomposition at 350 °C. The high desolvation temperature is presumably associated with the strong coordination of DMF (Zn–O = 1.977 Å).

The Zn<sub>7</sub>(μ<sub>4</sub>-O)<sub>2</sub> cluster has been observed in a number of discrete monocarboxylate complexes: ([Zn<sub>7</sub>O<sub>2</sub>(OAc)<sub>10</sub>(N-donor)]<sup>8a-d</sup> and [Zn<sub>7</sub>O<sub>2</sub>(2,6-difluorobenzoate)<sub>10</sub>(THF/MeCN)]<sup>8e</sup>. Coordination polymers have been formed by replacing monodentate groups with bridging N-donor atoms in the clusters.<sup>9</sup> None of these works<sup>8-10</sup> showed porous structures via gas sorption. Using a dicarboxylate, Fang et al.<sup>10</sup> reported a MOF with this SBU, [Zn<sub>7</sub>O<sub>2</sub>(phenylenediacrylate)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>], and studied H<sub>2</sub>, water, and methanol sorption. The cluster in this MOF is like in CALF-22 in that four pairs of carboxylates link in a plane with two carboxylates bridging perpendicularly. While the stability was not emphasized, water sorption was carried out (vide infra).

N<sub>2</sub> sorption at 77 K gave a type I isotherm (Figure 2) with a total uptake of 250 cm<sup>3</sup>(STP)/g. Fitting to Langmuir and Brunauer–Emmett–Teller models gave surface areas of 969 and 1022 m<sup>2</sup>/g, respectively. This is below the calculated surface area of 2142 m<sup>2</sup>/g based on the crystal structure<sup>11</sup> and indicates that activation was incomplete despite numerous approaches (vide infra).

For porous solids in general, but particularly for MOFs with well-coordinating solvents, optimal pore activation is a major challenge. Activation requires a balance between providing a sufficient driving force to remove solvent and maintaining the network. Numerous activation conditions were tested including solvent exchanges (CHCl<sub>3</sub>, toluene, and EtOH) to circulating exchange systems. In all cases, low-surface-area materials

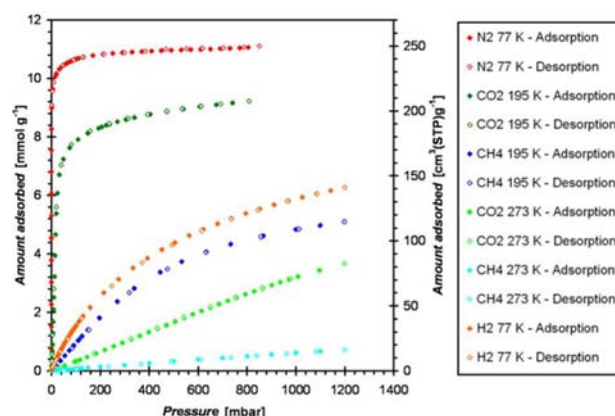


Figure 2. Gas-sorption isotherms performed on CALF-22.

resulted. The best procedure used solvent exchange of 1:1 DMF/EtOH followed by slow heating (0.2 °C/min) and holding at 130 °C for 6 h for an outgas rate of <1 μbar/min. Higher temperatures also gave reduced surface areas. Supercritical CO<sub>2</sub> is effective for activating MOFs,<sup>12</sup> but this was not available so, under the present activation, bare metal sites are not generated (Figure S4 in the SI).

CALF-22 adsorbed all gases (N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>) studied (Table S1 in the SI). The excess H<sub>2</sub> capacity (77 K, 1.2 bar) was 1.27 wt % with a reversible type I isotherm. CO<sub>2</sub> adsorption (273 K, 1.2 bar) gave good uptake of 3.67 mmol/g with a reversible and linear isotherm, with the latter indicating a homogeneous pore surface. While our experiment was limited to 1.2 bar, a higher pressure capacity can be estimated at lower temperature. The 195 K CO<sub>2</sub> isotherm gave a total capacity of 9.22 mmol/g. To compare, CH<sub>4</sub> sorption was low with maxima of 0.82 and 5.10 mmol/g at 273 and 195 K, respectively.

To study the gas–pore interaction, the isosteric heat of adsorption (*Q<sub>st</sub>*) was determined for CO<sub>2</sub> and CH<sub>4</sub>. For accuracy, the calculations were performed over three (CH<sub>4</sub>) and four (CO<sub>2</sub>) temperatures with excellent fits. The zero loading *Q<sub>st</sub>* for CO<sub>2</sub> was 21.5 kJ/mol, which increased to 24.5 kJ/mol with loading. For CH<sub>4</sub>, the *Q<sub>st</sub>* was 10.6 kJ/mol at zero loading and increased to 15.4 kJ/mol. The increases in *Q<sub>st</sub>* with loading are attributed to favorable gas–gas interactions. Overall, these *Q<sub>st</sub>* values indicate weaker interactions and corroborate that metal sites were not activated. To compare, in MIL-100 the Δ*H<sub>ads</sub>* for CO<sub>2</sub> is 62 kJ/mol due to binding to Cr.<sup>13</sup> Additionally, TGA of the post-adsorption sample (Figure S3 in the SI) shows 8.45% mass loss from 250 to 320 °C (calcd 8.69 wt % for two DMF molecules) and <sup>1</sup>H NMR spectra (Figure S4 in the SI) corroborate that DMF cannot be removed without framework collapse.

The use of nitro-substituted linkers in MOFs is not widely studied.<sup>7</sup> The electron-withdrawing nature of the nitro group would be expected to strongly impact coordination (*pK<sub>a</sub>*: H<sub>2</sub>BDC-NO<sub>2</sub>, 1.73; H<sub>2</sub>BDC, 3.54). It has been studied in isomorphous families of jungle-gym coordination polymers,<sup>7a,b</sup> where the nitro group affected the sorption of protic guests, and in tuning of the electronic structure of aromatics for photochemistry in MOFs.<sup>7c</sup> Surprisingly, a study reporting *Q<sub>st</sub>* for gases in nitro derivatives of MOFs does not exist. Here, particularly for CO<sub>2</sub>, the low *Q<sub>st</sub>* (21.5 kJ/mol) shows that the –NO<sub>2</sub> group is *not* interacting strongly with the gases (cf. 40.1 kJ/mol in an amine-modified MOF<sup>6e</sup>). Lower than expected *Q<sub>st</sub>* values can be due to a functional group being masked by the

pore structure;<sup>14</sup> however, here the NO<sub>2</sub> groups are directed into the pores.

Demonstrating stability is key to the industrial application of MOFs. Powder X-ray diffraction of the postanalysis sample of CALF-22 showed no significant changes (even after an additional 1 month in air; Figure S12 in the SI), indicating that the structure was stable to activation and analysis. Notably, the N<sub>2</sub> isotherm was repeated and showed no significant change in the shape or total capacity. Ultimately, the same sample was used for 11 isotherms (sorption and desorption) with different gases. The 77 K N<sub>2</sub> isotherm was repeated after this and showed no change to the original run. This stability is higher than MOF-5<sup>15</sup> and reaffirms the stability of the Zn<sub>7</sub>O<sub>2</sub>(COO)<sub>10</sub> cluster suggested by the water sorption studies of Fang et al.<sup>10</sup>

Incorporation of the BDC-NO<sub>2</sub> linker gives a robust high-surface-area MOF that features the Zn<sub>7</sub>O<sub>2</sub>(COO)<sub>10</sub> cluster. CALF-22 shows that the cluster is significantly more robust than its Zn<sub>4</sub>O(COO)<sub>6</sub> cousin. The Zn<sub>7</sub>O<sub>2</sub>(COO)<sub>10</sub> cluster forms networks that are doubly reinforced in one plane and potentially offer bare metal sites for the binding of guests. Conversely, the nitro groups on the BDC linkers, somewhat surprisingly, appear *not* to play a significant role in augmenting gas sorption.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Details on the synthesis, structure, and gas-sorption analysis and a CIF file for CALF-22. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version.

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### Notes

The authors declare no competing financial interest.

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