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Journal Name

COMMUNICATION

The First Example of a Zirconium-Oxide Based Metal-Organic Framework Constructed from Monocarboxylate Ligands

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This work reports the first example of a Zr-based MOF which is exclusively constructed from the monocarboxylate ligand formate. Despite the low surface area, the new material exhibits an unexpectedly favourable affinity for carbon dioxide over nitrogen at room temperature.

Metal-organic frameworks (MOFs) are a rapidly expanding class of crystalline porous materials.[1] Owing to their exceptional chemical, hydrothermal, and mechanical stabilities, zirconium (Zr) based MOFs have attracted considerable attention since $[Zr_6O_4(OH)_4(bdc)_6]$ (where bdc = 1,4-benzenedicarboxylate, also known as UiO-66) was discovered in 2008.[2-4] Several structures containing Zr-oxo clusters have been reported in recent years, however, these have exclusively contained multidentate ligands (typically bi-, tri-, and tetracarboxylate ligands, ESI).[2, 3, 5-13] To date, no Zr-based frameworks constructed from monocarboxylate ligands have been reported.

Monocarboxylic acids, such as acetic acid, were first introduced to Zr-based MOFs by Schaate *et. al.* as modulators to regulate crystal growth and improve the crystallinity of the UiO-type isoreticular frameworks.[14, 15] Further studies have illustrated that during synthesis, monocarboxylic acids aid not only in the formation of the characteristic hexanuclear Zr-oxo clusters, but that they also directly compete with the multidentate carboxylate linkers for metal binding. Ultimately, this leads to materials in which the ligands are partially replaced by the modulator, resulting in defects and larger pores.[15-17] In addition, previous literature has illustrated that formate anions can act as monocarboxylate ligands for the construction of three-dimensional magnesium formate frameworks.[18-21]

From an industrial viewpoint, gas separations are one of the most promising applications for MOFs.[22] In particular, the capture of carbon dioxide (CO_2) from industrial processes such as natural gas sweetening and hydrogen purification represents a significant environmental challenge that may be addressed by the application of new separation materials.[22-24] A plethora of MOFs have been explored for such applications, and many of these materials have exhibited higher selectivities for adsorption compared with traditional porous materials including mesoporous silicas, carbon nanotubes and zeolites.[22, 23] Studies also indicate that modification of the physical/chemical environment of the cavities within MOFs can be used to tune the host-guest interactions, thus modulating the selectivity.[25, 26]

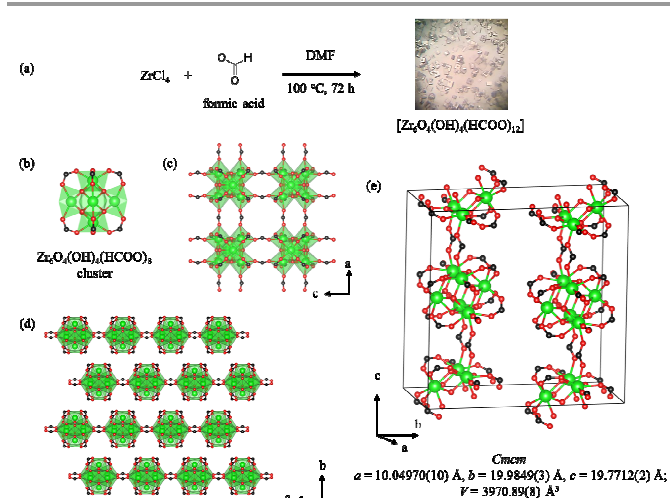Figure 1. (a) Synthetic strategy for ZrFA and an image of the colourless plate-like crystals; (b) the octahedral secondary building unit, $ZrO_4(OH)_4(HCOO)_8$; (c) the coordination modes for a single ZrFA layer through the *b*-axis; (d) 2D to 3D stacking of the framework along the *c*-axis; (e) unit cell and cell parameters of ZrFA. Colour scheme: Zr in green, O in red, C in black. H atoms and solvent molecules are omitted for clarity.

Herein we report the first example of a Zr-based framework constructed exclusively from the monocarboxylate ligand formate (FA). X-Ray diffraction analysis, thermal gravity analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) have enabled structural elucidation of the new material. The CO_2 adsorption

performance of the material at different temperatures has also been evaluated in order to provide a comparison with other widely-studied Zr-based MOFs.

The framework $[Zr_6O_4(OH)_4(FA)_{12}]\cdot DMF\cdot 6H_2O$ (denoted here as ZrFA) was synthesised as colourless plate-like crystals by the solvothermal reaction of Zr^{IV} chloride, formic acid and 3,5-pyridinedicarboxylic acid or 2,4-pyridinedicarboxylic acid in N,N'-dimethylformamide (DMF) at 100 °C for 72 h (Figure 1a, ESI). Single-crystal X-ray diffraction studies revealed that ZrFA crystallises in the orthorhombic space group $Cmcm$, with unit cell parameters $a = 10.04970(10)$ Å, $b = 19.9849(3)$ Å, $c = 19.7712(2)$ Å and $V = 3970.89(8)$ Å^3 (Figure 1e). In the absence of pyridinedicarboxylic acid, ZrFA was obtained as a powdered sample in a shorter reaction time (16 h) at 100 °C. The phase purity was confirmed by Le Bail refinement (ESI).

The structure of ZrFA consists of $Zr_6O_4(OH)_4$ secondary building units (SBUs), in which the triangular faces are alternately capped by μ_3-O and μ_3-OH groups. Eight vertices of the octahedral Zr_6-oxo cluster are occupied by intra-cluster formate ions (Figure 1b). In the ac plane, $Zr_6O_4(OH)_4(HCOO)_8$ units are bridged by two inter-cluster formate linkers to yield infinite two-dimensional (2D) covalently bonded square layers (Figure 1c). Ultimately, these 2D networks are stacked along the b-axis to form a three-dimensional structure (Figure 1d).

As mentioned above, monocarboxylic acids are typically employed as modulators to manipulate the crystal growth of Zr-MOFs by tuning the crystallinity, crystal size/shape, and the presence of defects within the lattice.[14-16] Two previous literature reports have demonstrated the linkage of Zr_{12} clusters (two Zr_6 sub-units via four acetate, propionate, vinyl acetate or 3,3'-dimentylacrylate ligands),[27, 28] and to the best of our knowledge, the present work represents the first report of such an intermolecular bridging mode for a monocarboxylate ligand in a zirconium framework.[6]
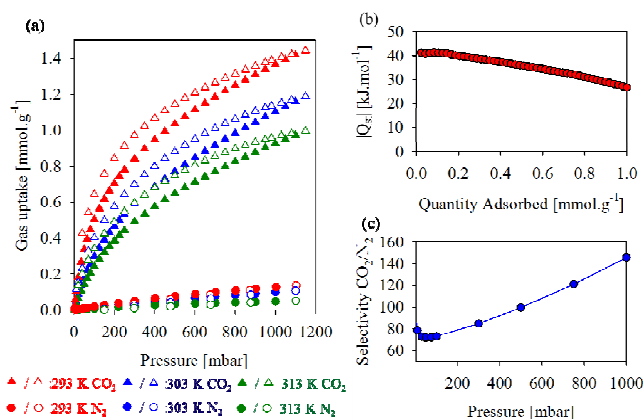
Thus, rather than functioning as a ligand, pyridinedicarboxylic acid performs the function of a modulator to favour the formation of ZrFA single crystals. In a recent report, a similar phenomenon was observed by Goodwin and co-workers during formate-modulated UiO-66(Hf) synthesis, where the appearance of an additional impurity phase (α hafnium formate vs. UiO-66(Hf)) was detected when the concentration of H_2bdc (1,4-benzenedicarboxylic acid) was very low compared to formic acid (ca. 200-fold excess).[29] Attempts to use a bulkier monocarboxylic acid (acetic acid, Van der Waals volume $V_{acetate} \sim 57$ Å^3 vs $V_{formate} \sim 40$ Å^3) for the synthesis of isostructural materials was unsuccessful, and has been attributed to the steric hindrance within the structure.

The total solvent-accessible volume of ZrFA was calculated to be 34.7% of the cell volume (SQUEEZE module of the PLATON routine). Residual electron density was found by Fourier analysis in the void space and was assigned to guest molecules (water and N,N'-dimethylformamide).

Table 1. Comparison of adsorption selectivity for CO_2/N_2 and heat of adsorption at zero coverage (Q_{st}^0) of CO_2 in different Zr-based MOFs.

Material	CO_2/N_2 selectivity[a]	Temperature [K]	$\|Q_{st}^0\|$ [kJ.mol^{-1}]	Ref.
ZrFA	31.0[a]	293	41.0	This work
UiO-67	9.4[a]	298	15.9	30
BUT-10	18.6[a]	298	21.8	30
BUT-11	31.5[a]	298	25.9	30, 31
UiO-66	22.8[b]	298	25.5	32
UiO-66-NH_2	32.3[b]	298	29.5	32
UiO-66-NO_2	25.5[b]	298	31.7	32
UiO-66-Br	25.3[a]	298	-	33
UiO-66-$(COOH)_2$	56.0[b]	303	34.8	34

[a] calculated at $P_{N2} = 750$ mbar and $P_{CO2} = 150$ mbar from single component isotherms; [b] calculated at $P_{N2} = 850$ mbar, $P_{CO2} = 150$ mbar from single component isotherms.

Figure 2. (a) CO_2 and N_2 isotherms for ZrFA at 293, 303 and 313 K; (b) isosteric heat (Q_{st}) of CO_2 adsorption; (c) IAST-predicted selectivities toward 15 : 85 CO_2/N_2 at 293K.

Unlike other Zr-based MOFs in the literature, the bidentate pyridinedicarboxylic acid, whose role as a modulator is essential for ZrFA single crystal formation, is not incorporated into the structure.[2, 3, 5, 6] This observation can be explained by the higher concentration of formic acid in the reaction medium compared with that of pyridinedicarboxylic acid. In general, a higher dosage of the modulator generates a higher level of defects in Zr-frameworks.[16] Considering that the concentration of formic acid is in ca. 800-fold excess compared with that of pyridinedicarboxylic acid, formate outcompetes pyridinedicarboxylate for binding to the Zr_6 cluster.

Prior to further analysis, as-synthesised ZrFA was washed with DMF (~10 mL) three times and then solvent-exchanged with acetone and dried at 60 °C under vacuum to remove any unreacted precursors and/or solvent molecules (ESI). TGA and variable temperature powder X-ray diffraction (VT-PXRD) analysis indicated that the thermal stability of ZrFA was lower than that of other reported Zr-MOFs (~120 °C vs. 400 °C for UiO-66).[15] The decreased stability has been assigned to the presence of a volatile non-aromatic carboxylate functionality.

ZrFA was shown to be essentially non-porous to N_2 gas at 77, 293, 303 and 313 K, but porous to CO_2 at elevated temperatures. Figure 2a shows that the uptake of N_2 at 293 K reaches a maximum of 0.13 mmol.g^{-1} at 1100 mbar. By contrast, the relatively higher CO_2 uptake at 1 atm indicates that the pore structure of ZrFA is accessible to this adsorbate over the temperature range 293-313 K. The total CO_2 uptakes at 1100 mbar and 293, 303 and 313 K are 1.44, 1.19 and 1.12 mmol.g^{-1}, respectively (Figure 2b). The observed hysteresis in the CO_2 isotherms can be attributed to the small pore windows in the MOF, which hinder the diffusion of guest molecules upon adsorption and desorption.

The calculated isosteric heat of CO_2 adsorption at zero coverage ($|Q_{st}|$) using adsorption data at 293, 303, and 313 K is 41 kJ.mol^{-1} for ZrFA. As a function of the surface coverage, Q_{st} decreases and reaches 27 kJ.mol^{-1} (Figure 2b). The μ_3-OH groups in the Zr_6-oxo clusters are believed to be the initial binding sites for CO_2 adsorption, as confirmed through neutron diffraction experiments and first-principles calculations in MOFs such as UiO-66.[16]

The relatively higher CO_2 uptake compared with the marginal N_2 uptake at ambient temperatures prompted an investigation of the

capacity of ZrFA to selectively adsorb CO_2 over N_2. The ideal selectivity of CO_2/N_2 was calculated using two methods: a single point method using a ratio of uptakes of the two pure component gases at relevant pressures; and Ideal Adsorbed Solution Theory (IAST).[35] Table 1 shows the results of the selectivity calculations for ZrFA at 293 K compared to several reference Zr-MOFs. The results indicate that although the CO_2 adsorption selectivity for ZrFA is lower than those values reported for carboxylate-functionalised Zr-MOFs, it is comparable to the selectivities for sulfone- and amino-functionalised ones. Additionally, the IAST CO_2/N_2 selectivity factor of ZrFA for a gas mixture containing 850 mbar N_2 and 150 mbar CO_2 at 293 K is 145.7, which reaffirms the previous observation that ZrFA outperforms other functionalised UiO-66 and UiO-67 frameworks with regards to its CO_2 selectivity (Figure 2c).

In summary, this work has demonstrated the synthesis, characterisation and CO_2/N_2 adsorption properties of a new zirconium-based framework, which represents the first example of a Zr-MOF constructed exclusively from monocarboxylate ligands. The CO_2 adsorption selectivity over N_2 found in ZrFA is comparable to that reported for related materials such as UiO-66 and UiO-67 with functional groups such as $-NH_2$, $-NO_2$, and $-SO_2$ based on single component isotherm data. The results presented here may provide useful information for the future design of Zr-based MOFs for industrial applications.

Notes and references

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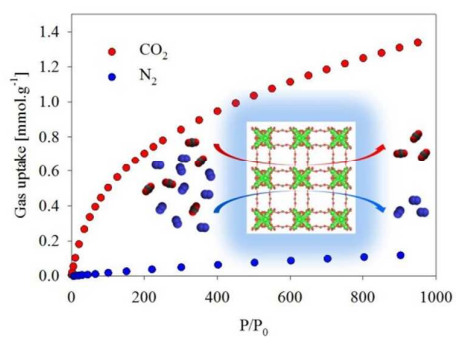
† **Crystal Data** for $[Zr_6O_4(OH)_4(FA)_{12}]\cdot DMF\cdot 6H_2O$ ($M =$1377.58), (CCDC 1023946): orthorhombic, space group *Cmcm* (no. 63), $a =$ 10.04970(10) Å, $b =$ 19.9849(3) Å, $c =$ 19.7712(2) Å, $V =$ 3970.89(8) Å^3, $Z = 4$, $T = 150(2)$ K, $\mu(CuK\alpha) = 13.618$ mm^{-1}, $D_{calc} = 2.304$ g/mm^3, 35477 reflections measured ($8.84 \leq 2\theta \leq 151.78$), 2259 unique ($R_{int} = 0.0467$, R$_\sigma$ $= 0.0165$) which were used in all calculations. The final R_1 was 0.0546 ($>2\sigma(I)$) and wR_2 was 0.1729 (all data).

Electronic Supplementary Information (ESI) available: Single crystal and powder X-ray diffraction summaries, FT-IR, TGA and adsorption analyses. See DOI: 10.1039/c000000x/

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Dalton Transactions Accepted Manuscript

TOC Graphic and Text

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