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Engineering New Defective Phases of UiO Family Metal-Organic Frameworks with Water

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Stability of UiO-67(Hf) family MOFs



Fig. S1 Stability of hcp UiO-67(Hf) synthesised using water



Fig. S2 Stability of hns UiO-67(Hf) synthesised using water

Refinement of hcp UiO-66 (F₄BDC)



Fig. S3 Pawley refinement of UiO-66 (F₄BDC) in space group P63/mmc and with parameters 14.82(1) Å and 36.18(1) Å (R_{wp} 3.086).

Details of Subsequent Refinement against a Proposed Structure.

Refinement against an optimised model **hcp** UiO-66 (F₄BDC) structure was carried out in space group $P6_3$ /mmc and gave a good fit, with cell parameters 14.793(8) Å and 35.75(5) Å (R_{wp} 8.839). The background was modelled using a freely refining Chebyshev polynomial with seven parameters. In order to account for the (hkl)-dependent peak broadening, an additional term was introduced using second order spherical harmonics. A Lorentzian size-broadening term and a scale factor based on $sin(\theta)$ (which corrects the peak intensities arising from the sample being thin relative to the beam penetration depth) were also applied. The discrepancies in low-Q peak intensities are likely to be due to the presence of guests in the pores.⁵¹

hcp UiO-66(Hf)



Fig. S4 Pawley refinement of hcp UiO-66, synthesised with 0.4 mL water and 1.5 mL formic acid, in space group $P6_3$ /mmc and with parameters 14.708(5) Å and 36.54(2) Å (R_{wp} 2.483).

Details of Subsequent Refinement against a Proposed Structure.

Refinement against the **hcp** UiO-66 structure was carried out in space group $P6_3$ /mmc, and gave cell parameters 4.742(3) Å and 6.50(2) Å (R_{wp} 5.259). The background was modelled using a freely refining Chebyshev polynomial with nine parameters. In order to account for the anisotropic peak broadening, an additional term was introduced using second order spherical harmonics. A Gaussian size-broadening term, a scale factor based on $sin(\theta)$ and a preferred orientation term along [001] were also applied. The discrepancies in low-Q peak intensities are likely to be due to the presence of guests in the pores.^{S1}

Synthesis of UiO-66(Hf) with high concentrations of water and formic acid



Fig. S5 UiO-66 synthesised with 2 mL formic acid and varying amounts of water, showing the decrease of crystallinity as the water concentration increases, although the phase remains **hcp**.



Fig. S6 Improvement of crystallinity of **hcp** UiO-66 synthesised with 2.5 mL H_2O , by increasing the amount of formic acid in the synthesis.



Fig. S7 UiO-66 synthesised with very high concentrations of water and formic acid; the phase remains **hcp**.

Stability of hcp UiO-66(Hf)



Fig. S8 Stability of activated hcp UiO-66(Hf) over time.

TGA model of fcu and hcp UiO-66(Hf)

TGA can be used to help determine the number of defects in a MOF sample. Since the final product of the oxidation of UiO (Hf) MOFs is HfO₂, TGA can be used to determine the mass fraction of other molecules in the material. Discrepancies between the expected mass fraction of linkers and the experimental fraction indicate the presence of defects.⁵²

The loss of a dicarboxylate linker from between two clusters in UiO MOFs requires the presence of compensating "capping" molecules at both coordination sites, in order to charge-balance the clusters. These capping molecules are usually derived from other species present during the synthesis, such as modulating acid, water, or hydroxide.^{S1,S3,S4} While two monodentate anions derived from the modulating acid would be required to replace one missing bidentate linker, two hydroxides and six water molecules could also compensate for a linker vacancy in UiO-66, i.e. with a hydroxide and a water molecule bound to each metal centre pair, with a third water molecule adding stability via hydrogen bonds.^{S5}



Fig. S9 2*n* capping molecules replace n bidentate linkers. For clarity, the double clusters are shown as polyhedral, and only one BDC linker per double cluster is shown. The BDC is replaced by: left, a formate anion; right, a hydroxide anion and two water molecules.

As long as these defect-compensating molecules are quite small, the replacement of *n* dicarboxylate linkers with 2*n* capping molecules results in the mass of the framework being lower than would be expected for a perfect framework. This means that, by calculating the mass fractions at different stages of the framework decomposition, the ratio of capping molecules to linkers can be determined (if the identity of the capping molecules is known) and therefore the concentration of missing-linker defects in the sample can be estimated.

Understanding the changes to the framework during heating is necessary in order to deduce the composition of the intact defective framework.



Fig. S10 Schematic of changes during TGA heating of hcp UiO-66

Initial mass losses below 150°C are due to the loss of solvent molecules.⁵⁶ Under the proposed model, the hydrogen-bonded water molecules are lost in this step.⁵⁵ After this loss, the sample will consist of the metal clusters with BDC linkers, formate, hydroxide and water in a ratio dependent upon the synthesis and activation conditions.

The second significant mass loss occurs between 250 and 300°C, corresponding to the dehydroxylation of the $Hf_6O_4(OH)_4$ cluster to Hf_6O_6 .⁵⁶⁻⁵⁸ In defective UiO-66 materials where formate molecules have replaced some linkers, formate ligands are lost over a similar temperature range.^{59,510} The metal-bound water molecules are also lost during this stage.⁵⁵ However, during dehydroxylation and loss of formate, the cluster must remain charge-balanced; due to high levels of water nearby, it is likely that the formate molecules are replaced by hydroxide. For the **hcp** model, an additional assumption is that the six cluster-bridging μ_2 -OH are not lost in the dehydroxylation step.

The largest step in the TGA curve, at around 520-540°C, corresponds to the decomposition of the remaining framework and the formation of HfO_2 ; as noted above, a smaller-than-expected final mass loss is likely to be due to a deficiency of linkers in the sample.^{56, S10-12}

Thus the size of the final mass loss step can be used to find the number of BDC linkers and, working backwards, the composition of the original framework [Table S1].

Table S1 Mass changes under heating of UiO-66 frameworks. "BDC_{1/2}" represents the number of half-BDC ligands attached to each cluster (i.e. for perfect **fcu** UiO-66, BDC_{1/2} = 12; for perfect **hcp** UiO-66, BDC_{1/2} = 18).

T (°C)	fcu UiO-66 (for comparison)	hcp UiO-66
150-250	$Hf_6O_4(OH)_4(BDC_{1/2})_x(FcO)_y(OH)_z \cdot zH_2O$	(Hf ₆ O ₄ (OH) ₄) ₂ (OH) ₆ (BDC _{1/2}) _x (FcO) _y (OH) _z ·(z+6)H ₂ O
350-500	$Hf_6O_6(BDC_{1/2})_x(OH)_{z+y}$	$(Hf_6O_6)_2(OH)_6(BDC_{1/2})_x(OH)_{z+y}$
>550	HfO ₂	HfO ₂
	Total Mass Loss	
520-540	x(BDC _{1/2}) + (6+x+y)(OH) – 12O	x(BDC _{1/2}) + (z+y)(OH) -60

For the defective sample synthesised with 1.5 mL formic acid and 0.4 mL water, known from PXRD to be **hcp** UiO-66, the ratio of formate to BDC is known from solution NMR, i.e., in the equations above, y = 0.292x/2. For the defective sample synthesised with 1.5 mL formic acid and 1.5 mL water, this ratio gives y = 0.583x/2.

TGA data for hcp UiO-66(Hf) synthesised with varying amounts of water



Figure S11 TGA under air of UiO-66 samples synthesised with 1.5 mL FcOH and varying concentrations of water. The samples with 0.4 mL and 1.5 mL water were both phase-pure **hcp** by PXRD.

Solution ¹H NMR of hcp UiO-66(Hf)



Fig. S12 ¹H NMR spectra of **hcp** UiO-66 synthesised with 0.4 mL H_2O and 1.5 mL FcOH, washed and activated. Left, full spectrum; right, zoomed spectrum.



Fig. S13 ¹H NMR spectra of **hcp** UiO-66 synthesised with 1.5 mL H₂O and 1.5 mL FcOH, washed and activated. Left, full spectrum; right, zoomed spectrum.

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