As defects significantly affect the properties of metal-organic frameworks (MOFs)–from changing their mechanical properties to enhancing their catalytic ability–obtaining synthetic control over defects is essential to tuning the effects on the properties of the MOF. Previous work has shown that synthesis temperature and the identity and concentration of modulating acid are critical factors in determining the nature and distribution of defects in the UiO family of MOFs. In this paper we demonstrate that the amount of water in the reaction mixture in the synthesis of UiO family MOFs is an equally important factor, as it controls the phase which forms for both UiO-67(Hf) and UiO-66(Hf) (F4BDC). We use this new understanding of the importance of water to develop a new route to the stable defect-ordered hcp UiO-66(Hf) phase, demonstrating the effectiveness of this method of defect-engineering in the rational design of MOFs. The insights provided by this investigation open up the possibility of harnessing defects to produce new phases and dimensionalities of other MOFs, including nanosheets, for a variety of applications such as MOF-based membranes.
Engineering New Defective Phases of UiO Family Metal-Organic Frameworks with Water†

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As defects significantly affect the properties of metal-organic frameworks (MOFs)–from changing their mechanical properties to enhancing their catalytic ability–obtaining synthetic control over defects is essential to tuning the effects on the properties of the MOF. Previous work has shown that synthesis temperature and the identity and concentration of modulating acid are critical factors in determining the nature and distribution of defects in the UiO family of MOFs. In this paper we demonstrate that the amount of water in the reaction mixture in the synthesis of UiO family MOFs is an equally important factor, as it controls the phase which forms for both UiO-67(Hf) and UiO-66(Hf) (F4BDC). We use this new understanding of the importance of water to develop a new route to the stable defect-ordered hcp UiO-66(Hf) phase, demonstrating the effectiveness of this method of defect-engineering in the rational design of MOFs. The insights provided by this investigation open up the possibility of harnessing defects to produce new phases and dimensionalities of other MOFs, including nanosheets, for a variety of applications such as MOF-based membranes.

1 Introduction

The UiO family of MOFs is of great interest for real-world applications, including sensing and energy storage, Uri UiO-66 (the prototypical UiO framework) is particularly thermally and chemically stable, due to the high coordination of its hexanuclear M₆(µ₃-O)₄(µ₃-OH)₄ metal clusters (M = Hf, Zr) by 12 linear dicarboxylate linkers in a face-centred cubic topology. As well as stability, this family of MOFs possesses catalytic activity and gas sorption capabilities, and the use of organic linkers with different functionalities can give access to new or improved properties such as increased CO₂ adsorption.

Zirconium and hafnium MOFs, including the UiO family, exhibit a wide range of defect chemistry. As defects alter the properties of the framework, obtaining control over the type, location and concentration of defects will in turn allow control over the properties of the MOF. UiO-66 is an ideal system for studying defective MOFs as it commonly incorporates both linker and cluster vacancies. The framework remains stable despite the presence of these defects due to the strong metal-linker coordination and high connectivity of the framework.

Missing-linker defects require compensating 'capping' ligands at coordination sites on the metal cluster left vacant by the absence of linkers; these capping ligands are usually derived from other species (such as solvent or counterions) present during the synthesis. Defects can therefore be deliberately introduced via the inclusion of these species in the reaction mixture. In 'modulated' synthesis, a monocarboxlic acid modulator is included in the synthesis, giving a ready source of monocarboxylate groups that compete with the linker to coordinate to the cluster, thereby creating missing-linker defects. While modulated synthesis was originally devised as a method of controlling the morphology of MOF crystals via capping coordination sites on the faces of the MOF crystal, the linker vacancies introduced by modulated synthesis can be incorporated within the framework, leading to a defective structure. By altering the identity and concentration of the modulator included in the synthesis, the concentration of linker vacancies in a MOF can be tuned systematically.

In our previous work, we showed that the use of modulating formic acid enabled control over the spatial distribution of defects in UiO family MOFs. In UiO-66(Hf), correlation of missing-linker defects around the clusters, compensated by the modulator, leads to the introduction of cluster vacancies correlated along ⟨100⟩ directions in the fcc matrix, forming correlated domains with the reo (primitive cubic) topology [Fig. 1].
Fig. 1 Reported phases of UiO-66 (top; formed with terephthalate (‘BDC’) linkers) and UiO-67 (bottom; formed with biphenyldicarboxylate (‘BPDC’) linkers). Dashed arrows show the differences in the synthesis conditions required in order to obtain different phases; solid arrows show postsynthetic treatments. Structural models derived from crystallographic information files reported in Refs. 6,9,19.

UiO-66(Hf), complete defect ordering is prevented by the concomitant formation of a Hf₆O₄(OH)₄(FCO)₁₂ hafnium formate layered framework as modulator concentration increases. 19,24 However, using modulating formic acid in the synthesis of UiO-67(Hf) results in the formation of a new defect-ordered phase. 6 In this UiO-67(Hf) phase, the missing-linker defects order within a (111) plane of the parent fcu structure, resulting in the condensation of pairs of 12-coordinate M₆(µ₃-O)₄(µ₁-OH)₄ clusters into 18-coordinate [M₆(µ₃-O)₄(µ₁-OH)₄]₂(µ₂-OH)₆ double clusters, giving a hexagonal hcp topology [Fig. 1]. The structural relationship between the fcu and hcp frameworks can be visualised by distorting the cubic structure along the [111] direction, so that the (111) plane of the fcu structure corresponds to the (001) plane of the hcp. This relationship means that the powder X-ray diffraction patterns are also closely related, as the fcu (111) reflection, corresponding to the close-packed plane, is replaced by reflections corresponding to the (002), (100) and (101) pseudo-close-packed planes in the hcp structure. Therefore, these two phases can be differentiated by the presence of these reflections. Rather than nano-domains, hcp UiO-67(Hf) is obtained as an ordered single phase bulk material.

These new defective frameworks have different properties from the parent non-defective UiO frameworks. Nano reo UiO-66(Hf) displays significantly enhanced high-pressure gravimetric gas sorption compared to fcu UiO-66(Hf). 11 In hcp UiO-67(Hf), the directionality of the structure means that selective topotactic delamination under gentle conditions produces the crystalline layered hxl structure, and under more forcing conditions (such as sonication or grinding) gives two-dimensional nanosheets, hereafter named hns UiO-67(Hf). 12,13

While defect engineering is becoming increasingly recognised as an important technique for tuning the properties of frameworks, the factors determining control over the degree and correlation of defects are not well understood. In contrast to the use of modulated synthesis, 14 the influence of water in the reaction mixture on the formation of defect phases of UiO family MOFs is not well-explored. This is despite water being essential for the formation of the metal cluster in UiO family MOFs, and in a wider chemical context, playing a critical role in zirconium and hafnium solution chemistry. 23,25,39–41 Additionally, while hydrothermal syntheses of UiO family MOFs are particularly environmentally attractive, as they remove the need to use toxic organic solvents such as DMF, there has been little specific investigation into the potential effects on the phase of the MOF framework of using water as a solvent. Previously reported syntheses of UiO-66 (F₂BDC) (UiO-66 with tetrafluoroterephthalate linkers) with and without water produce diffraction patterns indicative of different phases, but this has until now not been explained. 13,43 Additionally, although the hcp topology has been reported for UiO MOFs formed from other ligands, such as 2,2’-bipyridinedicarboxylate and (nitro)triphenyldicarboxylate, since our synthesis of hcp UiO-67(Hf), the archetypal UiO-66(Hf) material was until recently unknown, and has only been synthesised using ionic liquids rather than a more standard solvothermal synthesis. 45

In this work we systematically investigate the role of water in the formation of defect phases of UiO family MOFs, using a combination of synthesis, powder X-ray diffraction, thermogravimetric analysis and quantum chemical calculations. By varying the amount of water in the synthesis we demonstrate that, alongside formic acid, water is crucial to the successful synthesis of hcp UiO-67(Hf) and, additionally, that water allows the direct synthesis of the layered-nanosheet phase hns UiO-67(Hf). We use this knowledge to explain both reported and new phases of UiO-66(Hf) (F₂BDC) and then to synthesise hcp UiO-66(Hf) using conventional solvents. All UiO MOFs synthesised for this report are the hafnium analogues, unless otherwise specified.

2 Experimental

2.1 Synthesis

All reagents used were obtained from commercial suppliers and used without further purification.

2.1.1 Synthesis of UiO-67(Hf) defect phases.

Procedure modified from Ref. 9. HfCl₃ (Acros Organics, 99 %, 0.3 mmol, 96.1 mg) and biphenyldicarboxylic acid (H₂BPDC) (Acros Organics, 98 %, 0.3 mmol, 72.6 mg) were added to a 23 mL PTFE-lined steel autoclave, followed by dry N,N-dimethylformamide (DMF) (Sigma Aldrich, 99.85 % anhydrous DMF) (4 mL), and varying amounts of formic acid (Fisher, 98/100 %) (0.25–2 mL) and water (0–0.2 mL). The autoclave was sealed and heated at 150°C for 24 hours. The resulting white microcrystalline powder was filtered under vacuum, washed on the filter (DMF, Alfa Aesar, 99 %, 5 mL) and the solid product
dried. Phase-pure hcp UiO-67 formed with 1 mL formic acid and 0.05 mL water. Phase-pure hns UiO-67 formed with 1 mL formic acid and 0.2 mL water.

2.1.2 Synthesis of UiO-66(Hf) defect phases.

HfCl₄ (Acros Organics, 99 %, 0.3 mmol, 96.1 mg) and terephthalic acid (H₂BDC) (Alfa Aesar, 98 %, 0.3 mmol, 49.8 mg) were added to a 23 mL PTFE-lined steel autoclave, followed by dry N,N-dimethylformamide (Sigma Aldrich, 99.85 % anhydrous DMF) (4 mL), and varying amounts of formic acid (Fisher, 98/100 %) (0.5–3.0 mL) and water (0–3.5 mL). The autoclave was sealed and heated at 150°C for 24 hours. The resulting white microcrystalline powder was filtered under vacuum, washed on the filter (DMF, Alfa Aesar, 99 %, 5 mL) and the solid product dried. Phase-pure hcp UiO-66 formed with 1.5 mL formic acid and 0.4 mL water.

2.1.3 Hydrothermal synthesis of UiO-66(Hf) (F₂BDC) phases.

Procedure adapted from Ref. 43. HfCl₄ (Acros Organics, 99 %, 0.1 mmol, 32.0 mg) and tetrafluoroterephthalic acid (H₂F₂BDC) (Sigma, 97 %, 0.1 mmol, 23.8 mg) were added to a 23 mL PTFE-lined steel autoclave, followed by varying ratios of water and acetic acid (Sigma-Aldrich, >99.7 %) (0.96 mL solvent in ratios from 0:100 to 100:0 water:acid v/v). The autoclave was sealed and heated at 120°C or 150°C for 24 hours. The resulting white microcrystalline powder was filtered under vacuum, washed on the filter (water, 5 mL) and the solid product dried. Phase-pure hcp UiO-66(Hf) (F₂BDC) was synthesised at 120°C, with 60:40 water:acetic acid. This synthesis was further scaled up to HfCl₄ (0.3 mmol, 96.1 mg), H₂F₂BDC (0.3 mmol, 71.4 mg), water (1.73 mL) and acetic acid (1.15 mL). The hcp zirconium analogue was synthesised under the same conditions but with ZrCl₄ as the source of metal ions. The hcp structure was also produced when the modulating acetic acid was replaced with the same volume of formic acid.

2.1.4 Anhydrous synthesis of fcu UiO-66(Hf) (F₂BDC).

Procedure adapted from Ref. 44. HfCl₄ (Acros Organics, 99 %, 0.1 mmol, 32.0 mg) and tetrafluoroterephthalic acid (H₂F₂BDC) (Sigma, 97 %, 0.1 mmol, 23.8 mg) were added to a 23 mL PTFE-lined steel autoclave, followed by tetrahydrofuran (THF) (Fisher, analytical grade, 4 mL) and hydrochloric acid (Honeywell Fluka, fuming, 36.5-38 %, 42 µL). The autoclave was sealed and heated at 80°C for 24 hours. The resulting white microcrystalline powder was filtered under vacuum, washed on the filter (THF, Fisher, analytical grade, 5 mL) and the solid product dried.

2.2 Characterisation

2.2.1 Sample washing and activation method.

Procedure adapted from Ref. 14. Unreacted ligand was removed from the sample by washing with DMF at 70°C for 24 hours, followed by two further 2-hour washing cycles. After each wash, residual DMF was removed after centrifugation of the mixture at 8000 rpm for 15 minutes. Finally, any residual DMF was removed by heating at 200°C for 24 hours.

2.2.2 Powder X-ray diffraction.

The crystal structure, purity and crystallinity for all samples were assessed via their powder X-ray diffraction (PXRD) patterns, measured using a PANalytical Empyrean diffractometer (Cu Kα radiation, λ = 1.541 Å) over the 2θ range 3–40°, using a step size of 0.017° and a scan speed of 0.13° s⁻¹. Longer scans on some samples were performed with a step size of 0.017° and scan speed of 0.022° s⁻¹. Analysis of all powder diffraction data was carried out using the TOPAS Academic 4.1 structure refinement software. Simulated powder patterns of different MOF phases were obtained using Mercury and Vesta software.

2.2.3 Solution NMR.

Solution NMR was used to probe the nature of the organic components of the samples. The samples were prepared using a method adapted from Ref. 14. 10 mg of sample, washed and activated as described above, was digested in 1 M NaOH (Breckland Scientific Supplies Ltd.) in D₂O (Euro Isotop, 99 %, 600 µL). ¹H spectra of the resultant suspension [Figs. S12, S13 †] were collected with a standard ¹H 500 MHz Bruker Avance AVIII HD Smart Probe.

2.2.4 Thermogravimetric Analysis.

 Thermogravimetric analysis of samples was performed on a Mettler Toledo TGA/SDTA 851 thermo balance. Samples of 5–15 mg were heated to 700°C at a rate of 10°C min⁻¹. Measurements on samples were performed both under a constant flow (80 mL min⁻¹) of N₂ and under a constant flow (80 mL min⁻¹) of air (19-22 % O₂ in N₂), provided by Air Liquide UK Limited.

2.2.5 Scanning Electron Microscopy.

Samples were sputter coated with Pt to a thickness of 10 nm. Scanning electron microscopy was performed using a TESCAN MIRA3 FEG-SEM electron microscope operated at 5.0 kV, using the secondary electron detector.

2.2.6 Adsorption Measurements and Isotherms.

N₂ adsorption isotherms were carried out at 77 K on a Micromeritics 3Flex gas adsorption analyser. Samples were degassed in situ under vacuum at 120°C for 20 hours using the internal turbo pump. Warm and cold free-space correction measurements were performed using ultra-high purity He gas (grade 5.0, 99.999 % purity). Ultra-high purity N₂ (99.9992 %) was provided by Air products.

Grand canonical Monte Carlo (GCMC) simulations of N₂ adsorption were performed using the code RASPA. During each GCMC cycle, translation, rotation, insertions, deletions, and regrow moves were attempted, using 10,000 equilibration cycles and 10,000 production cycles. Van der Waals interactions were described by 12-6 Lennard-Jones potential using a cut-off distance of 12.8 Å. The force field parameters for N₂ were taken from the TraPPE force field. The Lennard-Jones parameters for the framework atoms were taken the Universal Force Field (UFF). All MOFs were treated as rigid in the simulations. Adsorbate-adsorbate and adsorbate-adsorbent van der Waals interactions were taken into account by Lorentz-Berthelot mixing rules.
Fig. 2 a-b) PXRD patterns of UiO-67(Hf), synthesised with a) different concentrations of formic acid, b) with 1.0 mL of formic acid and different water concentrations, showing the dependency of the phase formed on the concentration of water. The calculated powder patterns of fcu, hcp, and hxl UiO-67(Hf), and the hafnium formate MOF are shown for comparison. Dark red dashed lines indicate the evolution of peaks specific to the hcp phase, and black dashed lines show peaks which are common to more than one phase. Synthesis with 1.0 mL formic acid and 0.05 mL water gives phase-pure hcp UiO-67(Hf), and 0.2 mL water gives phase-pure hns UiO-67(Hf).

3 Results and discussion

3.1 The Role of Formic Acid and Water on UiO-67(Hf) Phases

Inspired by our previous work showing that formic acid plays a crucial role in the formation of the hcp UiO-67(Hf) phase, we investigated the effect of different concentrations of formic acid in the synthesis of UiO-67(Hf) [Fig. 2a)]. This series of syntheses was performed in DMF (99 %) but with no added water (i.e. we did not dry the as-received DMF).

Below 1 mL formic acid, the fcu phase is seen. hcp UiO-67(Hf) is formed when 1 mL formic acid (1:4 formic acid:DMF by volume) is used in the solvothermal synthesis: the observation of the hcp-characteristic peaks, (002), (100) and (101), in the region 0.28–0.41 Å⁻¹ clearly indicate that the phase is different from fcu, which in this region only has a (111) reflection in the same position as the (101) reflection of hcp. As the volume of formic acid is increased above 1 mL, a new phase forms; at 1.5 mL FcOH this phase crystallises concomitantly alongside the known hafnium formate MOF. At around 2 mL formic acid only the formate MOF forms; at high concentrations of formic acid compared to that of BPDC, the formate anions outcompete in binding to the clusters.

The powder X-ray diffraction (PXRD) pattern of the new material, seen most clearly in the PXRD patterns at 1.25 and 1.5 mL formic acid, strongly resembles that of the layered hxl UiO-67(Hf) material we previously reported but with absent l-dependent peaks, such as the (101) reflection, and with the remaining peaks displaying Warren-type line shapes. This combination of absent peaks and line broadening indicates the formation of a layered phase similar to hxl UiO-67(Hf), but with turbostratic disorder in the c-direction. We propose the prefix hns (“hexagonal nanosheet”) for this disordered layered phase.

Fig. 3 SEM image of the hns phase of UiO-67(Hf), illustrating the hexagonal nano-sheet morphology.

Noting that dissociated water can compensate for missing-linker defects in UiO-66, we then systematically investigated the effect of water in the synthesis of the hcp UiO-67(Hf) material. We now used anhydrous DMF solvent and added known volumes of water [Fig. 2b)]. At low concentrations of water (i.e. where only a small amount of ambient water was present), fcu UiO-67 forms, along with a minor phase of hcp. The crystallinity and phase-purity of hcp UiO-67(Hf) is improved with small amounts of water used in the synthesis, as the added water suppresses the formation of any fcu impurity phase. At higher water concentrations, the hns phase forms, becoming phase-pure at 0.2 mL water (0.2:4 water:anhydrous DMF by volume) as shown.
3.2 The Role of Water on UiO-66(Zr/Hf) (F$_{4}$BDC)

Observing the key role of water in the phase selection of UiO-67(Hf), we then examined other previously reported solvothermal syntheses of UiO materials where water was used as a solvent. The modulated hydrothermal methodology proposed by Ref. 43 provides a green and scalable approach to synthesising several frameworks isoreticular to fcu UiO-66(Zr). However, we noted that the material assigned as the cubic fcu UiO-66(Zr) (F$_{4}$BDC) displays a characteristic splitting of the reflection indexed to the fcu (111) reflection into two peaks at 0.49 Å$^{-1}$ and 0.52 Å$^{-1}$, and an additional reflection is present at 0.35 Å$^{-1}$. These features could be explained by this phase being the hcp rather than the fcu structure.

We therefore repeated the reported synthesis, producing both Zr and Hf analogues with experimental PXRD patterns consistent with those of Ref. 43. We were able to index the PXRD pattern of the Hf analogue using a hexagonal cell, and we carried out Pawley refinement to obtain accurate unit cell and instrumental parameters [Fig. S3].

Using the experimental structure as a constraint, a model structure was derived from the known hcp UiO-67 structure. This structure was then optimised using quantum chemical calculations. Density functional theory (DFT) calculations were performed both with and without the full crystal symmetry, to account for the tilting of the linkers. Optimisation with the full crystal symmetry constrains the linkers to be flat, which does not reflect the rotational disorder present in reality. Aside from the linker tilting, the model structures with and without the full symmetry are otherwise equivalent, giving no evidence of a symmetry-lowering distortion away from the hexagonal structure and suggesting that the overall symmetry of the UiO-66(Hf) (F$_{4}$BDC) structure is P6$_{3}$/mmc, like hcp UiO-67.

This triclinic optimised model, with linker tilting present, was then compared and validated against the experimental dataset, using the instrumental parameters obtained from the Pawley refinement [Fig. 4]. The background was modelled using a freely refining Chebyshev polynomial. Peak shapes were modelled using additional terms to account for anisotropic and size broadening and 2θ dependence. Due to the small crystallite size and resultant peak broadening, it was not possible to carry out Rietveld refinement.

While this water-rich synthesis of UiO-66 (F$_{4}$BDC) results in a hcp framework, it has been recently reported that an alternative route, with no added water and using THF as a solvent and hydrochloric acid as a modulator, produced the non-defective fcu phase. Therefore, to understand the effect of the water content of the reaction on the phase of the resultant material, we systematically investigated the synthesis of UiO-66 (F$_{4}$BDC) with varying concentrations of water [Fig. 5]. In this series of syntheses, acetic acid was used as the modulator for consistency with the original reported hydrothermal synthesis.

For UiO-66(Hf) (F$_{4}$BDC) synthesised hydrothermally with modulating acetic acid at both 120°C and 150°C, the phase which crystallises depends on the ratio of water to acid in the reaction mixture. These materials are very sensitive to the synthetic conditions, and the sample crystallinity is poor with low concentrations of modulating acetic acid. We found that with increasing concentrations of water the hcp material emerges, followed by a phase resembling hns. Thus both modulating acid and the presence of water are crucial to the formation of the hcp phase.

Furthermore, the hcp UiO-66(Hf) (F$_{4}$BDC) sample, like hcp UiO-67(Hf), transformed into a highly crystalline hns phase upon washing with DMF or methanol and activation [Fig. 5], showing that the creation of the defect-ordered hcp phase gives straightforward access to the layered-nanosheet material. SEM imaging [Fig. 6] shows the morphological differences between the fcu, hcp and hns phases; the hcp material shows a hexagonal intergrowth, with a characteristic ‘desert rose’ appearance, while the hns phase shows a delamination into sheets.

3.3 Synthesis of hcp UiO-66(Hf)

From the above two investigations, we have established that both modulating acid and water in the synthesis affect the phase of the material formed: increasing the concentration of acid and water simultaneously tends to promote the formation of the hcp phase rather than the fcu or nano-reo structures. We then applied this understanding of the key role of water in synthesis, in combination with formic acid, to the pursuit of the hcp phase of UiO-66.

With high concentrations of water and formic acid we were able to synthesise phase-pure hcp UiO-66(Hf). At lower concent-
trations of either formic acid or water, the fcu (111) peak broadens into the region where hcp (100) and (101) peaks would be expected, but the individual hcp peaks are not seen, indicative of a low concentration of hcp (fcu remaining the major component); phase-pure hcp UiO-66(Hf) only forms once volumes of 0.4 mL water and 1.5 mL formic acid are used [Fig. 7(a-d)]. The PXRD pattern of this material is consistent with that recently reported by Ref. 46 for the hcp UiO-66(Zr) material.

To confirm the assignment of this phase as hcp, a model structure of hcp UiO-66(Hf) was created based on our optimised structure for hcp UiO-66(Hf) (F₄BDC). Using the same approach as used to analyse the PXRD pattern of hcp UiO-66(Hf) (F₄BDC), the PXRD pattern of hcp UiO-66(Hf) was indexed, and accurate unit cell and instrumental parameters obtained from Pawley refinement [Fig. S4]. These parameters were then used in a comparison of the experimental hcp dataset against the model structure, which gave a good fit [Fig. S3(a,b)]. The background and peak shapes were modelled using the same approach as for the hcp UiO-66(Hf) (F₄BDC) structure, with an additional term to account for preferred orientation along [001]. Again, due to the small crystallite size, it was not possible to carry out Rietveld refinement.

Further increasing the volumes of water and formic acid in the reaction mixture to a maximum of 3.5 mL and 3.0 mL respectively produced neither the hafnium formate phase previously reported for both UiO-66(Hf) and UiO-67(Hf), nor the phase-pure delaminated hns phase seen in the investigation of hcp UiO-67 [Figs. S5-S7]. Thus again water, alongside modulating acid, is important in obtaining the hcp phase of UiO-66, both by promoting the formation of the hcp structure over the fcu, and by suppressing the hafnium formate phase. The washed and activated hcp UiO-66(Hf) material synthesised in this manner is stable in ambient conditions, with little change observed in the PXRD after nine months (at the time of writing) [Fig. S8].

3.4 Investigation of Defect Concentrations in hcp UiO-66(Hf) Phases via TGA and ¹H NMR Studies

While the formation of hcp UiO-66(Hf) occurs at higher concentrations of both formic acid and water (0.4 mL water and 1.5 mL formic acid in 4 mL anhydrous DMF) than for hcp UiO-67(Hf) (0.05 mL water and 1 mL formic acid), missing-linker defects are formed more easily in fcu UiO-66 than in UiO-67 and it is likely that a higher concentration of defects can be stabilised in fcu UiO-66(Hf) compared to fcu UiO-67(Hf) before the defect-ordered hcp phase forms.

It is well known that modulated synthesis of fcu UiO-66, of-
Fig. 7 a-c) PXRD patterns of UiO-66 synthesised with varying water concentrations and a) 0.5 mL FcOH; b) 1.0 mL FcOH; c) 1.5 mL FcOH. d) Plot of the intensity ratio of \textit{hcp} vs \textit{fcu} peaks, showing the emergence of the \textit{hcp} UiO-66 phase only at higher concentrations of both formic acid and water. PXRD patterns are compared with the predicted patterns for the \textit{fcu}, \textit{reo}, and \textit{hcp} UiO-66 structures.
ten introduces missing-linker defects, whereas these are rare in fcu UiO-67. These missing-linker defects are compensated by modulating acid, water, or hydroxide. While the recently-reported hcp UiO-66(Zr) was briefly noted to contain missing-linker defects, we have investigated the presence of defect-compensating molecules in hcp UiO-66(Hf), to establish whether water and formic acid in the synthesis not only determine the phase, as we have demonstrated, but also control the concentration of missing-linker defects in the hcp phase, just as in fcu UiO-66.

We used thermogravimetric analysis (TGA) to calculate the amount of missing-linker defects. The TGA analysis of UiO-66 family frameworks shows three distinct steps, corresponding to different stages of decomposition. The first significant mass losses (below 150°C) are due to the loss of solvent molecules and hydrogen-bonded water. The mass losses between 250 and 300°C correspond to the dehydroxylation of the Hf₆O₄(OH)₄ cluster to Hf₆O₄[OH] as well as loss of missing-linker-compensating formate or water molecules. The final and largest mass loss, used to calculate the linker-cluster stoichiometry, corresponds to the decomposition of the remaining framework and the formation of HFO₂. TGA analysis of hcp UiO-66 samples [Fig. S11] likewise displays mass losses at similar temperatures; however, in the ‘dehydroxylation’ step, we assumed that the Hf₁₂ double cluster does not dissociate via loss of the six µ₂-OH, instead losing formate (FCO) and hydrogen-bonded water as with fcu UiO-66 to give a (Hf₆O₄)₁₂(OH)₆ dehydroxylated double cluster. A detailed discussion of the mass losses in the TGA can be found in the ESI.

Of the UiO-66 samples synthesised with 1.5 mL formic acid, those with >0.4 mL water are phase-pure hcp UiO-66 by PXRD. However, the ratios of initial to final masses for these samples are lower than for perfect hcp, indicating the presence of defects, and also show a correlation between the lowering of the framework mass and the concentration of water in the synthesis [Fig. S11]. Samples with 0–0.3 mL water in the reaction mixture are mixed-phase; their mass ratios compared to HFO₂ are lower than for perfect fcu, as expected for a fcu/hcp mixture since hcp UiO-66 has a lower metal:linker ratio than fcu. However, without the PXRD data, these TGA curves could be erroneously modelled as extremely defective fcu. This demonstrates the need for care when using TGA data to calculate the defect concentration in UiO samples: if a sample is mixed phase, or the wrong model structure is used, there will be large systematic errors in the estimated defectivity.

The presence of formate (FcO) in the above activated phase-pure hcp UiO-66 frameworks was confirmed by solution ¹H NMR [Figs. S12,S13]; further deviations from the expected mass fraction indicate the presence of water or hydroxide as additional capping molecules. Where the formula of defect-free hcp UiO-66(Hf) is [Hf₆O₄(OH)₁₂(OH)₆(BDC)]₉, the formulae of defective samples containing defect-compensating formate, water and hydroxide molecules can be written as [(Hf₆O₄(OH)₁₂(OH)₆(BDC)]₉(OH)₆(FcO)); nH₂O. The hcp UiO-66 sample synthesised with 0.4 mL water and 1.5 mL formic acid is found to have x = 6.63(11), y = 2.82(22), z = 1.93(4), n = 8.81(22), i.e. with 26(1) % of terephthalate (BDC) linkers replaced. For the sample synthesised with 1.5 mL water and 1.5 mL formic acid, this gives x = 4.81(11), y = 5.58(22), z = 2.80(7), n = 11.58(22), i.e. with 47(1) % of BDC linkers replaced [Fig. 9, Table S2]. Therefore the hcp material can incorporate missing-linker defects to a high level, compensated by both formate and water/hydroxide, as in fcu UiO-66. Water in the synthesis also allows control over the phase purity of the sample. Hence not only the phase but also the defectivity of the sample can be tuned by adjusting the water concentration in the synthesis.

3.5 Adsorption Isotherm Measurements of hcp UiO-66(Hf)

The change in the structure due to the cluster condensation from fcu to hcp affects the surface area and size of the pores in the sample, as demonstrated by its sorption behaviour [Fig. 10]. The new phase hcp UiO-66 (Hf) has a Brunauer-Emmett-Teller (BET) area (N₂) of 422 m²g⁻¹ (when synthesised with 0.4 mL water),
which is lower than the 655–940 m²g⁻¹ of the fcu UiO-66 (Hf) phase. This is expected due to the greater density of the double-cluster material as opposed to the single cluster phase, and is also displayed in hcp compared to fcu UiO-67 and, more generally, in the cluster condensation of oxide materials.

The simulated N² adsorption isotherms [Fig. 10], using grand canonical Monte Carlo (GCMC) calculations, based on the model hcp UiO-66 crystal structure, agree well with the experimentally-observed isotherms at saturation pressures. At lower pressure, they show a typical overprediction of the host-guest interaction. The simulations were performed using two hcp UiO-66 structures generated from the model hcp structure of UiO-66 (F₄BDC). The first structure (hcp UiO-66 (opt)) corresponds to the geometrically optimized material after exchanging all F atoms to H while keeping the unit cell parameters fixed. The second structure (hcp UiO-66 (UCopt)) was generated by optimizing the geometry while relaxing the unit cell parameters. The simulations for both of these structures, carried out at 77 K, almost overlap, suggesting that the proposed hcp UiO-66 structure is very close to the known hcp UiO-66 (F₄BDC) structure and does not show any flexibility. For comparison, the BET area of 370–380 m²g⁻¹ calculated for hcp UiO-66 (F₄BDC) from these simulations agrees with the published BET value of 328 m²g⁻¹. Usually for microporous powder samples, a Type I isotherm is seen, corresponding to the filling of the narrow pores with large affinity to the guest (N²) molecules; this is seen in the simulated isotherm, performed on a perfect model crystal without any defects. In our case, however, the experimental isotherm of hcp UiO-66 is of Type II, displaying a small positive slope in the range 0.0001–0.9 P/P₀, followed by a suddenly increased uptake at high P/P₀, and therefore indicating the presence in the sample of mesoporosity.

In this regard, missing-linker defects in fcu UiO-66 are known to create mesopores in UiO-66 samples with missing-linker defects and known mesoporosity; pore volumes of up to 1.0 cm³g⁻¹, corresponding to pore apertures of 11.5 Å, and diameters even of 1–5.5 nm have been observed. This is in comparison to purely microporous UiO-66, which yields pore volumes of 0.426 cm³g⁻¹, with 6 Å apertures and 30 Å diameter. Here, calculations from the isotherms of hcp UiO-66 give a Horvath-Kawazoe pore width of 7.13 Å and average pore diameter of 68.7 Å, which support the existence of mesopores in the hcp sample.

### 4 Conclusions

#### UiO-66

| Form | Notes |
|------|-------|
| fcu  | HCP   |
| hcp  | HCP   |

Fig. 10 Simulated and experimental N² isotherms for hcp UiO-66 (right: semi-logarithmic scale). The simulated N² adsorption isotherm for UiO-66 (F₄BDC) is plotted for comparison.

In this work, we have demonstrated that water plays a key role in the synthesis of defect phases of UiO family MOFs. We have shown that both water and formic acid are instrumental in allowing control over the phase formed, causing the condensation of the metal clusters into the Hf₁₂ double clusters characteristic of the hcp phase. Starting from the first known example of the hcp phase, hcp UiO-67, we applied the discovery of the critical role of water in phase-selection to other members.
of the UIO family and used this understanding to synthesise the hcp phase of the canonical UIO-66, using conventional solvents rather than complex or expensive systems. We have also established that water and hydroxide can introduce missing-linker defects into this framework by replacing the bidentate dicarboxylate linkers, and therefore that by controlling the concentration of water in the synthesis the number of such defects in the sample can be tuned. Characterisation of the hcp UIO-66(Hf) material has shown that it can sustain missing-linker defects to high concentrations compensated by the introduction of formate, water and hydroxide groups, creating mesopores as shown by pore size measurements. Moreover, the introduction of directionally-correlated missing-linker defects through this defect-engineering process has allowed us to directly synthesise two-dimensional UIO MOF nanosheets with hexagonal topology, hns UIO-66 ([F$_4$BDC]) and hns UIO-67 [Fig. 11].

While the key role of water, as well as formic acid, in the creation of missing-linker defects and hence these new defect-engineered phases is evident, and a degree of control over the phase formation and purity has been obtained, work is now in progress to investigate the mechanism through which this occurs. Moreover, the inclusion at different locations of new water and hydroxide groups may create new sites of Brønsted acidity and affect the sorption behaviour, hydrophilicity and catalytic behaviour of the framework. Finally, the creation of novel stable Zr/Hf MOF-based nanosheets in this way represents a potential strategy for synthesising MOF membranes.

Conflicts of interest
There are no conflicts to declare.

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

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Supporting Information

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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
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.$^{31}$
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 H₂O, 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 HfO$_2$, 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.$^{51,53,54}$ 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.$^{55}$

Fig. S9 $2n$ 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 $2n$ 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. Under the proposed model, the hydrogen-bonded water molecules are lost in this step. 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 Hf₆O₄(OH)₄ cluster to Hf₆O₆. In defective UiO-66 materials where formate molecules have replaced some linkers, formate ligands are lost over a similar temperature range. The metal-bound water molecules are also lost during this stage. 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 μ₂-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 HfO₂; as noted above, a smaller-than-expected final mass loss is likely to be due to a deficiency of linkers in the sample.

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$_6$O$_4$(OH)$_4$(BDC$_{1/2}$)$_x$(FcO)$_y$(OH)$_z$·zH$_2$O | (Hf$_6$O$_4$(OH)$_4$)$_x$(BDC$_{1/2}$)$_x$(FcO)$_y$(OH)$_z$·(z+6)H$_2$O |
| 350-500 | Hf$_6$O$_6$(BDC$_{1/2}$)$_x$(OH)$_y$ | (Hf$_6$O$_6$)$_x$(BDC$_{1/2}$)$_x$(OH)$_y$ |
| >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) -6O |

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 $^1$H NMR of hcp UiO-66(Hf)

Fig. S12 $^1$H NMR spectra of hcp UiO-66 synthesised with 0.4 mL H$_2$O and 1.5 mL FcOH, washed and activated. Left, full spectrum; right, zoomed spectrum.

Fig. S13 $^1$H NMR spectra of hcp UiO-66 synthesised with 1.5 mL H$_2$O and 1.5 mL FcOH, washed and activated. Left, full spectrum; right, zoomed spectrum.
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