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## Modulated self-assembly of hcp topology MOFs of Zr/Hf and the extended 4,4'-(ethyne-1,2-diyl)dibenzoate linker†

Sophia S. Boyadjieva,<sup>a</sup> Francesca C. N. Firth,<sup>b</sup> Mohammad R. Alizadeh Kiapi,<sup>c</sup> David Fairen-Jimenez,<sup>c</sup> Sanliang Ling,<sup>d</sup> Matthew J. Cliffe<sup>e\*</sup> and Ross S. Forgan<sup>a\*</sup>

Careful control of synthetic conditions can enhance the structural diversity of metal–organic frameworks (MOFs) within individual metal–linker combinations. Herein, we show that hcp topology MOFs of both Zr(IV) and Hf(IV), linked by the extended (ethyne-1,2-diyl)dibenzoate linker, can be prepared by modulated self-assembly. The controlled addition of acetic acid and water to solvothermal syntheses is essential to generate these phase pure hcp topology materials, which are characterised experimentally and computationally. The central alkyne unit of the linker can be quantitatively brominated, but this results in partial degradation of the hcp phase, in contrast to the more stable fcu topology analogues. Nevertheless, the MOFs represent new members of the hcp topology isorecticular series showing high crystallinity and porosity, and demonstrate that new materials can be discovered in existing MOF phase spaces through judicious adjustment of key synthetic parameters.

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## Introduction

Metal–organic frameworks (MOFs) comprise metal ion or metal cluster nodes (also referred to as secondary building units, or SBUs) connected by multitopic organic ligands into multidimensional network structures.<sup>1</sup> To date, it is estimated that over 100 000 MOF structures have been deposited in the Cambridge Structural Database,<sup>2</sup> with this huge number attributed to the chemical diversity in the choice of both metal SBU and organic ligand.<sup>3</sup> In addition, it is possible to isolate multiple phases from the same metal–ligand combination—topological diversity—by careful control of reaction parameters.<sup>4</sup> A pertinent example is that of trivalent metals linked by linear ditopic dicarboxylates, which can yield structurally rigid (MIL-101) and flexible (MIL-88 and MIL-53) phases.<sup>5</sup> Furthermore, we have also previously shown that, in

the specific case of Fe(III) MOFs with 1,4-benzenedicarboxylate (BDC<sup>2-</sup>), coordination modulation—the addition of reagents to MOF syntheses that can tune the coordination and pH equilibria during self-assembly<sup>6</sup>—is a viable strategy for kinetically selecting a specific material from a complex phase landscape.<sup>7</sup>

The multiple series of MOFs comprising Zr(IV) or Hf(IV) SBUs connected by linear ditopic dicarboxylate ligands present a particularly striking case study into the isolation of different MOF phases *via* synthetic control.<sup>8</sup> Predominant among MOFs prepared from Zr(IV) or Hf(IV) and BDC<sup>2-</sup> or its derivatives is the UiO-66 series, in which [M<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(RCO<sub>2</sub>)<sub>12</sub>] metal clusters (M = Zr, Hf, Fig. 1a) are connected by twelve linear dicarboxylate linkers in a face-centred cubic (fcu) topology MOF (Fig. 1b). UiO-66(Zr) specifically exhibits the ideal formula [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>6</sub>]<sub>n</sub>,<sup>9</sup> and a wide range of isorecticular derivatives of these materials, including interpenetrated UiO-66 topology phases, have been reported with both longer and functionalised linkers.<sup>9–15</sup>

Varying the reaction composition can also affect the resultant MOF structure. For example, changing the metal source from ZrCl<sub>4</sub> to Zr(OiPr)<sub>4</sub> has led to the discovery of a polymorph of UiO-66 with a different connectivity and hex topology.<sup>16</sup> Addition of monotopic carboxylic acids as coordination modulators has induced formation of “defect” phases where the modulators themselves are incorporated as charge-compensating defects. Such defect phases can form in

<sup>a</sup> WestCHEM School of Chemistry, University of Glasgow, Joseph Black Building, University Avenue, Glasgow G12 8QQ, UK. E-mail: ross.forgan@glasgow.ac.uk

<sup>b</sup> Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

<sup>c</sup> The Adsorption & Advanced Materials Laboratory (A2ML), Department of Chemical Engineering & Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, UK

<sup>d</sup> Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

<sup>e</sup> School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK. E-mail: matthew.cliffe@nottingham.ac.uk

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**Fig. 4** a) Thermogravimetric analyses of GUF-12(Zr) and GUF-12(Hf) in air. b)  $N_2$  adsorption-desorption isotherms (77 K) of GUF-12(Zr) and GUF-12(Hf) with c) pore-size distributions ( $N_2$  at 77 K on carbon, slit pore, QSDFT, equilibrium model) calculated from the isotherms. d) Portion of the DFT model structure of GUF-12(Zr) viewed down the crystallographic  $c$  axis to visualise the hexagonal channel 11 Å in diameter.

subsequent TGA residue).<sup>41</sup> This is commensurate with  $^1H$  NMR spectra of acid-digested samples (see ESI,† Section S5), which show the presence of acetate even after activation, indicating that the acetate groups are present as charge compensating defects rather than pore-bound solvents. Resonances that could be assigned to formate, produced by decomposition of DMF, were not observed in the materials.

A pristine defect-free **hcp** structure would have formula  $[M_{12}O_8(OH)_{14}(EDB)_9]$ .  $^1H$  NMR spectroscopic analysis of activated, then acid-digested GUF-12(Zr) gives a 1:3.3 ratio of acetate to linker; assuming that one  $EDB^{2-}$  is replaced by two acetates gives a formula of  $[Zr_{12}O_8(OH)_{14}(EDB)_{7.8}(CH_3COO)_{2.4}]$ , which would leave a theoretical 42.5% wt  $ZrO_2$  residue after thermogravimetric analysis, matching well with the observed 42.1% wt. For GUF-12(Hf), the acetate content measured by  $^1H$  NMR spectroscopy is higher, at an approximate 1:2.5 acetate to  $EDB^{2-}$  ratio. Similar levels of defectivity have been observed elsewhere for the **hcp** phase prepared from Zr(IV) and  $BDC^{2-}$  using acetic acid modulated syntheses; these defects enhance its catalytic activity.<sup>33</sup> Taking a similar approach, a formula of  $[Hf_{12}O_8(OH)_{14}(EDB)_{7.5}(CH_3COO)_{3.0}]$  for GUF-12(Hf) would correlate with the NMR spectroscopic data and leave a theoretical  $HfO_2$  residue of 56.3% wt, close to the experimental value of 56.8% wt. This greater acetate incorporation of the Hf(IV) congener may be reflected in its lower overall thermal decomposition temperature compared to the Zr(IV) analogue, as observed by TGA (Fig. 4a). The decomposition temperatures are broadly similar to the **fcu** analogues.<sup>13</sup>

The reliability of the synthetic method allowed us to upscale the synthesis of the **hcp** phases to quantities suitable for porosity analysis.  $N_2$  adsorption/desorption isotherms of GUF-12(Zr) and GUF-12(Hf) were collected at 77 K after activation of the samples at 120 °C for 20 h under vacuum (Fig. 4b). Both MOFs exhibit typical type I isotherms, associated with microporous materials, with small increases in uptake between 0.9 and 1.0  $P/P_0$ , indicating adsorption occurring in interparticle spacing or surface roughness. This can be explained by the aggregated “desert rose” morphology of the  $\sim 100$  nm thick hexagonal particles, which feature multiple surfaces and crevices where nitrogen can be adsorbed. Brunauer–Emmett–Teller (BET) areas were

calculated from the experimental adsorption isotherms using BETSI, a publicly available software package that fully implements the extended Rouquerol criteria for an unambiguous BET area assignment (see ESI,† Section S6).<sup>44</sup> The BET areas were found to be  $1798\text{ m}^2\text{ g}^{-1}$  and  $1005\text{ m}^2\text{ g}^{-1}$  for GUF-12(Zr) and GUF-12(Hf), respectively, with pore volumes of  $1.03\text{ cm}^3\text{ g}^{-1}$  and  $0.59\text{ cm}^3\text{ g}^{-1}$ . As expected,<sup>30,35</sup> these are lower than those reported for the **fcu** analogues ( $3280\text{ m}^2\text{ g}^{-1}$  and  $2000\text{ m}^2\text{ g}^{-1}$ , for the Zr and Hf congeners, respectively).<sup>13</sup> Grand Canonical Monte Carlo (GCMC) simulations were performed to assess the potential total porosity of the two MOFs (see ESI,† Section S7). Simulated  $N_2$  adsorption isotherms for both GUF-12(Zr) and GUF-12(Hf) showed higher  $N_2$  uptakes and larger predicted BET areas ( $2765\text{ m}^2\text{ g}^{-1}$  and  $2127\text{ m}^2\text{ g}^{-1}$ , for the Zr and Hf congeners, respectively). GCMC simulations often overpredict porosity compared to experiment, but the magnitude of the difference between the experimental and simulated  $N_2$  uptakes suggest that the isolated MOFs may be partially amorphized or not fully activated.

In each isotherm, small type H4 hysteresis loops are discernible, which are indicative of minor levels of mesoporosity that could be a consequence of defectivity in the samples. Pore-size distributions (Fig. 4c), calculated from the experimental isotherms ( $N_2$  on carbon at 77 K, slit pore/QSDFT equilibrium) show a significant pore around 11 Å in diameter for each MOF, which correlates closely to the hexagonal pore evident along the crystallographic  $c$  axis (Fig. 4d), and is smaller than the major pore observed in the **fcu** analogues ( $\sim 12.5$  Å).<sup>13</sup> A broad feature is observed around 34 Å for each **hcp** MOF, which may be indicative of the defectivity implied by  $^1H$  NMR spectroscopy and TGA. This combination of high porosity and significant defectivity indicates the potential for application of the GUF-12 congeners in catalysis.<sup>33</sup>

We and others have previously shown that MOFs linked by ligands with internal alkene<sup>12,45–48</sup> and alkyne<sup>12,13,49,50</sup> subunits can be postsynthetically modified by halogenation. Specifically, we have demonstrated that the Zr(IV) and Hf(IV) **fcu** phases linked by  $EDB^{2-}$  can be quantitatively brominated in a single-crystal to single-crystal manner.<sup>13</sup> With two different linker environments in the **hcp** phases in this work,



we wished to determine if (i) the linkers were accessible to bromination, and (ii) if this would result in a reactive delamination to form a nanosheet phase. Under conditions identical to those we have previously utilised for the **fcu** analogue,<sup>13</sup> it was possible to quantitatively brominate the EDB<sup>2-</sup> ligands of the **hcp** materials, as assessed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy of acid-digested samples. However, PXRD analysis of the brominated materials showed that stability was an issue when samples were scaled up, with inconsistent results. In the case of GUF-12(Hf), additional Bragg reflections were present that may represent degradation of the MOF or delamination, underlining the metastability of the **hcp** MOFs (see ESI,† Section S8).

## Conclusions

We have shown that, by careful consideration of synthetic conditions, it is possible to synthesise Zr(IV) and Hf(IV) MOFs of EDB<sup>2-</sup> with the **hcp** topology to complement their established **fcu** analogues. The role of both water and acetic acid has been explored to optimise syntheses and reliably reproduce the materials on an increased scale, allowing characterisation of their porosity and possible defectivity, suggesting potential applications in heterogeneous catalysis. The **hcp** phases are likely kinetic products relative to the analogous **fcu** topology MOFs; moreover, the **hcp** materials are metastable, as demonstrated by partial degradation of GUF-12(Hf) during attempts to postsynthetically brominate the EDB<sup>2-</sup> linkers, in contrast to the stability of the **fcu** phase under identical conditions.<sup>13</sup> Nevertheless, this work shows that careful control of modulated self-assembly allows access to new MOF materials exhibiting desirable physical properties within well-established phase spaces.

## Conflicts of interest

There are no conflicts to declare.

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