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## Tuning the Properties of the UiO-66 Metal Organic Framework by Ce Substitution<sup>†</sup>

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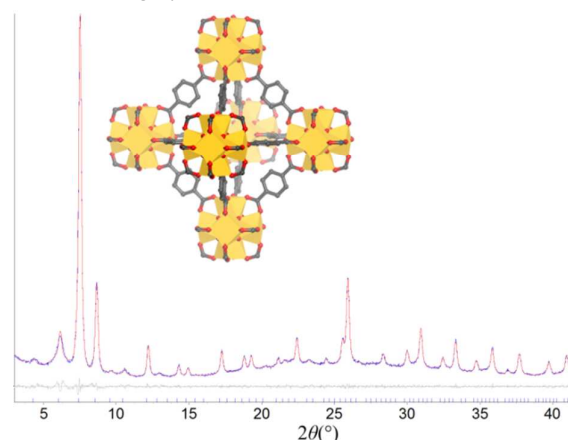
**Crystallisation of a mixed-metal form of the porous framework UiO-66 in which Zr is partially replaced by Ce produces a ligand-defective material, that contains some Ce(III) as well as a majority of Ce(IV). Infrared spectroscopy shows enhanced binding of methanol in the substituted material that leads to catalytic decomposition of the alcohol, which may be due to a combination of defects and redox activity.**

Substitution of one metal cation by another in metal-organic frameworks provides an interesting strategy to tune the properties of porous materials towards practical applications, borrowing from the idea of substitutional chemistry used in conventional solid-state chemistry.<sup>1</sup> Examples already presented in the literature include mixed lanthanide frameworks with highly tuneable luminescent properties,<sup>2</sup> a modification of the breathing behaviour of the flexible MOF by using mixtures of transition-metal ions<sup>3, 4</sup> the development of effective hydrogen storage materials with mixed, open metal sites,<sup>5</sup> and examples of cooperative effects of combination of metals in catalysis.<sup>6</sup> Synthesis of mixed-metal MOFs may be direct, under solvothermal conditions, by post-synthesis metal exchange,<sup>7</sup> or by secondary building unit rational design.<sup>8, 9</sup>

The Zr(IV) material UiO-66,<sup>10</sup> is a well-studied metal-organic framework due to its thermal, mechanical and hydrothermal robustness. The material is constructed from a hexameric oxocluster, consisting of eight-coordinate zirconium atoms with square-antiprismatic arrangement of coordinating oxygens and linked in three-dimensions with 1,4-benzenedicarboxylate (BDC) ligands, or more extended dicarboxylates to give isorecticular materials. UiO-66 has properties suited to gas adsorption,<sup>11, 12</sup> catalysis<sup>13</sup> and separation of hydrocarbons,<sup>14</sup> and post-synthesis modification allows chemical tagging to tune properties.<sup>15</sup> In terms of metal incorporation, recent work has focussed on post-synthesis

replacement of some of the Zr<sup>4+</sup> by Ti<sup>4+</sup> to improve dramatically the gas transport properties of MOF-polymer membranes.<sup>16</sup> Ce is another attractive candidate for substitution into UiO-66: Ce<sup>4+</sup> adopts eight coordination in its common oxide CeO<sub>2</sub>, and the properties of CeO<sub>2</sub>-ZrO<sub>2</sub> solid solutions are well established in redox catalysis and for their oxygen storage properties.<sup>17</sup> Indeed CeO<sub>2</sub> itself finds considerable application in important contemporary field of catalysis, such as a component in automotive three-way catalytic converters, and catalysts supports in areas such as the water gas shift reaction, and hydrocarbon and alcohol oxidation.<sup>18</sup>

The new mixed Ce/Zr UiO-66 material was obtained under solvothermal conditions, from a mixture of 166 mg 1,4-benzenedicarboxylic acid (1 mmol), 186.4 mg of zirconium(IV) chloride hexahydrate (0.8 mmol) and 74.5 mg of cerium(III) chloride (0.5 mmol) in 5 mL *N,N*-dimethylformamide (DMF) which was heated in Teflon lined vessel and heated to 393 K (at 1 K min<sup>-1</sup>) for 24 hours. After cooling, the solution was filtered and the recovered powder washed with DMF, distilled water and acetone to remove any free, unreacted 1,4-benzenedicarboxylic acid. Powder X-ray diffraction (PXRD), Figure 1, of the material UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) can be indexed using a primitive cubic unit cell.



**Fig. 1** Profile fitted powder X-ray diffraction pattern of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) ( $\lambda = 1.5406 \text{ \AA}$ ;  $a = 20.7353(1) \text{ \AA}$ ,  $Pm\bar{3}m$   $R_{wp} = 4.18$ . Data points are blue, the red line the fitted profile, the grey line the difference curve and the blue ticks are the positions of allowed Bragg reflections.

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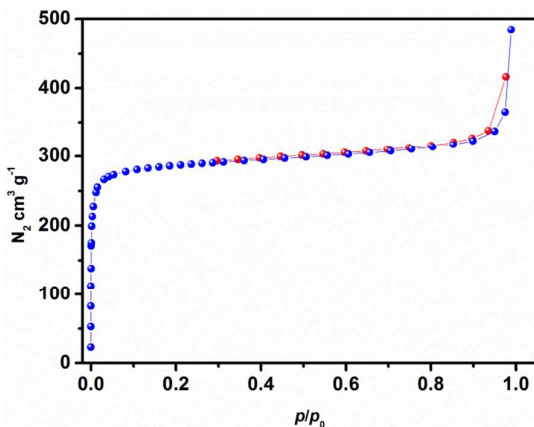
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<sup>†</sup> Electronic Supplementary Information (ESI) available: thermogravimetric analysis, thermodiffraction, further IR spectra and temperature programmed reduction/oxidation. See DOI: 10.1039/x0xx00000x

This is lower symmetry than the ideal F-cubic UiO-66 structure<sup>10</sup> and the extra 'symmetry forbidden' Bragg peaks are known to be associated with extended defects, in particular due to ordered regions of missing linkers.<sup>19, 20</sup> The refined cubic lattice parameter UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) of 20.7353(1) Å is larger than 20.7004(2) Å reported for the parent Zr material,<sup>10</sup> consistent with inclusion of Ce in the structure since both common oxidation states of Ce are expected to have larger ionic radius than Zr<sup>4+</sup>.<sup>21</sup>

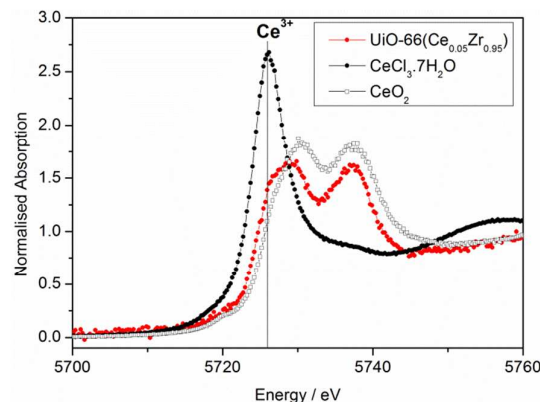
*In situ* PXRD on heating in air (ESI) shows that UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) collapses at ~573 K with loss of crystallinity; this is somewhat lower than reported for the pure Zr analogue (~673 K<sup>22</sup>). The symmetry forbidden low-angle reflections show no change on heating, suggesting that no annealing of the defects occurs in the mixed-metal material. Thermogravimetric analysis (ESI) confirms the presence of significant ligand defects, with loss of organic corresponding to a chemical formula of the as-made material of [(Ce<sub>0.05</sub>Zr<sub>0.95</sub>)<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>n</sub>].solvent, with *n* = 4, instead of 6 in the ideal UiO-66 structure. Such a level of ligand deficiency has been seen previously for pure Zr UiO-66 materials, depending on synthesis method.<sup>23</sup> Removal of solvent (7 hours activation at 423 K *in vacuo*) produces a material with a surface area, measured using nitrogen adsorption and the BET method, Figure 2, of ~1150 m<sup>2</sup> g<sup>-1</sup> and mean pore volume of ~0.75 cm<sup>3</sup> g<sup>-1</sup>. These are values comparable to UiO-66(Zr) literature<sup>22</sup> and show how the average crystal structure is maintained upon Ce incorporation.



**Fig. 2** Nitrogen adsorption (blue points) and desorption (red points) isotherms of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) (77 K, *P*<sub>0</sub> = 1 atm).

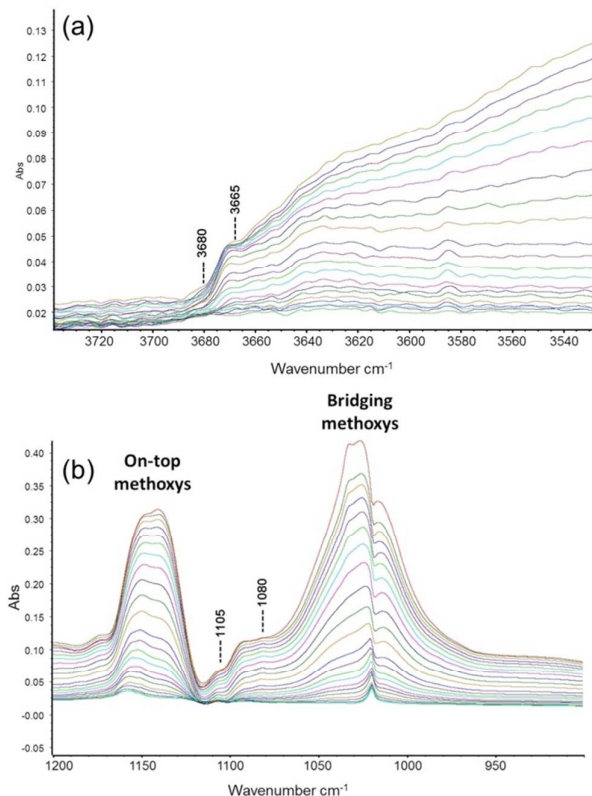
The oxidation state of Ce in UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) was examined using Ce L<sub>III</sub>-edge X-ray absorption near edge structure (XANES) spectroscopy (measured using B18 of Diamond Light Source, UK), Figure 3. This was important to investigate since it is well known that Ce(III) and Ce(IV) are both stable valence states under ambient conditions and indeed can be readily interconverted. Both also have ionic radii that would be compatible with the Zr sites in UiO-66.<sup>21</sup> The spectrum is compared with reference materials for Ce(III) and Ce(IV), both of which have oxygen environments for cerium, and qualitative inspection clearly show while the majority of Ce in the material is present as Ce(IV), there is also some Ce(III) present, as shown by the distinctive 'white line' of the lower oxidation state, indicated on Figure 2. The amount of Ce(III) can be quantified by using the edge position (50 % of edge step) as a reference point,<sup>24</sup> and this analysis gives an average Ce oxidation state of +3.8, resulting in a 20/80% content of Ce<sup>3+</sup>/Ce<sup>4+</sup> in UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>).

This is consistent with the PXRD and TGA that proved regions of defective linkers in the material, since the framework is substituted by a metal centre of lower positive charge and so has less charge to be balanced by the anionic carboxylate linkers.



**Fig. 3** Ce L<sub>III</sub>-edge XANES of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) compared with crystalline CeO<sub>2</sub> and CeCl<sub>3</sub>·7H<sub>2</sub>O reference materials.

To assess the properties of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) we used *in situ* IR spectroscopy to analyse its thermal behaviour and also its interactions with various guest molecules. The Ce containing material shows total dehydroxylation and evacuation of free acids and DMF between 473 and 523 K, in contrast to the pure Zr parent UiO-66 that showed dehydroxylation and evacuation of DMF and free acid at a temperature higher than 573 K. Upon surface rehydroxylation (Figure 4a), a band between 3650 and 3640 cm<sup>-1</sup> revealed the presence of OH groups bridged over Ce<sup>4+</sup>,<sup>25</sup> increasing in intensity with the amount of Ce in the sample (see ESI); while a weak shoulder at 3680 cm<sup>-1</sup> is consistent with the presence of Ce<sup>3+</sup>. For both CO adsorption and CD<sub>3</sub>CN adsorption the UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) sample showed a weaker host-guest interaction than the parent material (ESI). In the case of methanol, however, UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) showed a distinctive behaviour: in addition to the on-top and bridged methoxy species on metal sites, additional features were observed at ~1100 and 1040 cm<sup>-1</sup> (Figure 4b), assigned to methoxy groups linearly or bridged coordinated on Ce<sup>4+</sup>, respectively.<sup>26</sup> This is highlighted by subtracting the spectrum of adsorbed species on UiO-66(Zr) from that of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) (ESI): the intensity of methoxy bands is increased, showing that in the presence of cerium the methanol dissociative adsorption is enhanced. Moreover, the bands of linearly and bridged coordinated species are more evident, and a feature at ~1080 cm<sup>-1</sup> become visible, evidence for the presence of Ce<sup>3+</sup> cations. We also examined catalysis properties using *operando* IR spectroscopy<sup>27</sup> to investigate the behaviour of pure and Ce-substituted samples towards methanol reactivity. Upon introduction of 700 ppm of methanol diluted in Ar and 20% of oxygen, in a continuous flow inside a reactor-cell containing the sample methanol is dissociatively adsorbed to form methoxy moieties first, and then it is dehydrated to dimethylether. Around 473 K a partial oxidation (15%) of the reacting methanol into CO<sub>2</sub> is measured. It is possible that its catalytic activity is related to its acid/base properties, favouring the dehydration and dehydrogenation steps of methanol and dimethyl ether into methyl formate, successively decomposing into CO<sub>2</sub>. Considering the Ce-containing sample, new sites for methanol dehydration during the adsorption step are created, as shown by both IR spectra of the adsorbed species and MS in the gas phase.



**Fig. 4** IR spectra (a) showing the OH region upon rehydroxylation (bottom to top), and (b) the interaction of methanol (by introduction of increasing aliquots on the sample) with UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>), with bands unique to the Ce material indicated.

The activity of UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) can be compared with ZrO<sub>2</sub>, which itself is known for transforming methanol into dimethylether (unlike CeO<sub>2</sub>). It is also worth noting that deliberate inclusion of defects in UiO-66 is known to enhance Lewis acid catalytic properties,<sup>13</sup> and it is therefore likely that the additional defects induced by Ce inclusion are important in the activity of our new material. To investigate the possibility that redox activity of the Ce in the doped UiO-66 is also at play, we have made preliminary temperature programmed reduction/oxidation studies under dilute hydrogen (see ESI). These show a low temperature reduction at less than 200 °C for UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) (a lower temperature than surface reduction of CeO<sub>2</sub>), which can be reversed on heating in oxygen, while complementary *in situ* XRPD under dilute hydrogen flow shows the structure remains intact under the same temperatures. This proves redox activity in UiO-66(Ce<sub>0.05</sub>Zr<sub>0.95</sub>) and paves the way for future redox catalysis based applications.

In conclusion, cerium has been successfully incorporated in the structure of the robust zirconium MOF UiO-66 and by various characterisation techniques we have demonstrated its presence in the hexameric building units, in the form of two oxidation states: predominantly Ce(IV), but also minor amounts of Ce(III). The mixed-metal material shows enhanced binding of methanol and this allows catalytic decomposition of methanol into CO<sub>2</sub>. Further studies are required to determine the mechanism of the reactivity, which may be a combination of defect induced acidity and redox activity of

Ce<sup>4+</sup>. Given the use of cerium oxides in oxidative catalysis applications and considering the large number of robust and highly porous Zr polycarboxylate MOFs available as potential candidates for Ce doping, we envisage that study of Ce(IV) MOFs might be an important area for future research, of which there are few examples in the literature so far.<sup>28,29</sup>

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## Table of Contents Entry

Replacement of Zr by Ce in a metal organic framework gives defects and redox activity for use in heterogeneous catalysis

