Supporting Information

Tuning the Properties of the Thermally Stable UiO-66 Metal Organic Framework by Ce Substitution

Farid Nouar, Matthew I. Breeze, Betiana C. Campo, Guillaume Clet, Marco Daturi, Thomas Devic, Alexandre Vimont, Richard I. Walton, Christian Serre

S1: Thermogravimetric analysis

Figure S1: TGA under air

Consistent with the literature, the first mass loss before 100 °C is accounted for by solvent loss, followed by dehydroxylation to ~ 400 °C.\textsuperscript{1,2} This yields the composition \((\text{Ce}_{0.05}\text{Zr}_{0.95})_6\text{O}_6\text{OH}_4\text{BDC}_n\), which upon further heating collapses with total loss of ligands by 500 °C to give \((\text{Ce}_{0.05}\text{Zr}_{0.95})\text{O}_2\).

This analysis would suggest around 4 BDC ligands per hexameric unit \((n = 4\), see Table S1), consistent with UiO-66 analysed by Katz \textit{et al.}\textsuperscript{2}

<table>
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<th>Table S1: TGA Analysis</th>
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<td><strong>Experimental % Mass Loss</strong></td>
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S2: Thermodiffraction

Loss of Bragg peaks of UiO-66 occurs just before 350 °C upon heating in air, consistent with the TGA analysis.

Figure S2: Thermodiffraction of heating UiO-66(\text{Ce}_{0.05}\text{Zr}_{0.95}) in air.
S3: Further IR spectroscopy

Figure S3: IR spectra of CO adsorption at low temperature

Figure S4: CD$_3$CN adsorption
Figure S5: OH region highlighting the effect of Ce inclusion and comparison with the pure Zr material.

Figure S6: Difference IR spectrum for methanol absorption in UiO-66(Ce_{0.05}Zr_{0.95}) and in UiO-66(Zr)
S4: Temperature Programmed Reduction and Oxidation

Temperature Programmed Reduction is the standard test for reducibility of materials and a standard high surface area ceria was used for comparison. The upper temperature for the UiO-66 material is limited by its thermal stability, but H$_2$ uptake is seen before this.

Figure S7: Temperature Programmed Reduction under 10% H$_2$ in N$_2$

Temperature Programmed Oxidation was done on the sample immediately after the TPR to look at oxygen uptake following reduction using 10 % O$_2$ in He. This shows some reoxidation of the sample.

Figure S8: Temperature Programmed Oxidation (after reduction) of UiO-66(Ce$_{0.05}$Zr$_{0.95}$) under 10% O$_2$ in He
In situ powder XRD under 5% H₂-N₂ confirms that the material is stable to 350 °C under reducing conditions and in fact collapse is delayed compared to heating in air, possibly due to hindered oxidation of the organic.

Figure S9: In situ powder XRD under 5% H₂-N₂ of UiO-66(Ce₀.₀₅Zr₀.₉₅)