Supporting Information

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

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S1: Thermogravimetric analysis

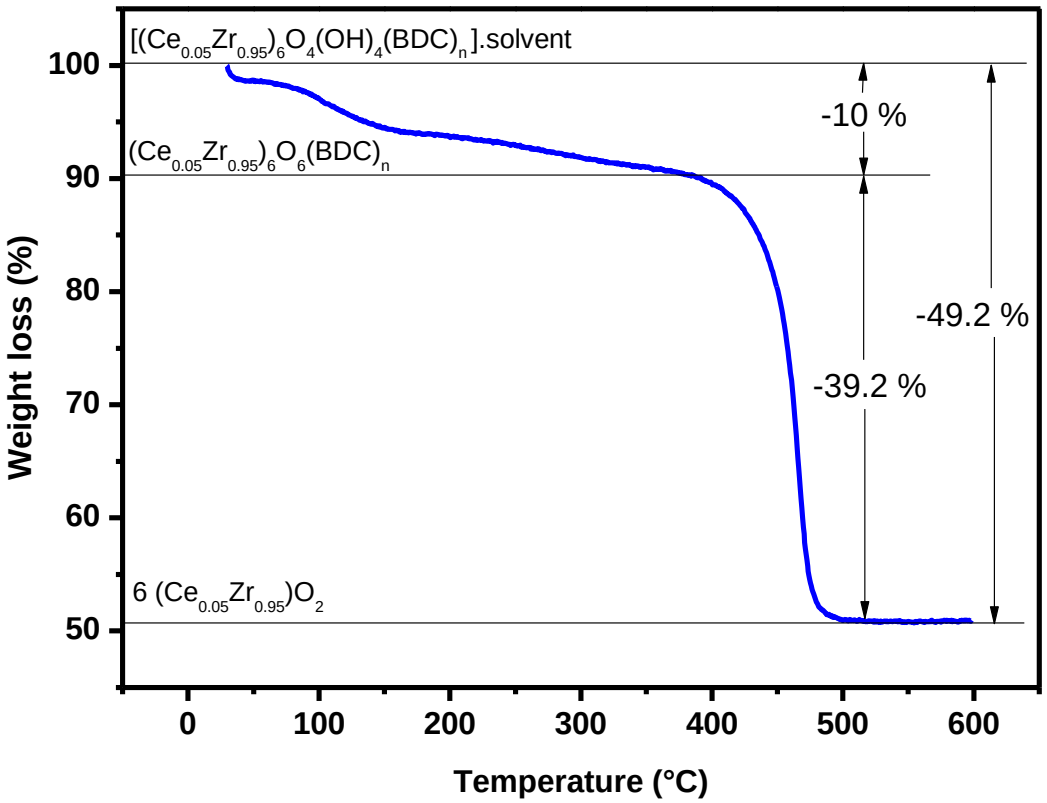

Figure S1: TGA under air

Consistent with the literature, the first mass loss before 100 °C is accounted for by solvent loss, followed by dehydroxylation to ~ 400 °C.[1, 2]. This yields the composition $((Ce_{0.05}Zr_{0.95})_6O_6(BDC)_n$, which upon further heating collapses with total loss of ligands by 500 °C to give $(Ce_{0.05}Zr_{0.95})O_2$.

This analysis would suggest around 4 BDC ligands per hexameric unit (n = 4, see Table S1), consistent with UiO-66 analysed by Katz *et al.*[2]

Table S1: TGA Analysis

Experimental % Mass Loss	Calculated $n = 3$	Calculated $n = 4$	Calculated $n = 5$	Calculated $n = 5$
39.2	34.4	42.6	49.0	54.1

S2: Thermodiffraction

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

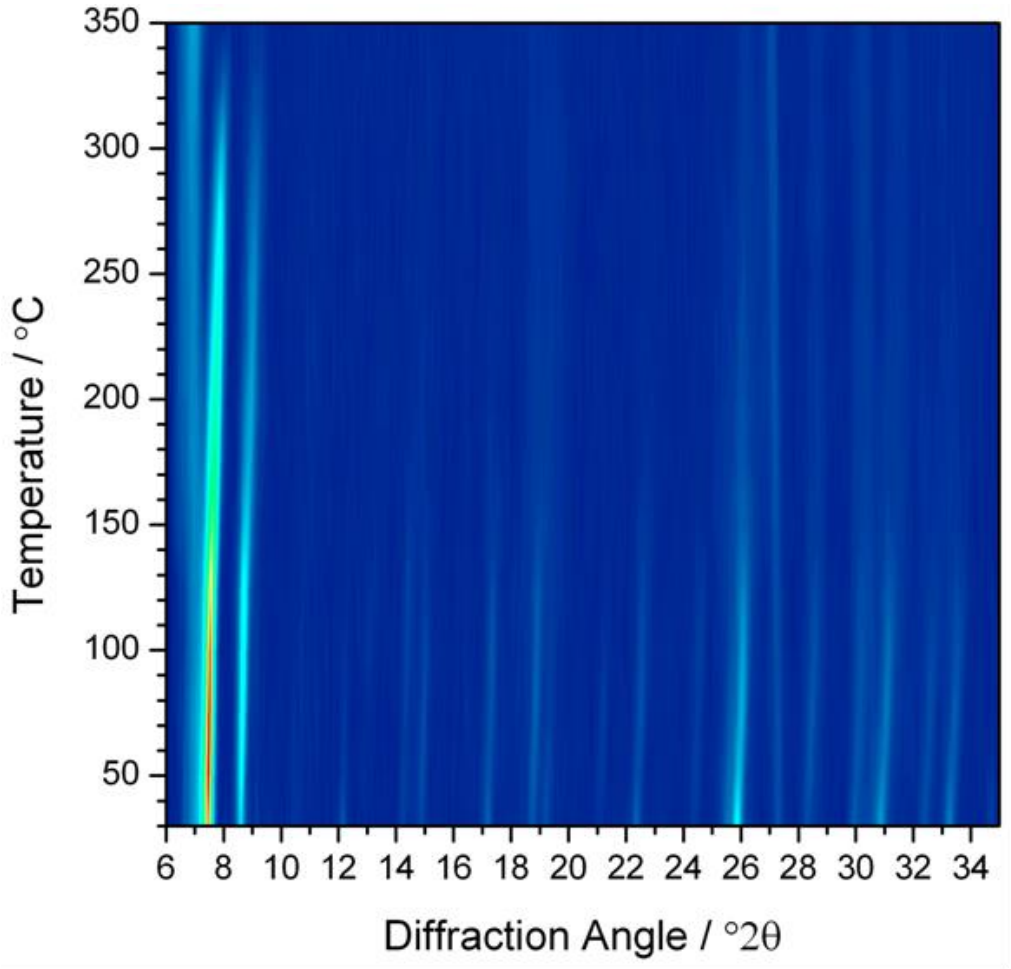

Figure S2: Thermodiffraction of heating UiO-66($Ce_{0.05}Zr_{0.95}$) in air.

S3: Further IR spectroscopy

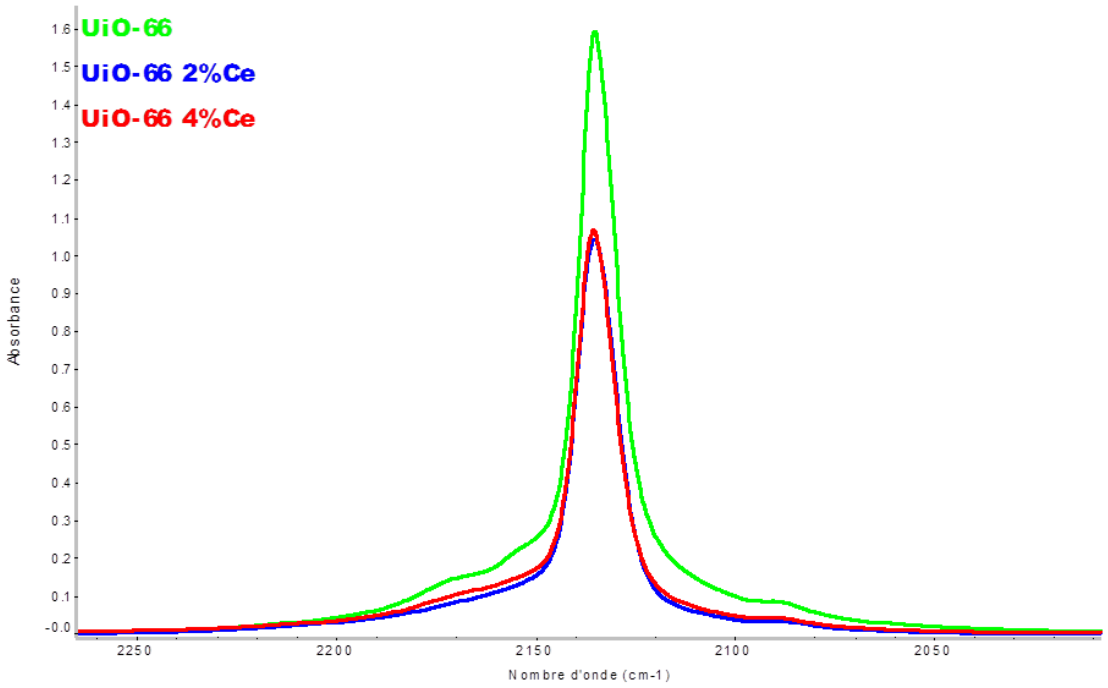

Figure S3: IR spectra of CO adsorption at low temperature

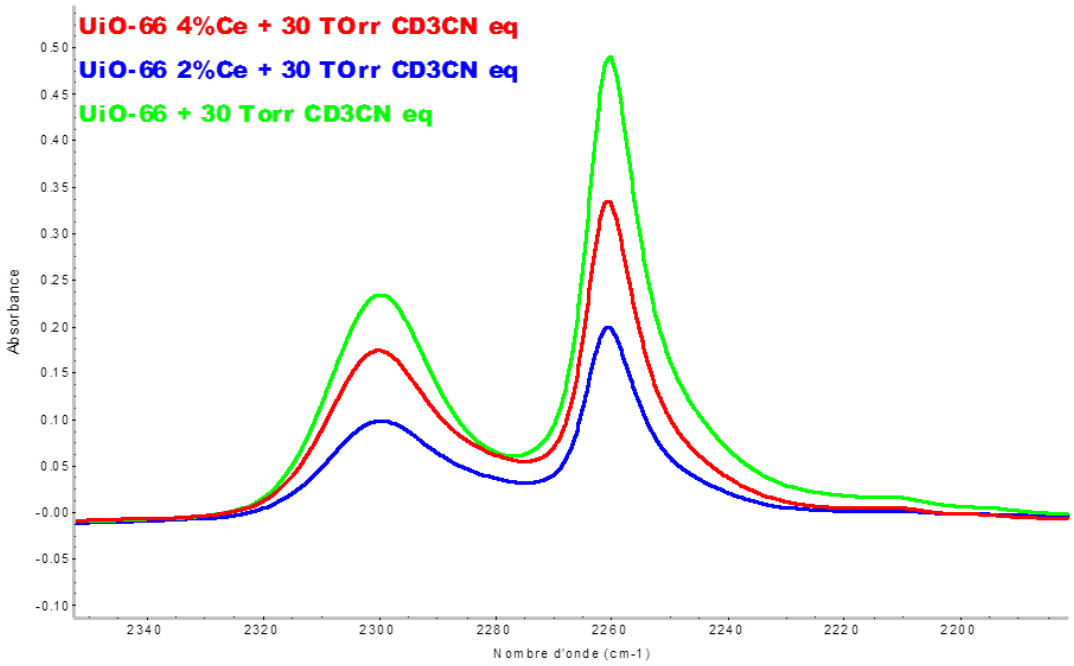

Figure S4: CD_3CN adsorption

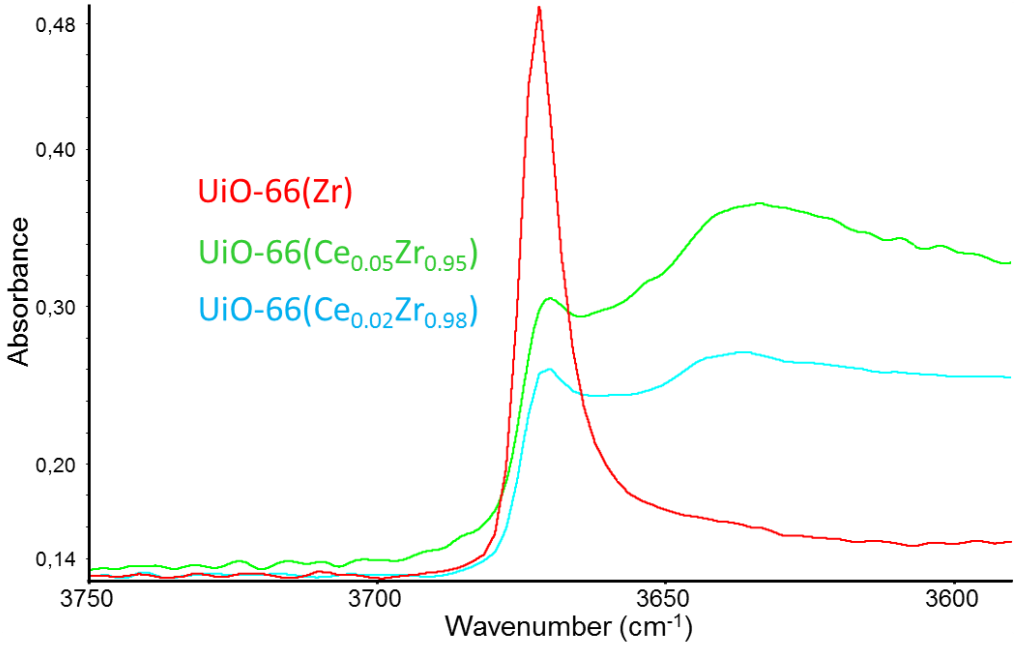

Figure S5: OH region highlighting the effect of Ce inclusion and comparison with the pure Zr material.

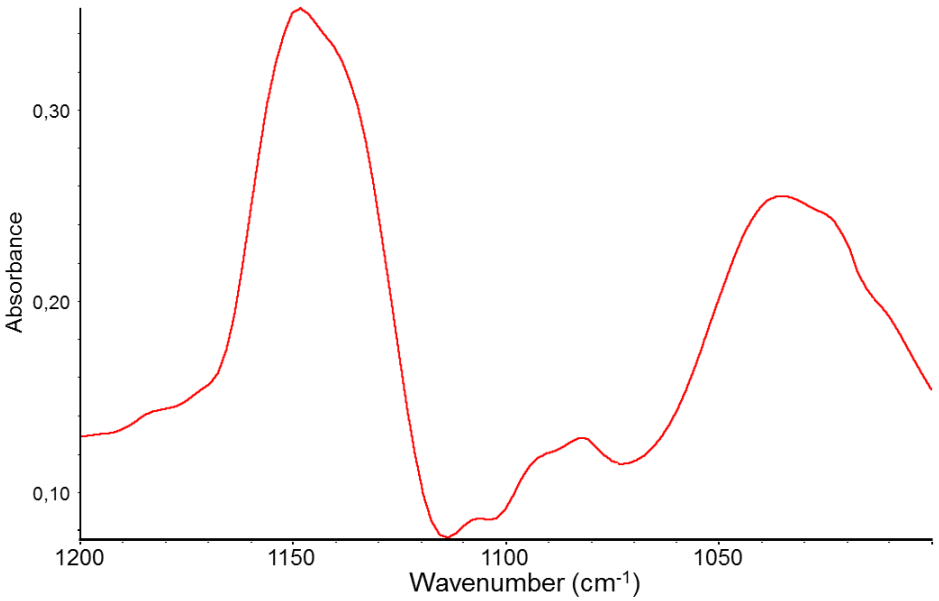

Figure S6: Difference IR spectrum for methanol absorption in UiO-66($Ce_{0.05}Zr_{0.95}$) and in UiO-66(Zr)

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.

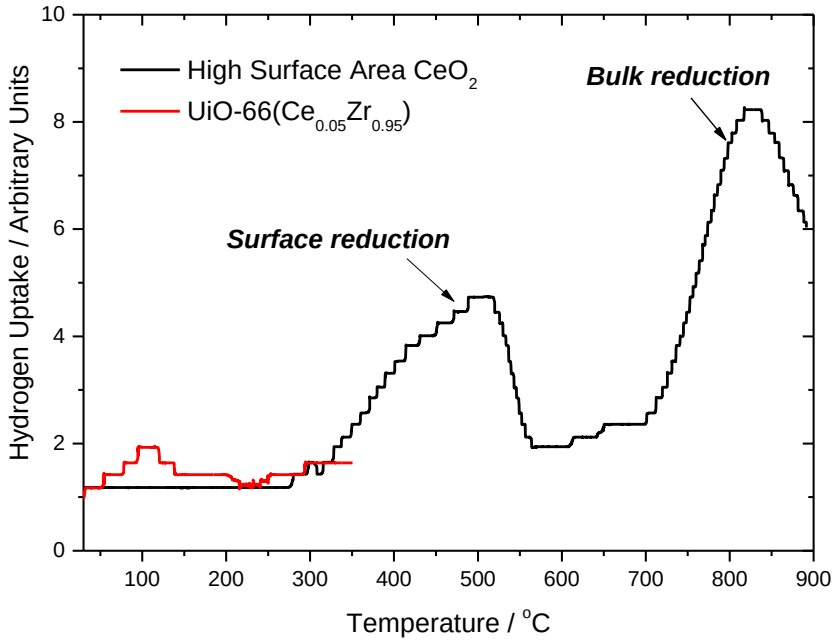

Figure S7: Temperature Programmed Reduction under 10% H_2 in N_2

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.

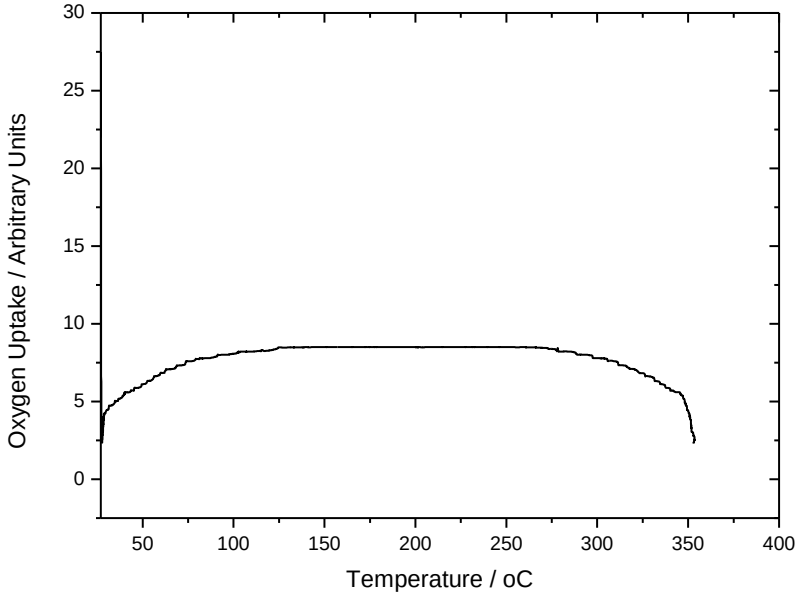

Figure S8: Temperature Programmed Oxidation (after reduction) of UiO-66($Ce_{0.05}Zr_{0.95}$) under 10% O_2 in He

In situ powder XRD under 5% H_2-N_2 confirms that the material is stable to 350 ^oC under reducing conditions amd in fact collapse is delayed compare to heating in air, possibly due to hindered oxidation of the organic.

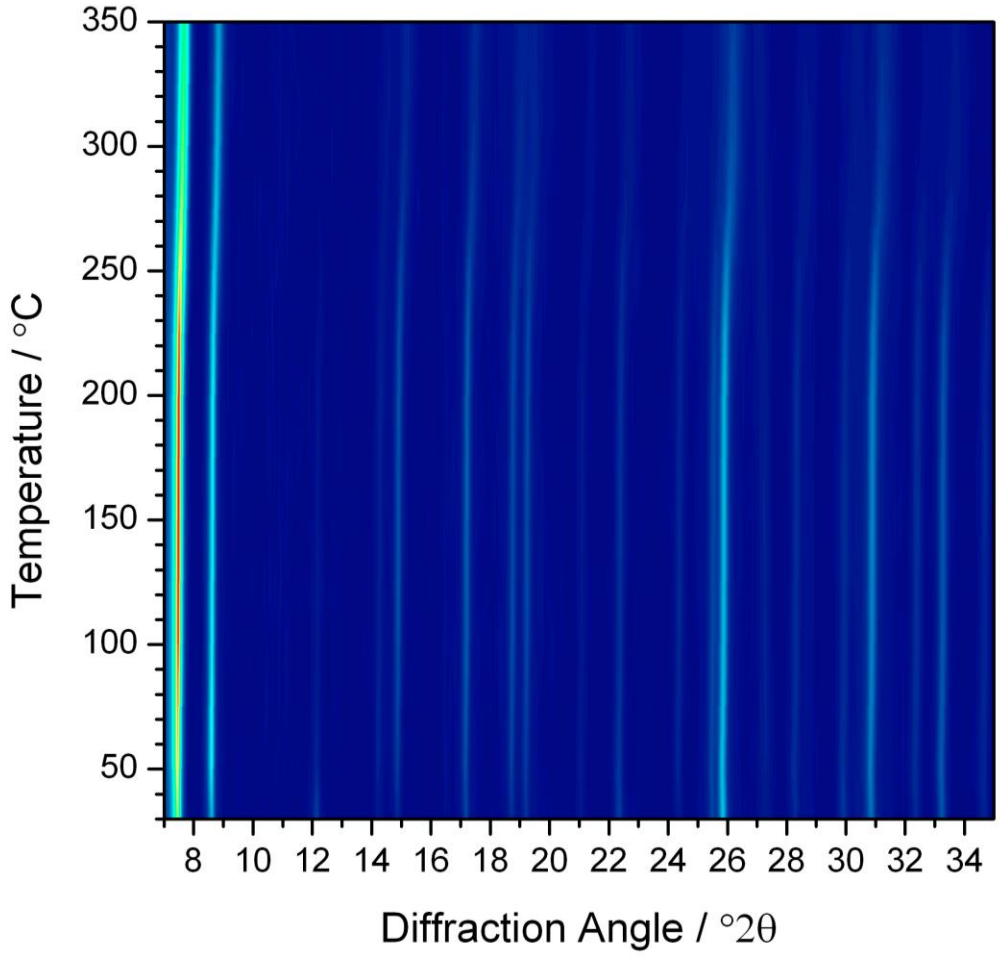

Figure S9: *In situ* powder XRD under 5% H_2-N_2 of UiO-66($Ce_{0.05}Zr_{0.95}$)

1. L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700.
2. M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449.