# SUPPORTING INFORMATION

## Synthesis of mixed-linker Ce-UiO-67 metal-organic framework

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#### S1. Synthetic procedure for g-scaled Ce-UiO-67

Ce-UiO-67 was synthesized according to Lammert *et al.*<sup>1</sup>, albeit upscaled to larger quantities. First, 1.2405 g of H<sub>2</sub>BPDC was mixed with 28.8 mL of DMF under stirring at 100 °C. After the preparation of a deionized water solution 0.5333 M of ammonium cerium(IV) nitrate  $(NH_4)_2Ce(NO_3)_6$ , 9.6 mL of this solution were added to the synthetic mixture. The resulting stoichiometry for the synthetic mixture was 1  $(NH_4)_2Ce(NO_3)_6$  : 1 H<sub>2</sub>BPDC : 73 DMF. After 15 min under stirring at 100 °C in an oil bath, the mother liquor was removed by centrifuging the product (10000 rmp, 15 °C, 5 min). The material underwent the following washing procedure, differently from the literature: 1 x DMSO (20 mL) and 2 x DMF (20 mL), sonicating for 5 min at 60 °C prior to each centrifuging. The material was dried in a static oven overnight at 70 °C. This procedure corresponded to 70% yield. The desolvated MOF yield, corrected by the solvent loss in its TGA profile at 250 °C, corresponds to 40%.

This synthetic procedure was further upscaled by using these quantities: 3.7215 g of H<sub>2</sub>BPDC in 86.4 mL of DMF adding 28.8 mL of deionized water solution 0.5333 M of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, keeping the same molar ratios. The washing procedure was parallelly adjusted for centrifugation dividing the reaction mixture in 3 Falcon tubes and washing them separately with 3 x DMSO (20 mL) and 3 x DMF (20 mL), sonicating for 5 min at 60 °C prior to each centrifuging. Interestingly, this further upscaled procedure corresponded to a higher yield 92%. The desolvated MOF yield, corrected by the solvent loss in its TGA profile at 250 °C, corresponds to 53%.



### S2. Additional information on basic characterization

**Figure S1**. PXRD pattern of #1 Ce-UiO-67-5% BPyDC synthesised without the addition of benzoic acid as modulator, showing a non-crystalline PXRD pattern.



**Figure S2**. PXRD pattern of #1 Ce-UiO-67-5% BPyDC synthesised at 80 °C with the addition of benzoic acid as modulator, showing a non-crystalline XRD pattern for the MOF.



**Figure S3**. PXRD pattern of #2 Ce-UiO-67-5% BPyDC synthesised varying the reaction time from the standard 15 min (a), exploring 30 min (b), 1 h (c), 3 h (d), 6 h (e) up to 24 h (f). Intensities normalized to the 5.58° peak.



**Figure S4**. TGA and DTA curves (exo up) for **A)** Ce-UiO-67 and for the three batches of Ce-UiO-67-5% BPyDC: **B)** #1, **C)** #2 and **D)** #3, respectively.

Figure S5 displays the <sup>1</sup>H-NMR spectrum of #1 Ce-UiO-67-5% BPyDC, as an example for this type of mixed-linker materials. At 4.75 ppm the feature of water in deuterium oxide dominates the spectrum. Upon the overnight digestion DMF, that is the pore-filling solvent of all these MOFs, is hydrolysed to formic acid (detected as formate at 8.4 ppm, more visible in Figure S4) and to dimethylamine (DMA at 2.1 ppm). There are no features ascribable to benzoic acid (as benzoate showing 3 peaks in the range 7-8 ppm <sup>2,3</sup>) possibly connected to the Ce clusters as missing linker defects.

The <sup>1</sup>H-NMR spectra of #1-#3 Ce-UiO-67-5% BPyDC in the  $\delta$  interval of interest 7 – 9 ppm are highlighted in Figures S6-S8. The two features, centred at 7.5 ppm and 7.7 ppm respectively are related to the original linker, H<sub>2</sub>BPDC, and their integrals have been set to 1 (despite being aware that their signals integrate 2 protons). On the other hand, the features of H<sub>2</sub>BPyDC are centred at 7.81 ppm, 8.06 ppm and 8.75 ppm. Table 1 summarises the percentages of BPyDC insertion in the Ce-UiO-67 framework on the basis of the <sup>1</sup>H-NMR integrated peak areas according to the following equation:





**Figure S5**. Entire NMR spectrum of #1 Ce-UiO-67-5% BPyDC taken as example for all the three samples. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.



**Figure S6**. NMR spectrum of #1 Ce-UiO-67-5% BPyDC in the  $\delta$  range of interest. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.



**Figure S7.** NMR spectrum of #2 Ce-UiO-67-5% BPyDC in the  $\delta$  range of interest. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.



**Figure S8.** NMR spectrum of #3 Ce-UiO-67-5% BPyDC in the  $\delta$  range of interest. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.



**Figure S9**. NMR spectrum of #2 Ce-UiO-67-5% BPyDC synthesised for 30 min in the  $\delta$  range of interest. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.



**Figure S10**. NMR spectrum of #2 Ce-UiO-67-5% BPyDC synthesised for 1 h in the  $\delta$  range of interest. Under each integrated feature (green sign), the value of the corresponding integral is reported in blue digits.

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| Material             | % BPyDC introduced |  |
|----------------------|--------------------|--|
| #2 Ce-UiO-67-5%BPYDC | 5 7                |  |
| for 15 min           | 5.7                |  |
| #2 Ce-UiO-67-5%BPYDC | 2 5                |  |
| for 30 min           | 2.5                |  |
| #2 Ce-UiO-67-5%BPYDC | 3 3                |  |
| for 1 h              | 0.0                |  |

The quantification of the defectivity of the materials has been obtained following this calculation: since no benzoate is visible from the <sup>1</sup>H-NMR spectra of the digested MOFs, we could hypothesize the hydroxylated MOFs formula as

 $Ce_6O_4(OH)_4(BPDC)_{6(1-x)}(BPyDC)_{6x}$ 

where x is the % BPyDC insertion obtained from NMR spectra. Hence, the molar mass of the MOF can be computed for the dehydroxylated materials having formula as

 $Ce_6O_6(BPDC)_{6(1-x)}(BPyDC)_{6x}$ 

It can be compared to the inorganic residue of the materials after TGA, corresponding to the 100% final plateau and to  $6 \text{ CeO}_2$ , with molar mass 1032 g/mol, obtaining the factor y as

 $y = \frac{molar \ mass \ dehydroxilated \ MOF}{molar \ mass \ ceria}$ 

By proportion, if the factor *y* is multiplied by 100 %, what we obtain is the weight % at which the plateau for the dehydroxylated MOF ideally is in the TG analysis. The ideal dehydroxylated plateau is compared then with the experimental dehydroxylated plateau observed from the TG curves, finding the factor z as:

 $z = \frac{weight (\%) experimental dehydroxilated MOF}{weight (\%) ideal dehydroxilated MOF}$ 

and then obtaining the defectivity in % as d = (1 - z)\*100.

**Table S2**. Resuming the experimental dehydroxylated molar mass in g/mol of the MOFs deriving from the % BPyDC effectively inserted, the corresponding ideal dehydroxylated TGA plateau in %, the experimentally observed dehydroxylated TGA plateau in %, the factor z as the ratio of the two plateaux and the defectivity d (%).

|           | Dehydroxylated | Ideal Experimental            |                 | z    | d    |
|-----------|----------------|-------------------------------|-----------------|------|------|
|           | MOF (g/mol)    | dehydroxylated dehydroxylated |                 |      | (%)  |
|           |                | TGA plateau (%)               | TGA plateau (%) |      |      |
| #1        | 2379           | 230.33                        | 222.01          | 0.96 | 3.61 |
| #2        | 2379           | 230.34                        | 224.46          | 0.97 | 2.55 |
| #3        | 2379           | 230.35                        | 222.74          | 0.97 | 3.30 |
| Ce-UiO-67 | 2378           | 230.27                        | 226.67          | 0.98 | 1.56 |



**Figure S11**. N<sub>2</sub> adsorption-desorption isotherm at 77 K of Ce-UiO-67. For the sake of clarity, we have selected one each three adsorption points up to  $150 \text{ cm}^3/\text{g}$  STP and then one every other.



**Figure S12**. N<sub>2</sub> adsorption-desorption isotherms at 77 K in the range of interparticle voids at relative pressures p/p<sup>0</sup> approaching 1: **A)** #1 Ce-UiO-67-5% BPyDC, **B)** #2 Ce-UiO-67-5% BPyDC, **C)** #3 Ce-UiO-67-5% BPyDC and **D)** Ce-UiO-67.



**Figure S13**. Linear BET regression in the 0.001<p/p<sup>0</sup><0.03 relative pressures range for Ce-UiO-67 (A) and for #1 Ce-UiO-67-5% BPyDC (B).



**Figure S14**. Linear BET regression in the 0.001< $p/p^{0}$ <0.03 relative pressures range for #2 Ce-UiO-67-5% BPyDC **(C)** and for #3 Ce-UiO-67-5% BPyDC **(D)**.



**Figure S15**. Linear regression of the *t*-Plots for **A**) Ce-UiO-67 and for the three repetitions of Ce-UiO-67-5% BPyDC, **B**) #1, **C**) #2 and **D**) #3. They were fitted in the thickness curve range 0.39 - 0.42 nm to maximize the R<sup>2</sup>.



**Figure S16**. PXRD pattern of Ce-UiO-67 and #3 Ce-UiO-67-5% BPyDC acquired after the volumetric assessment of the materials for crystallinity check. Intensities normalized to the 5.58° peak.



**Figure S17**. PXRD pattern of #1 Ce-UiO-67-5% BPyDC compared to the same material for crystallinity check after 18 months from the synthesis. Intensities normalized to the 5.58° peak.



**Figure S18.** N<sub>2</sub> adsorption-desorption isotherms at 77 K comparing #1 Ce-UiO-67-5% BPyDC as synthesized and after 18 months. For the sake of clarity, we have selected one each three adsorption points up to 150  $cm^3/g$  STP and then one every other.



**Figure S19**. N<sub>2</sub> adsorption-desorption isotherms at 77 K in the range of interparticle voids at relative pressures  $p/p^0$  approaching 1: **A**) #1 Ce-UiO-67-5% BPyDC and **B**) #1 Ce-UiO-67-5% BPyDC after 18 months.



**Figure S20**. Linear BET fit in the  $0.001 < p/p^0 < 0.03$  relative pressures range for #1 Ce-UiO-67-5% BPyDC (A) and #1 Ce-UiO-67-5% BPyDC after 18 months (B).



**Figure S21**. Linear regression of the *t*-Plots for #1 Ce-UiO-67-5% BPyDC **(A)** Ce-UiO-67 together with #1 Ce-UiO-67-5% BPyDC after 18 months **(B)**. They were fitted in the thickness curve range 0.39 - 0.42 nm to maximize the R<sup>2</sup>.

**Table S3**. Resuming the textural properties of of #1 and #1 Ce-UiO-67-5%BPyDC after 18 months, obtained by using the by the BET theory for SSA and the t-plot method for micropore SSA and micropore volume.

| Material                                | BET SSA<br>(m²/g) | Micropore SSA<br>(m²/g) | Micropore Volume<br>(cm³/g) |
|---|-------------------|-------------------------|-----------------------------|
| #1 Ce-UiO-67-5%BPyDC                    | 2189              | 2132                    | 0.79                        |
| #1 Ce-UiO-67-5%BPyDC<br>after 18 months | 2098              | 2016                    | 0.75                        |

### S3. Additional information on spectroscopic characterization



**Figure S22**. Simulated Raman spectra for BPDC (pink) and BPyDC (purple). Asterisks underline the similarities between #3 Ce-UiO-67-5% BPyDC (Figure S16, green) and the simulated H<sub>2</sub>BPyDC linker (purple).



**Figure S23**. ATR-IR spectra of the H<sub>2</sub>BPDC linker (dashed pink) and H<sub>2</sub>BPyDC linker (dashed purple) in powder form. Transmission IR spectra for Ce-UiO-67 (black) and #3 Ce-UiO-67-5% BPyDC (green) in pellet form after activation at 110 °C for 4 h. Asterisks underline the similarities between #3 Ce-UiO-67-5% BPyDC (green) and H<sub>2</sub>BPyDC linker (dashed purple).



**Figure S24**. Simulated IR spectra for the BPDC (pink) and the BPyDC (purple) linkers. Asterisks underline the similarities between #3 Ce-UiO-67-5% BPyDC (Figure S23, green) and the simulated H<sub>2</sub>BPyDC linker (purple).



**Figure S25**. Transmission IR spectra of Ce-UiO-67 exposed to air (pristine) and after activation in dynamic vacuum for 4 h at 110 °C.



**Figure S26**. Transmission IR spectra #3 Ce-UiO-67-5% BPyDC exposed to air (pristine) and after activation in dynamic vacuum for 4 h at 110 °C.



**Figure S27**. UV-vis diffuse reflectance spectra of Ce-UiO-67 (black) and #3 Ce-UiO-67-5% BPyDC (green) in powder form before (dashed lines) and after (solid lines) activation at 110 °C for 4 h. The spectra are shown in normalized Kubelka-Munk units.



**Figure S28**. PXRD pattern of Ce-UiO-67 and #3 Ce-UiO-67-5% BPyDC acquired for crystallinity check on the pelletized materials after IR experiments. Intensities normalized to the 5.58° peak.

## Bibliography

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