

# Supplementary Materials: Adsorption Properties of $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$ MOF

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## Synthesis of $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$ MOF

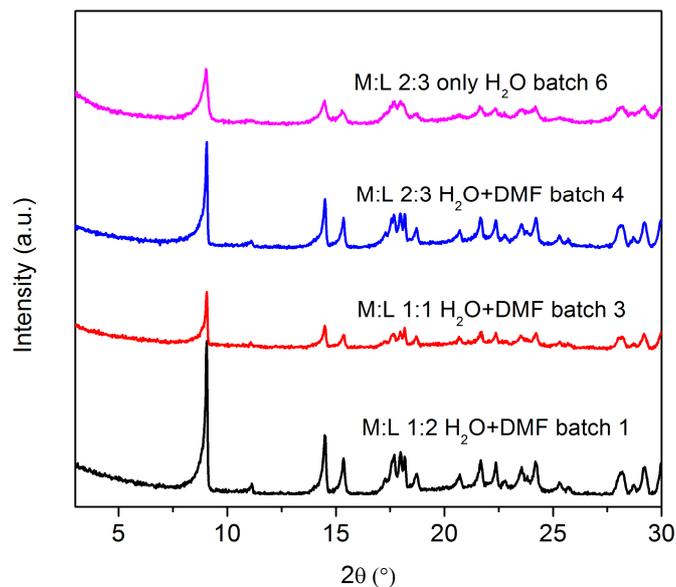
80 mL of DMF are placed in a 250 mL round-bottom flask then 0.9962 g (6 mmol) of  $\text{H}_2\text{BDC}$  are mixed to complete dissolution and 1.768 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (4 mmol) are subsequently added and stirred. The flask is maintained at 140 °C for 15 h on a stirring hotplate equipped with a DrySyn adapter under solvent reflux, then the yellow precipitate is filtered, still hot, washed twice with 10 ml of DMF in a small Erlenmeyer flask shaking with a vortex mixer and dried for 2 h in a 50 °C still oven.

## Synthesis Procedure Development

First, a similar synthesis procedure followed for MOF-76-Ce ( $\text{H}_3\text{BTC}$  ligand) [1] was adopted by employing  $\text{H}_2\text{BDC}$  ligand and by changing metal to linker ratio and solvents (DMF/ $\text{H}_2\text{O}$ ). The first obtained materials (see batches 1, 3, 4, 6) were white powders with a PXRD pattern very similar to a lanthanum terephthalate found on the PDF crystallographic database (card 00-034-1984) [2], as reported in Figure S1. Figure S2 shows different batches obtained by using DMF as a solvent and changing synthesis temperature and time, by keeping constant the metal to ratio; in all the cases a yellow powder is obtained. Batch 19 showed the best obtained diffractogram and for this reason its synthesis conditions are declared as the optimized ones.

D'Arras et al. [3] synthesized a material having an almost identical PXRD pattern (see Figure S3), starting from a Ce(IV) precursor, by claiming the  $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$  formula, which will be adopted also for the material reported in the present work.

Once optimized the synthesis conditions, a scale-up synthesis procedure (reactants increased by four times the reagents quantities) was adopted.



**Figure 1.** Diffractograms of 1,3,4 and 6 batches: adopted solvent and metal to linker ratio (M:L) are reported.

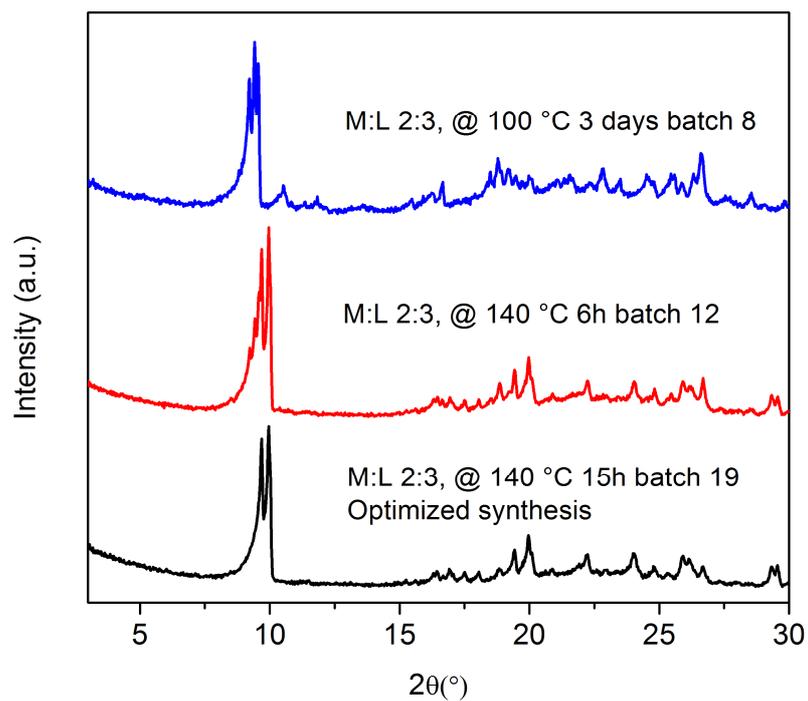


Figure 2. Diffractograms of 8, 12, 19 batches: reaction conditions are reported.

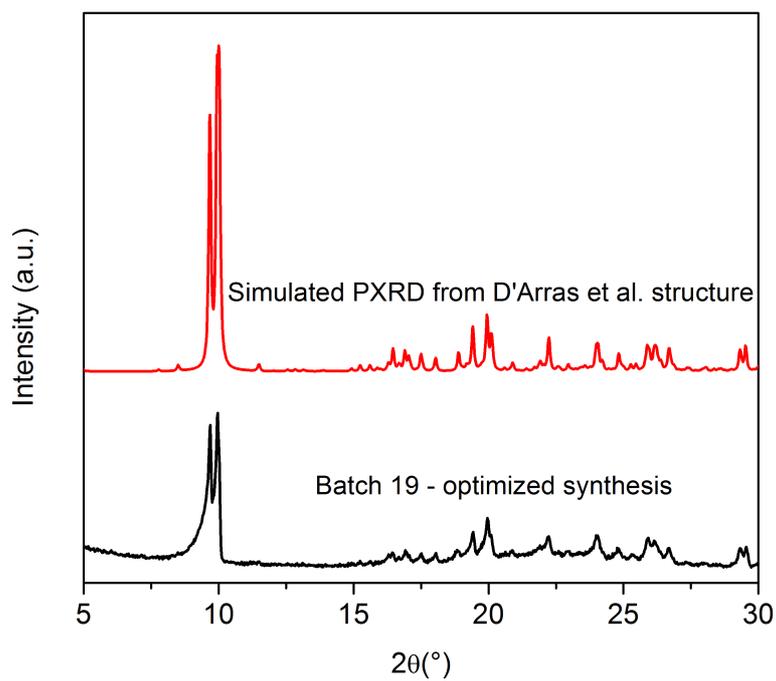


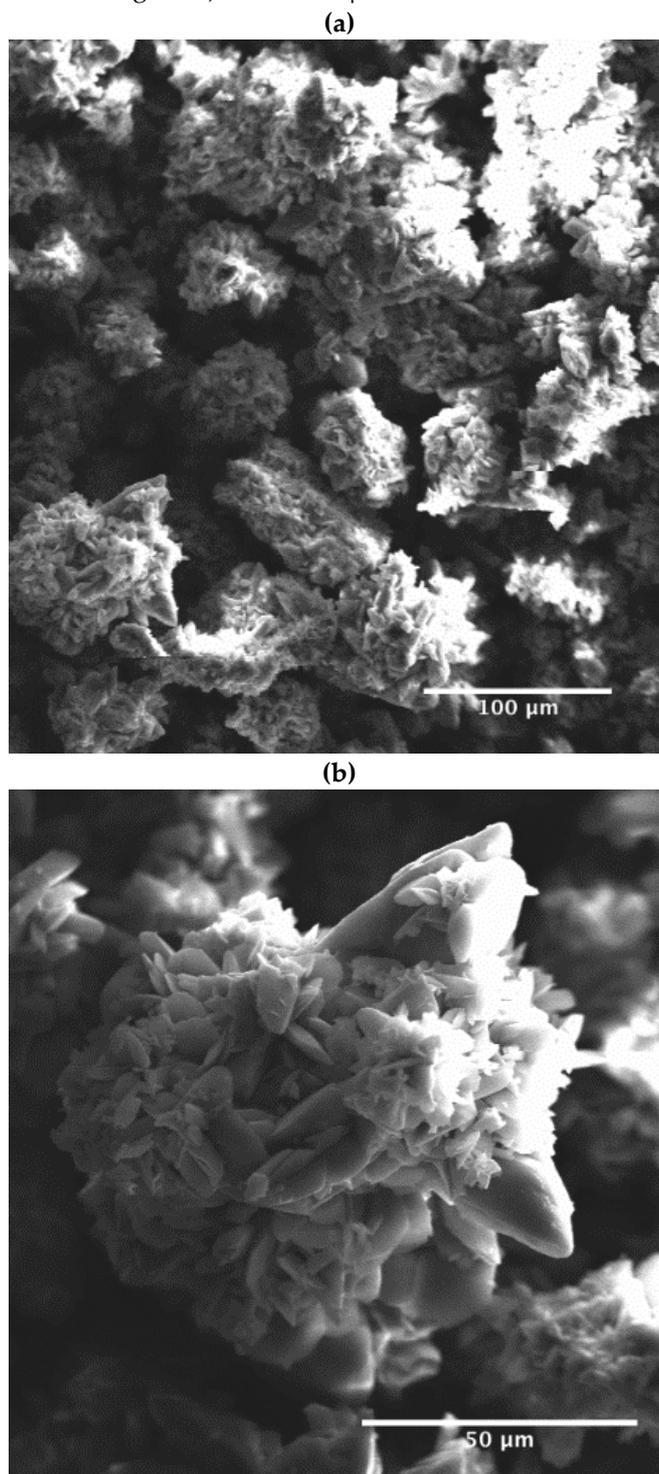
Figure 3. Diffractograms of batch 19 and the MOF reported by D'Arras et al. [3].

## Characterization of $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$ MOF

### SEM Microscopy

The SEM micrographs were collected using a Zeiss Evo 50 xvp microscope equipped a  $\text{LaB}_6$  crystal electron source working at 20 kV of accelerating potential. The sample was coated in gold with a sputterer to make it electrically conductive.

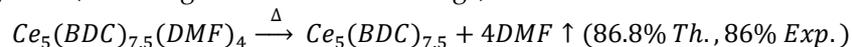
SEM images show a inhomogeneous mixture of aggregates of different sizes in the 50-150  $\mu\text{m}$  range while a magnification on a small particle exhibits a flower-like morphology made by many crystallites (probably twinned together) of about 5  $\mu\text{m}$  size.



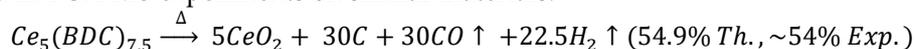
**Figure 4.** SEM images of  $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$  MOF. Part (b) reports a magnification of a portion reported in part (a).

### Thermogravimetric Analysis (TGA)

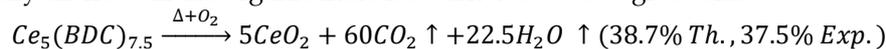
TGA in N<sub>2</sub> and dry air flow was performed on Ce<sub>5</sub>(BDC)<sub>7.5</sub>(DMF)<sub>4</sub> MOF sample (see Figure S5). The first weight loss, occurring in the 200–300 °C range, is due to DMF molecules loss.



The other transformation occurs after 500 °C in N<sub>2</sub> flow and it is assigned to the thermal degradation to ceria and carbon, perhaps following some intermediate steps like the loss of benzene as observed in TGA-MS experiments on similar materials.

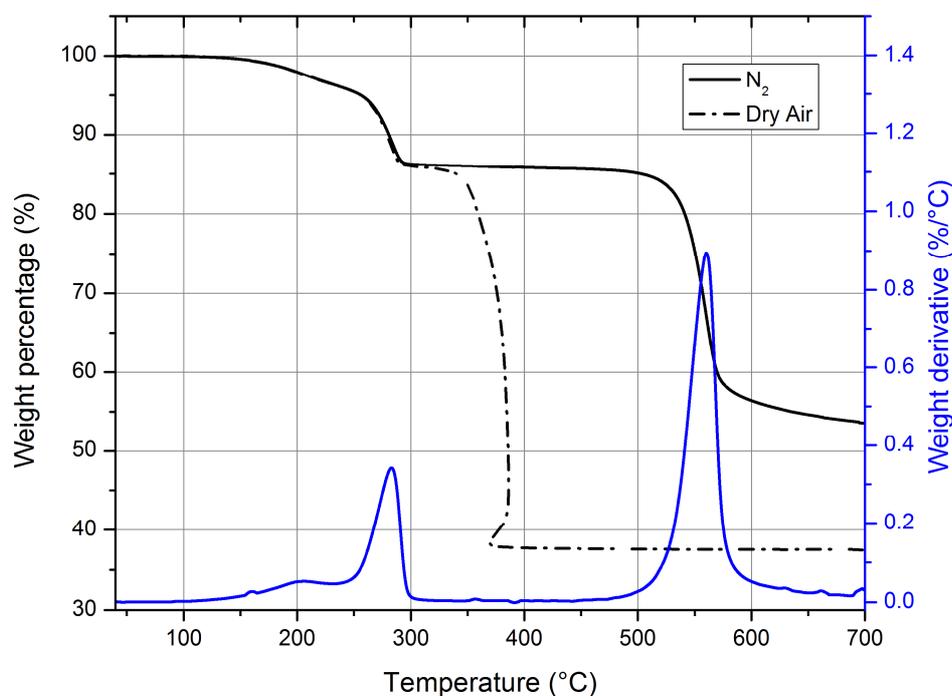


Under dry air flow all the organic moieties burn at 355 °C to give ceria.



The colours of the final products confirm the hypothesized reaction: carbon black for the N<sub>2</sub> flow measurement and pale yellow (as expected for ceria) for the dry air experiment.

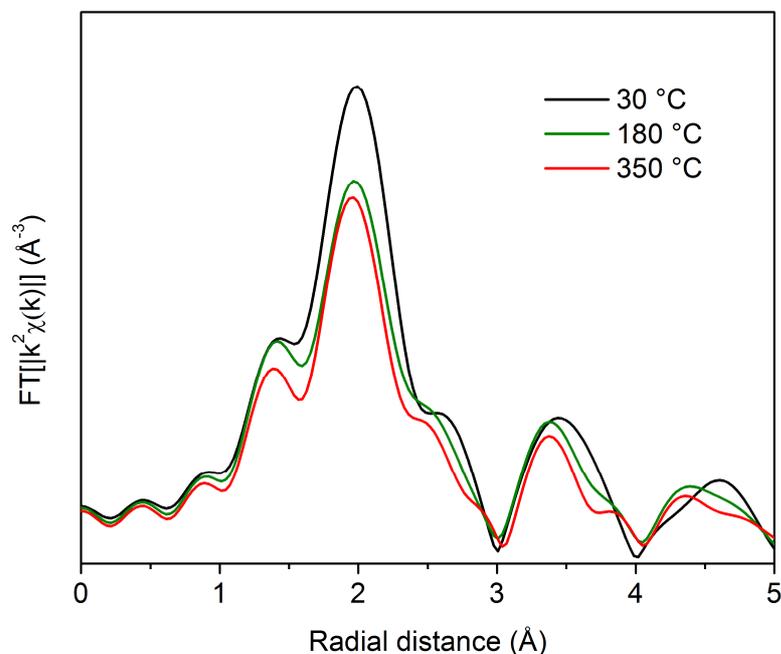
The little discrepancy between theorized and experimental weight losses can be due both to non-structural DMF that wets the sample or to some impurities. Beside that a purity assessment can be done on this thermogravimetric data: being theorized and measured values close within 1% the synthesized product is likely to have a purity higher than 99%.



**Figure 5.** TGA in N<sub>2</sub> (solid line) and dry (dash-dotted line) air flow of Ce<sub>5</sub>(BDC)<sub>7.5</sub>(DMF)<sub>4</sub> MOF.

## EXAFS

The EXAFS data (see Figure S6) report mainly a peak at 2 Å which is greatly reducing during activation. This can be due both to the loss of DMF molecules (as evidenced also by VTXRD in the main text and TGA in Figure S5) in the first coordination shell of cerium atoms and increase of Debye-Waller factor caused by the higher temperature. Only two out of five cerium atoms in the crystalline cell have coordinated DMF molecules that are outgassed during activation. The loss of coordination is confirmed in the EXAFS datum which is an average of all Ce atoms in the MOF.



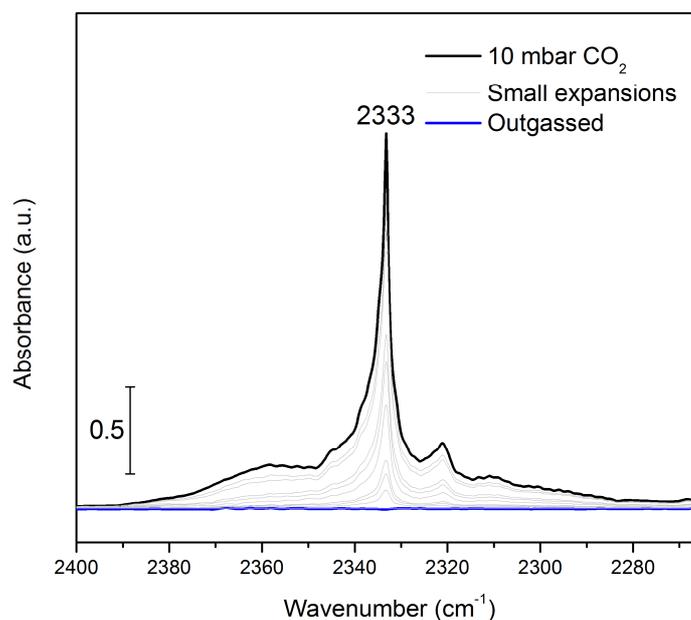
**Figure 6.** Magnitude of the Fourier transform of  $k^2\chi(k)$  EXAFS signal (phase uncorrected) at different temperatures of  $\text{Ce}_5(\text{BDC})_{7.5}(\text{DMF})_4$ .  $2.74 < k < 9.874 \text{ \AA}^{-1}$  range for the transform is used.

### CO<sub>2</sub> Adsorption FTIR Spectra

CO<sub>2</sub> adsorption FTIR spectra has been recorded at RT on the sample activated at 350 °C in vacuo for 1 hour (see Figure S7). A pressure of 60 mbar of CO<sub>2</sub> was dosed and then expansions were done. A narrow peak at 2333 cm<sup>-1</sup> dominates over the other ones and it is due to the asymmetric stretching of condensed CO<sub>2</sub> in the pores [4]. No open metal site is clearly detected. Even if available it would be hardly detected by means of CO<sub>2</sub> probe molecule being in this case the vibrational mode frequency very similar to the one of the physisorbed probe.

As can be seen in Figure S7 the adsorption of CO<sub>2</sub> is easily and fully reversible at room temperature.

Those data can be interpreted as an evidence of porosity of the material in the activated state, which is also confirmed by N<sub>2</sub> adsorption experiments.



**Figure S7.** Background subtracted CO<sub>2</sub> adsorption FTIR spectra at RT on Ce<sub>5</sub>(BDC)<sub>7.5</sub>(DMF)<sub>4</sub> activated 350 °C for 1 h.

### References

1. Ethiraj, J.; Bonino, F.; Vitillo, J.G.; Lomachenko, K.A.; Lamberti, C.; Reinsch, H.; Lillerud, K.P.; Bordiga, S. Solvent-Driven Gate Opening in MOF-76-Ce: Effect on CO<sub>2</sub> Adsorption. *ChemSusChem* **2016**, *9*, 713–719.
2. Sherif, F.G. Heavy Metal Terephthalates. *Ind. Eng. Chem. Prod. Res. Dev.* **1970**, *9*, 408–412.
3. D'Arras, L.; Sassoye, C.; Rozes, L.; Sanchez, C.; Marrot, J.; Marre, S.; Aymonier, C. Fast and continuous processing of a new sub-micronic lanthanide-based metal–organic framework. *New J. Chem.* **2014**, *38*, 1477.
4. Vitillo, J.G.; Savonnet, M.; Ricchiardi, G.; Bordiga, S. Tailoring metal–organic frameworks for CO<sub>2</sub> capture: The amino effect. *ChemSusChem* **2011**, *4*, 1281–1290.