Defective Ce-Doped Mixed Ligand-UiO-66 MOFs with Controlled Fluorination for CO_2 Conversion: Synthesis and Thorough Characterization

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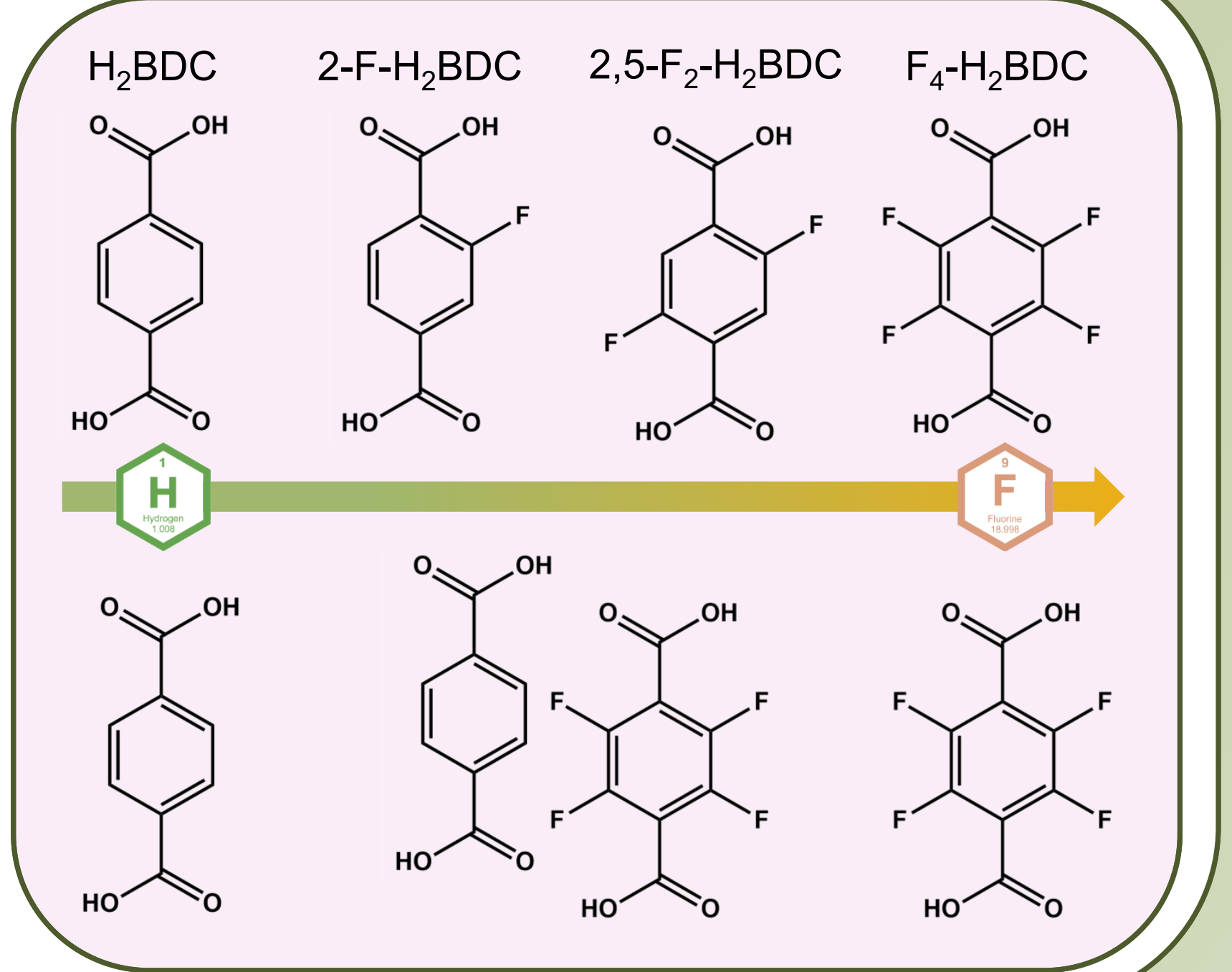
Introduction

UiO-66 is one of the most robust and versatile MOFs, widely employed in gas adsorption, catalysis, and separation. Recently, defect engineering on this material has gained more attention: missing linker and cluster defects can be selectively introduced to create more reactive exposed metal sites. Additionally, substituting Zr Lewis acid sites with Ce ions can enhance reactivity, particularly towards the conversion of CO_2 and methanol into dimethyl carbonate (DMC)[1]. This reaction is important for CO_2 fixation, as DMC is a greener alternative to phosgene and dimethyl sulphate, used in polycarbonate synthesis, carbonylations, methylations, and fuel additives.

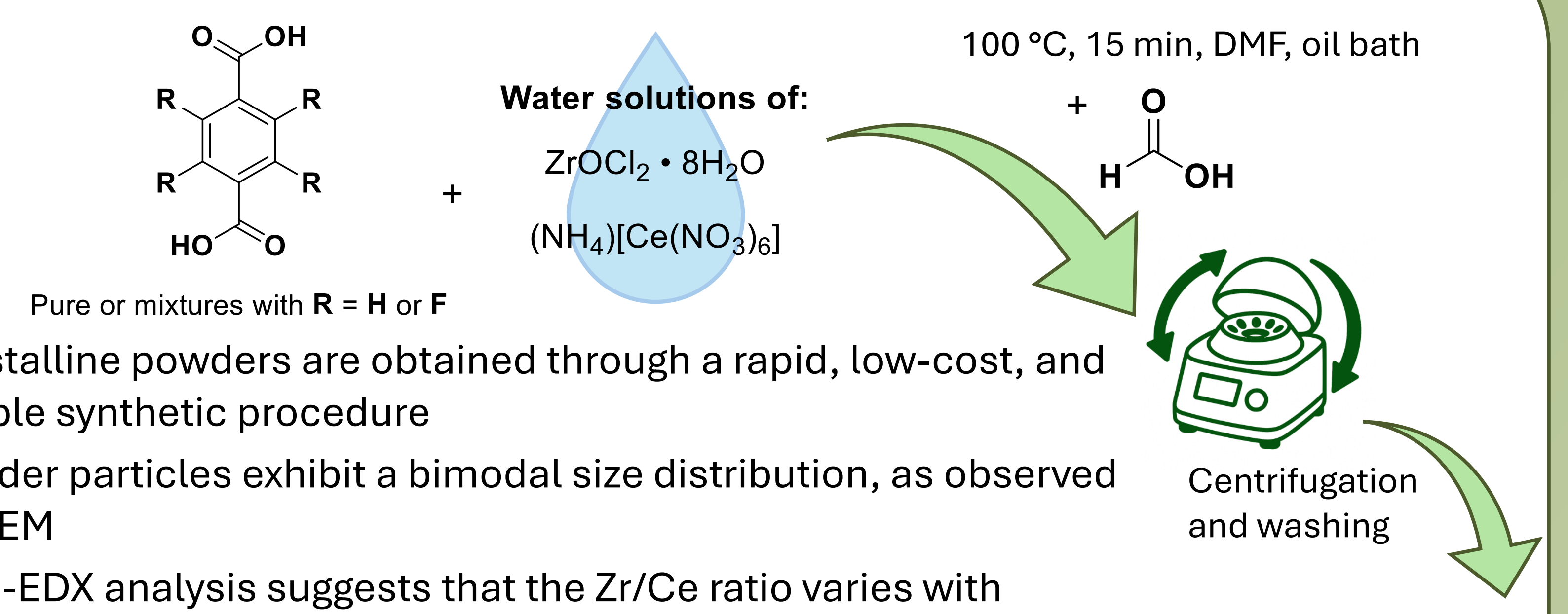
Studies on Zr and Ce-based MOF-derived oxides have shown that water produced during the reaction deactivates Ce sites, lowering catalytic activity[2]. Using UiO-66 to maintain an even distribution of active sites, could slow water diffusion to Lewis acid centres and improving activity. Moreover, trifluoroacetic acid-modulated UiO-66 catalysts have demonstrated improved performance in DMC synthesis[3], highlighting the role of hydrophobicity in water expulsion.

With this in mind, we succeeded in the synthesis of a series of potential $Zr_{0.9}Ce_{0.1}$-UiO-66 catalytic systems by substituting the ligand with fluorine-containing ones and applying a mixed linkers approach by introducing mixtures of fluorinated and non-fluorinated ligands at different ratios.

These materials are subject of a deep characterization, involving PXRD, porosimetry, TGA, SEM-EDX and ICP-OES analysis as well as synchrotron radiation techniques, HR-PXRD and *in-operando* AP-XAS.



Synthesis and Elemental Analysis



Pure or mixtures with **R** = **H** or **F**

Water solutions of:
$ZrOCl_2 \cdot 8H_2O$
$(NH_4)[Ce(NO_3)_6]$

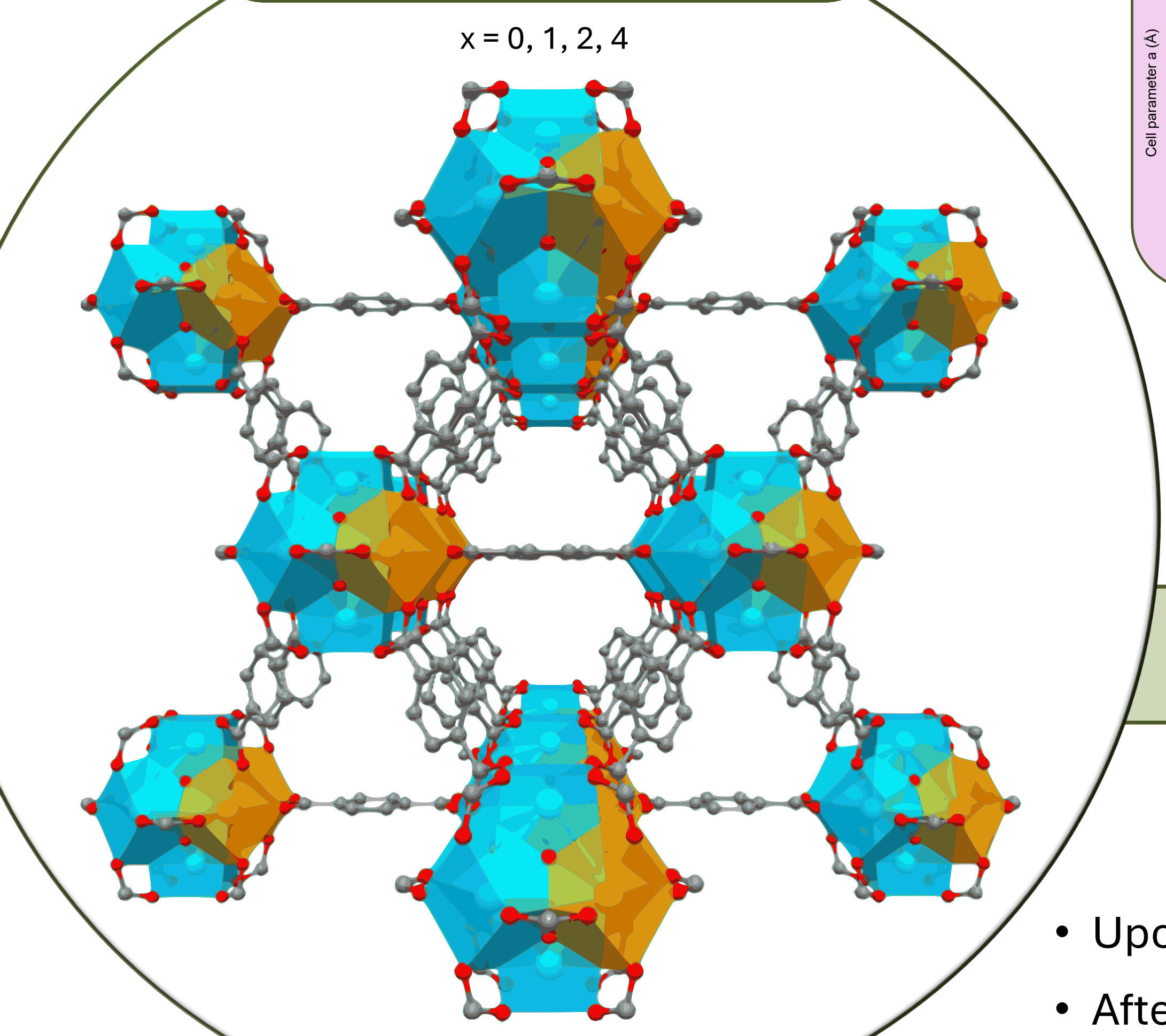
100 °C, 15 min, DMF, oil bath

Centrifugation and washing

- Crystalline powders are obtained through a rapid, low-cost, and simple synthetic procedure
- Powder particles exhibit a bimodal size distribution, as observed by SEM
- SEM-EDX analysis suggests that the Zr/Ce ratio varies with particle size, but further investigation is required
- Cerium incorporation is not correlated with the degree of linker fluorination and follows the expected stoichiometry, as confirmed by ICP-OES

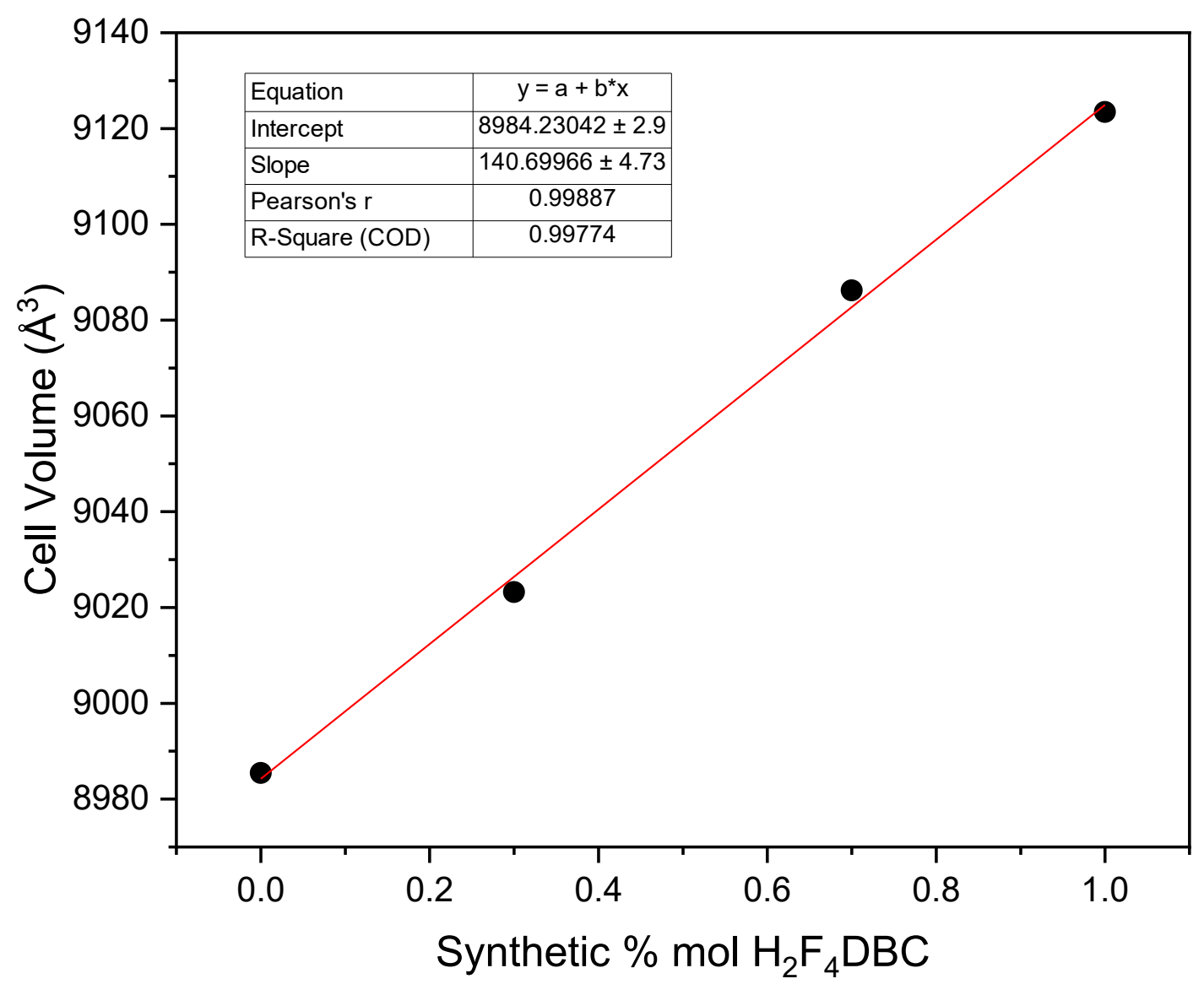
ICP-OES	Zr %mol	STD Zr %mol	Ce %mol	STD Ce %mol
BDC	91.5	0.5	8.50	0.07
F-BDC	89	1	10.70	0.03
F2-BDC	88.9	0.4	11.06	0.02
F4-BDC	89.9	0.3	10.11	0.07
70F4-30BDC	88	1	12.02	0.03
50F4-50BDC	88	2	12.0	0.2
30F4-70BDC	85.1	0.7	14.87	0.02

Zr/Ce-F_x-UiO-66



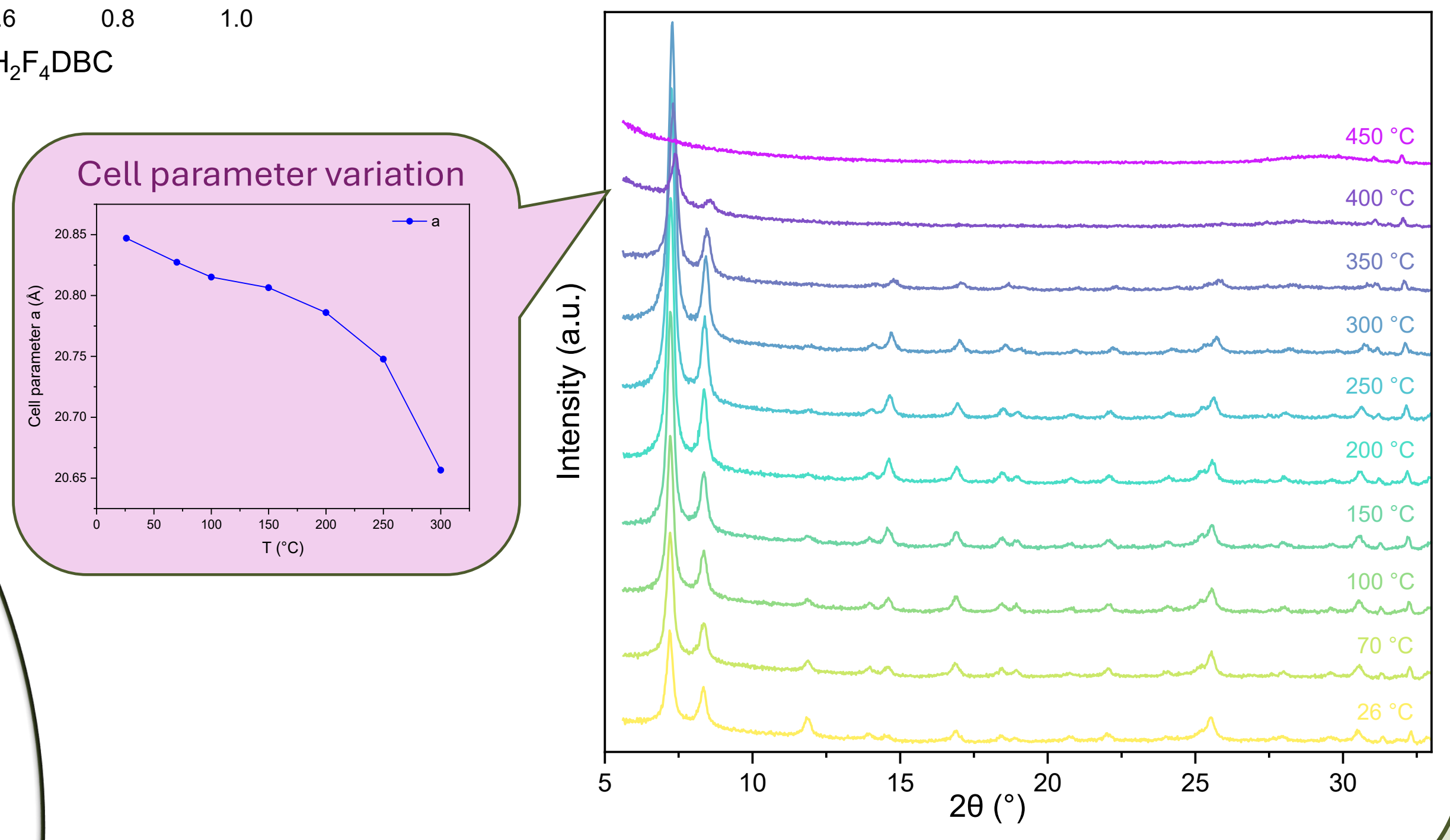
x = 0, 1, 2, 4

Powder X-Ray Diffraction



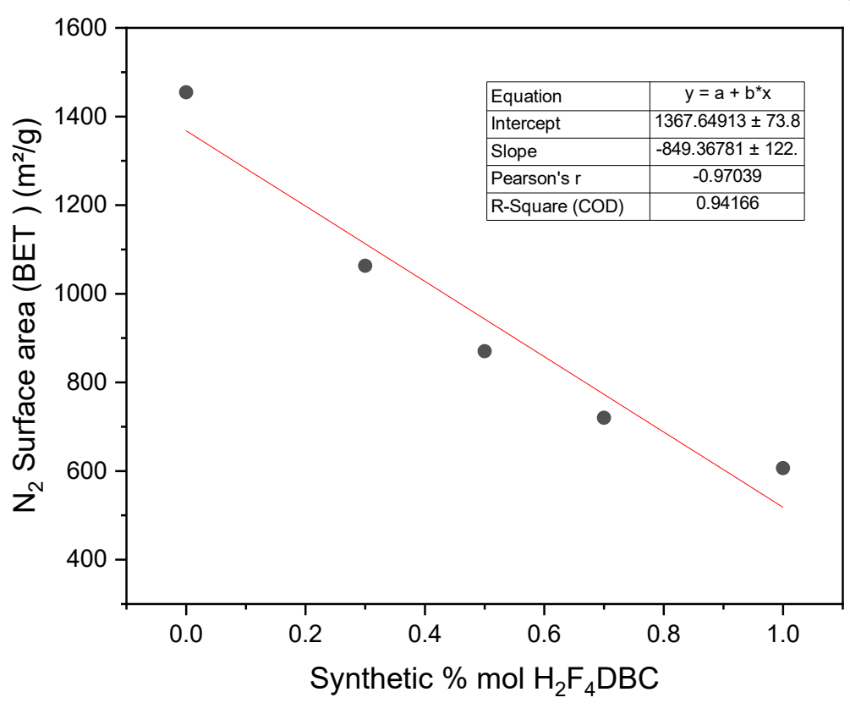
- Fluorination via mixed-linker approach induces a linear expansion of the unit cell
- The compounds display overall good thermal stability, as evidenced by TGA and VT-PXRD data, with unit cell compression observed upon thermal activation

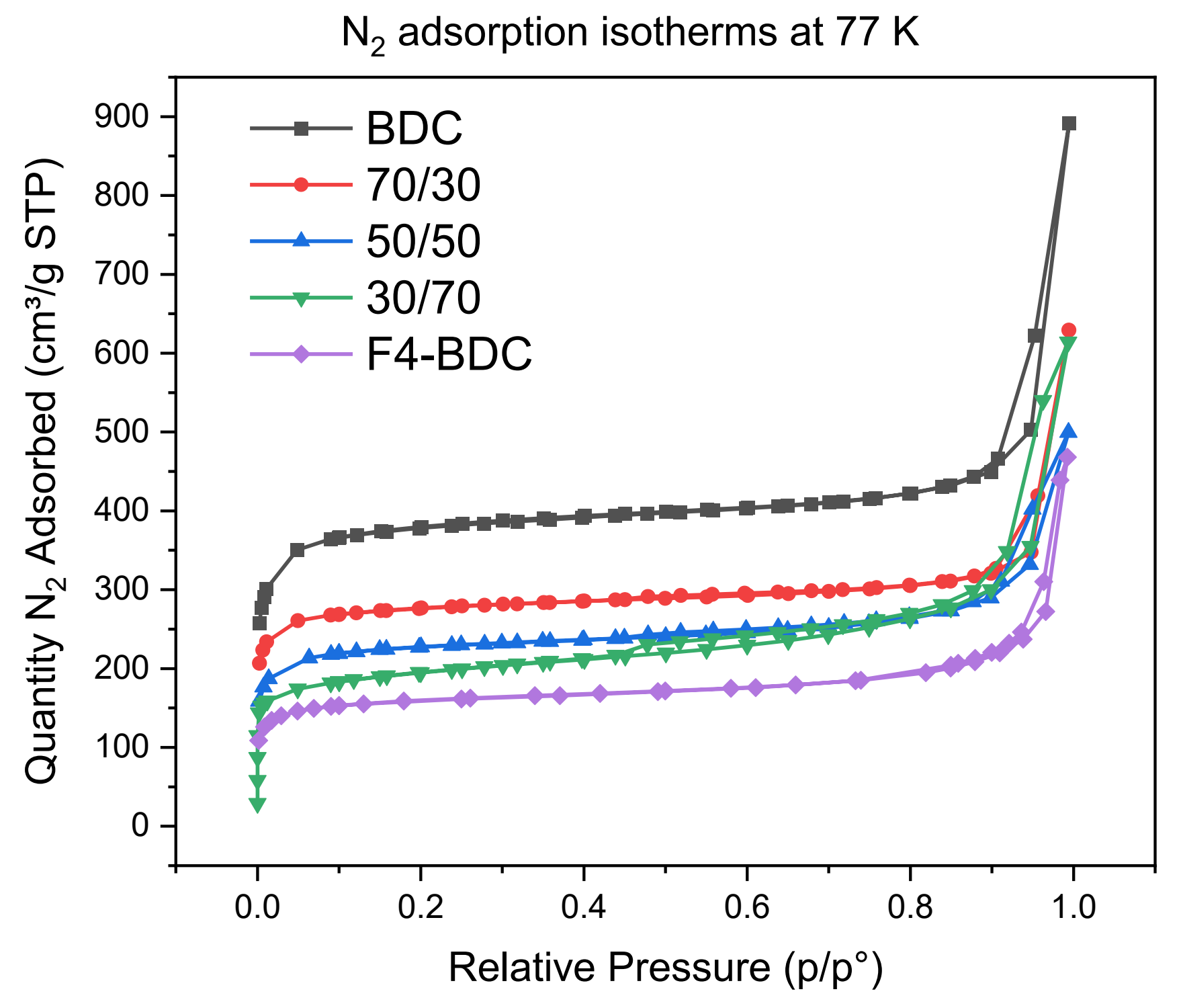
VT-PXRD

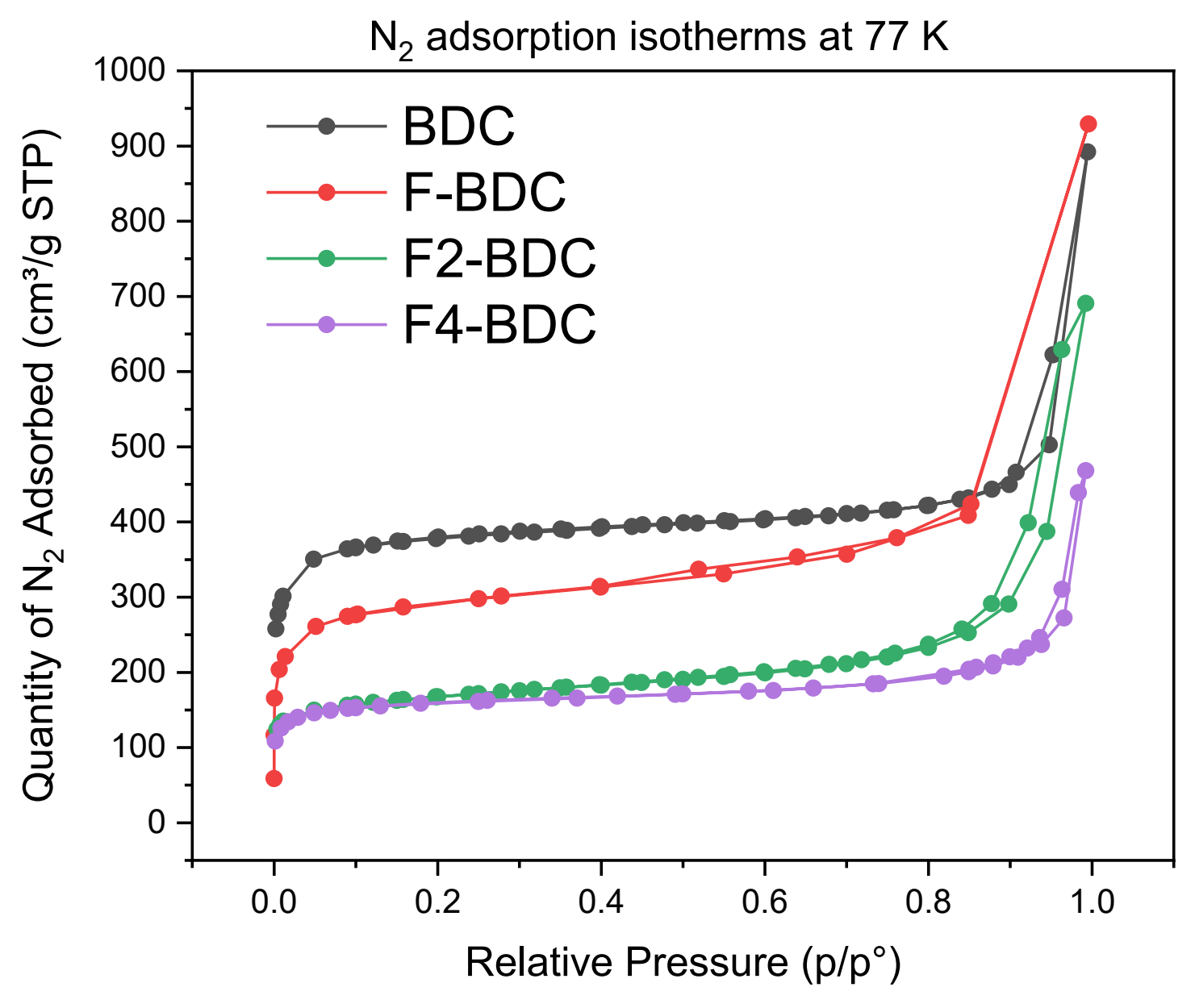


Adsorption Properties

- The compounds exhibit high surface areas that decrease linearly across the mixed-linker series
- Fluorine atoms partially block the pores, leading to a reduced maximum N_2 uptake





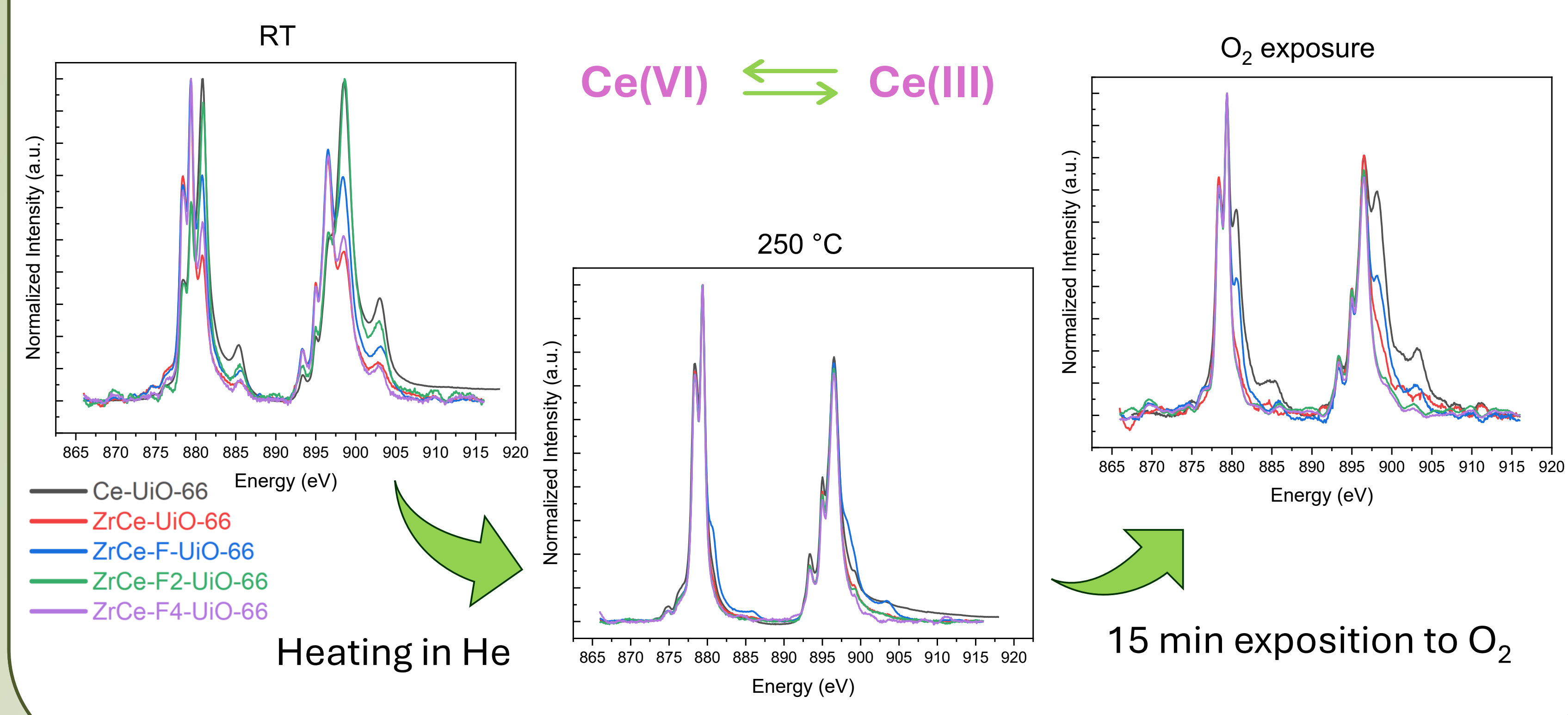


operando *soft*-XAS

Elettra, APE-HE

- Upon thermal activation, almost all Ce(IV) is reduced to Ce(III)
- After exposure to an O_2/He gas flow (15/15 ml/min) for 15 minutes, a partial reoxidation of Ce(III) to Ce(IV) is observed
- As reported in literature[4], the reduction process is associated with the decoordination of labile molecules (e.g., –OH, H_2O) from Ce centers

Ce $M_{4,5}$ edge



Heating in He

15 min exposition to O_2

[1] L. Huo, L. Wang, J. Li, et al., *Journal of CO2 Utilization* **2023**, *68*, 102352.
[2] S. Rojas-Buzo, D. Salusso, A. Jouve, et al., *Appl. Catal. B: Environment and Energy* **2024**, *346*, 123723.
[3] K. Xuan, Y. Pu, F. Li, et al., *Journal of CO2 Utilization* **2018**, *27*, 272–282.
[4] S. Rojas-Buzo, D. Salusso, F. Bonino, M. C. Paganini, S. Bordiga, *Mater Today Chem* **2023**, *27*, 101337.

Future Perspective

- Verify the robustness of the correlation between cell parameter, linker concentration, and BET surface area
- SEM-EDX mapping studies would be helpful to understand local grain composition
- Perform Rietveld refinement and structure solution to confirm pore blockage by fluorine atoms
- Conduct contact angle tests and dielectric constant measurements to evaluate hydrophobicity
- Carry out eventual catalytic tests for CO_2 conversion to DMC

DIPCHI
DIPARTIMENTO DI CHIMICA

Elettra Sincrotrone Trieste