ESRF	**Experiment title:** Structure, redox and luminescence properties of hexanuclear Ce/Zr clusters in new bimetallic MOFs with various connectivities	**Experiment number**: CH-6121
Beamline: BM23	**Date of experiment**: from: 17/02/2022 to: 21/02/2022	**Date of report**: 30/03/2022
Shifts: 12	**Local contact(s)**: Cesare Atzori	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Cesare Atzori* (ESRF)

Jonas Gosch* (Christian-Albrechts-Universität zu Kiel, Germany)

Christoph Meier* (Christian-Albrechts-Universität zu Kiel, Germany)

Diletta Morelli Venturi* (Universita' degli studi di Perugia, Italy)

Niklas Ruser* (Christian-Albrechts-Universität zu Kiel, Germany)

Norbert Stock (Christian-Albrechts-Universität zu Kiel, Germany)

Report:

Proposal summary:

Due to their unique properties metal-organic frameworks (MOFs) remain the object of intense studies and a huge number of new materials with different structures and properties are reported every year. MOFs based on the 12 fold (**12-c**) connected hexanuclear $\{Zr_6O_4(OH)_4\}$ cornerstones, e.g. UiO-66, are known for their thermal stability and high surface area. Catalytic and sensing properties of these materials can be improved by introducing redox-active Ce(IV) ions and synthesizing MOFs with low cluster connectivity.

Synthesis of MOFs have been carried out mainly through solvothermal techniques where water and/or DMF is used as a solvent to react the Ce containing salt to the linker molecules to yield the MOF. In such conditions it is quite common to observe an *in situ* reduction of Ce(IV) to Ce(III)[1] and the oxidation of the linker or the solvent especially at high temperatures and long residence times.

In this proposal, the goal was to follow the synthesis of Ce-based MOFs and to assess the reducibility of Ce centers during the synthesis by collecting quasi-simultaneous PXRD and XAS data for a selection of materials with ditopic linker molecules. This was made possible by the use of a cell designed for running solvothermal chemical reactions[2] and in the meantime shine a X-ray beam through the glass vial for PXRD/XAS experiments.

Secondarily, the structure of clusters with formula $[Ce_6O_4(OH)_4(C_7H_4O_2Cl)_8(DMF)_4(NO_3)_4]\cdot 4DMF$ was probed via XAS measurements in various solvents.

Photocatalytic reduction of some organic dyes by the means of Ce-MOFs have also been investigated by measuring the XANES spectra of MOF materials before and after the photocatalytic reaction.

Experimental description:

A series of reactions involving acetonitrile solutions of CAN (Cerium(IV) Ammonium Nitrate) and various dicarboxylic acid linkers (see Figure 1) was heated to 140°C while collecting quasi-simultaneous XAS at the Ce K-edge and PXRD data at 38.5 keV (the time duration of a complete XAS+PXRD cycle was about 15 minutes).

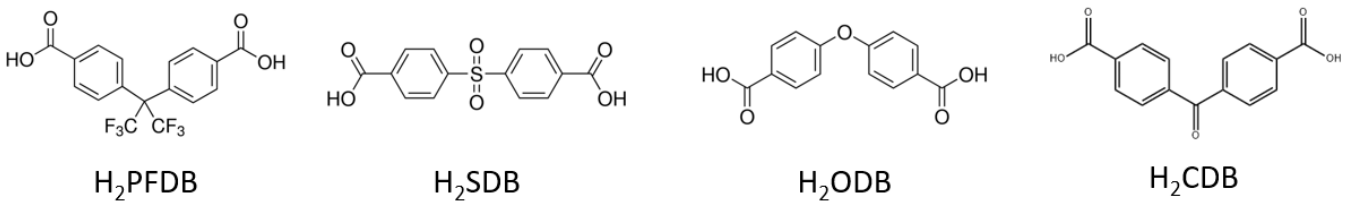

Figure 1 – Structural formulas of the linkers reacted with CAN in acetonitrile solution.

The XAS spectra of solutions of the molecular cluster $[Ce_6O_4(OH)_4(C_7H_4O_2Cl)_8(DMF)_4(NO_3)_4]\cdot 4DMF$ have been measured at the Ce K-edge in solution of various solvents (DCM, MeOH, THF, dioxane, Acetone, EtOH and 2M HCl) at room temperature. In order to investigate the photocatalytic role of some Ce-containing MOFs those materials were measured by means of XAS before and after the photocatalytic reaction at both Ce K and L_3 edges in pellet form and also the solution where the reaction were run was measured at Ce L_3-edge in fluorescence mode, because of the low concentration of Ce leaked into the solution itself (data not shown in the present report).

Results and discussion:

The results obtained during the beamtime confirmed that Ce(IV) centers do reduce to Ce(III), as shown by the shift of the absorption edge towards low energies, during the solvothermal reaction before reacting further with the linker to precipitate the MOF crystals. The kinetics of the reduction process are generally faster than those of the crystallization (10-20 minutes vs. 2-5 hours). This is clearly depicted by the quasi-simultaneous XANES and PXRD data shown in Figure 2 limitedly to the CeCDB case.

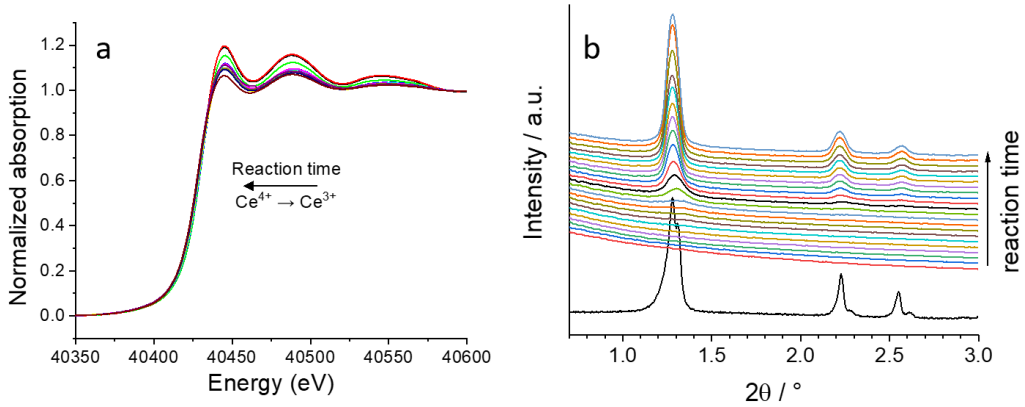

Figure 2 – Quasi-simultaneous XAS (a) and PXRD (b) collected during the synthesis of CeCDB MOF reacting H_2CDB and Cerium Ammonium Nitrate in acetonitrile solution.

By comparing the EXAFS signal collected on the molecular cluster collected in crystalline form and in solution of various solvents (Figure 3) we can infer that this compound is stable in those solvents while, conversely, it reacts in acidic media to yield a Ce(III) compound with a totally different chemical surroundings around Ce centers.

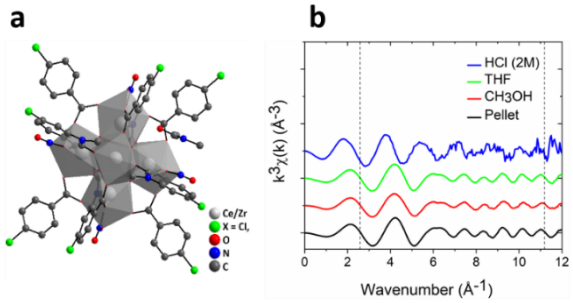

Figure 3 – (a) Hexanuclear molecular Ce/Zr-O cluster (1-Cl). (b) Ce K-edge EXAFS of 1-Cl in different solvents and as solid (in HCl changes of the spectra are due to the decomposition of the cluster)..

Conclusions:

1) The experiment proved that Ce(IV) reduces to Ce(III) before crystallizing the MOF in all materials tested.
2) Hexanuclear molecular Ce/Zr-O cluster are stable in solution and thus they can be further exploited in MOF synthesis

References

[1] Jacobsen, J.; Ienco, A.; D'Amato, R.; Costantino, F.; Stock, N. The Chemistry of Ce-Based Metal–Organic Frameworks. Dalton Transactions, 2020, 49, 16551–16586. https://doi.org/10.1039/d0dt02813d.
[2] Heidenreich, N.; Rütt, U.; Köppen, M.; Inge, A. K.; Beier, S.; Dippel, A.-C.; Suren, R.; Stock, N. A Multi-Purpose Reaction Cell for the Investigation of Reactions under Solvothermal Conditions. Review of Scientific Instruments, 2017, 88, 104102. https://doi.org/10.1063/1.4999688.