

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: X-ray Diffraction Studies of a Metal-Organic Framework, M-BTTri (M = Mn, Fe, Co, Cr, Cu, Ni)	Experiment number: 31-01-13
Beamline: BM 31	Date of experiment: from: 24 Sep 2016 to: 27 Sep 2016 from: 02 Nov 2016 to: 05 Nov 2016	Date of report: 09/19/2017
Shifts: 12	Local contact(s): Wouter Van Beek	<i>Received at ESRF:</i>

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Report:

This experiment was divided into two different section. One section was dedicated to the collection of X-ray Absorption Spectroscopy (XAS) data and the other section was dedicated to *in-situ* diffraction measurements. The brief description of these experiments have come below:

(1) XANES and EXAFS measurement of different metal clusters and MOFs in transmission mode:

This part of the work has already been published¹. The abstract and part of the result has come below:

Metal- organic frameworks (MOFs) have attracted much attention in the past decade owing to their unprecedented internal surface areas, tunable topologies, designable surfaces, and various potential applications. One bottleneck in the field regarding MOF synthesis is controlling the metal-containing secondary building unit (SBU) incorporated into the structure. In this work, we report the synthesis and characterization of five trimeric $[M_3(\mu_3-O)(CH_3CO_2)_6]_x$ clusters (where M = Fe³⁺, Cr³⁺, Fe³⁺/Cr³⁺, Fe³⁺/Co²⁺, or Fe³⁺/Ni²⁺ and x = +1 or 0). The monocarboxylate capping ligand, acetate in this case, readily undergoes exchange with several difunctional counterparts, including 1,4-benzenedicarboxylic acid (H2-BDC) and biphenyl-4,4'-dicarboxylic acid (H2-BPDC), for the formation of an isostructural series of MOFs, several of

¹ Peng, Li, et al. "Using Predefined M3 (μ_3 -O) Clusters as Building Blocks for an Isostructural Series of Metal-Organic Frameworks." *ACS Applied Materials & Interfaces* 9.28 (2017): 23957-23966.

which are newly reported (for $M = \text{Fe}^{3+}/\text{Cr}^{3+}$, $\text{Fe}^{3+}/\text{Co}^{2+}$, and $\text{Fe}^{3+}/\text{Ni}^{2+}$) and show excellent CO_2 adsorption properties. In this report, a host of techniques including NMR, ICP, and ESI-MS are used to probe the ligand exchange process and composition of the SBUs, and XAS is used to monitor the Fe^{3+} and Cr^{3+} environment throughout the reactions, giving strong evidence that the clusters stay intact throughout the MOF synthesis. This work reveals that predefined SBUs is an effective means to create metal-substituted analogues of known frameworks. Further, CO adsorption and in situ IR are used to probe accessibility of the metals after solvent removal. We show for the first time that the incorporation of the neutral clusters, containing weaker Lewis acids like Ni^{2+} and Co^{2+} , can promote the formation of open metal sites in the MOF frameworks, structural features known to enhance the binding energy of small guest molecules like CO_2 .

(2) Collection of variable temperature data on a crystalline MOF (Cu-BTTri) dosed with different dosing level of CO_2 :

In the second part of the experiment, a crystalline Metal organic Framework, Cu-BTTri, was dosed with different levels of carbon dioxide. Based on the adsorption sites obtained from Rietveld refinement of the data with the sequential dosing level of CO_2 and the relative occupancy of these sites at different dosing levels, the four strongest adsorption sites have been determined. These adsorption sites have been shown in Fig.2. The sequential Rietveld analysis on the variable temperature data is in progress. The manuscript is under preparation as well.

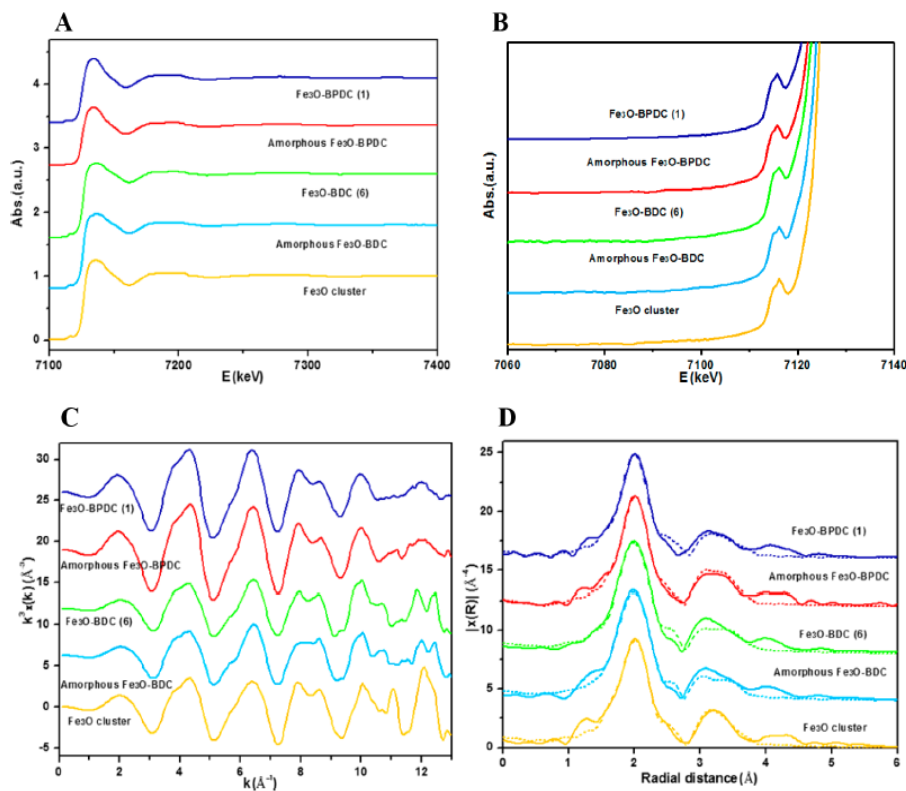


Figure 1-(A) XANES spectra for $\text{M}_3(\mu_3\text{-oxo})$ trimeric cluster, the amorphous $\text{Fe}_3\text{O-BPDC}$ isolated after 3 h, the final crystalline product $\text{Fe}_3\text{O-BPDC}$ (1). (B) Fe pre-edge spectra for $\text{M}_3(\mu_3\text{-oxo})$ trimeric cluster, the amorphous $\text{Fe}_3\text{O-BPDC}$ isolated after 3 h, the final crystalline product $\text{Fe}_3\text{O-BPDC}$ (1). (C) Fe K-edge EXAFS spectra for $\text{Fe}_3(\mu_3\text{-oxo})$ trimeric cluster, the amorphous $\text{Fe}_3\text{O-BPDC}$ isolated after 3 h, and the final crystalline product, $\text{Fe}_3\text{O-BPDC}$ (1). (D) Fit (dashed lines) to the samples' Fourier transformed EXAFS functions (solid lines) of Fe_3O trimeric cluster, the amorphous $\text{Fe}_3\text{O-BPDC}$ isolated after 3 h, the final crystalline product, $\text{Fe}_3\text{O-BPDC}$ (1), the amorphous $\text{Fe}_3\text{O-BDC}$ isolated after 3 h, and the final crystalline product, $\text{Fe}_3\text{O-BDC}$ (6) in the R domain

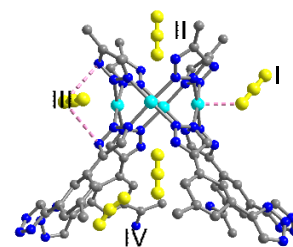


Figure 2- The CO_2 adsorption sites inside the structure of Cu-BTTri