EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.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.

ESRF	**Experiment title:** Understanding the mechanism of carbon dioxide adsorption on a series of Zeolitic Imidazolate Frameworks (ZIFs) using single x-ray diffraction study	**Experiment number**: **01-02-1129**
Beamline: **BM 01**	**Date of experiment**: from: 31 August 2016 to: 04 Sep 2016	**Date of report**: 09/19/2017
Shifts: **6**	**Local contact(s)**: Iurii Dovgaliuk	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

This beam time was our first beam time in the ESRF. We had two different goals at this beam time:

(1) Testing and commissioning of gas dosing manifold and in-situ sample cells:

The main purpose of this beam time was to test and commission our gas dosing manifold and *in-situ* single crystal and powder cell that has been used and will be used normally in our *in-situ* diffraction experiments in ESRF.

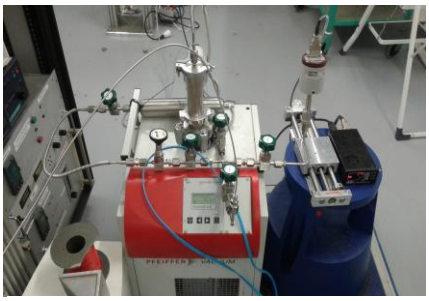

Figure 1- The gas dosing manifold designed for connection of the sample cell to vacuum or different gas sources

We had designed our gas dosing manifold (Fig. 1), the *in-situ* powder cell (Fig. 2) and the *in-situ* single crystal cell (Fig. 3). The picture of the sample cell on the beam (in BM01) has been shown in Fig. 4. The gas dosing manifold in addition to the both sample cells were tested on the beam in BM01 and their reliability were confirmed by conduction of the preliminary experiments. In addition, as many MOFs are not highly stable, the beam sensitivity of some of the samples were checked in advance in order to design the next *in-situ* experiments. For example, for some of ZIF samples, we found that when they are located at 100 °C while the diffraction pattern was continuously being measured, they are going under partial beam damage and therefore the reduction of the crystallinity. Therefore enough thought and care had to be taken in this kind of *in-situ* activation measurements. As a result, the next experiments that were done in BM01, BM02, and BM31 were designed in

Figure 2- Designed in-situ powder cell

such a way that exposure to beam becomes minimal. For some other samples like Cu-BTTri, the beam damage was not considerable.

(2) Collection of ex-situ diffraction pattern for single crystal and powder samples:

The ex-situ powder and single crystal diffraction pattern was measured on some samples where high quality data was needed for certain purposes or collection of the pattern in standard lab based instrument was not possible due to the small size of the sample or lack of high enough quality of the crystal. Having these data, already one paper has been published[1]. The full reference detail has come in the footnote. In the mentioned work, the crystal structures with the CCDC deposition number of **1539823** and **1539825** have been measured in BM01, SNBL ESRF. The abstract of the above published work has come as following:

Figure 3- Designed in-situ single crystal cell

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 $[M_3(\mu_3\text{-}O)(CH_3CO_2)_6]x$ clusters (where M = Fe^{3+}, Cr^{3+}, Fe^{3+}/Cr^{3+}, Fe^{3+}/Co^{2+}, or Fe^{3+}/Ni^{2+} 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 which are newly reported (for M = Fe^{3+}/Cr^{3+}, Fe^{3+}/Co^{2+}, and Fe^{3+}/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.

Figure 4- Picture of in-situ cell on the beam (at BM01)

[1] Peng, Li, et al. "Using Predefined M3 (μ3-O) Clusters as Building Blocks for an Isostructural Series of Metal–Organic Frameworks." *ACS Applied Materials & Interfaces* 9.28 (2017): 23957-23966.