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*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Ultra-fast Switchable Dipolar Rotors in Metal Organic Frameworks at 4 K	**Experiment number**: HC-4781
Beamline: ID-22	**Date of experiment**: from: 22/02/2022 to: 25/02/2022	**Date of report**: 12/09/2022
Shifts: 9	**Local contact(s)**: Ola gjonnes Grendal	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Experiment HC-4781

We collected successfully PXRD patterns of the 5 MOF compunds at several distinct temperatures, down to liquid He temperature, as programmed in the approved proposal.

We mainly focused on the study of two novel isoreticular Al-based MOFs which contain apolar and dipolar bicyclopentane molecular rotors, respectively. Powder X-ray diffraction patterns for these 2 samples were collected from 298 K down to 4 K using a He cryostat available at ID-22 beamline. Sample stability under synchrotron radiation was tested and an optimised measurement protocol was established to ensure data consistency along the measurements. Data collections were performed at more than 15 different temperatures. The PXRD data collected at the various temperatures allowed the crystal structure refinement by the Rietveld method: the results supported the modeling of the rotor conformation and its dependence with temperature. Specifically, the results allowed the identification and refinement of a complex and unprecedented behaviour of the polar molecular rotors at very low temperatures, that lead to the discovery of an order-disorder transition accompanied by a change in the motional regime in the solid state. PXRD results collected at syncrothron source strongly corroborate the rotor dynamic studied with solid state NMR in the same temperature range and supported DFT calculations to clarify the correlated motional mechanism. Moreover, the results provided fundamental insights in the breathing mechanism of MOF structures at very low temperatures. The results are reported in an upcoming paper (under revision in *Angew. Chem. Int. Ed.*). The abstract is reported below.

Abstract. Dynamics of dipolar rotors in solid matter is still a challenge as Coulombic interactions and hydrogen-bonding occurring in polar systems conflict with molecular reorientation, especially at extremely-low temperatures. The synthesis of Al-based MOFs, comprising a wheel-shaped ligand with geminal rotating fluorines, produced benchmark mobility of correlated dipolar rotors at 2K, with practically null activation

energies (E_a=0.017 kcal/mol). The unprecedented rotor dynamics of dipoles was measured over a wide temperature range (2K-300K) by ^{1}H-NMR relaxation times, which revealed multiple distinct configurations and attempt frequencies typical of correlated rotor dynamics. A synergistic approach comprising synchrotron radiation XRD at 4K, DFT, Molecular Dynamics and phonon calculations showed the fluid landscape of configurations and pointed out a cascade mechanism running throughout the structures, which converts dipole configurations into each other. Gas accessibility, shown by HP-Xe NMR, allowed for chemical stimuli intervention: CO_2 entering the channels triggers dipole reorientation, hampering their collective motion and stimulating a change of dipole configuration from disorder to order. Dynamic materials under conditions of limited thermal noise and high responsiveness facilitate the fabrication of molecular machines and controllable chemical and physical properties.

We collected for comparison the PXRD pattern of corresponding MOFs based on the same lignds and Zr^{4+} ions at room temperature and at 100 K to determine and refine the unit cell and model a reference disordered structure of BCP units inside these materials. The structural determination and refinement was interesting and promoted the discovery of ultra-fast molecular rotors modulated by disorder: the results are going to be submitted soon.

Moreover, the collection of PXRD pattern of a Hf-based MOF comprising highly luminescent ligands allowed the refinement of its crystal structure, fundamental for the evaluation of the empty volume enclosed inside the unit cell. The data will appear in an upcoming paper, to be published.