EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Controlled surface-supported synthesis of 2D COFs	**Experiment number**: **26-02-912**
Beamline:	**Date of experiment**: from: 24/June/2021 to: 01/July/2021	**Date of report**: 10/August/2021
Shifts:	**Local contact(s)**: Daniel Hermida merino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Masoumeh Keshavarz: Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

Report:

During this time slot, we performed *in situ* measurements in solution to track 2D COF nucleation and growth over time for various concentrations ranging from 5.0×10^{-5} M to 5.0×10^{-4} M. This experiment was performed over a period of 8 hours on the droplets deposited on different supports during the polymerization in order to probe the in-plane and out-plane structures and reveal the preferencial stacked structure along the support as well as providing the interlayer distances between the stacked sheets of the organic material. However, the signal was extremely low, and the synthesis procedure required more optimization to achieve the goal. Instead, to make an efficient use of time, we switched to another project entitled "Tuning the optoelectronic properties of 2D perovskites by dielectric confinement engineering through substitution/mixing of intralayer organic cations". This project has been granted by the same beamline with the number 26-02 939 for GIWAXS measurements. Some hypothetic experiments as described below have been performed assuring the success of our proposal for the next measurement round.

The goal for the alternative project was to explore the effect of variation of different atomic groups on the structure of a two dimensional perovskite with the chemical formula $MA_2(BA/EA/GA)_{n-1}Pb_n(I/Br/Cl)_{3n+1}$. A mix of monovalent cations is employed as spacers with BA/EA (n-butylammonium/ Ethylammonium) or BA/GA (n-butylammonium/ Guanidinium). The structural modification of the 2D perovskites will permit to achieve optimum efficiency and color rendering for application in LEDs. Preliminary results on temperature dependent photoluminescence (PL) measurements reveal clear changes in the PL spectra at lower temperatures illustrating different exciton binding energies as well as a differing fine structure of the excitons. Until now, the origin of the changes in the *T*-dependent photoluminescence spectra remains unclear. Moreover, a higher efficiency has been observed for LEDs made of mixed cations hinting to a better charge transportation through highly oriented layers relative to the substrate compared to the single cation-based devices. Specifically, we focused on the effect of two different groups: cation and, anion groups. These parameters can change the packing of the atomic groups in the system and hence their optoelectronic properties.

GIWAXS experiments were performed at the Dutch-Belgian Beamline at the European Synchrotron Radiation Facility (ESRF) station BM26B in Grenoble (12 keV, λ = 1.033 Å). The 2D scattering patterns were recorded using a PILATUS 1M Dectris detector. We have used a variable incident angle ranging from 0.17° to 1.8° for the measurements. Next, we used a Linkam stage to control the temperature ranging from 400 K down to 90K. The 2D scattering patterns were recorded at each temperature (every 25 K) to probe the effect of temperature on the arrangement of the interlayer cations in the structure of the materials and their structural phases. This study was performed for various concentration/ratios of the cations and at different temperatures. We also examined the effect of the substrate for a few of the samples.

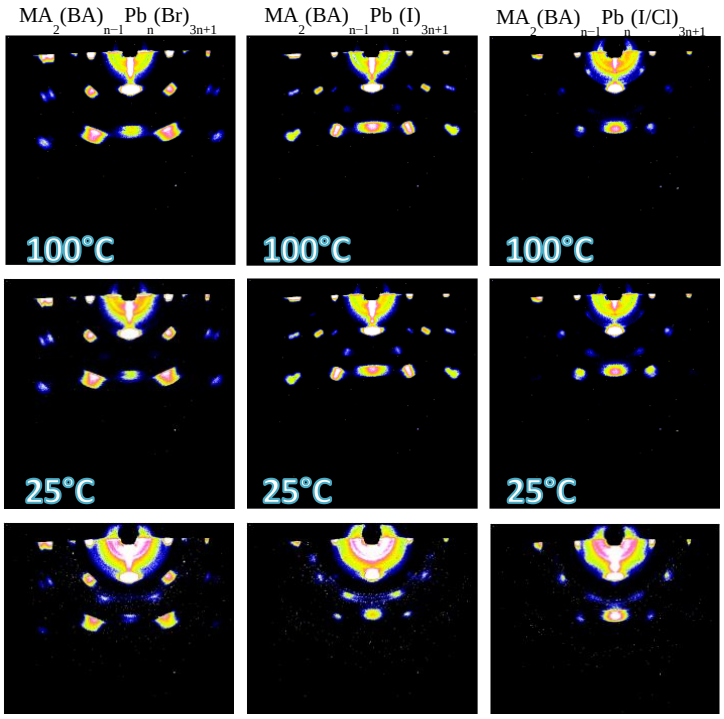

Figure 1. 2D scattering patterns of 2D perovskites upon halide group substitution and versus temperature indicating the structural changes (unpublished data).

Figure 1 illustrates examples of the 2D scattering patterns of three different samples with different halide groups (Br, I and I/Cl) at fixed incidence angle and at different temperatures. As can be seen in the initial analysis, the structure changes upon halide substitution and temperature variation corroborating with the PL measurements.

We are working on the analysis of the body of the results obtained during this measurement time and the initial analysis is promising. To summarize, not only the scientific results obtained made this time extremely fruitful but also, I benefited from becoming familiar with the setup and measurement technique as well as the data analysis.