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:** Tracking In-Situ Assembly of CsPbBr3 Nanocrystal Superlattices by Time-Resolved SAXS/WAXS	**Experiment number:** **SC-5243**
Beamline: ID02	**Date of experiment:** from: 22 Apr 2022 to: 25 Apr 2022	**Date of report:** 14 June 2022 *Received at ESRF:*
Shifts: 9	**Local contact(s):** BOESECKE Peter	

Names and affiliations of applicants (* indicates experimentalists):

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Report: Lead halide perovskite nanocrystals (NCs) exhibit bright, stable, and spectrally narrow color tunable fluorescence properties which makes them interesting for application in high performance photonic devices. The self-assembly of colloids into larger periodic structures upon controlled solvent evaporation is the most common way to produce highly ordered superlattices.

Because the self-assembly of different NCs is influenced by multiple assembly conditions, various self-assembled structures can be obtained. In that regard, it is important to understand the assembly mechanism in real time in order to manufacture targeted superlattices. Synchrotron *in situ* small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) are the techniques of choice for studying of the time-resolved assembly of NCs into superlattices with subsecond temporal and micrometer spatial resolution [1-3].

During the allocated beamtime, we tracked the *in situ* transitions from the colloidal suspension to the self-assembled superlattice state using a combination of SAXS and WAXS. A dedicated sample environment [4] was used to obtain the controlled assembly conditions, where the NCs, upon solvent evaporation, self-organized into ordered NC solids along the X-ray transparent silicon nitride membranes. In a single experiment, approximately 25 µl of the colloidal suspension were evaporated in a solvent vapor saturated atmosphere so that the evaporation rate for the solvent (heptane or toluene) was as low as 0.25 – 0.3 µl/min. This slow evaporation at

the controlled experimental conditions allowed for monitoring of the slightest changes in the superlattice states.
The experimental parameters of the beamline were as follows. The energy of the incident X-ray beam was set to 12.23 keV and the beam size was 25 x 25 μm^2. The SAXS data were recorded by the Eiger2 4M detector at the sample-to-detector distance of 1.52 m. Images were collected with exposure times of 0.2 – 0.5 seconds. For the chosen exposure times no beam damage of the sample was observed.
Monodisperse lead halide perovskite NCs were produced at the KU Leuven by a hot-injection method at different sizes in the range of 4-30 nm in diameter and stabilized by oleic acid / oleylamine ligands. We studied the effect of the NC chemical composition ($CsPbCl_3$, $CsPbBr_3$, $CsPbI_3$), size, solvent (heptane and toluene) as well as shape (cubic or hexagonal particles) on the self-assembly outcome during the provided beamtime.
The representative SAXS data revealing a transition from the colloidal suspension into the NC superlattice state – visible by the appearance of Bragg reflections – as a function of evaporation time are shown in Figure 1. Upon formation of the superlattice state, several transitions are evident, which are the subject of the ongoing analysis.

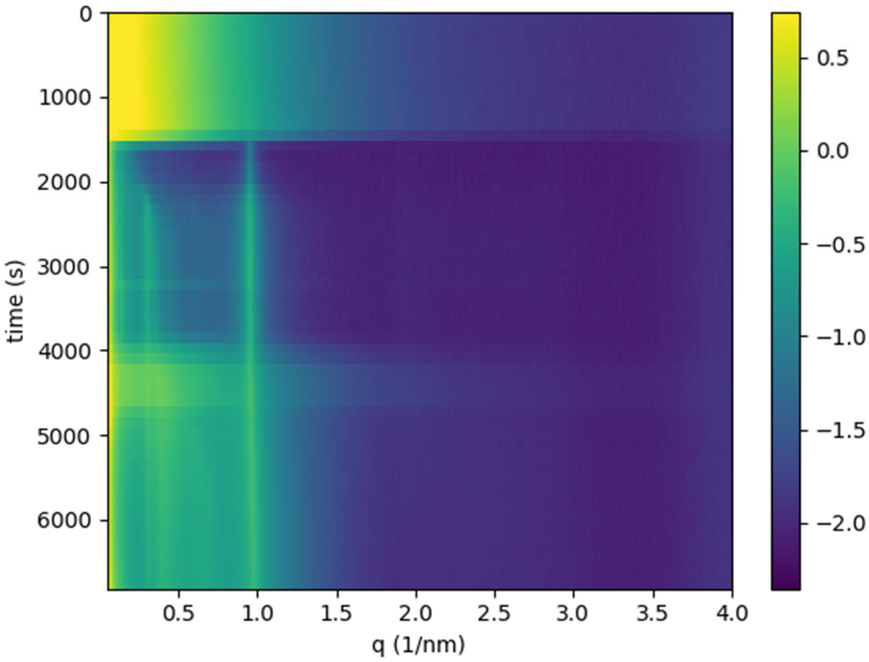

Figure 1. Time-resolved SAXS transitions from cubic $CsPbBr_3$ NC suspension into self-assembled superlattices during controlled solvent evaporation.

[1] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, Small 15, 1900438 (2019)
[2] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, J. Phys. Chem. Lett. 10, 6331–6338 (2019)
[3] I. Lokteva, M. Dartsch, F. Dallari, F. Westermeier, M. Walther, G. Grübel, F. Lehmkühler, Chem. Mater. 33, 6553 (2021)
[4] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, Rev. Sci. Instrum. 90, 036103 (2019)