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:** Blue-emitting confined metal clusters with Precise Numbers of Atoms	**Experiment number:** 26-01 1151
Beamline: DUBBLE A	**Date of experiment:** from: 25/07/2018 to: 28/07/2018	**Date of report:**
Shifts: 9	**Local contact(s):** Dipanjan banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Eric Breynaert*

Dirk Dom

Wauter Wangermez

Sambhu Radhakrishnan

Report:

Transition metal clusters of sub-nanometre size exhibit unique optical(and catalytic)properties depending on their precise number of atoms, structure and confinement. The main goal of this proposal is to reach a unified description of well-defined confined Cu, Pb and Pt metal clusters with precise numbers of atoms based on fluorescence microscopy, TEM, XAS and NMR.

With their well-defined pore structure, zeolites are highly versatile host materials to confine and stabilize molecular metal clusters with different sizes and structures. Cu nanodots exhibit blue fluorescence, and confined element Cu clusters could represent a promising alternative to supported noble metal clusters for many application as phosphor for lighting, as chemical sensors or in catalysis. Solid-state NMR spectroscopy could assist here by providing local chemical information of the clusters of interest. ^{63}Cu is an NMR-active nuclei with spin ½ or 3/2 and a natural abundance high enough to allow NMR studies without isotopic enrichment and at frequencies within the range of commercial broadband probes.

The spectroscopic signature of transition metal atoms in a cluster depends on their location within the cluster. All these signatures are summed upon detection, making it extremely challenging to disentangle the different chemical environments.

In combination with XAS, a new generation of NMR/TEM characterization tools is being developed for this type of clusters which could truly capitalize on the vastly superior spectral detail intrinsically present in NMR. This will help to understand the relation between the structure of the clusters and their luminescent behavior.

Starting from NH_4^+ exchanged zeolites, Cu cations were exchanged onto specific sites of the zeolite framework. Ion-exchanged samples were then thermally activated to induce reduction and cluster formation. After the synthesis of the loaded zeolites, an initial characterisation with UV-VIS absorption ans ESR was made. TEM was performed to visualize the clusters in the pores of the materials. In view of the limited number of shifts allocated (9 shifts) XANES spectra were recorded on all samples to assist in revealing local structure, oxidation and electronic state. Only on selected samples EXAFS spectra were recorded. Cu K-edge XANES and EXAFS spectra were recorded at 110k to prevent beam induced changes to the oxidation state (especially in the case of Cu), and at between 230 an 298K to allow correlation with the temperature dependent NMR results. All samples characterised with EXAFS have been heavily characterised with multinuclear NMR: ^{1}H, ^{27}Al , ^{29}Si and ^{63}Cu.

Combination of these datasets, with Rietveld refinement on the HR-PXRD data will yield a reference dataset that can be used for structure analysis of fully unknown samples. At present all these datasets are being combined in a molecular scale model which will serve to perform theoretical modelling of structure and properties of the clusters. Once finished these models will need more experimental verification. This work is ongoing.