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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.

	Experiment title: Investigating the Electronic Structure of Ionic liquids and Platinum Complexes Confined in Single-Walled Carbon Nanotubes	**Experiment number**: 28-01/1053
Beamline: BM28	**Date of experiment**: from: 28/06/2014 to: 01/07/2014	**Date of report**: 01/09/2014
Shifts: 9	**Local contact(s)**: Paul Thompson	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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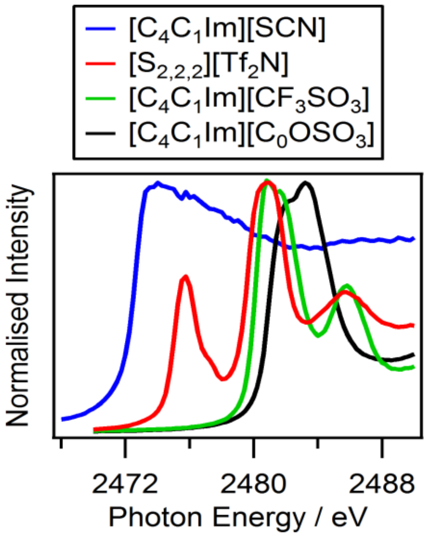
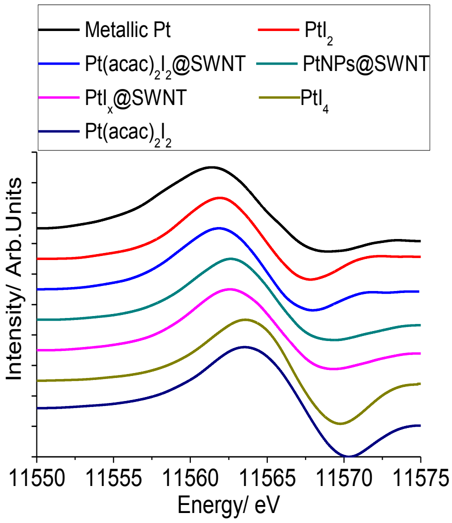
The aim of our experiments for this beamtime was firstly to use NEXAFS spectroscopy to investigate the electronic structure of a group of neat ionic liquids (salts composed entirely of mobile cations and anions) containing sulfur and chloride. Knowledge of the electron distribution in ionic liquids is key to understanding the link between ion composition and macromolecular properties such as viscosity. The second aim was to investigate the electron density distribution of a series of Pt compounds confined in single-walled carbon nanotubes(SWNTs) using NEXAFS spectroscopy. SWNTs can be used as templates for the synthesis of a range of nanostructures and can increase reaction rates for catalysts confined within them. Therefore knowledge of how confinement affects the electronic structure of species is important for designing new catalysts and tuning the properties of nanostructures synthesised in SWNTs. Furthermore ionic liquids confined within nanotubes can act as a model for supercapacitors, therefore the results from these experiments may be used for future investigations into using ionic liquids in supercapacitors.

In total 13 ionic liquid samples were studied using the S 1s edge and 4 samples were studied with the Cl 1s edge. Furthermore 7 samples were studied at the Pt $2p_{3/2}$ edge and 5 at the I $2p_{3/2}$ edge. The sample holder used (Figure 1) contained multiple sample loading slots, which enabled the rapid sample transfer required for studying a large number of samples. All experiments were carried out under high vacuum conditions and both fluorescence and drain current were measured. A strong fluorescence signal was observed for all samples and as a result clearly defined edges were obtained.

Figure 1. The sample holder used in these experiments





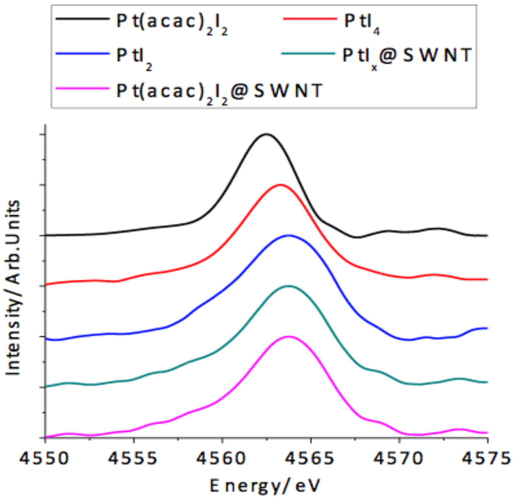


Figure 2. Sulfur fluorescence intensity *vs.* $h\nu$ for the S 1s edge for four sulfur-containing ionic liquids.

Figure 3. Platinum first derivitive fluorescence intensity *vs.* $h\nu$ for the Pt $2p_{3/2}$ edge

Figure 4. Iodine first derivitive fluorescence intensity *vs.* $h\nu$ for the I $2p_{3/2}$ edge.

The edge energies for both S 1s and Cl 1s were found to vary between different ionic liquids (Figure 2). Higher edge energies can be interpreted as lower electron density on the element probed (Cl and S in this case). Therefore these results provide information on the charge distribution in the ionic liquids studied and spectra of neat ionic liquids will also be useful for further investigations.

For the Pt containing species a wide range of Pt edge energies was observed (Figure 3) while a smaller range is present for the I edge (Figure 4). This was expected due to the lower range of oxidation states possible for Iodine. The results show that confinement in SWNTs causes an increase in electron density (lower edge energy) for the Pt but a decrease for the I (higher edge energy) for the $Pt(acac)_2I_2$. It was also found that that the oxidation state of the Pt atoms within both discrete nanoparticles (PtNPs) and extended PtI_x nanorods (which are formed by halogenation of PtNPs) was very similar. The Pt in these species was found to have an electron density intermediate between PtI_2 and PtI_4 reference samples

The results obtained in these experiments show that it is possible to carry out high-throuhput NEXAFS spectroscopy on BM28 using standard apparatus. These were the first experiments we have carried out using SWNTs and it has been demonstrated that clear spectra can be obtained from confined species. Due to the success of these experiments further work is planned, both studying particles confined in nanotubes and systems containing ionic liquids. Furthermore we currently have two papers being prepared for publication as a result of this work.