EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

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.

ESRF	**Experiment title: Ionic Liquids Confined in Nanotubes as Models for Supercapacitors: Investigating Electronic Interactions**	**Experiment number**: 28-01-1081
Beamline: BM28	**Date of experiment**: from: 28/01/2015 to: 31/01/2015	**Date of report**: 06/09/2016
Shifts: 9	**Local contact(s)**: Paul Thompson	*Received at ESRF:*

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Report:

The first aim of our experiments was to investigate how confinement in nanotubes affects the electronic structure of ionic liquids. Understanding the electronic structure of confined ionic liquids is key for applications such as supercapacitors, supported ionic liquid phase catalysis and lubrication. In particular ionic liquids confined in nanotubes is a good model for in supercapacitors (whereby ions are confined in nanopores). The second aim of our experiments was to investigate the effects of a co-solvent (water) on the electronic structure of ionic liquids. The use of ionic liquid:molecular solvent mixtures is currently hindered by a lack of understanding of how a co-solvent affects the electronic structure of ionic liquids. Water is an especially important co-solvent, due to low cost and its presence as a common contaminant in ionic liquids (which are often highly hygroscopic).

NEXAFS spectra were collected for six ionic liquids at the S 1s edge and one ionic liquid at the Cl 1s edge (spectra were collected for both the neat and confined ionic liquids in all cases). Furthermore spectra for ionic liquid:water mixtures were recorded for three separate ionic liquids (two at the S 1s edge, one at the Cl 1s edge). Samples were deposited on a silicon wafer and mounted onto an 8-slot sample holder, allowing sample changes to be kept to a minimum. NEXAFS spectra were recorded in fluorescence detection mode with the samples under a helium atmosphere.

Confinement of ionic liquids in single-walled nanotubes (SWNTs) led to narrower NEXAFS peaks, compared to neat ionic liquids, resulting from confinement restricting the number of possible ion environments (Figure 1). However, the magnitude of confinement effects varied significantly between different ionic liquids. However, the magnitude of the confinement effect on electronic structure varied between ionic liquids.For example, confinement of $[N_{2210}][TfO]$ led to a shift in edge energy of <0.1 eV, compared to +0.2eV for $[C_2C_0Im][NTf_2]$ (the shift in edge energy is due to peak narrowing). For $[C_4C_1Im][SCN]$ a shoulder appeared below the edge energy for confinement in

SWNTs, but not for the wider grapite nanofibers (GNF). This result indicates the presence of wall-sulfur interactions significantly altering the electronic structure of $[C_4C_1Im][SCN]$ upon confinement (due to the width of GNFs only a small number of sulfur-wall interactions are possible, hence the lack of the pre-edge shoulder).

The effect of water on electronic structure of ionic liquids was found to be strongly dependent on the ionic liquid studied (Figure 2). For $([C_4C_1Im][SCN])_x(H_2O)_{1-x}$ mixtures (x=mole fraction ionic liquid) only a small shift (+0.1 eV) was observed between x=0.0 and x=0.99. The small shift in edge energy for $[C_4C_1Im][SCN]$ upon addition of water suggests the the sulufr does not form strong interactions with water molecules in $([C_4C_1Im][SCN])_x(H_2O)_{1-x}$ mixtures. A peak narrowing was observed for $[C_4C_0Im][HSO_4]$ (edge energy shifted +0.2 eV from x=0.0 and x=0.99) upon addition of water, likely as a result of anion-water hydrogen bond formation lowering the number of possible environments for sulfur.. In contrast, a significant increase in edge energy (up to +0.7 eV) was observed upon addition of water to $[C_8C_1Im]$ Cl. Addition of water to $[C_8C_1Im]$ Cl led to a step-change in electronic structure between $x=0.4$ (1.5 Cl per water molecule) and $x=0.5$ (1 Cl^- per water molecule); increasingly water concentration past 0.5 mole fraction made no further difference to the edge energy. The step change indicates that a strong specific (e.g hydrogen bonding) interaction between Cl^- and water is responsible for the shift in energy (which is why the shift occurs when there is one H_2O per Cl^-).

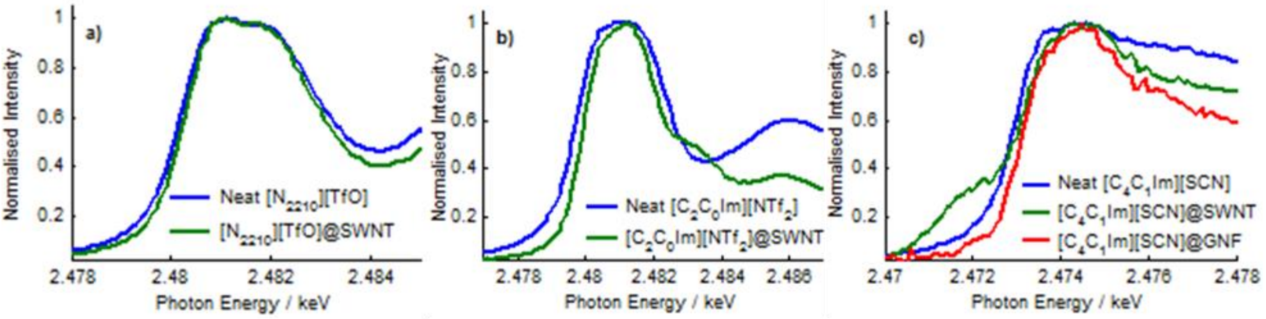

Figure 1. S 1s NEXAFS spectra of neat and confined (@SWNT and @GNF) ionic liquids, a) $[N_{2210}][TfO]$, b) $[C_2C_0Im][NTf_2]$ and c) $[C_4C_1Im][SCN]$.

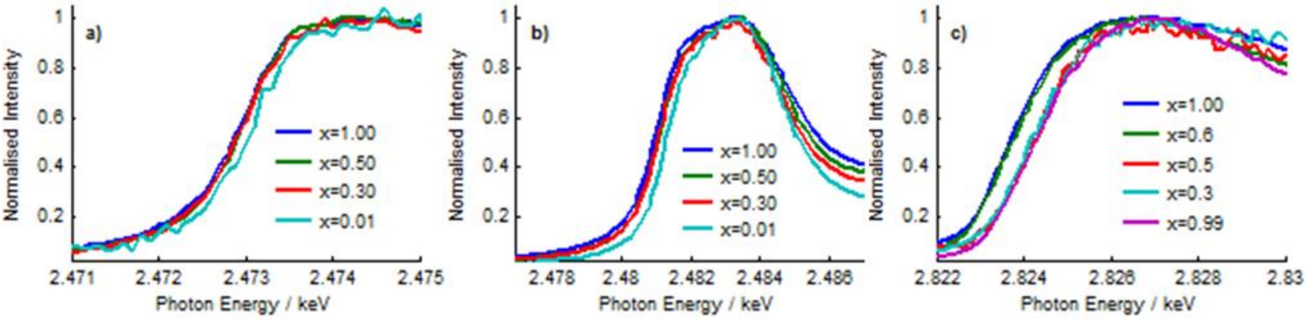

Figure 2. NEXAFS spectra of $(\text{Ionic Liquid})_x(H_2O)_{1-x}$ mixtures (x= mole fraction ionic liquid). a) S1s edge for $([C_4C_1Im][SCN])_x(H_2O)_{x-1}$, b) S1s edge for $([C_4C_0Im][HSO_4])_x(H_2O)_{x-1}$ and c) Cl 1s edge for $([C_8C_1Im]\ Cl)_x(H_2O)_{x-1}$.