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

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: Reactivation and Suppression of Deactivation of An Immobilised Cp*IrCl₂ Catalyst for Robust Industrial Transfer Hydrogenation	**Experiment number**: 28-01-1192
Beamline: BM28/ XMaS	**Date of experiment**: from: 01 July 2017 to: 04 July 2017	**Date of report**:
Shifts: 9	**Local contact(s)**: Paul Thompson	*Received at ESRF:*

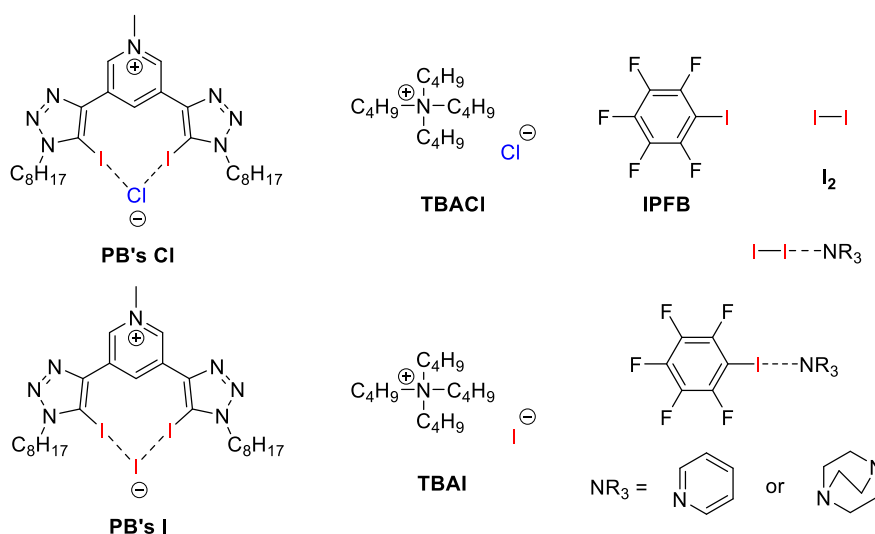**Names and affiliations of applicants** (* indicates experimentalists):

Bao N. Nguyen*, University of Leeds

Rachel Nicholls, University of Leeds
Joseph Sheppard, University of Leeds
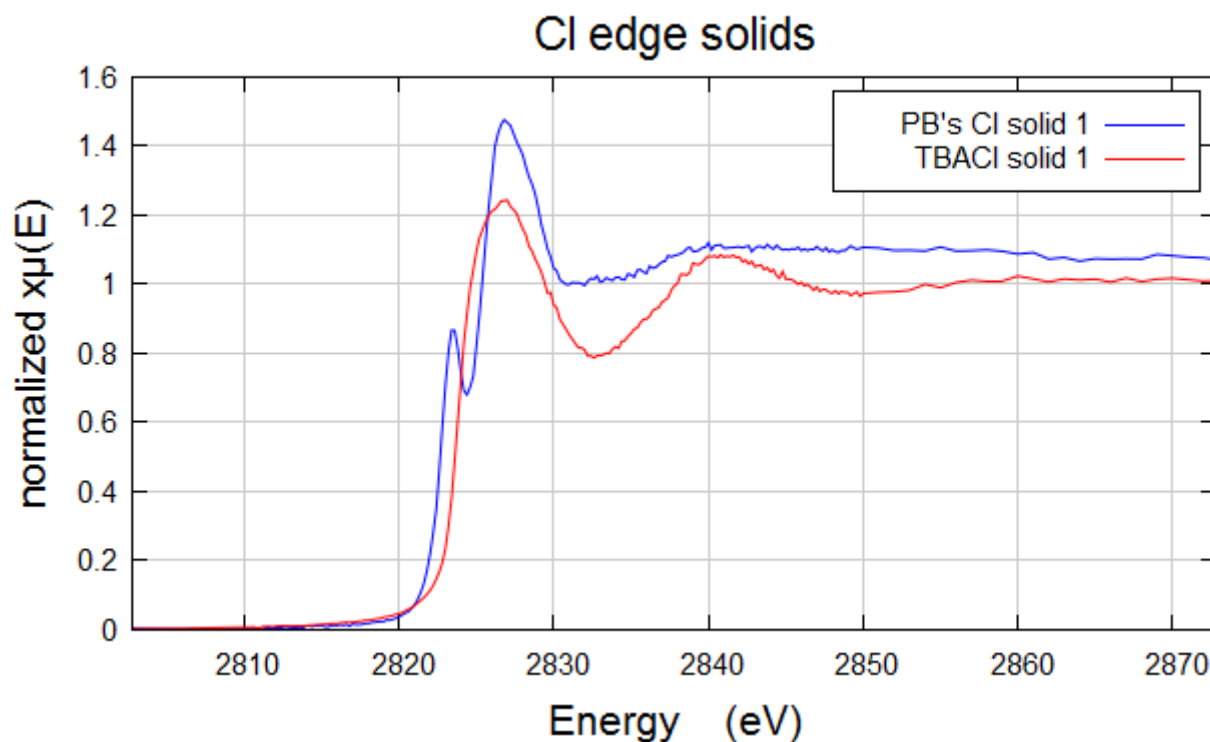Blanca Ivonne Vergaras, University of Leeds

Report: Cl K-edge and I L3-edge XANES spectra of a series of solid and solution samples were measured using the low energy XAS facilities at BM28. The data were were analysed using the Athena software of the Demeter package. Raw data from the beamline was extracted and combined for each scan using a Python script.
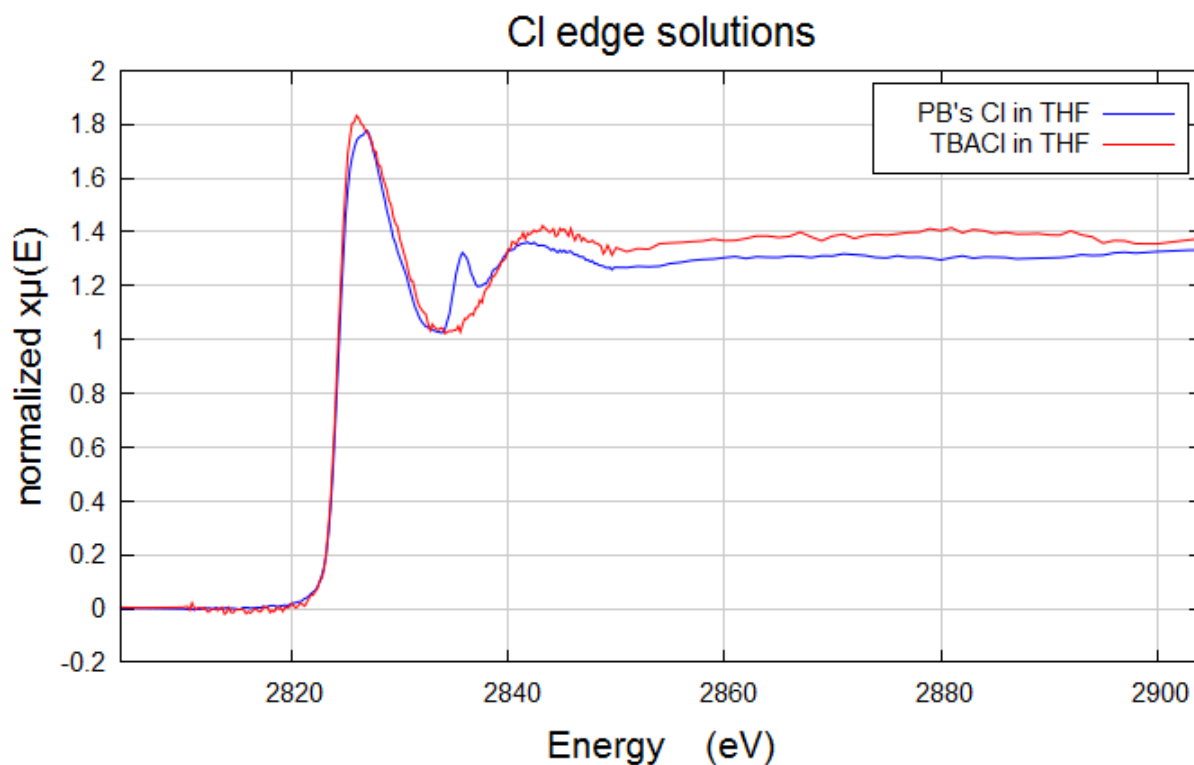
The samples which were measured are shown below:

Solid samples were mounted on carbon tape and solution samples were prepared in Tol/MeOH (1:1), THF and cyclohexane with concentration in the range of 2.5-25 mM (depending on solubility with typical conc. 15-20 mM).

Cl K-edge spectra of solid samples showed a clear difference between halogen bonded Cl (PB's Cl) and free chloride (TBACl). Halogen bonding resulted in a pre-edge feature, high whiteline and a small shift in the edge position to higher energy (~ 2 eV).
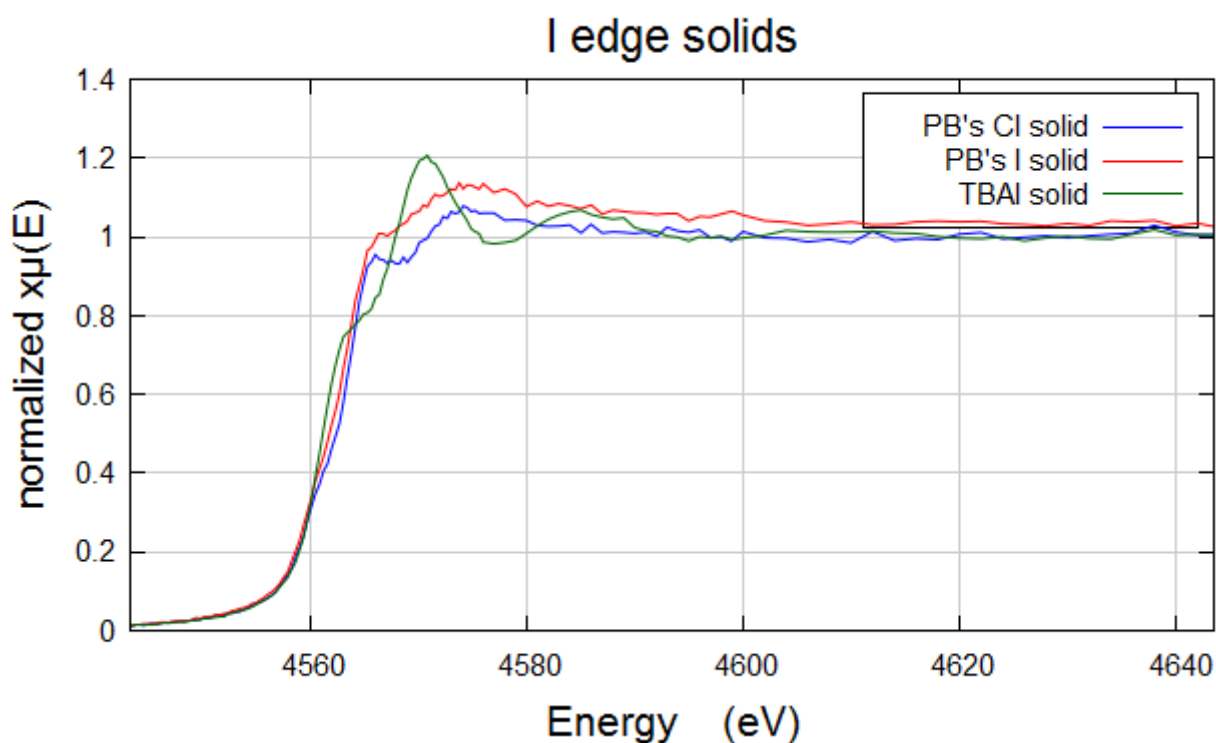

These spectra changed significantly in solution using THF. The pre-edge feature in PB's Cl sample (9 mg in 5 mL) disappeared and was replaced by a new peak after the whiteline. Otherwise, the two spectra are nearly identical with the same edge position. This detectable difference will allow reliable detection of halogen bonds to chloride anion in THF solutions.
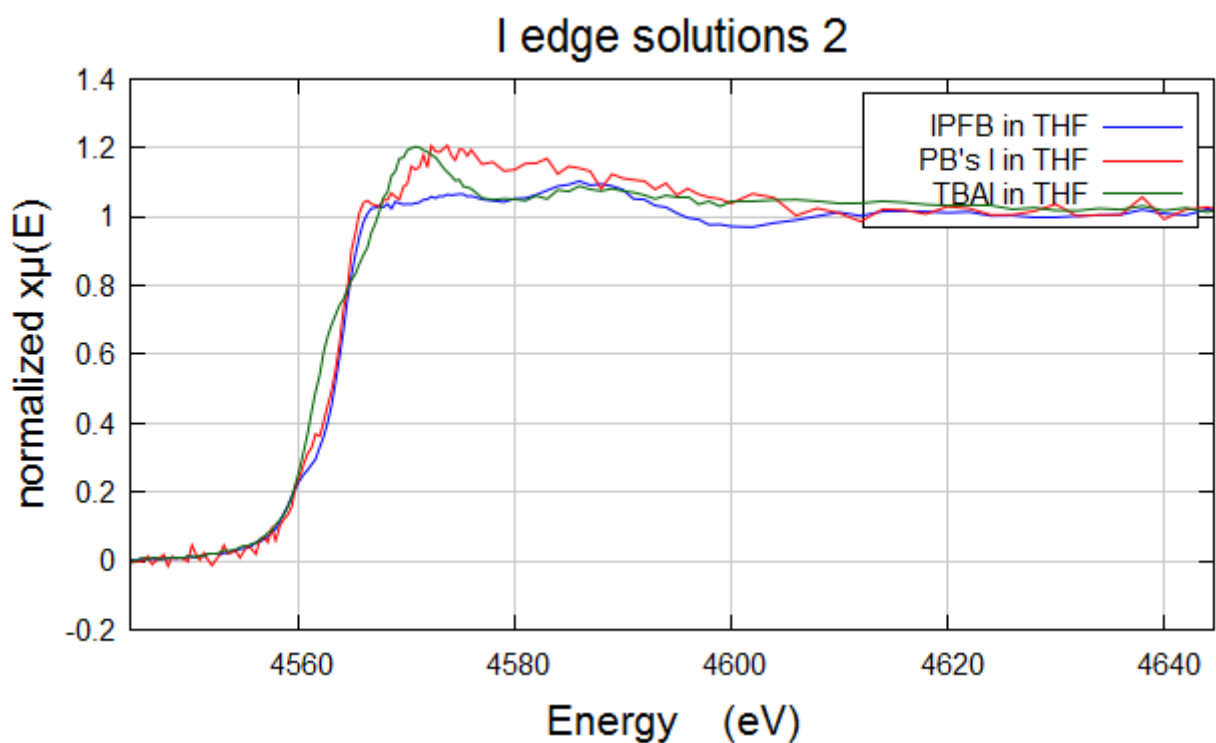

Similar measurements were performed at I L_3-edge. PB's I sample has 2 different I environment (donor and acceptor) while PB's Cl sample has only one (acceptor). Their spectra are boardly similar with little to no
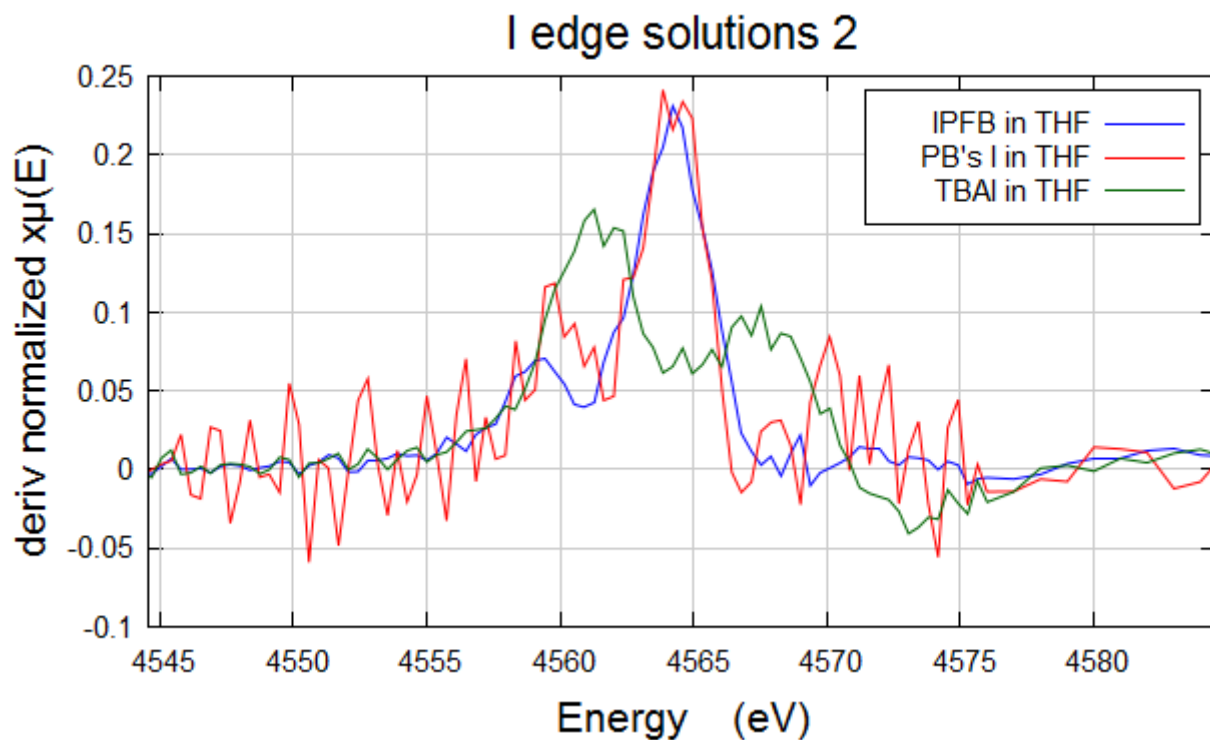
whiteline feature, in contrast with the spectrum of TBAI. The differences between halogen bonded iodide and non-halogen-bonded iodide spectra in solid state are thus established.
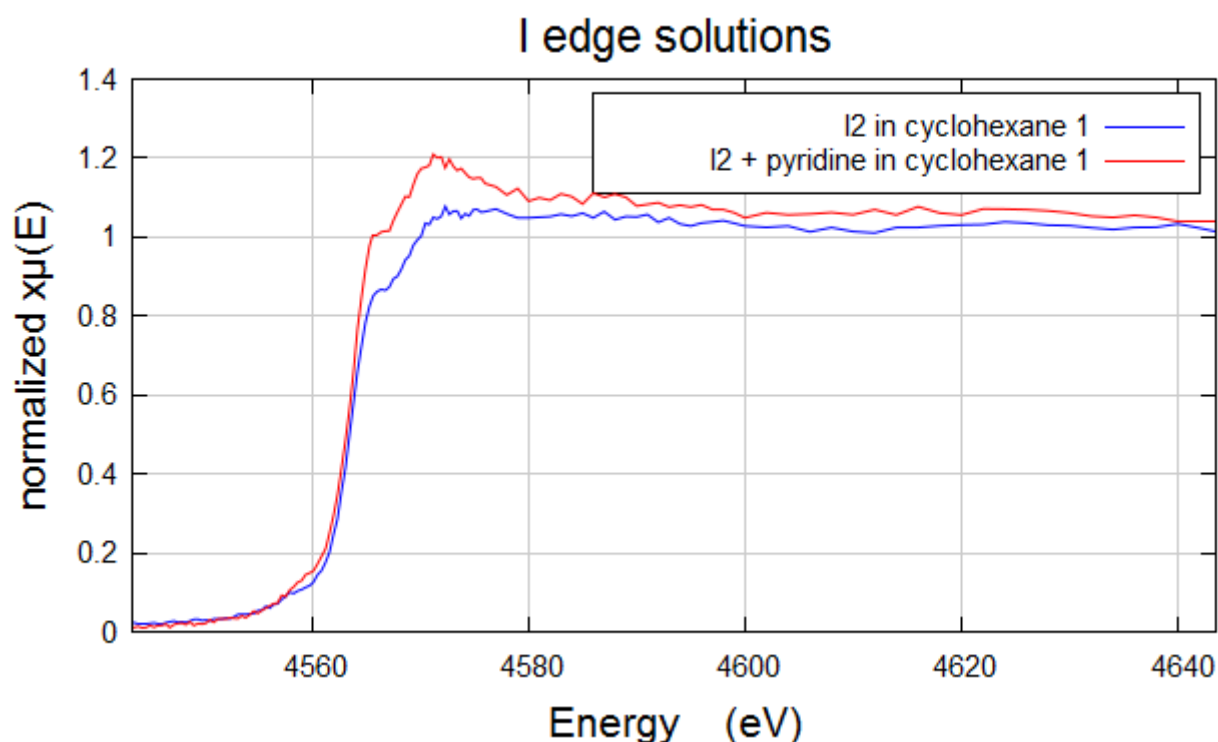

In solution, the spectra of TBAI and PB's I did not change significantly other an increased boardening of the peaks. The XANES spectrum of IPFB showed no whiteline.
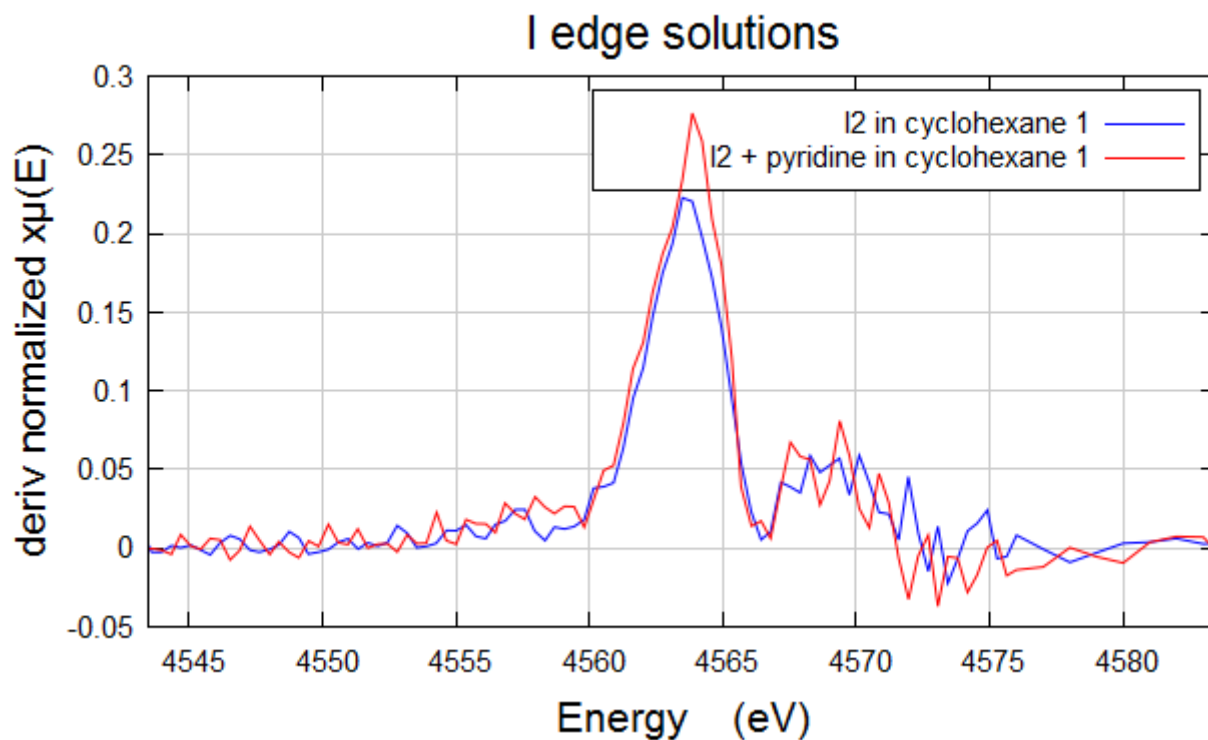

The derivative plot of the edge region showed a clearer picture: the spectra of PB's I corresponds to a combination of aryl iodide (e.g. IPFB) and iodide (e.g. TBAI) signal.

I edge solutions 2

Thus, it is difficult to determine whether the halogen bond I…I exist in solution using I L_3-edge XANES. To verify this, spectra of I_2 and I_2+pyridine in cyclohexane were collected. The halogen bond between I_2 and pyridine in cyclohexane has been established previously using UV/Vis measurements, and comparison of these spectra will confirm if the intereaction is detectable by I L_3-edge XANES.

I edge solutions

I edge solutions

Little difference was detected between the two spectra, proving that I L3-edge XANES is unsuitable for detection of halogen bonds with iodide anions in solution.

Conclusions: While Cl K-edge XANES proved effective in detecting halogen bonding to chloride anion, I L_3-edge XANES proved ineffective. Characterisation of halogen bonds with iodide will likely require measurements at I K-edge (33.18 keV). These will also benefit from the availability of EXAFS, which will provide vital information on halogen bond length in solution.