	IN SITU ULTRAFAST CRYSTALLOGRAPHY FOR THE STUDY OF THE EXCITED STATE OF DYES FOR PHOTOVOLTAIC SOLAR CELLS	**Exp. number**: CH-3181
Beamline:	**Date of experiment**: from: 26/02/2011 to: 01/03/2011	**Date of report**: 23/03/2011
Shifts: 9	**Local contact(s)**: Dr. Michael Wulff	*Received at ESRF:*

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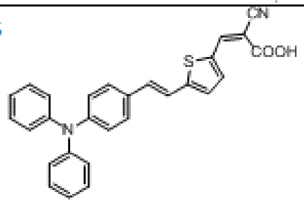
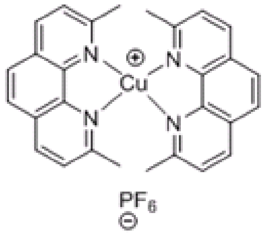
Introduction and list of measured samples

This proposal aimed at investigating one of the key step of dye sensitized solar cells (DSSC, also known as "Graetzel cells")[1] functioning, i.e. the structure of the excited state of the dye. Excited state of dyes used in DSSC have been studied with ultrafast spectroscopy, electrochemistry methods and by theoretical calculations[2] but not at the molecular level by ultrafast crystallography. In this experiment, the structures of dyes after illumination with a pulsed laser were studied with a time resolution at the picoseconds scale. 4 samples were measured: two typical DSSC dyes (N719 and D5) and two reference molecules, the first being a fast relaxing system inducing only solvent heating (DR1), the latter being an analogue of copper phenantroline molecule (CuPhen), widely studied by solid-state ultrafast spectroscopy.[3,4]

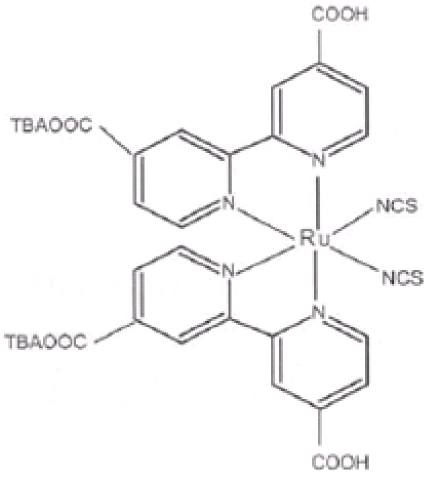
D5



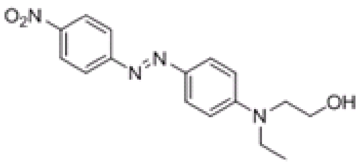
CuPhen

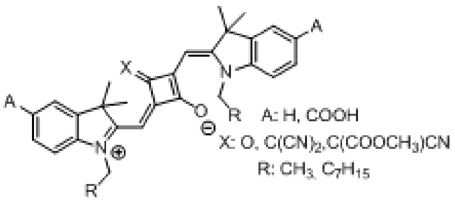


N719



DR1



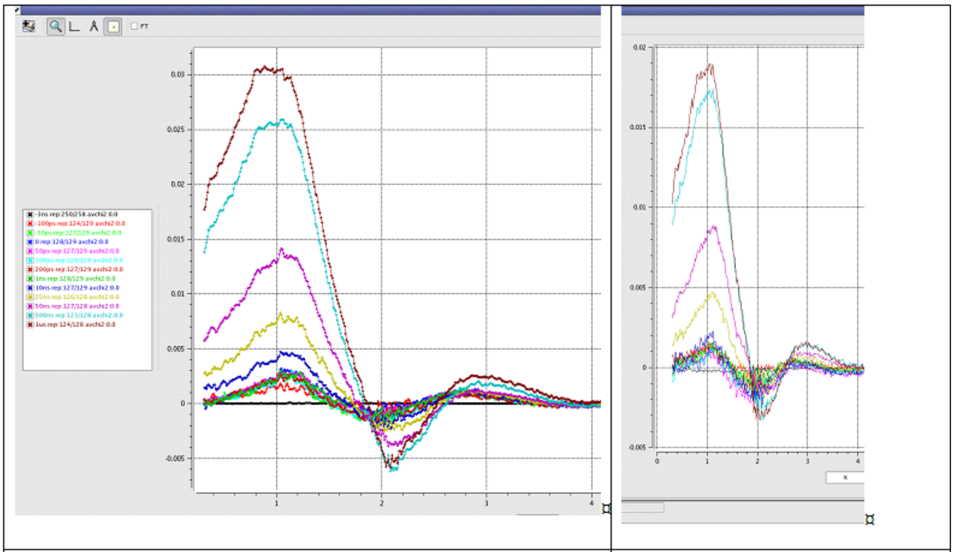


General structure of the Squaraine dyes

In situ crystallography has been carried out on liquid samples instead of solid ones, exploiting the possibility of flushing continuosly the solution under the laser beam, thus improving the overall stability of the sample. The four selected samples allowed maintaining fixed the laser wavelenght, saving time during the beamline setup. Conversely squaraines,[5] present in CH-3181 proposal, were not measured because they adsorb in another spectral region (around 600 nm) and there was no time of changing laser emission wavelength during EXP CH-3181.

Obtained results

Ultrafast solution X-ray scattering data were collected in the 100 ps-1μs time scale on D5, DR1, N719 and CuPhen. The preliminary analysis resulted encouraging and the main results are: i) one fast relaxing compound (DR1) was collected successfully and will be used as a reference materials for data analysis; ii) two DSSC dyes (N719 and D5), showing different time scale in the life time of the excited state, were successfully recorded; iii) a compound (CuPhen) belonging to a family deeply studied by solid-state ultrafast crystallography was analyzed to compare the behaviour in solution (this experiment) and in the solid-state.[3]



N719 dye with life time in the ns range (blu curve is 10 ns)

Ref. dye with very short life time

Figure 2

Significant signals were collected in all cases, promising successful structural characterization of the excited states in the different dyes.

Figure 2 shows the difference between the reference dye with short lifetime, i.e. DR1 (right), where only the signal of the heat transfer from excited molecules to the liquid is measured, and N719 in the ns time scale (violet yellow blue curves, left picture), differences that can be due to structural change in the excited state.

The second dye studied (D5) has relaxation times closed tothe limit of ID9 beamline (actually results very similar, but not identical to DR1), where a different signal from the simple transfer of energy from the molecule to the solvent can be still detected (blue line in figure 3a). In figure 3b the data concerning Cuphen are showed. Large signals can be detected and will be interpreted and compared to the results by solid-state ultrafast crystallography[3] to understand the effect of the surrounding environment (the solvent) of the excited structure.

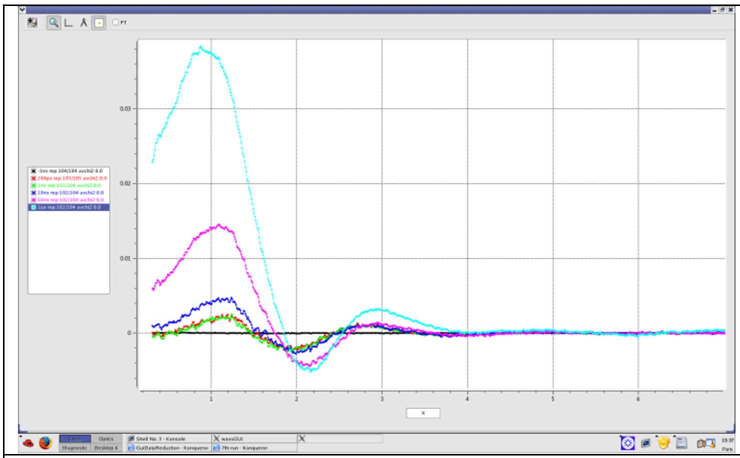
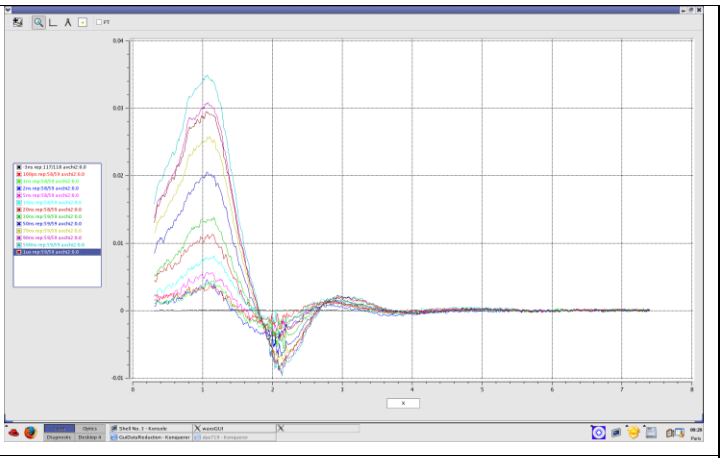


Figure 3a D5



b CuPhen

Conclusions and further developments

The preliminary analysis of collected data is encouraging and a publication is in preparation. Indeed a new experiment with a more monochromatic X-ray beam to collect data with higher resolution, especially in the faster time scales, is needed to collect a sufficient number of data point for an exhaustive analysis. Moreover lasers at different wavelengths will be useful to investigate NIR absorbers (i.e.: squaraine dyes). A proposal for the continuation of experiment CH-3181 was therefore presented in March 2011 deadline.

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[1] M. Graetzel, *Acc. Chem. Res.*, 2009, 42(11), 1788.

[2] M.K. Nazeeruddin, G. Viscardi, M Graetzel & al., *J. Am. Chem. Soc.* 2005, 127, 16835.

[3] P. Coppens et al. J. Am. Chem. Soc. 2004, 126, 5980-5981

[4] J.V. Lockard et al., *J. Phys. Chem. B* 2010, *114*, 14521–14527

[5] J.J. McEwen & al., *Chem. Commun.*, 2009, 6339.