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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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:** Structural Properties of Excimer Formation in Perylene Crystals	**Experiment number:** CH-2404
Beamline: ID09B	**Date of experiment:** from: 27/04/2007 to: 04/05/2007	**Date of report:** Friday, August 24, 2007
Shifts:	**Local contact(s):** Marco Cammarata	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Purpose/Results Expected

The purpose of the beamtime was to investigate the structural kinetics of the exciplex formed between tetrakis-μ-pyrophosphito-diplatinate(II) (PtPOP)and Thallium(I).

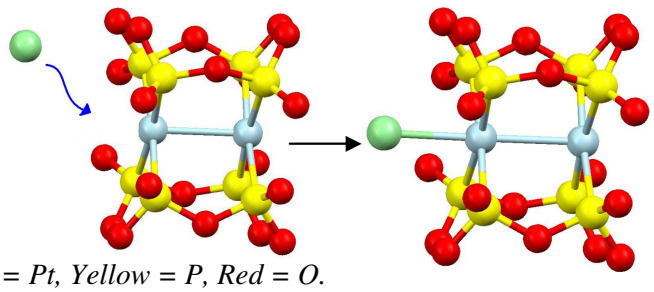

Figure 1. *The excited state complex (exciplex) formation between PtPOP and Thallium(I).Steel green = Tl, Steel Grey = Pt, Yellow = P, Red = O.*

The components of an exciplex (excited state complex) remain separated in the ground state, and will only form a complex as long as one of the components is in an electronically excited state. The Tl-PtPOP exciplex constitutes an ideal system for the study of reversible association reactions, since the exciplex (3 heavy nuclei in close proximity) scatter X-rays more efficiently than the separated ground state components (2+1 nuclei far apart).

From our study we expected to obtain knowledge of the exciplex structure (e.g. Tl-Pt distance) as well as the formation kinetics of the system.

Method

The pump probe setup for diffraction of liquids at beamline ID09B was used. An array of three rotating chopper wheels is capable of isolating a single X-ray pulse from the synchrotron, through absorption of

excess pulses. The sample can be excited by a femtosecond laser pulse prior to arrival of the X-ray pulse, and in this way, diffraction images of excited state systems can be recorded.

A solution of Thallium(I)-sulphate and PtPOP was made in argon-purged water, and brought into circulation of the liquid jet. The resulting liquid sheet (300 μ thickness) was subsequently pumped by a laser pulse (λ = 390 nm) stretched to 2 ps and probed by the X-ray beam at various time delays.

Results:

Difference curves are constructed by subtraction of radially integrated images. The curves shown below are from an experiment with a PtPOP concentration of 12 mM and 0.6 equivalents of Thallium(I) for every PtPOP molecule. At very short delays (100 ps and 200 ps) only the difference signal of excited state PtPOP is seen, but at longer delays, the signal from the diffusion controlled exciplex formation can be seen as a drastic increase in the difference signal at low q. This behaviour is in extremely good agreement with a diffusion controlled association reaction

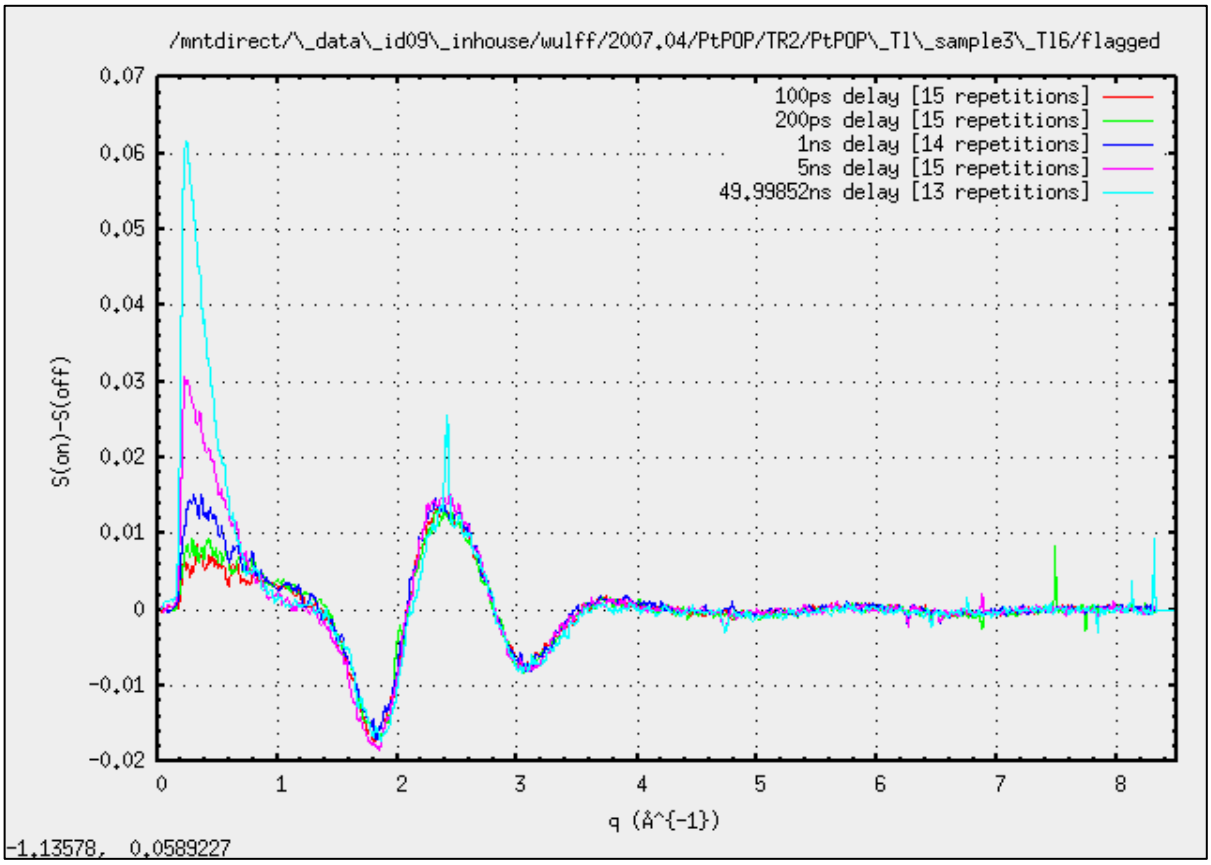

Figure 2: *Excerpt from the ID09B log with difference scattering curves of the Tl-PtPOP exciplex. The diffusion controlled formation of the exciplex manifests itself in the strong grow-in signal at q<1. The occasional spikes (e.g. at q = 2.4 for the 50 ns delay) is caused by radiative decay in the detector material. Corrections are applied for this phenomenon during the data analysis.The measured difference scattering is zero behind the beamstop (0< q < 0.2 $Å^{-1}$)*

Analysis

Shown below are preliminary fits to the data recorded at 5 ns and 50 ns from the solution with [PtPOP] = 12.0 mM and [Tl(I)] = 7.2 mM.

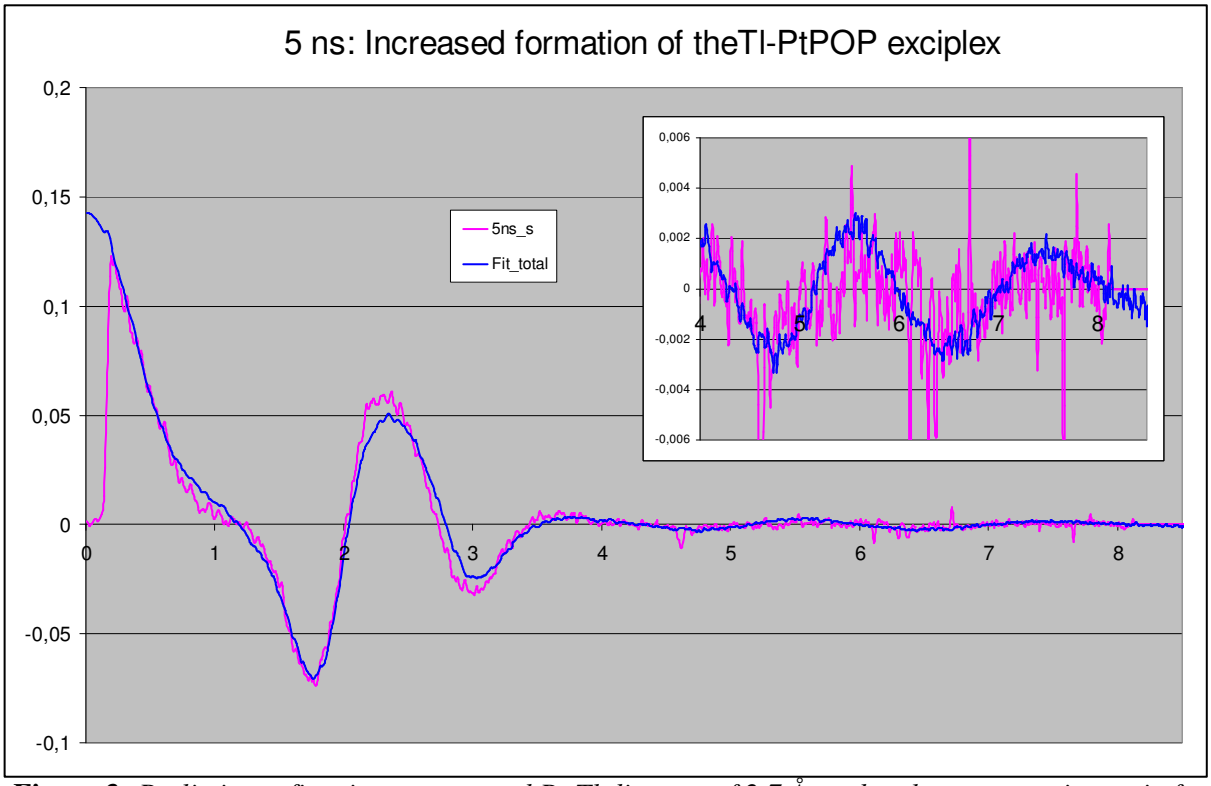

Figure 3: *Preliminary fit using an assumed Pt-Tl distance of 2.7 Å, and a photo conversion ratio for PtPOP of 4.2 %. Out of the excited state PtPOP units, 25 % have formed exciplexes with Tl(I)*

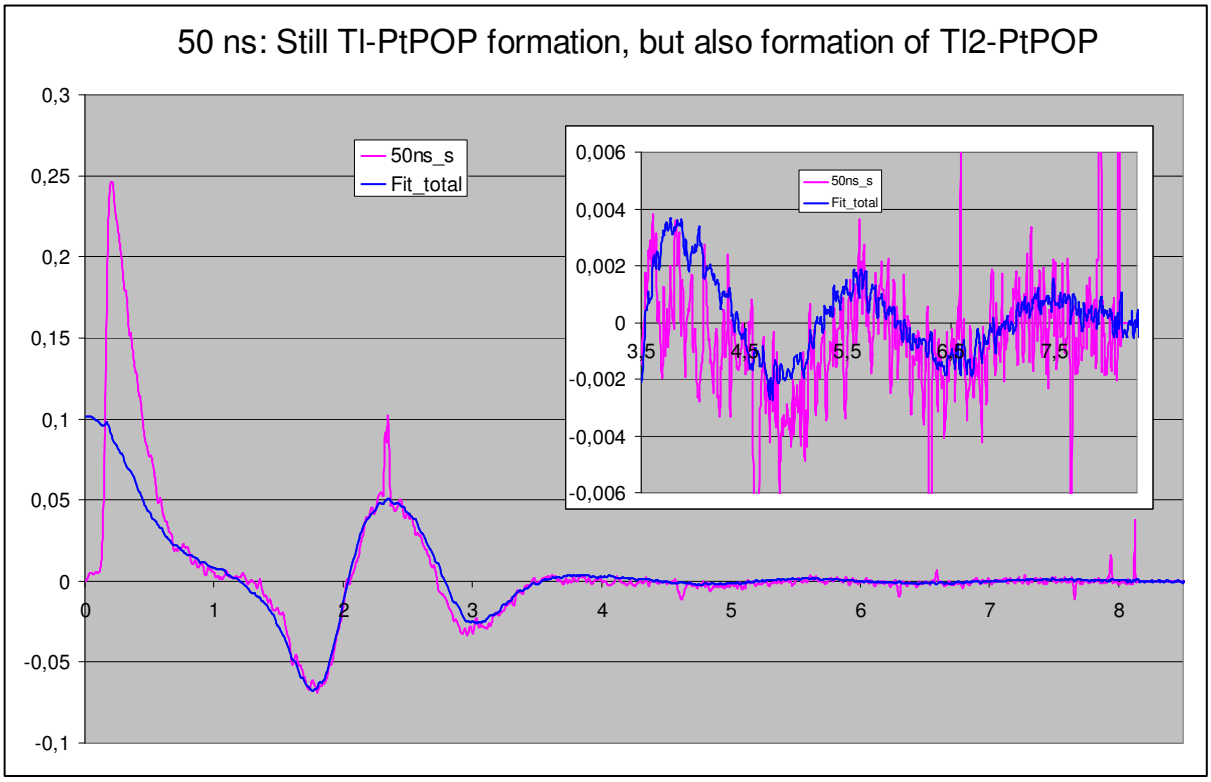

Figure 4: *Preliminary fit assuming a Pt-Tl distance of 2.7 Å. Excitation rate for PtPOP is 2.5 % out of which 30 % form exciplexes with Tl(I). So far, our model only partly can account for the peak at q<1. We assume this to be due to the formation of a* ***second*** *exciplex with* ***two*** *Tl(I)-ions bonded to PtPOP. The spikes (e.g. at q = 2.4) are artefacts as explained in fig. 2.*

At 50 ns our present model can only partly account for the observed difference signal. But we see an increasingly stronger signal at low q, which we (tentatively) attribute to the formation of a second exciplex where PtPOP forms an excited state complex with *two* Tl(I) ions as shown in fig. 5:

We are currently developing a model to account for the observed kinetic behaviour a well as a refinement of the exciplex structure. However, this is compromised by the relatively high level of noise in the data due to the difficulties experienced during the beamtime as explained in the following section on the 7/8+1 mode (see below).

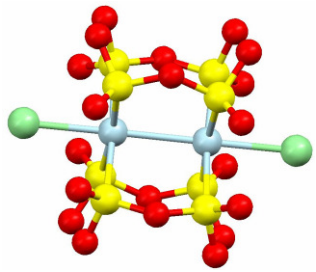

Figure 5. *The tetra-nuclear Tl-PtPOP-Tl exciplex, colourcoding as in Fig. 1.*

Experience with the 7/8+1 mode

Experiment CH-2404 was the first time-resolved experiment to run in the new 7/8+1 mode at ID09B at the ESRF. In this new mode, a 2 mA single pulse is placed in the centre of a 352 ns gap in the 200 mA bunch train which fills out the remaining 7/8 of the storage ring. Compared to e.g. the 16-bunch mode, the heatload on the pulse exclusion chopper wheels is significantly higher than what has previously been experienced. As a result of this, the NdFeB-magnets in the pickup system of the first heatload chopper (HC) was heated above the Curie Temperature and lost their magnetization. The HC thus could not be used, and had to be removed. In order to lower the heatload on the remaining beamline components, the beamsize was reduced by a factor of 4. Despite this reduced flux, we found it necessary to regularly stop the experiment in order to prevent overheating of the single-pulse triangular chopper.

Compared to the 16-bunch mode, the shorter pulse length in the 7/8+1 mode provides a better temporal resolution. However, the current of the single bunch in the 7/8+1 mode is only 1.04 mA on average compared to 5.5 mA in 16-bunch mode. This furthermore reduced the X-ray flux by a factor of 4. With a lifetime of 10 hours, the single bunch is rapidly decaying considering refill is only every 12 hours, so a single-bunch top-up would be very welcome, at least every 6 hours, maybe even every 3 or 4 hours.

All in all, the new 7/8+1 bunch mode proved useful for time-resolved experiments, albeit the HC problems and the rapid bunch decay is estimated to have caused an intensity decrease in the order of a factor of 16 compared to the flux we have previously used in 16-bunch mode. However, due to the enthusiasm and hard work of the beamline staff, we still managed to get very good results, as can be seen in figures 2, 3 and 4.

Conclusion and perspectives

We observed the first ever association process on ID09B. Despite the beamline working far from its optimum, the experiment proved the fundamental idea of monitoring the formation of an excited state complex. The difference signals are very strong, and the signature of the exciplex is clearly seen as a grow-in in the low-q region. An exciplex structure with a Tl-PtPOP distance of 2.7 Å was capable of producing decent fits to the results observed. However, a more accurate structural refinement is compromised by the relatively high level of noise in the measurements, caused by the less than optimum flux available during the experiment

We are currently analyzing the collected data with the aim of improving the conditions for a detailed structural study of the Tl-PtPOP exciplex. We thus hope to be able to perform a data collection at optimum concentrations of PtPOP and Tl, at the delay where the Tl-PtPOP exciplex is present in the highest concentrations. Further analysis is expected to yield conditions for a structural study of the second Tl-PtPOP-Tl exciplex, as well as a study of the dynamics of this system.