ESRF	**Experiment title: Ultrafast X-ray investigation of the Photoinduced spin transition.**	**Experiment number:** CH-2825
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Shifts: 12	**Local contact(s):** Laurent GUERIN	*Received at ESRF:*

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Report: The possibility of tuning by light the macroscopic state of some molecular crystals is a fascinating feature which may lead to the photo-control of physical properties of materials: optical, magnetic, conduction… This involves changes in the molecular identity, such as charge or spin between degenerate or quasi-degenerate ground states. In some systems, intermolecular interactions are strong enough to generate photo-induced cooperative phenomena leading to macroscopic phase transitions (new electronic and structural order with new physical properties). These are very different in nature from independent photochemical processes.

Spin transition is the prototype of molecular bistability in the solid state. This type of transition can be induced by light, and present a high efficiency in a variety of metal-based molecular complexes [1]. In such systems, Fe ions in a nearly octahedral field possess two possible spin states: high spin (HS) or low spin (LS). We focussed on the [(TPA)Fe(TCC)]PF_6 ferric catecholate spin crossover system which presents the advantage of a short relaxation time (~ 1 ms) [2] well adapted to the repetition rate of the laser pump and the RX chopper (~1kHz) at ID09B. Prerequisite ultra-fast optical pump-probe experiments had been performed in Rennes.

(a) 

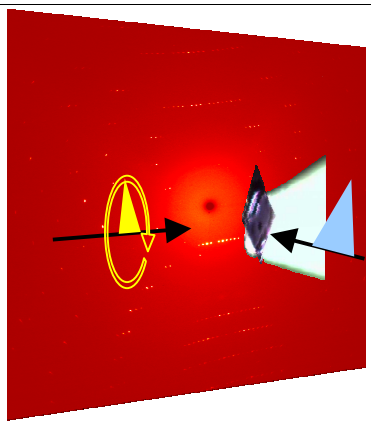
(b) 

Fig.1 (a) Single crystal of the orthorhombic polymorph of [(TPA)Fe(TCC)]PF_6 glued on the back of the (a,c) plane. The crystal is less than 5 µm thick; (b) Schematic representation of the experimental set-up: laser pulse in yellow and X-ray pulse in blue.

The main goals set for CH2825 were the following: firstly, to improve on our previous experiment (CH2599, [3]) by maintaining homogeneity of the excitation during the sample oscillation; and secondly to study the new orthorhombic polymorph of the [(TPA)Fe(TCC)]PF_6. This orthorhombic polymorph [4] grows in a plate form and these crystals were mounted onto a rotating capillary by their back surface, which crystallographically is the *(a,c)* plane (Fig. 1). Thus mounted crystals were oscillated around their **b** axis with X-rays propagating through the crystal parallel to the *(a,c)* plane at any one delay time and any angle of oscillation. The laser field was circular polarised to lift the effect of excitation anisotropy following the oscillation angle. The laser propagation vector was normal to the *(a,c)* plane, and so perpendicular to the X-ray propagation, meaning the effective photoconversion was independent of the crystal oscillation.

As previously, we used 800nm femtosecond pulse to excite the crystal. On the X-ray side we used monochromatic beam at 16keV throughout the experiment. In our previous experiment (CH-2599, [3, 5-6], we evidenced three main steps of the photo-conversion, amongst which the photo-conversion at the molecular level occurring at constant volume. This sequence was also observed in the new orthorhombic crystal. During CH2825, we were able to demonstrate that this first process can also be detected via time evolution of Bragg peaks of which the intensity is sensitive to the molecular spin state change (Fig. 2a). Moreover, we have succeeded in collecting a complete dataset on one single crystal for solving the average structure at 9 different delays, spanning the 3 steps of different time-scales (Fig. 2b). Quality of the collected data allows data refinement with the reliability factor R ≈ 2-4 % [7]. This improvement is due both to the new data collection strategy and the new FRELON detector used.

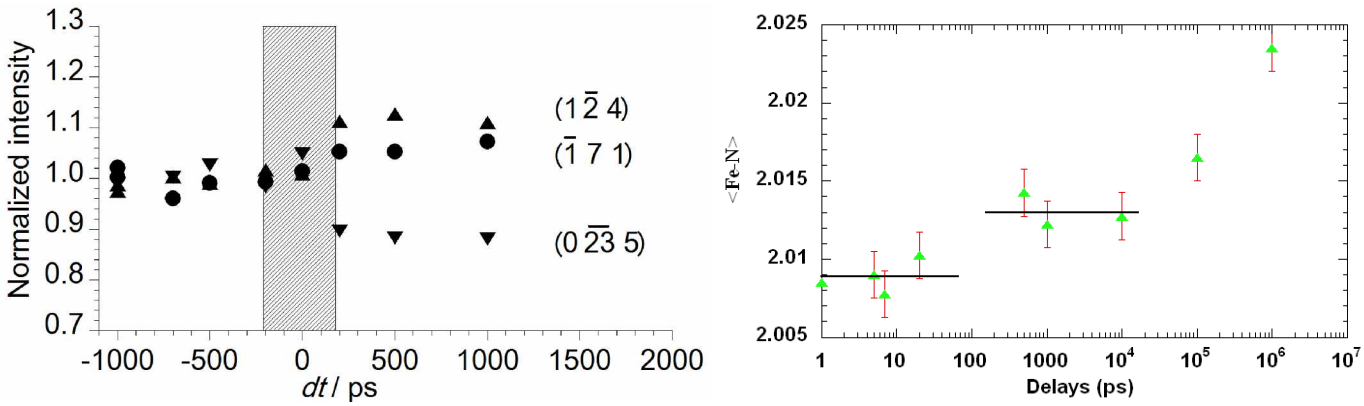


Fig.2 (a) Intensity evolution of selected Bragg peaks as a function of time; (b) Evolution of the average <Fe-N> bond length as a function of time (logarithmic scale)

At longer time scale (100ns to 30 µs), our optimized experimental conditions also allow us to observe the elastic strains induced by the volume expansion (Fig. 3a), revealed now by the shape of the Bragg peaks (Fig. 3b). In particular, we have demonstrated the homogeneous nature of the transient excited state at 10 µs (elongated bonds and expanded volume, but the width of Bragg peaks back to that prior to the excitation).

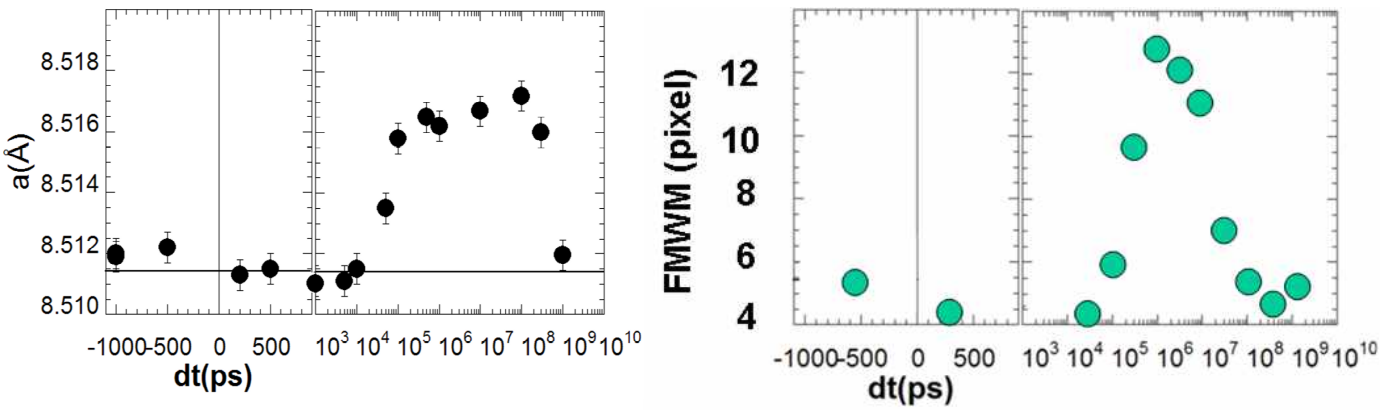


*Fig.3 (a) Time evolution of the unit-cell parameter **a**; (b) Bragg peak deformation in time*

During this experiment, we have significantly improved the experimental conditions in comparison to those used during CH-2599. We are now able to study plate-like crystals with a satisfying homogeneity of the laser excitation. The very high sensitivity allows to observe weak Bragg intensity changes as well as elastic stress.

References

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