



Experiment title: Ultrafast X-ray investigation of the Photoinduced spin transition.

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CH-2398

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Report: The possibility of tuning by light the macroscopic state of some organic 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, the coupling with the lattice degrees of freedom is large 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 conventional independent photochemical processes.

The photoinduced spin transition is a prototype of the molecular multi-stability driven by light, which is present and very efficient in a variety of molecular solids [1]. In such systems, Fe ions in a nearly octahedral field possess two possible spin states: high spin (HS) or low spin (LS). Up to now, it was mainly investigated under continuous laser irradiation at very low temperature where permanent states are reached [1-6]. All the structural analysis we performed for different compounds [2,3,5,6], show strong structural signatures, associated with the change of the spin state. Our experiment at ID09B aimed to investigate the dynamics of such transformation in the time domain. Therefore we check in our laboratory the lifetime of different compound by using our ultra-fast optical pump-probe experiment. Among them, we decided to focus on the [(TPA)Fe(TCC)]PF₆ ferric catecholate spin crossover system which presents the advantage of a shorter relaxation time (~ 1 ms) of the photoexcited state [7] compared to the primarily proposed systems discussed in the proposal.

We investigated the structural signatures associated with the photoinduced transition from LS state to the HS, by the optical pump and x-ray probe technique. In order to maximise the transformation rate, we used a double laser excitation (incidence 180°) on 10 μm thick needle-shaped crystals, on the monoclinic polymorph of this system we recently evidenced.

The laser was polarized along the crystal axis for which the penetration depth is larger. We collected partial and complete diffraction data from which structures were solved and refined at different delays with good quality and in very good agreement with the structures we get in our laboratory at thermal equilibrium. Here are summarized the results we obtained:

- the structural modifications at the molecular level seen through the evolution of the metal to ligand average bond length (Fe-N, *fig.a*) shows an instantaneous transformation at the molecular scale after laser excitation, within the experimental time resolution. Such an increase is also characteristic of the spin state change during thermal conversion.

- the volume of the crystal (and unit cell *fig.b*), increases latter around 10 - 100 ns. It corresponds to the time required for acoustic waves propagation (order of 1000m/s).

- From changes of the Debye-Waller factor in the time-domain, compared to thermal equilibrium evolution check in our laboratory, we could estimate the temperature evolution of the crystal, following excitation (*fig.c*).

These results show that the change at the molecular level is ultra-fast (complementary optical data are under investigation) and that the first stage of the transformation occurs at constant volume. Then, the stress associated with the increase of the molecular volume drives an increase of the crystal volume and so of the unit cell. Thermalization of the out of equilibrium crystal occurs on a longer time-scale, with an increase of $T \approx 30\text{K}$. These promising results will settle the base of our future femtosecond optical pump-probe experiments on this spin-

crossover system as the question of the short time scale evolution (from 0 to 1 ns) remains to be deeply explored. Exploring and improving the data collected so far in this time range using the 100 ps time-resolved x-ray diffraction on ID09B will be of great interest to probe the mechanisms in the early stage of the transformation.

References

- [1] *Spin Crossover in Transition Metal Compounds I-III*, Ed P. Gülich & H.A. Goodwin (Springer, 2004),
- [2] N. Huby et al, Phys. Rev. B Rapid Com, **69**, 020101(R) (2004).
- [3] K. Ichiyanagi et al, Phys. Rev. B Rapid Com, **73**, 060408(R) (2006).
- [4] N.O. Moussa et al, Phys. Rev. Lett. **94**, 107205 (2005).
- [5] N.O. Moussa et al, Phys. Rev. B **75**, 054101 (2007).
- [6] J. Hébert, E. Collet et al, in preparation.
- [7] C. Enachescu et al, Chem. Phys. Chem., **7**, 1127-1135 (2006)

