

Supplementary Information

Experimental techniques:

The experiment monitors the HS fraction based on optical pump-probe technique whereby a light pulse called “pump” excites the material and another pulse called “probe”, of lower intensity and delayed in time, checks the state of the system at a given delay. This technique allows to derive the information on temporally varying photo-physics or photo-chemistry, for instance in our case the evolution of electronic molecular state.

The setup used for this experiment is unique in that it covers 10 decades in time from the hundreds of femtosecond (10^{-13} s) to the millisecond (10^{-3} s) time scale. Two routines are used to generate the delay between pump and probe: a mechanical delay line covering 0-2 ns range and electronic pulse selector for 13 ns – 1 ms range. The complete setup as well as technical specification is described in detail elsewhere [1].

Optical density change is a common marker of the spin state switching, and it can be used to track the evolution of the HS fraction in the time domain [2]. Indeed, the spin state switching results in significant shifts, and sometimes suppression or creation, of absorption bands related to HS and LS states. To first approximation accounting only for linear terms, optical density of a spin crossover system can be written as :

$$OD(\lambda) = L \times (X_{HS}\varepsilon_{HS}(\lambda) + X_{LS}\varepsilon_{LS}(\lambda))$$

where L stands for the thickness of the material, X denotes the fraction of the given electronic spin state and $\varepsilon(\lambda)$ is the extinction coefficient at the given probe wavelength. As the experiment measures the transient change in transmitted intensity, it is rather straightforward to express the observable with the following formula:

$$\Delta OD(t) = -\log\left(\frac{\Delta I(t)}{I} + 1\right)$$

The transient optical density change is related to the molecules photo-converted to the HS state, representing a fraction X_{HS} of all molecules in the crystal, with the following formulae:

$$\Delta X_{HS}(t) = \frac{\Delta OD(t)}{\Delta OD_{thermal}}$$

When $\Delta OD_{thermal} = OD(X_{HS} = 1) - OD(X_{LS} = 1)$

In the experiment, the material is optically pumped at 800 nm within an LMCT optical band therefore inducing efficient LS to HS conversion [3, 4], and probed at 550 nm where the optical density between spin states changes most in the visible spectra. By monitoring this change, one can follow the evolution of the converted HS fraction ΔX_{HS} in the time domain. As such, this fraction is not the X_{HS} in the sample but the increase of HS fraction in the sample following photo-excitation. HS fraction can be non-zero before excitation.

Complementary results:

We show in Fig S1, all the raw data that were used to plot figures 2 to 5 representing a systematic temperature and excitation densities study. We also investigate the relaxation dynamics at the μs time scale that corresponds to the recovery of thermal equilibrium, Fig. S2.

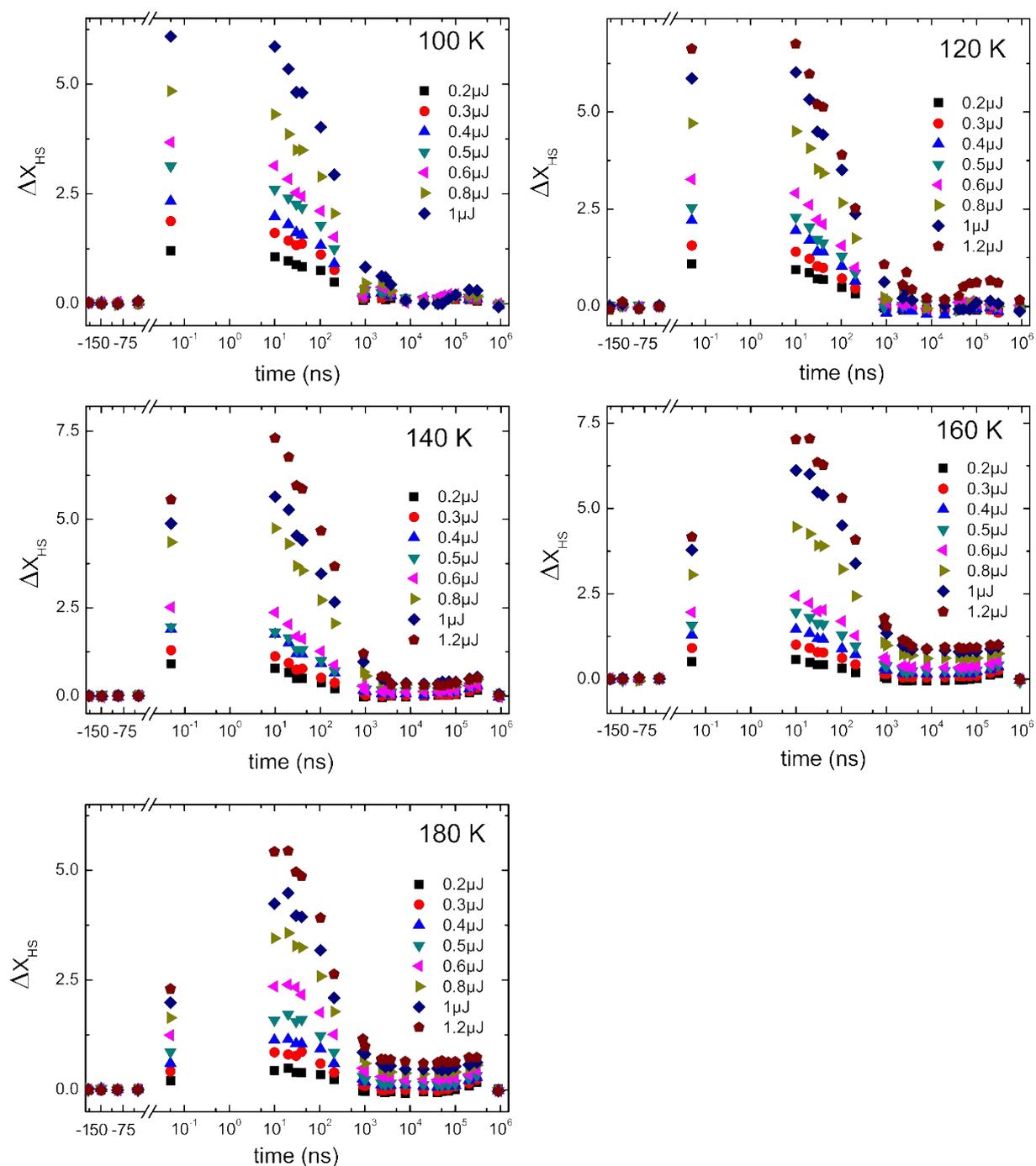


Fig. S1 Transient change of HS fraction, ΔX_{HS} , following a femtosecond excitation as function of pump excitation energy and sample temperature.

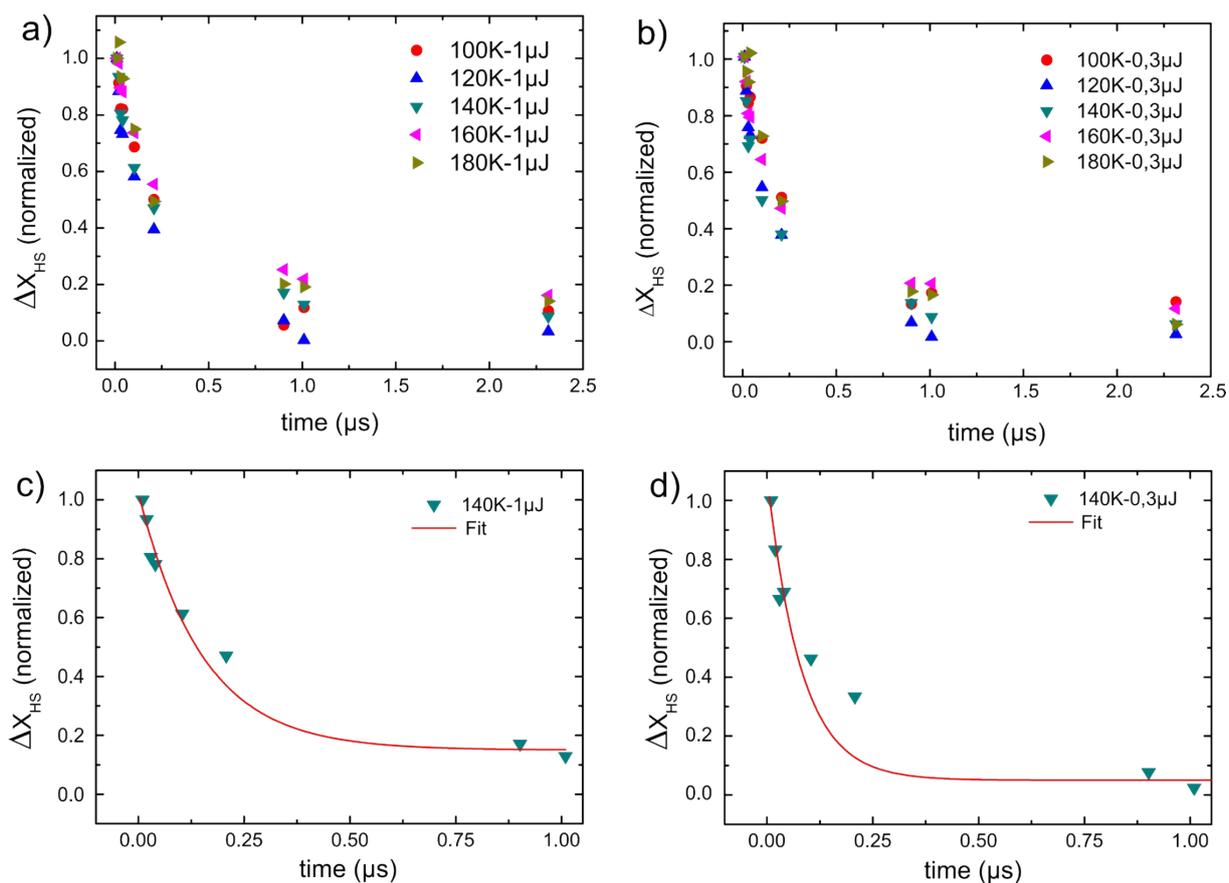


Fig. S2 Relaxation of the switched HS fraction as function of temperature at two excitations a) $1\mu\text{J}$ and b) $0.3\mu\text{J}$. Fit of the relaxation with a mono-exponential decay (red) provides respective time constant of 250 ± 60 ns for $1\mu\text{J}$ excitation c) and 140 ± 55 ns for $0.3\mu\text{J}$ excitation d).

For simplicity, all relaxation curves were normalized. First and foremost, these curves do not fit with mono-exponential decay, Fig. S2c-d. Secondly, they do not resemble self-accelerating sigmoidal curves, characteristic of cooperative relaxation process, but rather have self-decelerating character. As originally proposed by Hauser et al. [5], this relaxation character can be caused by a distribution of relaxation rates in spin-crossover centers. The apparent relaxation curve can also be explained by the thermalization rather than relaxation. In view of very weak temperature dependency of the relaxation rates observed in our experiments, Fig.S2 a-b, we are inclined to think that thermalization is the valid scenario.

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[2] M. Lorenc, J. Hébert, N. Moisan, E. Trzop, M. Servol, M. Buron-Le Cointe, H. Cailleau, M. L. Boillot, E. Pontecorvo, M. Wulff, S. Koshihara and E. Collet, *Phys. Rev. Lett.*, 2009, **103**, 2–5.

[3] R. Bertoni, M. Lorenc, A. Tissot, M. Servol, M. L. Boillot and E. Collet, *Angew. Chemie - Int. Ed.*, 2012, **51**, 7485–7489.

[4] A. Tissot, R. Bertoni, E. Collet, L. Toupet and M.-L. Boillot, *J. Mater. Chem.*, 2011, **21**, 18347.

[5] A. Hauser, *Spin Crossover in Transition Metal Compounds II*, Springer Berlin Heidelberg, 2004.