Electronic Supplementary Information

Probing the Anisotropic Distortion of Photoexcited Spin Crossover Complexes with Picosecond X-Ray Absorption Spectroscopy

Sophie E. Canton, Xiaoyi Zhang, Latévi M. Lawson Daku, Amanda L. Smeigh, Jianxin Zhang, Yizhu Liu, Carl-Johan Wallentin, Klaus Attenkofer, Guy Jennings, Charles A Kurtz, David Gosztola, Kenneth Wärnmak, Andreas Hauser and Villy Sundström

SI1. Determination of the excited state fraction in the picosecond XA experiment

Independent experiments were conducted to acquire the reference spectra necessary to lock the fraction of excited state α at Δt= 200 ps. The transient XANES spectrum of $[Fe(bpy)_3]^{2+}$ dissolved in MeCN (at 1.7 mM) was recorded under high laser excitation (tight laser beam focusing) so as to saturate the optical transition. In order to obtain reliable normalization far from the edge energy, large sampling steps were done in the EXAFS region. When varying the incident fluence with neutral density filters inserted in the path of the laser beam (from no attenuation down to OD2), no variation in the intensity of feature W_1' at 7124 eV was observed (see Figure 2 in the main text), and X-ray kinetics were taken. Single exponential fitting including the convolution with a Gaussian instrument response function of 80 ps FWHM delivers a time constant of 1370 ± 10 ps. The spatial overlap of the pump and probe beams was checked before and after the experiment, ensuring its stability during the accumulation. After normalization and correction for the factor exp [–(Δt/1370)] associated to the lifetime of the HS state, the difference spectrum $\Delta\mu$ is in excellent agreement with the one reported in Figure 6 of [1] for which α = 60% was found. The similarities between Figure 6 and Figure 7 in [1] indicate that these particular spectra are not distorted by self-absorption. Identical steps were followed for $[Fe(terpy)_2]^{2+}$ in MeCN (at 1.7 mM). Since the extinction coefficients of $[Fe(bpy)_3]^{2+}$ and $[Fe(terpy)_2]^{2+}$ are comparable at 527 nm (see Figure 4 in the main text), the absorption for $[Fe(terpy)_2]^{2+}$ was also saturated for the same laser intensities. The experimental settings employed for $[Fe(bpy)_3]^{2+}$ were kept (i.e. laser and X ray beams focus, jet conditions). X-ray kinetics were taken at 7124 eV. The single exponential fitting including the convolution with a Gaussian instrument response function of 80 ps FWHM provides a time constant of 4250 ± 53 ps. It should be noted that the time constant extracted under these conditions is in excellent agreement with the one obtained at lower fluence (τ = 4210 ± 40 ps, see Figure 3 in the main text). This allows ruling out any contribution from non-linear effect to these measurements. The difference spectrum $\Delta\mu$ was then acquired. After normalizing and correcting by the factor exp [–(Δt/4250)] associated to the lifetime of the HS state, this calibrated spectrum where the intensity is directly related to a known α can be used to extract by simple scaling this parameter for the difference spectra $\Delta\mu$ that were accumulated until good S/N in the EXAFS region was reached (with reduced laser power and larger spot size to guarantee long-term stability and sample integrity).

References

[1] Lima, F. A. ; Milne, C. J. ; Amarasinghe, D. C. V.; Rittmann-Franck, M. H.; van der Veen, R. M.; Reinhard, M.; Pham, V. T.; Karlsson, S.; Johnson, S. L.; Grolimund, D.; et al. A High-Repetition Rate Scheme for Synchrotron-Based Picosecond Laser Pump/X-ray Probe Experiments on Chemical and Biological Systems in Solution. *Rev. Sci. Instrum.* **2011**, *82*, 063111.