

# Supporting information for: Direct probing of spin state dynamics couples with electronic and structural modifications by picosecond time-resolved XAFS.

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## Experimental setup for picosecond time-resolved XAFS

Time-resolved XAFS experiments using the pump-probe technique were conducted at the undulator beamline NW-14A of the Photon Factory Advanced Ring (PF-AR) in Tsukuba. The 794 kHz x-ray was monochromatized using a Si(111) double-crystal monochromator, and higher-order harmonics were removed with a harmonic-rejection mirror. A femtosecond Ti:Sapphire laser was used as a pump source, and the fundamental wavelength of the laser was up-converted to 400 nm with a BBO crystal. The output power density of the laser on the sample was  $0.35 \text{ J/cm}^2$ . The XAFS spectra were collected in the fluorescence mode using a fast scintillation detector. X-ray signals were detected just before and just after the emission of the laser pulse using gated integrators synchronized with the pulse (945 Hz). The sample was composed of aqueous solutions of 50 mM  $[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ . 50 mM aqueous solutions of  $[\text{Fe}^{\text{II}}(2\text{-CH}_3\text{-phen})_3]^{2+}$  were utilized as a HS analog, both samples having been prepared using previously published methods.<sup>1</sup> The liquid sample was pumped into the sample chamber with a magnetic gear pump at the flow rate of 180 ml/min to reduce the radiation damage by the laser, and shaped to stable 300  $\mu\text{m}$  thick jet by a sapphire nozzle. Detailed information on the experimental methods for the time-resolved XAFS technique are also given elsewhere.<sup>2</sup>

## Details of EXAFS Analysis

The Fourier transformed EXAFS functions  $k^2 \times f(k)$  of the LS, HS analog, and photo-excited HS at  $\tau = 50 \text{ ps}$  are shown in Figure 3b of the main text as lines. The  $k$  ranges in the Fourier transformation were 2 to  $9.5 \text{ \AA}^{-1}$ . The transient HS EXAFS spectrum  $f(k, \tau)_{\text{HS}}$  was obtained by the expression

$$f(k, \tau)_{\text{HS}} = F(\tau) \Delta f(k, \tau) + f(k)_{\text{LS}}, \quad (1)$$

where  $F(\tau)$  is the scale factor at the delay time  $\tau$  (at  $\tau = 50 \text{ ps}$ , this value was 1/15 and was obtained by the static and transient difference spectra, and corresponds to the population of the excited state

at this time delay),  $f(k)_{LS}$  is the absorption spectrum of the LS ground state, and  $\Delta f(k, \tau)$  is the difference absorption spectrum at  $\tau$ . A curve-fitting analysis using the Fe–N and Fe–C shells was performed in  $k$  space after Fourier filtering of the peak of interest and the subsequent inverse Fourier transformation. The scattering amplitudes and the phase shifts were derived from the FEFF 8.20 code from the crystal structure of  $[\text{Fe}^{\text{II}}(\text{phen})_3](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ .<sup>3</sup> The  $R$  range employed in the curve-fitting analysis of the LS sample was  $\Delta R_{CF} \sim 1\text{--}2.4 \text{ \AA}$  and the HS analog and the transient HS samples were  $\Delta R_{CF} \sim 1\text{--}2.7 \text{ \AA}$ . Throughout the curve-fitting analysis, the parameters of the coordination numbers  $N$  of the Fe–N and the Fe–C shells were held constant at 6.0, the amplitude reduction factor  $S_0^2$  was fixed, and  $\Delta E_0$  in all spectra was assumed to be 0 because in the rising edge of the feature  $A(A')$ , indicated in Figure 2a of the main text, and each inflection point obtained by the first derivation does not change within the energy resolution. The bond length  $R$  and the Debye-Waller disorder factor  $\sigma^2$  were obtained as fitting variables. Fitting results are shown in Figure 3b of the main text as dotted lines and are listed in Table 1 of the main text. The thumbnails of the molecular structures of LS and photo-excited HS were generated by *Spartan*, molecular modeling software, using bond-lengths obtained from the time-resolved EXAFS analysis.

## Transient differences of EXAFS spectra

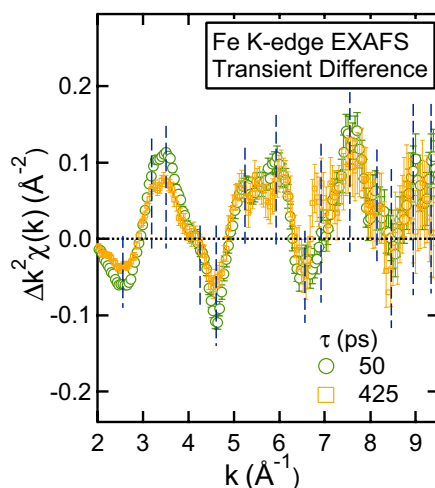


Figure S1: The transient difference of EXAFS spectra, weighted by  $k^2$ , at 50 and 425 ps.

The transient differences of EXAFS spectra observed at 50 and 425 ps after photo-excitation are shown in Figure S1. In the EXAFS oscillation, the period does not change in either spectrum, while the amplitude at 425 ps is decreased by  $\sim 25\%$  compared with that at 50 ps. This spectral time course in the EXAFS oscillation indicates that the transient spectral changes observed in the XAFS in the picosecond time scale correspond to the inter- and intramolecular vibrational relaxations in the two-level system from the photo-excited HS state to the LS ground state. This also verifies Eq. (1) with a scale factor  $F(\tau) = F_0 \exp(-\tau/t)$ , where  $F_0$  is a constant and  $t$  is the lifetime of the photo-excited HS (690 ps) state.

## Complete Ref. 30

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