



	<b>Experiment title:</b> Sub-nanosecond dynamics of spin crossover in Fe(II) polypyridyl complexes by complementary WAXS and XES	<b>Experiment number:</b> CH-4130
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**Report:**

In this report we describe the measurements and project status for our past experiment at ID09, which overall was quite successful. The experiment was performed as proposed on  $[\text{Fe}(\text{terpy})_2]^{2+}$  molecule in water solution, concentration of 15 mM, flown in a 300  $\mu\text{m}$  flat jet. We combined pump-probe XES and WAXS measurements to observe, respectively, the electron spin switching and structural changes in the nanosecond-lived quintet (HS) state upon excitation with optical picosecond laser pulses. The excitation was performed at 518 nm from the TOPAS system for wavelength conversion. We took advantage of the “pink” beam of U20 undulator and performed the time-resolved XES on Fe  $K\beta$  line with incoming X-ray spectrum centred at 12 keV to enhance the emission yield while still keeping moderate heatload on the beamline optics and the choppers. After confirming the existence of the HS state and measuring its lifetime with the XES, we continued with the time-resolved WAXS measurements using “pink” beam of U17 undulator centred at 18 keV at identical experimental conditions for consistency. Once the full kinetics was obtained with the scattering as well (Fig. 1), we switched the incoming photon energy to 25.2 keV which is the third harmonic of U20 undulator and used the multilayer monochromator (W coating) to select the narrow spectrum (1.6% BW). The high energy photons allowed us to significantly broaden coverage of the reciprocal space up to  $12 \text{ \AA}^{-1}$  thus gaining structural resolution in the scattering experiment. Since X-ray flux of the monochromotized beam is almost an order of magnitude lower compared to the “pink” beam the scattering signal was only collected at one positive delay of 100 ps and one negative delay of -3 ns as a reference. The respective difference signal is presented in Fig. 2A.

The total difference WAXS signal is a superposition of solute and solvent responses. Therefore for both the “pink” and the 25.2 keV configurations, the transient response of pure water to ultrafast heating was independently collected with IR laser excitation (1250 nm from TOPAS). As mentioned, the full kinetics of the HS state recovery to the ground state was acquired using the “pink” 18 keV beam providing the WAXS signal up to  $Q_{\max}=8.5 \text{ \AA}^{-1}$  (not shown here). Using the DFT calculated LS and HS structures and the measured solvent response, we fitted the WAXS signals to extract the HS state population kinetics (shown in Fig.1). From the transient XES spectral shape, the HS fraction was estimated using the reference compound and yields about 80% at 100 ps. To compare with the WAXS result, one

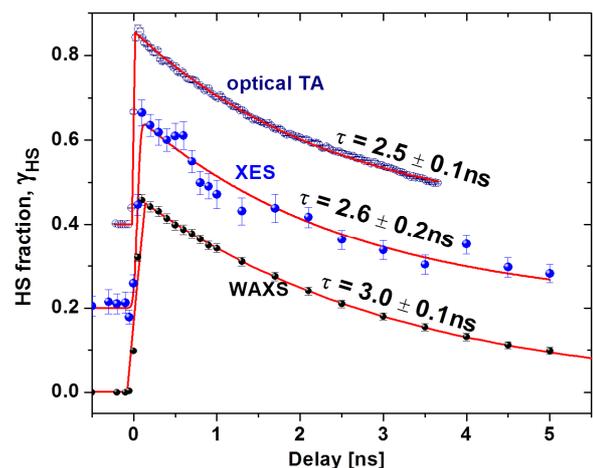


Fig.1 HS state population kinetics as acquired by three independent techniques demonstrating a fair agreement.

needs to correct for the X-ray and laser absorption in the sample, since the emission is collected from the front surface and WAXS is an average through the sample. After the correction, the maximum HS fractions from the two techniques are in the good agreement both giving about 45%. The HS state lifetime was measured from the XES by monitoring the signal recovery at a fixed energy on the peak of the Fe  $K\beta$  line of 7.058 keV. Additionally, following the experiment we performed a standard transient absorption measurement with an all-optical pump-probe setup at ID09. The HS lifetime was also extracted from optical transient absorption and it agrees well with the WAXS and XES kinetic traces (Fig.1).

The high resolution difference scattering at 100 ps delay (Fig. 2A) allowed us to optimized the molecular structure of the 2.5ns-lived HS excited state, taking as initial guess on the structure the DFT results of the ground and the excited stated. The ground state structure is assumed to be predicted well by DFT (b3lyp) as it is known to provide accurate result for the ground state of octahedral polypyridyl iron complexes. Structure of the HS state was varied in terms of metal-ligand distance and the ligand angle (Fig. 2B) to obtain optimal agreement with the experiment. A specific electronic quintet state was identified as most probable judging by the optimized structure. Overall, the data analysis and interpretation of results have been completed by now and the respective manuscript is in preparation.

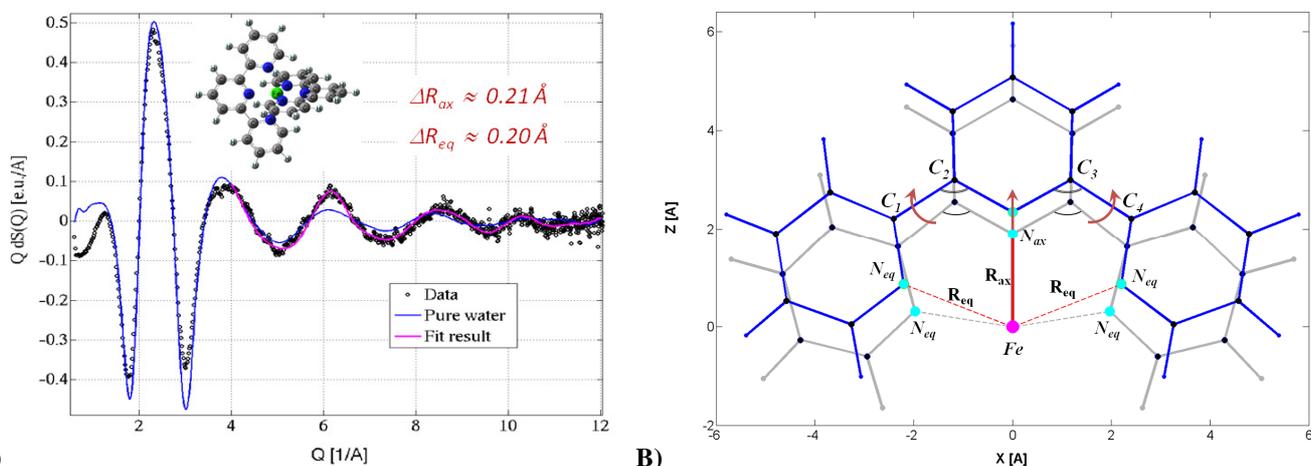


Fig.2 A): the terpyridine ligand structural change upon the HS transition: the Fe- $N_{ax}$  bond ( $R_{ax}$ ) elongation is accompanied with the  $C_1$ - $C_2$ - $N_{ax}$  or  $C_4$ - $C_3$ - $N_{ax}$  angle ( $\psi$ ) change. Right: setup for combined time-resolved WAXS and XES