

**Experiment title:**Angular-dependent EXAFS to solve the high-spin structure of  $[\text{Fe}(\text{terpy})_2]^{2+}$ **Experiment number:**

HC 764

<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: April 24th to: April 29 <sup>th</sup> 2013	<b>Date of report:</b> April 30, <sup>th</sup> 2013
<b>Shifts:</b> 15	<b>Local contact(s):</b> Gleb Parakhonskyi	<i>Received at ESRF:</i>

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**Report:**

The main goal of this experiment was to study the structure of the anomalous metastable photoexcited quintet state of  $[\text{Fe}(\text{terpy})_2]^{2+}$  (terpy: 2,2':6,2''-terpyridine) doped into  $[\text{Zn}(\text{terpy})_2](\text{PF}_6)_2$  applying polarisation dependent Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. This low-spin (LS) complex embedded in such matrices (similar Mn-, Cd-, or Zn-terpy compounds) shows a very anomalous behaviour: at low temperature its light-induced high-spin (HS) state is more than 10 orders of magnitude longer lived than what is expected from theory [1,2] and observed for  $[\text{Fe}(\text{terpy})_2]^{2+}$  in the neat compound. *Ab initio* calculations suggest that the structure of the HS state is unconventional, since besides the usual Fe–N elongation, its formation also requires a bending of the terpy ligand [3,4]. We expected through this experiment to bring an experimental evidence of the theoretically expected structure of the HS state, which may lead to a more complete understanding of the unusually long lifetime. This could pave the way for designing novel switchable compounds with a slow relaxation rate at much higher temperatures than expected from the prevailing relaxation model [1].

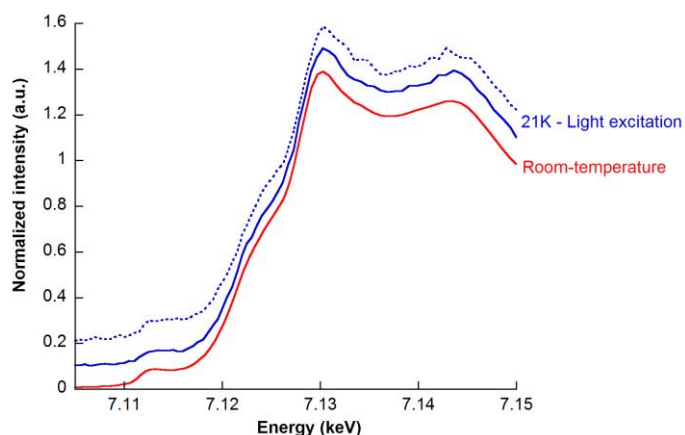
We investigated during this beamtime two different samples: (i) a single-crystal, for which the polarisation of the x-ray incoming beam was perpendicular to the **c** axis of the molecular crystal, and (ii) a pellet, in order to get access to the isotropic signal. Single-crystals were grown so the Zn:Fe ratio in the compound was 98:2; the biggest one was kept for the angular-dependent measurement and the smallest ones were crushed to prepare the pellet. This enabled to have both samples originating from the same solution and therefore presenting the same composition. In addition a reference sample ( $\text{FeCl}_2$ ) was measured to constraint the  $S_0^2$  in the EXAFS fitting of the  $[\text{Fe}(\text{terpy})_2]^{2+}$  spectra. Both samples were measured in fluorescence using a Vortex detector. The single crystal was measured in an almost 90° configuration: the incoming beam and the detector were placed at 90° from each others, but the perpendicular to the sample surface was at 7° from

the x-ray beam. The pellet was measured in the classical 45° configuration. For the low-temperature measurements, a diode was placed next to the sample to precisely measure its temperature in the cryostat.

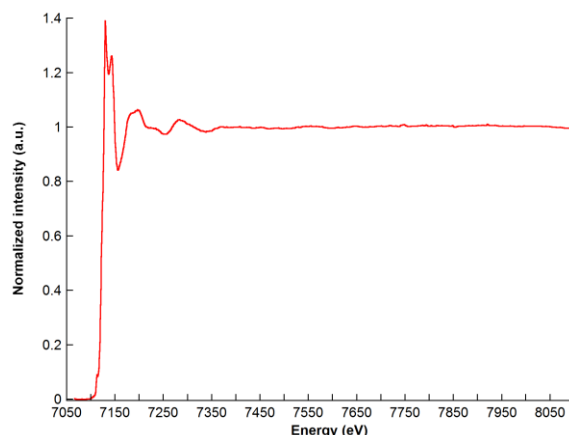
Most of the shifts were used to try to excite the system towards the high-spin state, especially with the improvement of the spatial overlap of the x-ray beam with the laser (for instance by inserting a 1mm-diameter pinhole on the sample). After each modification of the setup, we recorded a XANES spectrum, since the spin-transition can be easily monitored through variations of the pre-edge and of the two most intense peaks of the edge. Unfortunately, despite our several attempts, the excited high-spin state was never reached (Fig.1), and therefore no EXAFS data were acquired for the high-spin state at low-temperature under light-excitation. Several facts can explain this failure, and could quite easily be solved for a future attempt:

- (i) the power of the laser (3 mW, class 3R) : a class 3B laser is mandatory (Power >5mW)
- (ii) the weak beam in the 16-bunch mode : the experiment should be performed within the uniform or 7/8+1 modes, to have a higher intensity of the incoming x-ray beam and thus contribute efficiently to the excitation towards the high-spin state also through the x-ray beam
- (iii) the too large x-ray beam (6mm horizontally for these shifts) : a focus of the beam down to 1mm (equivalent to the size of the laser spot) would have helped to gain a factor of 6 for the incoming x-rays.

However, high-quality EXAFS spectra were easily obtained at room-temperature for the pellet sample (Fig. 2). In the case of the single-crystal, given the particular beam-sample-detector configuration, the signal-to-noise ratio was smaller than for the pellet. Despite a more important number of scans could have significantly increased it, we did not try to improve the quality of the spectrum here, since the room-temperature measurements cannot be used without those of the excited-state.



**Figure 1.** Isotropic normalized Fe K-edge XANES spectrum of  $\text{Zn}_{0.98}\text{Fe}_{0.02}(\text{terpy})_2 \cdot (\text{PF}_6)_2$  at room temperature (red) and 21K under light-excitation (blue). The continuous blue spectrum was measured for a x-ray beam slightly bigger than the laser spot; the dotted blue spectrum was measured with the x-ray beam and the laser aligned through a 1mm pinhole placed on the pellet.



**Figure 2.** Isotropic normalized Fe K-edge EXAFS spectrum of  $\text{Zn}_{0.98}\text{Fe}_{0.02}(\text{terpy})_2 \cdot (\text{PF}_6)_2$  at room temperature (Average of 10 scans, measured over a  $16,5 \text{ \AA}^{-1}$   $k$ -range, with a constant step in  $k$ )

## References

- [1] A. Hauser (1991) *Journal of Chemical Physics* 94 :2741
- [2] F. Renz et al. (2000) *Angewandte Chemie Int. Ed.* 39:3699
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- [4] A. Hauser et al. (2006) *Coordination Chemistry Review* 250:1642