

**Experiment title:**Pump-probe EXAFS at MHz repetition rates to solve the structure of the light-induced high-spin state of $[\text{Fe}(\text{tpy})_2]^{2+}$ **Experiment number:**
CH-4044

Beamline: ID26	Date of experiment: from: 05/03/2014 to: 11/03/2014	Date of report: 23/04/2014
Shifts: 18	Local contact(s): Pieter GLATZEL	<i>Received at ESRF:</i>

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Report:

The goal of the proposed experiment was to determine the structure of the anomalous metastable photoexcited state of $[\text{Fe}(\text{terpy})_2]^{2+}$ (terpy: 2,2':6',2''-terpyridine) by MHz pump-probe Extended X-ray Absorption Fine Structure (EXAFS) and high-resolution X-ray Absorption Near-Edge Structure (XANES) spectroscopies. This low-spin complex indeed presents an anomaly long photoinduced high-spin state, and the key to understand this unconventional behavior may lie in its structural deformation during the spin transition. However, such experiments require a MHz repetition-rate laser. For this beamtime, the laser of the FXE beamline of the European XFEL (Hamburg, Germany) was planned to be brought onto the ID26 beamline for several experiments, including this one. Nevertheless, due to a delay in the setup of the new mirrors on the ID26 beamline and other technical issues, the arrival of the laser has been postponed to a yet not defined time. This prevented the realisation of the initially proposed experiment on the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex. Therefore we took the opportunity to investigate by static spectroscopies another family of switchable molecular compounds, which present a charge transfer phenomena with temperature, pressure or light-excitation.

Among the charge-transfer molecular compounds, the Prussian Blue Analogues (PBA) represent a model family, which have been extensively studied for their promising switching properties. For instance, CoFe PBAs can be stabilized with a long lifetime in a diamagnetic $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ state (0) or a magnetic $\text{Co}^{\text{II}}\text{Fe}^{\text{III}}$ one (1) following a light impulsion, a temperature or a pressure change [1]. Moreover, recent results for a 'one-molecule' Prussian blue derivative showed that such effects are retained even at a nanometric scale [2]. In order to deeply understand the driving mechanism of the photomagnetic transition and the role of the alkali cation present in the structure, PBA are being investigated by conventional magnetometry, X-Ray Diffraction, visible and infrared spectroscopies, X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) at the K-edge or XAS at the $L_{2,3}$ edges. Nevertheless, to our knowledge, no study has been performed using high-resolution spectrometer such as the one available on the ID26 beamline. Therefore we took the opportunity with this beamtime to investigate some PBA compounds by High-Energy

Resolution Fluorescence Detected (HERFD-) XAS, X-ray Emission Spectroscopy (XES) and Resonant XES (RXES, *aka* Resonant Inelastic X-ray Scattering).

During this beamtime, we investigated three PBA samples : $\text{Rb}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3}\cdot n\text{H}_2\text{O}$ (denoted RbCoFe), $\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7}\cdot n\text{H}_2\text{O}$ (denoted CoFe) and $\text{Ni}_4[\text{Fe}(\text{CN})_6]_{2.7}\cdot n\text{H}_2\text{O}$ (denoted NiFe). For the three of them, we measured Fe K-edge HERFD-XANES, Fe $\text{K}\beta$ XES (the main lines and the valence-to-core) and Fe K-edge $1s3p$ -RXES. In the case of RbCoFe, measurements were performed for the diamagnetic state (at room temperature) and the magnetic one (at 10K, using the cryostat of the beamline); for the latter, the transition was triggered by the X-rays. For all the samples, $1s3p$ -RXES planes were acquired in the pre-edge region but also in the low energy transfer range in order to investigate the d-d excitations in these compounds. Finally, Co K-edge data were also acquired for RbCoFe but only at room-temperature.

In the case of RbCoFe, the photo-induced transition from the $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ state to the $\text{Co}^{\text{II}}\text{Fe}^{\text{III}}$ and the thermal relaxation were well observed (Fig. 1): the spectral features display significant variations both in the edge and the pre-edge. The energy shift of the white line is consistent with the increase of the Fe oxidation state. Changes were also observed in the $\text{K}\beta$ and valence-to-core XES spectra, as well as in the $1s3p$ RXES plane. More particularly, in the low energy transfer range (0-10 eV), features were observed for the Fe^{III} state (Fig. 2) but none for the Fe^{II} one. These features were seen on the RXES planes of all the Fe^{III} -bearing compound (RbCoFe at 10K under photoexcitation, CoFe and NiFe). Additional spectra were taken at a fixed incident energy to scan these features as a function of the transfer energy. 1D well-resolved scans were obtained, and preliminary multiplet calculations showed a good overall agreement with the experimental spectra. More detailed calculations will thus allow a full interpretation of these spectra and hence a better understanding of the d-d excitations observed by hard X-ray spectroscopy.

To conclude, we have efficiently used this beamtime to investigate reference compounds of the PBA family using all the techniques offered by the ID26 spectrometer (HERFD-XAS, XES, RXES). The stability of the beamline and of the cryostat, as well as the high quality of the spectrometer, enabled to record high-quality data. Their interpretation will bring fundamental information on the charge transfer transition that can be observed for some PBA compounds, as well as on the d-d excitations, which are still not well understood. These results are also an important milestone for further investigation of these switchable magnetic molecular materials using high-resolution hard X-ray spectroscopies.

[1] O. Sato *et al.* (1996) Science 272:704-705

[2] D. Li *et al.* (2008) J. Am. Chem. Soc. 130:252-258

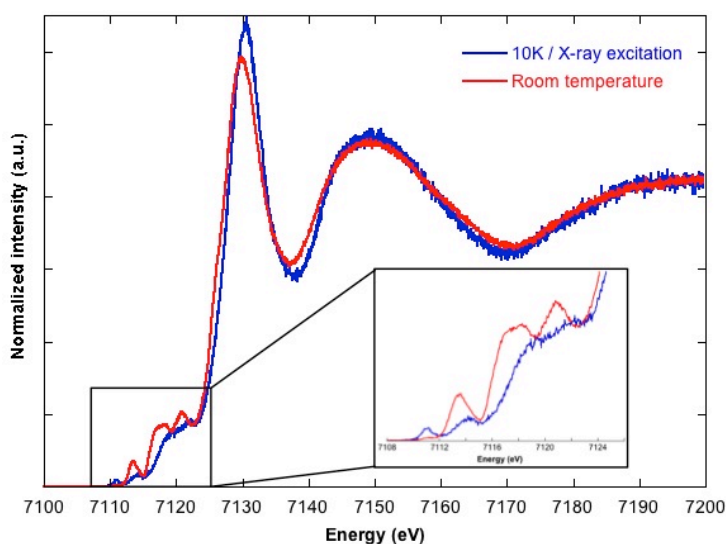


Figure 1. Fe K-edge HERFD-XANES spectra of the RbCoFe compound, at room temperature ($\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ state) and at 10K under photoexcitation ($\text{Co}^{\text{II}}\text{Fe}^{\text{III}}$ state).

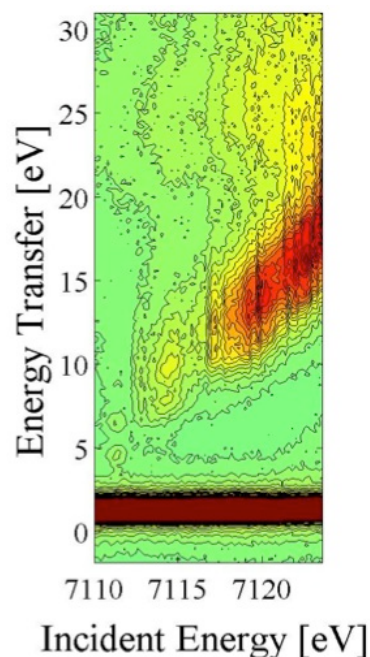


Figure 2. Fe K-edge $1s3p$ -RXES plane of the RbCoFe compound at 10K under photoexcitation. The d-d excitations are the features around 7112 eV for the incident energy and 0-10 eV for the transfer one.