

Structural probes to investigate the photomagnetic properties in cyanometalate compounds

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The rational design of molecular systems, which exhibit light-switchable physical properties is a subject of the intense research activity. Over the past, chemists have investigated the synthesis of magnetic and photoresponsive complexes through rational choices of cyanido-based building blocks. This approach has been extremely successful, and various molecular architectures have been obtained with remarkable properties such as spin crossover,¹ electron-transfer process,² and photoinduced magnetism.^{3,4} To unambiguously elucidate the photo-induced mechanism, the use of structural X-ray probes is extremely helpful.

In this presentation, we will focus on two compounds exhibiting photomagnetic properties. The first system, a dinuclear pair, namely $[(\text{Tp})\text{Fe}^{\text{III}}(\text{CN})_3\text{Co}^{\text{II}}(\text{PY5Me}_2)]^+$, has been studied using a combination of X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements done at Fe and Co $L_{2,3}$ edges and at K edges. These local structural measurements, as well the bulk magnetic measurements have shown the reproducibility and the full reversibility of the photo-induced and the thermal-induced electron transfer (figure).⁵ The second system is the mononuclear compound $\text{K}_4[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ for which the photomagnetic properties can be only understood with the help of photocrystallography study that reveals important reorganization of the Mo coordination sphere.

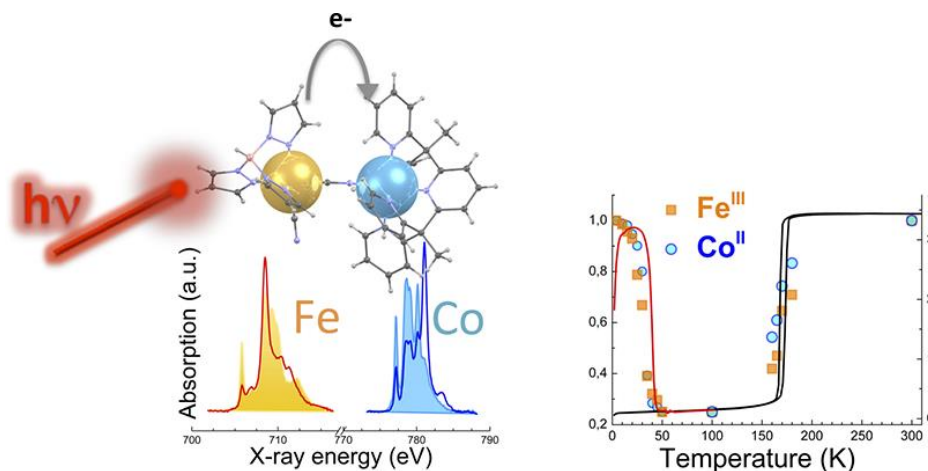


Figure. Left Top: Structure of $[(\text{Tp})\text{Fe}(\text{CN})_3\text{Co}(\text{PY5Me}_2)]^+$ and scheme of photo-induced electron transfer between Fe^{II} and Co^{III} . Left Bottom: L_3 edges XAS spectra measured after light excitation at 10 K (Fe^{III} : orange shape and Co^{II} : blue shape) and after thermal relaxation at 50 K (Fe^{II} : orange line and Co^{III} : blue line). Right: Comparison of Fe (yellow dots) and Co (blue dots) fractions obtained from XAS and magnetic properties under the variation of temperature (dark) and after light excitation red).

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