

X-ray Magnetic Spectroscopy Study of Switchable Photomagnetic Cubes

Niéli Daffé,¹ Juan-Ramón Jiménez,² Michał Studniarek,¹ Marie-Anne Arrio³, Rodrigue Lescouëzec,² and Jan Dreiser¹

¹SLS, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland ²IPCM, Université Pierre et Marie Curie, FR-75005 Paris, France ³IMPMC, Université de Pierre et Marie Curie, Paris, France

Email: nieli.daffe@psi.ch

Switchable molecules exhibiting tunable physical properties as a function of external stimuli (electric or magnetic fields, temperature, light, pressure) find an increasing interest for their potential use in molecule-based electronic devices such as molecular switches, sensors or qubits. One of the most encouraging group of compounds has emerged from the family of Fe/Co Prussian Blue Analogues (PBAs) which exhibit concomitant changes in their optical and magnetic properties based on a metal-to-metal electron transfer coupled to a spin transition that can be reversibly controlled by light irradiation or temperature modification. However, their integration into devices requires the transfer of their properties to lower dimensional analogues. Therefore, the past decade has witnessed considerable interest in the design of novel molecular systems based on PBAs [1]. Better insight into the metal-to-metal electron transfer at the molecular level in these systems is essential and requires the determination of the ligand-field geometries and the oxidation and spin states of the coordinated atoms.

To this end, we have studied heterocubane complex cages including Co and Fe ions (“Fe/Co cubes”) linked by cyanide bridges [2], using a combination of X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). Upon application of stimuli of light and temperature, we follow the changes in oxidation states using XAS at the $L_{2,3}$ edges of the 3d transition metals. These results are combined with XMCD measurements which yield the element specific magnetic moments delivering insight into the spin state of the metal ions. We show unambiguously that (i) the 300 K and 2 K ground states are formed mainly from diamagnetic $\text{Fe}_{\text{LS}}^{\text{II}} - \text{CN} - \text{Co}_{\text{LS}}^{\text{III}}$ pairs, (ii) the 2 K light-induced excited state is built from paramagnetic $\text{Fe}_{\text{LS}}^{\text{III}} - \text{CN} - \text{Co}_{\text{HS}}^{\text{II}}$ pairs. Similar conversion rates for $\text{Co}_{\text{LS}}^{\text{III}} \rightarrow \text{Co}_{\text{HS}}^{\text{II}}$ on the one hand and $\text{Fe}_{\text{LS}}^{\text{II}} \rightarrow \text{Fe}_{\text{LS}}^{\text{III}}$ on the other hand are obtained for a given laser intensity which evidence the metal-to-metal electron transfer process. In the photo-excited state, the total magnetic moment of Co ions is larger than the one of Fe. The magnetic moments of the Fe and Co ions exhibit paramagnetic behavior, with their moments oriented in the same direction. The original state can be restored by heating up the sample to room temperature demonstrating the reversibility of the conversion process. XAS and XMCD investigation of this system provide an atomic scale picture of the switching mechanism and address the pertinent question on the nature of the magnetic interaction between the Fe and Co ions in molecular PBAs. Our results provide a feedback to the synthesis of such molecular cages that can help in return to design cages with further improved properties.

[1] Aguilà, D. *et al.*, *Chemical Society Reviews* **45**, 203 (2015)

[2] Garnier, D. *et al.*, *Chemical Science* **7**, 4825-4831 (2016)