X-ray induced metal-to-metal electron transfer in a cyanido-bridged $[Fe_2Co_2]$ square molecule

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Switchable coordination compounds offer a possibility to control by temperature and/or light two or more distinct electronic states based on spin crossover [1], metal-to-metal [2] or metal-to-ligand [1] electron transfer. In both phenomena, electronic states with different configurations are involved and can be optically and/or thermally manipulated. For characterizing such changes of electronic states, X-ray absorption spectroscopy (XAS) appears to be the method of choice.

XAS has been used for the studies of the 3D photomagnetic Co/Fe Prussian Blue Analogs and obtained results provide an experimental proof of the electron transfer mechanism (oxidation and reduction of Fe and Co sites, respectively) [3]. More recently, several switchable Fe/Co square molecules have been synthesized [2] and photo- and thermally induced electron transfer has been probed using XAS and XMCD techniques [4]. Here we show that X-ray beam is also able to promote the metal-to-metal electron transfer, i.e., the X-ray beam is used during the same experiment as a pump and as a probe. Using a rather modest flux of incident X-rays, we have been able to follow the electron transfer kinetics recording XAS spectra at the K-edges of the both metal ions involved in the process. As expected outcomes, the full reversibility and the reproducibility of the electron transfer have been clearly confirmed. Moreover, the XAS results show a symmetric conversion of the reduced and oxidized species created by the electron transfer either thermally induced or under X-ray irradiation.

References

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