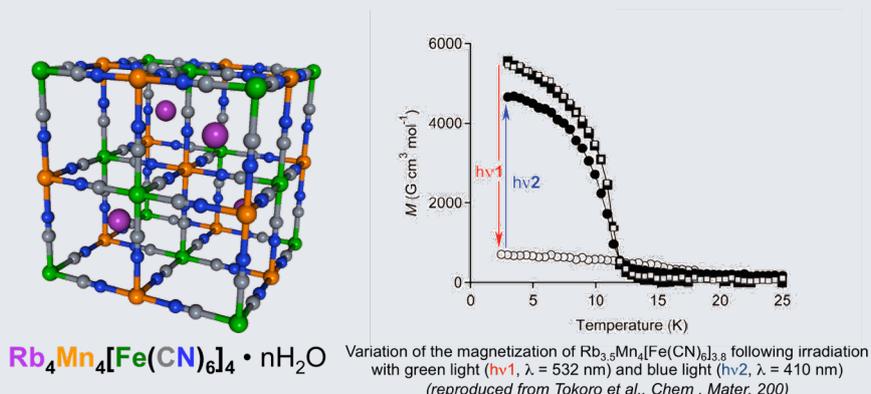


# Inside the visible-light-induced reversible charge transfer in Prussian blue analog.

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Optically-addressable functional nanomaterials are of great interest for the renewal of materials for high-density data storage. Among them, Prussian blue analog (PBA) are promising candidates, as several PBAs revealed a charge-transfer induced either by light (x-ray or in the visible range), pressure or temperature.



The  $\text{Rb}_{3.5}\text{Mn}_4[\text{Fe}(\text{CN})_6]_{3.8}$  PBA revealed to be particularly interesting, as it presents both thermally- and visible light-induced charge-transfer between the  $\text{Mn}^{\text{II}}\text{-Fe}^{\text{III}}$  and the  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$  states. Tokoro et al. first showed that, following the thermally-induced  $\text{Mn}^{\text{II}}\text{-Fe}^{\text{III}} \rightarrow \text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$ , a  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}} \rightarrow \text{Mn}^{\text{II}}\text{Fe}^{\text{III}}$  charge transfer could be triggered at low temperature by visible light in the green color range ( $\lambda = 532 \text{ nm}$ ). Using a xenon filtered lamp ( $\lambda = 410 \pm 30 \text{ nm}$ ), this optically-driven charge transfer could be reverse, leading back to the  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$  state. They proposed a mechanism to describe this visible-light-induced reversible charge transfer. The optical switching from the  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$  state to the  $\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}$  one occurs through a metal-metal charge transfer; in contrast, the reverse process originates from an optical transition from the  $\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}$  state to the  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$  state through the  $\text{CN}^- \rightarrow \text{Fe}^{\text{III}}$  ligand-to-metal charge transfer. Finally, Tokoro et al. also demonstrated the existence of a photostationary state between the low-temperature green-light-induced  $\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}$  state and the low-temperature blue-light-induced  $\text{Mn}^{\text{III}}\text{Fe}^{\text{II}}$  one.

This pioneer study thus established the different charge transfers occurring for the  $\text{Rb}_{3.5}\text{Mn}_4[\text{Fe}(\text{CN})_6]_{3.8}$  PBA and proposed a mechanism. Nevertheless, the inside of the mechanism still needs to be investigated with time-resolved experiment. Also, knowledge on the impact of temperature on these different charge-transfers and the corresponding mechanism is still missing. This study is the next step of our project thanks to the last developments for pump-probe transition metal K-edge X-ray absorption spectroscopy on the ODE beamline; the spectral signature of the  $\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{III}}$  ions can indeed be unambiguously identified by Mn K-edge XAS, as the white line of each oxidation state is separated by several eV. Also, the new cryostat designed for photoexcitation studies will allow resolving the impact of temperature on these optically-driven charge transfers.

H. Tokoro, T. Matsuda, T. Nuida, Y. Moromoto, K. Ohoyama, E.D.L. Dangui, K. Boukhedaden and S. Ohkoshi, *Visible-light-induced reversible photomagnetism in rubidium manganese hexacyanoferrate*, Chem. Mater. 20, 423-428 (2008)

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