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Ultrafast Spin and Charge Dynamics in CoFe Prussian Blue Analogues

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Spin and charge dynamics are at the heart of many photoinduced properties in molecular materials, including photomagnetism or artificial light harvesting [1]. The precise knowledge of the associated mechanisms requires to follow in real time the ultrafast processes occurring after light absorption, involving electronic, nuclear and spin motion. In this context, Prussian Blue Analogues (PBAs) are very attractive compounds, based on two cyanide-bridged metal centers. Photoinduced intermetallic charge transfer (CT) is indeed coupled to metal-centered spin transition as well as lattice deformation, thus governing the photoinduced properties.

In this work, we investigated the femtosecond dynamics occurring after visible light excitation in CoFe PBA nanoparticles. Light absorption is known to switch the compound from a Co^{III}(S=0)-Fe^{II}(S=0) state to a Co^{II}(S=3/2)-Fe^{III}(S=1/2) state, i.e., with coupled CT and spin-crossover [2]. Using visible transient absorption measurements, we show that 540nm excitation induces the spin-crossover mechanism on the Co site first, followed by CT on the 200 fs timescale (Figure 1), as confirmed by time-resolved X-ray absorption experiments [3]. In PBAs, different types of metal-centered and intermetallic excitations exist. We further propose to explore the interplay between spin and charge dynamics by performing direct CT transition, using tunable pump excitation. These results shed new light for investigating the ultrafast properties of multimetallic materials and spin-crossover compounds.

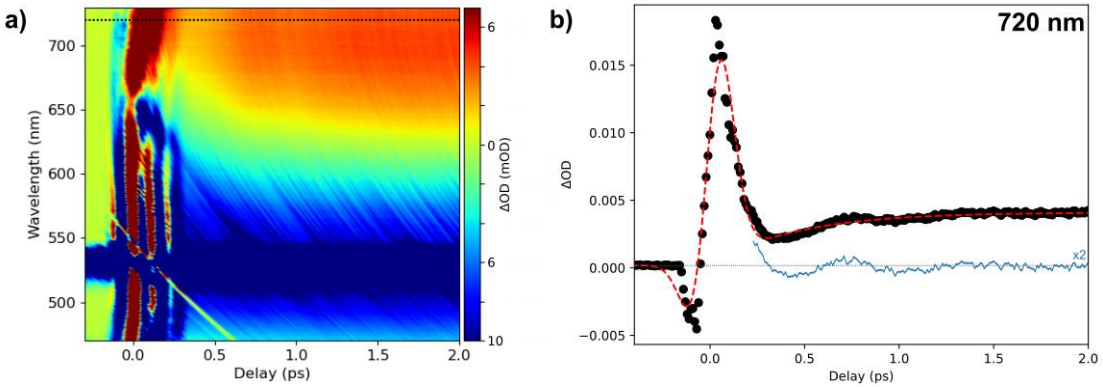

Figure 1: a) Transient absorption spectrum of CoFe PBA following 540nm excitation. b) Extracted time-resolved signal at 720nm (black dots), together with its fit (red dashed curve) including solvent response and an exponential population, accounting for the CT process. Residuals of the fit is shown in blue, where 600 fs oscillations correspond to vibrational activation induced by the spin transition on the Co site.

[1] S. Ohkoshi, H. Tokoro, Acc. Chem. Res. **45**, 1749–1758 (2012).
[2] S. Zerdane et al, Eur. J. Inorg. Chem. **2018**, 272-277 (2018).
[3] M. Cammarata et al, Nat. Chem. **13**, 10-14 (2021).