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Unraveling charge transfer dynamics in switchable molecular magnets through X-ray absorption spectroscopy

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Cyano-bridged coordination systems are widely studied in molecular magnetism due to the strong superexchange magnetic interactions facilitated by CN ligands. Their flexible cyano-bridged linkages also allow structural deformations in response to external stimuli, potentially enabling switchability or memory effects. One of the interesting phenomena observed in coordination networks is the possibility of triggering metal-to-metal charge transfer (MMCT) by temperature, pressure, or sorption of small molecules. MMCT entails electron transfer between metal ions, creating valence isomers with different electronic configurations. This process alters spin states, coupling interactions, and charge distribution, significantly impacting the material's magnetic, electric, and optical properties and bond lengths.

MMCT process was investigated in 1D bimetallic chains $\{(NH_4^+)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_\infty$, where the Ni(II/III) and Fe(II/III) redox pair is influenced by water sorption/desorption, temperature, and pressure [1]. Using X-ray absorption spectroscopy (XAS) at Fe and Ni K-edges, we probe the reversibility and reproducibility of the intramolecular Fe/Ni redox process (Figure 1).

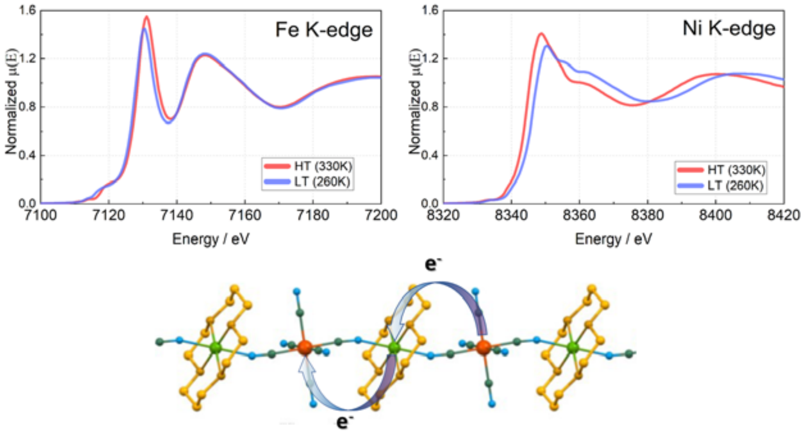

Figure 1. Normalized absorption coefficient at Fe and Ni K-edge recorded for $\{(NH_4^+)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_\infty$ at temperatures: 330K and 260K showcasing the antagonist change of XANES characteristics between Fe and Ni K-edges, due to the charge transfer effect).

To further tune the MMCT characteristics, Fe was substituted with Ru, whose higher reduction potential stabilizes the Ni(III)-Ru(II) phase. Notably, in this system rehydration, though partially reversible, does not restore the MMCT process. XAS measurements reveal that Ru remains in the Ru(II) oxidation state, challenging the previous assumption of electron transfer from Ru to Ni leading to Ru(III) formation [2]. This study underscores the power of XAS in probing fragile electron transfer and redox-active systems at a local scale. Furthermore, it highlights the technique's complementarity with traditional structural, optical, and magnetic measurements, offering a more comprehensive understanding of complex redox processes.

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References

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