SPIN CROSSOVER COUPLED WITH AN ELECTRON TRANSFER IN HOFMANN-TYPE COORDINATION POLYMERS

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Hofmann coordination polymers (CPs) that couple a spin transition [1] with an electron transfer (ET) at room temperature are an innovative strategy towards multifunctional metal organic frameworks (MOFs). Here, we developed 2D planar $\{Fe(Me\text{-}pbpy)_2[M(CN)_4]_2\}$ compounds (M= Pt^{II} or Ni^{II}), where the axial ligand consists of an infinitely π-stacked, redox-active bipyridinium derivative (Me-pbpy) (Fig. 1a, inset). UVvisNIR measurements (Fig. 1a) show that the compounds absorb over a large range, including a strong band around 500 nm that can be attributed to the reduced, radical form of the bipyridinium unit, which is known to be stabilized by a MOF structure [2]. Replacing Fe^{II} by Zn^{II} affords an isostructural MOF (Fig. 1a), where the band around 500 nm attributed to the electron transfer (ET) cannot be detected, indicating that the interaction between Fe^{II} and the redox-active Me-pbpy unit is crucial. The magnetic properties of the obtained materials show a gradual spin crossover (SCO) between 150 and 250 K with a slight double step (Fig. 1b) that could be related to the ET at high temperature, leading to an interesting coupling between SCO and a thermo-induced ET. These observations are further confirmed by DFT calculations for simplified fragments, single crystal XRD studies and Mossbauer spectroscopy.
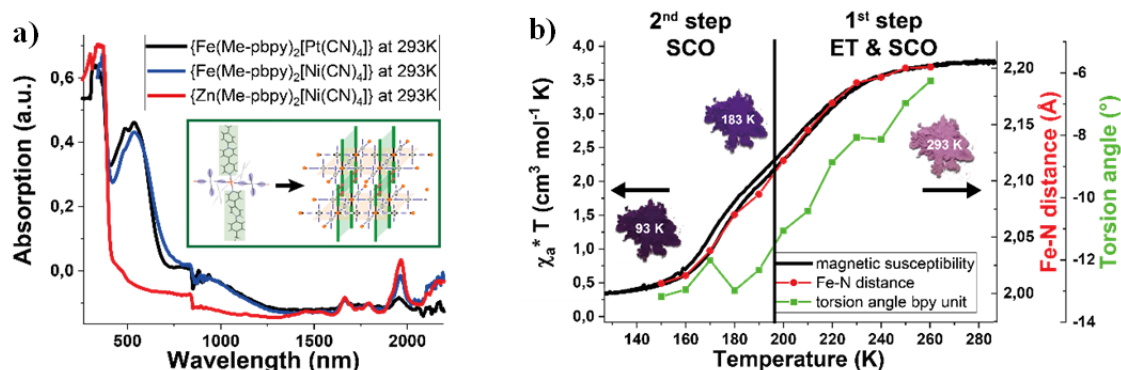

Figure 1: a) UVvisNIR absorption of $\{Fe(Me\text{-}pbpy)_2[M(CN)_4]_2\}$ compounds (M= Pt^{II} or Ni^{II}) in comparison to the isostructural Zn^{II} MOF. Inset: unit cell and packing scheme of clathrates. **b)** Magnetic properties, evolution of Fe-N distances and torsion angle of Me-pbpy [3] for $\{Fe(Me\text{-}pbpy)_2[Pt(CN)_4]_2\}$.

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