Desolvation-induced multistep spin-crossover in the $[Fe(3\text{-bpp})_2](OTf)_2$ complex

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One of the most difficult issues in material chemistry is the fabrication of switchable compounds. These systems can serve as the foundation for the design of sophisticated sensors and data storage devices. The iron(II) spin-crossover (SCO) complexes that display switching between the low-spin diamagnetic state (LS, S= 0) and the high-spin paramagnetic state (HS, S= 2) in response to external stimuli (e.g., temperature, host molecules) are of particular interest in this field of switchable materials.[1,2] Additionally, these processes affect other characteristics (e.g., structural parameters, optical properties).

In this presentation, the results of structural, magnetic, and spectroscopic analyses for $[Fe(3\text{-bpp})_2](OTf)_2$·solvated phase (**1**·solv) and thermally desolvated phase, where 3-bpp= 2,6-di-(1H-pyrazol-3-yl) pyridine and OTf^-= triflate, will be discussed. A single crystal X-ray diffraction study revealed that **1**·solv is composed of layers of $[Fe(3\text{-bpp})_2]^{2+}$ separated by OTf^- anions and solvent molecules (Figure 1). Magnetic studies showed that upon heating, **1**·solv exhibits a reversible LS↔½HS SCO effect with a transition temperature ($T_{½}$≈ 300 K). The further heating process leads to irreversible desolvation-assisted ½HS↔HS SCO phenomena ($T_{½}$≈ 340 K). In the next cooling and heating cycles, desolvated sample **1** exhibited the reversible three-step SCO: gradual LS↔¼HS SCO ($T_{½}$≈ 110 K), gradual ¼HS↔½HS SCO ($T_{½}$≈ 175 K) and abrupt ½HS↔HS SCO with thermal hysteresis ($T_{½}^{\downarrow}$≈ 226 K and $T_{½}^{\uparrow}$≈ 234 K). Moreover, the desolvated sample reveals a thermal quenching effect below 85 K. Complex **1** is a rare instance of a desolvation-induced multi-step spin-crossover system.

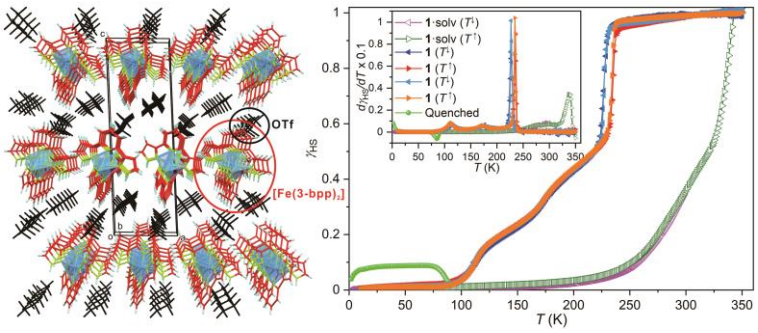

Figure 1. Structural unit and magnetic properties of **1** in 1 kOe.

1) S. Ohkoshi, K. Nakagawa, K. Imoto, H. Tokoro, Y. Shibata, K. Okamoto, Y. Miyamoto, M. Komine, M. Yoshikiyo, A. Namai, *Nat. Chem.* **2020**, *12*, 338. 2) A. Djemel, O. Stefanczyk, C. Desplanches, K. Kumar, R. Delimi, F. Benaceur, S. Ohkoshi, G. Chastanet, *Inorg. Chem. Front.* **2021**, *8*, 3210.