

Multifunctional Molecular Magnets: One- to Six- Step Spin-Crossover and Cluster-Based Single- Molecule Magnets Studies

李, 朝陽

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氏 名：李朝陽

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(多重機能性分子磁性体)

区 分：甲

論 文 内 容 の 要 旨

Molecular-based materials have attracted more and more attention owing to the potential application in the future molecular devices. Of which, the author was interested in the multifunctional spin-crossover (SCO), single-molecule magnet (SMM), and their photo effect in these systems. For the multifunctional SCO, series of Schiff ligands were designed, which are mainly discussed in chapter 2-4. Although the 5-Br-thsa ligand and its complexes have been studied before, our strategy is to design and synthesize neutral SCO compounds rather than the anionic ones based on the Fe(III) metal centre where it could show spin transition with suitable ligand field. For the SMMs, we rationally designed and synthesized series of hexanuclear compounds. Refer to the hexanuclear cluster, it should be noted that single-crystal-to-single-crystal transformation from hexanuclear cluster to a one-dimensional chain has been studied based on cyanide-bridged $\text{Fe}^{\text{III}}_4\text{M}^{\text{II}}_2$ cluster in our group. But in this dissertation we used tridentate ancillary ligand tptz to control the magnetic properties. Fortunately, we observed the slow magnetic relaxation behaviour for compound **5-2**, **5-3**, and **5-5a**.

In chapter 2, two Schiff ligands were synthesized and their single-crystal structures were characterized by X-ray diffraction, $\text{H}_2\text{-5-Cl-thsa-Et}$ (**L2-1**), $\text{H}_2\text{-5-Br-thsa-Et}$ (**L2-2**) (Scheme 2-1). Based on these two ligands, we aimed to synthesize mononuclear iron(III) SCO complexes that show large thermal hysteresis. Here, two neutral one-step SCO compounds, $[\text{Fe}(\text{H-5-Cl-thsa-Et})_2][\text{Fe}(\text{5-Cl-thsa-Et})_2]\cdot 2\text{H}_2\text{O}$ (**2-1**) and $[\text{Fe}(\text{H-5-Br-thsa-Et})_2][\text{Fe}(\text{5-Br-thsa-Et})_2]\cdot 2\text{H}_2\text{O}$ (**2-2**), were successfully synthesized. Compound **2-1** shows 70 K hysteresis loop, indicating strong cooperativity occurred in this compound. Compound **2-2** demonstrates one-step asymmetric spin transition with large thermal hysteresis. DSC has been done to confirm the phase transition of compound **2-1** and **2-2**.

In chapter 3, on neutral mononuclear ferric compound showing a two-step spin transition, $[\text{Fe}(\text{H-5-Cl-thsa-Me})(\text{5-Cl-thsa-Me})]\cdot \text{H}_2\text{O}$ (**3-1**), was synthesized. This two-step spin transition behaviour was confirmed by X-ray crystallography, magnetic measurement, DSC, variable-temperature IR and Mössbauer spectroscopy. Another new mononuclear compound,

[Fe(H-5-Br-thsa-Me)(5-Br-thsa-Me)]·H₂O (**3-2**), exhibiting three-step spin transition behaviour, was obtained and characterized by powder X-ray diffraction. More importantly, dielectric anomalies and photo-response were observed for these two compounds, suggesting the multifunctional properties of compound **3-1** and **3-2**.

In chapter 4, **4-1** exhibited six- and five-step spin transitions during cooling and heating processes, respectively. Two-step symmetry breaking ($P2_1/n \rightarrow Pn \rightarrow P2_1/n$, loss of the screw axis 2_1) without any cell multiplication was observed. The structural modification of the ligand and resonance-assisted hydrogen bonding (RAHB) should be related to the strong intermolecular interactions that play a dominant role in the multi-step SCO. DFT calculation is helpful for understanding the importance of the proton for such symmetry breaking SCO. Future studies will focus on deuterium, neutron diffraction and the possible ferroelectricity.

In chapter 5, we have described the synthesis and properties of a novel family of hexanuclear complexes exhibiting considerable magnetic anisotropy and slow magnetic relaxation. These Fe^{III}₄M^{II}₂ compounds have been characterized by X-ray crystallography, static and dynamic magnetic susceptibility measurements. X-ray crystallography studies reveal that the compound **5-1~5-3** with low symmetry $P-1$ space group and **5-4~5-5** with relatively high symmetry $P2_1/c$ space group. Magnetic studies suggest that the magnitude of the magnetic exchange between the Fe(III) and Co(II)/Ni(II) centres can be controlled via ancillary ligand choice compared with Oshio and our cases. Five hexanuclear complexes in this chapter, of which, **5-2**, **5-3**, and **5-5** show ferromagnetic coupling. The ac magnetic susceptibility of **5-2**, **5-3**, and **5-5** exhibit the characteristics of slow magnetic relaxation. Taken together, these studies establish the first class of hexanuclear transition metal complexes in which slow magnetic relaxation has been observed, and the structural data provide a starting point for further studies into the magnetic properties of this promising family of coordination compounds. In the future, we will explore the photo effect of these two series of hexanuclear compounds.

Though we have obtained some exciting results for the spin-crossover compounds and cluster-based single-molecule magnets, there are still some problems need to be solved in the future work. For example, for the compounds we discussed in the chapter 2, we will study the photo effect and the dielectric properties. For compound **3-2** the single-crystal structure is necessary to further understand the three-step spin transitions. More importantly, for compound **4-1** – the multistep spin transition, neutron diffraction is needed to explore the mechanism that involved the role of proton. For the compounds we discussed in the chapter 5, photo irradiation experiments are also needed to study the possible charge transfer and ac susceptibility change for the light excited phase.