

学位論文要旨

Chirality and Magnetism in Metal Organic Frameworks $[\text{Mn}^{\text{II}}(\text{L})]_x[\text{M}^{\text{III}}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$

M = Cr or Mn, L = aspartate, aminoalanine, serine or 1,2-diaminopropane

(配位重合体 $[\text{Mn}^{\text{II}}(\text{L})]_x[\text{M}^{\text{III}}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$ におけるキラリティーと磁性

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In molecular magnets, the structural building blocks are molecules carrying the magnetic moments. These building blocks are either purely organic molecules, coordination compounds or a combination of both. Unlike the conventional magnets, molecular magnets allow more room for design by chemical tailoring, and most are transparent in the visible region. Recently, the exploration for multifunctional molecular magnetic materials to introduce the additional properties to magnetism became significant to satisfy various applications. These combinations mainly include magnetism and electrical and ionic conductivities, optical activity and porosity with guest dependence.

Our main research interest is the chiral magnets which combine structural chirality and magnetism, specifically, we are expecting a chiral magnetic structure by introducing the structural chirality within an ordered magnet. Generally magnetic materials have the parallel ($\uparrow\uparrow$ ferromagnetism) or antiparallel ($\uparrow\downarrow$ antiferromagnetism) spin arrangements determined by the near-neighbor magnetic exchange interaction. When chirality appears in the structure of a magnet, it affects the way that the magnetic moments of unpaired electrons organize themselves through the Dzyaloshinskii-Moriya (DM) interactions which drives the neighbor spins toward perpendicular alignment to each other and thus may stabilize a chiral magnetic structure. The chiral magnets feature several new phenomena like Magneto-chiral dichroism (MChD), chiral spin soliton, and skyrmion.

In this work, we designed the chiral molecular magnets $[\text{Mn}^{\text{II}}(\text{L})]_x[\text{M}^{\text{III}}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$ (M=Mn, Cr; L=chiral ligands) by introducing the chiral ligands into the cyanide-bridged bimetallic Prussian Blue analogues and study the crystal structure and magnetic properties as well as proposing the magnetic structures. This work can be divided into two parts. First, we utilize the amino acid as the ligands which have versatile coordination towards various structures and high dimensional frameworks. Using this approach, two 3D chiral molecular

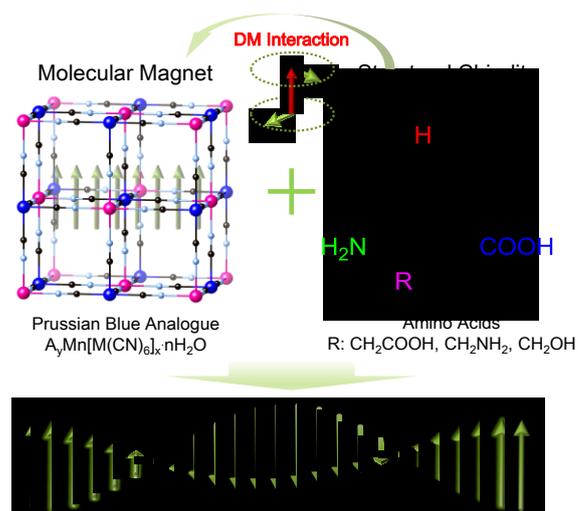


Figure 1. Approach of this study.

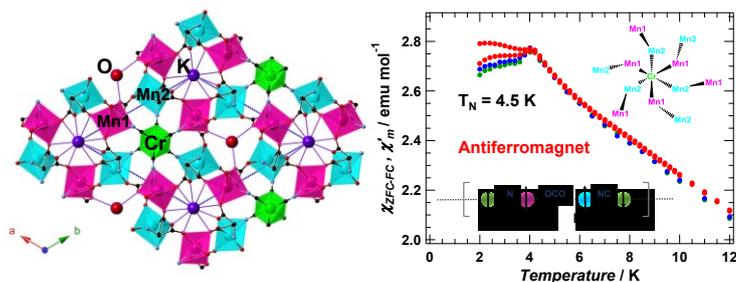


Figure 2. Crystal structure and the magnetic properties of 1.

magnets, $K_3[Mn^{II}(L-asp)]_6[Cr^{III}(CN)_6] \cdot 2H_2O$ (**1**) and $[Cr(CN)_6]_2[Mn_2(L-serK)2H_2O][Mn(L-ser)_{0.5}1.5H_2O] \cdot 3.5H_2O$ (**2**) have been obtained. **1** had the highest Mn-Cr ratio of 6:1 in this type compounds thus results in the largest saturation magnetization. Magnetic study shows **1** is the first CN bridged Mn-Cr antiferromagnet with a ordering temperature of 4.5 K. Crystal **2** has a complex modulated structure caused by the disorder of the *L*-serine or H_2O . After dehydration in a N_2 flow at room temperature, the superlattice disappeared indicating it is generated because of the disorder of water. Through the magnetic measurements, **2** is determined to be a ferrimagnet with $T_C = 53.5$ K which is one of the highest among CN bridged Mn-Cr molecular magnets.

Second, replacing the Cr^{III} by Mn^{III} is expected to improve the magnetic hardness as well as to strengthen the DM interaction. To verify the expected properties, we synthesized $[Mn^{II}(S-pnH)(H_2O)][Mn^{III}(CN)_6]H_2O$ (**3**) which is essentially the same as the reported compound $[Mn^{II}(S-pnH)(H_2O)][Mn^{III}(CN)_6] \cdot 2H_2O$. Single crystal magnetic measurements revealed it show a coercive field of 800 Oe at 2 K which is several 10 times large than that of $[Mn^{II}(S-pnH)(H_2O)][Cr^{III}(CN)_6]H_2O$. It also shows reversibly single-crystal to single-crystal phase transitions without great loss of crystallinity in similar mechanism to that of Mn^{II} - Cr^{III} isomorph. We also obtained the $[\{Mn(D/L-NH_2ala)\}_3\{Mn(CN)_6\}] \cdot 3H_2O$ (**4**) which is the first molecular magnet to show two very different magnetic ground states, spin-glass ($T_N = 7.5$ K) and ferrimagnet ($T_C = 18$ K), for one chiral structure. Crystallographic study indicates the progressive change between the two phases can be attributed to the change of geometry of $Mn(CN)_6$. Applying pressure transforms the spin glass to ferrimagnet while dehydration has the opposite effect. Variable geometry of $Mn(CN)_6$ adds to novel control of magnetism in chiral systems. Additionally, large non-linear AC susceptibilities which is one of the character of the chiral magnet have been confirmed on the ferrimagnetic phase.

Although the lack of neutron diffraction experiments to confirm the chiral magnetic structures, this work brings out several new chiral molecular magnets which demonstrated that: (a) high number of coordinating atoms in the chiral organic ligands increases the ratio of Mn^{II} to Mn^{III} thus increase the saturation magnetization and thus increase the BH_{max} ; (b) introducing anisotropy via ions with high spin-orbit coupling, for instance replacing Cr^{III} by Mn^{III} , increases the coercive field which also can increase the BH_{max} . And in the very special case of $[\{Mn(D/L-NH_2ala)\}_3\{Mn(CN)_6\}] \cdot 3H_2O$, two very distinct magnetic ground states, spin-glass and ferrimagnet have been stabilized for the first time, where the transformation between two states can be controlled by tuning the geometry of $Mn(CN)_6$ by pressure and by dehydration.

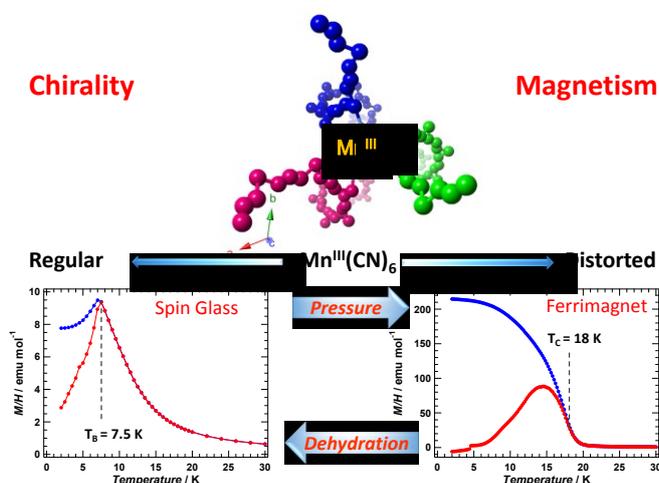


Figure 3. Crystal structure and the relationship between the two magnetic ground states of **4**.