

論文の内容の要旨

Chiral cyanido-bridged Mn–Nb magnets composed of achiral building blocks and their non-linear optical effect

(アキラルな構築素子から成るキラルなシアノ架橋型 Mn–Nb 磁性体及びその非線形光学効果)

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Abstract

1. Introduction

Molecule-based magnets are good candidates for functional magnets because their functionalities can be designed by selecting appropriate components from a large number of building blocks such as metal cations and organic ligands. Compounds which show both chirality and long range magnetic ordering are called chiral magnets. Chiral magnets attract strong attention as functional magnets because they exhibit a cross linking effect between optical and magnetic properties, such as magnetization induced second harmonic generation. There is a considerable number of reports of chiral molecule-based magnets by introducing enantiopure building blocks. However, reports of chiral magnets composed of achiral building blocks by the spontaneous chiral resolution are relatively rare. In 2014, our laboratory reported a chiral photomagnet synthesized from achiral building blocks, $[\text{Fe}(\text{4-bromopyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$. I studied analogues of this compound to obtain new chiral magnets. In my master course study, I prepared metal substituted compounds, $[\text{M}(\text{4-bromopyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ ($M = \text{Mn}, \text{Ni}, \text{Zn}$), and analyzed their crystal structures and magnetic properties. In this work, I will report the synthetic method, crystal structure, magnetic properties and second harmonic generation (SHG) phenomena of octacyanidonioate-based metal assemblies synthesized from achiral building blocks, namely, $[\text{Mn}(\text{4-iodopyridine})_4]_2[\text{Nb}(\text{CN})_8]$ (**MnNbIpy**),

$[\text{Mn}(\text{4-bromopyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot 0.5\text{H}_2\text{O}$ (**MnNbBrpy**), and $[\text{Mn}(\text{4-chloropyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot 0.5\text{H}_2\text{O}$ (**MnNbClpy**). All three compounds show ferrimagnetism. **MnNbIpy** and **MnNbBrpy**, which have chiral structures, show SHG phenomena.

2. Materials

The powder samples of target compounds were synthesized by reacting aqueous solutions of $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ to mixed water–ethanol or aqueous solutions of 4-halopyridine, manganese chloride, and sodium L-ascorbate. Crystalline samples were prepared by using the slow diffusion method. Spectroscopic studies revealed that **MnNbIpy**, **MnNbBrpy**, and **MnNbClpy** contain 4-halopyridine ligands and that the Mn ions are divalent. Elemental analysis show that formulae are $[\text{Mn}(\text{4-iodopyridine})_4]_2[\text{Nb}(\text{CN})_8]$ (for **MnNbIpy**), $[\text{Mn}(\text{4-bromopyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot 0.5\text{H}_2\text{O}$ (for **MnNbBrpy**), and $[\text{Mn}(\text{4-chloropyridine})_4]_2[\text{Nb}(\text{CN})_8] \cdot 0.5\text{H}_2\text{O}$ (for **MnNbClpy**).

Single crystal X-ray structural analysis showed that **MnNbIpy** has a chiral tetragonal structure ($a = b = 20.8730(7) \text{ \AA}$, $c = 14.2157(4) \text{ \AA}$) with a space group $I4_1$ and **MnNbBrpy** also has a chiral tetragonal structure ($a = b = 20.6168(12) \text{ \AA}$, $c = 14.0220(4) \text{ \AA}$) with a space group $I4_122$. This space group $I4_122$ is one of the supergroup of the space group $I4_1$. On the other hand, **MnNbClpy** shows an achiral orthorhombic structure ($a = 13.9379(3) \text{ \AA}$, $b = 26.6853(5) \text{ \AA}$, $c = 31.5931(6) \text{ \AA}$) with a space group $Fddd$.

MnNbIpy, **MnNbBrpy**, and **MnNbClpy** have similar coordination geometries. The Mn^{2+} ions adopt distorted octahedral geometries where four equatorial 4-halopyridine and two axial cyanido N atoms are coordinated and the Nb^{4+} ions adopt distorted square antiprism geometries, where eight cyanido C atoms are coordinated. Among the eight cyanido ligands coordinated to one Nb^{4+} ion, four are bridging ligands to Mn^{2+} ions and the other four are terminal ligands. These compounds show three-dimensional (3-D) cyanido-bridged coordination networks. One Nb^{4+} ion connects to four Nb^{4+} ions via $-\text{CN}-\text{Mn}-\text{NC}-$ moieties.

In these 3-D coordination networks, there are helical structures along the c -axis (for **MnNbIpy** and **MnNbBrpy**) or the a -axis (for **MnNbClpy**). There are two types of helical structures in **MnNbIpy** and **MnNbBrpy**, while only one type is founded in **MnNbClpy**. This differences in the two helical structures are the reasons for chiral structures of **MnNbIpy** and **MnNbBrpy**. There are halogen bondings along the direction of the coordination helices between the halogen atom of the 4-halopyridine ligands and the N atom of the terminal cyanido ligands. Halogen bonding in **MnNbIpy** and **MnNbBrpy** is stronger than that of **MnNbClpy**. In **MnNbIpy** and **MnNbBrpy**, the coordination geometries around the Mn^{2+} ions are distorted by halogen bonding, forming the two types of helical structures that lead to the chiral structure.

3. Magnetic Properties

Magnetic measurements were conducted on the powder samples. The product ($\chi_M T$) of magnetic susceptibility (χ_M) and temperature (T) vs temperature (T) plots ($\chi_M T - T$ plots) show that the $\chi_M T$ values at room temperature are $8.7 \text{ K} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ (for **MnNbIpy**), $8.4 \text{ K} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ (for **MnNbBrpy**), and $8.5 \text{ K} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ (for **MnNbClpy**). These values are

similar to the calculated spin only $\chi_M T$ value ($9.1 \text{ K}\cdot\text{cm}^3\cdot\text{mol}^{-1}$) assuming two Mn^{2+} ($S = 5/2$) and one Nb^{4+} ($S = 1/2$) ions per formula. The field cooled magnetization curves revealed that these three compounds show long range magnetic ordering with the Curie temperatures (T_C) of 22 K, 28 K, and 28 K for **MnNbIpy**, **MnNbBrpy**, and **MnNbClpy**, respectively. Magnetic property measurements show that these three compounds are ferrimagnetic. Magnetization vs. external magnetic field plots show that the saturation magnetization values are close to $9 \mu_B$ for all three compounds, which is the calculated value assuming ferrimagnetism with a $\{\text{Mn}^{\text{II}}_2\text{Nb}^{\text{IV}}_1\}$ unit per formula. Therefore, these compounds are ferrimagnetic, where the magnetic moments of Mn^{2+} and Nb^{4+} ions order antiparallely under the T_C .

4. Second Harmonic Generation Measurement

SHG measurements for **MnNbIpy** and **MnNbBrpy** were conducted because these compounds have chiral structures. The form of SH susceptibility tensors from point group of **MnNbIpy** and **MnNbBrpy** are depicted below.

$$\chi = \begin{pmatrix} 0 & 0 & 0 & \chi_{14} & \chi_{15} & 0 \\ 0 & 0 & 0 & \chi_{15} & -\chi_{14} & 0 \\ \chi_{31} & \chi_{31} & \chi_{33} & 0 & 0 & 0 \end{pmatrix} \quad (\text{for } \mathbf{MnNbIpy})$$

$$\chi = \begin{pmatrix} 0 & 0 & 0 & \chi_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\chi_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (\text{for } \mathbf{MnNbBrpy})$$

A 775 nm laser light, derived from a frequency doubled Ti:sapphire laser passed through filters, was focused and irradiated on the samples. The reflected light was passed through filters to remove the fundamental light and focused into a photomultiplier tube equipped with a band pass filter. The power of the 775 nm irradiated laser light was altered by changing neutral density filters. The observed light is monochromatic at 388 nm, and represent quadratic function of the power of the fundamental light well. These characteristics show the observed lights are SH light. **MnNbIpy** shows stronger SH light than that of **MnNbBrpy**, probably due to the difference of the number of non-zero elements of the SH susceptibility tensor resulting from the space group difference.

5. Conclusion

I synthesized three cyanido-bridged magnetic materials from achiral building blocks. **MnNbIpy** and **MnNbBrpy** are chiral compounds and **MnNbClpy** is an achiral compound. These three compounds have three dimensional coordination networks and similar coordination geometries. Magnetic property measurements revealed that these three compounds are ferrimagnetic where magnetic moments on Mn^{II} and Nb^{IV} order antiparallely and the T_C values are 22 K, 28 K, and 28 K for **MnNbIpy**, **MnNbBrpy**, and **MnNbClpy**, respectively. Additionally, thanks to the chiral structures, **MnNbIpy** and **MnNbBrpy** exhibit SHG phenomena. The results suggest that halogen bondings are worth considering as fine tuning to make a chiral structure in molecule-based magnets.