Fabrication and magnetic properties of columnar liquid crystals based on holmium dinuclear complexes

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Keywords: holmium, liquid crystal, magnetic material
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Abstract
Lanthanide elements are known to exhibit unique functions such as luminescence and magnetic properties. In this study, we fabricated the magnetic liquid crystal material based on holmium dinuclear complexes. It was found that the obtained dinuclear complexes formed hexagonal columnar phase and showed improved magnetic properties compared to the mononuclear complexes.

1. Introduction
Lanthanide elements exhibit unique luminescence and magnetic properties derived from 4f orbital electrons that are not involved in bonding. We have reported magnetic field-responsive polymeric materials using holmium (Ho), one of the lanthanide elements, which has a high magnetic moment[1,2)]. Recently, we have been working on the preparation of liquid crystal materials based on Ho complexes using Ho as the central metal. The resulting mononuclear complexes were found to self-organize into different ordered structures such as tetragonal columnar (Col_t) and cubic (Cub) phases, depending on the length of alkoxy side chains on the ligands (**Figure 1a**). In this work, we fabricated the Ho dinuclear complex **[HoC8(6)]$_2$bpm** with two Ho elements in a molecule to create new molecular assemblies with excellent magnetic properties. **[HoC8(6)]$_2$bpm** was prepared by reacting 2,2'-bipyrimidine (bpm) and the mononuclear complex **HoC8(6)**, which exhibits Cub phase. We investigated self-assembly behavior of **[HoC8(6)]$_2$bpm** and its magnetic properties.

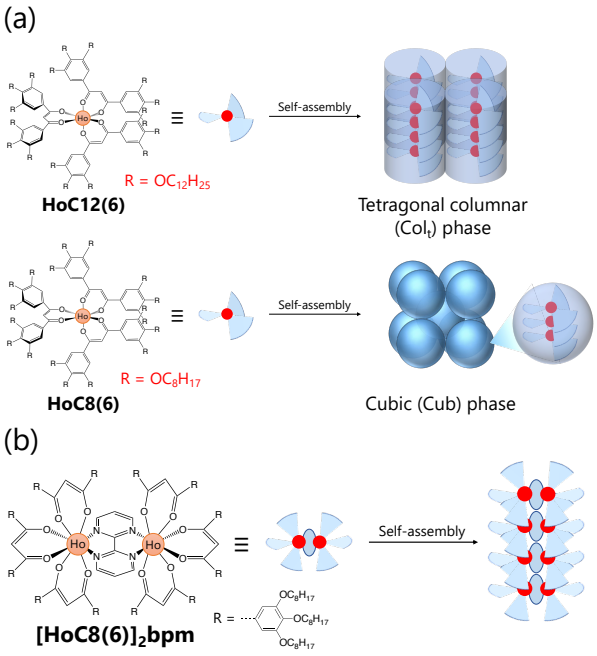

Figure 1. (a) Previous work and (b) this work.

2. Experiment
[HoC8(6)]$_2$bpm was prepared by coordination with **HoC8(6)** and bpm at 2:1 molar ratio. The formation of **[HoC8(6)]$_2$bpm** was confirmed by elemental analysis. The assembled structure of **[HoC8(6)]$_2$bpm** was investigated by polarized optical microscopy (POM) and X-ray

diffraction (XRD). The magnetic properties were evaluated by superconducting quantum interference device (SQUID).

3. Results and discussion

The good agreement between the calculated and measured values of elemental analysis suggested that **[HoC8(6)]$_2$bpm** formed the dinuclear Ho complexes with the expected composition. POM observation of **[HoC8(6)]$_2$bpm** showed optical texture, suggesting that the dinuclear complexes formed anisotropic liquid crystal phase at room temperature (**Figure 2a**). Therefore, it was found that the structural change from mononuclear to dinuclear complex altered self-assembly behavior of the complexes. Several peaks were observed from XRD measurements and the Miller indices were attributed to hexagonal columnar (Col$_h$) phase (**Figure 2b**). Generally, molecules with large aspect ratio tend to form columnar structures due to the effective interaction between the molecules. **[HoC8(6)]$_2$bpm** has larger molecular aspect ratio than **HoC8(6)**, which is thought to facilitate columnar stacking over long distances. SQUID measurements showed a linear plot of mass magnetization versus the external magnetic field, confirming that **[HoC8(6)]$_2$bpm** is paramagnetic at room temperature (**Figure 3**). Moreover, the values of the mass susceptibility of **[HoC8(6)]$_2$bpm** and **HoC8(6)** were 0.200 and 0.157 m^3 kg^{-1}, respectively, indicating that the dinuclear complex has improved magnetic properties compared to the mononuclear complex.

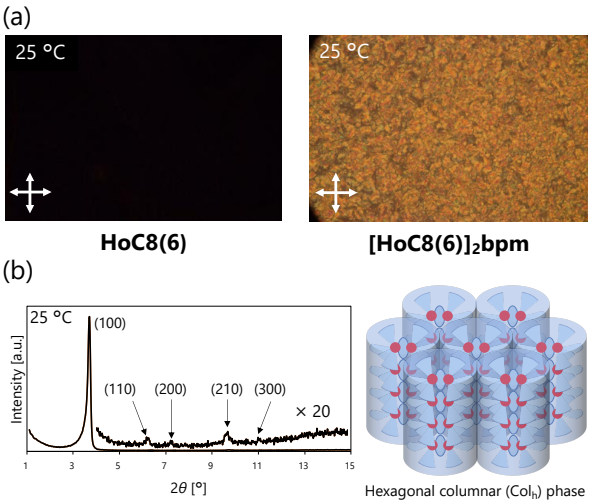

Figure 2. (a) POM images of **HoC8(6)** and **[HoC8(6)]$_2$bpm**. (b) XRD pattern of **[HoC8(6)]$_2$bpm** and diagram of Col$_h$ phase.

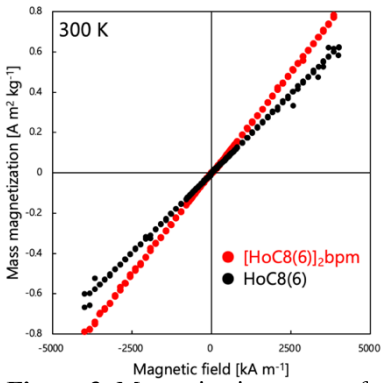

Figure 3. Magnetization curve of **[HoC8(6)]$_2$bpm** and **HoC8(6)**.

4. Conclusions

In summary, we fabricated the Ho dinuclear complex and confirmed that **[HoC8(6)]$_2$bpm** exhibited Col$_h$ phase. Furthermore, **[HoC8(6)]$_2$bpm** showed larger mass susceptibility than **HoC8(6)**, indicating that we succeeded in fabrication of a new magnetic liquid crystal material with superior magnetism.

Acknowledgments

We acknowledge Prof. Hirofumi Kanoh of Chiba University for the SQUID measurements.

References

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2) K. Kohaku et al., ACS. Appl. Polym. Matter., 2, 1800–1806 (2020). DOI: https://pubs.acs.org/doi/full/10.1021/acsapm.0c00038