

Synthesis of cyanide-bridged metal complex clusters with polar structures

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Cyanide-based organic inorganic hybrid materials (OIHM) have attracted much attention due to their functionalities such as phonon, optical, magnetic and ferroelectric properties.^[1] They form mainly double metal ion type with the general formula of $A_2MM'(CN)_6$, where A = organic cation; M = alkali metal cation and M' = transition metal ion. However, such cyanide-based OIHM have been synthesized by using highly symmetric cyanide metal complex units. In this study, we focused on asymmetric metal complex $[MnN(CN)_4]^{2-}$ for constructing new polar cyanide-anion based OIHM.

Herein, we synthesized $(NEt_4)_{1.75}Rb_{0.25}[MnN(CN)_4]$ (**1**). Single crystal X-ray structural analysis for **1** at 100 K shows that **1** consists of cyanide-bridged tetranuclear clusters by self-clustering of $[MnN(CN)_4]^{2-}$ units (**Fig 1**). The tetranuclear clusters incorporate one Rb cation, thereby they have a unique Janus-type anisotropic structure. The anisotropic clusters arrange same directions in **1** to form polar crystal (Space group: $P4$). In order to investigate the phase transition behavior, we carried out differential scanning calorimetry (DSC) measurement. DSC curves for **1** show several anomalies involving solid-solid phase transition (**Fig 2**). Furthermore, other alkali metal cations such as Na^+ , K^+ and Cs^+ have also been used to synthesize the cyanide-based OIHM to investigate their assembled structures.

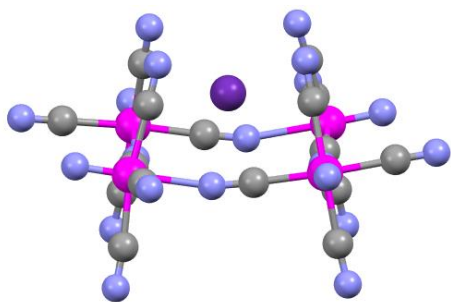


Fig 1. The structure of a polar cluster in **1**

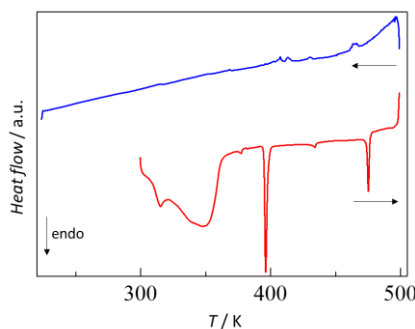


Fig 2. DSC curves of **1**

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