

## Development of 3d-4f heterometallic polynuclear complexes with a large magnetocaloric effect

(<sup>1</sup> Graduate School of Pure and Applied Sciences, University of Tsukuba) ○Takuya Shiga,<sup>1</sup> Haruka Miyamoto,<sup>1</sup> Honami Ito,<sup>1</sup> Hiroki Oshio,<sup>1</sup> Masayuki Nihei<sup>1</sup>

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Heterometallic polynuclear complexes exhibit interesting physical properties and functions derived from their unique electronic and magnetic interactions. Control of the molecular structures, electronic states, and magnetic properties is important for the construction of functional molecular materials.

In this work, a series of planar 3d-4f mixed-metal tetranuclear complexes,  $[M^{II}_3Ln^{III}(L)_3(X)_m](Y)_n$  ( $M = Cu, Ni, Co, Mn, Zn$ ;  $Ln = La, Gd, Dy, Tb$ ;  $X$  and  $Y = NO_3^-, solv.$ ), were synthesized by using a tetraketone ligand  $H_2L$  ((3*z*,5*z*)-4,5-dihydroxy-3,5-octadiene-2,7-dione) (Fig. 1a). X-ray structural analyses of all complexes reveal the complexes have planar triangular structures comprised of three deprotonated ligand  $L^{2-}$ , three 3d metal ions, and one 4f metal ion (Fig. 1b).

The cryomagnetic study revealed that ferromagnetic interactions between  $M$  and  $Ln$  ions except for the case of diamagnetic  $M = Zn$  and  $Ln = La$  were operative. In the case of  $[Cu_3Tb]$ ,  $[Cu_3Dy]$ , and  $[Co_3Tb]$  complexes, single-molecule magnet behavior was observed.  $[Mn_3La]$  complex shows very weak antiferromagnetic interactions between terminal  $Mn(II)$  ions, which has  $S = 5/2 + 5/2 + 5/2$  spin ground state. On the other hand,  $[Mn_3Gd]$  complex shows relatively strong ferromagnetic interactions between  $Mn(II)$  and  $Gd(III)$  ions, which has  $S = 11$  spin ground state (Fig. 1c). The magnetic entropy change of  $[Mn_3Gd]$  complex was measured, and the large  $\Delta S = 66.3 \text{ J kg}^{-1} \text{ K}^{-1}$  was observed at 4.5 K under 5 T. We believe that the developments of discrete polynuclear complexes with giant magnetocaloric effect will have an impact on material designs for low-temperature magnetic refrigeration.

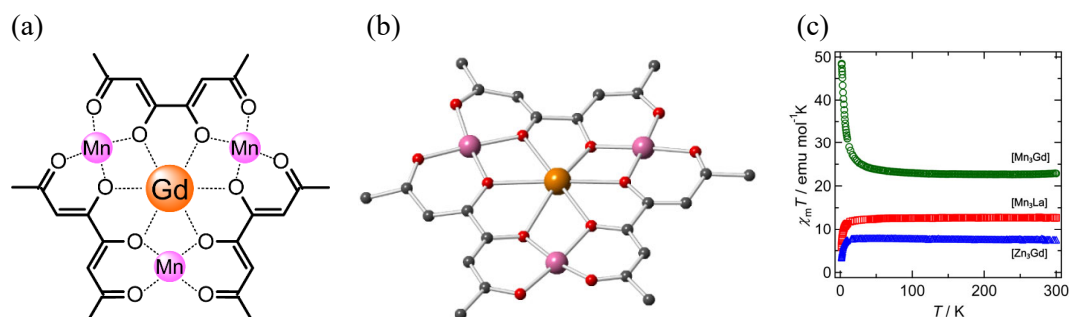


Fig. 1 (a) Schematic drawing of  $[Mn_3Gd]$  complex, (b) Crystallographic structure of  $[Mn_3Gd]$  complex, (c) Magnetic properties of  $[Mn_3Gd]$ ,  $[Mn_3La]$ , and  $[Zn_3Gd]$  complex.