High-Frequency/Field Electron Paramagnetic Resonance and High-Field Magnetization Studies on Wheel-like Clusters

Abstract: A family of 3d-4f wheel-like clusters {Fe_8Ln_8} (Ln = Gd, Tb, Dy, Ho, Er) and a giant 4f wheel-like cluster {Dy_{20}} were isolated and studied by high-frequency/field electron paramagnetic resonance (HF-EPR) and high-field magnetization. HF-EPR spectra aere observed in {Fe_8Ln_8}, which can help to exact the magnetic exchange-coupling constants, while magnetic hysteresis loops were observed for {Dy_{20}}, indicating a wheel-like single-molecule magnet.

Wheel-like clusters sometimes display fantastic magnetic properties because of their non-collinear arrangement of their spins. For example, the giant hetero-spin ring {Cr_8Dy_8} is a single-molecule magnet with open magnetic hysteresis loop at 0.5 K [1]. Toroidal behavior were observed in {$CrTb_6$} and {$CrHo_6$} molecules at low temperatures [2], and {$CrDy_6$} analogy displays a ferrotoroidic ground state [3]. Such behaviors are probably arising from magnetic coupling with strong single-ion anisotropy. Understanding of the exchange coupling in wheel-like clusters is of great importance to design complexes with toroidal moments and molecule-based multiferroics.

Herein, A series of hexadenuclear heterometallic wheel-like molecular clusters {Fe_8Ln_8} (Ln = Gd, Tb, Dy, Ho, Er, Y) and a family of giant lanthanide {Dy_{20}} were isolated. Their structures were studied by single crystal X-ray diffraction, revealing similar giant ring structure for all complexes. High-frequency/field electron paramagnetic resonance (HF-EPR) and high-field magnetization measurements were carried out for those complexes at low temperature to investigate the exchange coupling in those wheel-like clusters.

Fig.1 shows HF-EPR spectra at 4.2 K for {Fe_8Gd_8} (1a), {Fe_8Tb_8} (1b), {Fe_8Dy_8} (1c), {Fe_8Ho_8} (1d), and {Fe_8Er_8} (1e) with crystal structure for {Fe_8Ln_8} (1f). From the crystal structure, the Fe(III) ions and Ln(III) ions are arranged alternately to form a ring. The Fe···Ln separations are in the range from 3.39 to 3.48Å. To get the exchange couplings in those clusters, both magnetic and HF-EPR measurements were carried out. In the {Fe_8Gd_8} system, ferromagnetic interactions between Fe-Gd metal centers were found to be dominant from the magnetic susceptibilities, while with HF-EPR studies, the level-crossing field (H_C), together with the *g* factor and energy gap (ΔE) can be determined from extrapolation in these plots (Figure 1 and table 1). Combined with the magnetic susceptibilities, we are going to determine the exchange couplings between Fe(III) ions and Ln(III) ions with the method reported by Prof. Hiroyuki Nojiri et al .[4-5].

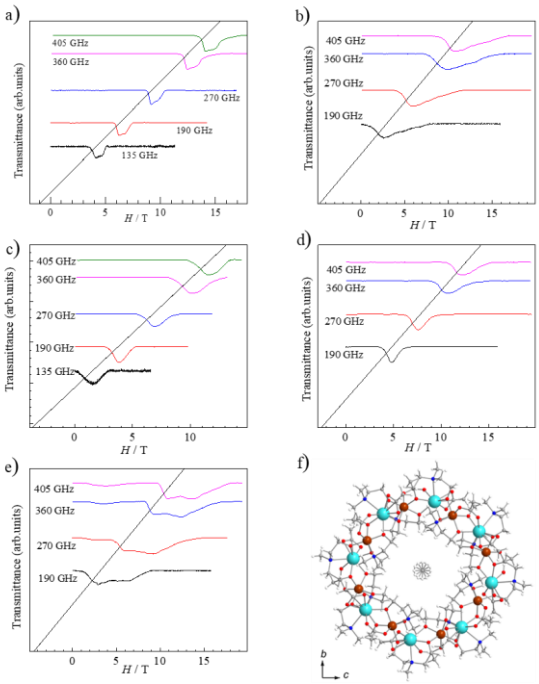

Fig. 1 Selected HF-EPR spectra of [Fe_8Ln_8] measured at 4.2 K [Ln = (a) Gd, (b) Tb, (c) Dy, (d) Ho and (e) Er]. The spectra are offset in a linear scale of the frequency. Straight line are drawn from the linear fitting in the frequency field plot. (f) Ball-and-stick modes of the molecular structures of {Fe_8Ln_8} wheels.

Table 1 The level-crossing fields (H_C) and energy gap (ΔE) from linear fitting in the frequency field plot for {Fe_8Ln_8} wheels.

	Fe_8Gd_8	Fe_8Tb_8	Fe_8Dy_8	Fe_8Ho_8	Fe_8Er_8
H_C / T	-0.60	-4.35	-3.30	-2.18	-4.02
ΔE/GHz	16.45	111.72	88.32	58.45	105.35

The structure of another wheel-like cluster {Dy_{20}} was shown in the Fig 2a, which is consisting of 20 Dy(III) ions bridged by 20 piv and 30 2-pa ligands with central water molecules and inner pyridine rings as template and terminal OH^- groups to balance the positive charge. At 0.45 K, magnetic hysteresis loops can be clearly observed (Fig 2b), which is indicative of a single-molecule magnet. Such behavior is in good agreement with its temperature dependent ac susceptibility data above 2 K, in which tail of out-of-phase signals can be observed. The energy barrier is probably very low with strong quantum tunnelling of the magnetization.

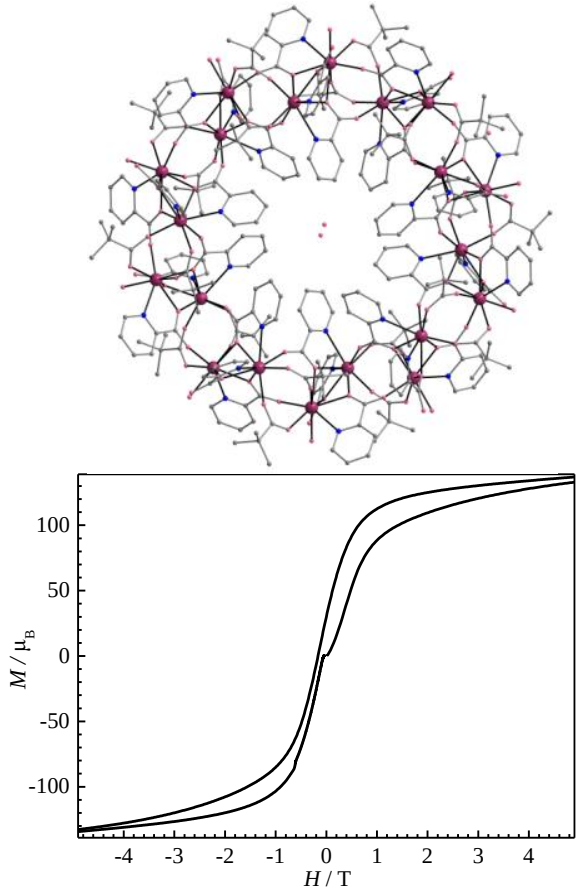

Fig. 2 (a) Molecular structure of {Dy_{20}}. Color code: Ln, purple; O, pink; N, blue; C, grey. (b) Magnetic hysteresis loop at 0.45 K for {Dy_{20}}

also carried out for a three-coordinated Fe(III) momer {$Fe(NTMS_2)_3$}, a two-coordinated Cr(II) momer {$Cr(SDipp)_2$} and a giant 3d-4f cluster {$Ni_{36}Ln_{96}$}. High-field magnetization measurements were carried for wheel-like molecular clusters {Fe_8Ln_8} (Ln = Gd, Tb, Dy, Ho, Er, Y). Analysis of those data were undergoing and we believed we believe we can get a lot of useful information from those data.

In conclusion, we got some HF-EPR spectra and high-field magnetizations for two kinds of wheel-like clusters. With magnetic susceptibilities and theoretical studies, we will have a clear understanding about electronic structure in those wheel-like clusters. With better and clearer understanding of the magneto-structural correlation, electronic structure and energy levels of those wheel-like clusters, single-molecule toroidal behavior may be clarified. We wish to publish three research papers in high-profile journals using these results.

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