



Double and triple pyridine-*N*-oxide bridged dinuclear Dysprosium(III) dimers and single-molecule magnetic properties

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ABSTRACT

A series of dinuclear lanthanide complexes bridged by three pyridine-*N*-oxide (PyNO) ligands with formula $[\text{Dy}_2(\text{hfac})_6(4\text{-cpyNO})_3] \cdot 4\text{H}_2\text{O}$ (**Dy1**), $[\text{Gd}_2(\text{hfac})_6(4\text{-cpyNO})_3] \cdot 4\text{H}_2\text{O}$ (**Gd1**), $[\text{Dy}_2(\text{hfac})_6(4\text{-mepyNO})_3]$ (**Dy2**), $[\text{Gd}_2(\text{hfac})_6(4\text{-mepyNO})_3]$ (**Gd2**) ($\text{hfac}^- = \text{hexafluoroacetylacetonate}$, $4\text{-cpyNO} = 4\text{-cyanopyridine } N\text{-oxide}$, $4\text{-mepyNO} = 4\text{-Methylpyridine } N\text{-oxide}$), and series of dinuclear lanthanide complexes bridged by two PyNO ligands with formula $[\text{Dy}_2(\text{hfac})_6(4\text{-cpyNO})_2]$ (**Dy3**), $[\text{Y}_2(\text{hfac})_6(4\text{-cpyNO})_2]$ (**Y1**), $[\text{Gd}_2(\text{hfac})_6(4\text{-cpyNO})_2]$ (**Gd3**), $[\text{Dy}_2(\text{hfac})_6(4\text{-mepyNO})_2]$ (**Dy4**), $[\text{Y}_2(\text{hfac})_6(4\text{-mepyNO})_2]$ (**Y2**), $[\text{Gd}_2(\text{hfac})_6(4\text{-mepyNO})_2]$ (**Gd4**), were structurally and magnetically characterized. The crystal structures revealed that pyridine-*N*-oxide serves as an effective bridge to link two Ln(III) centers, and periphery β -diketonate ligands complete the coordination sphere. The number of PyNO bridge can be rationally controlled by the stoichiometric ratio of reagents, which leads to different local coordination models and intramolecular Ln-Ln distances. Furthermore, elaborate modulation on the strength of magnetic coupling transmitted by PyNO bridge was successfully carried out by introducing electron-donating or -withdrawing substituents on the bridge ligand backbone. Magnetic measurements revealed that complex **Dy3** displayed significant double zero-field slow magnetic relaxation process, while **Dy1** and **Dy2** showed field-induced SMM behavior. Significantly enhanced SMMs performance was observed in **Dy4** with a hysteresis temperature of 2.5 K. The distinct slow magnetic relaxation behaviors were strongly related to their different individual Dy(III) ion magnetic anisotropy and Dy(III)-Dy(III) coupling, which were further confirmed by *ab initio* calculation.

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1. Introduction

The lanthanide-based single-molecule magnets (SMMs) or mononuclear SMMs also refer to single-ion magnets (SIMs) are attracting increasing interest due to their potential applications in high-density information storage, spintronics devices [1–6], quantum computing [7] and magnetic refrigeration [8]. Increasing the total spin *S* and retaining and aligning the high anisotropy of

individual ions are supposed to be effective strategies to achieve the high blocking temperature (T_B) and anisotropic energy barrier (U_{eff}) for the magnetization reversal [9]. Since the first double decker phthalocyanine (Pc) complex TbPc_2 show slow relaxation of the magnetization [9], a variety of lanthanide-containing SMMs were reported in the literature [10]. To date, both the highest energy barriers and hysteresis temperature are recorded by the lanthanide-based SMMs [11–17]. The record of U_{eff} has been broken continually, more than 1000 K [16,17b,c] until now, and the highest T_B increased from 14 K [13c] up to 20 K [18] for the dinuclear Ln_2 SMMs. More strikingly, the higher T_B of mononuclear Dy-based SMMs have reached from 20 K [15] quickly up to 60 K T_B [17b,c] recently. Despite it is an efficient way to improve the relaxation performance of SIMs by tuning the symmetry and strength of the

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local ligand field, however, it is difficult to build such SMMs like the pentagonal bipyramidal Dy(III) single-ion magnets (SIMs) because lanthanide-based complexes usually possess high coordination number and flexible coordination modes [15–17a]. On the other hand, it is also an efficient way to enhance the whole molecular magnetic anisotropy by introducing magnetic exchange interactions, especially for the dinuclear lanthanide systems, the $20 K T_B$ was recorded by a dinuclear Tb_2N_2 system with strong magnetic exchange coupling [18]. Although it has been proved that introducing radical ligands was successful in providing strong exchange interactions, the exploration and further application of such radicals are limited because it is rarely found to directly bridge Ln(III) ions and difficult to isolate [13b,c,18,19,27c]. Compared to the radical ligand, the corresponding neutral ligand could provide proper exchange interactions, albeit it is weak but enough to influence the magnetic anisotropy of the whole molecule [20,21a]. Obviously, it is highly expected to enhance the SMM performance by establishing the high local axial symmetry in combination with appropriate intramolecular coupling. However, it is actually difficult to generate this joint effect, especially for lanthanide ions which are liable to form the high coordination numbers and low local coordination symmetry surrounding 4f ions.

This is a way to enhance molecule magnetic anisotropy by controlling the number of bridges in dinuclear SMMs to lengthen or shorten the distance between two spin centers, and consequently modulating the strength of intramolecular coupling. Pyridine-*N*-oxide compounds are these efficient ligands to bridge two lanthanide ion centers, and the corresponding double and/or triple bridged dinuclear lanthanide-based SMM systems are reported recently in which the neutral PyNO ligands serve as the ideal candidates for introducing magnetic exchange interactions [21].

In this work, neutral 4-RpyNO ligands (R = –CN, –CH₃) are utilized to form series of dinuclear Ln(III) complexes with two modes

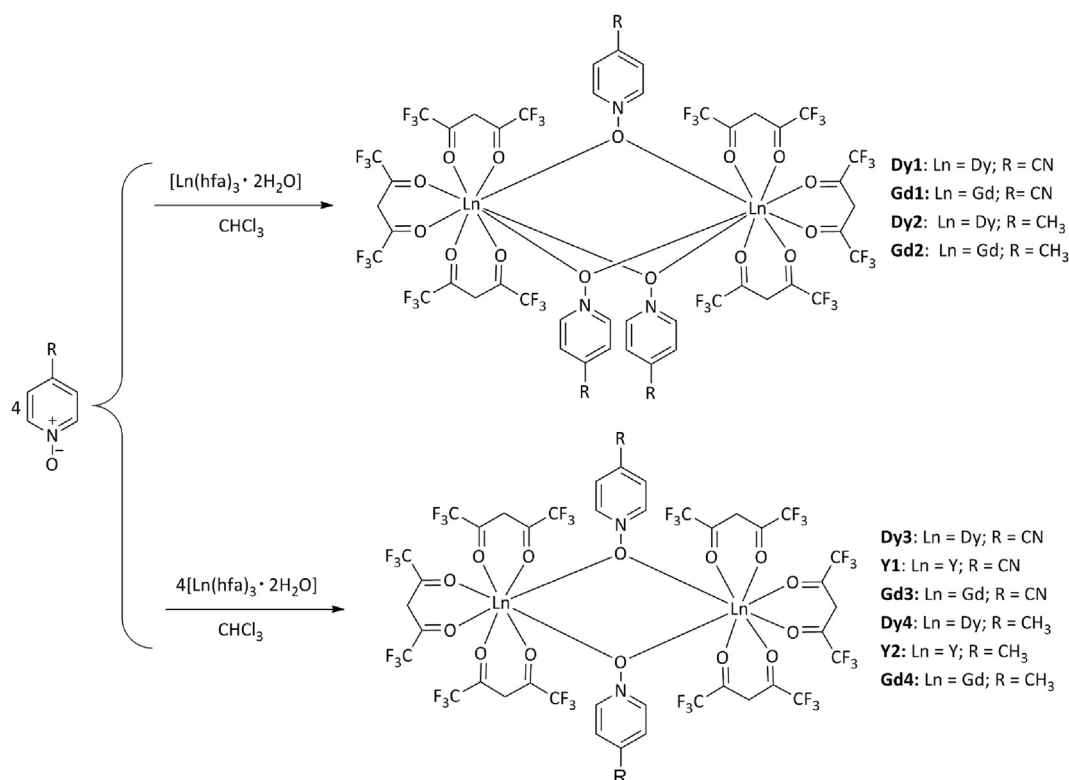
(Scheme 1). One is triple bridged mode, another is double bridged mode, in which three and two 4-RpyNO ligands bridge two Ln(III) ions, respectively. The distinct bridged modes lead to different structures and slow magnetic relaxation behaviors. Although similar double and/or triple bridged systems were reported before, these works are only a separate study of the double or three bridge systems [21,22]. For this work, the favourable Dy(III)–Dy(III) coupling in combination with the individual coordination symmetry result in the improvement from field-induced SMMs to the zero-field SMMs. We described herein the preparations, structures and SMM properties of the following Ln(III) complexes [Dy₂(hfac)₆(4-cpyNO)₃·4H₂O (**Dy1**), [Gd₂(hfac)₆(4-cpyNO)₃·4H₂O (**Gd1**), [Dy₂(hfac)₆(4-mepyNO)₃] (**Dy2**), [Gd₂(hfac)₆(4-mepyNO)₃] (**Gd2**), [Dy₂(hfac)₆(4-cpyNO)₂] (**Dy3**), [Y₂(hfac)₆(4-cpyNO)₂] (**Y1**), [Gd₂(hfac)₆(4-cpyNO)₂] (**Gd3**), [Dy₂(hfac)₆(4-mepyNO)₂] (**Dy4**), [Y₂(hfac)₆(4-mepyNO)₂] (**Y2**), [Gd₂(hfac)₆(4-mepyNO)₂] (**Gd4**) (hfac[−] = hexafluoroacetate, 4-cpyNO = 4-cyanopyridine *N*-oxide, 4-mepyNO = 4-Methylpyridine *N*-oxide) and the impact of the modulation of PyNO bridge on the magnetic relaxations was discussed.

2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents were obtained from commercial sources and used as received without further purification. All complexes were characterized by IR spectroscopy (Fig. S1[†]). The phase purity of the bulk samples were confirmed by XRD analyses as shown in Fig. S2[†].

Elemental analyses (EA) for C, H and N were performed using a Perkin-Elmer 2400 analyzer. Fourier transform (FT) IR spectra were recorded using a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr pellets. The elements (Dy, Y) were



Scheme 1. The syntheses of all complexes.

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