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A Purely Lanthanide-Based Complex Exhibiting Ferromagnetic Coupling and Slow Magnetic Relaxation Behavior

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Two lanthanide−organic frameworks, $\{\mathrm{Ln(TDA)_{1.5}(H_2O)_2}\}_n$ [TDA = thiophene-2,5-dicarboxylic acid anion; Ln = Gd (**1**), Dy (**2**)], were structurally and magnetically characterized. The magnetic studies revealed that the ferromagnetic coupling existed between adjacent lanthanide ions in **1** and **2**, and only **2** displays slow magnetic relaxation behavior with $\tau_0 = 2.4 \times 10^{-8}$ s and $\Delta E/k_B = 44.2$ K. To our knowledge, it is rather rare that ferromagnetic coupling and slow magnetic relaxation coexist in three-dimensional lanthanide-based frameworks.

The magnetic explorations of complexes associated with lanthanide ions, especially for single-molecule magnets (SMMs) and single-chain magnets (SCMs), have attracted more and more attention because they were considered as appealing candidates for future devices.[1] Taking advantage of the strong easy-axis-type magnetic anisotropy and larger J ($L + S$) value originating from lanthanide ions, both physicists and chemists joined their efforts to fabricate and magnetically characterize these kinds of compounds, and many excellent reports witnessed the remarkable progress of this field.[2−13] Noticeably, the most of these investigations focused on heteronuclear compounds based on langthanide and transition-metal ions or radicals. For example, the SMMs displaying slow magnetization relaxation behavior include the $\{\mathrm{Dy^{III}Mn^{III}}\}$ and $\{\mathrm{Ce^{IV}Mn^{III}}\}$ series from Christou's group[2] and Pecoraro's group,[3] the $\{\mathrm{Tb^{III}Cu^{II}}\}$ series reported by Matsumoto's group[4a] and Costes' group,[4b,c] the $\{\mathrm{Dy^{III}Cu^{II}}\}$ series of Sessoli's group,[5] Ishida's group,[6] and Luneau's group,[7] the $\{\mathrm{Dy^{III}Fe^{III}}\}$ series of Yamashita's group,[8] the $\{\mathrm{Mn^{III}Gd^{III}}\}$[9a] and $\{\mathrm{Mn^{III}Mn^{IV}Ln^{III}}\}$[9b] systems of Powell's group, and the $\{\mathrm{Co(Ni)^{II}Ln^{III}}\}$ series of Chandrasekhar's group,[10] and the SCMs include lanthanide- and radical-based systems reported by Gatteschi's group.[11] Only several purely lanthanide-based systems were reported by Powell's group,[9c,d] Ishikawa's group,[12] and Coronado's group.[13] Although the magnetic studies of lanthanide-based complexes have been well documented, it was hardly observed that ferromagnetic coupling and slow magnetic relaxation coexisted in three-dimensional (3D) lanthanide-based frameworks.

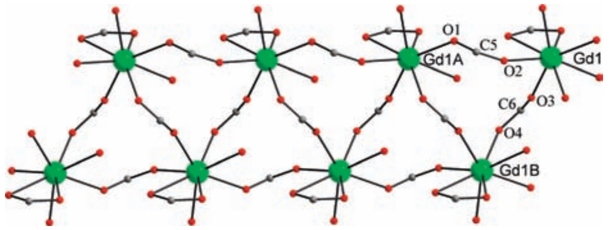

Figure 1. Along the *b* direction, a 1D beltlike chain constructed by the triangular $\{\mathrm{Gd_3}\}$ motif as a repeat unit. Color codes: green, Gd; red, O; gray, C. Other atoms were omitted for clarity.

In this contribution, two lanthanide−organic frameworks, $\{\mathrm{Ln(TDA)_{1.5}(H_2O)_2}\}_n$ [TDA = thiophene-2,5-dicarboxylic acid anion; Ln = Gd (**1**), Dy (**2**)],[14] were structurally and magnetically characterized. The results revealed that the ferromagnetic coupling existed between adjacent lanthanide ions in **1** and **2**. Interestingly, further magnetic analysis exhibits that **2** displays slow magnetic relaxation behavior, and to the best of our knowledge, it is rather rare that ferromagnetic coupling and slow magnetic relaxation coexist in three-dimensional lanthanide-based frameworks.

The structural analyses reveal that complexes **1** and **2** are isomorphous with space group *C*2/*c* and the structure of complex **1** described here representatively. The asymmetric unit in complex **1** [Figure S1 in the Supporting Information (SI)] consists of one unique $\mathrm{Gd^{3+}}$, one and half TDA molecules, and two coordinated water molecules. The coordination geometry around the eight-coordinated $\mathrm{Gd^{3+}}$ is a distorted bicapped trigonal prism (Figure S1 in the SI). The bond length of Gd−O falls into the range from 2.304(2) to 2.550(2) Å. Three adjacent $\mathrm{Gd^{3+}}$ ions are bridged only by carboxylic groups to generate a triangular $\{\mathrm{Gd_3}\}$ motif with nearly identical edges [Gd1−Gd1A, 5.790(4) Å; Gd1−Gd1B, 5.966(4) Å; Gd1B−Gd1A, 5.966(4) Å]. Along the *b* direction, the $\{\mathrm{Gd_3}\}$ motif as a repeat unit was connected into a one-dimensional (1D) beltlike chain by carboxylic groups (Figure 1). The TDA molecules in **1** exist in

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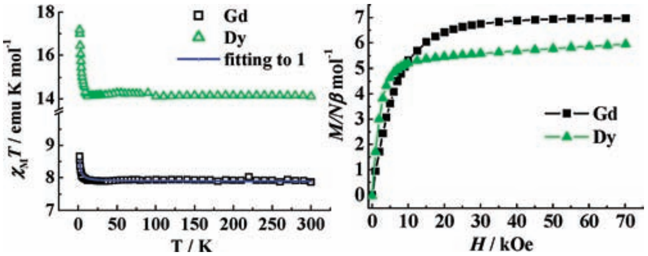

Figure 2. (Left) Plots of variable-temperature magnetic susceptibilities of **1** and **2** in the form of $\chi_M T$ vs T. (Right) Field dependence of magnetization of complexes **1** and **2** at 1.8 K.

two kinds of coordination modes (Figure S2 in the SI). By the two coordination modes of TDA molecules, the adjacent chains are further constructed into a highly ordered 3D framework (Figure S4 in the SI), and among neighboring chains bridged by TDA molecules, the shortest Gd···Gd separation between adjacent chains is about 9.2 Å.

The magnetic properties of complexes **1** and **2** were measured on microcrystalline samples using a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. Variable-temperature magnetic susceptibilities in the temperature range 1.8−300 K at an applied field of 1 kOe were investigated, and the $\chi_M T$ vs T plots are shown in Figure 2. For complex **1**, the $\chi_M T$ value almost keeps a constant of 7.90 emu·K·mol^{-1} in a large temperature range from 300 to 12 K, which is fairly close to the value of 7.88 emu·K·mol^{-1} based on one spin-only Gd^{3+} ion. Below 10 K, the $\chi_M T$ value sharply goes up with system cooling, but only a very small increase was observed, which reaches 8.65 emu·K·mol^{-1} at 1.8 K, indicating the presence of weak ferromagnetic coupling between Gd^{3+} ions. No appropriate theory model to analyze the magnetic property of the beltlike chain was reported. To estimate the coupling interaction, Hatfield's deduction[15a] is used here: the alternating chain model can be extended to a ladderlike chain. According to the structure of **1**, there are only two kinds of bridges between Gd^{3+} in the beltlike chain: an edged one, O1C5O2, and a gridded one, O3C6O4. So, this beltlike chain is very similar to the ladder in Hatfield's report. Thus, J_{edge} and J_{grid} are roughly calculated using the alternative chain model reported by Cortés et al.,[15b] as shown in Figure 2, and the best-fitting results give $g = 1.98$, $J_{edge} = J_{grid} = 0.0065$ cm^{-1}, and $zj' = 0$ with $R = 2 \times 10^{-3}$ ($R = \sum[(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2 / \sum(\chi_M T)_{obs}{}^2$), where zj' is the interchain interaction as a correction by the molecule field theory. This result indicates that the ferromagnetic coupling between adjacent Gd^{3+} ions within the chain is very weak and there is no remarkable magnetic interaction between chains. Two equal coupling constants within the chain may be attributed to the same bridging style of all carboxylic bridges.

For complex **2**, the $\chi_M T$ value at room temperature is nearly equal to the expected value of 14.17 emu·K·mol^{-1} (Figure 2) for one Dy^{3+} ion with the ground state $^6H_{15/2}$ and $g = {}^4/_3$.[16] With decreasing temperature, the $\chi_M T$ value almost remains unchanged from 300 to 10 K, and upon further cooling, the $\chi_M T$ value dramatically increases to a maximum of 17.18 emu·K·mol^{-1} at 1.8 K. This behavior indicates that spin−orbital coupling leads the 4f^n configuration of Ln^{3+} to split into $^{2S+1}L_J$ states, and further into Stark components under the crystal-field perturbation, and the effect of depopulation of the Stark components of Dy^{3+} is nearly equal of the ferromagnetic coupling between Dy^{3+} ions in the higher temperature range. The increase of $\chi_M T$ in the low-temperature range obviously implies the presence of ferromagnetic coupling between Dy^{3+} ions within the chain in **2**, and it is strong enough to overcome the effect of depopulation of the Stark components of Dy^{3+}.

The magnetizations of **1** and **2** vs field were measured at 1.8 K (Figure 2). Below 4 kOe, both of them increase sharply and the slope is very steep. Above this field, the magnetization of **1** increases slowly, reaching a saturation value of 7.0 μ_B at 30 kOe. Also, the magnetization curve confirms the ferromagnetic coupling in **1**, but the coupling interaction is very weak because

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(14) Syntheses for **1** and **2**: A mixture of H_2TDA (0.3 mmol, 51.7 mg), 0.2 mmol of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Gd (**1**), 90.6 mg; Dy (**2**), 91.3 mg), and 10 mL of water was heated in a 20 mL Teflon cup at 160 °C for 3 days and then cooled to room temperature at a rate of 1.5 °C·h^{-1}. The crystals of **1** and **2** were collected in 52% and 47% yields, respectively, based on Ln after being washed by water and diethyl ether. Elem anal. Calcd for **1**: C, 24.10; H, 1.57; S, 10.72. Found: C, 24.33; H, 1.64; S, 11.01. Calcd for **2**: C, 23.82; H, 1.56; S, 10.60. Found: C, 23.80; H, 1.58; S, 10.69.

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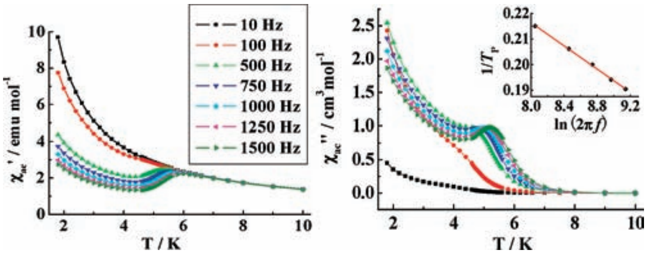

Figure 3. ac magnetic measurements for **2** at $H_{ac} = 3$ Oe and $H_{dc} = 0$. Inset: Solid line representing the least-squares fit of the experimental data to the Arrhenius equation for **2**.

the experimental curve is close to the calculated results for two isolated centers with $S = {}^7/_2$ and $g = 2$ (Figure S5 in the SI). For **2**, the saturation magnetization is not reached even at 70 kOe, and the value of 5.9 μ_B for **3** is close to that the reported by Powell's group.[9c] This may be explained by the fact that the energetically isolated spin state was not reached because of the field-induced level crossing and a high density of states.[3,12b]

To further explore the dynamics of magnetization, we performed alternating current (ac) magnetic measurements of **1** and **2**. Interestingly, in complex **2**, both the real χ_M' and the imaginary χ_M'' parts of the ac susceptibilities below 7 K exhibit strong frequency dependences (Figure 3). Comparably, no available signal was observed in complex **1** (Figure S6 in the SI). In plots of both χ_M' and χ_M'' for **2**, the peaks are observed above 500 Hz and shift to high temperature with increasing frequencies, which is the nature of slow magnetic relaxation.[11] Noticeably, both χ_M' and χ_M'' below about 4 K increase with decreasing temperature, which is similar to superparamagnetism plus paramagnetism. In our magnetic measurements, several crystals were picked out, crushed, and then measured in order for impurities to be excluded. Furthermore, the purity of both samples was confirmed by a comparison of experimental and simulated powder X-ray diffraction (Figure S7 in the SI). In fact, this behavior is also observed in the work reported by Ishida et al.[6] It may be the intrinsic characteristics of Ln^{3+}-based complexes, especially for Dy^{3+}, but we did not understand it very well because such examples are infrequently updated.

The peak temperatures, T_p, obtained by the Lorentzian peak function fitting from plots of $\chi_M''-T$ educe a linear plot of $1/T_p$ vs ln(2πf) and obey the Arrhénius law $1/T_p = -k_B/\Delta E[\ln(2\pi f) + \ln(\tau_0)]$ (Figure 3, inset), where f is the frequency. The best fitting yields the energy barrier $\Delta E/k_B = 44.2$ K and the relaxation time $\tau_0 = 2.4 \times 10^{-8}$ s. At 1.8, 2.3, 3.0, and 5.5 K, respectively, the frequency dependence of ac susceptibilities leads to the semicircle Cole−Cole plots of χ_M'' vs χ_M' (Figure S8 in the SI). The least-squares fitting results of the data are in good agreement with a distribution of single relaxation processes with α parameters of 0.03−0.18 (α = 0 corresponding to an infinitely narrow distribution of relaxation times), which is compatible with the value reported.[11,17] The shift of the peak temperature (T_p) of χ'' is measured by a parameter $\phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.25$, which falls in the range of a normal value for a superparamagnet. On the other hand, the frequency dependence of ac χ'' for **2** was also fitted by the conventional critical scaling law of the spin dynamics as described by $\tau = \tau_0[(T_p - T_f)/T_f]^{-zv}$, where $\tau = 2\pi f$, giving $zv = 2.7$ ($zv = 4-12$ for spin glass; Figure S9 in the SI). The above results suggest that the interestingly magnetic behavior in **2** could not originate from the spin glass.[18]

The variable-temperature magnetic properties in Figure 2 and the results analyzed above indicate that the carboxyl groups mediate the very weak ferromagnetic coupling between lanthanide ions, so the slow magnetization relaxation of **2** may originate from the single-ion behavior of Dy^{3+},[12] just as was theoretically investigated.[12e] Under the effect of the ligand field, the splitting of the ground-state multiplet of Dy^{3+} gave rise to strong magnetic anisotropy. It is suggested that the strong anisotropy D and high ground-state spin S of Dy^{3+} lead to a large enough energy $U = |D|S^2$ for reversal spin. Actually, this kind of phenomenon observed in other lanthanide complexes may associate with the strong anisotropy of the lanthanide ions.[2−13]

Additionally, the energy barrier and relaxation time in this work are comparable with those of the reported work.[2−13] The ferromagnetic coupling also exists between adjacent Dy^{3+} ions in a reported two-dimensional Dy complex,[19] but slow magnetization relaxation was not observed, and frequency dependence on an ac susceptibility signal only occurs when a direct current (dc) field (5 kOe) was applied.

In summary, two lanthanide−organic frameworks **1** and **2** were prepared and structurally characterized. Systematic magnetic studies for them have been performed, and only **2** exhibits a remarkable slow magnetic relaxation, although they are isostructural and magnetic interactions between lanthanide ions all display ferromagnetic coupling. To our knowledge, it is hardly observed that ferromagnetic coupling and slow magnetic relaxation coexist in 3D lanthanide-based frameworks.

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Supporting Information Available: Structural drawings and CIF files of **1** and **2**; additional magnetic data and analyses for **1** and **2**; and experimental and simulated powder X-ray diffraction of both **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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