

Two-Dimensional 3d–4f Networks Containing Planar Co₄Ln₂ Clusters with Single-Molecule-Magnet BehaviorsYue Liu,[†] Zhi Chen,[†] Jia Ren,[†] Xiao-Qing Zhao,^{*,‡} Peng Cheng,[†] and Bin Zhao^{*,†}[†]Key Laboratory of Advanced Energy Material Chemistry, MOE, and TKL of Metal and Molecule Based Material Chemistry, Department of Chemistry, Nankai University, Tianjin 300071, China[‡]College of Life and Science, Sichuan Agricultural University, Ya'an 625014, China

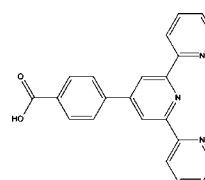
Supporting Information

ABSTRACT: Two novel two-dimensional 3d–4f networks based on planar Co₄Ln₂ clusters supported by rigid 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine afford the first examples of high-dimensional networks with 3d–4f clusters behaving as single-molecule magnets.

The discovery of the first [Mn₁₂] cluster with slow paramagnetic relaxation stimulates the renaissance of molecular magnetism and initiates the emerging subject of single-molecule magnets (SMMs), which can be viewed as potential candidates for information storage devices, quantum computing, and spintronics devices.^{1–3} The SMMs feature the presence of energy barriers deriving from the combination of a large spin ground state (*S*) and a uniaxial Ising-like magneto-anisotropy (*D*). In the past 2 decades, numerous complexes have been observed, and the most studied examples are based on 3d transition metals, especially Mn^{III} ions. However, the magnetic relaxation blocking temperatures of 3d metal SMMs remain low. Hence, it is of great significance to pursue new SMMs with high blocking temperatures. Because of many 4f ions with strong magnetic anisotropy, especially for Tb^{III} (⁷F₆), Dy^{III} (⁶H_{15/2}), and Ho^{III} (⁵H₈), significant effort is devoted to constructing SMMs containing 3d–4f or pure 4f systems.^{4,5} Most of the reported lanthanide-based SMMs so far contain anisotropic Dy^{III} ions, which can provide large spin and high spin–orbit coupling. In addition, compared with other 3d metal ions, the Co^{II} ion in an octahedral environment has a large single-ion anisotropy afforded by spin–orbit coupling, which can also be a good candidate ion for SMMs, and then there are some Co-based SMMs reported in recent years.^{6,7} Therefore, the combination of Co^{II} and Ln^{III} ions in one system may be a new and interesting strategy to obtain novel SMMs. To our knowledge, the Co^{II}–Ln^{III} SMMs are very limited.⁷

Generally speaking, an SMM is an isolated molecule, and the intermolecular magnetic interactions are negligible. As a consequence, it is rather scarce that multidimensional networks exhibit SMM behaviors, and the metal-ion-embedded frameworks focused on d or f ions rather than d–f mixed ones.⁸ On the other hand, the organic ligands in SMMs play an important role in constructing metal clusters and separating each magnetic unit. 4'-(4-Carboxyphenyl)-2,2':6',2''-terpyridine (HL; Scheme 1) follows the soft–hard concept that N and O donors fulfill the coordination affinities of 3d and 4f ions, respectively, so as to introduce 3d and 4f ions into one system. Furthermore, HL

Scheme 1. Representation of the Ligand HL



can separate metal clusters from each other, which fulfills the precondition of an isolated molecule for an SMM.

Considering those aspects as above-mentioned, we use HL ligands to build Co–Ln complexes. Two novel two-dimensional (2D) Co–Ln networks constructed of rare planar hexanuclear Co₄Ln₂ clusters and L[−] anions were isolated, formulated as {[Co₄Dy₂(L)₄(CO₃)₄(HCOO)₂(H₂O)₂]·2DMF·5H₂O}_n (**1**; DMF = *N,N*-dimethylformamide) and {[Co₄Ho₂(L)₄(CO₃)₄(HCOO)₂(H₂O)₂]·2DMF·2H₂O}_n (**2**) on the basis of crystal structure analyses. The magnetic study reveals that **1** exhibits slow magnetic relaxation. It may be noted that **1** is the first example of a high-dimensional 3d–4f framework containing heterometallic clusters that exhibits SMM behavior, although one example with a one-dimensional 3d–4f chain showing slow magnetic relaxation has been reported.⁹

1 and **2** were successfully obtained by a one-pot reaction of HL, Co(CH₃COO)₂·4H₂O, and Ln(NO₃)₃·6H₂O (Ln = Dy, Ho) in a mixed DMF/H₂O solution under solvothermal conditions (Supporting Information, SI), and the yields are 17% and 25% (based on Ln), respectively. Single-crystal X-ray analyses reveal that both **1** and **2** consist of a 2D network based on nearly planar hexanuclear Co₄Ln₂ clusters, lattice DMF, and H₂O molecules for crystallization, and the difference between **1** and **2** is the number of lattice H₂O molecules. Hence, **1** is chosen to depict the structure in detail. The hexanuclear Co₄Dy₂ cluster and its planar core are depicted in Figure 1a,b. The planar core of **1** contains a [Co₄Dy₂(CO₃)₄]⁶⁺ cluster with four Co^{II} and two Dy^{III} ions held together by four CO₃^{2−} anions from decomposition of DMF.¹⁰ On the basis of bond valence sum (BVS) analyses of Co sites,¹¹ the BVS of Co ions falls into the range from 1.868 to 1.968 (Table 3 in the SI), confirming the 2+ oxidation state of Co ions in **1** and **2**. Two CO₃^{2−} in η²:η²:η²:μ₄-bridging mode act as hexadentate ligands to chelate two Co^{II} ions (Co1 and Co2) and two Dy^{III} ions.

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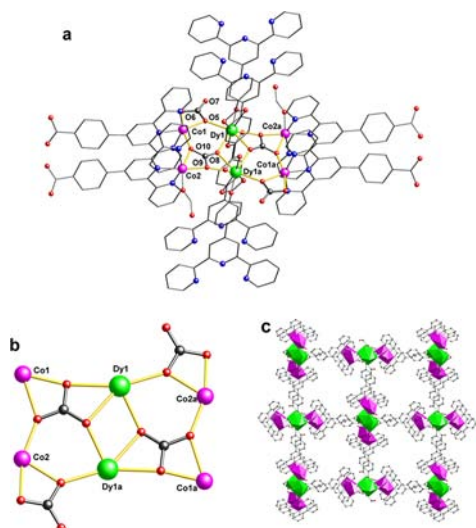


Figure 1. Hexanuclear Co_4Dy_2 cluster (a), its planar core (b), and the 2D network (c) of **1**. H atoms are omitted for clarity. Color code: green polyhedra, $[\text{DyO}_8]$; purple polyhedra, $[\text{CoN}_3\text{O}_3]$.

Dy1 and Dy1a are double-bridged by two μ_2 -O atoms from two μ_4 - CO_3^{2-} to form a Dy_2O_2 rhombus with angles of $110.54(33)$ and $69.46(29)^\circ$ for Dy–O–Dy and O–Dy–O, respectively. The remaining two CO_3^{2-} as tridentate ligands in $\eta^1:\eta^2:\mu_2$ -bridging mode link Dy1 and Co1 at the edge of the core. Four Co^{II} ions (Co1, Co2, Co1a, and Co2a) are precisely coplanar, while two Dy^{III} ions (Dy1 and Dy1a) slightly deviate from the plane and lie above and below with deviations of 0.2885 \AA . The eight-coordinated environment of Dy1 is completed by two L^- anions and one H_2O molecule, close to a distorted double-capped trigonal prism. The six-coordinated geometries of Co^{II} ions are completed by three N atoms from L^- anions and three O atoms from CO_3^{2-} and/or formate anions, forming distorted octahedra. It should be stated that formate is the product of decomposition of DMF.¹² In the core, the Dy...Dy and Co...Co distances are $3.930(1)$ and $4.125(3) \text{ \AA}$, respectively, and those of Dy...Co are $4.003(6)$ (Dy1...Co1) and $4.501(6) \text{ \AA}$ (Dy1...Co2).

Each hexanuclear Co_4Dy_2 cluster is encapsulated by eight L^- ligands, as shown in Figure 1a. Each Co^{II} ion in the cluster coordinates to three N atoms from one L^- , while the Dy^{III} ion is coordinated with one monodentate and one bidentate carboxyl groups from two L^- above and below the planar core, indicating two coordination modes of L^- : tetradentate and pentadentate. Both of them bridge two metal ions (Dy1, Co1 and Dy1, Co2, respectively). Finally, L^- ligands use their chemical characteristics of N and O atoms to fulfill the affinities of Co^{II} and Dy^{III} ions and connect those clusters to form a 2D network (Figure 1c). Considering Co_4Dy_2 as a four-connected node, the topology can be analyzed as a 2D 4^t -net with a distance of 17.669 \AA between nodes (Figure S1 in the SI). The 2D motifs are stacking along the c direction in a staggered –AB– mode (Figure S2 in the SI).

The calculated and experimental powder X-ray diffraction patterns were compared in Figure S3 in the SI, and the results confirm the purity of **1** and **2**. The direct-current (dc) magnetic properties of **1** and **2** were investigated under a 1 kOe field in the temperature range 2–300 K, and plots of $\chi_{\text{M}}T$ vs T are depicted (Figure S4 in the SI). The $\chi_{\text{M}}T$ values at 300 K of 42.30 and $40.26 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** and **2**, respectively, are

more than the those expected for four spin-only Co^{II} ions ($S = 3/2$) and two Ln^{III} ions in the ground state. As reported in many of the Co^{II} -containing compounds, the room temperature $\chi_{\text{M}}T$ value is usually higher than the expected spin-only one as a result of the orbital contribution of the high-spin Co^{II} ions in the octahedra to the magnetism.¹³ With decreasing temperature, the $\chi_{\text{M}}T$ value gradually decreases until 50 K and then drops sharply to reach minimum values of 11.23 and $7.80 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K for **1** and **2**, respectively. Thermal evolution of the $\chi_{\text{M}}T$ value observed suggests antiferromagnetic behavior; however, it is difficult to depict the interactions of Co–Co, Co–Ln, and Ln–Ln in **1** and **2** because both Co^{II} and Ln^{III} ions have intrinsically complicated magnetic characteristics (including the presence of spin–orbit coupling and magnetic anisotropy). The field dependences of magnetization data for **1** and **2** have been measured at 2, 3, and 5 K (Figures 2, S5 in

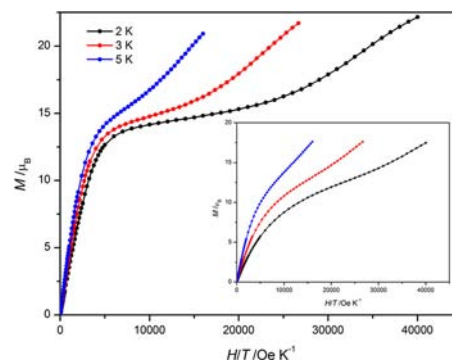


Figure 2. M vs H/T plots at different temperatures below 5 K for **1** and **2** (inset).

the SI). At 2 K, the magnetization of **1** and **2** quickly increases with enhancement of the field below 1 T. From 1 to 5 T, the value of **1** slowly rises similarly to that of reported $[\text{DyCo}]$ systems⁷ and then linearly increases above 5 T, which may be the peculiarity of the powder magnetization reported in Powell's work.^{4f} The lack of magnetic saturation even at 8 T and the nonsuperposition of M vs H/T plots (Figure 2) indicate the presence of magnetic anisotropy and/or low-lying excited states.

L^- ligands in **1** and **2** link Co_4Ln_2 clusters and effectively separate these clusters from each other, as well as the presence of significant magnetic anisotropy and unpaired electrons in those Co–Ln systems; as a result, both **1** and **2** may exhibit interesting magnetic behavior. In order to probe any SMM behavior, ac magnetic susceptibilities were performed for **1** and **2** in the temperature range 2–20 K with zero dc field, and frequency-dependent out-of-phase signals for **1** were observed, meaning that **1** has an Ising-type anisotropy, but the maximum of χ'' is lower than 2 K (Figure S6 in the SI). Comparably, out-of-phase susceptibility for **2** is negligible (Figure S7 in the SI). The behavior of **1** indicates the presence of slow magnetization relaxation, but the relaxation time and energy barrier cannot be deduced from these data because of the restriction of the instruments without full peak observed above 2.0 K. This phenomenon may originate from the presence of quantum tunneling of magnetization (QTM), and QTM may be suppressed by applying a static dc field.¹⁴ Therefore, the frequency dependence of ac susceptibility was obtained under a static dc field of 5000 Oe for **1**. As expected, QTM is partially suppressed, and the maxima of the χ'' values were shifted to

higher temperature above 2.0 K and detected for frequencies higher than 3111 Hz for **1** (Figure 3). The relaxation time was

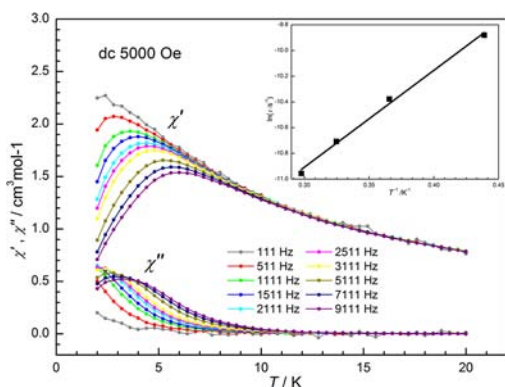


Figure 3. Temperature dependence of ac susceptibilities under a dc field of 5 kOe for **1**. Inset: Arrhenius plot for **1** using the ac data at frequencies of 3111–9111 Hz.

extracted from the temperature of the maximum $\chi''(\omega)$ as $\tau(T_{\max}) = \omega^{-1}$, and the magnetization relaxation time (τ) follows the Arrhenius law, $\tau = \tau_0 \exp(E_a/k_B T)$. The solid line in Figure 3 (inset) shows the result of a least-squares fit of the ac susceptibility relaxation data between 3111 and 9111 Hz to the Arrhenius equation, giving an energy gap (E_a/k_B) of 7.6 K and a preexponential factor $\tau_0 = 1.9 \times 10^{-6}$ s for **1**.

The obtained parameters are in the region of some reported Dy^{III} SMMs (the lowest-energy barrier reported is 6.2 K)¹⁵ and confirm the SMM behavior of 2D complex **1**. The magnetic slow relaxation behavior of Co₄Dy₂ complex **1** cannot be clearly concluded because of the nature of the Co^{II} and Dy^{III} ions; however, because no out-of-phase signals were observed for Co₄Ho₂ analogues, the SMM behavior of **1** may mainly be associated with the anisotropic Dy^{III} ions.

In summary, two Co^{II}–Ln^{III} coordination polymers (**1** and **2**) have been produced using a rigid HL ligand under solvothermal conditions, exhibiting novel 2D networks built from planar Co₄Ln₂ clusters. Compound **1** exhibits slow relaxation of magnetization, indicating SMM behavior. It is the first time that a 2D 3d–4f heterometallic coordination polymer exhibits SMM behavior. The results presented herein indicate that the construction of multidimensional networks with metal clusters is a feasible approach to preparing novel magnetic materials and will broaden the field of SMMs.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files of **1**, **2** (CCDC 860042, 860043, CIF), experimental details, Figures S1–S7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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