Field-Induced Relaxation of Magnetization in a Three-Dimensional LnMOF with the Second Bridging Ligand Squarate

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Supporting Information

ABSTRACT: A three-dimensional (3D) dysprosium(III) metal-organic framework with nicotinate N-oxide (NNO\(^{-}\)) and squarate (C\(_4\)O\(_4\)\(^{2-}\)) mixed bridging ligands, [Dy(NNO)-\((\text{C}_4\text{O}_4)(\text{H}_2\text{O})\)]\(_n\) (I), has been hydrothermally synthesized. The dysprosium(III) ions are linked to each other by the squarate anions to form a unique dysprosium(III) squarate double-layered network; the NNO\(^{-}\) anions then bridge such layers to complete the 3D framework. Complex I exhibits a two-step relaxation of magnetization under a dc field of 1000 Oe, with effective energy barrier values of 8.5 and 14.3 K, respectively.

INTRODUCTION

Recently, lanthanide(III) ions have been widely used to design and construct metal-organic frameworks (MOFs) not only due to their higher coordination numbers with respect to those of transition metal ions but also due to their unique 4f electrons, which may create structural diversity and result in interesting optical and magnetic properties.1-3 First, photoluminescence is the main subject of a study of lanthanide MOFs (LnMOFs); the interest stems from the fact that most lanthanide(III) cations display characteristic narrow fluorescent emissions in virtue of the ligands’ antenna effect.2 Further, single-molecule magnet (SMM) behaviors have also been observed in some LnMOFs, especially Dy(III) MOFs quite recently, because most lanthanide(III) ions have big magnetic moments and an obvious magnetic anisotropy, which meet the two corresponding prerequisites for an SMM.3 SMMs are characterized by slow magnetic relaxation and magnetic bistability, making them potential molecular materials in high-technique areas, such as quantum computing, high-density information storage devices, and spintronics.4-6 Only limited LnMOFs showing SMM behaviors have been explored,4-6 although a great advantage has been shown by 2D and 3D LnMOFs in which the lanthanide(III) ions, each of which corresponds to a single-ion magnet, are arranged as highly ordered “nanoscale-separation dots”. This is very useful for molecular devices of density information storage devices, and spintronics.6-7 Organic carboxylates, especially binary carboxylates, are often adopted as organic linkers to assemble LnMOFs because they have rich binding patterns and the oxygen atoms have a high affinity to the lanthanide(III) cations. Notably, the second bridging ligand to construct LnMOFs is an important aspect of the study. This improved approach can increase the flexibility and diversity of assembly, producing more LnMOFs with beautiful structures and interesting properties. Notably, oxalate (C\(_2\)O\(_4\)\(^{2-}\)) has been successfully utilized as the second bridging ligand to assemble many novel LnMOFs.8-10 In contrast, LnMOFs with a noncarboxylic acid type of organic polyacid as the second bridging ligand are documented rarely in the literature. For example, the squarate anion, which can be considered as an analogue of the oxalate anion (Scheme 1),11 is seldom chosen as the second bridging ligand to construct LnMOFs. Nevertheless, both the carbonyl oxygen atom and the hydroxyl oxygen atom can bind to lanthanide(III) ions easily, which makes the squarate anion have rich coordination modes and show excellent bridging ability. In this regard, we have used nicotinate N-oxide (NNO\(^{-}\)) as the main bridging ligand and squarate as the second bridging ligand to construct LnMOFs recently. In this article, we report the preparation, X-ray crystal structure, and properties of such a three-dimensional (3D) LnMOF, [Dy-(NNO)-(C\(_4\)\(_2\)O\(_4\))(\text{H}_2\text{O})\)]\(_n\) (I; C\(_4\)O\(_4\)\(^{2-}\) = squarate). Complex 1...
contains a unique dysprosium(III) squarate double-layered network, showing an interesting 3D topological structure. Notably, it exhibits a two-step magnetic relaxation under a dc field of 1000 Oe.

## RESULTS AND DISCUSSION

### Synthesis and XRD Spectrum

Similar to the preparation of LnMOFs with the second bridging ligand oxalate, the hydrothermal reaction technique was utilized to avoid yielding the lanthanide(III) squarate precipitate directly, and the lanthanide(III) starting materials may react with squaric acid and nicotinic acid N-oxide synchronously under hydrothermal conditions. Complex 1 was hydrothermally prepared by the reaction of squaric acid, nicotinic acid N-oxide, Dy(NO₃)₃·5H₂O, and 15 mL of H₂O at 170 °C for 5 days; only one crystalline phase was formed; the same product was obtained if double the quantity of nicotinic acid N-oxide was utilized, but the yield became smaller. The purity of the as-synthesized crystalline-phase product was examined by comparing its XRD spectrum with the ideal patterns simulated from the single-crystal structure (Figure S1); their peaks match well with each other.

### Crystal Structure

As shown in Figure 1, the 3D framework of complex 1 comprises dysprosium(III) squarate double layers and antiparallel NNO⁻ double bridging ligands, whereas water molecules just act as terminal ligands binding to dysprosium(III) atoms. There is only one crystallographic independent dysprosium(III) atom, which adopts an eight-coordinated geometry, completed by four oxygen atoms from four squarate anions, two oxygen atoms from the carboxylate group of one NNO⁻ anion, one oxygen atom from the N-oxide group of the neighboring antiparallel NNO⁻ anion, and one oxygen atom belonging to the water terminal ligand. The Dy₁−O bond distances [average 2.374 Å] are in accord with the normal values. The exact coordination geometry of the Dy₁ atom was analyzed in detail using the Shape software. The results indicate that it mostly belongs to the biaugmented trigonal prism, in which the deviation value from the standard C₂ᵥ symmetry is only 1.230 (Table S1).

The most fascinating structural feature of 1 is that the Dy³⁺ ions are connected to each other by the 4-connected squarate bridges, generating a unique dysprosium(III) squarate double-layered network along the bc plane (Figure 2). Each squarate anion bridges two Dy³⁺ ions from the above layer and two Dy³⁺ ions from the bottom layer, adopting the coordination mode shown in Scheme 1e. These squarate anions link to the Dy³⁺ ions along the short diagonal line and long diagonal line of the bc plane, forming a double-layered network similar to the famous single-layered (4, 4) network. Notably, such a double-layered network has never been observed in the LnMOF system before; it thus represents a new structural paradigm of lanthanide squarate, although the single-layered structure of lanthanide squarate has been recently observed in a 2D LnMOF displaying a large magnetocaloric effect, [Gd(C₄O₄)·(OH)(H₂O)]ₙ, in which the squarate anion adopts the 3-connected bridging mode shown in Scheme 1d. In the dysprosium(III) squarate double-layered network of 1, the Dy···Dy separation within each plane layer is 6.064 Å, whereas the shortest Dy···Dy separation between two plane layers is 6.041 Å.

Interestingly, several 3D Ln(III) MOFs with both the NNO⁻ bridging ligand and oxalate bridging ligand have also been reported recently. In all of these compounds, each oxalate anion just links to two opposite lanthanide(III) cations as a bisbidentate ligand; this 2-connected coordination mode is quite different from the 4-connected coordination mode observed in 1, so it is impossible to generate the similar

**Figure 1.** (a) The coordination environment of the Dy₁ atom in 1: symmetry codes: a: 1 − x, 1 − y, 1 − z; b: x, 1/2 − y, 1/2 + z; c: 2 − x, 1/2 + y, 1/2 − z; d: 2 − x, 1 − y, 1 − z; (b) 3D MOF of 1 viewed along the [001] direction.

**Figure 2.** Dysprosium(III) squarate layer viewed along the (a) [100] direction and (b) [001] direction.
“dysprosium(III) squarate oxalate layer network” in these compounds.

To complete the 3D framework of 1, the dysprosium(III) squarate layers are linked to each other through the bridging of NNO\(^{-}\) anions, which always appear in pairs, forming antiparallel double bridges. The corresponding Dy···Dy distance, separated by the NNO\(^{-}\) double bridges, is 8.169 Å. Taking the squarate ligand as a 4-connected node and the antiparallel NNO\(^{-}\) double bridges as a single linker, this 3D topological structure may be simplified into a (4, 5)-connected network, which was then analyzed by the Olex program, giving the long topological (O’Keeffe) vertex symbol of 4.4.4.4.4.4.6.6.6.6 and the short (Schläfli) vertex symbol of 4\(^{6}\)6\(^{4}\) (Figure 3). As far as we know, complex 1 is the first LnMOF with both the heterocyclic carboxylate bridging ligand and the squarate bridging ligand.

Magnetic Properties. As shown in Figure 4, the magnetic susceptibilities determined in a dc field of 1000 Oe indicated that the room temperature \(\chi T\) value of 14.19 cm\(^3\) K mol\(^{-1}\) is in accordance with the theoretical value of 14.17 cm\(^3\) K mol\(^{-1}\), corresponding to one isolated Dy\(^{3+}\) ion (\(^{9}H_{15/2}, S = 5/2, L = S,\) and \(g = 4/3\)). Upon cooling, the \(\chi T\) product placidly decreases up to around 50 K and then drops sharply to reach 12.16 cm\(^3\) K mol\(^{-1}\) at 2 K. The Curie–Weiss equation was utilized to fit the magnetic susceptibility data for 2–300 K; the \(C\) and \(\theta\) values of 1 were calculated to be 14.19 cm\(^3\) K mol\(^{-1}\) and −1.15 K, respectively (Figure S2). The small negative \(\theta\) value suggests that the \(\chi T\) decline with a decrease in temperature mainly results from thermal depopulation of the Dy\(^{3+}\) ions of the excited Stark sublevels, which is generally induced by crystal-field perturbation.\(^{3,4}\) The dipole–dipole antiferromagnetic interactions among the Dy\(^{3+}\) ions, if existent, will be very weak owing to the large Dy···Dy separations, as mentioned above. The field-dependent magnetization of 1 was measured at 2–6 K; nonsuperimposed M versus \(H/T\) plots are clearly presented as the inset of Figure 4, indicating the existence of magnetic anisotropy in 1.

Ac magnetic susceptibilities of 1 were also recorded to probe the dynamic magnetic properties. The out-of-phase (\(\chi''\)) signals are almost negligible when the dc field is zero (Figure S3). However, these signals become significantly intense and strongly frequency-dependent under a dc field. The field-dependent ac susceptibilities recorded at 997 Hz and 2.5 K (Figure S4) indicate that the optimum field is 1000 Oe, which may suppress the quantum-tunnelling effects; with this dc field, the susceptibility peaks could be seen obviously when the frequency was greater than 165 Hz (Figure 5a). These results suggest that there exist quantum-tunnelling effects; such effects can be decreased by applying a dc field of 1000 Oe to eliminate the Dy(III) ion’s ground-state degeneracy.\(^{46,47}\)

The Arrhenius law, \(\tau = \tau_{0} \exp(U_{\text{eff}}/kT)\) (\(\tau\) is the relaxation time of the magnetization), was adopted to calculate the
Table 1. Coordination Geometry, Symmetry, Magnetic Interaction, and Energy Barrier of Some High-Dimensional Dy(III) MOFs

| chemical formula | dimension | coordination geometry/symmetry | ferromagnetic? | energy barrier (Hk) | reference |
|------------------|-----------|-------------------------------|---------------|---------------------|-----------|
| [Dy(3-py-4-mpc) (C2O4)3(H2O)] | 2D | SAPR-8/D4d | yes | 186 K | 9 |
| [Dy(hfac)3]2(4,4-tmp) | 3D | PBPY-7/Dsh | yes | 131 K | 16 |
| [Dy2(4,4-tmp) (C2O4)0.5(OH)(H2O)] | 2D | JTCTPR-9/Dsh | yes | 64 K, 57 K (2 kOe) | 25 |
| [Dy2(INO)4(NO3)2] | 3D | TCTPR-9/Dsh | yes | 36 K, 33 K (1.2 kOe) | 12 |
| [Dy2(TDA)2(bipy)2(H2O)] | 2D | OH-8/D4d | no | 75 K (1 kOe) | 14 |
| [Dy2(HCAM)3(H2O)5]2 | 2D | JCSAPR-9/Dsh | no | 23 K (2 kOe) | 24 |
| [Dy(CO3)1.5(C2O4)1.5(H2O)] | 3D | SAPR-8/D4d | yes | 36 K, 33 K (1.2 kOe) | 12 |
| [Dy2(TDA)3(bipy)2NO)2] | 2D | SAPR-8/D4d | no | 32 K (1 kOe) | 27 |
| [Dy(CO3)1.5(H2O)] | 3D | SAPR-8/D4d | no | 18 K (1 kOe) | 13 |
| [Dy(BTC)·2H2O] | 2D | SAPR-8/D4d | no | 18 K (1 kOe) | 13 |
| [Dy2(C2O4)1.5DMF]·H2O | 2D | TCTPR-9/Dsh | no | 4 K, 11 K (0.7 kOe) | 11 |
| [Dy2(C2O4)1.5DMF]·H2O | 2D | TCTPR-9/Dsh | no | 19 K (0.9 kOe) | 18 |
| [Dy(3-py-4-pmc) (C2O4)0.5(OH)(H2O)] | 2D | TCTPR-9/Dsh | no | 14 K (1 kOe) | this work |

*SAPR-8, square antiprism; PBPY-7, pentagonal bipyramid; OH-8, octahedron; TCTPR-9, spherical tri capped trigonal prism; TDD-8, triangular dodecahedron; JCSAPR-9, capped square antiprism; PBPY-7, pentagonal bipyramid; JETBPY-8, Johnson elongated triangular bipyramid; BTBPY-8, bi augmented trigonal prism; JTCTPR-9, tricapped trigonal prism; JCSAPR-9, capped square antiprism J10.

effective thermal barrier. As shown in Figure 5b, the ln(τ) versus 1/T plots, which are based on the χ′ peak temperatures at different frequencies, could be fitted by the Arrhenius law, affording two effective energy barrier values, $U_{eff}/k = 8.5$ K ($τ_0 = 1.2 \times 10^{-5}$ s) and $U_{eff}/k = 14.3$ K ($τ_0 = 7.8 \times 10^{-7}$ s), for the fast relaxation phase (FR, in the low-frequency region) and slow relaxation phase (SR, in the high-frequency region), respectively. The $τ_0$ values coincide with the expected values for SMMs/SIMs (10$^{-3}$–10$^{-11}$ s). The $U_{eff}/k$ values of 1 are in the normal range for high-dimensional carboxylate-bridged Dy(III) MOFs, but they are not remarkable. There are several factors related to the effective energy barrier. As shown in Table 1, the carboxylate-bridged Dy(III) MOF with the largest $U_{eff}/k$ value contains the hydroxyl anion bridging ligand, suggesting that the use of mixed carboxylate/hydroxy bridges yields high $U_{eff}/k$ values, but this type of compound is rare. Another favorable factor is ferromagnetic interactions between Dy(III) ions. However, complex 1 does not show any ferromagnetic interactions. The third favorable factor is the high ligand field symmetry of the Dy(III) ion. For complex 1, the ligand field symmetry of the bi augmented trigonal prism for the Dy(III) ion ($C_3v$) is not as high as that of the square antiprism ($D_{sh}$), the pentagonal bipyramid ($D_{5h}$), and the octahedron ($D_{oh}$), so the $U_{eff}/k$ values of 1 are not large. In addition, the degree of dependence of the χ′ peak temperatures on frequencies could be assessed by the parameter $Φ = (∆T/τ_0)/Δ(\log f)$ (f is the frequency). The $Φ$ value of 1 is 0.52, which is in good agreement with the $Φ$ value of the superparamagnet ($Φ \geq 0.1$), but it is much larger than the $Φ$ value ($Φ \leq 0.01$) of spin glass, confirming the SM behaviors of 1.

To better understand the relaxation characteristics of magnetization, the isothermal frequency-dependent ac susceptibilities of 1 were also measured under a dc field of 1000 Oe. Five χ′ versus χ″ plots at 2.0–2.8 K are presented in Figure 6; all of them show hooklike shapes, confirming a two-step relaxation process. Obviously, the left and right parts of the hook-shaped curves are ascribed to the FR and SR phases, respectively. All of these hook-shaped curves might be fitted utilizing the sum of two modified Debye functions:

$$\chi_{ac}(ω) = \frac{X_S - X_0}{1 + (iωτ_{SR})^{1−α_S}} + \frac{X_S - X_0}{1 + (iωτ_{FR})^{1−α_F}} + X_0$$

(1)

Table S2 lists seven calculated parameters, $X_0$, $χ_0$, $χ_F$, $τ_F$, $τ_R$, $α_F$, and $α_R$ at 2.0, 2.2, 2.4, 2.6, and 2.8 K. The best fitting results are also visually presented in Figures 6 and S5–S9. The $α_S$ values, 0.35–0.46, are somewhat smaller than the $α_F$ values, 0.61–0.76, but all of these values are not small, indicating that the relaxation time distribution is not narrow not only for the FR phase but also for the SR phase. As mentioned above, complex 1 has one only crystallographic independent dysprosium(III) atom; therefore, the two-step thermal magnetic relaxation of 1 is ascribed to the field-inducing role. Notably, such
a dc field-inducing two-step relaxation of magnetization is seldom observed in high-dimensional Dy(III) MOFs, only two 3D Dy(III) MOFs and two 2D Dy(III) MOFs behave similar multiple relaxation of magnetization. Additionally, no any magnetic hysteresis of I could been seen at 1.9 K (Figure S10).

Because the magnetic interactions among the Dy$^{3+}$ cations are almost negligible in I, its magnetic properties are mainly ascribed to single-ion behaviors. If we assume existence of a Ising ground state in I, which is very frequent for low symmetry Dy$^{3+}$ complexes, the electrostatic model installed in the Magellan program could be applied for estimating the magnetic anisotropy in I. The calculated results are shown in Figure S7, the magnetic axis directionality of the dysprosium(III) ion is very close to the Dy$^1$–O$^3$ bond, with a small separation angle of 6.67°.

Figure 7. Magnetic axis of the Dy$^{3+}$ ion in I, calculated using an electrostatic method.

In summary, we have hydrothermally prepared a 3D LnMOF comprising a novel dysprosium(III) square double-layered network. It shows a (4, 5)-connected 4$^6$6$^4$ topological structure. Magnetic investigations reveal that it displays field-induced two-step magnetic relaxation under a dc field of 1000 Oe, with $\mu_{\text{eff}}/k_B$ values of 8.5 and 14.3 K for the FR and SR phases, respectively. Such a field-induced multiple thermal magnetic relaxation is rarely found in high-dimensional Dy(III) MOFs. Our work demonstrates that noncarboxylic acid type of organic polyprotonic acids can be also used as second bridging ligands to construct mixed-bridge LnMOFs with novel structures and interesting physical properties, like SMM behaviors; more such molecular materials may be explored.

## METHODS

### Materials and Equipment

All chemicals are commercially available. The elemental analyses were carried out using a FLASH EA1112 elemental analyzer. The infrared spectrum was determined on a BRUKER TENSOR-27 spectrophotometer with a pressed KBr pellet. The X-ray powder diffraction (XRD) pattern was recorded on a Rigaku D/max 2500 diffractometer with Cu Kα (λ = 1.5418 Å) radiation. The magnetic susceptibility measurements were performed using Quantum Design MPMS-XL5 with polycrystalline samples. Demagnetization corrections were evaluated from Pascal’s constants of all constituent atoms.

### Synthesis of 1

Squaric acid (1.0 mmol), 1.0 mmol of nicotinic acid N-oxide, 1.0 mmol of Dy(NO$_3$)$_3$·$\text{C}_2\text{H}_2\text{O}_4$, and 15 mL of H$_2$O was mixed in a Teflon-lined stainless steel autoclave (25 mL) and maintained at 170 °C for 5 days. After the reactor had cooled to room temperature overnight, colorless block crystals of I (35% yield on the basis of Dy) were collected as the only crystalline phase. These crystals were then washed using water and dried at ambient temperature. Calcd for C$_9$H$_6$DyNO$_8$ (1): C, 27.89; H, 1.42; N, 3.22%. Found: C, 27.83; H, 1.42; N 3.22%. IR (KBr pellet, cm$^{-1}$): 3427(b, s), 3207(b, m), 3150(m), 3086(w), 1615(s), 1588(s), 1565(s), 1424(s), 1282(w), 1122(m), 1189(w), 1106(w), 1085(w), 1023(w), 948(m), 897(w), 818(m), 769(m), 691(w), 671(w), 595(w), 575(w), 550(w), 520(w), 451(w), 427(w).

### X-ray Single-Crystal Crystallography

A carefully chosen single crystal of I, with dimensions of 0.33 × 0.28 × 0.11 mm$^3$, was fixed on a Bruker SMART APEX-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) for collecting diffraction data at 173(2) K. The $\varphi$ scan was applied for empirical absorption corrections. Cell parameters were calculated by global refinement of the positions of all collected reflections. The direct method was used to solve the crystal structure of I, and a full matrix least-squares technique based on F$^2$ was applied to refine this structure using the SHELXL 97 program. All hydrogen atoms were refined isotropically, but all nonhydrogen atoms were refined anisotropically. The main crystallographic data and structure determination parameters are reported in Table S3.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00083.

CIF file of complex 1, CCDC 1478335 (CIF)

More structural and magnetic pictures and tables (Figures S1–S10 and Tables S1–S3) (PDF)

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#### Notes

The authors declare no competing financial interest.

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