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Journal:	*Dalton Transactions*
Manuscript ID:	DT-ART-10-2014-003093.R1
Article Type:	Paper
Date Submitted by the Author:	06-Feb-2015
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Photo-control of the Magnetic Properties of Dy(III) and Ho(III) Homometal Coordination Polymers Bridged by a Diarylethene Ligand

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b00000000x

Two-dimensional Dy(III) and Ho(III) homometal coordination polymers containing the photochromic ligand 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (DTE) with the general formula $[Ln_2(DTE)_3(bipyridine)_2(H_2O)_2]_n$ (Ln = Dy and Ho) were obtained, and their magnetic properties of the open (**Dy-o** and **Ho-o**) and closed forms (**Dy-c** and **Ho-c**) were investigated. The Dy complexes exhibited slow magnetic relaxation without an external dc field. The magnetic properties of the Dy complexes were irreversibly affected by the conformation of the ligand.

Introduction

Single-molecule magnets (SMMs) are complexes that exhibit magnetic hysteresis or slow magnetic relaxation of a purely molecular origin.[1] These complexes show great promise for use in spintronic and quantum computing devices. Thus, it is necessary to design SMMs with a way to reversibly switch their magnetic properties by applying external stimuli,[2] such as temperature, light, pressure, electric field, magnetic field, oxidation-reduction, spin injection, etc.[3–6] It is convenient to incorporate photochromic compounds, which can be used to switch the magnetic properties, and we incorporated a dithienylethene compound functionalized with two carboxylato groups (DTE), which can coordinate to magnetic centers.[7] DTE derivatives are thermally stable and show fatigue-resistant photochromic performance in solution and in the solid state.[8–14] DTE reversibly isomerizes between ring-opened and -closed isomers when irradiated with UV and visible light, respectively,[15,16] which affects its geometric and electronic structures. The closed form is conjugated and chiral, whereas the open form is non-conjugated and only exhibits axial chirality (Figure 1).

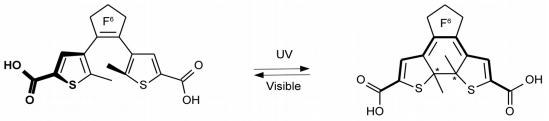


Fig. 1 Photochromic DTE ligand with two carboxylic groups in the open and closed form.

DTE coordinates to lanthanide ions to form an SMM complex, and the magnetic properties of these complexes are sensitive to the crystal field. Isomerisation of DTE affects the coordination sphere of the lanthanide ion and the electronic density on the coordinated oxygen atoms. In addition, there is electronic communication between two bridged SMMs through the closed form. Opening and closing the DTE ligand can be used to turn off and on the SMM behaviour of the complex. Previous work has shown that the magnetic properties of DTE bridged SMMs depend on the form of the ligand.[17–19]

In this work, we prepared two 2D homometal coordination polymers, $[Ln^{III}_2(DTE)_3(bipyridine)_2(H_2O)_2]_n$ (Ln = Dy, Ho). Crystal structures of the open forms of both complexes (**Dy-o** and **Ho-o**) were determined, whereas those of the closed form could not be determined. In addition, the static and dynamic magnetic properties of both forms of each complex were analyzed. The Dy complexes showed differences in their magnetic properties depending on whether the ligand was open or closed. **Dy-o** and **Dy-c** showed slow magnetic relaxation without an external dc field, whereas **Ho-o** and **Ho-c** did not.

Experimental Section

General considerations.

The ligand in the protonated form, 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (DTE), was prepared following a previously reported procedure.[7] Other chemicals and solvents used in this study were obtained from Tokyo Chemical Industry, Strem, or Wako Chemicals and were used without further purification. All operations reported here were carried out under an ambient atmosphere.

Preparation of Dy-o and Ho-o.

Solutions of DTE (53.6 mg, 0.12 mmol) in ethanol (10 ml), $DyCl_3•nH_2O$ (31.6 mg, 0.08 mmol) or $HoCl_3•nH_2O$ (33.6 mg, 0.08 mmol) in ethanol (10 ml), and 2,2'-bipyridine (14.5 mg, 0.08 mmol) in ethanol (10 ml) were mixed, and the resulting solution was stirred for 15 min. The pale blue turbid mixture was allowed to slowly evaporate in the dark in the presence of HCl vapour to give colourless crystals after several days. Evaporation was stopped by capping the vessel before all of the solvent evaporated. Yield: 33 mg (25%) for **Dy-o** and 20 mg (15%) for **Ho-o**. Anal. calc. (%) for $\{[Ho^{III}_2(DTE)_3(bipyridine)_2(H_2O)_2]\cdot 2EtOH\cdot 4H_2O\}_n$ $C_{75}H_{64}Ho_2F_{18}N_4O_{20}S_6$: C, 40.84; H, 2.92; N, 2.54. Found: C, 41.98; H, 3.30; N, 2.48; $\{[Dy^{III}_2(DTE)_3(bipyridine)_2(H_2O)_2]\cdot 2EtOH\cdot 4H_2O\}_n$ $C_{75}H_{64}Dy_2F_{18}N_4O_{20}S_6$: C, 40.84; H, 2.92; N, 2.54. Found: C, 41.86; H, 2.61; N, 2.79.

The low yield is due to the cessation of the evaporation before the ethanol totally evaporated (around 0.5 ml of solvent held) to avoid potential desolvation of the crystals. The elemental analysis ratio was calculated on the bases of the X-Ray diffraction data. The nature and amount of trapped solvent in the crystal lattice are estimations.

Single-Crystal X-ray diffraction.

All single-crystal crystallographic data were collected on a Rigaku Saturn70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) produced by a VariMax micro-focus X-Ray rotating anode source at 90 K. Data processing was performed using the CrystalClear crystallographic software package.[20] The structures were solved by using direct methods via SIR-92 or SIR-2011.[21] Refinement and further calculations were carried out using WinGX 2013.3 package[22] and SHELXL-2013.[23] The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. H atoms attached to the C atoms were positioned using idealized geometries and refined using a riding model. Positions of the H atoms on the water molecules were determined using the CALC-OH software[24] provide by WinGX.

The SQUEEZE instruction[25] in the PLATON software package was used to remove electron density due to disordered solvent molecules in the crystal lattice for both complexes. For **Dy-o**, 95 electrons were found in each void. Only water and ethanol were used during preparation of the complex, and thus, on the bases of the space group and symmetry of the void, we estimated that there were two ethanols and four waters per void. For **Ho-o**, there were four voids with two having a total of 97 electrons and the other two having 107 electrons, which correspond to two ethanols and four waters and two ethanols and 6 waters, respectively.

Powder X-ray diffraction.

The XRPD pattern was measured using a RIGAKU Smart-Lab diffractometer with Cu Kα radiation (λ = 1.5418 Å) for **Dy-o**. **Ho-o** was measured using a Brucker D2 Phaser with a Cu Kα radiation (λ = 1.5418 Å).

Physical Measurements.

Dc and ac magnetic susceptibility measurements were performed on solid polycrystalline samples on a Quantum Design MPMS-XL SQUID magnetometer in applied magnetic fields of 100 Oe in the T range of 1.8–20 K, 1000 Oe in the T range of 18–50 K, and 5000 Oe in the T range of 45–300 K. The experimental data were corrected for the diamagnetism of the sample holder, and the intrinsic diamagnetism of the materials was evaluated using Pascal's tables. Ac measurements were performed in a 3 Oe oscillating magnetic field with and without a static dc field. **Dy-c** and **Ho-c** were obtained by irradiating **Dy-o** and **Ho-o** samples, respectively, with UV light at 35000 cm^{-1} for 1 h in a dark room.

Solid-state absorption spectra were measured in $BaSO_4$ matrices on a Shimadzu UV-3150 spectrophotometer. Spectra of **Dy-o** and **Ho-o** were first acquired. Then they were irradiated with UV light at 35000 cm^{-1} for 30 min to obtain the close forms, which had a deep blue color, and spectra acquired again. To ensure the reversibility of the cyclization, a third set of spectra was acquired after leaving the samples in the sun for 1 day.

Results And Discussion

Crystal Structure Analysis.

Dy-o crystallized in the monoclinic space group *P*2/*n* (no. 13). The asymmetric unit of the complex is composed of one Dy ion, one and a half DTE ligands, one bipyridine ligand, and one coordinated water molecule (Figure 2). The full dinuclear complex was generated by applying the inversion operation, and the distance between the Dy ions was determined to be 4.533(1) Å. Two Dy ions are bridged by four carboxylato groups from the DTE ligands (Figure 3). The coordination sphere of each Dy ion is completed by two N atoms of a bipyridine ligand, one water molecule, and one oxygen atom from the carboxylato group of a DTE ligand in monodentate fashion. Overall the coordination spheres of the Dy ions are in a distorted square antiprism geometry, and the distortion was quantified using the software SHAPE 2.1 (Table 1).[26–27]

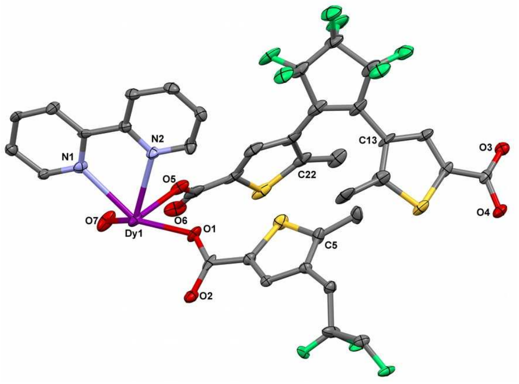


Fig. 2 ORTEP drawing of the asymmetric unit of **Dy-o**. Thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

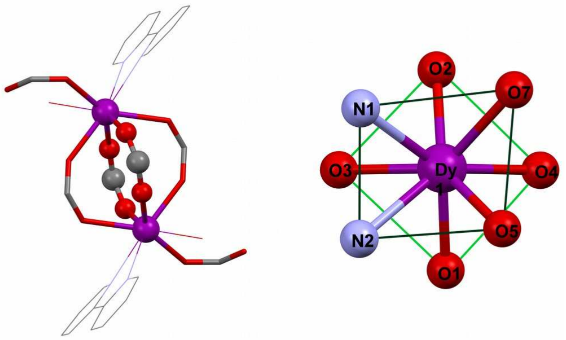


Fig. 3 Left: Ball and stick drawing of the Dy dimer with bipyridine and water ligands as wires. For clarity, only the carboxylato groups of the DTE ligands are shown, and the hydrogen atoms are omitted. Right: Representations of the coordination polyhedra in **Dy-o**. The light and dark green lines represent the bottom and top faces of the antiprism, respectively.

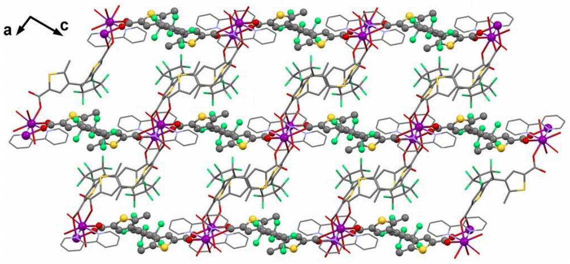


Fig. 4 Crystal packing of **Dy-o** in the ac plane.

Table 1 Possible geometries obtained using SHAPE 2.1. The smaller the values, the better the match between real and ideal polyhedral is.

			Dy	Ho1	Ho2
SAPR-8	D_{4d}	Square antiprism	0.745	0.621	0.758
BTPR-8	C_{2v}	Bi-augmented trigonal prism	1.365	1.381	1.226
JBTPR-8	C_{2v}	Bi-augmented trigonal prism J50	1.724	1.789	1.700
TDD-8	D_{2d}	Triangular dodecahedron	2.000	1.924	1.933

Furthermore, the Dy ion is not centred in its coordination sphere due to the different ligands (Table 2). The average Dy–N distance is 2.562(8) Å, whereas the Dy-OH$_2$ distance is 2.444(7) Å due to the oxophilic character of the Dy ions. The carbonyl O atoms have a negative charge, causing the **Dy-O** distance (2.322(7) Å to be shorter than that involving the coordinated H$_2$O.

Table 2 Selected bond lengths (Å) for **Dy-o** and **Ho-o**

	Dy	Ho1	Ho2
Ln–N	2.565(7)	2.559(5)	2.577(5)
Ln–N	2.560(8)	2.541(5)	2.524(5)
Ln–Ow	2.444(7)	2.405(5)	2.378(5)
Ln–O	2.344(7)	2.334(6)	2.360(4)
Ln–O	2.340(7)	2.326(4)	2.327(4)
Ln–O	2.317(7)	2.319(4)	2.308(5)
Ln–O	2.311(8)	2.311(5)	2.307(6)
n– O	2.299(7)	2.278(5)	2.300(5)

Two different DTE ligands were found. The first one (DTE1) was generated from the half ligand present in the asymmetric unit, and the entire DTE ligand was generated by applying the C2 axis of the *P*2/*n* space group, which also generated the 1D chains along the [101] direction (Figures 4 and S1). The four O atoms of the carboxylato groups on DTE1 coordinate to the Dy ions, and the shortest distance between the two Dy ions in the chain was determined to be 14.120(2) Å. DTE2 is the entire DTE ligand present in the asymmetric unit and links the 1D chains together (Figures 4 and S2) along the [100] direction to give a 2D coordination polymer in the (101) plane. Along the [100] direction, the shortest Dy···Dy distance was determined to be 13.821(3) Å. Between the planes, van der Waals interactions occur. The shortest Dy···Dy interplane distance was 8.703(2) Å. The C-C distances in DTE1 and DTE2 are 3.511 and 3.495 Å, respectively, which are short enough to allow for opening and closing of the DTEs.[10]

Table 3 X-ray data for **Dy-o** and **Ho-o**

Formula	$C_{71}H_{56}N_4O_{20}F_{18}S_6Dy_2$	$C_{71}H_{44}N_4O_{14}F_{18}S_6Ho_2$
Mr/g mol^{-1}	2144.62	2040.39
Crystal system	Monoclinic	Monoclinic
Space group	*P*2/*n* (no. 13)	*P*2/*n* (no. 13)
a/Å	14.599(3)	27.054(8)
b/Å	12.854(3)	12.490(3)
c/Å	23.641(4)	29.279(8)
β/°	97.627(4)	115.387(4)
V/Å^3	4397.12	8938.11
Z	2	4
T/K	93	93
Diffraction reflection	$4.11 \leq 2\theta \leq 27.48$	$3.05 \leq 2\theta \leq 27.55$
ρ_{calcd}/g cm^{-3}	1.620	1.517
μ/mm^{-1}	1.933	1.991
Number of reflections	34955	20773
Independent reflections	10005	19887
$F_0^2 > 2\sigma(F_0)^2$	5872	14887
Number of variables	586	1054
R_{int}, $R1$, $wR2$	0.1072, 0.0821, 0.1659	0.0715, 0.0614, 0.1443

Ho-o also crystallized in the monoclinic space group *P*2/*n*. However, the two Ho ions of the dimer are not symmetric (Figure 5). As a consequence, both the asymmetric unit of the complex, which contains two Ho ions, two bipyridine ligands, two coordinated water molecules, and three DTE ligands, and the cell volume were nearly twice those of **Dy-o**. The distance between the two Ho ions was determined to be 4.467(1) Å. Similar to **Dy-o**, the carboxylato groups on the DTE ligands bridge the Ho ions (Figure S3), and the coordination sphere of each ion is completed by the N atoms of the bipyridine ligand, one water molecule, and a monodentate carboxylato group from a DTE ligand. The coordination spheres of the two Ho ions are aligned in a distorted square antiprismatic geometry (Table 1 and Figure S4).

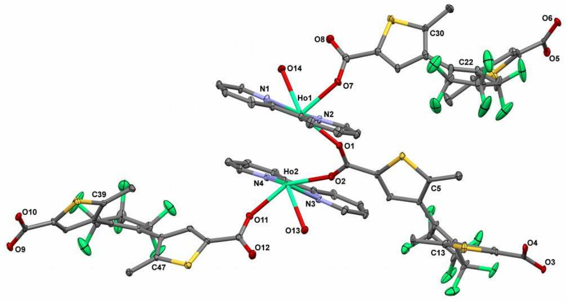
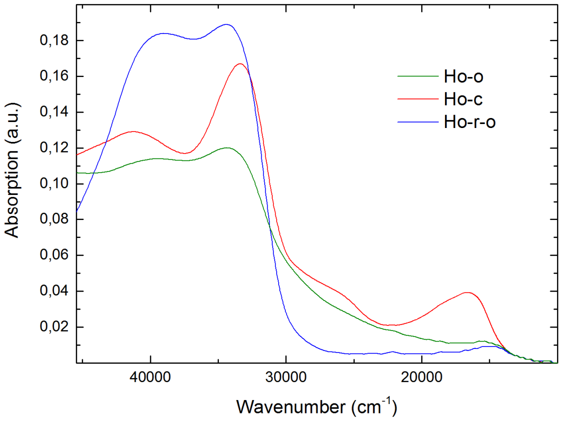


Fig. 5 ORTEP drawing of the asymmetric unit of **Ho-o**. Thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

Like **Dy-o**, two different DTE ligands were found in **Ho-o**. For DTE1, the four carboxylato O atoms coordinate to the Ho ions and generate a 1D chain along the [101] direction (Figure S5) with a distance between nearest dimers of 14.689(3) Å. For DTE2 and DTE3, only three of the four carboxylato O atoms are coordinated. These ligands link the 1D chains together along the [100] direction to give a 2D coordination polymer in the (101) plane (Figure S6). The shortest distances between dimers in the [100] direction were determined to be 14.103(3) and 14.051(4) Å for DTE2 and DTE3, respectively. van der Waals interactions occur between the planes, and the shortest interplane distance between dimers was determined to be 8.335(2) Å. The C-C distances are 3.53(1), 3.557(8) and 3.77(1) Å for DTE1, DTE2 and DTE3, respectively. All the distances are similar to those in **Dy-o**.

It has not been possible to obtain the X-ray structure of the complexes with the closed form of the ligand. After irradiation of the complexes with UV light, the crystals kept their shape but changed from colourless to blue, but no diffraction peaks were observed. The loss of crystallinity is irreversible. Crystallographic purity of open form of samples was determined by powder X-ray diffraction (Figure S10 - S11). Both samples, **Dy-o** and **Ho-o**, are in good agreement with the simulated spectra, no additional phase can be observed.



Solid-State Optical Properties.

Fig. 6 Solid-state UV-vis absorption spectra for **Ho-o**, **Ho-c** and **Ho-r-o**.

In UV-vis absorption spectra of **Ho-o**, there were two absorption bands at 40733 and 33000 cm^{-1} (Figure 6). The first one was attributed to a π-π* transition of the bipyridine ligand, and the second one corresponded to an S0 → S1 singlet intraligand (IL) transition localized on the photochromic ligand.[29]

After irradiating the sample at λ = 35000 cm^{-1} for 30 min, it became deep blue, and two additional bands are exalt at 26000 and 16780 cm^{-1} and were assigned as π-π* transition bands of the closed form of the ligand.[18] After exposition to the daylight for one day (**Ho-r-o** on Figure 6), the transition bands assigned to the closed form are no longer visible, attesting the reversibility of the photo-isomerisation. However the π-π* transition of the bipyridine ligand and the IL transition of the DTE are exalted after re-opening process due to the irreversible structure modification.

Magnetic properties.

The magnetic properties of the complexes with both forms of the ligand were determined. After measuring the magnetic properties of the open form of the complexes, the samples were irradiated at 35000 cm^{-1} for 1 hour, and then the magnetic properties of the sample were determined again. After irradiation of samples with UV light, they changed from colourless to deep blue (Figure S9).

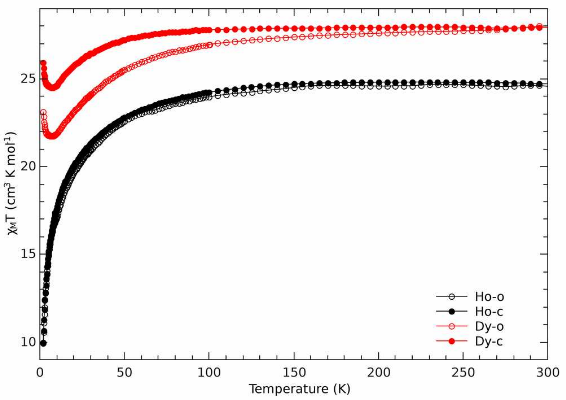


Fig. 7 *T* dependence of $\chi_M T$ for polycrystalline samples of the Dy and Ho complexes.

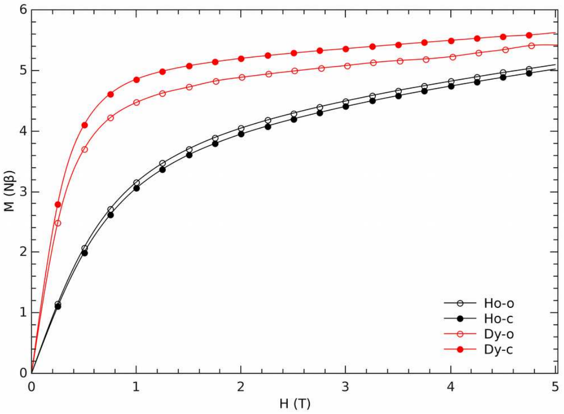


Fig. 8 Field dependence of the magnetization at 2 K for the complexes.

Static magnetic properties. The *T* dependences of $\chi_M T$ for polycrystalline samples of the complexes are shown in Figure 7. For both **Dy-o** and **Dy-c**, the $\chi_M T$ values at room T (27.93 cm^3 K mol^{-1}) were close to the expected value for two uncoupled Dy ions (28.34 cm^3 K mol^{-1}).[30] The values of $\chi_M T$ for the Dy complexes plateaued between 300 and 125 K, and then the values decreased to 23.11 and 24.48 cm^3 K mol^{-1} at 2 K with a minimum of 21.73 cm^3 K mol^{-1} at 6.8 K and 24.48 cm^3 K mol^{-1} at 7 K for **Dy-o** and **Dy-c**, respectively. The decrease between 125 K and 7 K is due to the depopulation of the mJ levels of the $^6H_{15/2}$ ground-state multiplet of the Dy^{III} ions. There is a significant difference in the depopulation processes for **Dy-o** and **Dy-c**, which were attributed to different energy splittings of the m_J sub-level of the ground state with a different m_J lowest state for the open and closed forms due to the crystal field around the metal ions. Closing the ligand causes a change in the crystal field, which affects $\chi_M T$ of the complex. The increase in $\chi_M T$ above 7 K is due to ferromagnetic interactions between the two Dy ions in the dimer through dipole-dipole interactions.

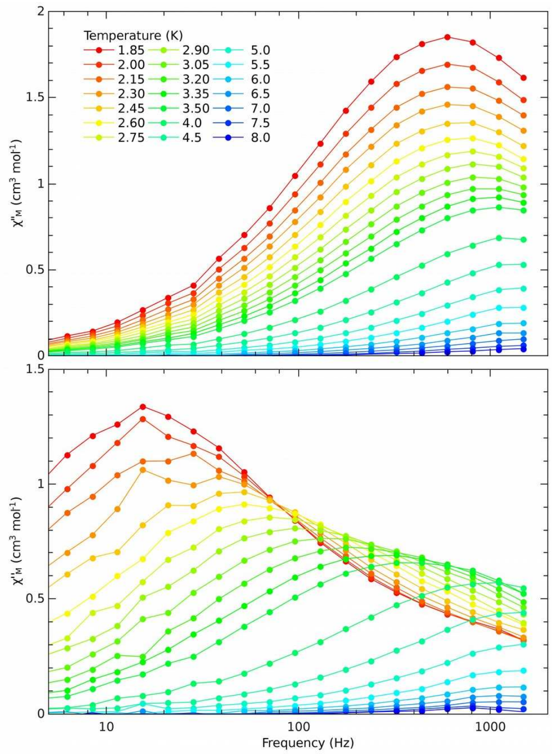


Fig. 9 *T* dependences of χ_M" of **Dy-o** at 0 Oe (top) and 1000 Oe (bottom).

The room-*T* values for **Ho-o** and **Ho-c** were determined to be 24.56 and 24.69 cm^3 K mol^{-1}, respectively. Like the Dy complexes, on cooling, $\chi_M T$ of both forms remained constant until 125 K, and then $\chi_M T$ decreased monotonically to 9.99 and 9.94 cm^3 K mol^{-1} for **Ho-o** and **Ho-c**, respectively, which indicate that the m_J levels of the $^5I_8$ ground-state multiplet of the Ho^{III} ions become thermally depopulated. A small difference in the depopulation process between the open and closed forms of the complexes was observed. No ferromagnetic interactions were observed in the Ho complexes. The ferromagnetic interactions may be too weak to offset the sub-level depopulation, or there may be no ferromagnetic interactions. Although antiferromagnetic interactions may occur, we could not determine the nature of the interactions graphically. Magnetization curves at 2 K for the complexes support that the m_J ground states of the open and closed forms of the complexes are different (Figure 8). The magnetisation values of **Dy-o** and **Dy-c** at 5 T were determined to be 5.418 Nβ and 5.625 Nβ, respectively. The different saturation values are due to differences in the energy splitting of the ground states.[31] Similar behaviour was observed for **Ho-o** and **Ho-c** with saturation values of 5.095 Nβ and 5.023 Nβ, respectively.

We are currently trying to extract the energy splitting of the four complexes from the $\chi_M T$ vs. *T* and *M* vs. *H* curves.

Dynamic magnetic properties. **Dy-o** showed an out-of-phase ac signal (χ_M") above 8 K in a zero dc field (Figure 9 top and Table S1). The frequency dependences in a zero dc field of the in-phase (χ_M') component and χ_M" of the ac susceptibility from 1.85 to 5 K were fitted using an extended Debye model:[32]

$$\chi_M{}' = \chi_{adia} + (\chi_{iso} - \chi_{adia}) \frac{1 + (\omega\tau)^{(1-\alpha)} \sin\frac{\alpha\pi}{2}}{1 + 2(\omega\tau)^{(1-\alpha)} \sin\frac{\alpha\pi}{2} + (\omega\tau)^{(2-2\alpha)}} \qquad (1)$$

$$\chi_M{}' = (\chi_{iso} - \chi_{adia}) \frac{(\omega\tau)^{(1-\alpha)} \cos\frac{\alpha\pi}{2}}{1 + 2(\omega\tau)^{(1-\alpha)} \sin\frac{\alpha\pi}{2} + (\omega\tau)^{(2-2\alpha)}} \qquad (2)$$

where χ_{dia} and χ_{iso} are the low- and high-frequency limits of the susceptibility, τ is the relaxation time, and α is the distribution of τ.

$$\tau = \frac{\tau_{TI}\,\tau_0 \exp\frac{-\mathit{\Delta}}{T}}{\tau_{TI} + \tau_0 \exp\frac{-\mathit{\Delta}}{T}} \qquad (3)$$

An Arrhenius law[33] (equation (3)) was used to determine the characteristic energy barrier ($\mathit{\Delta}$), thermally independent τ (τ_{TI}), and τ for infinite T (τ_0) of the sample.

α was about 0.21 in the T range studied. Below 3 K, a quantum relaxation process occurred with $\tau_{\mathrm{TI}} = 2.77 \times 10^{-4}$ s. Above 3 K, the relaxation process became unclear. Between 3 and 5 K, a transition between quantum relaxation and a thermal relaxation processes or a thermally activated regime with $\mathit{\Delta} = 14.5$ K and $\tau_0 = 5.33 \times 10^{-6}$ s was observed (Figure 10). The quantum relaxation was minimized in an external dc field of 800 Oe (Figure S7). From the frequency dependence of the ac susceptibility in a 1 kOe dc field in the T range of 1.85–5 K (Figure 9 bottom and Table S2), Δ was determined to be 21.7 K ($\tau_{\mathrm{TI}} = 9.6 \times 10^{-3}$ s and $\tau_0 = 8.1 \times 10^{-7}$ s). $\mathit{\Delta}$ is slightly higher than that calculated in a zero dc field, meaning that it is underestimated, and at 5 K, the complex is still in a transition regime between quantum relaxation and thermal relaxation processes. Furthermore, the quantum relaxation process was not fully suppressed below 2 K, and the external field caused an increase in α from 0.34 at 1.85 K to 0.28 at 5K with a maximum value of 0.37 at 2.45 K (see the Supporting Information). This increase in α is due to a higher magnetic inhomogeneity of the sample caused by the change in the geometry of the DTE ligands.

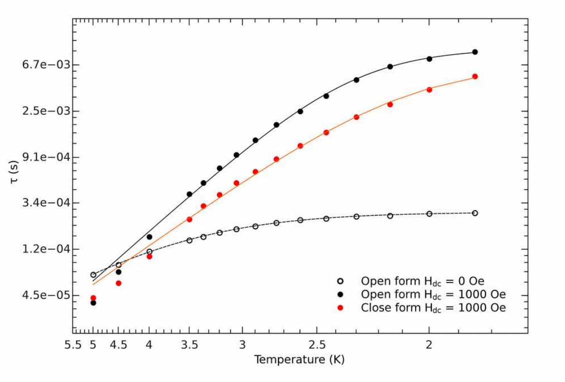


Fig. 10 Arrhenius plot with best-fit curves.

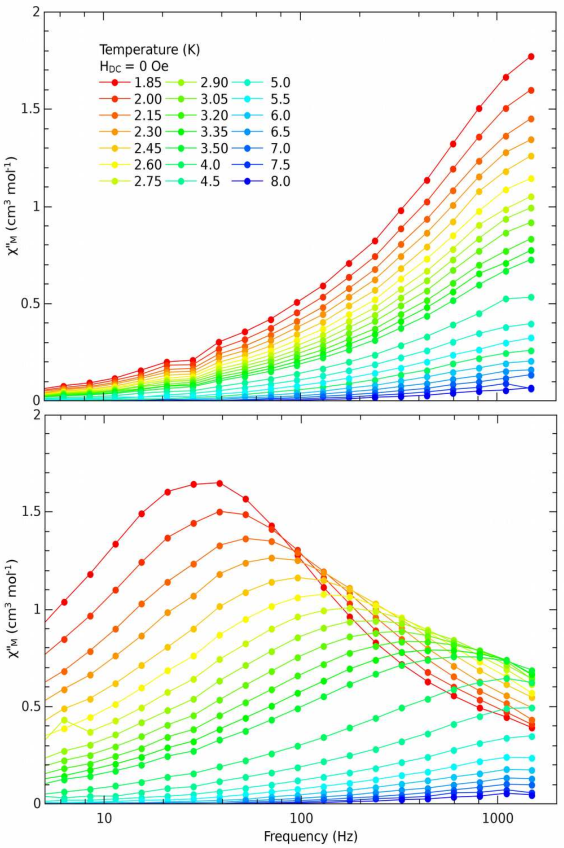


Fig. 11 *T* dependence of χ_M” of **Dy-c** at 0 Oe (top) and 1000 Oe (bottom).

For **Dy-c**, a χ_M” signal without an external dc field was observed (Figure 11). In comparison to the relaxation process for **Dy-o**, that for **Dy-c** is much faster. No maximum χ_M” value was observed in the range of 1–1500 Hz. The absence of peak at a frequency about 600 Hz indicates that most of sample is converted from open to closed forms and not just on the surface of the crystal. In a dc field of <1000 Oe (Figure 11 and Table S3), the relaxation process was slower, and a maximum, which corresponded to a thermal relaxation process with Δ = 17.1 K ($\tau_{\mathrm{TI}} = 6.9 \times 10^{-3}$ s and $\tau_0 = 1.9 \times 10^{-6}$ s) and an α value between 0.29 and 0.38, was observed. The Δ, α, and τ values are similar to those for **Dy-o** and **Dy-c** in external field of 1000 Oe. We think that the same thermal relaxation process occurs for the two complexes and that the differences at high frequency between **Dy-o** and **Dy-c** without an external dc field are due to a faster quantum relaxation process in the case of **Dy-c**. This change in the quantum relaxation process is due to the difference in the mJ level splitting observed with $\chi_M T$. In other words, we can control the quantum-tunneling relaxation process using a photochromic ligand. However, without the crystallographic structure of the open and closed forms of the ligand, the exact control mechanism remains unclear.

Ho-o and **Ho-c** did not exhibit a χ_M” signal above 1.85 K with or without an external dc field (Figure S8). There are two possible reasons for the absence of the SMM behaviour for these complexes. First, the same crystal field around the Dy and Ho ions does not produce the same energy splitting. In the case of phthalocyanato complexes,[34] the ground state of the Dy ions is $m_J = \pm$ 13/2, whereas that of the Ho ions is $m_J = \pm 5$. To obtain SMM behaviour, the highest m_J level must be stabilized, i.e., it is stabilized in the Dy complexes but not in the Ho ones. Second, the nature of intradimer magnetic interactions can play a role. Although there are clear ferromagnetic interactions in the Dy complexes, in the Ho complexes, the intradimer interactions are probably antiferromagnetic. In a previous study,[19] both Dy and Ho DTE bridged Ln dimer polymers show SMM behaviour, whereas the present 2D polymer does not. There are several possible reasons for this difference. I) Introduction of bipyridine as a coligand, instead of DMSO solvent, reduces degree of freedom of the coordination sphere. II) Substitution of two oxygen atoms by two nitrogen atoms in the coordination sphere of the ions induces a significant change in the crystal field and therefore a change in the energy splitting of the ground state. III) The DTE ligands coordinate differently. In the previous work, every carboxylato oxygen atom coordinates via one oxygen atom to bridge two Ho ions. However, in this work, one carboxylato oxygen atom does not coordinate, and there are no bridging atoms between the Ho ions.

Conclusions

Dy and Ho coordination polymers containing a photochromic DTE ligand were synthesized, and their properties were investigated by using UV-vis spectroscopy, X-ray diffraction, and SQUID magnetometry. The two complexes are isostructural with a lanthanide dimer bridged by three DTE ligands to create a 2D coordination polymer. In the coordination polymers, the

DTE ligands could be closed by irradiation with UV light. The Dy complexes exhibited slow magnetic relaxation without an external dc field when DTE was either opened or closed (Δ = 21.7 K and 17.1 K, respectively). The quantum-tunneling relaxation process was affected by the photo-isomerization of the ligand. Opening and closing the ligand changed its geometry, which affected the coordination sphere and the crystal field around the Dy ions. Thus, the energy splitting of the m_J level changed, meaning that the magnetic properties of the complex were drastically affected. In addition, there were weak intradimer magnetic interactions through the conjugated π-system of the DTE ligand. However, cyclization of the ligand caused the samples to become irreversibly amorphous. Theoretical calculations are needed to understand the relaxation mechanism for this complex in detail. Studies are in progress to utilize the photo-magnetic cross-effects of lanthanide-based complexes with a photochromic DTE ligand in photo-switches.

Notes and references

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† Electronic Supplementary Information (ESI) contains crystallographic diagram (Fig. S1-S6), *ac* susceptibility fitting parameters (Table S1-S3), Field dependancy of χ_M'' for **Dy-o** at 2 K (Fig. S7) and *T* dependence of χ_M'' and χ_M' for **Ho-o** in a zero dc field (Fig. S8). CCDC 1027622, CCDC 1027623. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000000x

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Photo-control of the Magnetic Properties of Dy(III) and Ho(III) Homometal Coordination Polymers Bridged by a Diarylethene Ligand

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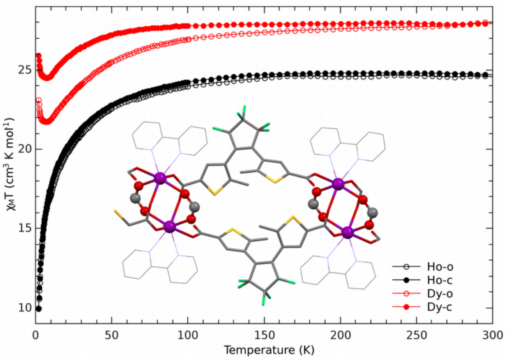

Two-dimensional Dy(III) and Ho(III) homometal coordination polymers containing the photochromic ligand 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (DTE) were obtained, and the magnetic properties of the open and closed forms were investigated. The Dy complexes exhibited slow magnetic relaxation, and its magnetic properties were greatly affected by the conformation of the ligand.