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Tetrathiafulvalene-Based Helicene Ligand in the Design of Dysprosium Field-Induced Single-Molecule Magnet

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ABSTRACT: The design of a coordination complex which involves a ligand combining both a tetrathiafulvalene core and helicene fragment was achieved thanks to the reaction between the new 2-{1-[2-methyl[6]helicene]-4,5-[4,5-bis(propylthio)-tetrathiafulvalenyl]-1H-benzimidazol-2-yl}pyridine ligand (**L**) and the Dy(hfac)₃·2H₂O metallo precursor. Magnetic investigations showed a field-induced Single-Molecule Magnet (SMM) behavior under an applied magnetic field of 1000 Oe for [Dy(hfac)₃(**L**)]·0.5CH₂Cl₂ while experimental oriented single crystal magnetic measurements allowed for the determination of the magnetic anisotropy orientation. The magnetic behavior was rationalized based on ab initio CASSCF/SI-SO calculations. This redox-active chiral field-induced SMM paves the route for designing switchable multi-properties SMMs.

Chemists are working hand in hand with physicists to design Single-Molecule Magnets (SMMs) displaying magnetic bistability at temperatures as high as possible. Recently a mononuclear Dy^{III}-SMM highlighted a blocking temperature of 60 K¹⁻³ jump-starting this kind of molecular objects suitable for potential applications in high-density data storage, quantum computing and spintronics.⁴⁻⁶ One more challenge is to combine the SMM behavior with others chemical, optical or physical properties such as ferroelectricity, redox-activity/conductivity, luminescence, non-linear optics, chirality/chiroptical activity in order to open the route to more potential applications.⁷⁻⁹ In the specific case of chiral SMMs, the chirality can come from highly optically-active ligands such as [n]helicenes,^{10,11} which are organic molecules with π -conjugated helical backbone made of *ortho*-fused aromatic rings with configurational stability for $n \geq 5$.¹² Subsequently the [n]helicenes can be decorated by an electroactive unit such as organometallic,¹³ quinone,¹⁴ pyridinium¹⁵ and tetrathiafulvalene¹⁶ (TTF) derivatives. The latter TTF core is a well-known electroactive fragment mainly used to design conducting materials ranging from semiconductors to superconductors.^{17,18} Its functionalization with a plethora of accepting groups allowed the TTF-based ligands to participate in the development of fluorescence switches,¹⁹ photovoltaic cells,²⁰ coordination of transition metals²¹ and finally

coordination of 4f elements. In particular, the combination of lanthanide ions with TTF-based ligands permitted to reach new classes of multi-properties compounds with redox-active luminescent SMM behaviour.^{7,22} To the best of our knowledge, no chiral SMM with a redox activity easily chemically accessible in common organic solvents has been reported to date. To reach such objective, we propose i) to combine both electro-active TTF and carbo[6]helicene in a unique ligand and ii) to coordinate such ligand to magnetically anisotropic Dy^{III} ion.

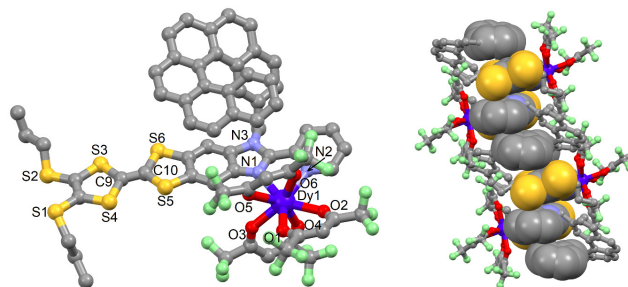


Figure 1. (Left) molecular structure of [Dy(hfac)₃(**L**)]·0.5CH₂Cl₂, the hydrogen atoms and dichloromethane molecule of crystallization were omitted for clarity. Selected bond lengths (Å): Dy1-N1, 2.466(5); Dy1-N2, 2.562(5); Dy1-O1, 2.330(4); Dy1-O2, 2.366(4); Dy1-O3, 2.332(4); Dy1-O4, 2.351(4); Dy1-O5, 2.372(4); Dy1-O6, 2.323(4); C9-C10, 1.343(7); carbon (C, gray); fluorine (F, green). (Right) crystal packing of [Dy(hfac)₃(**L**)] highlighting the π - π interactions along the *a* axis between the TTF-based molecular skeletons and the helicenic moieties (space-fill representation).

The functionalization of the molecular skeleton 4,5-bis(propylthio)-tetrathiafulvalenyl]-1H-benzimidazol-2-yl}pyridine²³ with the 2-bromomethyl[6]helicene²⁴ in its racemic form (85% yield, see S.I.) led to the 2-{1-[2-methyl[6]helicene]-4,5-[4,5-bis(propylthio)-tetrathiafulvalenyl]-1H-benzimidazol-2-yl}pyridine (**L**) ligand which reacted with the precursor Dy(hfac)₃·2H₂O (hfac⁻ = 1,1,1,5,5,5-hexafluoroacetylacetonate anion) to give the mononuclear complex [Dy(hfac)₃(**L**)]·0.5CH₂Cl₂.

Single-crystal X-ray diffraction confirms that this compound crystallizes in the triclinic space group P-1 (N°) (Table S1). The molecular structure attests the success of the alkylation of the TTF-based molecular skeleton by the 2-methylene-carbo[6]helicene derivative (Figures 1 and S1). The Dy^{III} ion is coordinated to the bischelating 1H-benzimidazol-2-ylpyridine (bzip) moiety and to the three hfac⁻ anions in a N_2O_6 surrounding. In a strict structural point of view, the first neighboring atoms create a D_{2d} symmetry polyhedron (Table S2, SHAPE analysis²⁵). The neutrality of the ligand **L** is confirmed by the C9=C10 central bond length of 1.343(7) Å. The benzimidazol-tetrathiafulvalene fragment is planar while the planes formed by the benzimidazole and pyridine moieties have a twist angle of 18.0(2) $^{\circ}$ resulting from the steric hindrance of the [6]helicene arm and optimized π - π interactions between the terminal benzene ring of the helicene and the bzip coordinated fragment. A quick overview of the literature on this kind of TTF-based ligands shows a zero twist angle when no alkylation is realized (amine, NH)²⁶ and for methyl-2-pyridine,²⁷ 4-methylpyridine-N-oxide,²⁷ 4,4'-dimethyl-2,2'-bipyridine²⁸ as alkylating arms while a twist angle of 12.2(3) $^{\circ}$ is measured for a bulkier arm such as 2,6-di(pyrazol-1-yl)-4-methylpyridyl²⁹. The crystal packing highlights the formation of a one-dimensional network of stacked **L** along the *a* axis which is formed by intramolecular π - π interactions between the helicene and bzip fragments and intermolecular π - π interactions between two "head-to-tail" ligands (Figure 1). The shortest intermolecular Dy-Dy distance is equal to 9.529 Å.

The redox properties of the ligand **L** and the complex $[Dy(hfac)_3(L)] \cdot 0.5CH_2Cl_2$ are investigated by cyclic voltammetry (Figure S2, Table S3). The cyclic voltammogram for the free ligand shows two mono-electronic oxidations at 0.53 V for the first oxidation and 0.93 V for the second oxidation, corresponding to the formation of a radical cation and a dication TTF fragment, respectively.^{23,26-29} The coordination of the $Dy(hfac)_3$ fragment has almost no significant effect on the oxidation potentials (0.55 V and 0.94 V) as observed for similar compounds.²⁶⁻²⁹ The electrochemical properties attest that the reversibility of the oxidation potentials and the redox-activity of the ligand are conserved after complexation.

The temperature dependence of $\chi_M T$ for a powdered sample of $[Dy(hfac)_3(L)] \cdot 0.5CH_2Cl_2$ shows a room temperature value of 14.06 $cm^3 K mol^{-1}$ in agreement with isolated Dy^{III} ion (Figure 2a). On cooling, $\chi_M T$ decreases monotonically down to 12.17 $cm^3 K mol^{-1}$ at 2 K. The first magnetization at 2 K highlights a classic behavior in the field range of 0-50 kOe for such isolated Dy^{III} ion (inset Figure 2a). The same sample shows frequency dependence in zero external dc field (Figures 2b and S3) but with a maximum of the χ_M'' vs. ν curve (ν the frequency of the ac oscillating field) that falls out of the frequency range of the experimental window. The application of an external dc field cancels the Quantum Tunneling of the Magnetization (QTM) and the maximum of the χ_M'' vs. ν curve shifts to lower frequency (Figure 2b). The 1000 Oe value was chosen as the optimum field since the relaxation is slowest and more intense (Figure 2b). In such applied field, the out-of-phase component of χ_M was observed in the temperature range of 2-8 K (Figures 2c and S4). The frequency dependence of the ac susceptibility can be analyzed in the framework of the extended Debye model both for field and temperature variations. The temperature dependence of the relaxation time at 1000 Oe is extracted from the extended Debye model between 2.0 and 6.0 K (Table S4). The Arrhenius plot of the relaxation time is well fitted by a Raman relaxation process $\tau = C \times T^n$ with $C = 2.4(4) \times 10^{-2}$ and $n = 5.5(1)$ (Figure 2d)²⁹. Theoretically, the expected value of the *n* exponent for Kramers ions is 9 and can be decreased down to 4, depending on the energies of the

ground state doublets.^{30,31} Recently it was shown that such exponent could reach a value close to 2 due to the presence of both acoustic and optic phonons in specific ligand environments.³² The Cole-Cole³³ plots normalized to their isothermal value are represented in Figure S5. The Dy^{III} ion lies in a N_2O_6 environment with the two nitrogen atoms coming from a bischelating imidazol-2-ylpyridine derivative while the six oxygen atoms come from three hfac⁻ anions. Thus the extracted dynamic parameters for the complex $[Dy(hfac)_3(L)] \cdot 0.5CH_2Cl_2$ can be compared with examples in which the common TTF-based skeleton is alkylated with different chemical arms.

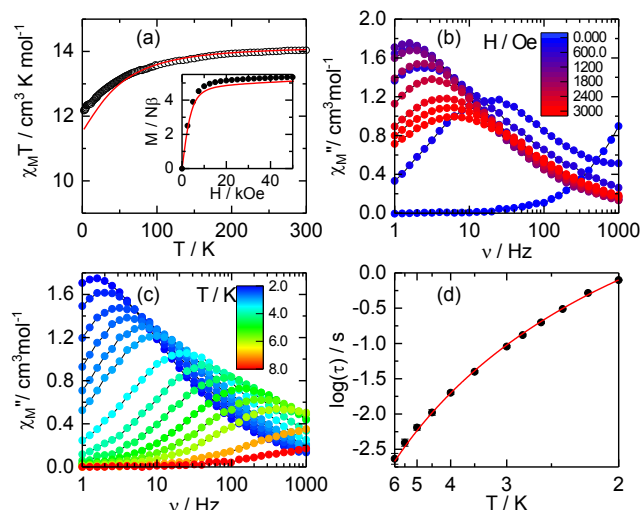


Figure 2. (a) Thermal variation of $\chi_M T$ for. In inset, first magnetization. Calculated curves are in red. (b) Scan field of the frequency dependence of χ_M'' of at 2 K. (c) Frequency dependence of χ_M'' between 2 and 8 K at 1000 Oe. (d) Temperature variation of the relaxation time measured in an external field of 1000 Oe with the best-fitted curve (red line) in the temperature range of 2-6 K.

In these compounds and others of the literature,³⁴ the effective energy barrier range from 18 K to 57 K. Nevertheless, starting from the same coordination polyhedron symmetry and N_2O_6 environment, it is clear that the nature of the alkylated group and/or the positions of the hfac⁻ anions (which can depend on the steric hindrance of the alkylated group) have a crucial importance on the value of the energy barrier. Since the complex $[Dy(hfac)_3(L)] \cdot 0.5CH_2Cl_2$ crystallizes in the triclinic P-1 space group and considering an effective spin $1/2$ at low temperature, the orientation of the *g*-tensor can be determined by measuring the magnetization of a single crystal in the three perpendicular planes (Figure S6). This oriented single crystal measurements revealed an uniaxial magnetic anisotropy with a Landé factor of 19.6 (20 expected for a pure $M_J = \pm 15/2$ ground state) with the orientation of the main magnetic axis along the most negatively charged direction of the coordination surrounding *i.e.* perpendicular to the plane containing the nitrogen atoms (Figure 3).

SA-CASSCF/SI-SO calculations were performed on $[Dy(hfac)_3(L)]$ to rationalize the observed magnetic properties (see computational details). Energy spectra and *g* tensors for the eight Kramer's doublets of the ground $^6H_{15/2}$ multiplet of the Dy^{III} ion are given in Table S5. The calculations confirm the axial character of the magnetic anisotropy tensor of the ground Kramer's doublet with a large g_z value of 19.09 for the Dy^{III} center and almost negligible g_x and g_y values. The decomposition in terms of pure $|J=15/2\rangle$ spin wavefunctions shows that the ground state has a majority (88%) $|\pm 15/2\rangle$ character with a non-negligible (10%) $|\pm 11/2\rangle$ component with a first excited state lying at more than 75 K above the ground state. Such discrepancy with the

hypothetic energy barrier coming from an Orbach process (21.1 K) supports the only operative Raman relaxation process in $[\text{Dy}(\text{hfac})_3(\text{L})]\cdot 0.5\text{CH}_2\text{Cl}_2$. The calculated ground-state easy axis (Figure 3) for the Dy^{III} ion is oriented perpendicular to the plane formed by the {tetrathiafulvalenyl-1*H*-benzimidazol-2-yl}pyridine moiety in agreement with experiment.³⁵

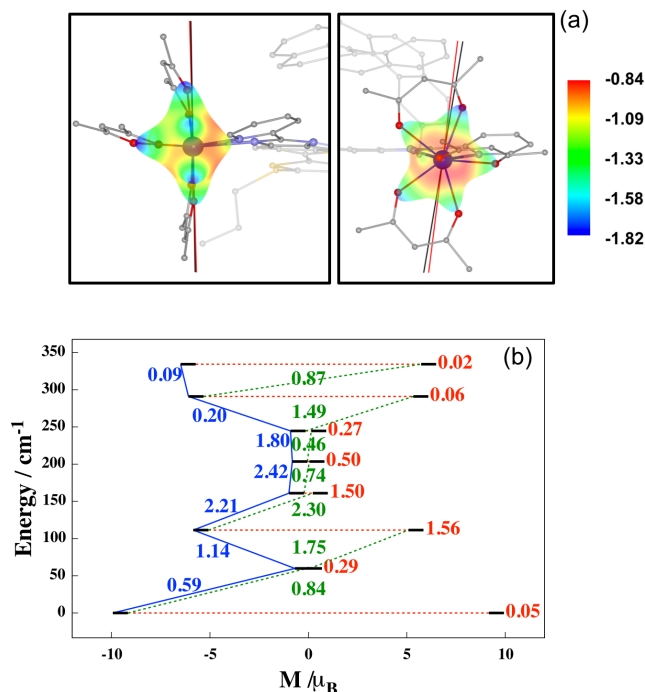


Figure 3. (a) Representation (two different orientations) of the ground state total molecular electrostatic potential around the Dy^{III} ion. The black and red lines correspond to experimental and theoretical main anisotropy axes, respectively. (b) Computed magnetization blocking barriers. Numbers provided on each arrow are the mean absolute values for the corresponding matrix elements of the magnetic transition dipole moment.

This orientation is further supported by the representation of the molecular electrostatic potential around the Dy^{III} ion using the home-made **CAMMEL** program (**C**alculated **M**ultipolar **E**lectrostatics; the description of the code is detailed in the Supporting Information). The total electrostatic potential is represented for the ground state along with both experimental and calculated axes in Figure 3a. As one can see, the most negative potential, containing the calculated magnetic axis, appears along the plane containing the two hfac⁻ ligands and perpendicular to the TTF plane. Moreover, the multipolar expansion of the total molecular electrostatic potential (Figures S7-S9) shows that quadrupolar contributions seem to be preponderant, as already observed in previous studies.^{36,37} Regarding the static magnetic properties, this electronic structure leads to a calculated magnetization at 2 K in good agreement with the experimental M vs H and to a quantitative agreement in the thermal dependence of the $\chi_{\text{M}}T$ product (Figure 2), with some small discrepancy at low temperatures that may be due to possible intermolecular dipolar interactions. The computed magnetization blocking barrier is reported in Figure 3b. Even though main relaxation mechanisms probably involve higher excited states (up to the third), calculations also support quantum tunneling relaxation mechanisms (QTM) within the ground state doublet. However, these transition moments allow only a qualitative evaluation of the magnetization barrier, since not all contributions (e.g. spin-phonon coupling) are included.³⁸⁻⁴⁰

In conclusion, a redox-active chiral field-induced SMM, $[\text{Dy}(\text{hfac})_3(\text{L})]\cdot 0.5\text{CH}_2\text{Cl}_2$, has been successfully synthesized by combination of a redox-active TTF-based skeleton and a [6]Helicene derivative followed by the coordination reaction of the $\text{Dy}(\text{hfac})_3$ precursor. This complex exhibits field-induced SMM behavior. This compound paves the route to the redox modulation of the electronic circular dichroism ECD signal and SMM behavior. To reach such aim, the synthesis of pure enantiomers of $[\text{Dy}(\text{hfac})_3(\text{L})]\cdot 0.5\text{CH}_2\text{Cl}_2$ and the oxidation of **L** are in progress.

ASSOCIATED CONTENT

Supporting Information

Ortep view of $[\text{Dy}(\text{hfac})_3(\text{L})]\cdot 0.5\text{CH}_2\text{Cl}_2$ (Figure S1), crystallographic data (Table S1-2), cyclic voltamograms (Figure S2, Table S3), additional magnetic data (Figures S4-9 and Tables S4-5), X-ray data in CIF format, experimental and material details and computational details.

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 interests.

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