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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 DyIII-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 other chemical, optical or physical properties such as ferroelectricity, redox-activity/conductivity, luminescence, nonlinear optics, chirality/chiroptical activity in order to open the route to more potential applications.5,9 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 ≥ 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.7,18 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.5,22 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 DyIII 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).
Single-crystal X-ray diffraction confirms that this compound crystallizes in the triclinic space group P-1 (N22) (Table S1). The molecular structure attests the success of the alkylation of the TTF-based molecular skeleton by the 2-methylene-carbobi6]helicene derivative (Figures 1 and S1). The DyII ion is coordinated to the bischelating 1H-benzimidazol-2-ylpyridine (bzip) moiety and to the three hfac- anions in a N2O6 surrounding. In a strict structural point of view, the first neighboring atoms create a D2 asymmetry polyhedron (Table S2, SHAPE analysis). 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)° 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) and for methyl-2-pyridine,27 4-methylpyridin-N-oxide,27 4,4'-dimethyl-2,2'-bipyridine28 as alkylling agents while a twist angle of 12.2(3)° 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)]·0.5CH2Cl2 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 to the formation of a radical cation and a dication TTF fragment, first oxidation and 0.93 V for the second oxidation, corresponding ligand shows two mono-electronic oxidations at 0.53 V for the isolated DyIII ion (inset Figure 2a). On cooling, M'' vs. T curve shifts to lower frequency with the maximum of the νM'' curve at 10.000 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 N2O6 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)]·0.5CH2Cl2 crystallizes in the triclinic P-1 space group and considering an effective spin ½ 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=±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).

Figure 2. (a) Thermal variation of νM'' for. Inset, first magnetization. Calculated curves are in red. (b) Scan field of the frequency dependence of νM'' of at 2 K. (c) Frequency dependence of νM'' 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.

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 1H15/2 multiplet of the DyIII 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 value of 19.09 for the DyIII center and almost negligible gx and gy values. The decomposition in terms of pure |J=15/2⟩ spin wavefunctions shows that the ground state has a majority (88%) |±15/2⟩ character with a non-negligible (10%) |±11/2⟩ 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 [Dy(hfac)₃(L)]·0.5CH₂Cl₂. The calculated ground-state easy axis (Figure 3) for the Dy⁺⁺ ion is oriented perpendicular to the plane formed by the {tetraphiafulvalenyl-1H-benzimidazol-2-yl}pyridine moiety in agreement with experiment.¹⁵

![Image](55x303 to 294x690)

**Figure 3.** (a) Representation (two different orientations) of the ground state total molecular electrostatic potential around the Dy'' 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'' ion using the home-made CAMMEL program (Calculated Molecular Multipolar Electrostatics; 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.¹⁵ 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 χM 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, [Dy(hfac)₃(L)]·0.5CH₂Cl₂, 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 Dy(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 [Dy(hfac)₃(L)]·0.5CH₂Cl₂ and the oxidation of L are in progress.

**ASSOCIATED CONTENT**

**Supporting Information**

Ortep view of [Dy(hfac)₃(L)]·0.5CH₂Cl₂ (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.

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**Notes**

The authors declare no competing financial interests.

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A redox-active chiral Field-Induced Single-Molecule Magnet was achieved through the coordination reaction of the \([\text{Dy(hfac)}_3]\) precursor to a ligand which combines a redox-active tetrathiafulvalene core and a chiral carbo[6]-helicene fragment. This multi-properties system was characterized using X-ray crystallography, magnetism and ab initio calculations.