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PHYSICAL REVIEW MATERIALS 00, 004400 (2018)

Radical-lanthanide ferromagnetic interaction in a Tb^{III} bis-phthalocyaninato complex 2 Dorsa Komijani,^{1,2} Alberto Ghirri,³ Claudio Bonizzoni,^{3,4} Svetlana Klyatskaya,⁵ Eufemio Moreno-Pineda,⁵ Mario Ruben,⁵ 3 Alessandro Soncini,⁶ Marco Affronte,^{3,4,*} and Stephen Hill^{1,2,†} 4 ¹Department of Physics, Florida State University, Tallahassee, Florida 32306, USA 5 ²National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA 6 ³CNR-Instituto Nanoscienze, via G. Campi 213A, 41125 Modena, Italy ⁴Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, via G. Campi 213A, 8 41125 Modena, Italy 9 ⁵Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Eggenstein-Leopoldshafen, Germany 10 ⁶School of Chemistry, The University of Melbourne, 3010 Victoria, Australia 11 (Received 27 December 2017; published xxxxx) 13 Recent studies have highlighted the importance of organic ligands in the field of molecular spintronics, via 14 which delocalized electron-spin density can mediate magnetic coupling to otherwise localized 4f moments 15 of lanthanide ions, which show tremendous potential for single-molecule device applications. To this end, high-16 field/high-frequency electron paramagnetic resonance (EPR) spectroscopy is employed to study a neutral terbium 17 bis-phthalocyaninato metalorganic complex, $[TbPc_2]^0$, with the aim of understanding the magnetic interaction 18 between the Ising-like moment of the lanthanide ion and the unpaired spin density on the coordinating organic 19 radical ligand. The measurements were performed on a previously unknown [TbPc₂]⁰ structural phase crystallizing 20 in the *Pnma* space group. EPR measurements on powder samples of [TbPc₂]⁰ reveal an anisotropic spectrum, 21 which is attributed to the spin- $\frac{1}{2}$ radical coupled weakly to the EPR-silent Tb^{III} ion. Extensive double-axis rotation 22 studies on a single crystal reveal two independent spin- $\frac{1}{2}$ signals with differently oriented (albeit identical) uniaxial 23 g-tensors, in complete agreement with x-ray structural studies that indicate two molecular orientations within 24 the unit cell. The easy-axis nature of the radical EPR spectra thus reflects the coupling to the Ising-like Tb^{III} 25 moment. This is corroborated by studies of the isostructural $[YPc_2]^0$ analog (where Y is nonmagnetic yttrium), 26 which gives a completely isotropic radical EPR signal. The experimental results for the terbium complex are well 27 explained on the basis of an effective model that introduces a weak ferromagnetic Heisenberg coupling between 28 an isotropic spin- $\frac{1}{2}$ and an anisotropic spin-orbital moment, J = 6, that mimics the known, strong easy-axis 29 $Tb \cdots Pc_2$ crystal-field interaction. 30 DOI: 10.1103/PhysRevMaterials.00.004400 31

I. INTRODUCTION

The study of electron delocalization involving spin-bearing 33 (radical) ligands coordinated to metal ions is relevant to a 34 wide range of research topics, including organic electronics, 35 photovoltaics, and catalysis, as well as many important biolog-36 ical processes and biomedical applications [1–4]. This subject 37 also became of interest within the molecular magnetism and 38 nanomagnetism communities, given the demonstration that 39 radical-bearing ligands can mediate strong exchange inter-40 actions between otherwise magnetically isolated lanthanide 41 (Ln) ions, resulting in a leap forward in the development 42 of spin-chain systems [5–7] and so-called single-molecule 43 magnets (SMMs) [8-10]-molecules that can be magnetized 44 below a characteristic blocking temperature T_B . More recently, 45 it has been recognized that delocalized electrons in organic 46 radicals play a key role in mediating coupling between lan-47 thanide magnetic moments and magnetic surfaces [11,12], or to 48 conduction electrons in spintronic devices [13,14]. Moreover, 49

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charge transport through organic ligands provides a means ⁵⁰ of addressing electron and nuclear quantum states associated ⁵¹ with lanthanide qubits integrated into single-molecule spin ⁵² transistors [15–17]. ⁵³

Although electron paramagnetic resonance (EPR) investi- 54 gations have previously been employed to study Ln-radical sys- 55 tems [18,19], transitions are typically silent or forbidden at the 56 low microwave frequencies of commercial EPR spectrometers; 57 this is due primarily to the large moment and strong crystal- 58 field anisotropy of most lanthanides, resulting in an Ising-type 59 coupling to the radical and appreciable zero-field gaps associ- 60 ated with allowed magnetic dipole transitions. Consequently, 61 the few EPR investigations targeted directly at understanding 62 Ln-radical interactions have been performed on homebuilt 63 high-field instruments [20,21]. Motivated by the potential use 64 of Tb^{III}-bis-phthalocyaninato (TbPc₂) sandwich complexes in 65 spintronic devices and quantum information processing appli-66 cations, as well as for magnetic interfaces, we set out to explore 67 whether the magnetic properties of the highly anisotropic and 68 sizable Tb^{III} moment can be probed via its coupling to a 69 nearby radical through the use of high-frequency microwave 70 techniques. To this end, we report single-crystal and powder 71 high-field EPR (HF-EPR) measurements on a neutral $[TbPc_2]^0$ 72

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FIG. 1. Molecular structure and packing of $[TbPc_2]^0$: (a) side view; (b) top view; and (c) packing diagram of the molecules in the unit cell, displaying two magnetically inequivalent sets of molecules with their easy axes (red/green arrows) tilted approximately 70° with respect to each other. Color scheme: Tb, purple; N, blue; C, gray; H atoms have been omitted for clarity.

complex for which the organic bis-phthalocyaninato ligand 73 is open shell; i.e., it carries an unpaired electron. A highly 74 anisotropic EPR signal can be attributed to the radical, sug-75 gesting an appreciable interaction with the Ising-like Tb^{III} ion. 76 As reported by Ishikawa et al. in 2003 [22], the 77 organometallic $[TBA]^+[LnPc_2]^-$ complex [Ln = Tb, Dy, and78 $TBA^+ = N(C_4H_9)_4^+$ was the first example of a SMM contain-79 ing just a single metal ion, in this case sandwiched between 80 the two organic Pc ligands. Oxidation of $[Tb(Pc)_2]^-$ results 81 in $[TbPc_2]^0$ (1), a neutral complex with an unpaired electron 82 now delocalized over the two Pc rings (Fig. 1) [23]. The 83 Tb^{III} ion has a spin-orbit coupled angular momentum ground 84 state of J = 6 (L = 3, S = 3), with the lowest (approximately 85 degenerate) substates as $m_1 = \pm 6$ derived on the basis of fits 86 to ¹He NMR paramagnetic shifts and temperature-dependent 87 magnetic susceptibility [24]. The easy axis of the terbium ion is 88 defined by the C_4 symmetry axis of the molecule, i.e., perpen-89 dicular to the planes of the Pc rings [Fig. 1(a)]. Meanwhile, 90 the next excited states $(m_J = \pm 5)$ lie more than $400 \,\mathrm{cm}^{-1}$ 91 above the $m_I = \pm 6$ states and are, thus, not populated at low 92 temperatures [24]. This large separation between the $m_J = \pm 6$ 93 and ± 5 substates is a direct consequence of the strong axial 94 nature of the crystal field imposed by the Pc2 ligands on the 95 nonspherical 4f electron density associated with the Tb^{III} ion. 96 This, in turn, results in highly pure $m_J = \pm 6$ states (tunnel 97 splitting \sim kHz) [25]. Thus, in contrast to recent studies of 98 a similar Ho^{III} compound with a 4f electron density that is 99 closer to spherical (tunnel splitting \sim K) [26], EPR transitions 100 between the ground substates in 1 cannot be observed directly 101 via EPR. However, the unpaired spin on the ligand provides 102 an indirect way to spectroscopically probe the Tb^{III} ion and its 103 coupling to the radical. 104

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II. EXPERIMENTAL DETAILS

The investigated complexes, $[TbPc_2]^0$ (1) and isostructural 106 $[YPc_2]^0$ (2), where Y is nonmagnetic, were synthesized according to previously established procedures [27]. Continuous 108 wave (cw) HF-EPR measurements were first performed at 109 low temperatures on a finely ground powder of 1 and 2 in 110 the frequency range from 52 to 412 GHz. A transmission- 111 type spectrometer was employed for these purposes in which 112 microwaves are propagated through cylindrical light pipes into 113 (and out of) a variable-flow He cryostat situated within the bore 114 of a 15/17 T superconducting magnet [28]. Microwaves were 115 generated using a phase-locked source (Virginia Diode) oper- 116 ating at a base frequency of 12–14 GHz followed by a chain 117 of multipliers. The returned microwave signal was recorded 118 using magnetic field modulation and a liquid He cooled InSb 119 bolometer. The fine powders were pressed into polyethylene 120 cups using a Teflon stopper to prevent mobilization in the 121 presence of the externally applied magnetic field. 122

Single-crystal measurements were carried out on 1 using 123 a cavity perturbation technique, employing a millimeter-wave 124 vector network analyzer (MVNA) in combination with various 125 microwave sources and detectors [29,30]. Field-swept HF-EPR 126 spectra were recorded in a 9-5-1 T superconducting vector 127 magnet, at fixed frequencies in the 50-104 GHz range. A 128 variable-flow He gas cryostat was again used for temper-129 ature control. A single needle-shaped crystal (approximate 130 dimensions $1.5 \times 0.4 \times 0.4 \text{ mm}^3$) was selected for study, and subsequently mounted horizontally on the base plate of a vertical cylindrical resonator. Due to the low-symmetry space 133 group of 1 (see below), the unit cell axes do not project 134 in a simple way onto the crystal shape. Consequently, ex- 135 tensive angle-dependent studies were first performed via in 136 situ double-axis rotation: the 9-5 T component of the vector 137 field was employed to rotate the applied field in the polar 138 angle θ in 10° increments ($\theta = 0^\circ$ corresponds to the field 139 being parallel to the vertical cylindrical axis of the resonator); 140 meanwhile, the azimuthal angle ϕ was varied in 20° increments 141 by physically rotating the resonator about its cylindrical axis. 142 EPR spectra were then recorded at 65.5 GHz and 2 K over a 180° range in θ , for 12 azimuthal planes of rotation in ϕ , 144 i.e., a full 4π steradians. Frequency-dependent measurements 145 were subsequently performed at field orientations parallel to 146 the deduced magnetic symmetry axes. All simulations were 147 performed using the program EASYSPIN [31]. 148

III. RESULTS

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Structural characterization. Single-crystal x-ray diffraction ¹⁵⁰ studies of **1** and **2** show that the molecules crystallize in ¹⁵¹ an orthorhombic unit cell (see the Supplemental Material ¹⁵² [32]). The crystals were obtained via slow vapor diffusion of ¹⁵³ dichloromethane into a solution of 1,1,2,2-tetrachloroethane ¹⁵⁴ containing the complex [27]. Interestingly, concentrations ¹⁵⁵ above 4.5 mM yield crystals in the $P2_12_12_1$ space group, ¹⁵⁶ while lower concentrations lead to the *Pnma* space group. In ¹⁵⁷ the $P2_12_12_1$ space group, a total of four distinct (differently ¹⁵⁸ oriented) molecules are contained within the unit cell while, ¹⁵⁹ in the *Pnma* space group, only two independent molecules are found. Due to these observations, we focus here exclusively ¹⁶¹



FIG. 2. Powder EPR spectra collected on samples of 1 and 2 at a frequency of 104.8 GHz and a temperature of 5 K; the data were recorded in derivative mode, dI/dB (I = absorption intensity).

on the complexes crystallizing in the *Pnma* space group because they are expected to exhibit less complex spectroscopic
behavior.

We describe only the structural characteristics of 1, as it 165 exhibits the most interesting spectroscopic properties. Single-166 crystal x-ray studies reveal only half of the molecule residing 167 in the asymmetric unit, with two differently oriented molecules 168 and a total of four molecules within the unit cell [Fig. 1(c)]. 169 The two spatially different molecules are related by a rotation 170 about the crystallographic b axis of $\sim 70^{\circ}$. Locally, the Tb^{III} ion 171 resides in a very symmetric environment. The eight isoindole 172 nitrogens of the Pc₂ ligands impose a square antiprismatic 173 coordination geometry on the Tb^{III} ion, with the two Pc ligands 174 arranged above and below in a near perfect staggered configu-175 ration. The average distance to the eight coordinating nitrogens 176 is 2.4186(2) Å, while the mean distance to the planes of the 177 Pc ligands is 1.4064(1) Å. Note that the distances observed 178 here for the neutral $[TbPc_2]^0$ (1) are slightly shorter than those 179 reported for the negatively charged analog, TBA+[TbPc2]-180 [33], where the $\langle Tb \cdots N \rangle$ and $\langle Tb \cdots Pc \rangle$ distances are 181 2.8245(3) and 1.4122(3) Å, respectively. The average twist 182 angle between the two Pc moieties is 45° [Fig. 1(b)], compared 183 to 44.1° for the TBA⁺[TbPc₂]⁻ analog. Therefore, the Tb^{III} ion 184 of **1** experiences a near ideal local D_{4d} crystal-field symmetry. 185 Spectroscopy. EPR spectra collected on powder samples of 186 and 2, at a frequency of 104.8 GHz and a temperature of 187 1 5 K, are shown in Fig. 2. The $[YPc_2]^0$ complex (2) displays 188 a sharp signal at \sim 3.75 T (peak-to-peak linewidth \sim 5 mT), 189 corresponding to an isotropic Landé g factor of 2.003(1)190 that can be ascribed to the spin- $\frac{1}{2}$ radical; the first derivative 191 line shape results from the lock-in detection of the field 192



FIG. 3. Angle-dependent EPR spectra for a single crystal of **1** for a full 180° rotation of θ (with $\phi = 120^{\circ}$), collected at a frequency of 65.5 GHz and temperature of 2 K; the dips in transmission correspond to the resonances. The green circles denote resonances for one of the two molecular orientations: note the smooth variation with angle from the cusplike maximum (at ~2.2 T), through a broad minimum (at ~1.4 T), with an overall 180° periodicity. An additional weak resonance is observed at two of the angles (marked with *), which we explain in Sec. IV.

modulated signal, dI/dB, where I represents the absorption 193 intensity. By contrast, the EPR spectrum of $[TbPc_2]^0(1)$ shows a significantly broader spectrum, with two prominent features 195 spanning all the way from the strong first derivative signal 196 at 2.93 T (peak-to-peak linewidth ~37 mT) to the weaker 197 asymmetric dip at the isotropic g = 2.00 position (~3.75 T). 198 Such a powder spectrum is typical for a species experiencing an 199 axial magnetic anisotropy, with the two features corresponding 200 to the parallel and perpendicular components. It is worth 201 noting that the EPR spectrum of the charged TBA⁺[TbPc₂]⁻ 202 derivative, for which the radical is absent, does not show any 203 visible EPR transition. This confirms a strong axiality and 204 negligible mixing within the ground $m_J = \pm 6$ substates of 205 the Tb^{III} ion, such that the transition between them is strongly $_{206}$ forbidden. Consequently, the entire spectrum recorded for the 207 $[TbPc_2]^0$ complex is ascribable to the radical. In turn, the 208 anisotropic nature of this spectrum provides the first indication 209 that the radical is coupled to the Tb^{III} ion, because an isolated 210 radical would otherwise give the same narrow spectrum as the 211 $[YPc_2]^0$ complex. 212

Single-crystal EPR measurements were subsequently carried out on **1** in order to study the effect of the lanthanide ion on the radical in more detail. Angle-dependent spectra collected at 65.5 GHz and 2 K for a full 180° rotation of θ (with $\phi = 120^{\circ}$) are shown in Fig. 3. Two sharp angle-dependent resonances of comparable linewidth to those observed for the pure radical (Fig. 2) are seen at essentially all angles (except at $\theta = 90^{\circ}$, 219 where they merge to a single asymmetric resonance). This, 220 together with the field dependence (*vide infra*), which ascribes g factors of ~2.00 to both resonances, corroborates their assignment to the spin- $\frac{1}{2}$ radicals. The fact that the separation of the parallel and perpendicular components of the 104.8 GHz powder spectrum (~0.82 T; see Fig. 2) is comparable to the range of the 65.5 GHz single-crystal data in Fig. 3 suggests 226

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FIG. 4. 3D color maps of the positions of the lowest- (a) and highest- (b) field 65.5 GHz EPR positions, highlighting the easy (blue) and hard (red) magnetization directions of the Tb^{III} ion, respectively; the black line in (a) marks the $\phi = 120^{\circ}$ plane of rotation, which intersects the easy axes of the two differently oriented molecules (see Fig. 3). (c) Resonance position for one of the two molecular orientations, clearly indicating an easy-axis anisotropy. The two hard planes and easy axes are tilted ~70° with respect to each other, in excellent agreement with the orientations of the two [TbPc₂]⁰ molecules (see Fig. 1).

a field-independent anisotropic interaction, likely involving a 227 coupling of the radical to the terbium ion, as the spectrum 228 would otherwise be isotropic. Meanwhile, the fact that two 229 EPR transitions are observed with distinct angle dependences 230 can be attributed to the existence of two differently oriented 231 molecules within the unit cell of compound 1 [Fig. 1(c)]. By 232 following the evolution of the resonance positions with angle, 233 it is straightforward to assign each one to a given molecular 234 orientation, as seen in Fig. 3. 235

Additional data sets under the same conditions as those 236 displayed in Fig. 3 were collected for multiple azimuthal 237 planes of rotation. Figure 4 displays three-dimensional (3D) 238 color maps representing these angle dependences mapped 239 onto a complete sphere. Because there is more than one 240 resonance for each field orientation, the data are presented in 241 several ways, emphasizing different aspects of the magnetic 242 anisotropy of 1: (a) plots the position of the lowest-resonance 243 field, highlighting the easy directions (dark blue); (b) plots 244 the position of the highest resonance field, accentuating the 245 hard directions (red); and (c) plots the resonance position for 246 only one of the two molecular orientations. The color maps 247 clearly indicate an easy-axis anisotropy for both molecular 248 orientations; i.e., the hard directions are confined to planes, 240 with easy directions along two axes that are orthogonal to the 250 hard planes. Moreover, the hard planes and/or easy axes are 251 tilted $\sim 70^{\circ}$ with respect to each other, in excellent agreement 252 with the orientations of the two $[TbPc_2]^0$ molecules determined 253

²⁵⁴ from x-ray diffraction measurements [Fig. 1(c)].
 ²⁵⁵ From the above measurements, it is straightforward to locate
 ²⁵⁶ the magnetic symmetry axesplanes for each molecular orienta-

the magnetic symmetry axesplanes for each molecular orienta-256 tion. In fact, the crystal was mounted within the resonator such 257 that the $\phi = 120^{\circ}$ azimuthal plane approximately intersects the 258 easy axes (and hard planes) of both orientations [see Fig. 4(a)]; 259 note that this corresponds to the situation in Fig. 3. For this 260 plane of rotation, one can therefore define polar angles, ψ_1 and 261 ψ_2 , that represent the alignment of the applied magnetic field 262 with respect to the easy axes of the two molecular orientations. 263 Such a transformation from the laboratory frame (θ, ϕ) to 264 local coordinates (ψ_i) is illustrated in Fig. 5, which displays 265 the ψ dependence of the resonance positions for one of the 266 molecular orientations in Fig. 3: The easy ($\psi = 0$) and hard 267 $(\psi = \pm 90^{\circ})$ directions are noted in the figure, and simulated 268 angle dependences (vide infra) are superimposed on the data. 269

Figure 6 plots the frequency dependence of resonance ²⁷⁰ positions for the easy ($\psi = 0$) and hard ($\psi = 90^{\circ}$) directions of ²⁷¹ [TbPc₂]⁰ (1). As noted above, the magnitude of the anisotropy, ²⁷² as measured by the separation of the $\psi = 0$ and 90° resonances, ²⁷³ is field independent. Moreover, agreement between the singlecrystal and powder data is good over the entire range investigated. Importantly, the ~26-GHz zero-field intercept/gap in the ²⁷⁶ spectrum cannot be explained in terms of noninteracting spin- $\frac{1}{2}$ ²⁷⁷ radicals; the Kramers theorem forbids such a gap [34]. Super ²⁷⁸ imposed on the data in Fig. 6 are simulations that assume a ²⁷⁹ ferromagnetic coupling between the radical and the Tb^{III} ion on ²⁸⁰ each molecule; details concerning these simulations, which assume an isotropic *g* factor of ~2.00 and just a single interaction ²⁸¹ garameter, are given in the following section. As can be seen, ²⁸³ agreement between the experiment and simulation is excellent. ²⁸⁴

IV. DISCUSSION

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The preceding experiments provide clear evidence that the ²⁸⁶ EPR signals seen for compounds 1 and 2 can be attributed, ²⁸⁷



FIG. 5. Plot of the resonance positions in Fig. 3 [see also Fig. 4(a)], for one of the two molecular orientations; the polar coordinate has been transformed ($\theta \rightarrow \psi$) to a local frame, where $\psi = 0$ represents field parallel to the easy axis of the molecule. The solid curves represent two different simulations described in Sec. IV, one exact and the other approximate.



FIG. 6. Frequency versus magnetic field plot of the combined single-crystal (at T = 2 K) and powder (at T = 5 K) EPR data for 1, with the field parallel ($\psi = 0^{\circ}$) and perpendicular ($\psi = 90^{\circ}$) to the easy axis of one of the molecular orientations; uncertainties in the determination of the resonance positions lie within the data points. The solid lines represent simulations described in Sec. IV.

to zeroth order, to the unpaired spin- $\frac{1}{2}$ on the Pc₂ radical. 288 We now consider the source of considerable anisotropy of 289 the radical signal in 1. While rare, EPR spectra exhibiting 290 similar degrees of anisotropy have been reported for crystals 291 of magnetically ordered organic radical ferromagnets [35,36]. 292 However, a smooth first-order angle dependence ($\sim \sin^2 \psi$) is 293 observed in these cases, as opposed to the cusplike behavior 294 observed at $\psi = 90^{\circ}$ in **1**. Moreover, the isotropic signal 295 observed for 2 would also seem to rule out the possibility 296 that long-range ordering of the radicals is responsible for the 297 anisotropy in 1. Hence coupling to the highly anisotropic Tb^{III} 298 ion represents the obvious starting point for an analysis of the 299 results. 300

We thus consider the simplest possible effective spin Hamiltonian of Eq. (1) that includes an isotropic (scalar) coupling between the radical and Ln moments, while absorbing all of the anisotropy into the zero-field-splitting (ZFS) Hamiltonian, \hat{H}_{ZFS}^{Tb} , of the terbium ion:

$$\hat{H}^{\text{eff}} = \hat{H}_{\text{ZFS}}^{\text{Tb}} + J_{\text{ex}}\hat{S}^{\text{rad}} \cdot \hat{J}^{\text{Tb}} + \hat{H}_{\text{Z}}^{\text{Tb}} + \hat{H}_{\text{Z}}^{\text{rad}}.$$
 (1)

Here, $\hat{S}^{\rm rad}$ and $\hat{J}^{\rm Tb}$, respectively, represent angular mo-306 mentum operators associated with the radical (spin) and 307 the lanthanide (spin orbital), while J_{ex} parametrizes the 308 scalar coupling between them. Meanwhile, we assume 309 isotropic Zeeman interactions, $\hat{H}_Z^{\text{Tb}} (= g_J \mu_B \vec{B}_0 \cdot \hat{J}^{\text{Tb}})$ and \hat{H}_Z^{rad} 310 $(=g_e \mu_B \vec{B}_0 \cdot \hat{S}^{rad})$, with g_e (=2.00) and g_J (= $\frac{3}{2}$ for Tb^{III}) 311 representing the Landé factors, and \vec{B}_0 the applied magnetic 312 field. 313

The anisotropic ZFS interaction of the Tb^{III} ion can be expressed in terms of extended Stevens operators [37]:

$$\hat{H}_{ZFS}^{Tb} = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q \hat{O}_k^q.$$
(2)

The \hat{O}_k^q terms are comprised of angular momentum oparr erators of rank k, which are then parametrized by their

accompanying B_{l}^{q} coefficients. The off-diagonal $(q \neq 0)$ terms 318 can be neglected for the purposes of this analysis, as they 319 are known to influence the magnetic behavior of the Tb ion 320 only at very low applied magnetic fields ($B_0 < 0.04 \text{ T}$) [25]. 321 This leaves only the cylindrically symmetric terms, $B_k^0 \hat{O}_k^0$ 322 (k = 2, 4, 6), containing only even powers of the *z*-component 323 angular momentum operator, \hat{J}_{z}^{k} , where we have dropped the 324 "Tb" superscript here for compactness. In principle, the B_k^0 325 coefficients are known from thermodynamic measurements 326 [24,25]. However, we find that the results of the simulations 327 are completely insensitive to these parameters provided they 328 are chosen so that the $m_J = \pm 6$ substates lie lowest in energy 329 and are well separated from the first excited state, as is known 330 to be the case experimentally. For these purposes, one can 331 simplify the analysis greatly by retaining only the leading term 332 $B_2^0 \hat{O}_2^0 = \{3\hat{J}_z^2 - \hat{J}(\hat{J}+1)\}$, so long as the B_2^0 parameter is 333 chosen to be negative and sufficiently large so that the Tb^{III} ZFS interaction dwarfs the remaining interactions in Eq. (1); 335 i.e., the EPR measurements do not constrain this parameter (or 336 any of the Tb^{III} ZFS parameters) [38]. 337

The approach outlined above leaves J_{ex} , the scalar cou- 338 pling, as the only free parameter in the model. The simu- 339 lations in Figs. 5 and 6 assume a ferromagnetic interaction, 340 $J_{\rm ex} = -0.147 \, {\rm cm}^{-1}$. It is now relatively straightforward to 341 understand the experimental observations within the context 342 of this relatively simple model. In zero field, the radical 343 is coupled only to the Tb^{III} ion, with doubly degenerate 344 eigenstates $|+6, +\frac{1}{2}\rangle$, $|-6, -\frac{1}{2}\rangle$, and $|+6, -\frac{1}{2}\rangle$, $|-6, +\frac{1}{2}\rangle$, em- 345 ploying here an $|m_J, m_S\rangle$ representation. The energy separation 346 between these states, $\Delta_0 = |6J_{ex}| = 0.88 \text{ cm}^{-1}$ or 26.4 GHz, ³⁴⁷ corresponds to the zero-field gap in the EPR spectrum (see 348 Fig. 6); as can be seen, the transitions $|+6,+\frac{1}{2}\rangle$ to $|+6,-\frac{1}{2}\rangle$ ³⁴⁹ and $|-6, -\frac{1}{2}\rangle$ to $|-6, +\frac{1}{2}\rangle$ involve a simple spin flip of the 350 radical under an exchange bias field due to the Tb^{III} ion; 351 i.e., the gap corresponds to the energy difference between the 352 ferromagnetic (F) and antiferromagnetic (A) configurations 353 (meaning up/up and up/down, not to be confused here with 354 long-range ordered states). 355

We next consider the field dependence of the EPR spectrum. ³⁵⁶ Because of the strong crystal-field anisotropy of the Tb^{III} ion, it ³⁵⁷ may be treated as an Ising-like moment; i.e., $\langle \hat{J}_x^{\text{Tb}} \rangle = \langle \hat{J}_y^{\text{Tb}} \rangle = 0$. ³⁵⁸ Consequently, from a semiclassical point of view, the Tb^{III} ³⁵⁹ moment is constrained along $\pm z$, the C_4 symmetry axis of ³⁶⁰ the molecule (or $\psi = 0^\circ$). Meanwhile, in the intermediate ³⁶¹ field regime, the radical spin follows B_0 ; here, "intermediate" ³⁶² implies that the radical Zeeman interaction, \hat{H}_Z^{rad} , is strong ³⁶³ enough to overcome the scalar coupling (i.e., $g_e \mu_B B_0 > \Delta_0$), ³⁶⁴ but that the field is not yet so strong that it can compete with ³⁶⁵ $\hat{H}_{ZFS}^{\text{Tb}}$. The scalar interaction energy then takes the form ³⁶⁶

$$J_{\text{ex}}\hat{S}^{\text{rad}} \cdot \hat{J}^{\text{Tb}} \approx \pm J_{\text{ex}} \left| \frac{1}{2} \frac{B_0}{B_0} \cdot 6\hat{z} \right| = \pm 3 |J_{\text{ex}} \cos \psi|, \quad (3)$$

where the \pm signs denotes the F (-) and A (+) cases. Likewise, $_{367}$ in this same intermediate field regime, the radical and Tb^{III} $_{368}$ Zeeman interactions may be written $_{369}$

$$\hat{H}_{Z}^{\text{Tb}} \approx \pm \frac{3}{2} \mu_{B} |\vec{B}_{0} \cdot 6\hat{z}| = \pm 9 \mu_{B} B_{0} |\cos \psi|,$$
$$\hat{H}_{Z}^{\text{rad}} \approx \pm \mu_{B} B_{0}.$$
(4)



FIG. 7. Exact solutions to Eq. (1) with the field applied parallel (a) and perpendicular (b) to the easy axis of the $[TbPc_2]^0$ molecule; note that each of the solutions in (b) is doubly degenerate. The red lines denote allowed EPR transitions at 65.5 GHz, corresponding to a spin-flip of the radical.

The absolute value of the cosine recognizes the timereversal invariance of the leading axial interaction, \hat{H}_{ZFS}^{Tb} , which means that the physics is the same regardless of whether the field is applied above or below the molecular hard plane. One can then write down expressions for the four energy eigenvalues, referenced to the uncoupled zero-field groundstate energy:

$$\epsilon_{0\pm} \approx -|3J_{\rm ex}\cos\psi| \pm 9\mu_B B_0|\cos\psi| \pm \mu_B B_0,$$

$$\epsilon_{1\pm} \approx +|3J_{\rm ex}\cos\psi| \pm 9\mu_B B_0|\cos\psi| \pm \mu_B B_0,$$
 (5)

where ε_0 and ε_1 correspond to the F and A cases, respectively (see Fig. 7); the inverted \mp in the second expression reflects the A coupling, i.e., the radical is "down" when the Tb^{III} is wup." Radical EPR transitions involve a change in the sign of the last terms in Eq. (5), but no change in the second terms (the Tb^{III} Zeeman energy). The ground-state transition, ϵ_{0-} to ϵ_{1+} , thus involves an energy,

$$\Delta \epsilon_0 \approx |6J_{\rm ex} \cos \psi| + 2\mu_B B_0. \tag{6}$$

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Although Eqs. (3)–(6) are approximate, they become exact for $\psi = 0^{\circ}$, because the Hamiltonian of Eq. (1) is diagonal in this limit. Therefore, $\Delta \epsilon_0 = \Delta_0 + 2\mu_B B_0$ for this orientation; i.e., the unperturbed transition energy ($g_e \mu_B B_0$, with $g_e =$ 2.00) for the radical is offset vertically by the zero-field gap, $\Delta_0 = |6J_{\rm ex}|, \text{ exactly as observed in Fig. 6. Meanwhile, for } _{390} \psi = 90^\circ, \text{ the scalar coupling and Tb}^{\rm III} Zeeman interactions } _{391} are identically zero in the intermediate field regime (because } _{392} \hat{S}^{\rm rad} \cdot \hat{J}^{\rm Tb} = \hat{B}_0 \cdot \hat{J}^{\rm Tb} = 0$), resulting in an EPR spectrum that } _{393} is indistinguishable from that of an isolated radical, i.e., a $g_e = _{394} 2.00$ resonance with no zero-field offset, again in reasonable } _{395} agreement with experiment (Fig. 6). } 396

The overall effect of the scalar coupling is to shift the 397 ground-state EPR positions by an amount 398

$$\Delta B_0 \approx - \left| \frac{3 J_{\rm ex} \cos \psi}{\mu_B} \right|,\tag{7}$$

below the isotropic g = 2.00 position (~2.34 T at 65.5 GHz), 399 where $|3J_{\rm ex}/\mu_B| \approx 0.94$ T. Here, one sees the reason for the 400 cusplike turning point of the resonance position at $\psi = 90^{\circ}$ 401 and the broad minimum at $\psi = 0^{\circ}$ (Fig. 5). The experimental 402 downshift of 0.94 T to 1.4 T at $\psi = 0^{\circ}$ is in excellent agreement 403 with experiment. However, the angle-dependent data presented 404 in Fig. 5 were obtained slightly below the "intermediate" field 405 regime, so that the approximation does not work as well when 406 the field rotates away from $\psi = 0^{\circ}$. The scalar interaction 407 dominates at low fields, meaning that there is a residual 408 coupling to the Tb^{III} ion even at $\psi = 90^\circ$, thus explaining 409 why the resonance occurs slightly below the g = 2.00 position. 410 Indeed, this is also the reason why Eq. (7) does not account 411 quantitatively for the experimental results in Fig. 5 quite as well 412 as the simulations involving exact diagonalization of Eq. (1); 413 comparisons between the exact and approximate expressions 414 at much higher fields do give near perfect agreement. 415

For the magnetic fields (>1 T) and temperatures (\sim 2 K) at $_{416}$ which the experiments were carried out, only the $|-6, -\frac{1}{2}\rangle$ (at 417 ϵ_{0-}) and $|-6,+\frac{1}{2}\rangle$ (at ϵ_{1+}) states are significantly populated 418 when the applied field has an appreciable component along 419 z; this is because of the strong Zeeman interaction associated 420 with the Tb^{III} ion $(\pm 9\mu_B B_0 | \cos \psi |)$. Hence only the ground- 421 state EPR transition is observed for most field orientations. 422 However, this is not necessarily the case when ψ is close to 90°. 423 In fact, the $\epsilon_{0\pm}$ and $\epsilon_{1\mp}$ states are quasidegenerate at exactly 424 $\psi = 90^{\circ}$, because the radical EPR transition is insensitive to 425 the state of the Tb^{III} ion, which lives in a nonmagnetic superposition of the $m_1 = \pm 6$ states (with a minuscule tunneling gap 427 on the order of kHz) [25]. Thus one may think of two (quasi-) 428 degenerate radical EPR transitions, one for each of the Tb^{III} 429 degrees of freedom. Meanwhile, slightly away from $\psi = 90^{\circ}$, 430 this degeneracy is lifted because of the weak longitudinal 431 (//z) field component, yet both transitions may be expected 432 to possess detectable Boltzmann weights, thereby explaining 433 the observation of an additional peak at some orientations close 434 to $\psi = 90^{\circ}$ in Fig. 3 (indicated by *). However, the intensity 435 of the higher-lying transition will rapidly lose weight as the 436 field rotates away from $\psi = 90^{\circ}$. 437

It is natural to question the validity of such a simple ⁴³⁸ model [Eq. (1)]. In particular, why assume a scalar coupling? ⁴³⁹ Exchange involving spin-orbital moments only couples the ⁴⁴⁰ spin part of the wave function and, for instance, in Ref. [12], ⁴⁴¹ we have expressed this Heisenberg interaction as $J_{ex}\hat{S}^{rad} \cdot \hat{S}^{Tb}$. ⁴⁴² However, our choice here does not alter the underlying physics, ⁴⁴³ because \vec{L} is strongly coupled to \vec{S} , and the net effect would ⁴⁴⁴ simply be a renormalization of the coupling parameter, J_{ex} , ⁴⁴⁵

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doubling its value in the case of Tb^{III}. Similarly, why not 446 consider an anisotropic coupling, such as an Ising or dipolar 447 interaction? The Ising character is already built into the model 448 via the ZFS interaction associated with the Tb^{III} ion. An 440 anisotropic coupling $(J_{ex}$ is now a tensor) would simply add su-450 perfluous parameters. We note that recent CASSCF (complete 451 active space self-consistent field) ab initio calculations [12,39] 452 on $[TbPc_2]^0$ using a minimal active space of 4 f orbitals and the 453 π -ligand singly occupied molecular orbital (π -SOMO), also 454 including spin-orbit coupling nonperturbatively, fully support 455 our current assumption that the radical-4f exchange coupling 456 is (i) much smaller than the gap between ground and first 457 excited crystal-field substates; and (ii) well described by an 458 isotropic exchange Hamiltonian. 459

Another potential source of anisotropic coupling that should 460 be considered is the purely through-space dipolar interaction 461 between the Tb^{III} ion and the spin density on the radical, which 462 can in principle be calculated precisely via ab initio methods. 463 However, one can also get a good sense for the magnitude of 46/ this interaction by assuming that the radical spin density is 465 localized on the C and N atoms of the ligand, and then perform 466 simple point-dipole calculations. Published density functional 467 theory (DFT) results suggest that most of the spin density 468 resides on the 16 inner C atoms (on average 0.05 $\mu_{\rm B}/{\rm C}$), which 469 are located at an average distance of 3.33 Å from the Tb^{III} 470 ion [17]. Meanwhile, the remainder of the density resides 471 on the 48 C atoms of the outer rings (0.005 $\mu_{\rm B}/{\rm C}$), with a 472 small negative polarization on the 16 coordinating N atoms 473 (about $-0.01 \,\mu_{\rm B}/\rm N$). Interestingly, based on a point-dipole 474 approximation, we find the coupling to be antiferromagnetic 475 for nearly all of these sites. The closest eight N atoms sit 476 at an average angle of 54.55° from the Tb ion, as measured 477 from the C_4 axis of the molecule. This is fractionally below 478 the magic angle of $\psi_m = 54.7^{\circ} [3\cos^2 \psi_m - 1 = 0]$, meaning 479 that the contribution of these sites to the dipolar interaction is 480 near negligible because of the axial symmetry of the molecule. 481 Moreover, because the polarization is negative at these sites, 482 their contribution to the coupling will be antiferromagnetic. 483 The remaining atoms all sit at angles beyond ψ_m . Therefore, 484 the remaining eight N atoms provide the only ferromagnetic 485 486 coupling. However, this contribution is overwhelmed by the carbon atoms, which all couple antiferromagnetically to the 487 Tb^{III} ion. A weighted sum of point-dipolar contributions gives 488 an estimate for the ZFS of $\Delta_0 \approx 1.3$ GHz, corresponding to a 489 $J_{\rm ex} = +7.2 \times 10^{-3} \, {\rm cm}^{-1}$. Thus not only is the sign incorrect, 490 but the magnitude of the coupling is more than an order of 491 magnitude too small. Therefore, the main contribution to the 492 coupling has to involve exchange, and Eq. (1) is expected to 493 capture the essential physics. 494

There have been a limited number of previous (and 495 conflicting) experimental and theoretical attempts to eval-496 uate the radical-lanthanide exchange interaction in bis-497 phthalocyaninato-type Ln complexes. The earliest study on 498 $LnPc_2$ ⁰ suggested a strong antiferromagnetic coupling (when 499 Ln = Gd, Tb, Ho) on the basis of relatively high-temperature 500 magnetic susceptibility measurements [18,19]. More recently, 501 both ferro- and antiferromagnetic interactions have been de-502 503 duced from single-molecule transistor experiments [15,17], 504 although a large anisotropic exchange term (amounting to 60%) of the isotropic component) was introduced in Ref. [17] in 505 order to explain some features of the observed Kondo reso-506 nance. Meanwhile, recent NMR/DFT studies on a $[TbPc_2]^0$ 507 complex very similar to the one studied here have suggested 508 ferromagnetic coupling due to the orthogonality between the broken-symmetry ligand-centered π -SOMO and the seven 4 f 510 magnetic orbitals with opposite spin polarization [40]. We 511 note, however, that the energies of the high- and low-spin 512 states of [GdPc₂]⁰ were not reported in Ref. [39], so it is 513 difficult to assess whether other exchange mechanisms (e.g., 514 spin polarization) could stabilize an antiferromagnetic ground 515 state, despite the orthogonality between magnetic orbitals. 516 Another quite recent DFT calculation shows that the exchange 517 coupling between the f electrons and the radical is mediated by 518 d electrons of the Tb^{III} ion that significantly overlap the N and C orbitals of the Pc ligands and, due to large spin-polarization effects, lead to antiferromagnetic coupling [11]. Meanwhile, 521 combined XMCD, CASSCF/RASSI-SO, and DFT studies of 522 $[TbPc_2]^0$ grafted onto surfaces point to ferromagnetic coupling 523 [12], although the results depend on the details of the modeling 524 and are sensitive to molecule configuration. 525

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The present EPR experiments undoubtedly demonstrate 526 a ferromagnetic Tb-radical exchange interaction in the bulk 527 $[TbPc_2]^0$ derivative crystallized in the *Pnma* space group. One 528 may actually expect such coupling on the basis of relatively 529 simple molecular point group symmetry considerations [38]. It 530 turns out that, for exact molecular D_{4d} symmetry, the π -SOMO 531 (ϕ_{π}) on the Pc₂ ligand system spans a $\Gamma_{\pi} = a_2$ irreducible 532 representation of D_{4d} , while the irreducible representations 533 spanned by the 4 f orbitals of the central Tb^{III} ion are $\Gamma_{4f} =$ 534 $b_2 + e_1 + e_2 + e_3$ [38]. Therefore, the kinetic contribution 535 to the exchange, proportional to the matrix element of a 536 totally symmetric Hamiltonian, h, inducing virtual transitions 537 between the π -SOMO and the Tb 4 f atomic orbitals, is clearly 538 zero by symmetry, i.e., $\langle \phi_{\pi} | h | 4f \rangle = 0$, since $\Gamma_{\pi} \times \Gamma_{4f}$ does 539 not include the totally symmetric irreducible representation. It 540 is this contribution that favors antiferromagnetic coupling [34]. 541 Therefore, its absence leaves only potential exchange within 542 the restricted excitation space of the π -SOMO and seven 4 f or- 543 bitals. This interaction is given by the exchange integral, which 544 is always ferromagnetic and necessarily isotropic. Considera- 545 tion of extended excitation spaces may introduce additional 546 (likely weaker) terms, both isotropic and anisotropic, and of 547 either sign [34,38]. However, the simple symmetry arguments 548 presented here seem to confirm the ferromagnetic coupling that 549 is found experimentally. 550

Finally, Branzoli et al. reported an antiferromagnetic in-551 termolecular exchange interaction between [YPc₂]⁰ radicals 552 (here, Y is nonmagnetic) from magnetization, ¹He NMR 553 paramagnetic shifts, and NMR T₁ measurements [41]. Mean-554 while, specific heat measurements on $LnPc_2$ (Ln = Y, Tb) also evidence the presence of extended spin excitations at low temperature [42]. Effects of such intermolecular interac-557 tions are not evident in the single-crystal EPR measurements 558 presented here; in particular, the observation of independent 559 (noninteracting) signals for the two molecular orientations 560 would seem to rule this out. However, weak satellite peaks 561 observed in the powder measurements (~ 0.15 T above and 562 below the strong low-field resonance in Fig. 1) at the low-563 est temperatures, may provide evidence for intermolecular 564

interactions in the $P2_12_12_1$ structure (γ phase). These satellite peaks have no counterpart in the single-crystal EPR measurements. However, x-ray structure studies of the powder sample employed in this study suggest a small contamination with the $P2_12_12_1$ phase. Future work aims to address the issue of intermolecular exchange interactions in Ln(Pc)₂ crystals in more detail.

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V. CONCLUSIONS

We present detailed high-field, high-frequency EPR mea-573 surements on a powder and a single-crystal sample of a 574 previously unreported structural phase (Pnma space group) of 575 the neutral terbium bis-phthalocyaninato metalorganic com-576 plex, [TbPc₂]⁰. An anisotropic EPR spectrum is observed, 577 which is attributed to the $s = \frac{1}{2}$ radical delocalized over the 578 Pc₂ ligand. The magnetic anisotropy results from a weak 579 coupling of the radical to the Ising-like spin-orbital moment 580 of the Tb^{III} ion. Angle-dependent EPR studies reveal two 581 differently oriented, magnetically independent molecules, in 582 agreement with x-ray structural studies. Analyses of the results 583 unambiguously demonstrate that the radical-Tb^{III} coupling is 584 due to a ferromagnetic exchange interaction. The essential 585 physics is captured via an effective spin Hamiltonian in which 586 the exchange is assumed to be isotropic ($J_{ex} = -0.147 \text{ cm}^{-1}$), 587

while the magnetic anisotropy is folded entirely into the singleion properties of the Tb^{III} ion. This model is rationalized on the basis of the simple symmetry considerations that dictate an orthogonality of the Tb 4f orbitals and the π -SOMO associated with the Pc₂ ligand, thereby suppressing virtual hopping transitions that mediate antiferromagnetic exchange interactions.

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