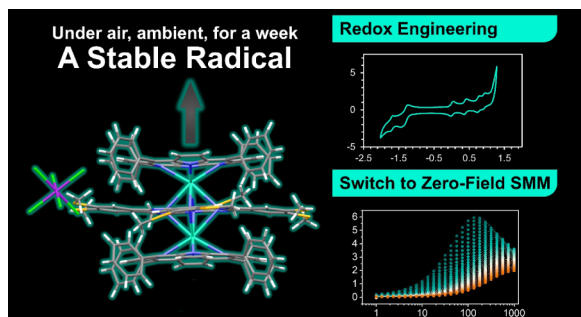


A Stable Radical in Cationic Dinuclear Rare-Earth Triple-Decker Complexes Featuring Switchable Magnetic Properties

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ABSTRACT: In quantum information processing, the implementation of qudits—multilevel qubits where d is the number of levels—has been a major challenge that, if resolved, could lead to the acceleration of certain computational tasks. Spin transport measurements demonstrate that tris(phthalocyaninato)-dinuclear rare-earth(III) molecules offer a promising platform for nuclear spin qudits with an increased Hilbert space. However, the absence of radicals in these systems has so far hindered studies on the coupling between lanthanide ions and conduction electrons. In this study, we report the synthesis of (phthalocyaninato)bis(porphyrinato)-dinuclear rare-earth(III) complexes functionalized with thiomethyl groups. The tailored oxidation of the neutral complexes facilitated their conversion to air-stable radicals.

CASSCF calculations and static magnetic measurements revealed a radical–lanthanide exchange coupling constant of $J_{\text{Ln-Rad}} = -0.45 \text{ cm}^{-1}$. Dynamic magnetic measurements demonstrated a shift in the magnetic properties due to exchange interaction, namely from field-induced single-molecule magnets (SMMs) to zero-field SMMs. The findings of this study, along with the strong bonding affinity of thiomethyl groups to gold electrodes, highlight the potential of these molecules as novel materials for the implementation of nuclear spin qudits with an increased Hilbert space.



1. INTRODUCTION

In the realm of information storage and quantum information processing (QIP), the development of molecule-based quantum devices has emerged as a prominent and highly ambitious goal. Among potential molecules, bis-(phthalocyaninato) terbium(III) (TbPc_2) has garnered considerable attention due to its role as both a single-molecule magnet (SMM) and a molecular qubit (Figure 1, top left).^{1,2} In 2003, Ishikawa et al. reported that terbium(III) in the TbPc_2 exhibits doubly degenerate ground states with substantial magnetic anisotropy, resulting in remarkably slow magnetization relaxation.³ Later, it was found that nuclear spin states are accessible through the magnetic relaxation of TbPc_2 via quantum tunneling of magnetization (QTM) in low-temperature μ -SQUID measurements.⁴ Nuclear spins are ideal platforms for QIP since they are well isolated from the environment, leading to long decoherence times.⁵ This renders terbium particularly promising since its sole naturally abundant isotope, ¹⁵⁹Tb, possesses a nuclear spin $I = 3/2$, yielding a four-level system where the multiplicity d is defined as $d = 2I + 1 = 4$. The potential of TbPc_2 for QIP was demonstrated by the successful implementation of Grover's quantum algorithm using its nuclear spin states via single-molecule spin transport measurements.^{6–8} Multilevel qubits, or qudits (with $d > 2$), have distinct advantages over traditional qubits, including the

ability to encode and manipulate more information per unit.⁹ Recent advances have highlighted the superiority of qudits in fidelity compared to multiqubit systems,¹⁰ as well as their potential for fault-tolerant quantum operations¹¹ and the design of advanced qudit-based processors.¹² These features establish TbPc_2 qudits as promising candidates for next-generation QIP systems. A key challenge in improving qudits is scaling up the dimension of d . Our group previously proposed that exponential scaling of the multiplicity $d = (2I + 1)^n$, where n is the number of the nuclear spin-bearing centers, could be achieved through multinuclear lanthanide sandwich complexes with phthalocyanine or porphyrin ligands, which are later called multiple-decker complexes (such as a triple decker).⁹ Later in 2021, this concept was demonstrated experimentally in a spin transport measurement on a triple-decker complex (Tb_2Pc_3 , Figure 1, top right).¹³

The utilization of multinuclear complexes as qudits depends on several factors, including SMM characteristics, the hyperfine

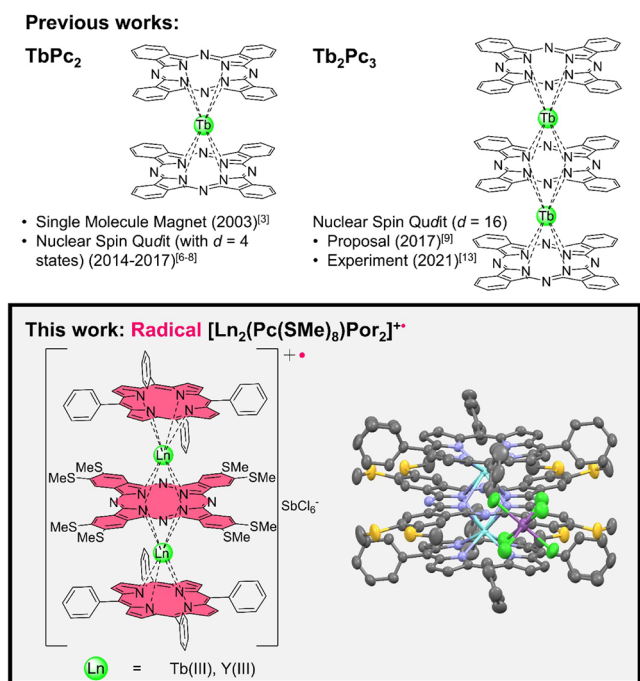


Figure 1. Previous work on bis(phthalocyaninato) terbium(III) (TbPc₂, top left), tris(phthalocyaninato) diterbium(III) (Tb₂Pc₃, top right), and this work on lanthanide(III) bis(porphyrinato)-(octathiomethyl)phthalocyaninato ([Tb₂Por₂(Pc(SMe)₈)]^{•+} SbCl₆⁻, bottom).

coupling between electron spin and nuclear spin, and the exchange coupling between the electron spins of lanthanides (J_{Ln-Ln}).^{2,9} In the case of triple deckers, the last mentioned

factor is particularly important, as several studies have reported weak J_{Ln-Ln} in such complexes.¹⁴⁻¹⁶ In spin transport, the exchange coupling between a radical and lanthanide spin (J_{Ln-Rad}) is also crucial, since nuclear-spin readout in spin transport is enabled by a “spin cascade” between the nuclear spin of ¹⁵⁹Tb, the total angular momentum of ¹⁵⁹Tb, and an organic radical.¹⁷ It is notable that, unlike the case of [TbPc₂]⁰, where J_{Rad-Tb} was investigated in a bulk sample using high-field EPR,¹⁸ J_{Rad-Tb} still remains unknown in triple deckers. J_{Ln-Rad} and J_{Ln-Ln} have been widely investigated in various radical-bridged dilanthanide complexes. Since 2011, these complexes have been explored in pursuit of high-performance SMMs.¹⁹⁻²² The radical, which bridges two lanthanides, induces either exchange bias^{21,23} or a giant spin effect,^{20,24,25} thereby enhancing SMM performance. Here, J_{Ln-Rad} is crucial, as the linear correlation between J_{Ln-Rad} and the energy barrier U_{eff} has been demonstrated.²⁶ However, a significant problem arises because, unlike [TbPc₂]⁰, neutral triple-decker molecules such as [Tb₂Pc₃]⁰ do not exhibit an organic ligand-based radical. The presence of a radical-bearing triple-decker has been reported in previous studies, for instance, through *in situ* UV-vis spectroscopy^{27,28} and *in situ* Kondo measurement using scanning tunneling spectroscopy.^{29,30} Beyond phthalocyanine/porphyrin triple-decker systems, there have been studies on phthalocyanine–corrole mixed-ligand systems.³¹⁻³³ However, none of these approaches fully satisfy our requirements, as the first two are not useful in bulk magnetometry, and the latter, due to broken symmetry, does not qualify as an SMM,³³ which falls outside our area of interest. In short, to develop more reliable qudits for quantum device applications, a triple-decker molecule is needed that possesses both SMM properties and the capability to be converted into a radical suitable for magnetic measurement.

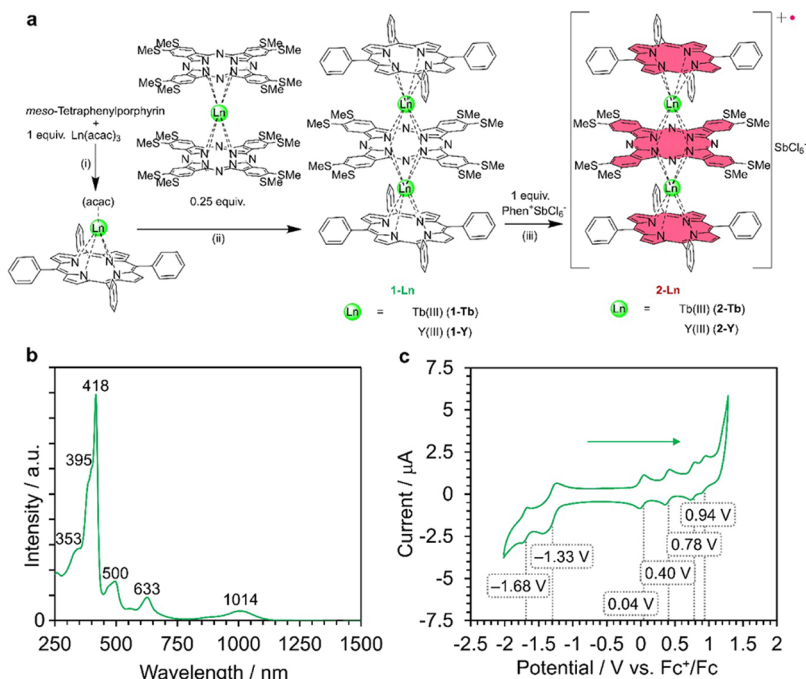


Figure 2. (a) Synthetic pathway for the preparation of triple-decker (porphyrinato)(phthalocyaninato) lanthanides (1-Ln and 2-Ln); (i) 1,2,4-trichlorobenzene/*n*-octanol, reflux, for 4 h. (ii) 1,2,4-Trichlorobenzene/*n*-octanol, reflux, for 16 h. (iii) At room temperature, under inert atmosphere, for 30 min. The synthesis of 16SMe–LnPc₂ is described in the [Supporting Information](#). (b) UV-vis-NIR spectrum of 1-Tb in CHCl₃. (c) Cyclic voltammogram of 1-Tb (0.5 mM) in a 0.1 M *n*Bu₄NPF₆/CH₂Cl₂ supporting electrolyte/solvent at a scan rate of 100 mV s⁻¹. The arrow represents the direction of the scan.

Herein, we present the synthesis and properties of porphyrin–phthalocyanine mixed-ligand heteroleptic triple-decker complexes functionalized with thiomethyl groups (Figure 1, bottom). The thiomethyl group was chosen due to its potential for strong binding affinity to gold electrodes^{34–38} and its electron-donating property.^{39,40} In this work, we focused on the latter property. Leveraging its electron-donating property, we pursued two objectives: (1) tuning the redox levels of the triple decker to enable conversion into a cationic radical and (2) studying the magnetic properties of the radical, particularly the exchange couplings ($J_{\text{Ln-Rad}}$ and $J_{\text{Ln-Ln}}$) and their influence on the SMM properties.

2. RESULTS

2.1. Synthesis and Characterization of 1-Tb and 1-Y.

The lanthanide(III) bis(porphyrinato)((octathiomethyl)-phthalocyaninato) triple-decker complexes (**1-Ln**, **Ln** = **Tb(III)**, **Y(III)**) were prepared using a two-step, tandem one-pot reaction based on a previously reported synthetic approach (Figure 2a).⁴¹ This method involves three key steps: (1) *in situ* formation of lanthanide(III) porphyrinato acetylacetonate ($\text{Ln}(\text{Por})(\text{acac})$) over 4 h, which acts as a template to overcome the instability of intermediate monoporphyrinates; (2) addition of a presynthesized bis-(phthalocyaninato) rare-earth(III) complex with thiomethyl groups (**16SMe-LnPc₂**, Figure 2a), which undergoes thermal splitting and reacts with $\text{Ln}(\text{Por})(\text{acac})$; and (3) slow formation of **1-Ln** under reflux conditions for 16 h. In previous work, the regioselectivity of this synthetic process was explained by quantum chemical calculations.⁴² First, the asymmetric electronic density distribution in the intermediate heteroleptic double-decker complex was shifted toward the phthalocyanine ligand, along with the charge density. Additionally, in the presence of electron-donating alkoxy groups, the coefficients of HOMO are ca. 34% and 66% at the porphyrin and phthalocyanine ligands, respectively (HOMO = the highest occupied molecular orbital). Consequently, the polarization of the molecule results in the selective interaction of monoporphyrinate at the phthalocyanine site of the LnPcPor complex. Similarly, the electron-donating thiomethyl groups of the LnPc_2 complex triggered the process regioselectively. As a result, the crude product could be easily purified using silica gel column chromatography (eluent: $\text{CHCl}_3/\text{hexane}$ = 2/1 at first, then 100% CHCl_3), yielding a green powder. Recrystallization from $\text{CHCl}_3/\text{hexane}$ produced crystalline particles suitable for single-crystal X-ray diffraction (XRD) (*vide infra*).

The UV–vis–NIR absorption spectrum of **1-Tb** is depicted in Figure 2b, and the peak positions and molar absorption coefficients are listed in Table S2. Electronic absorption spectroscopy is the most commonly used technique to characterize macrocyclic tetrapyrrolic compounds and their metal complexes.⁴³ The spectrum closely resembles those of previously reported bis(porphyrinato)(phthalocyaninato) triple deckers.^{41,44,45} Following previous reports, the peaks were assigned to electronic transitions specific to each ligand. The Soret bands of phthalocyanine and porphyrin appear at 353 and 418 nm, respectively. Meanwhile, the Q bands of the phthalocyanine ligand, with some contributions from the porphyrin ligands, are observed at 1014 nm. The absorptions at 500 and 633 nm are assigned to the Q-band mainly of Por^{2-} . Furthermore, the electron-donating substituent in phthalocyanine macrocycles affects their electronic structure, thereby

altering the energy of transitions in the UV and visible regions.^{39,40} The effect of the thiomethyl groups of **1-Tb** is evident in the additional peak at 395 nm, similar to what is observed for **16SMe-LnPc₂** (Figures S2a and S3a).

The infrared (IR) spectroscopic data (Figure S4a) reveal that the IR spectrum of **1-Tb** is similar to that of $\text{Tb}_2\text{PcPor}_2$,¹⁴ confirming their structural similarity. Additional peaks were also observed: one around 1200 cm^{-1} (*Ph-S* stretching) and 1400 cm^{-1} ($-\text{CH}_3$ umbrella motion).⁴⁶ As is the case of **16SMe-LnPc₂** (Figures S2b and S3b), these peaks are characteristics of *-SMe* groups, which is distinguished from isoindole stretching peaks.⁴⁷

High-resolution ESI–TOF–mass spectrometry (ESI-MS) was performed on **1-Tb**, showing signals from a single ion, whose isotopic pattern matched the simulated one (Figure S4b).

Likewise, a series of characterizations (UV–vis–NIR, IR, ESI-MS) was performed on **1-Y**, revealing its similar character to **1-Tb** (Figure S5 and Table S2). In addition, the ^1H and ^{13}C NMR spectra recorded in CD_2Cl_2 of the newly prepared diamagnetic triple-decker complex **1-Y** clearly demonstrated a molecular structure of $(\text{Por})\text{Y}(\text{Pc})\text{Y}(\text{Por})$ (Figures S6 and S7). The assignments of the spectra were achieved by the resolved multiplicity in the signals for the Pc α - and β -protons, the 2D NMR spectra, and were similar to the spectra of related triple-deckers.⁴⁸

The redox properties of **1-Tb** and **1-Y** were investigated by cyclic voltammetry (CV) in CH_2Cl_2 . **1-Tb** and **1-Y** showed redox properties typical of (phthalocyaninato)bis-(porphyrinato) triple deckers^{44,49} (Figures 2c, S5 and Table S1). Six quasi-reversible redox waves were observed at $E_{1/2}$ = 0.94, 0.78, 0.40, 0.04, -1.33 , -1.68 V vs ferrocene/ferrocenium (Fc/Fc^+) for **1-Tb**, and at $E_{1/2}$ = 0.95, 0.79, 0.39, 0.01, -1.31 , -1.67 V for **1-Y**. As previously reported,⁴⁴ such redox profiles are insensitive to the central metal ions but related to the ligand-centered redox reactions ($[\text{Ln}_2\text{PcPor}_2]/[\text{Ln}_2\text{PcPor}_2]^+$, $[\text{Ln}_2\text{PcPor}_2]^+ / [\text{Ln}_2\text{PcPor}_2]^{2+}$, and $[\text{Ln}_2\text{PcPor}_2]/[\text{Ln}_2\text{PcPor}_2]^-$, $[\text{Ln}_2\text{PcPor}_2]^- / [\text{Ln}_2\text{PcPor}_2]^{2-}$), as well as thiomethyl-associated oxidations. In contrast, a previous study⁴⁹ reported that electron-donating/withdrawing substituents on the porphyrin cause a shift in those redox potentials accordingly. The first oxidation potentials of **1-Tb** and **1-Y** are lower than those of $\text{Ln}_2(\text{Pc})(\text{TCIPor})_2$ or $\text{Eu}_2(\text{Pc})\text{Por}_2$ (TCIPor = 5,10,15,20-tetrakis(4-chlorophenyl)-porphyrin), suggesting that electron-donating substituents on the phthalocyanine macrocycle also lower the redox potentials of the complexes. The same trend was also observed in DFT calculations, where the HOMO of **1-Tb** (-4.43 eV) is higher in energy than that of $\text{Tb}_2\text{PcPor}_2$ (-4.53 eV) (Figure S10). The potential difference between the first oxidation and the first reduction $\Delta E^\circ_{\text{first Ox.} - \text{first Red.}}$ (= first Ox. – first Red.) is an important value for sandwich porphyrinato–phthalocyaninato complexes as it represents the HOMO–LUMO gap of the molecule (LUMO = the lowest unoccupied molecular orbital). Interestingly, when comparing $\Delta E^\circ_{\text{first Ox.} - \text{first Red.}}$ values of **1-Tb** and **1-Y** to those of previously reported Por–Pc–Por triple deckers (Table S1), it was observed that the (triple-decker) complexes possessing electron-donating groups tend to exhibit smaller $\Delta E^\circ_{\text{first Ox.} - \text{first Red.}}$ values, with this effect being most significant in **1-Tb** and **1-Y**. Thus, the ligand design strategy utilized in this work effectively stabilized the desired redox pair by tailoring the redox states. Furthermore, we performed cyclic voltammetry on **1-Tb** and **1-Y** over the range of -0.3 to 0.3 V

for 19 cycles (Figures S4c and S5f). No obvious change was observed after repeated cycles, suggesting that the oxidation of 1-Tb and 1-Y is not accompanied by any follow-up chemical reactions. The result here further supports the discussion about the stability of the oxidized species (2-Tb/2-Y, *vide infra*).

2.2. Synthesis, Characterization, and Stability Study of 2-Tb and 2-Y. Encouraged by the results of the cyclic voltammetry of neutral 1-Tb and 1-Y, we attempted to oxidize them to obtain cationic radicals (2-Tb and 2-Y, respectively). Hence, 1-Tb or 1-Y were reacted with an equimolar amount of phenoxathiine hexachloroantimonate(V) ($\text{Phen}^+\text{SbCl}_6^-$) in chloroform (Figure 2a, the third step). Upon mixing, both solutions immediately turned from green to brown. The resulting solution was transferred into test tubes placed in a hexane bath, allowing for the slow diffusion of hexane. Needle-like crystals of 2-Tb or 2-Y were obtained, which were suitable for single-crystal XRD analysis (*vide infra*).

Their UV-vis-NIR absorption spectra are shown in Figures 3a and S9b, and the peak positions and molar absorption

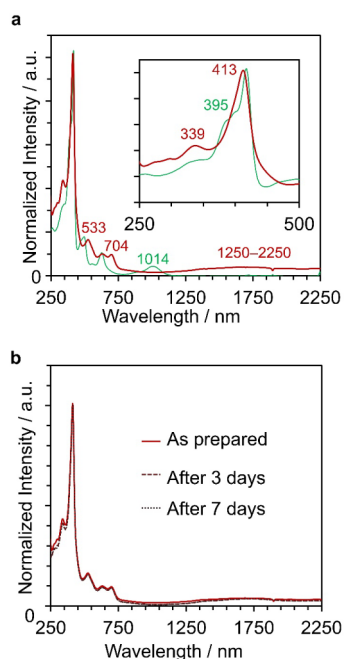


Figure 3. (a) Comparison of UV-vis-NIR spectra. Green: 1-Tb, Maroon: 2-Tb. (b) Time dependence of UV-vis-NIR spectra of 2-Tb.

coefficients are summarized in Table S2. Significant differences were observed between the spectra of the neutral (1-Tb and 1-Y) and those of the one-electron oxidized forms (2-Tb and 2-Y). Notable differences include a stronger peak at $\lambda = 339$ nm, the disappearance of peaks at $\lambda = 395$ and 1014 nm, a blue shift of the peak at $\lambda = 413$ nm, the broadening and redshift of the peak at $\lambda = 533$ nm, the appearance of peaks at $\lambda = 704$ nm, and the broad one in $\lambda = 1250$ – 2250 nm. These observations are consistent with previous reports, where one-electron oxidation of Tb_2Pc_3 complex causes a significant change in its electronic absorption.^{27,28} Notably, the broad peak in the NIR range is typically observed in tetrapyrrolic sandwich compounds with π radicals: monocationic Tb_2Pc_3 , neutral TbPc_2 and phthalocyanine–corrole mixed-ligand complexes.^{27,28,31,43,50} In the case of LnPc_2 , two bands are observed in the NIR range: the high-energy band is related to the radical

part and attributed to the SOMO–LUMO transition, while the lower-energy band is assigned to an intramolecular charge transfer (ICT), both of which are the fingerprints of the presence of a delocalized organic radical.^{43,51}

To assign the broad absorption band, TD-DFT calculations were performed for 2-Y (geometry based on the crystal structure). The calculations were carried out only for the yttrium analogue for simplicity in the spin states to be considered (only the doublet state) and due to the similar absorption band features between 2-Y and 2-Tb. The abstracted results of the TD-DFT calculations for 2-Y are summarized in Section S7. The results suggest that various electronic transitions may contribute to the observed absorption band in the 1250–2250 nm range. The electronic transitions ($f > 0.05$ above $\lambda = 1100$ nm) occur from the molecular orbitals distributed mainly over the Por rings (556β , 557β) or delocalized over the whole complex (559α) to orbitals distributed mainly over the Pc ring (559β or 560α , 561α ; see Figure S11). In short, these predicted transitions ($559\beta \leftarrow 556\beta$, $559\beta \leftarrow 557\beta$, $560\alpha \leftarrow 559\alpha$, $561\alpha \leftarrow 559\alpha$) are characterized as ligand-based IVCT with different CT characters. To ensure the accuracy of the assignment, we also carried out TD-DFT calculations on 2-Y-opt (optimized structure of 2-Y), yielding similar assignments of the broad absorption bands. The experimental broad absorption was also analyzed based on Marcus–Hush theory.^{52–55} The experimental line width is larger than the calculated value, and the presence of multiple excitation processes is anticipated by both the TDDFT calculations and the experimental spectra (Figure S29). Therefore, the actual line width could be narrower, indicating that the compounds (2-Tb and 2-Y) are on the borderline of the Robin-Day class II–III mixed-valence system.

Overall, these spectral changes indicate the formation of cationic radicals, which were further proven by their crystal structures and EPR (*vide infra*).

Furthermore, the sample used for UV spectroscopy was kept under ambient conditions (Figures 3b and S9a). Remarkably, the UV-vis-NIR absorption spectra of the sample remained unchanged even after 7 days, proving the air stability of 2-Tb and 2-Y under ambient conditions. The IR spectra of 2-Tb and 2-Y are similar to those of 1-Tb and 1-Y, except for a broad peak in 3000 – 3500 cm^{-1} (Figures S8a and S9c) attributed to O–H vibration, probably due to the condensation of water in air caused by the cold sample. Furthermore, the presence of the SbCl_6^- anion is proven by single-crystal XRD (*vide infra*). ESI-MS of 2-Tb and 2-Y shows two sets of peaks, whose isotropic pattern matches with those for $z = 1$ and $z = 2$, respectively (Figures S8b,c and S9d,e).

2.3. X-ray Crystallographic Analyses of 1-Tb, 1-Y, 2-Tb, and 2-Y. On obtaining crystals of 1-Tb, 1-Y, 2-Tb, and 2-Y (*vide supra*) their solid-state structures were determined by single-crystal XRD analysis (Figures 4 and S13). All of the complexes showed a triple-decker structure with a symmetrical Por–Ln–Pc–Ln–Por configuration. In the structures of 2-Tb and 2-Y, hexachloroantimonate(V) was included in a one-to-one ratio with the triple-decker complex. Considering charge balance, this proves the complexes 2-Ln to be cationic organic radicals, which was further proven by EPR (*vide infra*). Since molecular symmetry has a great impact on the magnetic properties,¹⁴ crystal parameters of 1-Tb, 1-Y, 2-Tb, 2-Y, and $\text{Tb}_2\text{PcPor}_2$ were compared in detail. First, the isostructural character of terbium and yttrium analogues (1-Tb and 1-Y, 2-Tb and 2-Y, respectively) was confirmed by similar values for

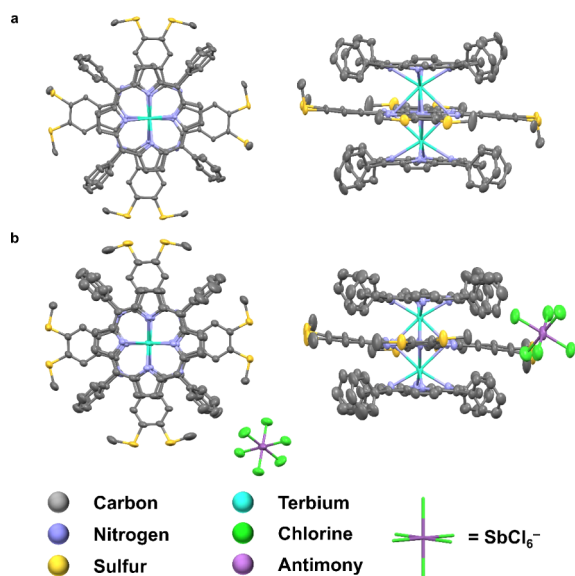


Figure 4. Molecular structures of 1-Tb (a) and 2-Tb (b) represented in the ellipsoids model. For both of them, the side view is shown on the left, while the top view is shown on the right. Solvent molecules and hydrogen atoms are omitted for clarity.

various crystal parameters and crystal packing indexes (Tables 1 and S6).^{1,43} Second, both 1-Ln and 2-Ln have inversion centers, making the two Ln centers equivalent. Based on this, the coordination geometries of the lanthanide centers are compared, where all local symmetries are best described as cuboid (Table S5).¹⁴ In addition, some crystal parameters were selected to quantitatively compare the differences in geometry (Table 1). Comparing 2-Ln to 1-Ln, some differences can be observed, such as the elongation of the Ln–Ln distance, the contraction of the Por–Pc distance, and a smaller twist angle for both Tb and Y. Their parameters are similar to those of Tb₂PcPor₂. Finally, the intermolecular distances in the crystal packing structure were closely investigated. The intermolecular Tb...Tb distances were estimated to be 13.11, 14.17, 15.97, 15.95 Å and 12.71, 18.86, 15.76, 15.93 Å for 1-Tb and 2-Tb, respectively (Figure S12). The values for the Y analogues were similar as well (Figure S14). Similar to Tb₂PcPor₂, their terbium ions between molecules are well isolated.¹⁴ To summarize, both 1-Tb and 2-Tb are centrosymmetric, where two Ln centers are in a cubic coordination environment. The structures obtained here were utilized for DFT or CASSCF calculations (see Section 2.5).

2.4. EPR Study of 2-Y. Prior to the EPR studies, a DFT calculation on the structure of 2-Y predicted that the spin density was fully delocalized over the Pc and Por ligands,

mainly on the carbon atoms (Figure 5a,b), similar to that of the previously reported YPc₂ and YPcPor.^{56,57}

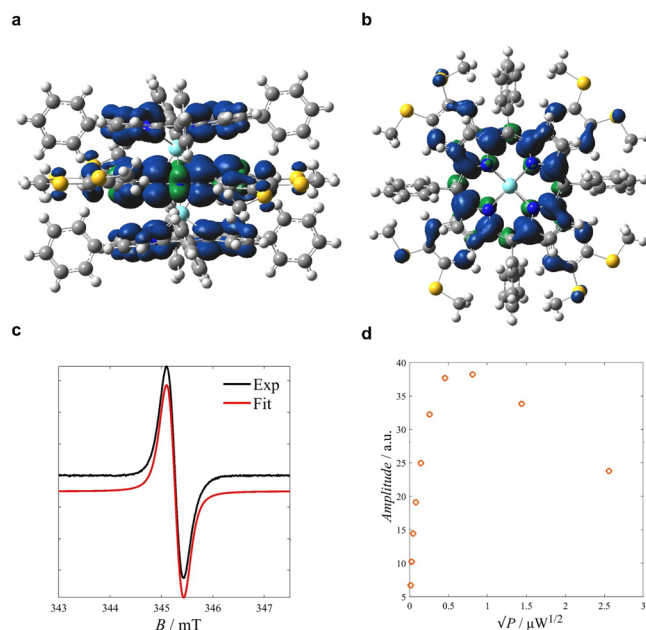


Figure 5. (a) Side and (b) top views of spin density distribution of 2-Y (without the counteranion) derived from DFT calculation at the TPSSh/def2SVP level (isocontour value = 0.0004). (c) Experimental (black) and calculated (red) CW EPR spectra from a frozen solution of radical compound 2-Y. Experimental parameters: $f_{MW} = 9.67742$ GHz, $\Delta B_{1(pp)} = 0.1$ mT, $P_{MW} = 0.207$ μ W, and $T = 92$ K. (d) Saturation curve for 2-Y. Integrated intensity as a function of MW power.

To prove the presence of the radical, a CW-EPR measurement was performed on a frozen solution of 2-Y in a 4:1 CD₂Cl₂/CDCl₃ mixture at 92 K (Figure 5c). It exhibited a simple resonance centered at $g = 2.0023$. Fits to an isotropic absorption yielded best-fit parameters: $g = 2.00237(7)$, $\sigma_{Gpp} = 0.25(1)$ mT, $\sigma_{Lpp} = 0.14(1)$ mT. The lack of hyperfine splitting is attributed to the low spin density on nitrogen atoms, as observed in the cases of YPc₂ and YPcPor previously reported.^{56,57} Indeed, the Mulliken spin density of nitrogen atoms in 2-Y is similar to that of YPc₂ (Tables S3 and S4, as well as Section S6). We also investigated the microwave power dependence of the integrated intensity of the EPR signal (Figure 5d). In agreement with related systems [YPc₂] and [YPcPor], the saturation curve indicated the very early onset of saturation, which is typical of systems that exhibit long spin–lattice relaxation times (T_1).

2.5. CASSCF Calculations. In advance of the magnetic study, we performed ab initio CASSCF calculations in order to

Table 1. Selected Crystal Parameters for 1-Tb, 2-Tb, 1-Y, 2-Y, and Tb₂PcPor₂

Compound	Ln–Ln/Å	Por–Pc/Å	Por–Ln/Å	Ln–Pc/Å	Twist Angle/° ^a
1-Tb	3.74	3.11	1.24	1.87	7.61
2-Tb	3.75	3.09	1.21	1.88	4.16
1-Y	3.72	3.07	1.21	1.86	7.55
2-Y	3.73	3.05	1.19	1.86	4.17
Tb ₂ PcPor ₂ ^b	3.72	3.10	1.24	1.86	3.90

^aThe angle between porphyrin (Por) and phthalocyanine (Pc) ligands, which was clearly described previously.¹⁴ ^bBased on ref 14, the parameters that are not described in the literature are recalculated using CCDC 989974.

predict the magnetic properties of the neutral complex **1-Tb** and cationic radical complex **2-Tb**. To keep the computational effort and required time low enough, modified molecular structures of the complexes were used, where one Tb ion was replaced with diamagnetic Y and the phenyl groups were replaced by methyl groups. For further details, see [Supporting Information](#).

As **1-Tb** does not contain a radical, the calculation is straightforward and was performed using standard approaches of a (8,7)-CASSCF calculation, considering all possible spin states $S = 3, 2, 1$, and 0 , with the maximum number of CI roots for each (see [Section S4.1](#)). Spin-orbit coupling was included via RASSI, and the magnetic properties were derived by using the SINGLE_ANISO routine. The 13 states corresponding to $J = 6$ are shown in [Table S7](#), and they are characterized by a quasi-doubly degenerated ground state, which is well isolated from the quasi-doubly degenerated first excited state ($\sim 200 \text{ cm}^{-1}$). The two ground states exist as a one-to-one mixture of $|\pm 6\rangle$, which hampers **1-Tb** from being a zero-field SMM (*vide infra*) ([Table S7](#)). This behavior arises due to the ligand field Hamiltonian, $\hat{H}_{\text{LF}} = \sum B_k^q \hat{O}_k^q$ ($\hat{O}_k^q$ is the Steven's operator), where non-negligible off-diagonal components $B_k^{q \neq 0}$ contribute to transverse anisotropy ([Table S8](#)).¹⁴ The easy axis of magnetization for terbium was found to align nearly parallel to the axis of the molecule ([Figure S16](#)).

Subsequently, the calculation of **2-Tb** was carried out. Following the approach of previous reports,^{58,59} a CASSCF (9, 8) calculation was executed using only $S = 7/2$ and $5/2$, including only the seven lowest CI roots for each state (see [Section S4.2](#)). This corresponds to a Tb(III) ion coupled either ferromagnetically ($S = 7/2$) or antiferromagnetically ($S = 5/2$) to a radical. The use of only the seven lowest CI roots prevents configurations where electrons of Tb jump to the ligand and vice versa. The 26 states are depicted in [Figure S17](#). All states are doubly degenerate. Overall, the energy diagrams look comparable for **1-Tb** and **2-Tb**, except for the ground state and the first excited state, whose degeneracy was lifted. Notably, this method inherently includes the effect of the radical and the exchange coupling $J_{\text{Ln-Rad}}$. It does, however, not allow for any disentanglement of these effects.

It is common practice to simulate interactions between magnetic centers using programs like PHI (*vide infra*) in order to obtain values of magnetic interaction by employing the 27 ligand field parameters of a given lanthanide ion. As the previously described calculation of **2-Tb** already includes the radical, the crystal field parameters are not applicable for such treatment. We have, therefore, performed an additional calculation of a fictional dicationic complex (**2-Tb** dication; see [Section S4.3](#)). This fictional molecule corresponds to **2-Tb** with the radical removed. This allows us to extract the crystal field parameters and employ them later in a simulation to couple to a radical. The obtained energy diagram for the **2-Tb** dication is similar to that of **1-Tb**, characterized by a semidegenerate ground state ([Figure S19](#)). As described, the energy diagram of **2-Tb** was simulated using the crystal field parameters of **2-Tb** dication coupled to an additional $S = 1/2$ using the PHI package⁶⁰ ([Figure S24](#)). As expected, the energy diagram is identical to that of the **2-Tb** dication when $J_{\text{Ln-Rad}} = 0 \text{ cm}^{-1}$ (besides all states being double degenerate), but as $J_{\text{Ln-Rad}}$ increases, the levels are split, and the overall energy diagram becomes closer to that of **2-Tb**. The calculated energy splitting of **2-Tb** was best reproduced when considering $J_{\text{Ln-Rad}}$

$= -2.67$ or 2.73 cm^{-1} . This result suggests that **2-Tb** can be modeled as a combination of the **2-Tb** dication, a radical, and an exchange coupling $J_{\text{Ln-Rad}}$.

To prove the validity of this method, we also performed a similar calculation on **1-Tb**, using only 7 CI roots and only the highest spin state (**1-Tb** simplified, see [Section S4.4](#)). The comparison between the full and simplified calculations is shown in [Section S4.3](#), revealing very similar results. Therefore, for further discussion, we will use the results from the simplified calculation.

2.6. Magnetometry on 1-Tb and 2-Tb. In order to study the static magnetic behavior of neutral **1-Tb** and cationic radical **2-Tb**, the direct current (DC) magnetic susceptibilities were measured in the temperature range from 300 to 2 K under an applied DC field of 1000 Oe ([Figure 6a](#)). The value

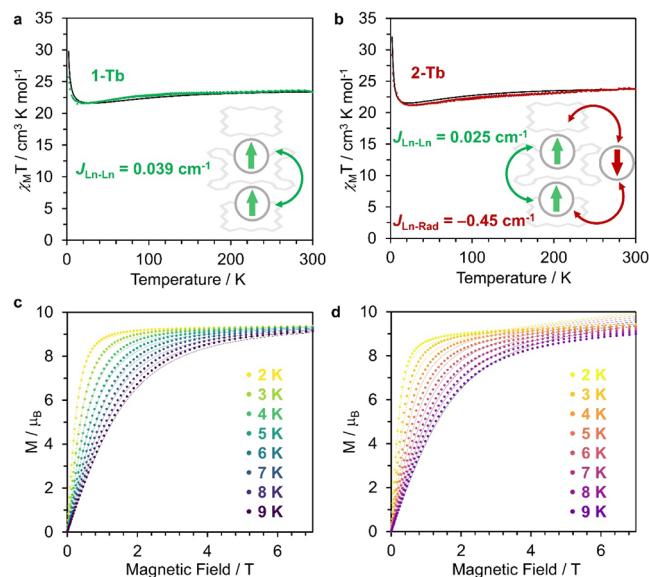


Figure 6. (a, b) Temperature dependence of $\chi_M T$ value of **1-Tb** (a) and **2-Tb** (b), calibrated at 300 K. Circles in green and maroon represent the experimental data, while the black solid lines are their fitting. (c, d) Magnetization versus field plots of **1-Tb** (c) and **2-Tb** (d). The circles correspond to the experimental data, and the solid lines correspond to the fits.

of $\chi_M T$ for **1-Tb** at 300 K was $24.9 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is in good agreement with the value expected for two Tb^{3+} ions ($23.6 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$).⁶¹ Upon cooling, $\chi_M T$ showed a slow decrease, followed by an abrupt increase around 23 K, suggesting ferromagnetic coupling between the two Tb(III) ions. On the other hand, the $\chi_M T$ value for **2-Tb** at 300 K was $24.6 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is also close to the expected value for two Tb^{3+} ions and one radical ($24.0 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$). Like the $\chi_M T$ of **1-Tb**, that of **2-Tb** also showed a slow decrease upon cooling and an abrupt increase at 28 K. The small mismatch in $\chi_M T$ values at 300 K was calibrated by normalizing to the expected values, as shown in [Figure 6](#). Comparing the two plots, the one for **2-Tb** exhibited a larger drop-off, indicating the presence of antiferromagnetic $J_{\text{Ln-Rad}}$. In addition, magnetization versus field ($M(H)$) curves were measured on **1-Tb** and **2-Tb** in the field range of 0–7 T at the temperature range of 2–9 K ([Figure 6c](#)). The $\chi_M T(T)$ and $M(H)$ data were fitted simultaneously, considering two lanthanide centers ([Figure 6a](#) inset), employing the Hamiltonian as follows:

$$\hat{H}_{1-\text{Tb}} = 2\hat{H}_{\text{LF}} + \hat{H}_{\text{Ex(Ln-Ln)}} \quad (1)$$

where $\hat{H}_{\text{LF}}$ is the ligand field (LF) Hamiltonian using the LF parameters obtained from the calculation of **1-Tb** simplified (Table S13), and $\hat{H}_{\text{Ex(Ln-Ln)}}$ is the lanthanide–lanthanide exchange Hamiltonian given as follows:

$$\hat{H}_{\text{Ex(Ln-Ln)}} = -2J_{\text{Ln-Ln}} \hat{S}_{\text{Tb}_1} \cdot \hat{S}_{\text{Tb}_2} \quad (2)$$

where $J_{\text{Ln-Ln}}$ is the lanthanide–lanthanide exchange coupling, and $\hat{S}_{\text{Tb}}$ is the spin operator for Tb center ($S = 3$). A single isotropic exchange variable gave a satisfactory fitting, resulting in $J_{\text{Ln-Ln}} = 0.039 \text{ cm}^{-1}$. Additionally, the $\chi_M T(T)$ and $M(H)$ plots of **2-Tb** were fitted simultaneously, considering a radical and two terbium ions (Figure 6b inset), using the following Hamiltonian:

$$\hat{H}_{2-\text{Tb}} = 2\hat{H}_{\text{LF}} + \hat{H}_{\text{Ex(Ln-Ln)}} + 2\hat{H}_{\text{Ex(Ln-Rad)}} \quad (3)$$

where $\hat{H}_{\text{LF}}$ is the LF Hamiltonian based on the LF parameters calculated for the **2-Tb** dication (the LF parameters are shown in Table S11), $\hat{H}_{\text{Ex(Ln-Ln)}}$ is the lanthanide–lanthanide exchange Hamiltonian defined as eq 2, and $\hat{H}_{\text{Ex(Ln-Rad)}}$ is the exchange Hamiltonian given as follows:

$$\hat{H}_{\text{Ex(Ln-Rad)}} = -2J_{\text{Ln-Rad}} \hat{S}_{\text{Tb}} \cdot \hat{S}_{\text{Rad}} \quad (4)$$

where $J_{\text{Ln-Rad}}$ is the lanthanide–radical exchange coupling, and $\hat{S}_{\text{Rad}}$ is the spin operator for the radical center. The satisfactory fitting was obtained with two single isotropic exchange variables: $J_{\text{Ln-Ln}} = 0.025 \text{ cm}^{-1}$ and $J_{\text{Ln-Rad}} = -0.45 \text{ cm}^{-1}$.

Alternating current (AC) magnetometry was performed on both **1-Tb** and **2-Tb** to investigate their dynamic magnetic properties. Initially, the field dependence of χ_M'' versus frequency plots at 2 K was investigated to examine the optimal field (Figure S25a,d). In **1-Tb**, the maximum was out of the measurement range (1–1000 Hz). This finding was confirmed by χ_M'' versus frequency measurements of **1-Tb** at zero field, where the maximum was not observed in the scan window within the temperature range (Figure S26b). Upon increasing the field, the peak shifted to lower frequencies (Figure S25a), suggesting that **1-Tb** is a field-induced SMM. The optimal field value of 1500 Oe was obtained based on the signal strength and frequency. Overall, the dynamic magnetic behavior of **1-Tb** is similar to that of $\text{Tb}_2\text{PcPor}_2$.¹⁴ On the other hand, in the case of **2-Tb**, χ_M'' (ν) showed a peak located around 200 Hz even at zero field, revealing its zero-field SMM character (Figure S25d). The marked difference in the behaviors of **1-Tb** and **2-Tb** evidenced that the radical has a substantial effect on the magnetic properties.

Afterward, the temperature dependence of χ_M' and χ_M'' versus frequency plots was measured at 1500 Oe for **1-Tb** and in zero-field for **2-Tb** (Figures 7a,b and S27). For **1-Tb**, the maximum in χ_M'' vs T was around 10 Hz at 2 K, which showed a gradual shift to higher frequencies upon heating and was observed up to 11 K. On the other hand, for **2-Tb**, the maximum was seen already around 100 Hz at 2 K and was observable up to 3.95 K.

The obtained results were fitted with a generalized Debye model using CC-FIT2.^{62,63} Figure 7c represents the relaxation time (τ in log scale) versus temperature (inverse) plot. The plot of **1-Tb** was fitted employing a combination of Orbach and Raman processes using eq 5:

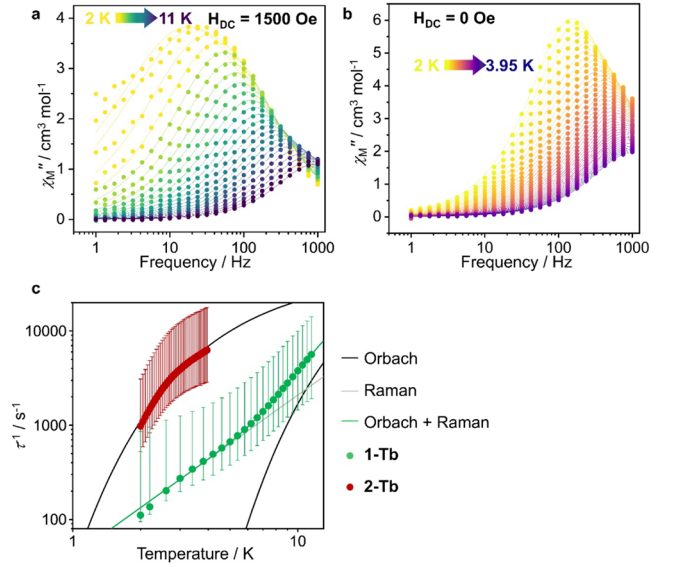


Figure 7. (a, b) Temperature dependence of χ_M'' versus frequency of **1-Tb** (a) and **2-Tb** (b). The solid lines represent the fitting of data of the corresponding color. (c) Relaxation time (τ^{-1}) versus temperature plot in log–log scale of **1-Tb** and **2-Tb** (circles in green and maroon, respectively). The solid lines represent each process: Orbach $\tau^{-1} = \tau_0^{-1} \exp\left(\frac{-U_{\text{eff}}}{T}\right)$ (black), Raman $\tau^{-1} = CT^n$ (gray), Orbach + Raman $\tau^{-1} = \tau_0^{-1} \exp\left(\frac{-U_{\text{eff}}}{T}\right) + CT^n$ (green). The best-fit parameters are described in the manuscript. Error bars are calculated from the log-normalized (ln) distribution.⁶²

$$\tau^{-1} = \tau_0^{-1} \exp\left(\frac{-U_{\text{eff}}}{T}\right) + CT^n \quad (5)$$

where the first term stands for the Orbach process, while the second represents the Raman process. It yielded the following parameters: $\tau_0 = (7.56 \pm 0.26) \times 10^{-6} \text{ s}$, $U_{\text{eff}} = 43.6 \pm 0.6 \text{ K}$, $C = 40 \pm 2 \text{ s}^{-1}$, $n = 1.71 \pm 0.03$. On the other hand, the plot of **2-Tb** was fitted only considering an Orbach process using the first term of eq 5. It was best fitted with the parameters as follows: $U_{\text{eff}} = 7.3 \pm 0.1 \text{ K}$, yielded the following parameters: $\tau_0 = (2.32 \pm 0.09) \times 10^{-5} \text{ s}$.

To understand their magnetic properties, the energy states of **1-Tb** and **2-Tb** were simulated using PHI,⁶⁰ with the parameters used to fit the DC data (LF parameters: Tables S11 and S13, and low-lying energy states: Table S18). For **1-Tb**, under zero field, the quasi-doubly degenerated ground states are in a one-to-one mixture of $|\pm 6, \pm 6\rangle$, which is commonly found in non-Kramers system. On the other hand, the doubly degenerated ground states of **2-Tb** consist solely $|+6, +6, -1/2\rangle$ or $|-6, -6, +1/2\rangle$, which is reasonably explained by the fact that **2-Tb** is a Kramers system. The first excited states include $|+6, -6, +1/2\rangle$ and so on, characterized by antiferromagnetic coupling between the Tb centers. Remarkably, the energy gap between the ground states and the excited states ($= 3.6 \text{ cm}^{-1}$) is close to the energy barrier U_{eff} of **2-Tb** ($= 7.3 \text{ K} = 5.1 \text{ cm}^{-1}$). For **1-Tb**, a Zeeman diagram was created (Figure S28). Upon applying the magnetic field of 1500 Oe, the degenerated states ($|\pm 6, \pm 6\rangle$) undergo Zeeman splitting. It is notable that although this Zeeman diagram explains the magnetic behavior well qualitatively, it does not match quantitatively, which was also true for the previously studied $\text{Tb}_2\text{PcPor}_2$.¹⁶

3. DISCUSSION

In this study, we designed porphyrin–phthalocyanine mixed-ligand triple-decker complexes functionalized with thiomethyl groups. We first synthesized the neutral molecules (**1-Tb** and **1-Y**) based on a refined approach for preparing lanthanide heteroleptic triple-decker complexes with a symmetrical Por–Ln–Pc–Ln–Por (**1-Tb** and **1-Y**) structure.⁴¹ This method leverages *in situ*-generated unstable intermediates to ensure the regiospecific formation of the target complexes through selective interactions governed by electronic and charge density distributions. **1-Tb** and **1-Y** were characterized using UV–vis–NIR, IR spectroscopies, HR ESI-MS, and ¹H- and ¹³C-NMR (only with **1-Y**). Cyclic voltammetry was performed on **1-Tb** and **1-Y**, revealing their lowered oxidation potential compared with those of other porphyrin–phthalocyanine mixed-ligand triple-decker derivatives. This result validates another key design objective: tailoring the redox state through the incorporation of electron-donating groups.

1-Tb and **1-Y** were converted into the corresponding cationic radicals (**2-Tb** and **2-Y**, respectively) by the addition of an equimolar amount of the oxidation reagent (phenoxathiine hexachloroantimonate (V)). **2-Tb** and **2-Y** were characterized using UV–vis–NIR, IR spectroscopies, and HR ESI-MS. As described in the introduction, to the best of our knowledge, this is the first bulk study on radicals based on triple-decker platforms. Remarkably, UV–vis–NIR spectra remained unchanged for 1 week in the solution of **2-Tb** and **2-Y** kept in air at room temperature, revealing their unprecedented air stability. EPR proved the presence of an organic radical $S = 1/2$ on **2-Y**. The amplitude was saturated quickly against increased microwave power, indicating its long spin–lattice relaxation time (T_1). In the field of molecular electron-spin QIP, organic radicals have attracted increased attention because their small spin–orbital coupling tend to give long T_1 .⁶⁴ Several attempts have been and are still being made to harness YPC₂ as an electron–spin qubit.^{57,65} The results presented here may offer **2-Y** as a new platform for an electron–spin qubit. However, pulse EPR studies on **2-Y** are needed to validate this hypothesis.

Crystalline materials of **1-Tb**, **1-Y**, **2-Tb**, and **2-Y** were obtained, which were suitable for single-crystal XRD, revealing their symmetrical Por–Ln–Pc–Ln–Por configuration. The monocationic character of the **2-Ln** complexes was confirmed by the one-to-one ratio of triple-decker to SbCl₆[−] anion in the lattice of **2-Ln**. Single-crystal XRD analysis provided essential parameters for understanding their structural and magnetic correlations. First, **2-Tb** exhibited the elongation of the Tb–Tb distance by 0.01 Å, the contraction of the Por–Pc distance by 0.02 Å, and a smaller twist angle of 3.45°. Previously, Horii et al.²⁷ revealed that upon two-electron oxidation ([Tb₂Pc₃]^{0/2+}), crystal parameters in Tb₂Pc₃ changed significantly, including the contraction of the Tb–Tb distance by 0.08 Å, the contraction of the Por–Pc distance by 0.07 Å, and a smaller twist angle of 12.4°. They performed a CASSCF study and concluded that the contraction in Tb–Tb induced a decrease in the energy barrier U_{eff} (from 279 to 217 cm^{−1}). Considering the subtle differences in the crystal parameters, the effect of the crystal field on the energy barrier differences between **1-Tb** and **2-Tb** is expected to be less prominent. On the other hand, the nearest intermolecular Tb⋯Tb distance was 13.1 Å for **1-Tb** and 12.7 Å for **2-Tb**. Similar to the previously reported Tb₂PcPor₂,¹⁴ it can be inferred that both of

them are sufficiently distant, allowing us to disregard the intermolecular Tb⋯Tb magnetic interaction. Furthermore, the phenyl groups perpendicular to the porphyrin plane and the lattice solvents increase the intermolecular distance (Figures S12 and S14), indicating that the intermolecular radical⋯radical magnetic interactions would also be minimized.

Static magnetic properties of **1-Tb** and **2-Tb** were investigated by a combination of CASSCF calculations and bulk magnetometry. The $\chi_M T(T)$ and $M(H)$ plots clearly showed different behaviors between **1-Tb** and **2-Tb**. The fitting of these plots was performed using the ligand field parameters obtained from CASSCF, yielding isotropic exchange coupling values of $J_{\text{Ln–Ln}} = 0.039$ cm^{−1} for **1-Tb**, while $J_{\text{Ln–Ln}} = 0.025$ cm^{−1} and $J_{\text{Ln–Rad}} = -0.45$ cm^{−1} for **2-Tb**. $J_{\text{Ln–Ln}}$ is similar for both, and they are of the same order of magnitude as those previously reported Tb₂Pc₃, Dy₂Pc₃, or Tb₂PcPor₂ (0.097 cm^{−1}, 0.2 cm^{−1}, and 0.012 cm^{−1}, respectively).^{16,66,67} Additionally, $J_{\text{Ln–Rad}}$ of **2-Tb** is of the same order as that of TbPc₂ and GdPc₂ ($J_{\text{Ln–Rad}} = 0.15$ cm^{−1} and 0.2 cm^{−1}, respectively).^{18,68} It is notable that exchange coupling is essential for the electronic read-out of nuclear spin states in spin-transport measurements.⁶

Dynamic magnetic properties of **1-Tb** and **2-Tb** differ significantly. The field dependence of χ_M'' versus frequency plots revealed that **1-Tb** is a field-induced SMM, while **2-Tb** is a zero-field SMM. We attribute this to the fact that **1-Tb** is a non-Kramers system, while **2-Tb** is a Kramers system. In addition, the temperature dependence of χ_M'' versus frequency plots and their fitting was performed on **1-Tb** and **2-Tb**. **1-Tb** was fitted with the combination of Orbach and Raman processes. The plot of **1-Tb** resembles that of Tb₂PcPor₂, where the value of U_{eff} is similar ($U_{\text{eff}} = 43.6 \pm 0.6$ K for **1-Tb**, while $U_{\text{eff}} = 25.9–34.6$ K for Tb₂PcPor₂).^{14,16} On the other hand, the plot of **2-Tb** was fitted solely with the Orbach process to give $U_{\text{eff}} = 7.3 \pm 0.1$ K. This value is in good agreement with the calculated energy gap, which supports the validity of our calculation. Overall, **1-Tb** and **2-Tb** showed significant differences in magnetic properties, namely the switch from field-induced SMM to zero-field SMM. As discussed in the introduction, various radical-bridged dinuclear lanthanide SMMs have been investigated for their improved magnetic properties.^{21,22} Radical-containing ligands have been adopted in transition-metal SMMs as well.^{21,69–71} An unambiguous “On/Off” switching of SMM activity was found in a dinuclear cobalt complex with *N,N*-diaryl- β -diketimines upon a ligand-centered redox reaction.⁷² On the other hand, regarding dinuclear lanthanide complexes, a switching behavior between field-induced SMM and zero-field SMM upon ligand-centered redox reaction was observed in systems with tetraoxolene ligands.^{73,74} However, to the best of our understanding, the contribution of structural change in such systems remains unclear. It is notable that, as mentioned in the introduction, the studies on radical-bridged dinuclear lanthanide SMMs aim for strong $J_{\text{Ln–Rad}}$ coupling, typically yielding a value of $J_{\text{Ln–Rad}}$ well above 1 cm^{−1}.^{19,26,73} In a weak coupling regime, TbPc₂ stands as a good example. Upon oxidation of anionic [TbPc₂][−], neutral [TbPc₂]⁰ exhibits a higher energy barrier due to structural change^{3,75} and a larger coercive field due to the suppression of QTM.^{76,77} Compared with these previously studied systems, our system is characterized by the following points: (i) switchable magnetic properties between field-induced and zero-field SMM, (ii) weak $J_{\text{Ln–Rad}}$ coupling, and (iii) a radical effect that is

reasonably explained by the theoretical models enabled by single-crystal structure analysis.

4. CONCLUSION

In summary, we have synthesized lanthanide porphyrin-phthalocyanine mixed-ligand triple-decker complexes functionalized with thiomethyl groups exclusively on Pc rings. A lowered oxidation potential enabled the synthesis of radical-bearing triple deckers with a well-defined crystal structure. To the best of our knowledge, this is the first example of a radical-bearing triple-decker complex with full bulk characterization. Furthermore, the introduced organic radical is stable under ambient conditions for over a week. Static magnetic measurements and CASSCF calculations afforded the exchange coupling ($J_{\text{Ln-Rad}} = -0.45 \text{ cm}^{-1}$). AC susceptibility revealed a transition from field-induced SMM to zero-field SMM, which was well explained by the theoretical model.

Our findings provide valuable insights into the field of quantum technology. For instance, the radical-bearing yttrium triple-decker is a promising candidate as an electron spin qubit, owing to its stability. Additionally, our approach suggests a new strategy to create a switchable SMM, transitioning from a field-induced SMM to a zero-field one. Above all, we highlight the potential of our molecule as a nuclear spin qubit with an increased Hilbert space. As explained in the introduction, one of our key design objectives was to enhance binding with gold electrodes. To achieve this, thiomethyl groups are positioned exclusively on the middle phthalocyanine ligands, which facilitates a junction configuration in which only the middle ligand interacts directly with the electrode. Combined with this targeted chemical design, the defined $J_{\text{Ln-Rad}}$ gives these complexes a distinct advantage over the previously studied Tb_2Pc_3 systems. Spin transport measurements on this molecular platform are currently in progress.

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Notes

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REFERENCES

- (1) Martynov, A. G.; Horii, Y.; Katoh, K.; Bian, Y.; Jiang, J.; Yamashita, M.; Gorbunova, Y. G. Rare-Earth Based Tetrapyrrolic Sandwiches: Chemistry, Materials and Applications. *Chem. Soc. Rev.* **2022**, *51* (22), 9262–9339.
- (2) Moreno-Pineda, E.; Godfrin, C.; Balestro, F.; Wernsdorfer, W.; Ruben, M. Molecular Spin Qudits for Quantum Algorithms. *Chem. Soc. Rev.* **2018**, *47* (2), 501–513.
- (3) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. Lanthanide Double-Decker Complexes Functioning as Magnets at the Single-Molecular Level. *J. Am. Chem. Soc.* **2003**, *125*, 8694–8695.
- (4) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets: Bis-(Phthalocyaninato)Terbium and Bis(Phthalocyaninato)Dysprosium Anions. *Angew. Chem., Int. Ed.* **2005**, *44* (19), 2931–2935.
- (5) Maurer, P. C.; Kucsko, G.; Latta, C.; Jiang, L.; Yao, N. Y.; Bennett, S. D.; Pastawski, F.; Hunger, D.; Chisholm, N.; Markham, M.; et al. Room-Temperature Quantum Bit Memory Exceeding One Second. *Science* **2012**, *336* (June), 1283–1286.
- (6) Vincent, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Electronic Read-out of a Single Nuclear Spin Using a Molecular Spin Transistor. *Nature* **2012**, *488* (7411), 357–360.
- (7) Thiele, S.; Balestro, F.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W. Supplementary Materials for Electrically Driven Nuclear Spin Resonance in Single-Molecule Magnets. *Science* **2014**, *344* (6188), 1135–1138.
- (8) Godfrin, C.; Ferhat, A.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Operating Quantum States in Single Magnetic Molecules: Implementation of Grover's Quantum Algorithm. *Phys. Rev. Lett.* **2017**, *119* (18), 1–5.
- (9) Wernsdorfer, W.; Ruben, M. Synthetic Hilbert Space Engineering of Molecular Qudits: Isotopologue Chemistry. *Adv. Mater.* **2019**, *31* (26), 1806687.
- (10) Janković, D.; Hartmann, J. G.; Ruben, M.; Hervieux, P. A. Noisy Qudit vs Multiple Qubits: Conditions on Gate Efficiency for Enhancing Fidelity. *Npj Quantum Inf.* **2024**, *10* (1), 1–10.
- (11) Chiesa, A.; Roca, S.; Chicco, S.; De Ory, M. C.; Gómez-León, A.; Gomez, A.; Zueco, D.; Luis, F.; Carretta, S. Blueprint for a Molecular-Spin Quantum Processor. *Phys. Rev. Appl.* **2023**, *19* (6), 1.
- (12) Mezzadri, M.; Chiesa, A.; Lepori, L.; Carretta, S. Fault-Tolerant Computing with Single-Qudit Encoding in a Molecular Spin. *Mater. Horiz.* **2024**, *11*, 4961–4969.
- (13) Biard, H.; Moreno-Pineda, E.; Ruben, M.; Bonet, E.; Wernsdorfer, W.; Balestro, F. Increasing the Hilbert Space Dimension Using a Single Coupled Molecular Spin. *Nat. Commun.* **2021**, *12* (1), 1–8.
- (14) Katoh, K.; Breedlove, B. K.; Yamashita, M. Symmetry of Octa-Coordination Environment Has a Substantial Influence on Dinuclear TbIII Triple-Decker Single-Molecule Magnets. *Chem. Sci.* **2016**, *7* (7), 4329–4340.
- (15) Horii, Y.; Katoh, K.; Cosquer, G.; Breedlove, B. K.; Yamashita, M. Weak DyIII–DyIII Interactions in DyIII-Phthalocyaninato Multiple-Decker Single-Molecule Magnets Effectively Suppress Magnetic Relaxation. *Inorg. Chem.* **2016**, *55* (22), 11782–11790.
- (16) Katoh, K.; Yasuda, N.; Damjanović, M.; Wernsdorfer, W.; Breedlove, B. K.; Yamashita, M. Manipulation of the Coordination Geometry along the C4 Rotation Axis in a Dinuclear Tb³⁺ Triple-Decker Complex via a Supramolecular Approach. *Chem.-Eur. J.* **2020**, *26* (21), 4805–4815.
- (17) Godfrin, C.; Thiele, S.; Ferhat, A.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Electrical Read-Out of a Single Spin Using an Exchange-Coupled Quantum Dot. *ACS Nano* **2017**, *11* (4), 3984–3989.
- (18) Komijani, D.; Ghirri, A.; Bonizzoni, C.; Klyatskaya, S.; Moreno-Pineda, E.; Ruben, M.; Soncini, A.; Affronte, M.; Hill, S. Radical-Lanthanide Ferromagnetic Interaction in a T^{III} Bis-Phthalocyaninato Complex. *Phys. Rev. Mater.* **2018**, *2* (2), 1–9.
- (19) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. Strong Exchange and Magnetic Blocking in N23– Radical-Bridged Lanthanide Complexes. *Nat. Chem.* **2011**, *3* (7), 538–542.
- (20) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. A N23–Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. *J. Am. Chem. Soc.* **2011**, *133* (36), 14236–14239.
- (21) Demir, S.; Jeon, I. R.; Long, J. R.; Harris, T. D. Radical Ligand-Containing Single-Molecule Magnets. *Coord. Chem. Rev.* **2015**, *289*–290 (1), 149–176.
- (22) Li, H. D.; Wu, S. G.; Tong, M. L. Lanthanide-Radical Single-Molecule Magnets: Current Status and Future Challenges. *Chem. Commun.* **2023**, *59*, 6159–6170.
- (23) Morita, T.; Damjanović, M.; Katoh, K.; Kitagawa, Y.; Yasuda, N.; Lan, Y.; Wernsdorfer, W.; Breedlove, B. K.; Enders, M.; Yamashita, M. Comparison of the Magnetic Anisotropy and Spin Relaxation Phenomenon of Dinuclear Terbium(III) Phthalocyaninato Single-Molecule Magnets Using the Geometric Spin Arrangement. *J. Am. Chem. Soc.* **2018**, *140* (8), 2995–3007.
- (24) Vieru, V.; Iwahara, N.; Ungur, L.; Chibotaru, L. F. Giant Exchange Interaction in Mixed Lanthanides. *Sci. Rep.* **2016**, *6*, 24046.
- (25) Liu, F.; Spree, L.; Krylov, D. S.; Velkos, G.; Avdoshenko, S. M.; Popov, A. A. Single-Electron Lanthanide-Lanthanide Bonds Inside Fullerenes toward Robust Redox-Active Molecular Magnets. *Acc. Chem. Res.* **2019**, *52* (10), 2981–2993.
- (26) Gould, C. A.; Mu, E.; Vieru, V.; Darago, L. E.; Chakarawet, K.; Gonzalez, M. I.; Demir, S.; Long, J. R. Substituent Effects on Exchange Coupling and Magnetic Relaxation in 2,2'-Bipyrimidine Radical-Bridged Lanthanide Complexes. *J. Am. Chem. Soc.* **2020**, *142* (50), 21197–21209.
- (27) Horii, Y.; Damjanović, M.; Ajayakumar, M. R.; Katoh, K.; Kitagawa, Y.; Chibotaru, L.; Ungur, L.; Mas-Torrent, M.; Wernsdorfer, W.; Breedlove, B. K.; et al. Highly Oxidized States of Phthalocyaninato Terbium(III) Multiple-Decker Complexes Showing Structural Deformations, Biradical Properties and Decreases in Magnetic Anisotropy. *Chem.-Eur. J.* **2020**, *26* (39), 8621–8630.
- (28) Martynov, A. G.; Polovkova, M. A.; Gorbunova, Y. G.; Tsivadze, A. Y. Redox-Triggered Switching of Conformational State in Triple-Decker Lanthanide Phthalocyaninates. *Molecules* **2022**, *27* (19), 6498.
- (29) Xia, H. N.; Minamitani, E.; Žitko, R.; Liu, Z. Y.; Liao, X.; Cai, M.; Ling, Z. H.; Zhang, W. H.; Klyatskaya, S.; Ruben, M.; Fu, Y. S. Spin-Orbital Yu-Shiba-Rusinov States in Single Kondo Molecular Magnet. *Nat. Commun.* **2022**, *13* (1), 1–7.
- (30) Liao, X.; Minamitani, E.; Xie, T.; Yang, L.; Zhang, W.; Klyatskaya, S.; Ruben, M.; Fu, Y. S. Altering Spin Distribution of Tb₂Pc₃ via Molecular Chirality Manipulation. *J. Am. Chem. Soc.* **2024**, *146* (9), 5901–5907.
- (31) Lu, G.; Li, J.; Yan, S.; Zhu, W.; Ou, Z.; Kadish, K. M. Synthesis and Characterization of Rare Earth Corrole-Phthalocyanine Heteroleptic Triple-Decker Complexes. *Inorg. Chem.* **2015**, *54* (12), 5795–5805.
- (32) Lu, G.; He, C.; Fang, Y.; Wang, L.; Zhu, W. Construction of Mixed Corrole-Phthalocyanine Europium Triple-Decker Complexes Involving: Meso -Substituted Trans -A2B-Corrole. *New J. Chem.* **2018**, *42* (4), 2498–2503.
- (33) Lu, G.; He, C.; Wang, K.; Sun, J.; Qi, D.; Gong, L.; Wang, C.; Ou, Z.; Yan, S.; Zeng, S.; Zhu, W. Dysprosium Heteroleptic Corrole-Phthalocyanine Triple-Decker Complexes: Synthesis, Crystal Structure, and Electrochemical and Magnetic Properties. *Inorg. Chem.* **2017**, *56* (19), 11503–11512.
- (34) Bogani, L.; Wernsdorfer, W. Molecular Spintronics Using Single-Molecule Magnets. *Nat. Mater.* **2008**, *7*, 179–186.
- (35) Wagner, S.; Kisslinger, F.; Ballmann, S.; Schramm, F.; Chandrasekar, R.; Bodenstein, T.; Fuhr, O.; Secker, D.; Fink, K.; Ruben, M.; Weber, H. B. Switching of a Coupled Spin Pair in a Single-Molecule Junction. *Nat. Nanotechnol.* **2013**, *8* (8), 575–579.

- (36) Heersche, H. B.; De Groot, Z.; Folk, J. A.; Van Der Zant, H. S. J.; Romeike, C.; Wegewijs, M. R.; Zobbi, L.; Barreca, D.; Tondello, E.; Cornia, A. Electron Transport through Single Mn12 Molecular Magnets. *Phys. Rev. Lett.* **2006**, *96* (20), 1–4.
- (37) Parks, J. J.; Champagne, A. R.; Costi, T. A.; Shum, W. W.; Pasupathy, A. N.; Neuscamman, E.; Flores-Torres, S.; Cornaglia, P. S.; Aligia, A. A.; Balseiro, C. A.; Chan, G. K. L.; Abruña, H. D.; Ralph, D. C. Mechanical Control of Spin States in Sp. *Science* **2010**, *328* (5984), 1370–1373.
- (38) Gehring, P.; Sowa, J. K.; Hsu, C.; de Bruijckere, J.; van der Star, M.; Le Roy, J. J.; Bogani, L.; Gauger, E. M.; van der Zant, H. S. J. Complete Mapping of the Thermoelectric Properties of a Single Molecule. *Nat. Nanotechnol.* **2021**, *16* (4), 426–430.
- (39) Topal, S. Z.; Işci, Ü.; Kumru, U.; Atila, D.; Gürek, A. G.; Hirel, C.; Durmuş, M.; Tommasino, J. B.; Luneau, D.; Berber, S.; et al. Modulation of the Electronic and Spectroscopic Properties of Zn(II) Phthalocyanines by Their Substitution Pattern. *Dalt. Trans* **2014**, *43* (18), 6897–6908.
- (40) Kobayashi, N.; Ogata, H.; Nonaka, N.; Luk'yanets, E. A. Effect of Peripheral Substitution on the Electronic Absorption and Fluorescence Spectra of Metal-Free and Zinc Phthalocyanines. *Chem. -Eur. J.* **2003**, *9* (20), 5123–5134.
- (41) Birin, K. P.; Gorbunova, Y. G.; Tsivadze, A. Y. Efficient Scrambling-Free Synthesis of Heteroleptic Terbium Triple-Decker (Porphyrinato)(Crown-Phthalocyaninates). *Dalt. Trans* **2012**, *41* (32), 9672–9681.
- (42) Birin, K. P.; Gorbunova, Y. G.; Tsivadze, A. Y. Novel One-Pot Regioselective Route towards Heteroleptic Lanthanide (Phthalocyaninato)(Porphyrinato) Triple-Decker Complexes. *J. Porphyr. Phthalocyanines* **2009**, *13* (2), 283–290.
- (43) Pushkarev, V. E.; Tomilova, L. G.; Nemykin, V. N. Historic Overview and New Developments in Synthetic Methods for Preparation of the Rare-Earth Tetrapyrrolic Complexes. *Coord. Chem. Rev.* **2016**, *319*, 110–179.
- (44) Sun, X.; Li, R.; Wang, D.; Dou, J.; Zhu, P.; Lu, F.; Ma, C.; Choi, C. F.; Cheng, D. Y. Y.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Synthesis and Characterization of Mixed Phthalocyaninato and Meso-Tetrakis-(4-Chlorophenyl)Porphyrinato Triple-Decker Complexes - Revealing the Origin of Their Electronic Absorptions. *Eur. J. Inorg. Chem.* **2004**, *2004* (19), 3806–3813.
- (45) Muranaka, A.; Matsumoto, Y.; Uchiyama, M.; Jiang, J.; Bian, Y.; Ceulemans, A.; Kobayashi, N. Definitive Assignments of the Visible-near-IR Bands of Porphyrin- Naphthalocyanine Rare-Earth Sandwich Double- and Triple-Decker Compounds by Magnetic Circular Dichroism Spectroscopy. *Inorg. Chem.* **2005**, *44* (11), 3818–3826.
- (46) Gellini, C.; Moroni, L.; Muniz-Miranda, M. High Overtones of the C–H Stretching Vibrations in Anisole and Thioanisole. *J. Phys. Chem. A* **2002**, *106* (46), 10999–11007.
- (47) Lu, F.; Bao, M.; Ma, C.; Zhang, X.; Arnold, D. P.; Jiang, J. Infrared Spectra of Phthalocyanine and Naphthalocyanine in Sandwich-Type (Na)Phthalocyaninato and Porphyrinato Rare Earth Complexes. Part 3. The Effects of Substituents and Molecular Symmetry on the Infrared Characteristics of Phthalocyanine in Bis(Phthal. *Spectrochim. Acta, Part A* **2003**, *59* (14), 3273–3286.
- (48) Sun, X.; Cui, X.; Arnold, D. P.; Choi, M. T. M.; Ng, D. K. P.; Jiang, J. The Electronic Absorption Characteristics of Mixed Phthalocyaninato Porphyrinato Rare Earth(III) Triple-Decker (TPyP)2(Pc). *Eur. J. Inorg. Chem.* **2003**, *2* (8), 1555–1561.
- (49) Jiang, J.; Liu, W.; Law, W. F.; Ng, D. K. P. Heteroleptic Triple-Decker (Phthalocyaninato)-(Porphyrinato) Europium (III) Complexes: Synthesis and Electrochemical Study. *Inorg. Chim. Acta* **1998**, *268* (1), 49–53.
- (50) Gasyna, Z.; Schatz, P. N.; Boyle, M. E. Analysis of the Intervalence Band in Lutetium Bis(Phthalocyanine): The System Is Delocalized. *J. Phys. Chem.* **1995**, *99* (25), 10159–10165.
- (51) Klar, D.; Candini, A.; Joly, L.; Klyatskaya, S.; Krumme, B.; Ohresser, P.; Kappler, J. P.; Ruben, M.; Wende, H. Hysteretic Behaviour in a Vacuum Deposited Submonolayer of Single Ion Magnets. *Dalt. Trans.* **2014**, *43* (28), 10686–10689.
- (52) Hush, N. S. Intervalence-Transfer Absorption. Part 2. *Theoretical Considerations And Spectroscopic Data* **1967**, *8*, 391–444.
- (53) Hush, N. S. Homogeneous and Heterogeneous Optical and Thermal Electron Transfer. *Electrochim. Acta* **1968**, *13* (5), 1005–1023.
- (54) Arnold, A.; Sherbow, T. J.; Bohanon, A. M.; Sayler, R. I.; Britt, R. D.; Smith, A. M.; Fetting, J. C.; Berben, L. A. Delocalization Tunable by Ligand Substitution in [L2Al]: N -Complexes Highlights a Mechanism for Strong Electronic Coupling. *Chem. Sci.* **2021**, *12* (2), 675–682.
- (55) Kurahashi, T.; Fujii, H. One-Electron Oxidation of Electronically Diverse Manganese(III) and Nickel(II) Salen Complexes: Transition from Localized to Delocalized Mixed-Valence Ligand Radicals. *J. Am. Chem. Soc.* **2011**, *133* (21), 8307–8316.
- (56) Boudalis, A. K.; Olivares-Peña, J. E.; Moreno-Pineda, E.; Fediai, A.; Wenzel, W.; Turek, P.; Ruben, M. Room-Temperature Spin Nutations in a Magnetically Condensed Phase of [Y(Pc)2]•. *Chem. Commun.* **2021**, *57* (87), 11505–11508.
- (57) Suryadevara, N.; Boudalis, A. K.; Olivares Peña, J. E.; Moreno-Pineda, E.; Fediai, A.; Wenzel, W.; Turek, P.; Ruben, M. Molecular-Engineered Biradicals Based on the VIII-Phthalocyanine Platform. *J. Am. Chem. Soc.* **2023**, *145* (4), 2461–2472.
- (58) Wysocki, A. L.; Park, K. Nature of Hyperfine Interactions in TbPc2 Single-Molecule Magnets: Multiconfigurational Ab Initio Study. *Inorg. Chem.* **2020**, *59* (5), 2771–2780.
- (59) Pederson, R.; Wysocki, A. L.; Mayhall, N.; Park, K. Multireference Ab Initio Studies of Magnetic Properties of Terbium-Based Single-Molecule Magnets. *J. Phys. Chem. A* **2019**, *123* (32), 6996–7006.
- (60) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. PHI: A Powerful New Program for the Analysis of Anisotropic Monomeric and Exchange-Coupled Polynuclear d- and f-Block Complexes. *J. Comput. Chem.* **2013**, *34* (13), 1164–1175.
- (61) Benelli, C.; Gatteschi, D. Magnetism of Lanthanides in Molecular Materials with Transition-Metal Ions and Organic Radicals. *Chem. Rev.* **2002**, *102* (6), 2369–2387.
- (62) Reta, D.; Chilton, N. F. Uncertainty Estimates for Magnetic Relaxation Times and Magnetic Relaxation Parameters. *Phys. Chem. Chem. Phys.* **2019**, *21* (42), 23567–23575.
- (63) Blackmore, W. J. A.; Gransbury, G. K.; Evans, P.; Kragsskow, J. G. C.; Mills, D. P.; Chilton, N. F. Characterisation of Magnetic Relaxation on Extremely Long Timescales. *Phys. Chem. Chem. Phys.* **2023**, *25* (25), 16735–16744.
- (64) Zhou, A.; Sun, Z.; Sun, L. Stable Organic Radical Qubits and Their Applications in Quantum Information Science. *Innovation* **2024**, *5* (5), 100662.
- (65) Komeda, J.; Boudalis, A. K.; Montenegro-Pohlhammer, N.; Anthaume, C.; Mizuno, A.; Turek, P.; Ruben, M. Selective Transition Enhancement in a G-Engineered Diradical. *Chem. -Eur. J.* **2024**, *30* (42), 202400420.
- (66) Moreno-Pineda, E.; Klyatskaya, S.; Du, P.; Damjanović, M.; Taran, G.; Wernsdorfer, W.; Ruben, M. Observation of Cooperative Electronic Quantum Tunneling: Increasing Accessible Nuclear States in a Molecular Qudit. *Inorg. Chem.* **2018**, *57* (16), 9873–9879.
- (67) Katoh, K.; Aizawa, Y.; Morita, T.; Breedlove, B. K.; Yamashita, M. Elucidation of Dual Magnetic Relaxation Processes in Dinuclear Dysprosium(III) Phthalocyaninato Triple-Decker Single-Molecule Magnets Depending on the Octacoordination Geometry. *Chem. -Eur. J.* **2017**, *23* (61), 15377–15386.
- (68) Gürek, A. G.; Basova, T.; Luneau, D.; Lebrun, C.; Kol'tsov, E.; Hassan, A. K.; Ahsen, V. Synthesis Structure, and Spectroscopic and Magnetic Properties of Mesomorphic Octakis (Hexylthio) -Substituted Phthalocyanine Rare-Earth Metal Sandwich Complexes. *Inorg. Chem.* **2006**, *45* (4), 1667–1676.
- (69) Yoshihara, D.; Karasawa, S.; Koga, N. Cyclic Single-Molecule Magnet in Heterospin System. *J. Am. Chem. Soc.* **2008**, *130* (32), 10460–10461.

- (70) Yoshihara, D.; Karasawa, S.; Koga, N. Heterospin Single-Molecule Magnets with Extra-Large Anisotropic Barrier. *Polyhedron* **2011**, *30* (18), 3211–3217.
- (71) Jeon, I. -R.; Park, J. G.; Xiao, D. J.; Harris, T. D. An Azophenine Radical-Bridged Fe₂ Single-Molecule Magnet with Record Magnetic Exchange Coupling. *J. Am. Chem. Soc.* **2013**, *135* (45), 16845–16848.
- (72) Fortier, S.; Le Roy, J. J.; Chen, C. H.; Vieru, V.; Murugesu, M.; Chibotaru, L. F.; Mindiola, D. J.; Caulton, K. G. A Dinuclear Cobalt Complex Featuring Unprecedented Anodic and Cathodic Redox Switches for Single-Molecule Magnet Activity. *J. Am. Chem. Soc.* **2013**, *135* (39), 14670–14678.
- (73) Zhang, P.; Perfetti, M.; Kern, M.; Hallmen, P. P.; Ungur, L.; Lenz, S.; Ringenberg, M. R.; Frey, W.; Stoll, H.; Rauhut, G.; et al. Exchange Coupling and Single Molecule Magnetism in Redox-Active Tetraoxolene-Bridged Dilanthanide Complexes. *Chem. Sci.* **2018**, *9* (5), 1221–1230.
- (74) Reed, W. R.; Dunstan, M. A.; Gable, R. W.; Phonsri, W.; Murray, K. S.; Mole, R. A.; Boskovic, C. Tetraoxolene-Bridged Rare-Earth Complexes: A Radical-Bridged Dinuclear Dy Single-Molecule Magnet. *Dalt. Trans.* **2019**, *48* (41), 15635–15645.
- (75) Ishikawa, N.; Sugita, M.; Tanaka, N.; Ishikawa, T.; Koshihara, S. Y.; Kaizu, Y. Upward Temperature Shift of the Intrinsic Phase Lag of the Magnetization of Bis(Phthalocyaninato)Terbium by Ligand Oxidation Creating an $S = 1/2$ Spin. *Inorg. Chem.* **2004**, *43* (18), 5498–5500.
- (76) Gonidec, M.; Davies, E. S.; McMaster, J.; Amabilino, D. B.; Veciana, J. Probing the Magnetic Properties of Three Interconvertible Redox States of a Single-Molecule Magnet with Magnetic Circular Dichroism Spectroscopy. *J. Am. Chem. Soc.* **2010**, *132* (6), 1756–1757.
- (77) Gonidec, M.; Krivokapic, I.; Vidal-Gancedo, J.; Davies, E. S.; McMaster, J.; Gorun, S. M.; Veciana, J. Highly Reduced Double-Decker Single-Molecule Magnets Exhibiting Slow Magnetic Relaxation. *Inorg. Chem.* **2013**, *52* (8), 4464–4471.