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Amplification of Lanthanide *f*-Orbital Differences by Redox-Non-Innocent Semiquinone Binding

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Abstract. A deeper understanding of the electronic structure of the lanthanides (Ln) is essential to harness their technological applications and enable responsible recovery/separation. Here, an isostructural series of tris(3,5-dimethyl-1-pyrazolyl)borate (Tp*)-supported Ln^{III} adducts of a redox non-innocent 3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ) ligand, (Tp*)₂Ln(DTBSQ), is characterized experimentally and computationally for all the early lanthanides La-Gd, except Pm. Computational simulations, together with spectroscopic measurements on selected systems, show the metals retain the trivalent oxidation state despite semiquinone binding with weak metal–radical coupling. While Ln^{III}-DTBSQ bond distances decrease with decreasing Ln^{III} ionic radii, theory suggests increased 4*f* -orbital mixing driven by the energetic accessibility of the *f* -shell with significant radical contributions to the bonding occur for Sm/Eu. Orbital analyses and multireference calculations confirm these effects originate from metal-ligand orbital energy matching rather than through-space overlap. The Ln^{III} 4*f* interactions are more covalent with the radical ligand than the Tp*, showing remarkably low 6*s* character. This contrasts with other common ligand-Ln studies and suggests that the DTBSQ-based orbitals have the appropriate symmetry and energy to preferentially interact with the 4*f* orbitals over the 6*s* orbital. This work provides new insights into Ln-radical interactions, revealing bonding characteristics for potential selective *f*-element chelators and extension into actinide chemistry.

Introduction

The electronic structure and chemical bonding of *f*-block complexes is one of the least understood areas of chemistry despite the critical importance of rare earth (RE) elements in modern technologies. The high technological value of the RE ions is due to their unique and tunable

magnetic and electronic properties,¹⁻³ driven by the availability of *f*-electrons in both molecules,⁴⁻⁶ and materials.^{7,8} Despite the ubiquity and criticality of various lanthanide (Ln) ions for modern applications, Ln separations remain environmentally costly and energetically intensive due to the need to selectively differentiate between neighboring Ln^{III} ions featuring relatively similar chemical bonding properties. Descriptions of such metal-ligand bonding in Ln complexes are typically simplified to models that are purely electrostatic in nature due to the core-like nature of the 4*f* orbitals in comparison to the more diffuse 5*d* shell. However, evidence shows observable levels of covalent mixing and notable electronic structure changes of 4*f* ions in various ligand fields.⁹⁻¹¹ With specific ligand frameworks, the energetic alignment between Ln^{III} and ligand orbitals can be fine-tuned for individual lanthanides. This enables precise control and a deeper understanding of the electronic structures that produce the most desirable properties. Additionally, selectively strengthening a particular lanthanide-ligand bond offers opportunities for targeted element separations by amplifying the subtle differences in the chemical bonding properties of neighboring Ln^{III} ions. Sets of molecules that exhibit interpretable trends can provide important insight into covalency, particularly for Ln species for which covalency differences between individual Ln complexes are relatively small.

Metal-ligand covalency is commonly explained by two main factors: orbital spatial overlap and the relative energy of the participating orbitals (**Figure 1**). Strong spatial overlap and a small energy difference between metal-ligand orbitals contribute to higher levels of covalency (**Figure 1**, left). For Ln species, for which the 4*f* orbitals are contracted and spatial overlap subsequently limited, Ln-L covalency can then be enhanced by minimizing the metal-ligand orbital energy difference in a Hubbard-type interaction.¹² The Hubbard model provides a simplified way to capture

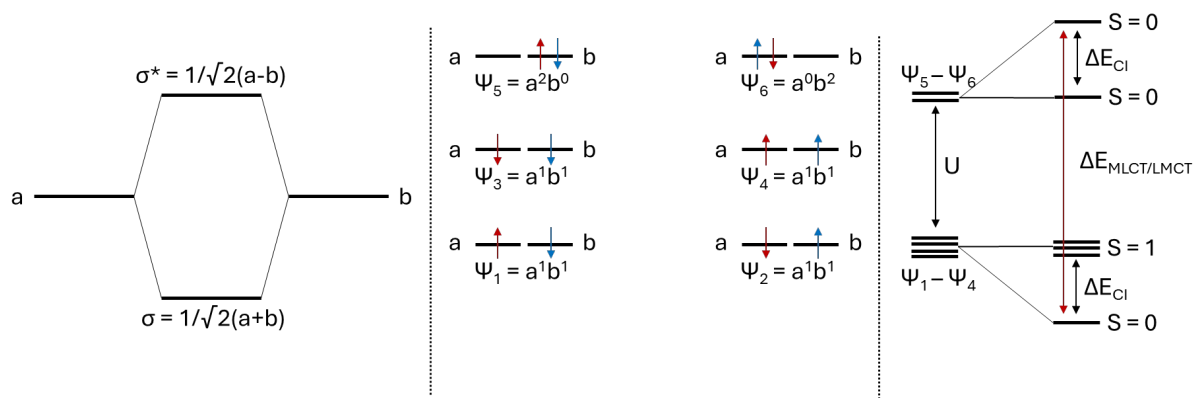


Figure 1. Depiction of the classical spatial overlap-driven, affording bonding (σ) and antibonding (σ^*) states (left) vs Hubbard type energy-driven descriptions of covalency (right) for mixing of states (center). U is the energy of the charge transfer state in the absence of interaction between the $4f$ and ligand orbitals, $\Delta E_{MLCT/LMCT}$ is the energy of the charge transfer state with M-L interactions, while ΔE_{CI} is the energetic stabilization afforded from configuration interaction

the basic transition between conducting and insulating electron behavior, by describing the competition between an electron's ability to traverse between different sites versus the repulsive

interactions of residing in the same orbital. Here, the similar energies of the metal and ligand frontier orbitals give rise to different electronic states that can mix, (**Figure 1**, center), resulting in multiconfigurational ground states (**Figure 1**, right). This multiconfigurational ground state is energetically stabilized from the configurational interaction with an MLCT/LMCT state, where the energy of the charge transfer state in the absence of interaction between the $4f$ and ligand orbitals, U , can be minimized to maximize this energetic stabilization, ΔE_{CI} . Such a model has been used to explain phenomena like metal-insulator transitions and magnetism, and applied to single-molecule systems for various purposes,¹³ quantitatively evaluating exchange coupling in $\text{Cp}^*_2\text{Yb}(\text{bipy})$,¹⁴ and elucidating the strong spin coupling observed in lanthanide-based single-molecule magnets (SMMs).¹⁴ In the latter case, the model has effectively described the interaction of lanthanide spins mediated by bridging N_2^{3-} radical ligands.

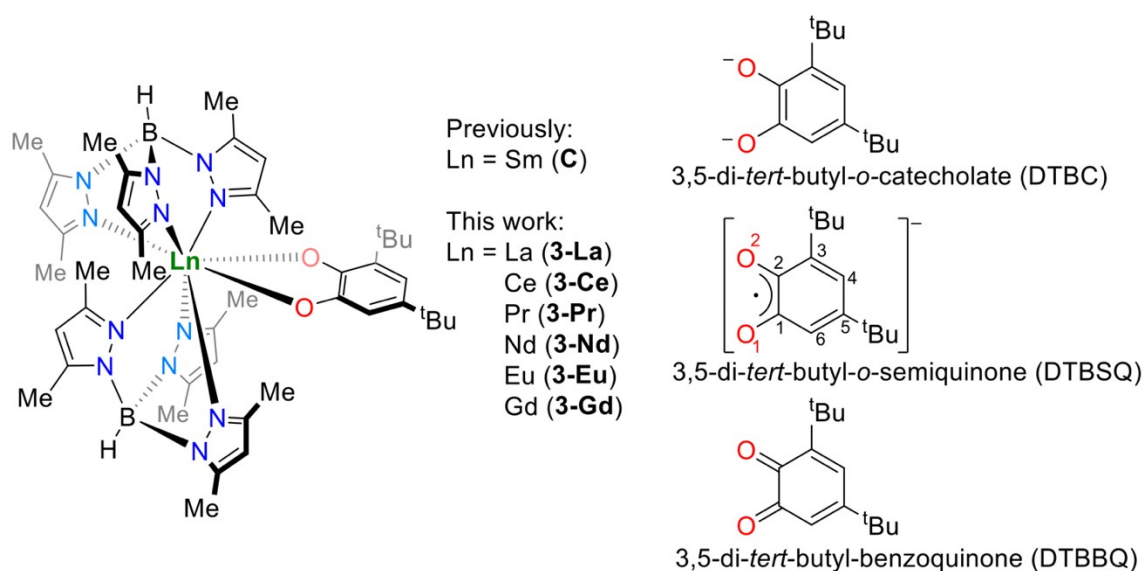


Figure 2. $(\text{Tp}^*)_2\text{Ln}(\text{DTBSQ})$ complexes made and studied here (left) and the reduction (upper right) and oxidation (lower right) products of the semiquinone radical, DTBSQ (shown as the anion middle right, with the numbering scheme).

Redox-active ligands both enable metals to maintain their thermodynamically preferred oxidation state, and in complexes where the metal ion is coordinated to redox-active ligands with similar orbital energies, can provide valuable information on covalency and yield interesting electronic and magnetic properties, along with tunable catalysis.^{15–18} Among radical ligands, the 3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ), **Figure 2**, is particularly attractive due to its redox activity that provides access to three different oxidation states between its reduced (3,5-di-*tert*-butyl-*o*-catecholate (DTBC)) and oxidized (3,5-di-*tert*-butyl-benzoquinone (DTBBQ)) forms (**Figure 2**, right), for which the redox potentials are well-matched with Ln^{III} species, such as Ce^{III} and Eu^{III} (see details in the SI, section 2). It has been used to induce unique electronic properties, such as combined conductivity and magnetism, in low oxidation state *d*-block complexes arising from the distinctive metal-ligand radical interactions.^{19–26} Similarly, the divalent $\text{Sm}^{\text{II}}(\text{Tp}^*)_2$ reduces 3,5-di-*tert*-butyl-benzoquinone, DTBBQ in **Figure 2**, to yield the Sm^{III} adduct of the semiquinone

organic radical complex $\text{Sm}^{\text{III}}(\text{Tp}^*)_2(\text{DTBSQ})$ (**C**,²³ also referred to below as **3-Sm** for simplicity as we include it in this study) through formal one-electron reduction of the organic ligand, highlighting the non-innocent nature of this ligand. $[\text{Tp}^*]^-$ is the monoanionic, methylated tris(pyrazolyl)borate anion $[\text{HB}(\text{C}_3\text{N}_2\text{HMe}_2)_3]^-$, a bulky redox-innocent supporting ligand often used in place of isoelectronic alkylated cyclopentadienyl ligands due to its steric bulk and redox stability.²⁴ Elsewhere, the rare earth metal-semiquinone motif has been isolated for heavier Ln, synthesized *via* a one-pot reaction through the addition of KOH to a mixture of either isolated or *in situ* generated $\text{Tp}_2\text{Ln}^{\text{III}}\text{X}$ (Ln = Eu, Gd, Tb, Dy, Ho, Yb; X = $[\text{NO}_3]^-$, $[\text{C}_6\text{H}_5\text{CO}_2]^-$) and H_2DTBC (Tp = tris(pyrazolyl)borate), with the Gd complex showing unusually strong antiferromagnetic coupling with the radical ligand.^{25–27}

Harnessing the resulting differences in donor strength of the semiquinone ligands could offer alternative strategies for lanthanide separations,^{28,29} yet early Ln-semiquinone complexes whose covalency can be studied have yet to be reported. The early Ln complexes are of particular interest since they possess a more radially extended and energetically accessible 4*f* shell compared to the later series, which should show an even greater ability to engage in covalent interactions. In both cerium and praseodymium oxides, the 4*f* orbitals interact covalently with the ligand 2*p* orbitals, as evidenced by pre-edge features in the O K-edge XANES spectra of LnO_2 .³⁰ It was proposed that this covalency is due to a Hubbard-type energetic match rather than spatial overlap. We hypothesized that such a match can be improved by utilizing redox-active ligands such as DTBSQ that both stabilizes the Ln center in its preferred oxidation state while also resulting in enhanced covalent bonding.

Here, we use the salt elimination reaction between Ln^{III} salts and the radical anion of the semiquinone as a straightforward route to all the early Ln-semiquinone complexes except Pm, which have a variety of accessible charge transfer states. We have characterized their bonding and electronic structure through single crystal X-ray diffraction, SQUID magnetometry, NMR, EPR, IR, and UV-visible-NIR spectroscopies in addition to a thorough computational investigation, including density functional theory (DFT) and multireference modeling to fully characterize the identified multiconfigurational ground states. These studies show the early Ln-DTBSQ bonding cannot be described by a pure electrostatic model; the primary factor dictating the Ln-DTBSQ bonding differences is the relative $4f$ orbital stabilization, with heightened levels of bonding interaction observed for Sm^{III} , and Eu^{III} systems. Notably, while predominantly ionic in nature, the Ln-DTBSQ bond exhibits unusual bonding characteristics that challenge conventional understanding. These findings not only deepen our comprehension of Ln-radical systems but also highlight their potential to inspire novel approaches towards rare earth ion separations, and discoveries in actinide chemistry.

Results and Discussion

Complex synthesis and characterization

Complexes **3-Ln** are isolated through either a salt elimination or redox route depending on the redox activity of the Ln^{3+} ion (**Scheme 1**). A salt elimination route between $\text{Ln}^{\text{III}} (\text{Tp}^*)_2\text{LnI}$ (**1-Ln**), made *in situ*, and the independently isolated potassium salt of 3,5-di-*tert*-butyl-*o*-semiquinone, $\text{K}[\text{C}_6\text{H}_2'\text{Bu}_2\text{O}_2]$ which is an organic radical ($\text{K}[\text{DTBSQ}]$, **2**), provides the most convenient access to $(\text{Tp}^*)_2\text{Ln}(\text{DTBSQ})$ **3-Ln** ($\text{Ln} = \text{La-Nd, Gd}$, **Scheme 1**). A redox reaction

between *in situ* generated $\text{Ln}^{\text{II}}(\text{Tp}^*)_2$ and 3,5-di-*tert*-butyl-*o*-quinone was found to be ideal for isolating **3-Eu** and the Sm complex **3-Sm** (**C**). As found computationally below, the easily accessible $\text{Eu}^{3+/2+}$ and $\text{Sm}^{3+/2+}$ redox couples (-1.55 for Sm and -0.35 V for Eu vs NHE)³¹ impact the electronic structure and bonding of the complexes. Experimentally, this translates to the need for a slight excess of oxidant in the redox reaction route to enable isolation of the complexes. Meanwhile, the salt metathesis route to **3-Eu** or **3-Sm** (**C**) yields a mixture of complexes, likely owing to reduction of the Ln^{III} center. The radical K[DTBSQ] **2** was made from the redox reaction of 3,5-di-*tert*-butyl-*o*-catechol (H_2DTBC) and 3,5-di-*tert*-butyl-benzoquinone (DTBBQ) in the presence of KOH and has no visible resonances in the ^1H NMR spectrum, confirming the lack of any residual catechol or quinone. Complexes **3-Ln** can be isolated as green solids after work-up from hexane in

moderate yields regardless of the synthetic route and have been fully characterized by a variety of methods, including single crystal X-ray diffraction, SQUID magnetometry, NMR, EPR, UV-vis-NIR, and IR spectroscopies (**Figure S1 - S27**). While the complexes were isolable in bulk for **3-La** through **3-Pr** and **3-Gd** from the salt metathesis route and for **3-Sm/3-Eu** through the redox route, we were unable to isolate **3-Nd** pure in bulk form. We can isolate single crystals of **3-Nd**, but the bulk material always contains unidentifiable impurities with the same solubility properties. Similarly to **2**, there are no observable resonances for the DTBSQ ligand in the NMR spectra of **3-La** and **3-Gd** due to the expectedly rapid nuclear spin relaxation for formally $4f^0/4f^7$ -organic radical systems. All the other **3-Ln** show paramagnetically shifted, assignable resonances.

Importantly, the set of six isolated **3-Ln** complexes provide sequential accessibility to the $4f$ shell, which, depending on the energetics of the involved orbitals, can enhance the bonding interactions and give rise to accessible low-lying charge transfer states.

Spectroscopic studies

The ^1H NMR spectra of the complexes were obtained (**Figure S1, S5, S11, S22, S25**, see SI). The spectra for **3-La** and **3-Gd** show that the proton resonances for the DTBSQ radical are NMR-silent, consistent with the expectation of a rapid spin relaxation across the molecule's formally $4f^{0/7}$ -organic radical electron configuration of **3-La** and **3-Gd** respectively. Additionally, while the proton resonances for the Tp^* ligand are observable and non-paramagnetically shifted for **3-La**, consistent with the formally $4f^0$ La^{III} center, these resonances are absent in the ^1H NMR spectrum of **3-Gd**, similarly consistent with the formally $4f^7$ Gd^{III} center. In contrast, the ^1H NMR spectrum of a C_6D_6 solution of **3-Ce** shows paramagnetically shifted resonances, suggestive of a

Ce^{III}, 4f¹-trapped organic radical analogous to **3-Sm (C)**²³ and is consistent with computational results. The ¹H NMR spectra of **3-Pr** and **3-Eu** solutions show paramagnetically shifted resonances similar to **3-Sm (C)**. While 24 resonances were still observed for **3-Eu**, the strongly paramagnetically formally 4f⁶ Eu^{III} center was found to impact the spin relaxation of the proton signals enough to significantly affect the observed integration of the resonances (**Figure S22**).

EPR spectra were measured for toluene solutions of **3-La** and **3-Ce**. The solution EPR spectrum (**Figure 3a**) for **3-La** at 270 K shows a multiline signal with the isotropic *g* value of 2.00502, most likely arising from the organic semiquinone radical on the DTBSQ. The spectrum is well-simulated using hyperfine couplings to two magnetic nuclei, ¹H (*I* = 1/2) and ¹³⁹La (99.91%, *I* = 7/2), with *A*_{iso} (¹H) = 9.29 MHz (or 3.31 gauss) and *A*_{iso} (¹³⁹La) = 8.59 MHz (or 3.06 gauss), respectively. The similar hyperfine couplings of ¹H and ¹³⁹La together give rise to the 9-line pattern. The ¹H hyperfine coupling is assigned as due to coupling to the 4-H proton of the DTBSQ as it is similar to that reported in a previous EPR study of Li(DTBSQ),³² confirming the ligand-based nature of this paramagnetic species. The hyperfine coupling of 4-H is further validated by ¹H ENDOR spectroscopy (**Figure 3b**). The dipolar ¹H hyperfine coupling (−[16.1, 1.1, 10.7] MHz, *A*_{iso} = 9.3 MHz) of the in-plane 4-H originates from a spin polarization mechanism, with C4 (**Figure 4**) being the most spin-bearing carbon. Splittings due to 6-H are not observed in the solution EPR spectrum, but its hyperfine coupling (*A* = [7.2, 4.0, 5.4] MHz, *A*_{iso} = 5.5 MHz) is also resolved in the ENDOR spectrum. The presence of a small ¹³⁹La hyperfine coupling is consistent with the close proximity of DTBSQ to the formally diamagnetic La^{III} center. In contrast, the EPR spectrum for **3-Ce** is featureless at 15 K (**Figure S6**). In combination with the paramagnetically shifted resonances in the ¹H NMR spectrum, a first approximation of the ground state electronic structure is thus a

singlet or triplet state containing the $\text{Ce}^{\text{III}} 4f^1$ electron and the DTBSQ electron. Computationally, **3-Ce**, along with all other f^n **3-Ln**, possesses a multiconfigurational ground state. In the case of **3-Ce**, it is dominated (98%) by triplet character with minor contributions (2%) from excited singlet configurations. These triplet and singlet configurations correspond to states where the $f^1 \text{Ce}^{\text{III}}$ center is ferromagnetically or antiferromagnetically coupled with the DTBSQ radical, respectively. Ce^{III} is the Ln^{III} most susceptible to oxidation to Ln^{IV} as this achieves the group oxidation state. However, here it is isolated as a Ce^{III} -DTBSQ and not a Ce^{IV} -DTBC complex, suggesting that all the other **3-**

Ln (which all have less accessible $\text{Ln}^{\text{IV/III}}$ redox couples) will favor a Ln^{III} -organic radical ground state. Eu^{III} is the most susceptible to reduction, as Eu^{II} achieves the half-full f^7 shell. Pleasingly here, it is isolated as predominantly Eu^{III} -DTBSQ rather than the Ln^{II} -DTBBQ complex, although the isolation is complicated due to the instability of the +3 oxidation state with this ligand set. The solid-state structures and computational studies below confirm these assignments.

Solid state structures

Complexes **3-Ln** are isostructural in the solid state (section 4 in SI) according to single crystal X-ray diffraction studies, similar to the previously reported structure for **3-Sm** (C). The

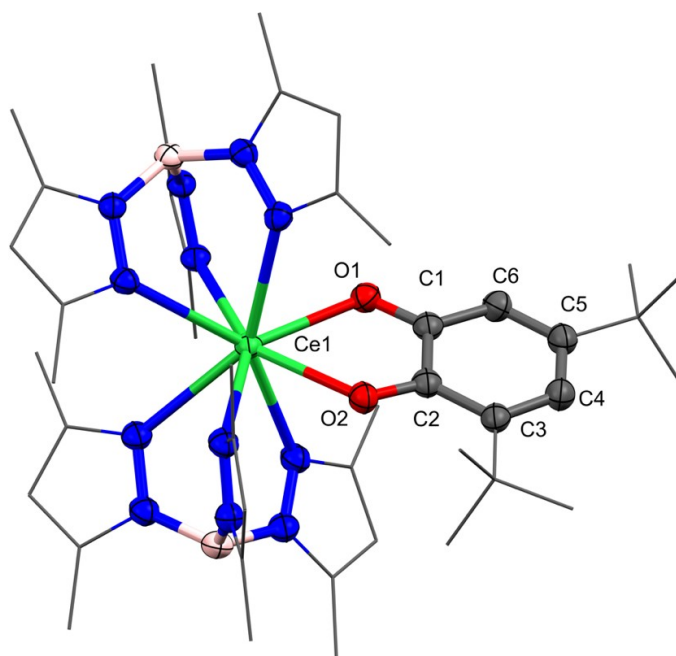


Figure 4. Solid state structure of **3-Ce**. Displacement ellipsoids for selected atoms set at 50%; other peripheral atoms drawn as wireframe; H atoms and lattice solvent omitted for clarity. C = grey, Ce = green, N = blue, B = pink, O = red.

structure of **3-Ce** is shown in **Figure 4**. All complexes crystallize in the $P\bar{1}$ space group and show an 8-coordinate Ln center, with two distinct Ln-O bonds to the DTBSQ and six distinct Ln-N bonds to the two Tp^* ligands. All complexes were found to crystallize with a lattice solvent, similar to the

previously observed structure for **3-Sm** (**C**), with the only difference here being that all structures were found to crystallize with a hexane molecule except for **3-Nd**, which was found to crystallize with a toluene molecule. The data show, as expected, increasingly shorter Ln-N and Ln-O bonds with increasing Ln atomic number and thus charge density; selected data for **3-La** to **3-Gd** are in **Table 1** and the optimized structural parameters are listed in **Table S3** (*vide infra*). The average Ln-N bond length decreases from 2.662(4) Å in **3-La** to 2.5662(5) Å in **3-Gd**. There are two different Ln-O and C-O bonds in each structure (see atom numbering in **Figure 2** and **Figure 4**). Both Ln-O1 and Ln-O2 lengths decrease from 2.453(3) Å and 2.502(3) Å for **3-La** to 2.371(5) Å and 2.403(4) Å for **3-Gd**, respectively. The two different C-O bond distances in all complexes are consistent with a semiquinone structure, by comparison with the C-O bond lengths of 1.301(4) and 1.244(4) Å in Na₄[DTBSQ]₄(THF)₄.³³ In contrast, H₂DTBC, which has two crystallographically distinct molecules in the asymmetric unit, has C-O bond lengths of 1.3805(15)/1.3827(15) and 1.4002(15)/1.3891(14) Å,³⁴ while DTBBQ has C-O bond lengths of 1.224(5) and 1.219(5) Å.³⁵ The

C1-O1 bond lengths in all **3-Ln** are in the range C1-O1 = 1.281(4)-1.290(7) Å, intermediate between the bond lengths observed for the Na semiquinone Na₄[DTBSQ]₄(THF)₄ and the free DTBBQ but significantly closer to the values for the Na semiquinone. Additionally, the C2-O2 bond distances are in the range C2-O2 = 1.267(10)-1.288(8) Å, intermediate between the Na semiquinone and the free H₂DTBC. That one C-O bond measure (C1-O1) is intermediate between the radical and its oxidized form for all **3-Ln** complexes while the other (C2-O2) is intermediate between the radical and its reduced form is further consistent with an overall semiquinone assignment, in line with our computational analysis showing the electronic structures of these complexes retain organic radical character.

The bulkier Tp* ligand also significantly impacts the structure compared to the non-methylated Tp ligand, for which Eu^{III} and Gd^{III} solid-state structures (Tp)₂Ln(DTBSQ) have been reported.^{25,26} For both, the methylated structures show Ln-O bond lengths greater than 0.015 Å longer than the non-methylated analogues, while the average Ln-N bond length is > 0.02 Å longer. The B-Ln-B angle is also significantly increased from less than 140° in the non-methylated complexes compared to almost 150° for the methylated complexes.

SQUID Magnetometry

The experimental temperature dependence of the χT product for **3-Pr** measured in the range 2–300 K under an applied magnetic field of 1 kOe is reported in **Figure 5**. The χT room temperature value is equal to 1.50 cm³ K mol⁻¹. This value is lower than the theoretically expected value for an isolated Pr^{III} ion plus a radical (1.6 + 0.375 = 1.975 cm³ K mol⁻¹). This situation resembles what has already been reported for other lanthanide ion-radical systems^{36,37} and can be

ascribed to the crystal field splitting effect.³⁸ Upon cooling down at 2 K, the χT value decreases to 0.21 cm³ K mol⁻¹. Such deviation from the Curie's law can be attributed to the thermal depopulation of the M_J states and/or the presence of antiferromagnetic interactions between the Pr^{III} ion and the DTBSQ radical. Differently, the temperature dependence of χT for **3-La** shows a nearly constant value in agreement with the presence of one unpaired electron from the DTBSQ radical ligand (**Figure S31**). The hypothesis of antiferromagnetic coupling in **3-Pr** is supported by the field dependence of the magnetization curves showed in **Figure 5a** and **Figure S30**. The M vs H plots never saturate, reaching a value equal to 0.85 μ_B under a magnetic field of 7 T at a temperature of 2 K. This value is lower than the value of 1 μ_B expected for an isolated radical. In contrast, the M vs H plot for **3-La** closely matches the behavior expected for a single isolated unpaired electron (**Figure S31**).

Computational analysis of electronic structures

The experimental structures of the **3-Ln** complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) were optimized assuming two scenarios (**Figure S32**): ferromagnetic coupling between radical electron and metal 4*f* electrons (high-spin, **Figure S32a**), and anti-ferromagnetic coupling, where the spin of the radical electron was flipped (low-spin, **Figure S32b**). The high-spin configuration is found to be slightly more energetically favorable (0.69-6.68 kcal/mol) for all the complexes but **3-Gd** (**Table 2**). The complexes **3-Ce**, **3-Pr**, **3-Nd**, and **3-Sm** exhibit weak coupling between the metal center and the radical ligand, a result consistently confirmed by calculations using alternative functionals (**Table S2**). In contrast, **3-Eu** shows stronger coupling (*vide infra*). In **3-Gd** although the energetic difference between the two spin configurations is too small to derive meaningful conclusions, the low-spin configuration is consistent with a previous observation of an antiferromagnetic coupling between the 7/2 and 1/2 spins of the Gd center and radical, respectively.²⁵ Notably, in **3-Ce**—unlike in the other systems—the antiferromagnetic configuration yields two distinct singlet solutions,

Table 2. Lanthanide and radical spin densities, along with the HS-LS energy difference calculated for the **3-Ln** systems. For each lanthanide, the formal *f*-electron count is indicated in the second column. In the radical, the expected spin density value is 1, which corresponds to one unpaired electron.

restricted and unrestricted, both of which must be considered (**Figure S32b**). Detailed analysis (see Computational Details, SI) reveals that while the lower energy of the two corresponds to the unrestricted broken-symmetry singlet Ce^{III}-DTBSQ state, the ferromagnetically-coupled triplet state—differing only by a spin flip at the radical ligand—is the lowest-energy configuration by approximately 1.03 kcal/mol (**Table 2**). This relatively small energy difference is suggestive of overall weak Ce-radical coupling. In contrast, the restricted singlet solution, corresponding to a formal Ce(IV)-DTBC species, lies significantly higher in energy (~9 kcal/mol).

To ensure consistency in the theoretical analysis, the electronic structure, bonding, and spectroscopy studies were performed using the high-spin structures for **3-Ce**, **3-Pr**, **3-Nd**, **3-Sm**, and **3-Eu**, while for **3-Gd**, the low-spin was used instead. The optimized structures show good agreement with the experimental data, where the average Ln-O and Ln-N bond lengths were predicted with errors of less than 1.5%, in the range of 0.01 and 0.04 Å (**Table S3**). Since the first

part of the lanthanide series is being analyzed, trends in terms of averaged M-O and M-N bond lengths were explored. As observed in **Figure S35**, a good correlation between the bond distances and the 8-coordinate Shannon radii³⁹ was observed, where, similarly to the experimental structures, the expected decrease in bond distances is consistent with the well-known lanthanide contraction.

Ground State Electronic Structure and Bonding Analysis

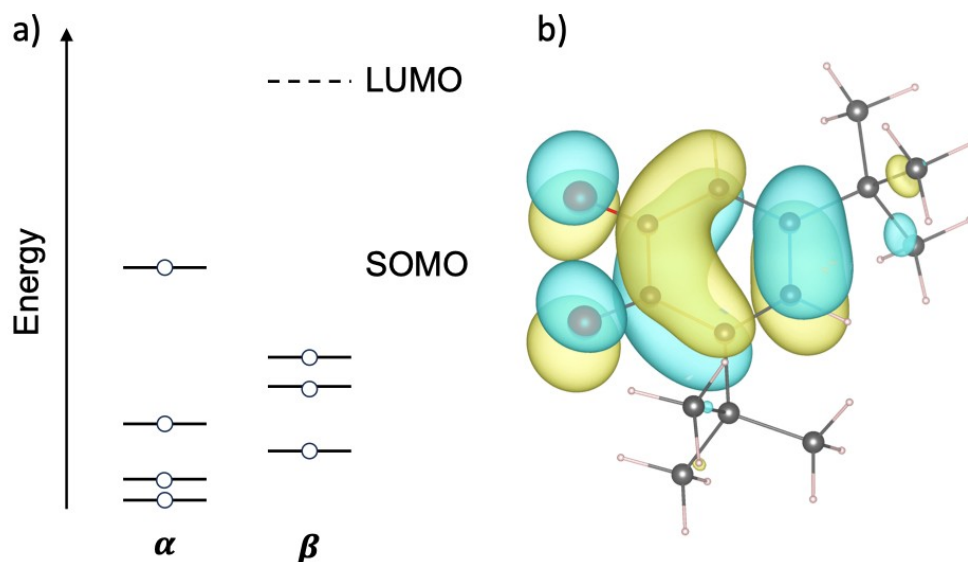


Figure 6. a) Qualitative representation of the frontier molecular orbitals of the DTBSQ radical, where white circles represent electrons. Occupied and empty orbitals are represented through solid and dashed lines, respectively. SOMO = single occupied molecular orbital and LUMO = lowest unoccupied molecular orbital. (b) Depiction of the α -SOMO. Isovalue=0.03. Grey=C, red=O, white=H.

The DFT analysis of the ground states of the complexes confirms the formulation of a Ln^{III} –trapped organic radical system, accompanied by a ferromagnetic arrangement between the Ln and radical electrons energetically favored by <2 kcal/mol for all but **3-Eu**. This scenario is further corroborated by spin-orbit CASSCF/MC-pDFT calculations, which also reveal a multiconfigurational nature of the ground states, primarily driven by the static correlation inherent to the 4f -shell. One notable aspect is that the DTBSQ radical has both the singly occupied molecular orbital (SOMO) and its unoccupied counterpart (down spin-state) displaying similar spatial functions but different energies (**Figure 6a**). This energetic splitting is rationalized due to the differential stabilization of the occupied α -spin component with respect to the β -spin, as discussed for radical species by Kasemthaveechok *et al.* in 2022.⁴⁰ As observed in **Figure 6b**, the unpaired electron is mainly delocalized among the π orbitals perpendicular to the aromatic ring and the oxygen atoms. As mentioned, upon lanthanide coordination, the radical-based SOMO is

maintained for all the systems except for **3-Ce**, where it displays 4*f* character (**Figure S37**). This is explained due to the energetic stabilization of the 4*f* -shell that occurs as the lanthanide series is traversed, unlike the energy of the 5*d* shell that remains almost unaltered (**Figure 7**). In terms of the canonical orbitals describing the Ln-radical interaction, negligible mixing was found for most of the systems, which suggests a predominantly ionic bond. However, slight deviations are noticed in **3-Sm (C)**, and **3-Eu**, where a favorable energy match between unoccupied metal 4*f*-MOs and radical orbitals originates the interactions depicted in **Figure S38**. This energy degeneracy driven orbital mixing has been observed in other *f*-element systems.^{41–43}

Besides the energetics of the molecular orbitals, the atomic spin densities (α - β electrons) of the metal and the radical ligand, derived from the Mulliken and Natural population analysis, were also analyzed (**Table 2**). Overall, the lanthanide centers have spin densities close to the expected formal value while the radical displays values consistent with one unpaired electron. The largest deviations were observed in the **3-Eu** complex, where the metal center exhibits a spin density of

6.12, slightly surpassing the formal value of 6.0. This was accompanied by a radical spin density of 0.74, lower than the expected value for a single unpaired electron in an isolated organic radical suggesting ligand to metal electron density donation.

Table 3. Composition of the spin-orbit ground states in terms of the most dominant configurations of the contributing spin-free states. To simplify the description of the metal - radical interaction, the main configurations are represented through multiplicities and arrows. The *5d* shell is not included to facilitate the analysis. (*)The ground state is doubly degenerate (Kramers doublet).

System	Ground State Configuration
3-Ce	98% $(\pi^{\uparrow}f^{\uparrow})_{\text{triplet}}$ + 2% $(\pi^{\downarrow}f^{\uparrow})_{\text{singlet}}$
3-Pr*	89% $(\pi^{\uparrow}f^{\uparrow\uparrow})_{\text{quartet}}$ + 11% $(\pi^{\downarrow}f^{\uparrow\uparrow})_{\text{doublet}}$
3-Nd	95% $(\pi^{\uparrow}f^{\uparrow\uparrow\uparrow})_{\text{quintet}}$ + 5% $(\pi^{\downarrow}f^{\uparrow\uparrow\uparrow})_{\text{triplet}}$
3-Sm (C)	87% $(\pi^{\uparrow}f^{\uparrow\uparrow\uparrow\uparrow})_{\text{septet}}$ + 12% $(\pi^{\downarrow}f^{\uparrow\uparrow\uparrow\uparrow})_{\text{quintet}}$ + 1% $(\pi^0f^{\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{septet}}$
3-Eu*	84% $(\pi^{\uparrow}f^{\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{octet}}$ + 13% $(\pi^{\downarrow}f^{\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{sextet}}$ + 3% $(\pi^0f^{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{octet}}$
3-Gd	98% $(\pi^{\uparrow}f^{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{nonet}}$ + 2% $(\pi^{\downarrow}f^{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow})_{\text{septet}}$

Due to the intrinsic degeneracy of the *f* shell combined to the quasi-degeneracy previously observed between both high-spin and low-spin Ln-radical configurations, the spin-orbit RASSCF/MC-pDFT multireference approach was employed to get insight on the nature of the ground states (see Computational Details, SI). Since the redox flexibility provided by the radical allows the Ln centers to be in their preferred oxidation state, the calculations initially assumed a Ln^{III} configuration. To be thorough, all the possible multiplicities originated from the metal-radical interaction were considered for complete validation (**Table S1**). Overall, the **3-Ln** systems display multiconfigurational ground states mainly associated to the static correlation present in the 4*f*-shell. At the spin-free (SF, without spin-orbit coupling) level, the ground state is nearly degenerate with other several low-lying electronic states (**Table S6**). For **3-Ce**, **3-Pr**, **3-Nd**, and **3-Gd**, the ground

state corresponds to the highest spin multiplicity, consistent with a ferromagnetically coupled metal–radical configuration. The next nearly degenerate state, appearing only 38 – 86 cm⁻¹ (0.1 – 1 kcal/mol) higher in energy, has the subsequent lower multiplicity and originates from a spin flip at the radical-centered electron. Similar observations were reported in a previous study on a Ce–bipy•⁻ complex, where analysis of the spin-free triplet states showed that the (f¹π¹) configuration was more stable, but energetically degenerate with singlet states.⁴⁴ This behavior parallels the DFT results, where ferro- and antiferromagnetic coupling between the metal and ligand are essentially isoenergetic, suggesting a weak Ln-radical coupling. In **3-Sm(C)** and **3-Eu**, a similar pattern is observed; however, the energetic gap relative to the next spin state is slightly larger being ~280 cm (~1 kcal/mol) (see **Table S6** for details).

At the spin–orbit level the analysis becomes more intricate, as the resulting states are linear combinations of the spin-free states. To facilitate interpretation, we quantified the SF contributions to the lowest SO state in **Table 3**, although more details are given in **Table S7**. In **3-Ce**, **3-Pr**, **3-Nd** and **3-Gd** the ground states are dominated by the highest multiplicities, triplet, quartet, quintet and nonet, respectively (**Table 3**). For example, in the case of **3-Ce**, the totality of the triplet configurations has one of the electrons in the π radical orbital while the other is in the 4f shell (π¹f⁴), suggesting a ferromagnetic coupling. In **3-Sm (C)** and **3-Eu**, the situation is similar to the one observed in **3-Ce** and **3-Pr** since the ground state is dominated by the highest multiplicity. However, excited states involving the reduction of the metal center contribute approximately 1% and 3% to the ground-state wavefunction of **3-Sm (C)** and **3-Eu**, respectively. This marks a notable difference compared to the other complexes, which can be attributed to the presence of low-lying, empty metal-based orbitals able of accepting electron density from the ligand. These findings are in line

with the accessible $\text{Ln}^{3+}/\text{Ln}^{2+}$ standard reduction potentials for Sm (-1.55 V) and Eu (-0.35 V) vs. NHE, contrasting with those of other lanthanides in the series.³¹ Furthermore, this agrees with the experimental observations, where a slight excess of oxidant was required to stabilize pure complexes in the Ln^{III} state. Similar studies^{45,46} on the Yb(III) complex $(\text{Cp}^*)_2\text{Yb}(\text{bipy})$ (where $\text{Cp}^* = \text{C}_5\text{Me}_5$) have reported analogous observations, noting that the electronic configurations associated with the metal reduction contribute to the ground state. This aligns with the accessible $\text{Yb}^{3+}/\text{Yb}^{2+}$ redox couple, which has a potential of -1.15 V vs NHE. Although smaller, in our case, the contributions of the reduced configurations are enough to reveal a more pronounced metal-radical interaction in Sm and Eu.

The SQUID magnetometry data for **3-Pr** are consistent with weak antiferromagnetic Pr–radical coupling; accordingly, we extended our theoretical analysis to further study the underlying magnetic interactions. To examine how the crystal field affects the lanthanide ions, we considered the anionic **[3-Pr]⁻** and cationic **[3-Pr]⁺** derivatives, in which the DTBSQ ligand is formally closed-shell (DTBC and DTBBQ, respectively; see Computational Details, SI). Spin-orbit CASSCF/NEVPT2 calculations indicate that both the first oxidation and reduction are ligand-centered, thereby providing access to a Pr^{III} reference electronic structure. Within this framework, we computed the crystal-field parameters for Pr^{III} and attempted to reproduce the magnetic data via fitting to an effective spin Hamiltonian.

Although the $\chi T(T)$ and $M(H)$ data are reasonably reproduced using the **[3-Pr]⁺** model with an eight-orbital active space that includes the formally vacant radical orbital (**Figure S41**), the fitting procedure does not provide a satisfactory simultaneous description of both observables. In particular, the χT values are systematically overestimated relative to experiment, precluding a

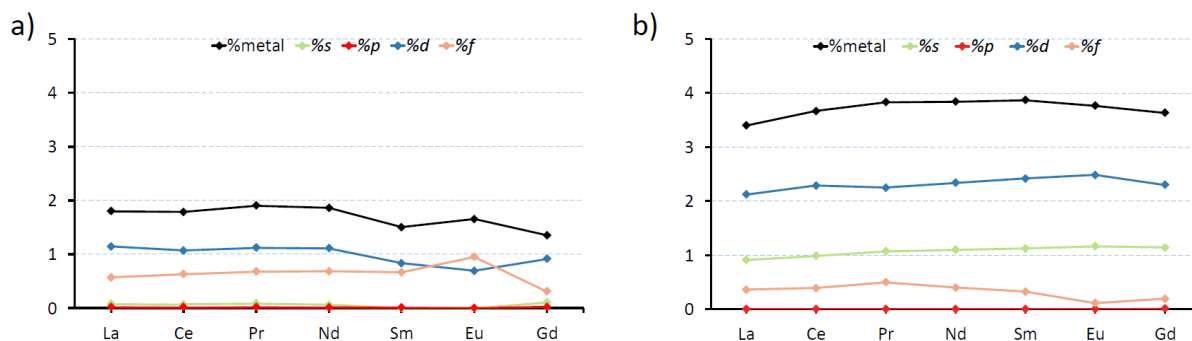


Figure 8. Analysis of NLMOs describing Ln-O (a) and Ln-N (b) interactions in **3-Ln** systems. The black lines indicate the total metal contribution to the bond, which is further decomposed in *s* (light green), *p* (red), *d* (blue) and *f* (orange) contributions.

reliable quantification of the metal–radical coupling. While these discrepancies may, in part, arise from limitations in the description of the crystal-field parameters and/or the treatment of dynamic correlation effects, it is important to note that similar issues have been reported in other Ln-radical^{14,44,47} and related systems.^{48,49} A more rigorous treatment of these effects warrants further investigation but lies beyond the scope of the present study.

Bonding analysis

To analyze the lanthanide-ligand (Ln-L) interactions, the natural bond orbital (NBO) program version 7.0 was employed.⁵⁰ This tool transforms a given density into a localized form, corresponding to the one-center (or “lone-pair”) and two-center (or “bond”) patterns of the Lewis structure picture. The molecular orbitals were visualized by using the software VESTA 3.5.8.⁵¹ The chemical bond was analyzed through the natural localized molecular orbital (NLMO) representation, where both metal and ligand participations were quantified and further decomposed in atomic (*s*, *p*, *d*, *f*) orbital contributions. The Ln-radical bond involves a couple of non-equidistant Ln-O interactions that are mainly described through σ , π , and lone pair orbitals (**Figure S42**),

which are slightly distorted in the longer Ln-O bond. Since the lone pairs displayed an almost negligible orbital mixing, they are not considered in the analysis unless stated otherwise. The metal involvement ranges between ~1% and 2% yielding orbitals heavily dominated by the DTBSQ radical. Overall, this suggests that the nature of these interactions is predominantly ionic with a small degree of ligand to metal donation.^{52–56} The metal participation in bonding is mainly driven by the contributions of the *4f*, *5d*, and *6s* orbitals. While the Ln-L interaction is typically dominated by electron donation from the *5d* and *6s* orbitals, the *4f* orbitals, despite being more radially contracted, can still participate in bonding if the symmetry and energy of the coordinating ligand orbitals are compatible. Additionally, although the *6s* orbital is more spatially extended than the *5d* orbitals, it is not always energetically accessible, which depending on the ligand framework, restricts its involvement in the bond. In this case, the small metal contribution is primarily derived from electrons in the *d* orbitals with contributions ranging from 0.9% to 1.2%. The exception to this behavior is seen in **3-Eu**, where the *4f* involvement is larger than that of the *5d*. This was rationalized based on the Eu *4f*⁶ ground state configuration, which is prone to be reduced to reach *4f*⁷ configuration, a more stable half-filled state. This leads to an increased ligand to *4f* shell donation and the contribution of this reduced configuration to its multiconfigurational ground state composition (**Table 3**). Previous reports on different isoelectronic *f*⁶ systems have also seen the same behavior.^{55,57–59} Interestingly, there is no *6s* involvement in the Ln-O interaction. Instead, the *4f* contribution, though small, dominates in all the **3-Ln** complexes. This is not common considering previous studies that investigated the bonding between lanthanides and chalcogen,⁶⁰ cyclopentadienyl,⁵⁴ carbenes,^{61,62} among other ligands,⁶³ where the *6s* involvement prevailed. So far, these observations suggest that the DTBSQ-based orbitals have the appropriate symmetry and

energy to preferentially interact with the $4f$ orbitals over the $6s$ orbital. We note that this is likely to become even more important when extrapolating to actinide complexes.

The Ln-Tp* interaction is described by three σ Ln-N bonds per ligand which are similar in terms of polarization and composition. The average metal participation to the bond ranges between 3.2% and 3.9% which is dominated by the d contribution. However, unlike the Ln-radical bonding, the $6s$ involvement in Ln-N bonds is larger than the $4f$, which remains below 1.5%. Notably, the $4f$ participation to the Ln-radical is slightly higher than in the Ln-Tp* case, despite the ~1.5% of increased total metal participation in the latter as a result of higher $5d$ participation (**Figure 8** and **S36**). This is reflected in the calculated Wiberg bond orders that are slightly larger for the Ln-DTBSQ compared to the Ln-Tp* across the series (**Figure S43**). The overall bonding analysis suggests that a combination of symmetry and energetic factors favors f -orbital mixing in the Ln-DTBSQ over the Ln-Tp* bond. Furthermore, in line with these factors, the delocalized electron in the DTBSQ radical reduces localized charge density and increases polarizability, all of which further amplifies the contribution of the f -orbitals to the bonding interaction. This also suggests that the metal-DTBSQ radical interaction shows lanthanide-dependent differences in bonding mainly reflected through an incremented donation to the f -shell.

Optical spectra

The electronic structure and vibrational features of the complexes were probed via UV-visible-NIR spectroscopy in toluene (**Figure 9, 10** and **S40**) and FTIR spectroscopy (see SI section 3). The UV-vis spectra of all **3-Ln** complexes contain a narrow, strong absorption at ~310 nm with a molar absorptivity of greater than $6,000 \text{ M}^{-1} \text{ cm}^{-1}$ and a broad shoulder at lower energy centered at

~350 nm with a molar absorptivity of 2,000-6,000 M⁻¹ cm⁻¹. In addition, broad, low intensity absorbances are observed at lower energies of 500-800 nm, with molar absorptivities of less than 1,000 M⁻¹ cm⁻¹ (**Figure 9** left, inset). Initially, both charge transfer and $4f \rightarrow 5d$ transitions were investigated via TDDFT at ZORA-CAMB3LYP/TZP level of theory. However, due to the missing spin-orbit interaction this approach does not predict intensities for the parity forbidden f - f transitions. Therefore, the SO-RASSCF/MC-pDFT multireference wavefunction-based approach was further employed (see Computational Details).

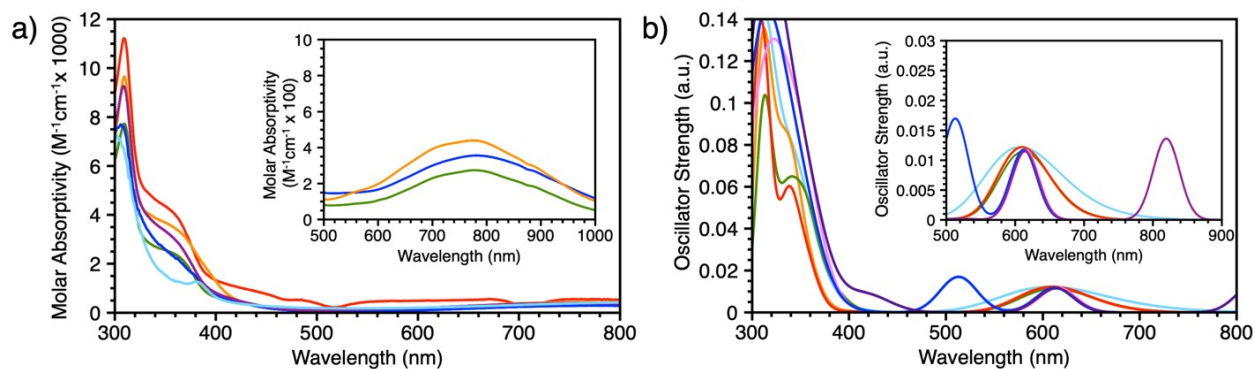


Figure 9. Experimental (a) and simulated (b) UV-visible spectra of **3-La** (red), **3-Ce** (orange), **3-Pr** (green), **3-Nd** (pink), **3-Sm** (C) (dark blue), **3-Eu** (purple) and **3-Gd** (light blue). Inset shows an expansion of the weaker, lower energy absorptions. Level of theory: ZORA-CAMB3LYP/TZP. Assignments of these peaks are given in **Table S8**.

The UV-visible-NIR spectra were successfully simulated to assign the absorbance bands (**Figure 9** and **Figure 10**). The intense peak at ~310 nm was found to belong to intra- and inter-ligand transitions involving both the DTBSQ and the Tp* ligands, while the less intense shoulder at ~350 nm peak corresponds mainly to π (radical) $\rightarrow 5d$ transitions. Additionally, an intra-radical transition was calculated at ~615 nm, which falls in the range of the low intensity experimental feature observed between ~500 and ~800 nm. A previous study by Sawyer *et al*⁶⁴ reports the UV-vis spectrum of the DTBSQ radical, where a low-lying band located ~630 nm was observed and ascribed to an intra-ligand transition, consistent with the theoretical assignment. These assignments agree with the experimental spectra as these spectroscopic transitions in the region between 300-800 nm mostly involve the ligands and $5d$ orbitals, whose energy remains nearly unaltered through the lanthanide series. As such, the spectra look reasonably similar among all the **3-Ln** systems. Conversely, differences arising from the energetic stabilization of the $4f$ shell as the lanthanide series is traversed were observed computationally. First, the position of the $4f \rightarrow 5d$ transitions varies depending on the systems, increasing in energy from Ce^{III} to Eu^{III}. In case of **3-Ce** which is

the system displaying the lowest-energy $4f \rightarrow 5d$ transition, they start at ~ 579 nm (see **Table 3**). In **3-Sm (C)** and **3-Eu**, where the $4f$ orbitals are more stabilized, a low-lying π (radical) $\rightarrow 4f$ transition was found at ~ 513 and ~ 780 nm, respectively, consistent with the weakly intense experimental feature found between ~ 500 and 800 nm. As explained by Binnemans in his seminal review,⁶⁵ Eu^{3+} is more prone to display low-lying CT bands given its unique electronic structure which makes this ion the easiest to reduce. However, these CT bands are difficult to identify experimentally given their low intensity and the overlap with other transitions. To try to observe these weaker, lower energy transitions, concentrated solutions of greater than 1 mM were measured. Samples were chosen for this analysis to represent early f^n (**3-Ce**, **3-Pr**) and middle f^n (**3-Sm (C)**) systems. Consistent with simulated spectra, the broad, low energy transitions at 500 - $1,000$ nm were able to be discerned at high concentrations less than 2 orders of magnitude in intensity than the central absorbance features at ~ 310 and ~ 350 nm. Interestingly, a recent study by Dunstan *et al.* that explored the chemistry of the second half of the Ln series coordinated to non-methylated Tp and DSTBSQ ligands (analogous to **3-Ln** systems) identified a band between 580 and $1,000$ nm two orders of magnitude less intense than the ones observed in the UV region, consistent with the data of these systems.²⁶ Since this band is broader and ~ 170 nm red-shifted with respect to the one observed in the spectrum of the isolated DTBSQ radical,⁶⁴ it is reasonable to think that some degree of metal participation can be the responsible for these differences in agreement with the theoretical assignment.

In the NIR energy region there are no observable absorbances for **3-Ce**, while **3-Pr**, and **3-Sm (C)** show a series of weak (less than $100 \text{ M}^{-1} \text{ cm}^{-1}$) absorbances, of much lower energy than those of **3-Ce** which were modeled via SO-CASSCF calculations and assigned to $4f \rightarrow 4f$ transitions. The

labeling of the bands was carried out within the intermediate coupling scheme, where the observed electronic states are best described as linear combinations of spin-free states mixed by spin–orbit coupling.

To verify structural similarities in the bulk solid material, FTIR data were collected for **3-Ln** (see SI). The vibrational spectra of the complexes are nearly identical for the series, with characteristic absorbances at 2,522 and 2,548 cm^{-1} attributable to the B-H stretches of the bound Tp* as previously observed for **3-Sm (C)**.²³ This is consistent with the similarity of the solid-state structures of single crystals of **3-Ln**.

Discussion

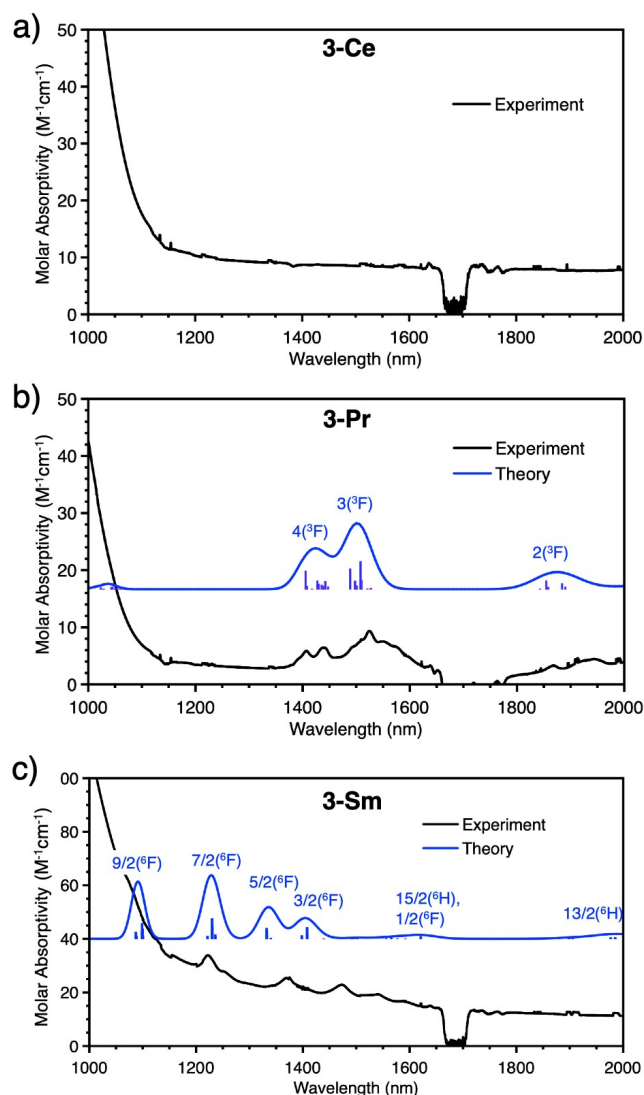


Figure 10. NIR Spectra of **3-Ce** (top), **3-Pr** (middle) and **3-Sm** (**C**) (bottom). The dip in the region 1,700 nm is due to solvent overtones. The assignment is performed in terms of predominant states labeled as $J(^{\circ}L)$, where J =total angular momentum quantum number ($L+S$), L =orbital angular momentum and S =spin angular momentum. To better match the experimental data, the simulated spectra of **3-Pr** and **3-Sm** were both red-shifted by 150 cm^{-1} .

In this work, we have synthesized and conducted a comprehensive investigation on a new family of isostructural **3-Ln** complexes featuring the non-innocent ligand DTBSQ, formulated as $(\text{Tp}^*)_2\text{Ln}(\text{DTBSQ})$ ($\text{Ln} = \text{La-Gd}$, excluding Pm). Experimental characterization using ^1H NMR, UV-vis-NIR, EPR spectroscopy, SQUID and X-ray crystallography confirms a scenario consistent with a Ln^{III} -trapped organic radical system, even for the redox active Ln^{III} , where the metal centers

adopt formal trivalent oxidation states coordinated to the DTBSQ radical that hosts the delocalized electron. This assignment is supported both by solid state X-ray structures, for which the DTBSQ ligand shows C-C and C-O bond metrics consistent with a semiquinone radical as opposed to a catecholate or benzoquinone ligand, as well as EPR and ^1H NMR spectroscopic data for which **3-La** and **3-Ce** are observed to show ground states approximated to a first-degree as $4f^0/4f^1$ -organic radical species respectively. SQUID magnetometry conducted on **3-La** and **3-Pr** further confirms the description of a Ln^{III} -radical system, in which the Pr^{III} ion and the DTBSQ radical exhibit a weak antiferromagnetic interaction.

Based on such spectroscopic results, we initially expected the ground state of **3-Ce** to be an open shell singlet, but calculations instead show the overlap between the $4f$ orbitals and the O $2p$ - π orbitals is too weak to stabilize this singlet state. Across the series, the low-lying vacant f -orbitals progressively approach the energy of the occupied DTBSQ-based orbitals, enhancing the propensity for ligand-to-metal electron donation. Theoretical analysis also reveals multiconfigurational ground states, primarily arising from the static correlation inherent to the $4f$ shell. However, notable differences were observed for both **3-Sm (C)** and **3-Eu**, where states associated with the reduction of the metal center contributed to the ground-state wavefunction via a Hubbard interaction, consistent with the accessible $\text{Ln}^{3+}/\text{Ln}^{2+}$ redox couples for these ions. This impact of the easily reducible Sm^{3+} and Eu^{3+} centers was also observed experimentally during the synthesis of the complexes. While the salt metathesis route was found to easily give **3-La**, **3-Ce**, and **3-Pr**, such a route was found to give impurities when targeting **3-Nd**, **3-Sm (C)** and **3-Eu**, including Ln^{III} ions more prone to reduction. Indeed, the easiest route to isolate **3-Sm (C)** and **3-Eu** was *via* formal oxidation of the known divalent $\text{Ln}^{\text{II}}(\text{Tp}^*)_2$ complexes with slight excess of DTBBQ.

In line with these observations, an analysis of the Ln^{III}–DTBSQ chemical bond confirms, as expected, a predominantly ionic interaction, with the metal contributing approximately 1.5–2% to the bonding.^{53–56,66} Consequently, the primary distinguishing factor in terms of bonding among the systems is the extent of orbital mixing, driven by the energetic degeneracy between the 4*f* orbitals and the radical-based orbitals, with the **3-Pr**, **3-Sm (C)** and **3-Eu** showing the most significant deviations. Interestingly, in the Ln–DTBSQ system, the 4*f* character dominates over that observed in the Ln–Tp* bond, a trend reflected in the calculated bond orders. This occurs despite the Ln–Tp* complexes exhibiting twice the overall metal participation in the M–L bonds compared to Ln–DTBSQ. These findings highlight the relatively softer nature of the DTBSQ ligand compared to typical anionic non-radical oxygen donor ligands, as evidenced by the enhanced *f*-orbital contribution to the bond. From a structural standpoint, while the average Ln^{III}–DTBSQ bond distances align well with the Shannon ionic radii, consistent with the expected lanthanide contraction, a detailed theoretical analysis uncovered subtle nuances in the bonding. These subtleties are primarily attributed to the unique electronic structure of the radical ligand, highlighting complexities beyond simple ionic interactions.

The experimental UV-vis-NIR spectra of all **3-Ln** complexes reveal high-intensity absorption bands in the 250–400 nm range, dominated by intra- and inter-ligand transitions. Additionally, unusual, less intense, low-lying spectroscopic features were observed in the **3-Ce**, **3-Pr**, and **3-Sm (C)** complexes, attributed to the unique electronic structure of the DTBSQ radical. These UV-vis-NIR spectra were analyzed using TDDFT and the multireference methodology described earlier, confirming the assignment of the high-energy bands to intra- and inter-ligand transitions as well as LMCT features. Interestingly, the low-lying bands observed experimentally in

the Ce^{III}, Sm^{III}, and Pr^{III} complexes were theoretically reproduced and identified in the other studied systems, where they were attributed to intraradical transitions. Notably, in the Sm^{III} and Eu^{III} complexes, additional bands associated with LMCT transitions from the radical to vacant 4*f* orbitals were identified at approximately 500 nm and 810 nm, respectively. These distinctive features are intrinsic to the electronic nature and identity of the metal centers.

Conclusions

The electronic structures and chemical bonding of the Ln-radical ligand fragment in a new, isostructural series of bis(Tp*) semiquinone Ln complexes have been studied for all early Ln, except Pm. Spectroscopic, magnetic and X-ray crystallographic data show that despite the redox activity of some Ln^{III} species, namely Ce and Eu, as well as the DTBSQ, remarkably all complexes can be isolated and characterized as (Tp*)₂Ln^{III}-organic radical species.

Theoretical investigations of the Ln-DTBSQ interaction reveal that it is predominantly ionic across the analyzed series, with significant deviations arising from 4*f* -shell stabilization. This stabilization can facilitate Hubbard-type interactions, as observed in the **3-Sm (C)** and **3-Eu** complexes. Additionally, notable differences in bonding between the Ln-DTBSQ and Ln-Tp* moieties were identified. The Ln-Tp* bond shows greater metal participation compared to the Ln-DTBSQ bond but the latter exhibits a slightly higher 4*f* -contribution, leading to increased bond order. This is unusual, since 6*s* involvement prevails in Ln bonding all commonly used ligands, underscoring the intriguing properties of organic radicals, where polarizability can facilitate a better mixing with Ln orbitals, and a resulting amplification of 4*f* participation in the bond.

Moving forward, this study offers valuable experimental and computational insights into the unique behaviors arising from the interplay between f -electrons and radical ligands. These findings not only deepen our fundamental understanding, but also open exciting opportunities for designing electronic-structure driven strategies in lanthanide separations. Building on this foundation, ongoing efforts are extending this approach to actinide systems, with the aim of advancing both bonding studies and separation technologies.⁶⁷

Experimental Details

General information

All materials were manipulated using standard high-vacuum Schlenk-line techniques and MBraun gloveboxes and stored under an atmosphere of dried and deoxygenated nitrogen unless noted otherwise. All glassware items and Fisher brand 1.2 μm retention glass microfiber filters were dried in a 160 °C oven overnight before use. Hexane, tetrahydrofuran (THF), and toluene for use with moisture and air sensitive compounds were dried using an MBRAUN SPS 800 Manual solvent purification system and stored over activated 3 Å molecular sieves. Benzene- d_6 was purchased from Cambridge Isotope Laboratories and refluxed over potassium metal for 24 hours, freeze-pump-thaw degassed and purified by trap-to-trap distillation prior to use. All solvents were purchased from Sigma-Aldrich or Fisher Scientific and stored over 3 Å molecular sieves for 4 hours before being used. $\text{LnI}_3(\text{Et}_2\text{O})_x$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}$),^{68,69} $\text{LnI}_2(\text{THF})_x$ ($\text{Ln} = \text{Sm}, \text{Eu}$),^{70,71} NaTp^* ,⁷² **A**, and **B**⁷³ were prepared according to literature methods. All other chemicals were purchased from commercial suppliers and degassed and/or dried under vacuum or over 3 Å molecular sieves for 12 hours before use. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and are referenced to residual protio solvent (7.16 ppm for benzene- d_6) for ^1H NMR spectroscopy with samples in NMR tubes fitted with J Young teflon valves. Chemical shifts are quoted in ppm. NMR spectra were measured at 25 °C unless otherwise noted. Elemental analyses were carried out by the microanalytic services in the College of Chemistry at the University of California, Berkeley. ATR-FTIR spectra were recorded on a Shimadzu IRSpirit FTIR spectrometer on neat powders. EPR experiments were carried out in the CalEPR center in the University of California, Davis. X-band continuous-wave spectra were recorded on the Bruker Biospin EleXsys E500 spectrometer equipped with a super high Q resonator (ER4122SHQE) and an ESR900 liquid helium cryostat with a temperature controller (Oxford Instrument ITC503), under slow-passage, non-saturating conditions. Spectrometer settings were as following: frequency = 9.4 GHz, conversion time = 60 ms, modulation amplitude = 0.1 mT, modulation frequency = 100 kHz. Q-band pulse EPR measurements were performed on a Bruker Biospin EleXsys E580 spectrometer equipped with a home-built R.A. Isaacson cylindrical TE011 resonator, using the following pulse sequence: Davies ENDOR, π -RF- $\pi/2$ - τ - π - τ -echo. The length of inversion (π) pulse in Davies ENDOR is 80 ns. EPR and ENDOR spectra were simulated using the EasySpin 6.0.0-dev.53 package in MATLAB 2023b.⁷⁴ Optical spectra were recorded on either a Varian Cary 50 for UV-visible spectra or Cary 5000 UV-Vis-NIR spectrophotometer for NIR measurements using either Schlenk-adapted quartz cuvettes with a 1 cm path length, sealed PTFE-taped screw-cap quartz cuvettes with a 1 cm path length, or sealed semi-micro, PTFE-taped screw-cap fluorimeter quartz cuvettes with 1 cm or 0.4 cm path lengths depending on the choice of angle. The samples were prepared under an N_2 atmosphere for all spectroscopic measurements. Single crystal X-ray diffraction data of all other compounds were collected using a Rigaku Xtalab Synergy-S diffractometer fitted with a HyPix-6000HE photon counting detector using $\text{CuK}\alpha$ ($\lambda = 0.154184$ Å) radiation at 100 K. All structures were solved using SHELXT in Olex2 and refined using SHELXL in Olex2.^{75,76} Absorption corrections were completed using CrysAlis PRO (Rigaku Oxford Diffraction) software. Analytical numeric absorption corrections used a multifaceted crystal model based on expressions derived by Clark and Reid.⁷⁷ Numerical absorption correction was based on a Gaussian integration over a multifaceted crystal model.

Syntheses

2 K[DTBSQ]

To a Schlenk flask was added 40.00 mL of a 0.1065 M aqueous KOH solution and 21.00 mL degassed ethanol. Light brown H₂DTBC (0.4734 g, 2.129 mmol) was added, affording an immediate clear blue solution. Volatiles were removed under reduced pressure at 60 °C, after which point DTBBQ (0.4688 g, 2.128 mmol, 0.9994 eq), a magnetic stirbar, and 40 mL of dry THF were added, giving an immediate dark blue suspension that was stirred for 5 minutes before the solvent was removed under reduced pressure to give K[DTBSQ], **2**, as a dark blue solid (1.0127g, 92% yield). The absence of any residual K₂DTBC or DTBBQ was confirmed by ¹H NMR spectroscopy, which contained no resonances.

3-La, LaTp*₂(DTBSQ)

To a 20 mL vial containing a thawing colorless THF suspension of LaI₃(Et₂O)_{1.56} and a magnetic stir bar (0.1683 g, 0.2649 mmol, 3.770 mL) was added a thawing THF solution of NaTp* (0.1876 g, 0.5859 mmol, 2.212 eq, 7.540 mL), dropwise over 10 minutes, giving a clear, pale solution that was stirred for a further 30 minutes. A thawing THF solution of K(DTBSQ) (0.0765 g, 0.295 mmol, 1.11 eq, 7.540 mL) was then added dropwise to the reaction mixture over 10 minutes with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 23 hours. The suspension was then filtered through a glass microfiber filter, giving a clear, dark green filtrate that was dried to a dark green residue. To the residue was added 8 mL toluene, giving a cloudy dark green suspension that was filtered through a glass microfiber filter, giving a clear, dark green filtrate that was dried to a dark green residue. To the residue was added 5 mL hexane, giving a dark brown cloudy suspension that was filtered through a glass microfiber filter, giving a clear dark green solution. An aliquot of the solution was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green LaTp*₂(DTBSQ), **3-La** (0.0536 g, 20 % yield). The complex was found to co-crystallize with lattice hexane that is retained upon drying under vacuum, as shown in the ¹H NMR spectrum with a substoichiometric amount of hexane present consistent with elemental analysis results. The DTBSQ ligand was found to be silent by ¹H NMR, consistent with a radical on the ligand; the resonances for the Tp* ligand are broadened and shifted; the H-B proton was not resolvable. Elemental analysis (CHN): Calculated for C₄₄H₆₄B₂LaN₁₂O₂·0.75(C₆H₁₄): C: 57.21 %. H: 7.37 %, N: 16.51 %. Found: C: 57.33 %, H: 7.21 %, N: 16.48 %. ¹H NMR (400 MHz, C₆D₆) δ 5.59 (6H, 6 Ar-H), 3.58 (1H, H-B), 1.3-2.5 (18H, 6 Ar-CH₃), 1.24 (hexane), 0.89 (hexane). FTIR (ATR, cm⁻¹): 2,522 (ν_{B-H}), 2,548 (ν_{B-H}).

3-Ce, CeTp*₂(DTBSQ)

To a 20 mL vial containing a thawing tan-colored THF suspension of CeI₃(Et₂O)_{2.99} and a magnetic stir bar (0.1000 g, 0.1347 mmol, 1.920 mL) was added a thawing THF solution of NaTp* (0.0977 g, 0.305 mmol, 2.27 eq, 3.840 mL), dropwise over 10 minutes, giving a clear, pale solution that was stirred for a further 30 minutes. A thawing THF solution of K(DTBSQ) (0.0387 g, 0.149 mmol, 1.11 eq, 3.840 mL) was then added dropwise to the reaction mixture with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 40 minutes. The suspension was then filtered through a glass microfiber filter, giving a clear, dark green filtrate that was dried to a greenish residue. To the residue was added 4 mL toluene, giving a cloudy dark green suspension that was filtered through a glass microfiber filter, giving a clear, dark

green filtrate that was dried to a dark green residue. To the residue was added 2 mL hexane, giving a cloudy dark green suspension that was filtered through a glass microfiber filter, giving a clear, dark green filtrate. An aliquot of the solution was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green CeTp*₂(DTBSQ), **3-Ce** (0.0865 g, 60 % yield). The complex was found to co-crystallize with lattice hexane that is retained upon drying under vacuum, as shown in the ¹H NMR spectrum, and 15 % incorporation of KI, which was not found to impact the spectroscopic results. Elemental analysis (CHN): Calculated for C₄₄H₆₄B₂CeN₁₂O₂·C₆H₁₄·0.15(KI): C: 56.34 %, H: 7.38 %, N: 15.77 %. Found: C: 56.49 %, H: 7.19 %, N: 15.74 %. ¹H NMR (400 MHz, C₆D₆) δ 27.78 (9H, Ar-Bu), 18.48 (3H, Ar-CH₃), 18.09 (3H, Ar-CH₃), 17.45 (1H, Ar-H), 12.94 (3H, Ar-CH₃), 7.16 (benzene), 6.71 (3H, Ar-CH₃), 6.00 (1H, Ar-H), 5.71 (9H, Bu-Ar), 5.12 (3H, Ar-CH₃), 4.60 (2H, 2 Ar-H), 3.0-4.0 (9H, 3 Ar-CH₃), 1.5-2.5 (4H, 2 H-B, 2 Ar-H), 1.24 (hexane), 1.02 (3H, Ar-CH₃), 0.89 (hexane), 0.31 (4H, 1 Ar-CH₃, 1 Ar-H), -7.75 (1H, Ar-H), -24.60 (6H, 2 Ar-CH₃). FTIR (ATR, cm⁻¹): 2,522 (ν_{B-H}), 2,548 (ν_{B-H}).

3-Pr, PrTp*₂(DTBSQ)

To a 20 mL vial containing a thawing yellow THF suspension of PrI₃(Et₂O)_{0.14} and a magnetic stir bar (0.1979, 0.3721 mmol, 3 mL) was added a thawing THF solution of NaTp* (0.2668 g, 0.8334 mmol, 2.240 eq, 6 mL), dropwise over 10 minutes, giving a clear, pale solution that was stirred for a further 30 minutes. A thawing THF solution of K(DTBSQ) (0.1101 g, 0.4245 mmol, 1.141 eq, 6 mL) was then added dropwise to the reaction mixture with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 18 hours. To the residue was added 10 mL toluene, giving a cloudy dark green suspension that was then filtered through a glass microfiber filter, giving a clear, dark green filtrate that was dried to a greenish residue. To the residue was added 5 mL hexane, giving a dark green cloudy suspension that was filtered through a glass microfiber filter, giving a clear dark green solution. An aliquot of the solution was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green PrTp*₂(DTBSQ), **3-Pr** (0.0459 g, 13% yield). The complex was found to co-crystallize with lattice hexane that is retained upon drying under vacuum, as shown in the ¹H NMR spectrum as well as a substoichiometric amount of KI salt, which was not found to impact the spectroscopic results. Elemental analysis (CHN): Calculated for C₄₄H₆₄B₂N₁₂O₂Pr·C₆H₁₄·0.15(KI): C: 56.00 %, H: 7.17 %, N: 16.36 %. Found: C: 56.36 %, H: 6.78 %, N: 16.02 %. ¹H NMR (400 MHz, C₆D₆) δ 41.22 (3H, Ar-CH₃), 36.53 (1H, Ar-H), 33.19 (9H, Ar-Bu), 21.56 (1H, Ar-H), 10.31 (9H, Ar-Bu), 7.98 (3H, Ar-CH₃), 7.16 (benzene), 5.14 (1H, Ar-H), 4.92 (3H, Ar-CH₃), 4.45 (1H, Ar-H), 4.24 (1H, Ar-H), 4.14 (1H, Ar-H), 2.36 (3H, 1 Ar-CH₃), 1.75 (4H, 1 Ar-CH₃, 1B-H), -0.20 (1H, Ar-H), -0.66 (1H, Ar-H), -0.85 (1H, Ar-H), -1.26 (1H, Ar-H), -1.66 (3H, Ar-CH₃), -2.05 (3H, Ar-CH₃), -4.96 (1H, Ar-H), -5.62 (3H, Ar-CH₃), -6.86 (3H, Ar-CH₃), -9.9 (1H, B-H). FTIR (ATR, cm⁻¹): 2,522 (ν_{B-H}), 2,548 (ν_{B-H}).

3-Nd, NdTp*₂(DTBSQ)

To a 20 mL vial containing a thawing blue THF suspension of NdI₃(Et₂O)_{0.34} and a magnetic stir bar (0.2036 g, 0.3717 mmol, 4 mL) was added a thawing THF solution of NaTp* (0.2671 g, 0.8341 mmol, 2.244 eq, 8 mL), dropwise over 10 minutes, giving a clear, light blue solution that was stirred for a further 30 minutes. A thawing THF solution of K(DTBSQ) (0.1068 g, 0.4115 mmol, 1.107 eq, 8 mL) was then added dropwise to the reaction mixture over 10 minutes with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 23 hours. The suspension was centrifuged for 5 minutes, giving a clear dark green

supernatant that was dried to a green residue. To the residue was added 8 mL toluene, giving a cloudy dark green suspension that was centrifuged for 5 minutes, giving a clear, dark green supernatant that was dried to a dark green residue. To the residue was added 3 mL hexane, giving a dark green cloudy suspension that was centrifuged for 5 minutes, giving a clear dark green supernatant. An aliquot of the supernatant was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. While single crystals were able to be probed for XRD studies, the bulk material was found to contain impurities through ¹H NMR that cocrystallize with the desired product following iterative recrystallization.

C (3-Sm, SmTp*₂(DTBSQ))

C was isolated through a modified literature procedure. To a 20 mL vial containing a thawing blue THF suspension of SmI₂(THF)_{2.7} and a magnetic stir bar (0.1038 g, 0.1732 mmol, 2 mL) was added a thawing THF solution of NaTp* (0.1382 g, 0.4318 mmol, 2.492 eq, 4 mL), dropwise over 5 minutes, giving a clear, light blue solution that was stirred for a further 30 minutes. A thawing brown THF suspension of DTBBQ (0.0585 g, 0.265 mmol, 1.53 eq, 4 mL) was then added dropwise to the reaction mixture over 5 minutes with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 23 hours. The suspension was centrifuged for 5 minutes, giving a clear dark green supernatant that was dried to a green residue. To the residue was added 4 mL toluene, giving a cloudy dark green suspension that was centrifuged for 5 minutes, giving a clear, dark green supernatant that was dried to a dark green residue. To the residue was added 1.5 mL hexane, giving a dark green cloudy suspension that was centrifuged for 5 minutes, giving a clear dark green supernatant. An aliquot of the supernatant was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green SmTp*₂(DTBSQ), **C** (0.0953 g, 46 % yield). The identity was then verified by elemental analysis, ¹H NMR, and XRD and the complex probed *via* UV-vis-NIR spectroscopy. Elemental analysis (CHN): Calculated for C₄₃H₆₂B₂N₁₂O₂Sm·1.05(C₆H₁₄)·0.85(KI): C: 50.07%, H: 6.54%, N: 14.21 %. Found: C: 50.35%, H: 6.17%, N: 13.87%. FTIR (ATR, cm⁻¹): 2,522 (ν_{B-H}), 2,548 (ν_{B-H}).

3-Eu, EuTp*₂(DTBSQ)

To a 20 mL vial containing a thawing yellow THF suspension of EuI₂(THF)_{2.44} and a magnetic stir bar (0.0607 g, 0.104 mmol, 1 mL) was added a thawing THF solution of NaTp* (0.0739 g, 0.231 mmol, 2.21 eq, 2 mL), dropwise over 5 minutes, giving a cloudy, yellow suspension that was stirred for a further 30 minutes. A thawing brown THF suspension of DTBBQ (0.0271 g, 0.123 mmol, 1.18 eq, 2 mL) was then added dropwise to the reaction mixture over 5 minutes with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 21 hours. The suspension was centrifuged for 5 minutes, giving a clear dark green supernatant that was dried to a green residue. To the residue was added 2 mL toluene, giving a cloudy dark green suspension that was centrifuged for 5 minutes, giving a clear, dark green supernatant that was dried to a dark green residue. To the residue was added 1 mL hexane, giving a dark green cloudy suspension that was centrifuged for 5 minutes, giving a clear dark green supernatant. An aliquot of the supernatant was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35 °C, giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green EuTp*₂(DTBSQ), **3-Eu** (0.0080 g, 8 % yield). For the ¹H NMR spectrum, while the expected 24 distinct resonances were

observed, the integration was not found to add up the expected value, likely a consequence of the strongly paramagnetic environment from the formally $4f^6$ metal center and the organic radical causing rapid spin relaxation of ligand ^1H resonances. The same resonances in the same ratio were observed in product isolated in multiple batches isolated through redox or salt metathesis methods. ^1H NMR: δ 30.66, 29.44, 17.44, 14.42, 13.43, 11.24, 6.75, 5.72, 4.13, 3.21, 2.99, 2.50, 2.35, 1.95, 1.87, 1.75, 1.58, 1.38, 0.30, -1.33, -2.22, -2.65, -15.88. Elemental analysis (CHN): Calculated for $\text{C}_{44}\text{H}_{64}\text{B}_2\text{EuN}_{12}\text{O}_2 \cdot 0.65\text{C}_6\text{H}_{14}$: C: 56.26 %, H: 7.20 %, N: 16.44 %. Found: C: 58.25 %, H: 5.14 %, N: 14.53 %. FTIR (ATR, cm^{-1}): 2,522 ($\nu_{\text{B-H}}$), 2,548 ($\nu_{\text{B-H}}$).

3-Gd, $\text{GdTp}^*_2(\text{DTBSQ})$

To a 20 mL vial containing a thawing grey THF suspension of $\text{GdI}_3(\text{Et}_2\text{O})_2$ and a magnetic stir bar (0.2035 g, 0.2677 mmol, 4 mL) was added a thawing THF solution of NaTp^* (0.1880 g, 0.5872 mmol, 2.194 eq, 8 mL), dropwise over 10 minutes, giving a cloudy grey suspension that was stirred for a further 30 minutes. A thawing THF solution of $\text{K}(\text{DTBSQ})$ (0.0775 g, 0.299 mmol, 1.12 eq, 8 mL) was then added dropwise to the reaction mixture over 10 minutes with stirring, giving an immediate cloudy dark green suspension that was allowed to stir for 23 hours. The suspension was centrifuged for 5 minutes, giving a clear dark green supernatant that was dried to a green residue. To the residue was added 7 mL toluene, giving a cloudy dark green suspension that was centrifuged for 5 minutes, giving a clear, dark green supernatant that was dried to a dark green residue. To the residue was added 5 mL hexane, giving a dark green cloudy suspension that was centrifuged for 5 minutes, giving a clear dark green supernatant. An aliquot of the supernatant was separated and used for SCXRD studies, with both the aliquot and bulk material stored at -35°C , giving green crystalline solid. Bulk material was dried *in vacuo* to yield dark green $\text{GdTp}^*_2(\text{DTBSQ})$, **3-Gd** (0.0154 g, 4 % yield). The complex was found to co-crystallize with lattice hexane that is retained upon drying under vacuum, as shown in the ^1H NMR spectrum as well as a substoichiometric amount of KI salt, which was not found to impact the spectroscopic results. The complex was found to be silent by ^1H NMR, with only solvent peaks observable as expected from a formal $4f^7$ -organic radical complex. Elemental analysis (CHN): Calculated for $\text{C}_{44}\text{H}_{64}\text{B}_2\text{GdN}_{12}\text{O}_2 \cdot 2.8\text{C}_6\text{H}_{14} \cdot 0.85(\text{KI})$: C: 53.59 %, H: 7.61 %, N: 12.54 %. Found: C: 54.36 %, H: 6.79 %, N: 11.76 %. The poor yield complicated the isolation of pure material in the bulk.

DC Magnetic studies

Direct current (dc) magnetic characterizations were performed on polycrystalline samples using a Quantum Design MPMS3 SQUID magnetometer. Measurements were conducted between 2 and 300 K in the presence of an external applied magnetic field. These measurements were all corrected for the intrinsic diamagnetic contribution of the compounds.

Theoretical Analysis

Computational details

Geometry optimization and bonding: Initially, the experimental structures of the **3-Ln** complexes (Ln = La, Ce, Pr) were optimized in AMS version 2023.104⁷⁸ using the meta-hybrid M06-2X functional in conjunction with Slater-type basis functions (STO) triple- ζ plus polarization (TZP). Additionally, the hybrid

PBE0 and meta-hybrid TPSSH functionals were also employed to provide a more comprehensive benchmarking of the level of theory.^{79–81} Due to the good agreement observed between optimized and crystal structures, the coordinates of the rest of **3-Ln** (Ln = Nd, Sm, Eu, Gd) systems were further optimized at the same level of theory. No symmetry or geometry constraints were imposed.^{82,83} The relativistic effects were incorporated through the zeroth-order regular approximation (ZORA) of the Dirac equation.⁸⁴ To accurately analyze the ground states of the systems, two scenarios were considered (**Figure S30**): ferromagnetic coupling between radical electron and metal 4f electrons (high-spin, **Figure S30a**), and anti-ferromagnetic coupling, where the spin of the radical electron was flipped (low-spin, **Figure S30b**). In the case of the **3-Ce** system, the LS configuration corresponds to a singlet, which adds complexity since this state can be either restricted (RKS), with opposite-spin electrons occupying the same spatial orbitals, or unrestricted (UKS), where opposite-spin electrons are allowed to occupy different spatial orbitals. To ensure robustness, both singlet configurations were considered. The restricted singlet was obtained by specifying a spin polarization of zero, which in ADF by default converges to the restricted solution. The unrestricted (broken-symmetry) singlet was generated using the SPINFLIP keyword, where a triplet solution is provided as input to subsequently flip one electron on the metal center to produce the desired spin polarization. All the structures used a gradient convergence criterion of 1×10^{-3} Ha/Å. Frequency calculations were further performed to confirm the optimized structures as true minima without imaginary frequencies.

To analyze the lanthanide-ligand (Ln-L) interactions, the natural bond orbital (NBO) program version 7.0 was employed.⁵⁰ This tool transforms a given density into a localized form, corresponding to the one-center (or “lone-pair”) and two-center (or “bond”) patterns of the Lewis structure picture. The natural localized molecular orbitals (NLMOs) set were used for this purpose, which were visualized by using the software VESTA 3.5.8.⁵¹

Spectroscopic Simulation Using Time-Dependent DFT calculations (TDDFT): To be able to simulate the spectroscopic bands located in the UV-vis region, the TDDFT approach was employed. The calculations were also performed in AMS 2023.104 using the same relativistic Hamiltonian and basis set described in the previous section. However, we varied the functional to the Coulomb-attenuated method (CAM-B3LYP) since it has proven useful in the characterization of long-range charge transfer (CT) bands.⁸⁵ Given the large size of these systems (125 atoms) and the computational cost associated to these simulations, we limited the calculation of excited states to 60 roots per system, which cover the energy region of interest (300–800 nm) including both near-IR and typical UV-vis range. However, to further validate the reliability of these results, we performed a test calculation with 150 roots for the **3-Ce** system where no significant differences compared to the spectra obtained using 60 roots were observed. The Tamm–Dancoff approximation (TDA) was employed in all cases.⁸⁶

Multireference calculations: The **3-Ln** complexes were further studied via *ab initio* wavefunction calculations using the OpenMolcas program to validate and complement the DFT results.⁸⁷ The initial wavefunctions were calculated with density functional theory using the PBE functional in conjunction with all-electron ANO-RCC Gaussian-type basis sets contracted to TZP quality.⁸⁸ Scalar relativistic effects were included via the 2-component Douglas-Kroll-Hess (DKH2) Hamiltonian.⁸⁹ The static correlation was accounted for by using the PBE density as input for restricted active self-consistent field (RASSCF) calculations.⁹⁰ The active space considered the 4f shell plus two radical-based orbitals (bonding and

antibonding) in RAS2 and the 5*d* shell in RAS3. In total, the active space included *n*+1 electrons (*n* = 4*f* electrons) distributed in 14 orbitals (**Figure S31**). The details of the number of roots and multiplicities are given in **Table S1**. The multiconfigurational pair-density functional theory (MC-pDFT) method with the tPBE on-top functional was used to recover the dynamic correlation present in these systems.^{91,92} Finally, the spin-orbit (SO) coupling was included through state interactions between RASSCF wavefunctions via restricted active space state interaction (RASSI) method (**Figure S32**).⁹⁰ To model the *f*-*f* transitions in **3-Pr** and **3-Sm**, we employed a model system where the DTBSQ was replaced for its oxidized form DTBBQ.

To simulate the optical spectra, the position of the different bands were obtained from energy differences (ΔE) of the different excited states relative to the ground state. Notably, while the MC-pDFT correction did not substantially affect the conclusions regarding the nature of the ground or CT states, it introduced deviations in the simulated *f* $\rightarrow$ *f* bands of the **3-Pr** and **3-Sm** complexes, where better agreement was obtained without this approximation. Therefore, the UV-vis-NIR spectra were modeled solely at the SO-CASSCF level. The oscillator strengths (*f*) were calculated from the associated transition dipole matrix elements as $f = 2/3(\text{TDM})^2/\Delta E$. Once we had the position and intensity of each transition, a gaussian broadening using a Full Width at Half Maximum (FWHM) equal to 0.05 eV was performed to the *f* $\rightarrow$ *f* bands and 0.3 eV to the rest (**Figure S42**). As a final step, the energies were converted to wavelengths (nm) to better match the experimental data.

Magnetic Calculations: Multireference calculations were performed for the optimized coordinates of the **3-Pr** system in ORCA 6.1.0.^{93,94} Initial densities were calculated using a restricted open Hartree-Fock (ROHF) wavefunction which greatly improves the convergence of the following CASSCF step. In this case we used this setup: ‘rohfcase sahfc’, ‘rohfnump 3’, ‘rohfnel[1] 1,2,1’ and ‘rohfnorb[1] 1,7,1’ to account for electrons and orbitals of both Pr and radical. Scalar relativistic effects were included *via* the second-order Douglas-Kroll-Hess (DKH2) Hamiltonian.⁹⁵⁻⁹⁸ The SARC2-DKH-QZVP basis set was used for Pr and DKH-def2-TZVP for ligand atoms^{88,99-101} in combination with the RIJCOSX approximation, a high-quality integration grid (defgrid3), the AutoAux function, and a tight SCF convergence criteria.

Since our main goal was to quantify the exchange coupling between Pr and the DTBSQ radical, we used a methodology previously employed for similar systems^{44,102,103} where the crystal field parameters of the 3+ lanthanide are obtained to subsequently model the experimental magnetic data via fitting with the Lines approach Hamiltonian.¹⁰⁴ To be able to access the 3+ center, we had two options: reducing or oxidizing the system to prevent an unpaired electron in the radical ligand. To account for both possibilities, we modeled both [**3-Pr**]⁺ and [**3-Pr**]⁻ analogs. While some previous studies—that we are using as reference—only included the 7 non-bonding 4*f*-orbitals,^{102,103} we attempted to increase the active space to resemble the one initially used (see above). However, in the case of [**3-Pr**]⁺ the originally singly-occupied radical orbital is now empty, which precludes of using exactly the same setup here. Therefore, in [**3-Pr**]⁺ we tested 3 active spaces: CAS(2,7) which only accounts for the 4*f*-shell, CAS(2,8) which also includes the empty DTBC orbital and CAS (2,10) which additionally incorporates a low-lying 5*d* orbital. The latter did not converge properly as the 6*s* Pr-based orbital rotated in. Similarly, in [**3-Pr**]⁻ it was very difficult to account for additional orbitals besides the 4*f*-shell since attempts to include the double occupied DTBBQ-based orbital resulted in non-convergence or rotations of core Pr *p*-orbitals. Once the CASSCF was converged, dynamic

correlation effects were included via N-electron valence second-order perturbation theory (NEVPT2) in its strongly contracted implementation.^{105,106} Finally, spin-orbit effects were accounted for via quasi-degenerate perturbation theory (QDPT). The SINGLE_ANISO routine was employed to calculate magnetic properties and extract crystal-field parameters.¹⁰⁷

The SO states associated with the $^3\text{H}_4$ ground multiplet for the $[\mathbf{3-Pr}]^+$ and $[\mathbf{3-Pr}]^-$ models are shown in **Figures S37** and **S38**. For $[\mathbf{3-Pr}]^+$, only minor differences in the splitting of the states are observed between the two active spaces considered. In contrast, more pronounced variations arise for the reduced $[\mathbf{3-Pr}]^-$ model, which exhibits a larger overall splitting ($\sim 700\text{ cm}^{-1}$ with PT2 correction) compared to $\sim 500\text{ cm}^{-1}$ for $[\mathbf{3-Pr}]^+$. The corresponding crystal field parameters extracted from each calculation are provided in **Table S5**. Despite these variations, none of the calculated parameter sets yielded satisfactory agreement with the experimental data within the Lines model, indicating that this approach is insufficient to accurately describe the magnetic behavior in this system.

The UV–vis–NIR spectra simulated using RASSCF/MC-pDFT + SOC calculations show reasonable agreement with the experimental data, shown in **Figure S42** for representative systems. As observed for **3-Ce** and **3-Pr**, the high-energy region between 300–400 nm is well reproduced (peaks A and B) and mainly corresponds to intraligand and charge-transfer (CT) transitions, in line with TD-DFT. However, the experimental low-energy feature around $\sim 600\text{ nm}$ is not reproduced. We attribute this discrepancy to an incomplete active space, which would require the inclusion of additional DTBSQ-based orbitals to properly account for these transitions.

Similar behavior is observed for **3-Sm**, although the high-energy bands appear slightly blue-shifted. Interestingly, in this case we were able to partially reproduce the low-energy band experimentally observed between 600–800 nm, which is consistent with LMCT transitions, in agreement with the TD-DFT assignment.

Despite the overall reasonable agreement, accurately reproducing the spectral region examined here would require expanding the active space to include additional ligand-based orbitals, which would significantly increase the computational cost and likely make the calculations impractical.

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Associated content

Supporting Information. The Supporting Information is available free of charge at [TO_BE_ADDED_IN_PAGE_PROOFS]. Supporting Information: Full experimental and

computational details (.docx); Crystallographic cif files deposited with the CCDC, codes 2410014, 2410029, 2410030, 2410032, 2410033, and 2410037 (.cif); Optimized XYZ coordinates (.xyz).

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