Tuning the Optical and Magnetic Properties of Lanthanide Single-Ion Magnets using Nitro-functionalized Trispyrazolylborate Ligands

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Abstract

We report the synthesis, crystal structures, photophysical and magnetic properties of 11 novel lanthanide complexes with the asymmetrically functionalized trispyrazolylborate ligand, 4-nitrotrispyrazolylborate, 4-NO$_2$Tp$^-$: [Ln(4-NO$_2$Tp)$_3$] (Ln = La – Dy, except Pm). In-depth photophysical characterization of the ligands via luminescence, reflectance and absorption spectroscopic techniques, decay lifetimes, quantum yields supported by time-dependent density functional theory (TD-DFT) and Natural Bond Order (NBO) analysis reveal that n-NO$_2$Tp$^-$ ligands are dominated by intra-ligand charge transfer (ILCT) transitions and that second-sphere interactions are critical to the stabilization of the T$_1$ state of n-NO$_2$Tp$^-$ ligands and hence their ability to sensitize Ln$^{3+}$ emission. The luminescence properties of the complexes indicate that 4-NO$_2$Tp$^-$ is a poor sensitizer of Ln$^{3+}$ emission, unlike 3-NO$_2$Tp$^-$. Moreover, the [Nd(4-NO$_2$Tp)$_3$] (crystallized as a hexane solvate) displays single-molecule magnet (SMM) properties, with longer relaxation times and larger barrier than the non-functionalized NdTp$_3$, attributed to the addition of the NO$_2$-group and subsequent rigidification of the molecular structure.

Introduction

Lanthanide (Ln) hybrid materials with tunable optical and magnetic properties have been attractive targets in fields such as opto-electronics and molecular magnetism.$^{1-3}$ While there has been great success with tailoring the optical properties of the lanthanides towards specific applications such as metal ion and explosives sensors,$^{4,5}$ thermometers,$^6$ information
storage devices\textsuperscript{7} etc., the ability to tune the molecular magnetic properties of the lanthanide ions remains quite elusive\textsuperscript{2,8}. The intrinsic, magnetic properties of 4\textit{f} ions, namely, their large single-ion anisotropy and high degree of spin-orbit coupling allow for Ln-materials to have applications such as high density, molecule-based information storage, spintronic devices and quantum computing\textsuperscript{9}. Recent reports on lanthanide molecular magnets that seek to harness the large single-ion anisotropy of the lanthanides, do so by engineering a wide variety of chemical environments including radical-bridged complexes to promote superexchange interactions\textsuperscript{10-15} low coordination number (CN < 8) complexes\textsuperscript{16-19} and many di-cyclopentadienyl (metallocene) complexes\textsuperscript{20-22}.

There has, however, been comparatively very little work done on optimizing both the optical and magnetic properties of the lanthanides simultaneously, or using the lessons learned from harnessing the optical properties to inform design of lanthanide molecular magnets\textsuperscript{23}. Bi-functional Ln-materials that display useful photophysical and magnetic properties are advantageous because they could display unusual properties, e.g. optical polarization of nuclear spin\textsuperscript{24} and yield insights into the fundamental properties of \textit{f}-electrons by studying excited state dynamics in a magnetic field. Such work would require a ligand platform that can: i) exert a large degree of control over the primary coordination sphere of the lanthanides, ii) sensitize lanthanide luminescence and iii) accommodate a wide variety of ring substituents to facilitate tunability of properties\textsuperscript{23}.

Pyrazolylborate ligands (H\textsubscript{4-x}BP\textsubscript{x}z\textsubscript{y}) meet all these criteria. They are widely used to make lanthanide chelates owing to their ability to control the spherical coordination environment of \textit{f}-block elements \textit{via} steric bulk/chelate effect\textsuperscript{25,26} and can accommodate a very diverse array of ring substituents\textsuperscript{27-29}. Moreover, lanthanide pyrazolylborates, Ln(H\textsubscript{4-x}BP\textsubscript{x}z\textsubscript{y})\textsubscript{y}, have been characterized as light-emitting devices (LEDs)\textsuperscript{30,31} single-molecule magnets (SMMs)\textsuperscript{32,33} and even magneto-luminescent materials that display both sensitized luminescence and SMM properties\textsuperscript{34}. Despite the breadth of work done on harnessing the desirable, opto-electronic and magnetic properties of the \textit{f}-elements using pyrazolylborate ligands, our understanding of how ring substituents affect the properties of Ln(H\textsubscript{4-x}BP\textsubscript{x}z\textsubscript{y})\textsubscript{y} materials is lacking, especially when compared to Ln-benzoate or Ln-\textit{β}diketonate systems\textsuperscript{35}. Latva et al.,\textsuperscript{36} Tsaryuk et al.,\textsuperscript{37,38} de Bettencourt-Dias et al.,\textsuperscript{39,40} Raymond et al.\textsuperscript{41} among others, have detailed descriptions on how to tune the optical properties of Ln hybrid materials using aromatic ring substituents to control the antenna effect. The antenna effect
describes the energy transfer from the S_1 or T_1 states of coordinated “antenna” ligands (organic chromophores) to lanthanide ions’ 2S+1LJ states by the Förster or Dexter energy transfer mechanisms. The influence of both electron-donating and electron-withdrawing groups, as well as the impact of the number of substituents and ring position on the photophysical properties of lanthanide complexes is well understood and has been implemented with great success.\textsuperscript{35} Conversely, less explored is the influence of said substituent effects on slow magnetic relaxation dynamics (SMM properties), considering both structural changes (intermolecular interactions) and perturbations of the crystal field experience by the Ln\textsuperscript{3+} ion. We are aware of only a single report, by Goswami, Venugopalan, Patra and coworkers on the influence of halo-substitution on the optical and magnetic properties of lanthanide amino-bisphenol complexes that addresses the impact of substituent (halogen) effects on magnetic properties of Ln-materials.\textsuperscript{42} Given the variety of lanthanide molecular magnets with pyrazolylborates and our lab’s recent work with selective functionalization of trispyrazolylborate (Tp\textsuperscript{-}) ligands,\textsuperscript{29, 43} we postulate that asymmetrically functionalized Tp\textsuperscript{-} ligands (Figure 1) are an ideal platform for establishing how aromatic ring substituents influence the properties of lanthanide molecular magnets.

![Diagrams of asymmetric trispyrazolylborate ligands](image)

Figure 1: Diagrams of asymmetric trispyrazolylborate ligands, left – 3-nitrotrispyrazolylborate (3-NO\textsubscript{2}Tp\textsuperscript{-}) and right – 4-nitrotrispyrazolylborate (4-NO\textsubscript{2}Tp\textsuperscript{-}).

We previously reported five families of lanthanide 3-nitrotrispyrazolylborates, Ln(3-NO\textsubscript{2}Tp\textsubscript{x})\textsubscript{y}, complexes that displayed tunable nuclearity and charge transfer mediated optical properties, and we elucidated the impact of strongly electron-withdrawing substituents on the coordination chemistry and photophysical properties of Ln(H\textsubscript{4-x}Pz\textsubscript{x})\textsubscript{y} complexes.\textsuperscript{44} We noted that the drastic difference in structural types and photophysical properties, when compared to other homoleptic Ln(H\textsubscript{4-x}BPz\textsubscript{x})\textsubscript{y} complexes was primarily due to the presence of new binding site via the oxygen of the nitro-group (Ln—O\textsubscript{NO\textsubscript{2}}) on the 3-NO\textsubscript{2}Tp\textsuperscript{-}. With this in mind, we substituted 3-NO\textsubscript{2}Tp\textsuperscript{-} for the 4-nitrotrispyrazolylborate
ligand, 4-NO$_2$Tp$^-$, to investigate the influence of the nitro-group on lanthanide pyrazolylborates without Ln—O$_{NO_2}$ coordination. Herein, we report that the coordination compounds of 4-NO$_2$Tp$^-$ with Ln$^{3+}$ ions are indeed 9-coordinate homoleptic complexes, [Ln(4-NO$_2$Tp)$_3$] (Ln = La – Dy, except Pm) analogous to the previously reported LnTp$_3$. Moreover, the inclusion of the non-coordinating nitro-group imparts control over the crystal packing and crystallographic symmetry of [Ln(4-NO$_2$Tp)$_3$] which may be used as a tool to influence the slow magnetic relaxation of [Nd(4-NO$_2$Tp)$_3$]. The photophysics of [Ln(4-NO$_2$Tp)$_3$] feature Ln$^{3+}$-selective singlet sensitization of Eu$^{3+}$ and Tb$^{3+}$ and various intra-ligand charge transfer (ILCT) transitions between the $S_n$ and $T_n$ states of the boron-bridged pyrazole and 4-nitropyrazole rings. We also provide a comparative analysis of the performance of Tp$^-$ vs n-NO$_2$Tp$^-$ ($n = 3$ or 4) as Ln$^{3+}$ sensitizers and SMM-generating ligands (Tp$^-$ vs 4-NO$_2$Tp$^-$).

Results

Synthesis of Ln(4-NO$_2$Tp)$_3$·Solvent

The reported complexes, [Ln(4-NO$_2$Tp)$_3$] (Ln = La – Dy, except Pm, 1 – 9) were synthesized by combining methanolic solutions of LnCl$_3$ salts with [TBA][4-NO$_2$Tp]. The solid crude product may be readily isolated by removing the methanol in vacuo and washing away tert-butylammonium chloride in isopropanol. The complexes are stable in acetonitrile (as indicated by their well-defined NMR spectra, see Figures S6 – S13). They are also soluble in common solvents such as dichloromethane and acetone, but only sparingly soluble in methanol and ethanol and insoluble in benzene and isopropanol. This differs drastically from the non-functionalized LnTp$_3$ complexes which are insoluble in all solvents when Ln = La – Gd and only sparingly soluble in benzene and dichloromethane for Ln = Dy and Tb.$^{45}$ Crude [Ln(4-NO$_2$Tp)$_3$] can be recrystallized as one of two polymorphs, a hexane solvate, [Ln(4-NO$_2$Tp)$_3$]·C$_6$H$_{14}$ (a) and a benzene solvate, [Ln(4-NO$_2$Tp)$_3$]·7 C$_6$H$_6$ (b).

Crystal Structures

Structural Description of [Ln(4-NO$_2$Tp)$_3$]·C$_6$H$_{14}$. Compounds 1a – 9a are all isomorphous and hence only the crystal structure of 4a will be discussed in detail. 4a contains one crystallographically unique Nd$^{3+}$ ion coordinated to 9 nitrogen atoms from three unique
4-NO$_2$Tp$^-$ ligands, with the Nd$^{3+}$ center exhibiting a tricapped trigonal prismatic coordination geometry of approximately $D_{3h}$ site symmetry. Ln—N bonds lengths range from 2.565(2) – 2.579(3) Å for the nitrogen atoms of the trigonal prism and 2.739(3) – 2.753(2) Å for the capping nitrogen atoms. The mononuclear [Ln(4-NO$_2$Tp)$_3$] complex displays an approximate $C_{3h}$ point symmetry, analogous to that of the 9-coordinate LnTp$_3$ complexes, with a $C_3$ axis passing through the Nd$^{3+}$ center perpendicular by the plane defined by the three nitropyrazoles. However, unlike in LnTp$_3$, there are three unique NO$_2$···H-C hydrogen bonds between adjacent Ln(4-NO$_2$Tp)$_3$ molecules, whereas LnTp$_3$ does not feature any significant intermolecular interactions. The NO$_2$···H-C hydrogen bonds as shown Figure 2(b) range from 3.1916(1) Å to 3.4382(1) Å, where two of the three H bonds occur between pyrazole and 4-nitropyrazole rings and the last between two 4-nitropyrazole rings. 4a crystallizes in the $C_2/c$ space group and it contains two highly disordered hexane sites in the lattice. The hexane molecule does not significantly separate the [Ln(4-NO$_2$Tp)$_3$] molecules, resulting in fairly dense crystal packing in 4a with the shortest intermolecular Nd$^{3+}$-to-Nd$^{3+}$ distance being 9.471(6) Å, similar to LnTp$_3$ at 9.686(1) Å. Interestingly this packing features sheets of [Ln(4-NO$_2$Tp)$_3$] molecules, along the [001] direction, such that a given sheet is sandwiched between a parallel one and another that is slighted canted by $19^\circ$. (Figure S1).

![Figure 2: (a) Asymmetric unit of 4a (with the hexane omitted for clarity) featuring the [Ln(4-NO$_2$Tp)$_3$] complex. (b) NO$_2$···H-C hydrogen bonding between [Ln(4-NO$_2$Tp)$_3$] complexes forming a 2-D layer in the xy plane.](image-url)
Structural Description of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3] \cdot 7\text{C}_6\text{H}_6$ ($5\text{b}$, Ln = Sm and $8\text{b}$, Ln = Tb). Compounds $5\text{b}$ and $8\text{b}$ constitute a second solvate polymorph of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$, crystallized with 7 solvent benzene molecules per molecule of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$. Since $5\text{b}$ and $8\text{b}$ are isostructural and only the structure of $5\text{b}$ will be discussed. The $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complex of $5\text{b}$ (Ln = Sm) is the same as $4\text{a}$ (Ln = Nd) (Figure S2), with Sm—N bond lengths that range from 2.5427(11) – 2.5440(13) Å for the trigonal prism nitrogrens and 2.7408(11) Å for the capping nitrogens, however it crystallizes in the R-3 space group. Additionally, the crystallographic 3-fold rotoinversion axis overlaps with the molecular $C_3$ that through Sm$^{3+}$, resulting in only a third of the $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complex being present in the asymmetric unit of $5\text{b}$, while the entire molecule is contained with the asymmetric unit of $4\text{a}$. There are 7 lattice benzene molecules per molecule of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$, resulting in significantly less dense crystal packing of the $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ units with fairly long intermolecular Sm$^{3+}$-to-Sm$^{3+}$ distances, the shortest being 12.667(1) Å. All of the [Sm(4-NO₂Tp)₃] complexes lie perfectly parallel to each other and there are no significant non-covalent interactions between the monomers (Figure 3).

Figure 3: Packing diagram of $5\text{b}$ (solvent benzene molecules omitted for clarity) where the [Sm(4-NO₂Tp)₃] molecules align collinearly in parallel planes.

Photophysical Properties of 4-NO₂Tp⁻ and $[\text{Ln}(4\text{-NO}_2\text{Tp})_3] \cdot \text{C}_6\text{H}_{14}$

Optical Properties of 4-NO₂Tp⁻. We utilized diffuse reflectance and luminescence spectroscopy techniques, in addition to time-dependent density functional theory (TD-DFT) to fully characterize the photophysical properties of 4-NO₂Tp⁻. Diffuse reflectance
measurements for K[4-NO₂Tp] (Figure S14) reveal a broad absorption band, spanning the UV to blue region, between 225 and 430 nm. The solid-state luminescence spectra of K[4-NO₂Tp], 1a (fluorescence) and 7a (phosphorescence) spectra respectively, for 4-NO₂Tp⁻, are summarized in Figure 4. La and Gd complexes are well known to yield emission spectra that display decay of Sₙ and Tₙ states almost exclusively⁴⁴, ⁴⁶, ⁴⁷ and are included to aid in characterization of those transitions/states with respect to 4-NO₂Tp⁻. The similar profiles for all three (emission) spectra, even 7a at 77K, indicate that the decay of the Tₙ states of 4-NO₂Tp⁻ is non-radiative (NR) and/or that T₁ state is unstable and excitation energy is readily lost. The most probable cause would be the NO₂-group intra-ligand charge transfer (ICLT) quenching pathway, described by Tsaryuk et al., where excitation energy is lost due to the non-radiative π*-n_NO₂ transition.⁴⁷, ⁴⁸

Figure 4: Top: Calculated S₀ → S₁ transition of Calc-1 as predicted by TD-DFT. Bottom: room temperature luminescence excitation (left, broken lines) and emission (right, solid lines) of K[4-NO₂Tp] (λ_exc = 393 nm, λ_em = 590 nm), 1a (λ_exc = 400 nm, λ_em = 481 nm) and 7a (at 77 K, λ_exc = 394 nm, λ_em = 481 nm). The excitation peak at 400 nm is assigned as S₀ → S₁ of 4-NO₂Tp⁻. * - background signal from the Xe arc lamp observable owing to very weak emission intensity of 1a and 7a.

To assign the S₀ → S₁ and T₁ → S₀ transitions of 4-NO₂Tp⁻ associated with the antenna effect, we carried out TD-DFT calculations on a geometry optimized model of 1, Calc-1 (Figure 4 and Figure S24). The population analysis of Calc-1 indicates that the HOMOs and LUMOs of the ligand are localized at the π systems of aromatic pyrazole (Pz) and 4-nitropyrazole (4-NO₂Pz) rings. There is good agreement between the calculated absorption spectrum of
Calc-1 and the solution absorption spectrum of crude 1 in acetonitrile (Figure 5). However, the low energy absorptions in the excitation spectra of K[4-NO₂Tp] and 1a at ~400 nm, that lead to radiative decay (ca 485 nm) are not predicted by TD-DFT nor are they present in the solution absorption spectrum. We attribute this to the nature of collecting luminescence excitation spectra where only transitions that lead to emission can be observed and not necessarily the transitions with large ε values, which is what is typically observed in an absorption spectrum. Since reflectance spectroscopy is sensitive to transitions with very low molar absorptivity/f-oscillator strengths (see Ln³⁺ absorptions in Figure S18 – S24), we note that the 400 nm transition of 4-NO₂Tp⁻ (which has a very low ε); is present in the reflectance spectrum of 1a. Given that the higher energy transitions with larger oscillator strengths do not lead to emission from 4-NO₂Tp⁻, assignment of the peaks in the excitation spectra is quite difficult. However, based on the TD-DFT calculations (Figure 5) and our previous work with the 3-NO₂Tp⁻ ligand and we assign the 4-NO₂Tp⁻ transitions as:

- Excitation peak at 400 nm: \( S_0 \rightarrow S_1, \pi_{NO_2} \rightarrow \pi^*_{4-NO_2Pz} \) ICLT,
- Emission at 485 nm: \( S_1 \rightarrow S_0, \pi^*_{4-NO_2Pz} \rightarrow \pi_{NO_2} \) ICLT,
- Theoretical emission of \( T_1 \rightarrow S_0 \) being \( \pi^*_{4-NO_2Pz} \rightarrow \pi_{NO_2} \) ILCT

Figure 5: Left – Electronic absorption spectrum (solid line) of crude 1 in acetonitrile (1.03x10⁻⁵ M) and calculated UV-VIS of Calc-1 in the gas phase. Right – TD-DFT output of the assigned \( S_0 \rightarrow S_1 \) as an ICLT \( \pi_{Pz} \rightarrow \pi^*_{4-NO_2Pz} \) transition and the calculated \( S_0 \rightarrow T_1 \) transition associated with the antenna effect.

*Luminescence Properties of [Ln(4-NO₂Tp)₃]·C₆H₁₄. All of the reported complexes (except 2a and 7a) display Ln³⁺ emission in the UV-visible region, however this emission is due primarily
to direct $f\cdot f$ transitions and not sensitization via the 4-NO$_2$Tp$^-$ ligand. Figure 6, which displays the excitation spectra of 1a–9a (except 2a and 7a) and the weak (or in some cases absent) absorption associated with 4-NO$_2$Tp$^-$, highlights that 4-NO$_2$Tp$^-$ is an inefficient sensitizer for Ln$^{3+}$ emission. Interestingly, the presence of several direct $f\cdot f$ absorption peaks in Figure 6 reveal that 4-NO$_2$Tp$^-$ does not directly quench Ln$^{3+}$ luminescence via Ln$^{3+}$-to-4-NO$_2$Tp$^-$ back-energy transfer and that direct $f\cdot f$ absorption and/or Ln$^{3+}$-to-Ln$^{3+}$ energy transfer (energy migration) are fairly efficient sensitization mechanisms. 2 likely does not display room temperature luminescence due to a fast $d_{\text{Ce}} \rightarrow \pi^*$ 4-NO$_2$Pz metal-to-ligand charge transfer (MLCT) and subsequent non-radiative $\pi^*$ 4-NO$_2$Pz $\rightarrow \pi NO_2$ transition, analogous to monomeric, [Ce(3-NO$_2$Tp)$_2$(NO$_3$)].

6a and 8a are the only compounds that feature a significant absorption band ca. 330–340 nm that could be attributed to ligand absorption and sensitization via 4-NO$_2$Tp$^-$. This band coincides somewhat with the absorption at 284 nm in the absorption spectrum of crude 1 and a $\pi_{\text{Pz}} \rightarrow \pi^*$ 4-NO$_2$Pz transition predicted at 276 nm for Calc-1 and therefore, this peak is assigned as the $S_0 \rightarrow S_7$, $\pi_{\text{Pz}} \rightarrow \pi^*$ 4-NO$_2$Pz ICLT transition. The disparity between the transitions observed in the absorption spectrum versus the excitation and emission spectra may be attributed to two distinct pathways associated with luminescence vs energy transfer to Eu$^{3+}$/Tb$^{3+}$; usually these pathways are identical (to be discussed later, see Figure 10). The ability of 4-NO$_2$Tp$^-$ to weakly sensitize Tb$^{3+}$ and Eu$^{3+}$ emission suggests that the $T_1$ state of 4-NO$_2$Tp$^-$ (which we could not determine experimentally), may have enough energy to sensitize Eu$^{3+}$ ($^5D_0$, 17,500 cm$^{-1}$) and Tb ($^5D_4$, 21,500 cm$^{-1}$) emission, yet may be too short lived to participate in energy transfer for the lanthanide ions studied, and that the rate of non-radiative decay via a fast $\pi^*$ 4-NO$_2$Pz $\rightarrow \pi NO_2$ transition is large ($k_{\text{nonrad}} \gg k_{\text{rad}}$). Another explanation for the sensitized emission in 6a and 8a and not the other lanthanides, may be a singlet energy transfer pathway via the $S_0 \rightarrow S_7$, $\pi_{\text{Pz}} \rightarrow \pi^*$ 4-NO$_2$Pz ICLT transition that typically only Eu$^{3+}$ and Tb$^{3+}$ can participate in, whereas triplet sensitization is usually necessary for more weakly luminescent lanthanides (Pr$^{3+}$, Sm$^{3+}$, Dy$^{3+}$).
Figure 6: 298 K temperature solid-state luminescence excitation (left, broken lines) and emission (right, solid lines) of $1a$ ($\lambda_{\text{exc}} = 400 \text{ nm}$, $\lambda_{\text{em}} = 481 \text{ nm}$), $3a$ ($\lambda_{\text{exc}} = 446 \text{ nm}$, $\lambda_{\text{em}} = 602 \text{ nm}$), $4a$ ($\lambda_{\text{exc}} = 350 \text{ nm}$), $5a$ ($\lambda_{\text{exc}} = 405 \text{ nm}$, $\lambda_{\text{em}} = 600 \text{ nm}$), $6a$ ($\lambda_{\text{exc}} = 394 \text{ nm}$, $\lambda_{\text{em}} = 700 \text{ nm}$), $8a$ ($\lambda_{\text{exc}} = 486 \text{ nm}$, $\lambda_{\text{em}} = 544 \text{ nm}$) and $9a$ ($\lambda_{\text{exc}} = 450 \text{ nm}$, $\lambda_{\text{em}} = 575 \text{ nm}$) with assignments of the various $4$-$\text{NO}_2\text{Tp}^-$ or direct $f$-$\text{to}-f$ $\text{Ln}^{3+}$ transitions. The emission spectrum of $4a$ collected using 350 nm may be a $4$-$\text{NO}_2\text{Tp}^-$ transition or Nd$^{3+}$ absorption at $\sim 350 \text{ nm}$ ($^4I_{11/2}$).
Magnetic Properties of \([\text{Ln}(4\text{-NO}_2\text{Tp})_3] \text{C}_6\text{H}_{14}\)

Figure 7: Temperature dependence of \(\chi m T\) product at 1000 Oe for 4a (Nd, ○), 8a (Tb, □) and 9a (Dy, △). Solid lines correspond to simulations using the crystal field parameters of set 1 in Table 1, dashed lines to those using set 2.

**Static Magnetic Measurements.** The magnetic susceptibility of 4a, 8a and 9a were studied under a static field of 1000 Oe (0.1 T) as shown in Figure 7. The room temperature \(\chi m T\) values were 1.65 cm\(^3\)K/mol, 11.85 cm\(^3\)K/mol and 13.93 cm\(^3\)K/mol for 4a, 8a and 9a respectively. These values agree well with those anticipated for free uncoupled \(\text{Ln}^{3+}\) ions at 1.64 cm\(^3\)K/mol (\(\text{Ln} = \text{Nd}, \quad ^{4}I_{9/2}, S = 3/2, L = 6, g = 8/11\)), 11.82 cm\(^3\)K/mol (\(\text{Ln} = \text{Tb}, \quad ^{7}F_6, S = 3, L = 3, g = 3/2\)) and 14.17 cm\(^3\)K/mol (\(\text{Ln} = \text{Dy}, \quad ^{6}H_{15/2}, S = 5/2, L = 5, g = 4/3\)). For all three compounds, \(\chi m T\) decreases with \(T\), owing to the depopulation of higher energy \(m_J\) states generated by crystal field splitting of the ground state.\(^{34}\) Assuming a perfect \(D_{3h}\) coordination sphere for the lanthanide center, the crystal field Hamiltonian can be expressed as:

\[
\hat{H}_{CF} = B_2^0 \theta_2 \hat{O}_2^q + B_4^0 \theta_4 \hat{O}_4^q + B_6^0 \theta_6 \hat{O}_6^0 + B_6^6 \theta_6 \hat{O}_6^6
\]

where \(B_k^q\) are the crystal field parameters (including orbital reduction parameters), \(\theta_k\), are the operator equivalent factors and \(\hat{O}_k^q\) the Stevens operator equivalents.\(^{51,52}\) A survey of the crystal field parameters between \(-5000\) and \(+5000\) cm\(^{-1}\) indicated that the best fits of the experimental data around \(B_0^6 = B_0^6 = 0\) for all three cations. While the negligible value of the sole equatorial plane of the tricapped trigonal prismatic coordination sphere, the \(B_0^6\) value is more surprising for 4f centers. Attempts to determine values for the \(B_2^0\) and \(B_4^0\) parameters were
unsuccessful owing to overparameterization of the systems (Figures S26 – S28). Even when further narrowing the possibilities by assuming a linear dependence of the crystal field parameters on the $f$-electron count of the metal center, two sets of parameters remained equally suited to account for the DC magnetization data (Table 1, Figure 7 and S29).

Table 1: Crystal field parameters suitable for simulations of the static magnetization.

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<tr>
<th>Crystal field parameters (cm$^{-1}$)</th>
<th>4a</th>
<th>8a</th>
<th>9a</th>
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<td>$B^0_2/B^0_3$ (set 1)</td>
<td>960/-300</td>
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<td>-460/-20</td>
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<td>$B^0_2/B^0_4$ (set 2)</td>
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Dynamic Magnetic Measurements. Dynamic (ac) magnetic susceptibility experiments were collected on 4a, 8a and 9a in the 0 – 1000 Hz frequency range between 1.8 and 9.8 K. None of the complexes displayed an out-of-phase signal in the absence of a magnetic field bias, but the Nd$^{3+}$ complex, 4a did so, under a small applied field (H = 400 Oe). $\chi''_m$ vs $f$ and $\chi''_m$ vs $f$ isotherms are presented in Error! Reference source not found.(a) and (b) respectively and the frequency dependence of $\chi''_m$ confirm that 4a is indeed a single-molecule magnet. The time dependence of the relaxation times, extracted using the CCFit2 program, can be modelled using equation 1, which contains a direct term (AT) and a two phonons Raman term.

$$\tau^{-1} = AT + \tau_0^{-1} \left( \frac{e^{-\frac{U_{eff}}{k_B T}}}{e^{-\frac{U_{eff}}{k_B T}} - 1} \right)^2$$

Since 4a is a field-induced SMM, no quantum tunneling parameter was included when modelling the relaxation data. Full details on all of the terms and parameters used for the fit are outlined in Figure 11 and S30. Initial inclusion of a Raman term (CT$^n$) yielded a power dependence $n$ term of $\sim$3.5; since this is a significant departure from the idealized Raman relaxation mechanism, we excluded any direct Raman contribution. Moreover, the use of a model with an Orbach ($\tau_0^{-1}e^{-\frac{U_{eff}}{k_B T}}$) and a direct term (AT) yielded a sufficient model, however the $U_{eff}$ was significantly smaller than what is expected for a true Orbach process at 14 cm$^{-1}$. We therefore turned to a model with direct and two-phonons Raman terms, which yielded a nearly identical $U_{eff}$, or rather $E_{vib}$ at 13 cm$^{-1}$ (Figure S30), corresponding to phonon-coupled under-barrier relaxation process rather than a true $\Delta m_1$ transition/Orbach process.
Discussion

Ligand Design for Tp−-based Antenna Ligands

Table 2: Photophysical data comparing [EuTp₃], [Eu(3-NO₂Tp)₂(NO₃)] and 6a

<table>
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<th>Compounds</th>
<th>τ₄₃5 /ms</th>
<th>τ₄₅5 /ms</th>
<th>Φ₄₃5 /%</th>
<th>Φ₄₅5 (Φ₄₅5’ /%)</th>
<th>k₄₅ /s⁻¹</th>
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<td>[EuTp₃]</td>
<td>1.84</td>
<td>9.00</td>
<td>43</td>
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<tr>
<td>[Eu(3-NO₂Tp)₂(NO₃)]</td>
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<td>0.113 ± 0.07</td>
<td>22</td>
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<td>506 ± 72</td>
<td>18.2</td>
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<td>[Eu(4-NO₂Tp)₃]C₆H₁₄ (6a)</td>
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<tr>
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<td></td>
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<td>395 ± 53</td>
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</table>

a – η₄₅ = (Φ₄₅ /Φ₄₅’ ) according to de Sá et al.⁵⁶, b – k₄₅ = Φ₄₅ /τ₄₅, c – k₄₅₉ = (1/τ₄₅) – k₄₅, d – Measured at 77 K, e – Measured with a 340 nm excitation, f – Measured with a 395 nm excitation.

Comparison of the optical properties of the [Ln(4-NO₂Tp)₃] complexes and those of previously published complexes [LnTp₃] and [Ln(3-NO₂Tp)₂(NO₃)] shows the markedly inferior sensitizing efficiency of the 4-NO₂Tp⁻ ligand. Given the similarity of 3-NO₂Tp⁻ and 4-NO₂Tp⁻, including the prevalence in both ligands of πₚ₂ → π*ₙ-NO₂P₂ charge transfer transitions, predicted by TD-DFT and confirmed experimentally, this difference is rather surprising. To elucidate the origin of the disparity between the n-NO₂Tp⁻ (n = 3 or 4) ligands, we determined the quantum yield (Φ₄₅), emission lifetime (τ₄₅), and derived their intrinsic quantum yield (Φ₄₅), the rates of radiative (k₄₅) and nonradiative decay (k₄₅₉) as well as their efficiency of

Figure 8: (a) In-phase molar susceptibility (χ’ₘ) vs frequency and (b) out-of-phase molar susceptibility (χ”ₘ) vs frequency of 4a between 2 and 9 K at H = 400 Oe.
sensitization ($\eta_{sens}$) (Table 2). The radiative lifetime for Eu$^{3+}$ is similar for all three complexes, with a slight reduction in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)]. Expectedly, 10-coordinate [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] has a lower intrinsic quantum yield than the two 9-coordinate complexes, which show nearly identical $\Phi_{Eu}^{Eu}$. The primary difference between the EuTp-complexes is their quantum yields. Consistent with the reduction in sensitization efficiency often associated with nitrated antenna ligands, the quantum yield and radiative decay rate of 6a are about half of those of [EuTp$_3$] (~2.4 % vs 4.6 % for $\Phi_{exp}$ and ~13 s$^{-1}$ vs 25 s$^{-1}$ for $k_{rad}$), however the quantum yield and radiative decay rate for [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] are 4 % and 21 s$^{-1}$ respectively, approximately equal to those of [EuTp$_3$]. The reduction in the radiative decay of 6a as compared to [EuTp$_3$] can be attributed to the fast decay/short lifetime of the T$_1$ state of 4-NO$_2$Tp$^-$ and inefficient energy transfer to Eu$^{3+}$ owing to the presence of the nitro-group. However, the nitro group appears to have no impact in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)].

![Figure 9](image.png)

<table>
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<th>NO$_2$–H–C Hydrogen Bond</th>
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<td></td>
<td><strong>5.90</strong></td>
<td><strong>1.59</strong></td>
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</table>

Figure 9: Top: Representative Natural Bond Orbitals (NBOs) of the $\pi$–$\pi$ stacking interactions in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] and the NO$_2$–H–C hydrogen bonding in 6a. Bottom: Table summarizing the donor and acceptor pairs and associated contribution to the stabilization energy in kJ/mol.

Examination of the differences between [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] and 6a seem to indicate that the triplet state of 3-NO$_2$Tp$^-$ is more stable/longer-lived than that of 4-NO$_2$Tp$^-$, given that the emission from 4-NO$_2$Tp$^-$ could not be observed at even 77 K, while we recorded room temperature T$_1$ emission from 3-NO$_2$Tp$^-$ in [Gd(3-NO$_2$Tp)$_2$(NO$_3$)]. TD-DFT calculations predict that both 3-NO$_2$Tp$^-$ and 4-NO$_2$Tp$^-$ should have similar triplet energies (422 and 404 nm respectively), indicating that the enhanced stability of 3-NO$_2$Tp$^-$ must be due to external
factors, outside of the energy of the molecular orbitals. One possible explanation is revealed by a comparison of the non-covalent interactions in the crystal structures of [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] and 6a. These interactions are π-π stacking and NO$_2$···H-C hydrogen bonding in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] and 6a respectively, both interactions involving the n-NO$_2$Pz ($n = 3$ or $4$) rings. Natural Bond Order (NBO) derived stabilization energies associated with each NCI (π-π stacking or NO$_2$···H-C hydrogen bonding) (Figure 9) and indicates that the π-π stacking interactions are significantly stronger than NO$_2$···H-C hydrogen bonding. We postulate that the stronger π-π stacking NCIs of [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] increase the rigidity of 3-NO$_2$Tp$^-$. The coordination of the 3-NO$_2$ group to the Ln$^{3+}$ centers is likely to also contribute to an increased rigidity, accounting overall for the higher sensitization efficiency observed in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] vs 6a. This is consistent with recent reports on NCIs stabilizing the triplet state of aromatic ligands.$^{57}$-$^{60}$ The enhanced stability afforded to the T$_1$ state of 3-NO$_2$Tp$^-$ in [Eu(3-NO$_2$Tp)$_2$(NO$_3$)] likely increased its lifetime enough that it could undergo substantial energy transfer with Eu$^{3+}$ (Figure 10), while the T$_1$ state of 4-NO$_2$Tp$^-$ undergoes a rapid non-radiative decay. By changing the position of the ring substituent in n-NO$_2$Tp$^-~(n = 3$ or $4)$ ligands, we can control the type and strength of NCIs in Ln(n-NO$_2$Tp)$_x$ complexes and consequently tune the efficiency of n-NO$_2$Tp$^-$-to-Ln$^{3+}$ energy transfer (s) using second-sphere interactions.
Ligand Design for Tp⁻-based Single-Molecule Magnets

The capped trigonal prismatic coordination sphere provided by the 4-NO₂Tp⁻ ligands corresponds to a relatively strongly axial crystal. Therefore, single molecule magnet properties are more likely to be obtained with lanthanide ions with an oblate electronic density along with a relatively high J value.⁸ Those include neodymium (J = 9/2), terbium (J = 6) and dysprosium (J = 15/2). Magnetic studies on 4a (Nd), 8a (Tb) and 9a (Dy) offer a preliminary confirmation of the axiality of the crystal field, as no B_k^q term with q ≠ 0 appears in the modelisation of the dc magnetization data. However, either set of crystal field parameters (Table 1) obtained from those fits indicate ground states with m_J = 0 for 8a and m_J = ½ for 9a, in agreement with the absence of single molecule magnetism observed for those complexes. Of the two sets obtained for 4a, the first corresponds to a ground state m_J = 3/2 compatible with the observed slow magnetic relaxation and should therefore be preferred to the second set which would indicate a m_J = ½ ground state.

In 4a, as in the unsubstituted analogue [NdTp₃]₃₂ slow relaxation can only be observed under a small external magnetic field. This indicates substantial quantum tunneling of the magnetization at zero field, and in turn the presence of some small equatorial contribution to the crystal field, albeit one that could not be quantified from the dc data. Interestingly, relaxation is about 5 times slower in 4a than in [NdTp₃] at the same temperature (Figure 11) despite the virtually identical geometry of the two complexes (and higher crystallographic symmetry in [NdTp₃]). Moreover, 4a’s relaxation barrier, E_vib is about 6 times larger than NdTp₃’s “Orbach” barrier (12.7 vs 2.8 cm⁻¹). [NdTp₃] was previously reported to have a small relaxation barrier (U_eff = 2.84 cm⁻¹, τ₀ = 4.2x10⁻⁹ s),³² likely not a “true” Orbach relaxation barrier but rather a value corresponding to under barrier relaxation due to vibronic coupling. Given that dilution of NdTp₃ with diamagnetic La³⁺ ions, did not significantly affect the relaxation behavior,³² the slight increase in intermolecular Ln³⁺-to-Ln³⁺ distances in 4a is likely not responsible for the improvement either, nor is the change from the parallel anisotropy axes in [NdTp₃]⁶¹ to the slightly canted layers of 4a, which would usually assumed to be detrimental to slow relaxation. A change in vibrational levels is therefore the most likely mechanism for the observed difference, linked to the lattice rigidifying effect of the NO₂···H-C
17 hydrogen bonding in 4a. This marked increase in relaxation times and under-barrier in 4a over [NdTp₃], signify that the former is a better SMM than the latter owing to the nitro-functionalization. The apparent similarity in the primary coordination sphere of 4a and [NdTp₃] facilitates the first example of the influence of a strongly electron-withdrawing group on relaxation dynamics via a direct comparison of the two Nd³⁺ chelates.

![Figure 11: Temperature dependence of the magnetic relaxation times, under a small bias field, of [NdTp₃] (black triangles, 100 Oe) with the reported Orbach fit (black line), and 4a (blue squares, 400 Oe) with the fit (blue broken line) generated using equation (1). From the fitted AC data (solid lines), [NdTp₃]: Uₑff = 2.84(2) cm⁻¹, τ₀ = 4.2(2)x10⁻⁴ s; 4a: A = 318 (8) K, Uₑff = 12.7(1.6) cm⁻¹ and τ₀ = 4.1(1.6)x10⁻⁵ s.](image)

### Conclusion

Eleven new lanthanide complexes with an asymmetric nitro-functionalized trispyrazolylborate ligand, 4-NO₂Tp⁻ were synthesized and their optical and magnetic properties are presented. The [Ln(4-NO₂Tp)₃] complexes display crystalline polymorphism based on the solvent used for recrystallization. The choice of lattice solvent can be used as a method of controlling crystal packing and supramolecular assembly (or lack thereof) via NO₂····H-C hydrogen bonding. An in-depth analysis of the optical properties of 4-NO₂Tp⁻ revealed two distinct pathways for luminescence and energy transfer comprised of several ILCT transitions such as nNO₂ → π*₄-NO₂Pz and πPz → π*₄-NO₂Pz absorptions and π*₄-NO₂Pz → nNO₂ and π*₄-NO₂Pz → πPz emissions. Moreover, 4-NO₂Tp⁻ is a poor sensitizer for Ln³⁺ emission (vs Tp⁻ and 3-NO₂Tp⁻), as a direct result of adding a non-coordinating nitro-group. With regard to the magnetic properties of the reported complexes, the opposite is true, whereby adding a nitro-group increased the relaxation times by a factor of 5 as well as the under-barrier of [Nd(4-NO₂Tp)₃] over [NdTp₃] by one order of magnitude. Our findings on the ability to control
the crystal packing/non-covalent interactions, diverse charge transfer optical properties and enhancement of relaxation barriers using 4-NO$_2$Tp$^-$ over Tp$^-$, in context with our previous work on [Ln(3-NO$_2$Tp)$_6$] complexes, highlights the utility of asymmetric Tp$^-$ ligands for tuning the properties of the lanthanides to generate and study magneto-luminescent materials and design better molecular magnets.

Associated Content

Electronic Supporting Information

The Electronic Supplementary Information is available free of charge on the ACS Publications website. Crystallographic information on CCDC 2226885 – 2226894, 2227039 can be obtained free of charge by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EK UK, emailing data_request@ccdc.cam.ac.uk or via their website http://www.ccdc.cam.ac.uk/data_request/cif.

PXRD patterns, IR, NMR and reflectance spectra, computational details, DC and AC SQUID data fits and parameters (PDF)

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The manuscript was written through contributions of all authors.
Notes
The authors declare no competing financial interests.

Acknowledgment
This material is based upon work supported by the Department of Energy National Nuclear Security Administration through the Nuclear Science and Security Consortium under Award Number DE-NA0003180. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or limited, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. This study is also supported by the Mary Hopkins Shepard Endowed Graduate Fellowship for Science Award through the Columbian College of Arts and Sciences (CCAS) at the George Washington University. This work was completed in part with resources provided by the High Performance Computing Cluster at the George Washington University, Research Technology Services. CHH acknowledges Alexander Marwitz (Georgetown University) for his help with determination of quantum yields and Grant Wilkinson (Georgia Institute of Technology) for collection of the static SQUID measurements.

Experimental
Materials. Lanthanide chloride salts, LnCl$_3$·7 H$_2$O (Ln = La$^{3+}$, Ce$^{3+}$, Fisher Scientific, 99.9%), PrCl$_3$·7 H$_2$O (Strem Chemicals, 99.9%), LnCl$_3$·6 H$_2$O (Ln = Nd$^{3+}$, Sm$^{3+}$ – Dy$^{3+}$, Aldrich, 99.9%) are commercially available and were used as received.
Synthesis of Tetrabutylammonium 4-nitrotrispyrazolylborate, [Bu₄N][4-NO₂Tp]. [Bu₄N][4-NO₂Tp] was prepared as described in the literature.²⁹, ⁴³ After each synthesis of [Bu₄N][4-NO₂Tp], a standard solution, typically 0.3 M, was prepared by dissolving the reaction product in methanol.

Synthesis of Potassium 4-nitrotrispyrazolylborate, K[4-NO₂Tp]. K[4-NO₂Tp] was prepared by dissolving 4-nitropyrazole (0.4485 g, 4 mmol) and potassium trispyrazolylborate (1.000 g, 4 mmol) in dry ethyl acetate and heating under reflux for 2 hours. Pentane (50 mL) was added to the cloudy mixture which was then placed in a refrigerator at 5 °C overnight. Two distinct phases were always isolated from this reaction, a white powder of K[4-NO₂Tp] in very low yield (> 5 %) and a yellow powdery mixture of K[4-NO₂Tp] and 4-nitropyrazole. Owing to the low yields, the solvent-free synthesis with the tetrabutylammonium salt was always used to generate the 4-NO₂Tp⁻.

Synthesis of Ln(4-NO₂Tp)₃·Solvent (1 – 9). Complexes of 1 – 9 were synthesized using the same procedure differing only in the recrystallization conditions. A standard solution of LnCl₃ was generated by dissolving an appropriate amount of the salt, e.g. LaCl₃ (0.4910g, 2.002 mmol) in methanol (20 mL, 0.1 M). Solutions of LaCl₃ (1 mL, 0.1 M, 1 mmol) and [Bu₄N][4-NO₂Tp] (1 mL, 0.3 M, 3 mmol) were combined in a scintillation vial. The solvent was removed in-vacuo and the oil-like residue was suspended in 3 mL 1:1 cyclohexane:isopropanol; vacuum filtration and washing with of isopropanol (3 x 3 mL) yielded dry, crude La(4-NO₂Tp)₃ as a white powder. Recrystallized solvates were prepared by dissolving the crude product in of methanol (3 mL, La – Eu) or 1:1 methanol:ethanol (3 mL, Gd – Dy). Hexanes or benzene for (6 mL) was layered on top of the solution. Single crystals of hexane (1a – 9a) or benzene (5b, 8b) solvates were observed after 1 day and the final product was isolated and collected after 3 days via vacuum filtration and washing with hexanes (3 x 3 mL). Crystals of the hexane polymorph had a tendency to re-dissolve in the mother liquor after 5 or 6 days. X-ray diffraction quality single crystals were collected when the recrystallization was carried out in a sealed scintillation vial, while a microcrystalline powder was obtained when the synthesis was done in a parafilmed 25 mL Erlenmeyer flask.
[La(4-NO2Tp)3]·C6H14 (1). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 51 %.

[Ce(4-NO2Tp)3]·C6H14 (2). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 52 %.

[Pr(4-NO2Tp)3]·C6H14 (3). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 45 %.

[Nd(4-NO2Tp)3]·C6H14 (4). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 51 %.

[Sm(4-NO2Tp)3]·C6H14 (5). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 36 %. \(\tau = 0.116 \text{ ms (} \lambda_{\text{exc}} = 340 \text{ nm (}^6\!P_{3/2}) , \lambda_{\text{em}} = 604 \text{ nm})\)

[Eu(4-NO2Tp)3]·C6H14 (6). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 30 %. \(\tau = 1.80 \text{ ms (} \lambda_{\text{exc}} = 394 \text{ nm (}^5\!L_6) , \lambda_{\text{em}} = 700 \text{ nm})\)

[Gd(4-NO2Tp)3]·C6H14 (7). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 33 %.

[Tb(4-NO2Tp)3]·C6H14 (8). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 50 %. \(\tau = 1.87 \text{ ms (} \lambda_{\text{exc}} = 486 \text{ nm (}^5\!D_4) , \lambda_{\text{em}} = 542 \text{ nm})\)

[Dy(4-NO2Tp)3]·C6H14 (9). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 36 %.

[Sm(4-NO2Tp)3]·7C6H6 (5b). White single crystals were isolated from methanol/benzene. Yield (recrystallized): 44 %.

[Tb(4-NO2Tp)3]·7C6H6 (8b). White single crystals were isolated from methanol/benzene. Yield (recrystallized): 40 %.

**X-ray Structure Determination.** Crystals of 1a – 9a, 5b and 8b, were harvested from mother liquors and mounted on 50 µm MiTeGen mounts. All measurements were made using monochromated microfocus Mo Kα (\(\lambda = 0.71073\)) radiation on a Bruker D8 Quest, equipped with a Photon II detector. All reflection data were collected at 100(2) K with 0.5° φ and ω scans. The data were reduced using SAINT,\(^6^2\) and empirical absorption corrections were applied using SADABS,\(^6^3\) for 1a – 9a, 5b and 8b. Structure solutions solved using intrinsic phasing were performed using the ShelXT package\(^6^4\) in APEX III. All data were subsequently refined using SHELXL-2014 in the program SHELXL.\(^6^5\) All atoms were refined anisotropically.
The reported CIFs for 1a – 9a, feature structural models that were refined with scattering contributions from the disordered hexane sites removed from the diffraction data using the bypass procedure in PLATON.66 The electron count from the “squeezed” model converged in good agreement with a single hexane molecule. Aromatic hydrogen atoms were placed in idealized positions and allowed to ride on the coordinates of the parent atom with isotropic thermal parameters (U\textsubscript{eq}) fixed at 1.2 U\textsubscript{eq} for all carbon atoms and at 1.5 U\textsubscript{eq} for all boron atoms. Details of the X-ray diffraction experiments and crystal data are summarized in Table 3.

Table 3: Crystallographic data for 1a – 9a, 5b and 8b.

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$R = R_2 = \sum |F_o| - |F_c| / \sum |F_o|$ for observed data only. $R_w = wR_2 = (\sum w(F_o^2 - F_c^2)^2)/(\sum w(F_c^2)^2))^{1/2}$ for all data.

**Powder X-ray Diffraction.** Powder X-ray diffraction (PXRD) data on the bulk recrystallization products from each sample were collected on a Rigaku Miniflex (Cu Kα 2θ = 5 – 60) and analyzed using the Match! software program. The PXRD patterns of the bulk products for 1a – 9a, 5b and 8b were used to check purity and reproducibility and are provided in ESI Figures S2 and S3.

**Infrared Spectroscopy.** Infrared spectra were collected from 650 to 4000 cm$^{-1}$ using a Perkin-Elmer Frontier FT-IR spectrophotometer with a diamond attenuated total reflectance (ATR) sample holder. The IR spectra of the bulk, recrystallized products for 1a – 9a, 5b and 8b were used to check purity and reproducibility and are provided in ESI Figures S4 and S5.

**1H Nuclear Magnetic Resonance Spectroscopy.** NMR spectra of crude 1 – 9 (no solvates) were recorded on a Varian 400 MHz spectrometer. Spectra of crude 1 – 9 (except 7) are provided in the ESI Figure S6 – S13.

**Photophysical Measurements.** Visible and NIR solid-state luminescence measurements were obtained at room temperature for 1a – 9a (and 77 K for 6). Luminescence spectra were collected with a Horiba Jobin Yvon Fluorolog-3 spectrophotometer using a 450 W xenon arc lamp combined with a double excitation monochromator and double emission monochromator. For spectra in the visible region, a photomultiplier tube at 950 V was used as the emission detector, whereas for spectra in the near-IR region, a liquid nitrogen cooled, Symphony II NIR InGaAs diode array detector was used as the emission detector. Data were collected and analyzed using the FluorEssence software package. The solid samples were mounted on a J1933 Solid Sample Holder using non-emitting high vacuum grease for room temperature scans. Low temperature luminescence measurements were collected on solid samples under vacuum using a Janis VPF-100 cryostat equipped with UV-grade fused silica windows coupled with a Lakshore model 325 temperature controller. Lifetime measurements were collected with a Horiba Jobin Yvon Flurolog-3 spectrophotometer adapted for time-correlated single photon counting (TCSPC) measurements using a xenon flash lamp as the
light source. Lifetime profiles for 5a, 6a and 8a were obtained using the TCSPC module and the data were fit using DAS6 software. Quantum yields measurements were collected in duplicate using a Horiba PTI QM-400 fluorometer using a PTFE powder holder under ambient conditions and an 8.9 cm integrating sphere with a Spectralon fluropolymer coating. The samples were crushed with a mortar and pestle, diluted with KBr in a 1:50 ratio of sample:KBr prior to data collection. Diffuse reflectance spectra were collected on solid samples at 298 K. The light source was a Mikropack DH-2000-BAL deuterium and halogen light source coupled with an Ocean Optics Flame detector. Scattered light was collected with a fiber-optic cable. Spectra were referenced with BaSO₄. Data were processed using OceanView spectroscopy software. The electronic absorption spectrum of 1 was collected on a SPECORD 600 UV-VIS diode array spectrophotometer.

**Magnetic SQUID Measurements.** Crystalline samples for static SQUID magnetometry were prepared inside a glovebox where a measured amount of sample was added to a half-sealed quartz tube using a glass pipet followed by a measured amount of eicosane. The top of the tube was then fitted to an Ultra Torr Swagelok adapter. This was taken out of the glovebox and the eicosane was melted using hot water to fix the sample. The assembly was then attached to a Schlenk line, and the top of the tube was sealed using an H₂/O₂ torch while the sample was under vacuum. The sealed tube was taped to a straw using Kapton tape and loaded onto the instrument. For the dynamic measurements, the samples were enclosed in a copper foil pouch and mounted on a quartz holder with Kapton tape. The molar diamagnetic susceptibilities of the compounds were estimated from their molar mass (\(\chi_{\text{dia}} \text{ (cm}^3\text{·mol}^{-1}) = -[\text{MW(g mol}^{-1}) \times 10^{-6}]/2\)) and subtracted from the experimental value. Data was collected at 0.1 T for static measurements and 0.04 T for dynamic measurements for using a Quantum Design SQUID MPMS3 magnetometer.

**Computational Methods.** Computational studies were conducted using the High-Performance Computing Cluster at The George Washington University. The input structure for Calc-1 was derived from the crystal structure of 1a. The frontier molecular orbitals and the UV/VIS spectrum of Calc-1 were computed using Density Functional Theory (DFT) in the Gaussian 16 software (Gaussian Inc.).⁶⁷ A ground state optimization was
performed on **Calc-1**, using the B3LYP\textsuperscript{68, 69} level of theory with the modified scalar-relativistic effective core potential (ECP) basis set def2-TZVP as implemented in the software with the def2-TZVP pseudopotential applied to La\textsuperscript{3+}.\textsuperscript{70-73} Geometry optimizations were performed on the input structure without symmetry constraints in the gas phase. Subsequent frequency calculations were performed on **Calc-1** to confirm that the optimized structure was its global minimum. No imaginary frequencies were present in the calculated IR and Raman spectra. Time-dependent DFT calculations were then conducted to determine the expected absorption spectra of **Calc-1** considering singlet (S\textsubscript{0} → S\textsubscript{n}) and triplet (S\textsubscript{0} → T\textsubscript{n}) transitions. 100 singlet and triplet states each were identified for **Calc-1**. NBO calculations were performed using **NBO7** on two models. Model A consisted of two molecules of [La(3-NO\textsubscript{2}Tp)\textsubscript{2}(NO\textsubscript{3})] (generated from crystallographically determined atomic coordinates of [Gd(3-NO\textsubscript{2}Tp)\textsubscript{2}(NO\textsubscript{3})]·\textsubscript{1/4} H\textsubscript{2}O) participating in a π-π stacking interaction. Model B comprised two [La(4-NO\textsubscript{2}Tp)]\textsuperscript{2+} units participating in a NO\textsubscript{2}···H-C hydrogen bond (generated from crystallographically determined atomic coordinates in **1a**). NBO second-order perturbation theory was applied to quantify the magnitude of the donor–acceptor interaction between adjacent complexes as well as to identify the atomic and molecular orbitals involved with Jmol as the visualization software.\textsuperscript{74}
References


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