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Tuning the optical and magnetic properties of lanthanide single-ion magnets using nitro-functionalized trispyrazolylborate ligands†

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We report the synthesis, crystal structures, photophysical and magnetic properties of 11 novel lanthanide complexes with the asymmetrically functionalized trispyrazolylborate ligand 4-nitrotrispyrazolylborate, 4-NO₂Tp⁻: [Ln(4-NO₂Tp)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*-NO₂Tp⁻ ligands are dominated by intra-ligand charge transfer (ILCT) transitions and that second-sphere interactions are critical to the stabilization of the T₁ state of *n*-NO₂Tp⁻ ligands and hence their ability to sensitize Ln³⁺ emission. The luminescence properties of the complexes indicate that 4-NO₂Tp⁻ is a poor sensitizer of Ln³⁺ emission, unlike 3-NO₂Tp⁻. Moreover, [Nd(4-NO₂Tp)₃] (crystallized as a hexane solvate) displays single-molecule magnet (SMM) properties, with longer relaxation times and larger barrier than the non-functionalized [NdTp₃], attributed to the addition of the NO₂-group and subsequent rigidification of the molecular structure.

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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 devices⁷ *etc.*, the ability to tune the molecular magnetic properties of the lanthanide ions remains quite elusive.^{2,8} The intrinsic, magnetic properties of 4f 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.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,^{10–15} low coordination number (CN < 8) complexes,^{16–19} and many dicyclopentadienyl (metallocene) complexes.^{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.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,²⁴ and yield insights into the fundamental properties of 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.²³

Pyrazolylborate ligands (H_{4–x}BPz_x) meet all these criteria. They are widely used to make lanthanide chelates owing to their ability to control the spherical coordination environment of f-block elements *via* steric bulk/chelate effect,^{25,26} and can accommodate a very diverse array of ring substituents.^{27–29} Moreover, lanthanide pyrazolylborates, [Ln(H_{4–x}BPz_x)_y], have been characterized as light-emitting devices (LEDs),^{30,31} single-

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molecule magnets (SMMs)^{32,33} and even magneto-luminescent materials that display both sensitized luminescence and SMM properties.³⁴ Despite the breadth of work done on harnessing the desirable, opto-electronic and magnetic properties of the f-elements using pyrazolylborate ligands, our understanding of how ring substituents affect the properties of [Ln(H_{4-x}BPz_x)_y] materials is lacking, especially when compared to Ln-benzoate or Ln-β-diketonate systems.³⁵

Latva *et al.*,³⁶ Tsaryuk *et al.*,^{37,38} de Bettencourt-Dias *et al.*,^{39,40} Raymond *et al.*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 S₁ or T₁ states of coordinated “antenna” ligands (organic chromophores) to lanthanide ions' ^{2S+1}L_J 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.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 Ln³⁺ ion. We are aware of only two reports, by Sushila *et al.* and Gálico *et al.*, on the influence of halo-substitution on the optical and magnetic properties of lanthanide amino-bisphenol and β-diketonate complexes respectively, that addresses the impact of substituent (halogen) effects on optical and magnetic properties of Ln-materials.^{42,43} Given the variety of lanthanide molecular magnets with pyrazolylborates and our lab's recent work with selective functionalization of trispyrazolylborate (Tp⁻) ligands,^{29,44} we postulate that asymmetrically functionalized Tp⁻ ligands (Fig. 1) are an ideal platform for establishing how aromatic ring substituents influence the properties of lanthanide molecular magnets.

We previously reported five families of lanthanide 3-nitrotripyrazolylborates, Ln(3-NO₂Tp)_x complexes that displayed tunable nuclearity and charge transfer mediated optical properties, and we elucidated the impact of strongly electron-with-

drawing substituents on the coordination chemistry and photophysical properties of Ln(H_{4-x}Pz_x)_y complexes.⁴⁵ We noted that the drastic difference in structural types and photophysical properties, when compared to other homoleptic Ln(H_{4-x}BPz_x)_y complexes was primarily due to the presence of new binding site *via* the oxygen of the nitro-group (Ln-O_{NO₂}) on the 3-NO₂Tp⁻. With this in mind, we substituted 3-NO₂Tp⁻ for the 4-nitrotripyrazolylborate ligand, 4-NO₂Tp⁻, to investigate the influence of the nitro-group on lanthanide pyrazolylborates without Ln-O_{NO₂} coordination. Herein, we report that the coordination compounds of 4-NO₂Tp⁻ with Ln³⁺ ions are indeed 9-coordinate homoleptic complexes, [Ln(4-NO₂Tp)₃] (Ln = La–Dy, except Pm) analogous to the previously reported [LnTp₃]. Moreover, the inclusion of the non-coordinating nitro-group imparts control over the crystal packing and crystallographic symmetry of [Ln(4-NO₂Tp)₃] which may be used as a tool to influence the slow magnetic relaxation of [Nd(4-NO₂Tp)₃]. The photophysics of [Ln(4-NO₂Tp)₃] feature Ln³⁺-selective singlet sensitization of Eu³⁺ and Tb³⁺ 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*-NO₂Tp⁻ (*n* = 3 or 4) as Ln³⁺ sensitizers and SMM-generating ligands (Tp⁻ vs. 4-NO₂Tp⁻).

Results

Synthesis of Ln(4-NO₂Tp)₃-solvent

The reported complexes, [Ln(4-NO₂Tp)₃] (Ln = La–Dy, except Pm, 1–9) were synthesized by combining methanolic solutions of LnCl₃ salts with [TBA][4-NO₂Tp]. 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 Fig. S7–S14†). 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 [LnTp₃] complexes which are insoluble in all solvents when Ln = La–Gd and only sparingly soluble in benzene and dichloromethane for Ln = Dy and Tb.⁴⁶ Crude [Ln(4-NO₂Tp)₃] can be recrystallized as one of two polymorphs, a hexane solvate, [Ln(4-NO₂Tp)₃]·C₆H₁₄ (a) and a benzene solvate, [Ln(4-NO₂Tp)₃]·7C₆H₆ (b).

Crystal structures

Structural description of [Ln(4-NO₂Tp)₃]·C₆H₁₄. Compounds 1a–9a are all isomorphous and hence only the crystal structure of 4a will be discussed in detail. 4a contains one crystallographically unique Nd³⁺ ion coordinated to 9 nitrogen atoms from three unique 4-NO₂Tp⁻ ligands, with the Nd³⁺ center exhibiting a tricapped trigonal prismatic coordination geometry of approximately D_{3h} site symmetry. Ln–N bonds lengths range from 2.565(2) to 2.579(3) Å for the nitrogen atoms of the trigonal prism and 2.739(3) to 2.753(2) Å for the capping nitro-

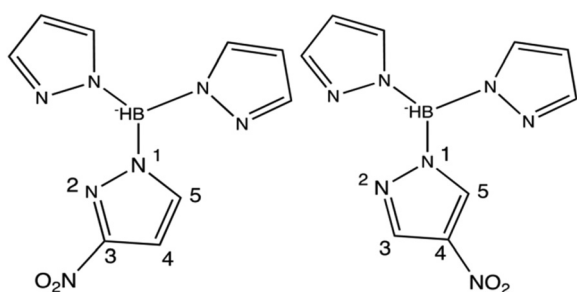


Fig. 1 Diagrams of asymmetric trispyrazolylborate ligands, left – 3-nitrotripyrazolylborate (3-NO₂Tp⁻) and right – 4-nitrotripyrazolylborate (4-NO₂Tp⁻).



gen atoms. The mononuclear $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complex displays an approximate C_{3h} point symmetry, analogous to that of the 9-coordinate $[\text{LnTp}_3]$ complexes,⁴⁶ with a C_3 axis passing through the Nd^{3+} center perpendicular to the plane defined by the three nitropyrazoles. However, unlike in $[\text{LnTp}_3]$, there are three unique $\text{NO}_2\cdots\text{H-C}$ hydrogen bonds between adjacent $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ molecules, whereas $[\text{LnTp}_3]$ does not feature any significant intermolecular interactions. The $\text{NO}_2\cdots\text{H-C}$ hydrogen bonds as shown Fig. 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. Compound **4a** crystallizes in the $C2/c$ space group and it contains two highly disordered hexane sites in the lattice. The hexane molecule does not significantly separate the $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ 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 $[\text{LnTp}_3]$ at 9.686(1) Å. Interestingly this packing features sheets of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ molecules, along the [001] direction, such that a given sheet is sandwiched between a parallel one and another that is slightly canted by 19° (Fig. S1†).

Structural description of $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]\cdot 7\text{C}_6\text{H}_6$ (5b**, Ln = Sm and **8b**, Ln = Tb).** Compounds **5b** and **8b** 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 **5b** and **8b** are isostructural and only the structure of **5b** will be discussed. The $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complex of **5b** (Ln = Sm) is the same as **4a** (Ln = Nd) (Fig. S2a†), with Sm-N bond lengths that range from 2.5427(11)–2.5440(13) Å for the trigonal prism nitrogens and 2.7408(11) Å for the capping nitrogens, however it crystallizes in the $R\bar{3}$ 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 **5b**, while the entire molecule is contained with the asymmetric unit of **4a**. 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 (Fig. S2b†), with fairly long intermolecular Sm^{3+} -to- Sm^{3+} distances, the shortest being 12.667(1) Å. All of the $[\text{Sm}(4\text{-NO}_2\text{Tp})_3]$ complexes lie perfectly parallel to each other and there are no significant non-covalent interactions between the monomers (Fig. 3).

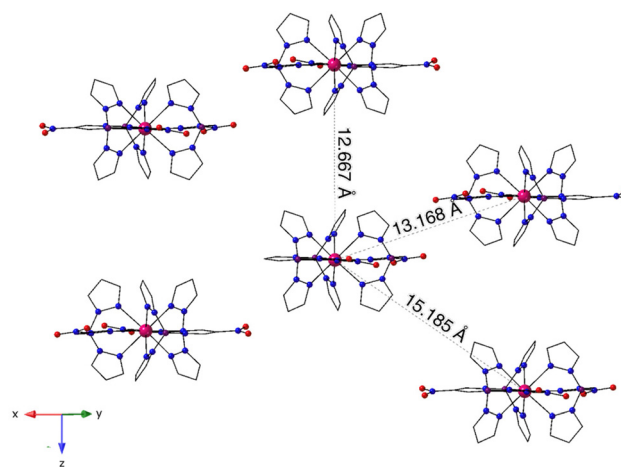


Fig. 3 Packing diagram of **5b** (solvent benzene molecules omitted for clarity) where the $[\text{Sm}(4\text{-NO}_2\text{Tp})_3]$ molecules align collinearly in parallel planes.

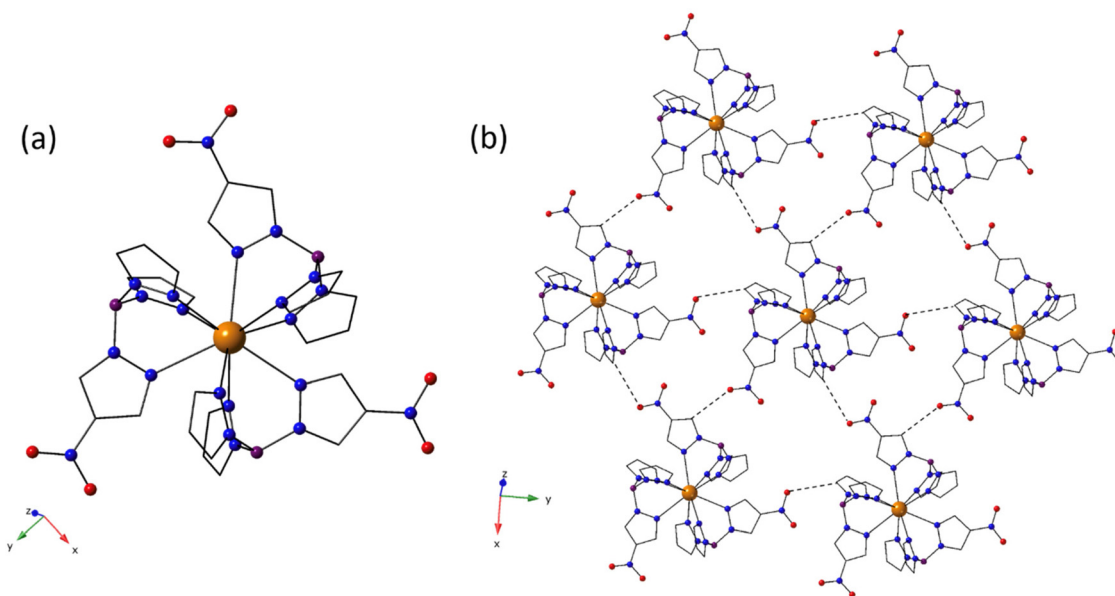


Fig. 2 (a) Asymmetric unit of **4a** (with the hexane omitted for clarity) featuring the $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complex. (b) $\text{NO}_2\cdots\text{H-C}$ hydrogen bonding between $[\text{Ln}(4\text{-NO}_2\text{Tp})_3]$ complexes forming a 2-D layer in the xy plane.



Photophysical properties of 4-NO₂Tp⁻ and [Ln(4-NO₂Tp)₃]-C₆H₁₄

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] (Fig. S16†) 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 Fig. 4. La and Gd complexes are well known to yield emission spectra that display decay of S_n and T_n states almost exclusively^{45,47,48} 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 77 K, indicate that the decay of the T_n 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 (ICTL) quenching pathway, described by Tsaryuk *et al.*, where excitation energy is lost due to the non-radiative π*–n_{NO₂} transition.^{37,38}

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** (Fig. 4 and Fig. S26†). 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 (Fig. 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 Fig. S19–S25†), 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

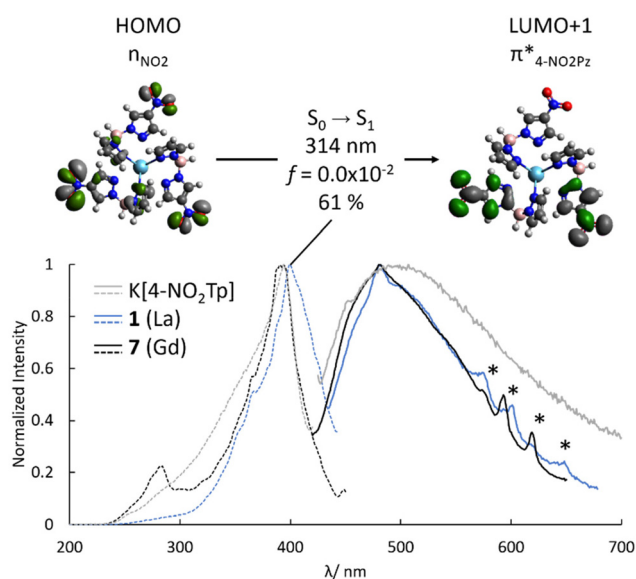


Fig. 4 Top: Calculated S₀ → S₁ transition of **Calc-1** as predicted by TD-DFT. Bottom: Room temperature luminescence excitation (left, broken lines) and emission (right, solid lines) of K[4-NO₂Tp] (λ_{exc} = 393 nm, λ_{em} = 490 nm), **1a** (λ_{exc} = 400 nm, λ_{em} = 481 nm) and **7a** (at 77 K, λ_{exc} = 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**.

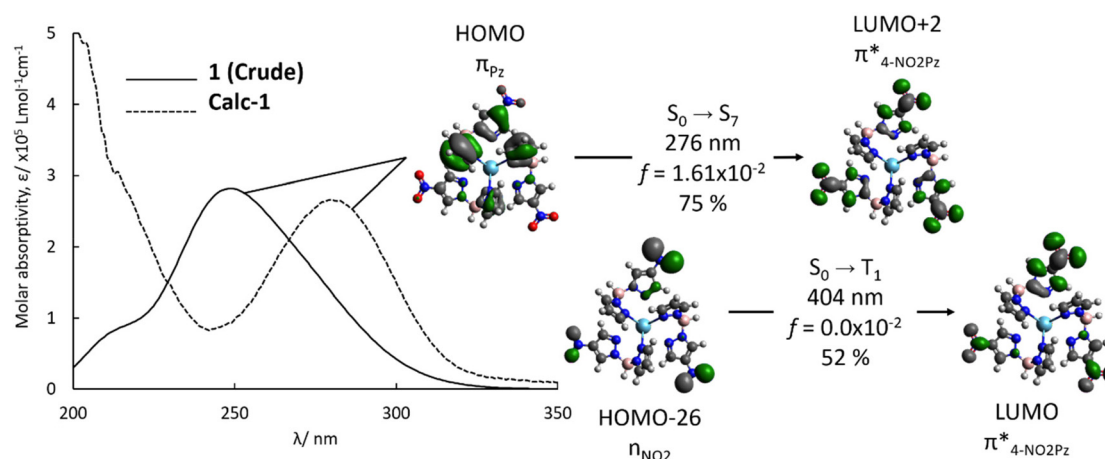


Fig. 5 Left – Electronic absorption spectrum (solid line) of crude **1** in acetonitrile (1.03 × 10⁻⁵ M) and calculated UV-VIS of **Calc-1** in the gas phase. Right – TD-DFT output of the assigned S₀ → S₇ as an ICTL π_{Pz} → π*_{4-NO₂Pz} transition and the calculated S₀ → T₁ transition associated with the antenna effect.



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 (Fig. 5) and our previous work with the 3-NO₂Tp⁻ ligand and we assign the 4-NO₂Tp⁻ transitions as:

excitation peak at 400 nm: S₀ → S₁, n_{NO₂} → π*_{4-NO₂Pz} ICLT,
emission at 485 nm: S₁ → S₀, π*_{4-NO₂Pz} → n_{NO₂} ICLT,
theoretical emission of T₁ → S₀: π*_{4-NO₂Pz} → n_{NO₂} ILCT.

Luminescence properties of [Ln(4-NO₂Tp)₃]·C₆H₁₄. All of the reported complexes (except **2a** and **7a**) display characteristic Ln³⁺ emission in the UV-visible region (Fig. 6). The profiles and relative intensities for **3a** (Pr), **4a** (Nd), **5a** (Sm), **8a** (Tb) and **9a** (Dy) emission spectra are typical for the line-like, f-f transitions of the trivalent lanthanides.^{34,45} The europium analogue, **6a**, features an emission spectrum with the expected ⁵D₀ → ⁷F_{*J*} (*J* = 1–4) transitions. Induced electric dipole (⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₄) transitions are allowed in **6a**, given the lack of a center of symmetry, while fully forbidden transitions, ⁵D₀ → ⁷F₀ and ⁵D₀ → ⁷F₃ are either not observable (⁵D₀ → ⁷F₀) or very weak (⁵D₀ → ⁷F₃). The intensity of magnetic dipole (⁵D₀ → ⁷F₁) transition is independent on any Eu³⁺-ligand interactions,⁴⁹ and just happens to coincide with ⁵D₀ → ⁷F₂. The difference in intensity between *J* = 2 and *J* = 4 is somewhat unexpected, as the former transition is usually considered hypersensitive and thus expected to be more intense.⁴⁹ This can be attributed to two factors: (i) lack of electric quadrupole contributions to *J* = 2 and (ii) a static coupling mechanism between Eu³⁺ and 4-NO₂Tp⁻, *i.e.* a weakly covalent Eu³⁺-4-NO₂Tp⁻ bond.^{50,51} A preliminary Judd–Ofelt analysis of the luminescence data performed on **6a** (Table S2†) provides some evidence for the latter with a low value for Ω₂.⁵⁰ Finally, the crystal field splitting observed for the ⁵D₀ → ⁷F_{*J*} (*J* = 1–4) transitions is in agreement with the high local symmetry (*D*_{3h}) of the europium center.⁵²

The observed emission spectra in Fig. 6 is due primarily to direct f-f transitions and not sensitization *via* the 4-NO₂Tp⁻ ligand. The excitation spectra of **1a–9a** (except **2a** and **7a**) and the weak (or in some cases absent) absorption associated with 4-NO₂Tp⁻, highlights that 4-NO₂Tp⁻ is an inefficient sensitizer for Ln³⁺ emission. Interestingly, the presence of several direct f-f absorption peaks in Fig. 6 reveal that 4-NO₂Tp⁻ does not directly quench Ln³⁺ luminescence *via* Ln³⁺-to-4-NO₂Tp⁻ back-energy transfer and that direct f-f absorption and/or Ln³⁺-to-Ln³⁺ energy transfer (energy migration) are fairly efficient sensitization mechanisms. **2** likely does not display room temperature luminescence due to a fast d_{Ce} → π*_{4-NO₂Pz} metal-to-ligand charge transfer (MLCT) and subsequent non-radiative π*_{4-NO₂Pz} → n_{NO₂} transition, analogous to monomeric, [Ce(3-NO₂Tp)₂(NO₃)].⁴⁵

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-NO₂Tp⁻. This band coincides somewhat with the absorption at 284 nm in the absorption spectrum of crude **1** and a π_{Pz} → π*_{4-NO₂Pz} transition predicted at 276 nm for **Calc-1** and therefore, this peak is assigned as the S₀ → S₇, π_{Pz} → π*_{4-NO₂Pz} 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 Eu³⁺/Tb³⁺; usually these pathways are identical (to be discussed later, see Fig. 10). The ability of 4-NO₂Tp⁻ to weakly sensitize Tb³⁺ and Eu³⁺ emission suggests that the T₁ state of 4-NO₂Tp⁻ (which we could not determine experimentally), may have enough energy to sensitize Eu³⁺ (⁵D₀, 17 500 cm⁻¹) and Tb (⁵D₄, 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 π*_{4-NO₂Pz} → n_{NO₂} transition is large (*k*_{nonrad} ≫ *k*_{rad}). Another explanation for the sensitized emission in **6a** and **8a** and not the other lanthanides, may be a singlet energy transfer pathway^{53,54} *via* the S₀ → S₇, π_{Pz} → π*_{4-NO₂Pz} ICLT transition that typically only Eu³⁺ and Tb³⁺ can participate in, whereas triplet sensitization is usually necessary for more weakly luminescent lanthanides (Pr³⁺, Sm³⁺, Dy³⁺).

Magnetic properties of [Ln(4-NO₂Tp)₃]·C₆H₁₄

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 Fig. 7. The room temperature χ_m*T* values were 1.65 cm³ K mol⁻¹, 11.85 cm³ K mol⁻¹ and 13.93 cm³ K mol⁻¹ for **4a**, **8a** and **9a** respectively. These values agree well with those anticipated for free uncoupled Ln³⁺ ions at 1.64 cm³ K mol⁻¹ (Ln = Nd, ⁴I_{9/2}, *S* = 3/2, *L* = 6, *g* = 8/11), 11.82 cm³ K mol⁻¹ (Ln = Tb, ⁷F₆, *S* = 3, *L* = 3, *g* = 3/2) and 14.17 cm³ K mol⁻¹ (Ln = Dy, ⁶H_{15/2}, *S* = 5/2, *L* = 5, *g* = 4/3). For all three compounds, χ_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:

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

where *B_k^q* are the crystal field parameters (including orbital reduction parameters), *θ_k* are the operator equivalent factors and *Ō_k^q* the Stevens operator equivalents.^{56,57} A survey of the crystal field parameters between –5000 and +5000 cm⁻¹ indicated that the best fits of the experimental data around *B₆⁰* = *B₆⁶* = 0 for all three cations. While the negligible value of the sole equatorial term *B₆⁰* is in agreement with the substantially longer Ln–N_{NO₂Pz} distances in the plane of the tricapped trigonal prismatic coordination sphere, the *B₆⁰* value is more surprising for 4f centers. Attempts to determine values for the *B₂⁰* and *B₄⁰* parameters were unsuccessful owing to overparameterization of the systems (Fig. S27–S29†). 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, Fig. 7 and S30†).

Dynamic magnetic measurements. Dynamic (ac) magnetic susceptibility experiments were collected on **4a**, **8a** and **9a** in



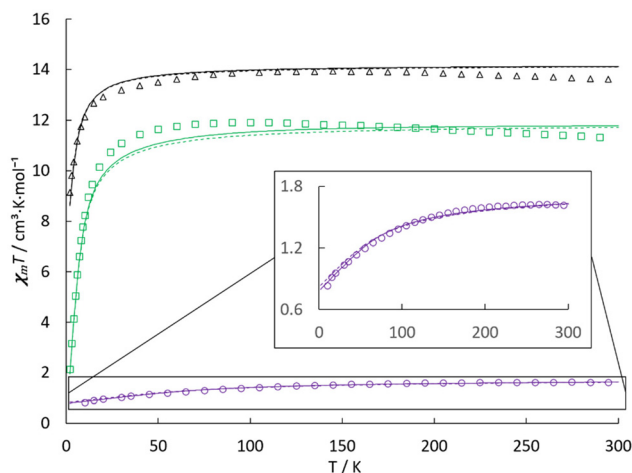


Fig. 7 Temperature dependence of $\chi_m T$ product at 1000 Oe for **4a** (Nd, \circ), **8a** (Tb, \square) and **9a** (Dy, Δ). Solid lines correspond to simulations using the crystal field parameters of set 1 in Table 1, dashed lines to those using set 2.

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

Crystal field parameters (cm^{-1})	4a	8a	9a
B_2^0/B_4^0 (set 1)	960/−300	−220/−70	−460/−20
B_2^0/B_4^0 (set 2)	−560/340	−610/10	−620/−50

modelled using eqn (1), which contains a direct term (AT) and a two phonons Raman term.⁵⁹

$$\tau^{-1} = AT + \tau_0^{-1} \frac{e^{-\frac{E_{\text{vib}}}{k_B T}}}{\left(e^{-\frac{E_{\text{vib}}}{k_B T}} - 1\right)^2} \quad (1)$$

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 Fig. 11 and S30.† Initial inclusion of a Raman term (CT^m) yielded a power dependence n term of ~ 3.5 ; since this is a significant departure from the idealized Raman relax-

ation mechanism, we excluded any direct Raman contribution.

Moreover, the use of a model with an Orbach $\left(\tau_0^{-1} \cdot e^{-\frac{U_{\text{eff}}}{k_B T}}\right)$ 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} (Fig. S30†), corresponding to phonon-coupled under-barrier relaxation process rather than a true Δm_j transition/Orbach process.

Discussion

Ligand design for Tp[−]-based antenna ligands

Comparison of the optical properties of the $[\text{Ln}(\text{4-NO}_2\text{Tp})_3]$ complexes and those of previously published complexes $[\text{LnTp}_3]$ and $[\text{Ln}(\text{3-NO}_2\text{Tp})_2(\text{NO}_3)]$ 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 $\pi_{\text{Pz}} \rightarrow \pi^*_{n\text{-NO}_2\text{Pz}}$ charge transfer transitions, predicted by TD-DFT and confirmed experimentally, this difference is rather surprising. To elucidate the origin of the disparity between the $n\text{-NO}_2\text{Tp}^-$ ($n = 3$ or 4) ligands, we determined the quantum yield (Φ_{exp}), emission lifetime (τ_{Eu}) and derived their intrinsic quantum yield ($\Phi_{\text{Eu}}^{\text{Eu}}$), the rates of radiative (k_{rad}) and nonradiative decay (k_{nonrad}) as well as their efficiency of sensitization (η_{sens}) (Table 2). The radiative lifetime for Eu³⁺ is similar for all three complexes, with a slight reduction in $[\text{Eu}(\text{3-NO}_2\text{Tp})_2(\text{NO}_3)]$. Expectedly, 10-coordinate $[\text{Eu}(\text{3-NO}_2\text{Tp})_2(\text{NO}_3)]$ has a lower intrinsic quantum yield than the two 9-coordinate complexes, which show nearly identical $\Phi_{\text{Eu}}^{\text{Eu}}$. The primary difference between the EuTp-complexes is their quantum yields. Consistent with the reduction in sensitization efficiency often associated with nitrated antenna ligands,³⁸ the quantum yield and radiative decay rate of **6a** are about half of those of $[\text{EuTp}_3]$ ($\sim 2.4\%$ vs. 4.6% for Φ_{exp} and $\sim 13 \text{ s}^{-1}$ vs. 25 s^{-1} for k_{rad}), however the quantum yield and radiative decay rate for $[\text{Eu}(\text{3-NO}_2\text{Tp})_2(\text{NO}_3)]$ are 4% and 21 s^{-1} respectively, approximately equal to those of $[\text{EuTp}_3]$. The reduction in the radiative decay of **6a** as compared to $[\text{EuTp}_3]$

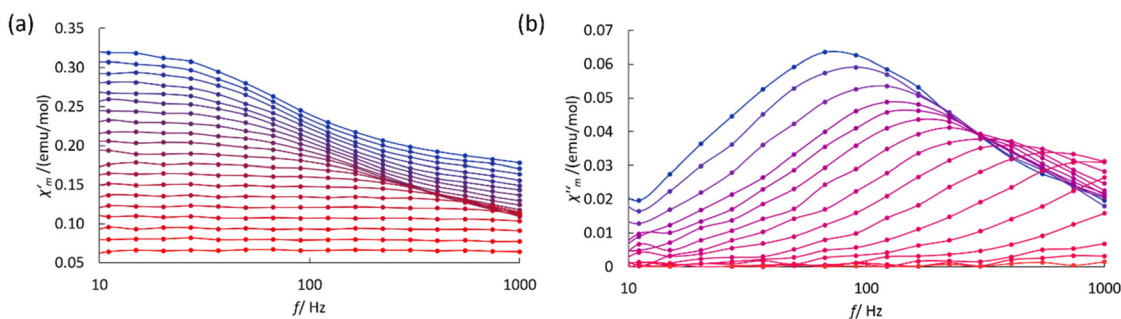


Fig. 8 (a) In-phase molar susceptibility (χ'_m) vs. frequency and (b) out-of-phase molar susceptibility (χ''_m) vs. frequency of **4a** between 2 and 9 K at $H = 400 \text{ Oe}$.



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

Compounds	$\tau_{\text{Eu}}/\text{ms}$	$\tau_{\text{ligand}}(\text{T}_1)/\text{ms}$	$\Phi_{\text{Eu}}^{\text{Eu}}/ \%$	$\Phi_{\text{exp}}(\Phi_{\text{Eu}}^{\text{Tp}^*})/ \%$	$k_{\text{rad}}/ \text{s}^{-1}$	$k_{\text{nonrad}}/ \text{s}^{-1}$	$\eta_{\text{sens}}/ \%$
[EuTp ₃]	1.84 (ref. 60)	1.90 (ref. 60), 9.00 (ref. 34) ^d	43 (ref. 60)	4.6 (ref. 60)	25	518	10.7
[Eu(3-NO ₂ Tp) ₂ (NO ₃)]	1.90 ± 0.27	0.113 ± 0.07 ^d	22	4.00	21 ± 3	506 ± 72	18.2
[Eu(4-NO ₂ Tp) ₃]-C ₆ H ₁₄ (6a)	1.82 ± 0.03 ^e 1.94 ± 0.20 ^f	N/A	45	1.8 ^e 2.9 ^f	9.9 ± 0.2 ^e 16 ± 1.6 ^f	539 ± 8 ^e 395 ± 53 ^f	4.0 ^e 6.4 ^f

^a $\eta_{\text{sens}} = (\Phi_{\text{exp}}/\Phi_{\text{Eu}}^{\text{Eu}})$ according to de Sá *et al.*⁶¹ ^b $k_{\text{rad}} = \Phi_{\text{exp}}/\tau_{\text{Eu}}$. ^c $k_{\text{nonrad}} = (1/\tau_{\text{Eu}}) - k_{\text{rad}}$. ^d Lifetime of [Gd(3-NO₂Tp)₂(NO₃)] measured at 77 K. ^e Measured with a 340 nm excitation. ^f Measured with a 395 nm excitation.

can be attributed to the fast decay/short lifetime of the T₁ state of 4-NO₂Tp⁻ and inefficient energy transfer to Eu³⁺ owing to the presence of the nitro-group. However, the nitro group appears to have no impact in [Eu(3-NO₂Tp)₂(NO₃)].

Examination of the differences between [Eu(3-NO₂Tp)₂(NO₃)] and **6a** seem to indicate that the triplet state of 3-NO₂Tp⁻ is more stable/longer-lived than that of 4-NO₂Tp⁻, given that the emission from 4-NO₂Tp⁻ could not be observed at even 77 K, while we recorded room temperature T₁ emission from 3-NO₂Tp⁻ in [Gd(3-NO₂Tp)₂(NO₃)].⁴⁵ TD-DFT calculations predict that both 3-NO₂Tp⁻ and 4-NO₂Tp⁻ should have similar triplet energies (422 and 404 nm respectively), indicating that the enhanced stability of 3-NO₂Tp⁻ 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-NO₂Tp)₂(NO₃)] and **6a**. These interactions are π - π stacking and NO₂...H-C hydrogen bonding in [Eu(3-NO₂Tp)₂(NO₃)] and **6a** respectively, both interactions involving the *n*-NO₂Pz (*n* = 3 or 4) rings. Natural bond order (NBO) derived stabilization energies associated with each NCI (π - π stacking or NO₂...H-C hydrogen bonding) (Fig. 9) and indicates that the π - π stacking interactions are significantly stronger than

NO₂...H-C hydrogen bonding. We postulate that the stronger π - π stacking NCIs of [Eu(3-NO₂Tp)₂(NO₃)] increase the rigidity of 3-NO₂Tp⁻. The coordination of the 3-NO₂ group to the Ln³⁺ centers is likely to also contribute to an increased rigidity, accounting overall for the higher sensitization efficiency observed in [Eu(3-NO₂Tp)₂(NO₃)] vs. **6a**. This is consistent with recent reports on NCIs stabilizing the triplet state of aromatic ligands.⁶²⁻⁶⁵ The enhanced stability afforded to the T₁ state of 3-NO₂Tp⁻ in [Eu(3-NO₂Tp)₂(NO₃)] likely increased its lifetime enough that it could undergo substantial energy transfer with Eu³⁺ (Fig. 10), while the T₁ state of 4-NO₂Tp⁻ undergoes a rapid non-radiative decay. By changing the position of the ring substituent in *n*-NO₂Tp⁻ (*n* = 3 or 4) ligands, we can control the type and strength of NCIs in Ln(*n*-NO₂Tp)_x complexes and consequently tune the efficiency of *n*-NO₂Tp-to-Ln³⁺ 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

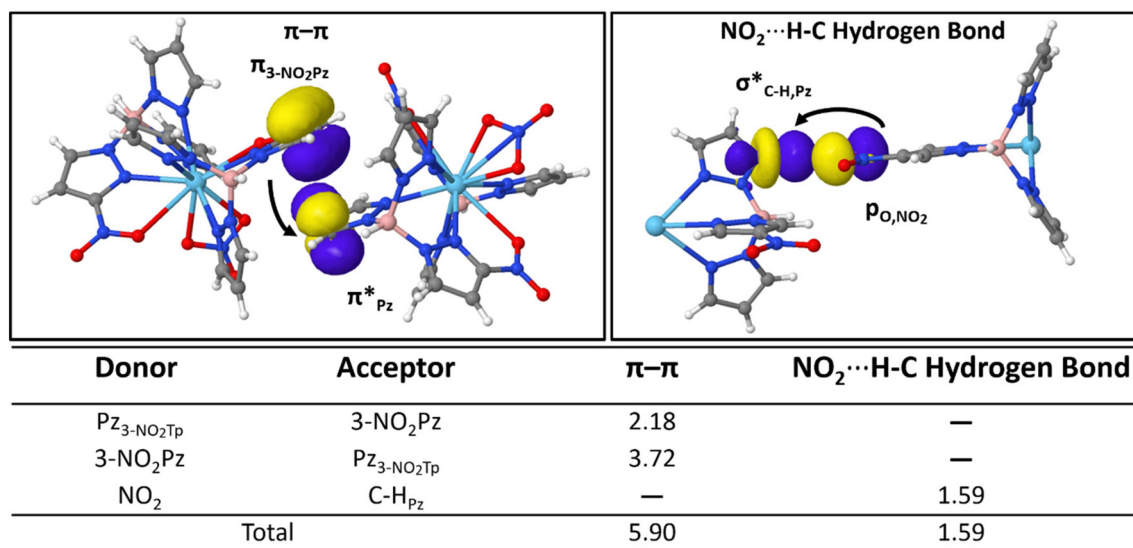


Fig. 9 Top: Representative natural bond orbitals (NBOs) of the π - π stacking interactions in [Eu(3-NO₂Tp)₂(NO₃)] and the NO₂...H-C hydrogen bonding in **6a**. Bottom: Table summarizing the donor and acceptor pairs and associated contribution to the stabilization energy in kJ mol⁻¹.



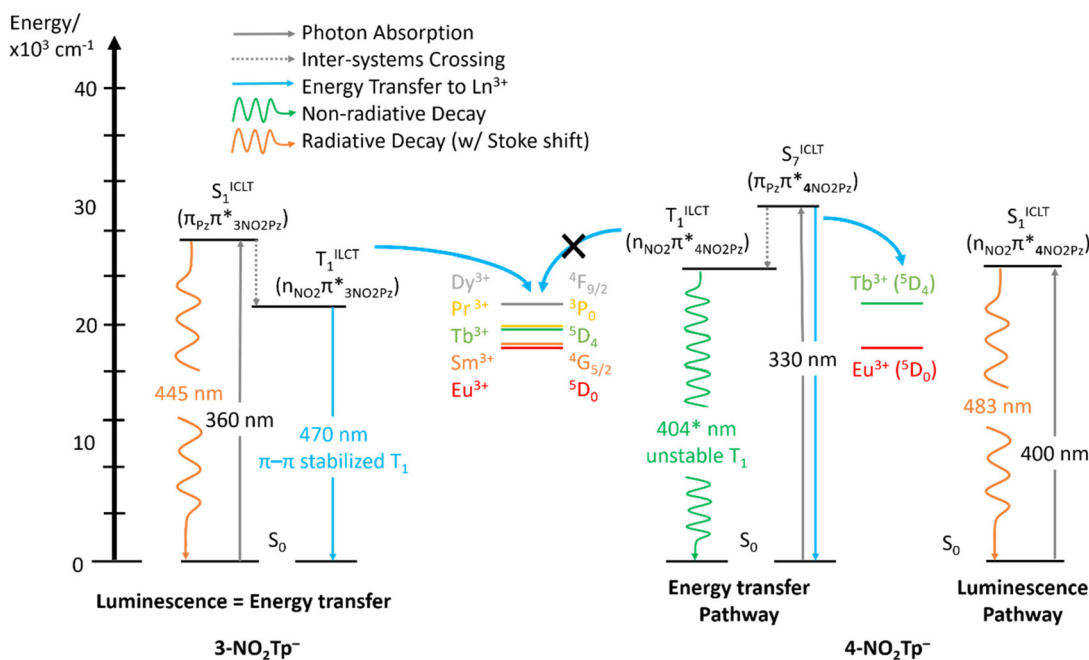


Fig. 10 Jablonski diagram comparing the luminescence and energy transfer pathways in 3-NO₂Tp⁻ and 4-NO₂Tp⁻.

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 axially of the crystal field, as no B_k^q term with $q \neq 0$ 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 $m_J = \frac{1}{2}$ 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 $m_J = \frac{1}{2}$ 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 (Fig. 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 ($U_{\text{eff}} = 2.84 \text{ cm}^{-1}$, $\tau_0 = 4.2 \times 10^{-5} \text{ s}$),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

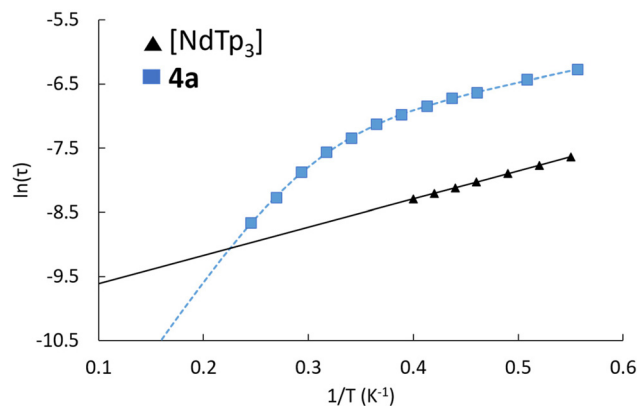


Fig. 11 Temperature dependence of the magnetic relaxation times, under a small bias field, of [NdTp₃] (black triangles, 100 Oe) with the reported Orbach fit (black line),³² and **4a** (blue squares, 400 Oe) with the fit (blue broken line) generated using eqn (1). From the fitted AC data (solid lines), [NdTp₃]: $U_{\text{eff}} = 2.84(2) \text{ cm}^{-1}$, $\tau_0 = 4.2(2) \times 10^{-5} \text{ s}$; **4a**: $A = 318(8) \text{ K}$, $U_{\text{eff}} = 12.7(1.6) \text{ cm}^{-1}$ and $\tau_0 = 4.1(1.6) \times 10^{-5} \text{ s}$.

change from the parallel anisotropy axes in [NdTp₃]⁶⁶ to the slightly canted layers of **4a**, which one would usually assume 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 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.

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 n_{NO₂} → π*_{4-NO₂Pz} and π_{Pz} → π*_{4-NO₂Pz} absorptions and π*_{4-NO₂Pz} → n_{NO₂} and π*_{4-NO₂Pz} → π_{Pz} 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-NO₂Tp⁻ over Tp⁻, in context with our previous work on [Ln(3-NO₂Tp)_x] 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.

Experimental

Materials

Lanthanide chloride salts, LnCl₃·7H₂O (Ln = La³⁺, Ce³⁺, Fisher Scientific, 99.9%), PrCl₃·7H₂O (Strem Chemicals, 99.9%), LnCl₃·6H₂O (Ln = Nd³⁺, Sm³⁺-Dy³⁺, 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.^{29,44} 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 (0.4910 g, 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 × 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 × 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 parafilm 25 mL Erlenmeyer flask.

[La(4-NO₂Tp)₃]·C₆H₁₄ (1a). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 51%. Elemental Anal. Calc. for LaC₃₃H₄₁O₆N₂₁B₃: C 39.67, H 4.11, N 29.45. Found: C 39.40, H 3.59, N 29.05.

[Ce(4-NO₂Tp)₃]·C₆H₁₄ (2a). Pale yellow single crystals were isolated from methanol/hexanes. Yield (recrystallized): 52%. Elemental Anal. Calc. for CeC₃₃H₄₁O₆N₂₁B₃: C 39.62, H 4.10, N 29.41. Found: C 39.21, H 3.88, N 29.55.

[Pr(4-NO₂Tp)₃]·C₆H₁₄ (3a). Green single crystals were isolated from methanol/hexanes. Yield (recrystallized): 45%. Elemental Anal. Calc. for PrC₃₃H₄₁O₆N₂₁B₃: C 39.60, H 4.10, N 29.39. Found: C 39.45, H 3.94, N 29.59.

[Nd(4-NO₂Tp)₃]·C₆H₁₄ (4a). Lilac single crystals were isolated from methanol/hexanes. Yield (recrystallized): 51%. Elemental Anal. Calc. for NdC₃₃H₄₁O₆N₂₁B₃: C 39.47, H 4.09, N 29.29. Found: C 39.29, H 3.94, N 29.13.

[Sm(4-NO₂Tp)₃]·C₆H₁₄ (5a). Pale yellow single crystals were isolated from methanol/hexanes. Yield (recrystallized): 36%. Elemental Anal. Calc. for SmC₃₃H₄₁O₆N₂₁B₃: C 39.22, H 4.06, N 29.11. Found: C 39.11, H 3.91, N 29.30. τ = 0.116 ms (λ_{exc} = 340 nm (⁶P_{3/2}), λ_{em} = 604 nm).

[Eu(4-NO₂Tp)₃]·C₆H₁₄ (6a). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 30%. Elemental Anal. Calc. for EuC₃₃H₄₁O₆N₂₁B₃: C 39.16, H 4.05, N



29.07. Found: C 38.87, H 3.87, N 29.07. $\tau = 1.80$ ms ($\lambda_{\text{exc}} = 394$ nm ($^5\text{I}_6$), $\lambda_{\text{em}} = 700$ nm).

[Gd(4-NO₂Tp)₃] \cdot C₆H₁₄ (**7a**). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 33%. Elemental Anal. Calc. for GdC₃₃H₄₁O₆N₂₁B₃: C 38.96, H 4.03, N 28.92. Found: C 38.91, H 3.97, N 29.04.

[Tb(4-NO₂Tp)₃] \cdot C₆H₁₄ (**8a**). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 50%. Elemental Anal. Calc. for TbC₃₃H₄₁O₆N₂₁B₃: C 38.90, H 4.03, N 28.87. Found: C 38.71, H 4.00, N 28.92. $\tau = 1.87$ ms ($\lambda_{\text{exc}} = 486$ nm ($^5\text{D}_4$), $\lambda_{\text{em}} = 542$ nm).

[Dy(4-NO₂Tp)₃] \cdot C₆H₁₄ (**9a**). White single crystals were isolated from methanol/hexanes. Yield (recrystallized): 36%. Elemental Anal. Calc. for DyC₃₃H₄₁O₆N₂₁B₃: C 38.76, H 4.01, N 28.77. Found: C 38.78, H 3.92, N 28.66.

[Sm(4-NO₂Tp)₃] \cdot 7C₆H₆ (**5b**). Pale yellow single crystals were isolated from methanol/benzene. Yield (recrystallized): 44%. Elemental Anal. Calc. for SmC₆₉H₆₉O₆N₂₁B₃: C 56.33, H 4.69, N 20.00. Found: C 55.41, H 4.66, N 20.61.

[Tb(4-NO₂Tp)₃] \cdot 7C₆H₆ (**8b**). White single crystals were isolated from methanol/benzene. Yield (recrystallized): 40%. Elemental Anal. Calc. for TbC₆₉H₆₉O₆N₂₁B₃: C 56.01, H 4.67, N 19.88. Found: C 55.40, H 4.70, N 20.43.

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 K α ($\lambda = 0.71073$) 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,⁶⁷ and empirical absorption corrections were applied using SADABS,⁶⁸ for **1a–9a**, **5b** and **8b**. Structure solutions solved using intrinsic phasing were performed using the ShelXT package⁶⁹ in APEX III. All data were subsequently refined using SHELXL-2014 in the program SHELXL.⁷⁰ 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.⁷¹ 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_{iso}) fixed at 1.2 U_{eq} for all carbon atoms and at 1.5 U_{eq} for all boron atoms. Details of the X-ray diffraction experiments and crystal data are summarized in Table 3.

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 K α $2\theta = 5$ –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 Fig. S3 and S4.†

Infrared spectroscopy

Infrared spectra were collected from 650 to 4000 cm^{-1} using a PerkinElmer 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 Fig. S5 and S6.†

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 Fig. S4–S14.†

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA. Samples were heated from 30–500 °C at 20 °C min^{-1} in air. TGA curves of **5a** and **5b** are given in Fig. S15† indicating thermal stability of [Ln(4-NO₂Tp)₃] up to ~240 K, with solvent loss at 185 °C for **a** (hexanes) solvate and 77 °C for **b** (benzene) solvate.

Elemental analysis

Elemental analyses were performed by ALS Environment for **1a** and **9a**, and Atlantic Microlab for **2a–8a**, **5b** and **8b**.

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 Fluorolog-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 fluopolymer 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 col-



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

	1a	2a	3a	4a	5a	5b
CCDC no.	2226885	2226886	2226887	2226888	2226889	2226890
Formula	LaN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	CeN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	PrN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	NdN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	SmN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	SmN ₂₁ O ₆ B ₃ C ₆₉ H ₆₉
Formula weight	913.04	914.25	915.04	918.37	924.49	1471.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Trigonal
Space group	C2/c	C2/c	C2/c	C2/c	C2/c	R $\bar{3}$
<i>a</i> , Å	24.473(5)	24.400(8)	24.369(6)	24.2443(7)	24.324(15)	21.6878(4)
<i>b</i> , Å	13.830(3)	13.801(3)	13.783(3)	13.7711(3)	13.756(10)	21.6878(4)
<i>c</i> , Å	29.778(4)	28.778(10)	28.792(7)	28.8113(11)	28.833(15)	25.7723(8)
α , °	90	90	90	90	90	90
β , °	116.898(5)	116.759(12)	112.453(8)	112.537(1)	112.49(2)	90
γ , °	90	90	90	90	90	90
<i>V</i> , Å ³	8988(3)	8954(5)	8937(4)	8921.3(5)	8913(10)	10 498.2(5)
<i>Z</i>	8	8	8	8	8	6
<i>T</i> , K	100	100	100	100	100	100
ρ_{calc} , g cm ⁻³	1.349	1.356	1.360	1.367	1.378	1.396
μ , mm ⁻¹	1.011	1.077	1.150	1.224	1.378	0.907
λ , Mo K α	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>R</i> _{int}	0.0483	0.0590	0.0455	0.0639	0.0673	0.0403
Residuals: ^a <i>R</i> ; <i>R</i> _w	0.0219; 0.0477	0.0236; 0.0546	0.0252; 0.0638	0.0295; 0.0651	0.0268; 0.0613	0.0175; 0.0426
Goodness of fit	1.022	1.042	1.049	1.007	0.996	1.071

	6a	7a	8a	8b	9a
CCDC no.	2226891	2226892	2226893	2227039	2226894
Formula	EuN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	GdN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	TbN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇	TbN ₂₁ O ₆ B ₃ C ₆₉ H ₆₉	DyN ₂₁ O ₆ B ₃ C ₂₇ H ₂₇
Formula weight	926.10	931.38	933.06	1479.80	936.63
Crystal System	Monoclinic	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group	C2/c	C2/c	C2/c	R $\bar{3}$	C2/c
<i>a</i> , Å	24.313(16)	24.296(6)	24.248(2)	21.6423(9)	24.291(5)
<i>b</i> , Å	13.724(10)	13.742(2)	13.7248(17)	21.6423(9)	13.695(3)
<i>c</i> , Å	29.722(15)	29.768(4)	28.843(4)	25.7873(17)	29.707(8)
α , °	90	90	90	90	90
β , °	115.893(13)	116.414(8)	112.506(4)	90	115.032(5)
γ , °	90	90	90	90	90
<i>V</i> , Å ³	8922(10)	8901(3)	8867.9(18)	10 460.3(11)	8954(4)
<i>Z</i>	8	8	8	6	8
<i>T</i> , K	100	100	100	100	100
ρ_{calc} , g cm ⁻³	1.379	1.390	1.398	1.409	1.390
μ , mm ⁻¹	1.466	1.551	1.656	1.082	1.729
λ , Mo K α	0.71073	0.71073	0.71073	0.71073	0.71073
<i>R</i> _{int}	0.0643	0.0608	0.0394	0.0800	0.0477
Residuals: ^a <i>R</i> ; <i>R</i> _w	0.0430; 0.0872	0.0251; 0.0629	0.0323; 0.0713	0.0355; 0.0689	0.0426; 0.0852
Goodness of fit	0.975	1.020	1.003	1.118	1.163

^a $R = R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ for observed data only. $R_w = wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ for all data.

lected 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 ($\chi_{\text{dia}}(\text{cm}^3 \text{mol}^{-1}) = -[\text{MW}(\text{g mol}^{-1}) \times 10^{-6}]/2$) 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.).⁷² A ground state optimization was performed on **Calc-1**, using the B3LYP^{73,74} 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 La³⁺.^{75–78} 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 ($S_0 \rightarrow S_n$) and triplet ($S_0 \rightarrow T_n$) 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-NO₂Tp)₂(NO₃)] (generated from crystallographically determined atomic coordinates of [Gd(3-NO₂Tp)₂(NO₃)]₄H₂O) participating in a π - π stacking interaction. Model B comprised two [La(4-NO₂Tp)]²⁺ units participating in a NO₂...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.⁷⁹

Author contributions

The manuscript was written through contributions of all authors.

Conflicts of interest

The authors declare no competing financial interests.

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