Utility of All-Pyrazole Heteroscorpionates in *f*-element Chemistry

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Utility of All-Pyrazole Heteroscorpionates in *f*-element Chemistry

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Abstract

Since their discovery in 1966, scorpionate ligands have been utilized to make coordination compounds for a variety of applications such as: studying organometallic reactions, biomimetic complexes, light-emitting materials and single -ion magnets. The recent development of a solvent-free pyrazole substitution chemistry has yielded the quantitative synthesis of asymmetrically functionalized all-pyrazole heteroscorpionate ligands. In this frontier article, we highlight the utility of all-pyrazole heteroscorpionates, specifically, nitro-trispyrazolylborates, in *f*-element chemistry. They offer great versatility in coordinating ability, donor strength, steric bulk and even optical charge transfer properties, all of which can be used to tune the properties of resultant complexes with metal ions. We show how they can impart structural diversity, sensitize Ln^{3+} luminescence and engender magnetic anisotropy and slow magnetic relaxation in the ion they coordinate. Additionally, we comment on the future of functionalized trispyrazolyl scorpionates, which includes enabling post-synthetic modifications of *f*-element complexes and becoming a platform to study the electronic properties of low oxidation state actinides.

Introduction

Trofimenko's discovery of potassium hydrotrispyrazolyborate (Tp^{-}), in the 1960's led to the development of the highly versatile class of chelating ligands known as "scorpionates".[1] Scorpionates are defined as anionic, $6e^{-}$ donor, face-capping ligands, and are known for being sterically demanding and very tunable with respect to pendant functional groups and ligand-to-metal donation.[2] Trispyrazolylborate, the original scorpionate, has since found wide application in *f*-element coordination and organometallic chemistry owing to its ability to readily enclose *f*-ions, thus facilitating chemical control over their usually unpredictable coordination modes-.[3-4] The resultant complexes feature robust catalytic activity,[5] 100 % quantum yield LEDs,[6-7] and single-ion magnets (SIMs) with-elements including: Nd^{3+}, Dy^{3+}, Yb^{3+}, U^{3+} and Pu^{3+}.[8-10] Tp^{-}, the first example of scorpionate, is a homoscorpionate: all of the donor sites are equivalent (pyrazole N); on the other hand, heteroscorpionates are an evolution of scorpionates, defined as anionic, $6e^{-}$ donor, face-capping ligand where not all three donor sites are identical.[11] Most research efforts involving scorpionates focus on generating different types of homologous scorpionate ligands (and derivative metal-scorpionate complexes) including: trisimidazolylborate,[12] trisbenzotriazolylborate,[13] trismercaptoarylborates and phenyltris(2-pyridyl)borates,[14] and tris(2-pyridyl)amines/phosphines.[15] We recommend the following reviews by Marques and coworkers for *f*-element scorpionate materials[3-4] and Smith,[2] and Pawar et al.,[14] for the versatility of scorpionate ligand in coordination chemistry.

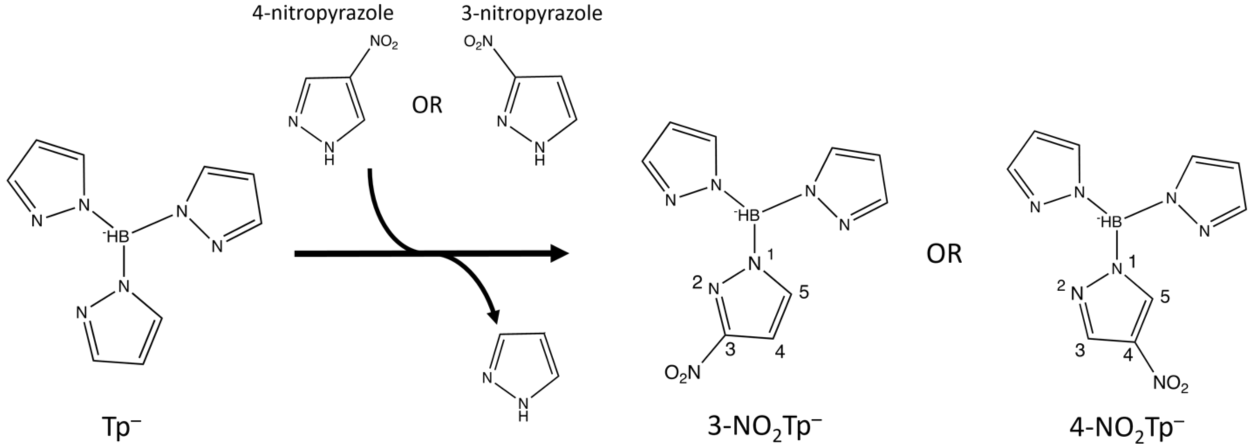


Figure 1: Schematic diagram of the synthesis of asymmetric n-NO_2Tp^{-} (n = 3 or 4) ligands *via* pyrazole substitution. Each Tp^{-} ligand has 3 sites per pyrazole ring (positions 3, 4 and 5), a total of 9 possible sites for functionalization.

There have been several groups interested in developing chemistry to generate heteroscorpionate via selective functionalization of Tp^-.[11, 16-23] The most effective method (Figure 1) involves the substitution of a normal pyrazole for another N- or S-donor aromatic ring.[11] Initial attempts at generating functionalized Tp^- involved reacting different types of aromatic amines with pyrazoles and MBH_4 (M = alkali metal) in a melt, however, this led to uncontrolled substitutions and mixed phases.[21-23] To overcome this, Vahrenkamp and coworkers, reacted potassium trispyrazolylborate (KTp) with thioimidazoles in a melt, to generate phase pure thiol-functionalized Tp^-ligands.[19] Desrochers and coworkers expanded this work with benzotriazoles and Tp^{Me_2-},[11, 16] and Warren et al, contributed with the substitution of 3'-pyridyl,5-methyl-pyrazole and $Tp^{^iPr_2-}$.[20] Our group is also interested in improving upon the desirable properties of homologous Tp^- ligands such as Tp^-, Tp^{Me_2}, $Tp^{^iPr_2-}$ etc., by generating *all-pyrazole heteroscorpionates*, with 2 identical binding sites *via* pyrazole nitrogens (claws) and 1 unique binding site *via* an *n*-nitropyrazole (stinger, *n* = 3 or 4), corresponding to a selective single substitution of one of nine sites available for the nitro group (Figure 1). We have developed a rich pyrazole substitution chemistry using tetrabutylammonium trispyrazolylborate, which allows us to synthesize asymmetric NO_2-Tp^- ligands Figure 1 with a controlled degree (1 or 2 NO_2-groups per Tp^-) and position (3-, 4- or 5-NO_2) of functionalization; and we paired those ligands with a host of transition metals and lanthanides for various optical and magnetic application. comment on future directions for this class of compounds in magneto-optical applications and *f*-element separations. The combination of NO_2-Tp^- with d-block metals such as Fe^{2+} generated solvatochromic, spin crossover (SCO) complexes with highly tunable SCO transition temperatures.[17-18] Substituting transition metals for *f*-elements such as Nd^{3+} resulted in a single-molecule magnet (SMM) while several other lanthanides (Pr^{3+}, Sm^{3+}, Eu^{3+}, $Tb^{3+}$and Dy^{3+}) yielded emissive materials ranging from the visible to NIR.[24-25] These advances, however, are mostly the result of the addition of a single NO_2-group and there is room for further diversification of Tp^-. With this in mind, we detail our progress with lanthanide complexes with all-pyrazole heteroscorpionates ligands, the asymmetric *n*-NO_2-Tp^- (*n* = 3 or 4) nitrotrispyrazolylborates, and discuss how selective functionalization of Tp^- influences their optical and magnetic properties. Moreover, we comment on future directions for this class of compounds in magneto-optical applications and *f*-element separations.

Structural Diversity

Functionalization of the trispyrazolylborate ligand with a single NO_2-group in either the 3- or 4-position on one of the pyrazole rings (Figure 1) and subsequent complexation with Ln^{3+} ions, leads to significant structural diversity among the resulting lanthanide complexes, which feature monomeric, dimeric and tetrameric structures. Unsurprisingly, 4-NO_2Tp^- follows Tp^- in generating with the larger lanthanide ions (La – Dy) nine-coordinate complexes with nearly identical coordination motifs of the κ^3 – Tp^- and 4-NO_2Tp^- ligands (top of Figure 2).[24] However, the solubilities and solid-state structures of the non-functionalized and nitro-functionalized compounds differ dramatically, likely due to the incorporation of the strongly electron-withdrawing NO_2 -group. [Ln(4-NO_2Tp)$_3$] is fairly soluble in several common organic solvents (acetone, dichloromethane, methanol) whereas [$LnTp_3$] is notoriously insoluble in most solvents and requires sublimation to grow single crystals of metal complexes.[24] The greater solubility of [Ln(4-NO_2Tp)$_3$] affords it greater variation in possible solid-state structures in the form of different solvates; a hexanes phase (Figure 3b) vs a benzene phase (Figure 3c).

The bulk of the structural diversity of Ln/NO_2Tp compounds is due to functionalization at position 3. In 3-NO_2Tp^- the introduction of a potential new binding site at the O of the NO_2-group yields a flexidentate ligand, which coordinates the lanthanide center in tri- or tetradentate fashion depending on its size. Specifically, 3-NO_2Tp^- is tridentate exclusively when paired with the smallest lanthanides (Yb, Lu), however the added bulk of the NO_2-group precludes the coordination of >1 3-NO_2Tp^-, as opposed to unfunctionalized Tp^-, which yields 8-coordinate [$LnTp_3$] (Ln = Ho – Lu) complexes with two tridentate and one bidentate ligand. For larger lanthanides (La – Gd), 3-NO_2Tp^- is usually tetradentate, which was unexpected as Fe/3-NO_2Tp^- compounds feature exclusively tridentate 3-NO_2-ligands. Medium size lanthanides (Dy – Tm) produce complexes with both tri- and tetradentate 3-NO_2Tp^-. Interestingly, the tetradentate coordination mode of 3-NO_2Tp^- appears exclusive to *f*-elements, as we have not been able to observe it in transition metal complexes. The combined effect of a flexidentate ligand and the lanthanide contraction resulted in six unique structural types being identified for Ln/3-NO_2Tp compounds. The remarkable structural diversity afforded by 3-NO_2Tp^- (Figure 2) allowed for the facile synthesis of a set of polynuclear lanthanide complexes to study the optical and magnetic properties as a function of Ln^{3+}-to-Ln^{3+} distance.[25] We speculate that this ligand platform can be used to potentially study An^{3+}-to-An^{3+} interactions in future iterations. This property of 3-NO_2Tp^- contrasts with that of Tp^- and 3,5-difunctionalized Tp^{R2-} (R= Me or ^{i}Pr) ligands that also feature some structural diversity. Examples of said diversity include: Ln^{2+} dimers with the unusual η^5-coordination of a pyrazole ring to a metal ion with Tp^-,[26] and trimers, tetramers and hexamers assembled *via* bridging hydride ligands with $Tp^{^iPr2-}$, Tp^{Me2-} and Tp^- respectively.[27-28] Figure 2 compares the structural diversity of 3-NO_2Tp^- against Tp^- and Tp^{R2-} (R = Me or ^{i}Pr). Homologous Tp^- ligands require substantial steric crowding *via* alkyl group substitution and harsh reductive conditions to display tunable nuclearity while 3-NO_2Tp^- can natively generate higher nuclearity complexes under simple ambient conditions.

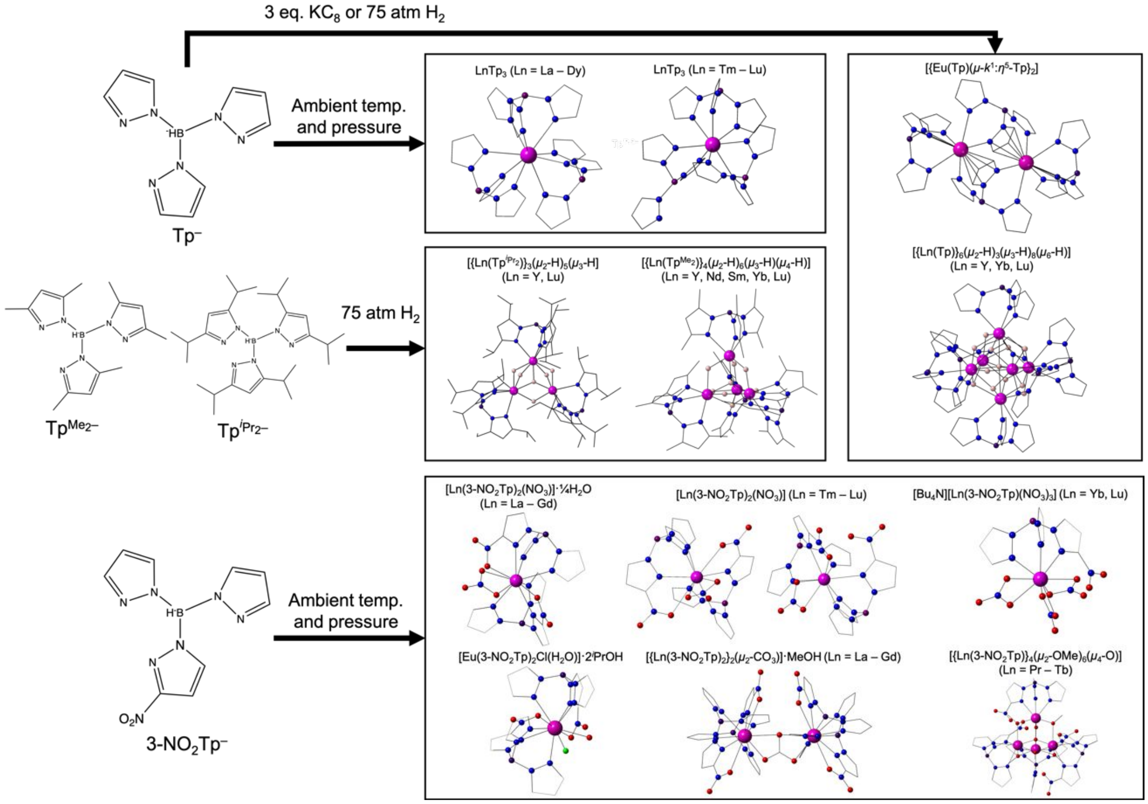


Figure 2: Structural diversity of lanthanide trispyrazolylborates. Top: Structures associated with non-functionalized Tp^-, where ambient reaction conditions yield [$LnTp_3$] complexes and reductive conditions yield dimers (with Eu^{2+}) or hexamers (with Ln^{3+}). Middle: Structure of 3,5-disubstituted alkyl Tp^- ligands and their resultant complexes with trivalent lanthanides (polynuclear complexes form under reductive conditions). Bottom: Structure of $3NO_2Tp^-$ and the six crystallographically unique structure types with various trivalent lanthanides which feature tunable nuclearity under simple ambient conditions.

Influence of Second-Sphere Interactions

Comparison of the crystal structures of [$LnTp_3$], the hexanes and benzene solvates of [$Ln(4\text{-}NO_2Tp)_3$] and the various Ln/3-NO_2Tp compounds (Figure 3) reveal a variety of second-sphere interactions throughout their solid-state structures and a correlation between nitro-substitution and the nature of the second-sphere interactions. Politzer and coworkers broadly define non-covalent (second-sphere) interactions as close contacts in crystal lattice that correlate with coulombic interactions between positive and negative regions of adjacent molecules.[29] As shown in Figure 3, [$LnTp_3$] does not feature any substantial 2nd sphere interactions, while [$Ln(4\text{-}NO_2Tp)_3$] displays interactions dependent on the recrystallization solvent, where hexanes yield $NO_2\cdots H\text{-}C$ hydrogen bonding and benzene yields no 2nd sphere interactions. Finally, Ln/3-NO_2Tp) compounds typically display π-π stacking interactions between 3-NO_2Pz and Pz rings (broken red lines in **Error! Reference source not found.**d and e). These intermolecular forces always involve the nitro-functionalized pyrazole ring, indicating that the NO_2-functionality is responsible for their appearance, and the position (3 vs 4) dictates the nature and strength of the interaction. That is, 4-NO_2Tp^- (with lattice hexanes) yields *weaker* $NO_2\cdots$H-C hydrogen bonding interaction or no interactions (with lattice benzenes) vs 3-NO_2Tp^- that usually generates *stronger* π-π stacking interactions, according to NBO7 calculations.[24] Moreover, such interactions can influence the complexes' optical properties. Analysis of the quantum yields of [Eu(3-NO_2Tp)$_2$(NO_3)]·¼H_2O and [Eu(4-NO_2Tp)$_3$]·C_6H_{14} revealed that 3-NO_2Tp^- is a better antenna ligand than 4-NO_2Tp^- owing to enhanced ligand rigidity in the tetradentate 3-NO_2Tp^- over the tridentate 4-NO_2Tp^-. The stronger 2nd sphere interaction in [Eu(3-NO_2Tp)$_2$(NO_3)]·¼H_2O (π-π stacking) over [Eu(4-NO_2Tp)$_3$]·C_6H_{14} ($NO_2\cdots$H-C hydrogen bonding), also contributes to this enhanced rigidity and consequently, Ln^{3+} sensitization efficiency.[24] Similarly, Bian and Liu have reported blue-light emitting Ce(III)/Tp^{Me_2} compounds with nearly 100 % quantum yields attributed to rigidity of the trispyrazolylborate framework.[6-7]

With respect to magnetic properties, Gil et al. highlighted that pronounced hydrogen bonding reduced axial anisotropy in Dy(III)/thiocyanate/crown ether SMMs and was detrimental to magnetic relaxation.[30] Interestingly, the improvement in SMM properties observed in [Nd(4-NO_2Tp)$_3$] over [NdTp$_3$] could be due to a change in the primary coordination sphere (the NO_2-group changing the basicity of the donor N in NO_2Pz vs non-functionalized Pz) and/or the change in the 2nd sphere (hydrogen bonding in [Nd(4-NO_2Tp)$_3$]). In light of this, more examples of the impact of prominent non-covalent interactions in Ln-SMMs are necessary to determine if and how 2nd sphere interactions affect magnetic properties.

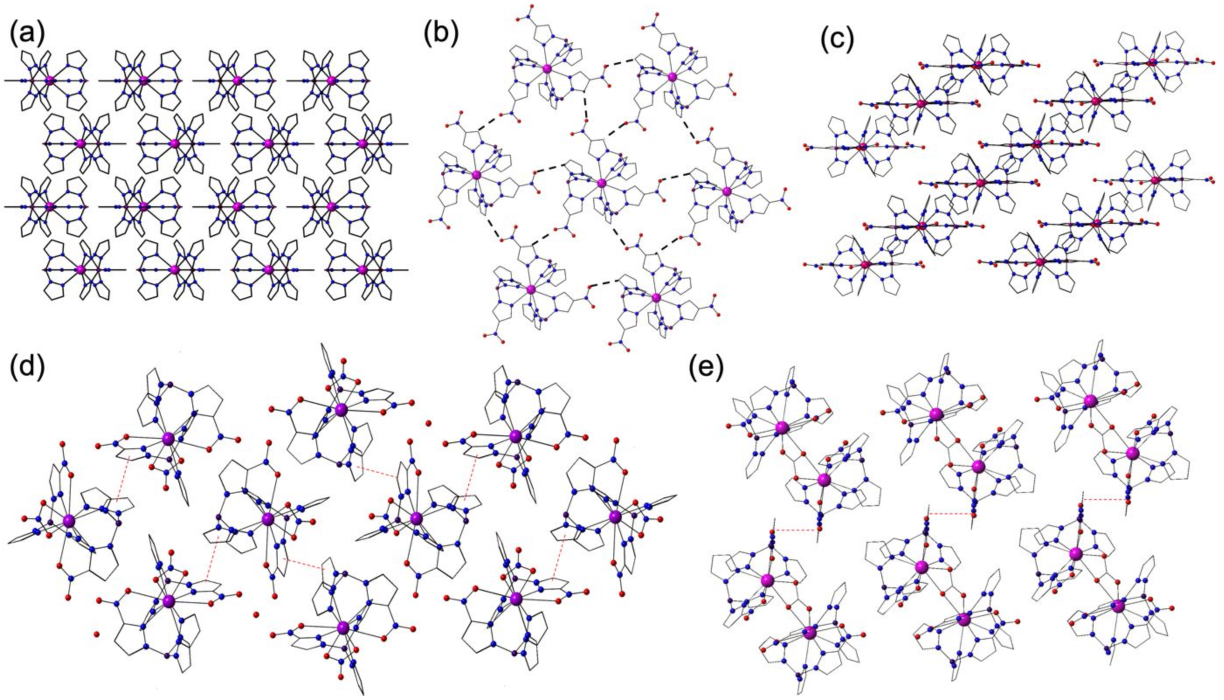


Figure 3: Solid-state structures of (a) nine-coordinate $LnTp_3$ (Ln = La – Dy) with no significant 2nd sphere interactions, (b) $Ln(4NO_2Tp)_3 \cdot C_6H_{14}$ (Ln = La – Dy) featuring $NO_2 \cdots HC$ hydrogen bonding (black broken lines), (c) $Ln(4NO_2Tp)_3 \cdot 7C_6H_6$ (Ln = La – Dy) with no significant 2nd sphere interactions, (d) $[Ln(3NO_2Tp)_2(NO_3)] \cdot ¼H_2O$ (Ln = La – Gd) featuring π-π stacking (red broken lines) and (e) $[\{Ln(3NO_2Tp)_2\}_2(\mu_2CO_3)] \cdot MeOH$ (Ln = La – Gd) displaying π-π stacking. Solvate molecules are excluded for clarity.

Optical Properties

The optical and photophysical properties of mono-substituted *n*-nitrotrispyrazolylborates-, $3\text{-}NO_2Tp^-$ and $4\text{-}NO_2Tp^-$ have been fully characterized recently by our group, *via* absorption and luminescence spectroscopies, in addition to modelling using TD-DFT.[24-25] A summary of the transitions involved in the antenna effect for Tp^-, $3\text{-}NO_2Tp^-$ and $4\text{-}NO_2Tp^-$ can be found in Figure 4. Tp^- complexes feature $\pi_{Pz} \rightarrow \pi_{Pz}^*$ transitions and triplet sensitization. $3\text{-}NO_2Tp^-$ species display a combination of intra-ligand charge transfer (ILCT) transitions, $\pi_{Pz} \rightarrow \pi_{3\text{-}NO_2Pz}^*$ and $n_{NO_2} \rightarrow \pi_{3\text{-}NO_2Pz}^*$ and triplet sensitization, while $4\text{-}NO_2Tp^-$ compounds exhibit $\pi_{Pz} \rightarrow \pi_{4\text{-}NO_2Pz}^*$ ILCT transitions and subsequent singlet sensitization. The dissimilarity in sensitization pathways of these Tp^- ligands is a direct result of the functionalization with a nitro-group, which either reduces the energy of the lowest lying triplet state, T_1 and/or affects the stability/lifetime of T_1. Thus, we can control the sensitization efficiency and overall performance of these complexes as optical devices by controlling the degree and position of the ring substitution. Looking ahead, the expansion into more functional groups will afford us even greater control over the materials' photophysical properties. Similar work has been done with lanthanide benzoates and pyridines, to ascertain which ring substituents enhance Ln^{3+} emission.[31-32]

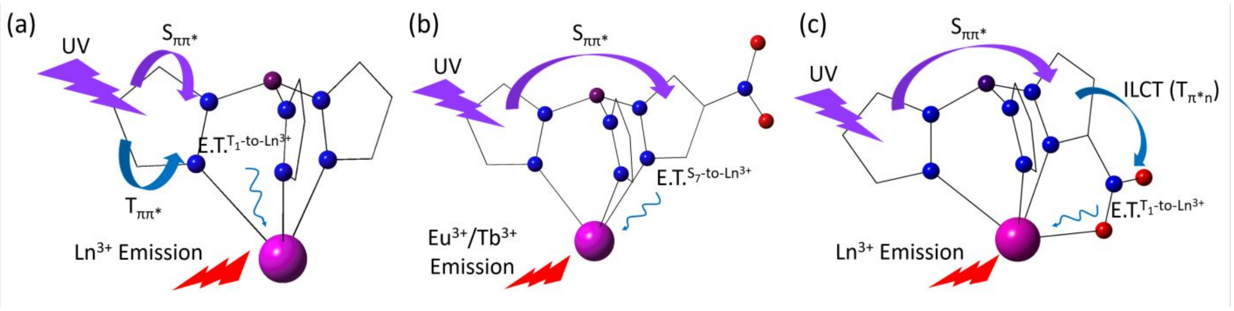


Figure 4: Diagrams of theoretical units, (a) [LnTp,] (b) [Ln(4-NO_2Tp)] and (c) [Ln(3-NO_2Tp)] displaying the transitions involved in RTp^--to-Ln^{3+} energy transfer/sensitization. Tp^- features singlet $\pi_{Pz} \longrightarrow \pi_{Pz}^*$ absorption upon UV excitation, intersystems crossing to triplet π_{Pz}^* state and Ln^{3+} sensitization *via* a triplet $\pi_{Pz}^* \longrightarrow \pi_{Pz}$ transition. 4-NO_2Tp^- features singlet $\pi_{Pz} \longrightarrow \pi_{4\text{-}NO_2Pz}^*$ absorption upon UV excitation, no intersystems crossing and Ln^{3+} sensitization *via* de-excitation of the $\pi_{4\text{-}NO_2Pz}^* \longrightarrow \pi_{Pz}$ transition. 3-NO_2Tp^- features singlet $\pi_{Pz} \longrightarrow \pi_{3\text{-}NO_2Pz}^*$ absorption upon UV excitation, intersystems crossing to triplet $\pi_{3\text{-}NO_2Pz}^*$ state and Ln^{3+} sensitization *via* a triplet $\pi_{3\text{-}NO_2Pz}^* \longrightarrow n_{NO_2}$ transition. Tp^- and 3-NO_2Tp^- can sensitize all of the lanthanides excluding Tm^{3+} for 3-NO_2Tp^-, while 3-NO_2Tp^- can only sensitize Eu^{3+} and Tb^{3+}.

Molecular Magnetism

Several lanthanide and most actinide single-molecule magnets have been synthesized using trispyrazolylborate ligands owing to their ability to crowd *f*-elements (Nd^{3+}, Dy^{3+}, Yb^{3+}, U^{3+} and Pu^{3+}) and generate stable complexes.[8-10, 33-37] In the design of molecular magnets, the geometry of the primary coordination sphere encompassing an *f*-element ion determines the barrier to magnetic relaxation, *U*, by an Orbach process, which is theoretically independent of the extended structure/crystal packing.[38] Functionalized Tp^- ligands offer an opportunity to precisely control the magnitude of *U via* crystal field effects, as ring substituents can drastically impact the basicity of the coordinating nitrogen atoms.[39] Rinehart and Long established that primarily axial coordination environments are optimal for ions with oblate (Nd^{3+}, Tb^{3+} and Dy^{3+}) electron densities, while strong equatorial interactions are best for prolate (Er^{3+}) ions, to maximize the single-ion anisotropy of those ions. However, *U* is not the sole determinant of SMM performance, as the effective, apparent barrier U_{eff} that can be determined experimentally is affected by a variety of factors e.g. phonons, intermolecular interactions, dipolar interactions,[38, 40] none of which are accounted for by the Orbach mechanism. As such, the ability to control the non-covalent interactions between Ln-containing molecules in a single-molecule magnet, using asymmetric Tp^- ligands, can a powerful tool that can be used to design SMMs.

Future Work and Outlook

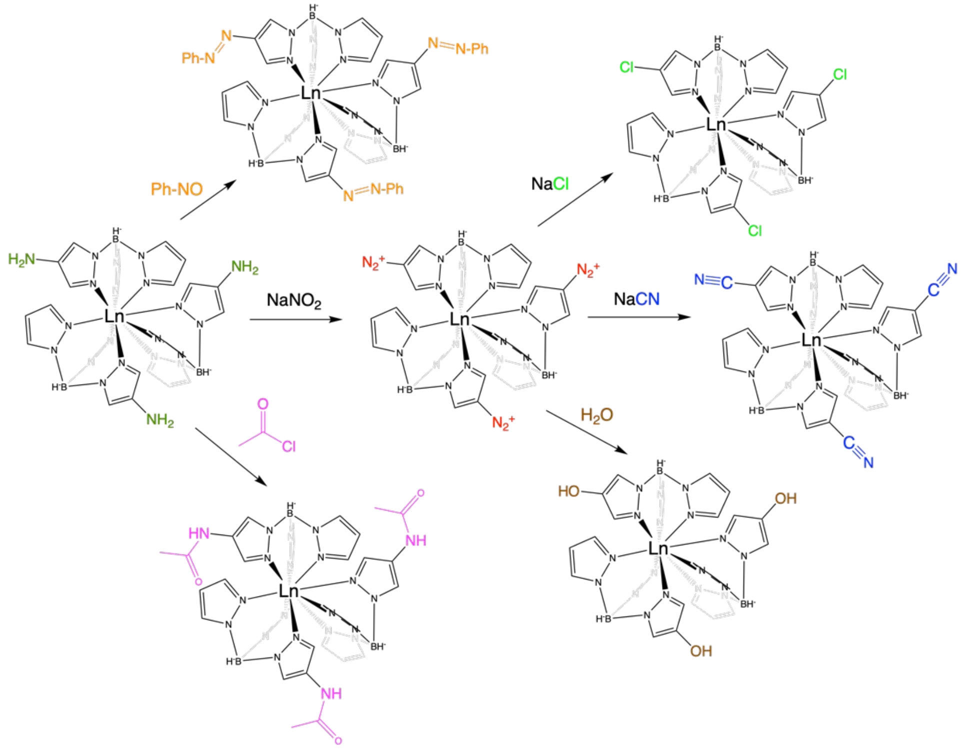
Simultaneous Optimization of Optical and Magnetic Properties. The observation of both luminescence and slow magnetic relaxation in Ln/Tp compounds makes them prime candidates for bi-functional magneto-luminescent materials.[24, 36-37, 41] Such compounds could find new applications in modern society including "information storage sensing (optical detection of magnetic compounds) and bio-imaging that combines Magnetic Resonance Imaging and fluorescence labelling," as described by Long et al.[41] They can also display interesting and unexpected properties such as the *optical polarization of nuclear spin* as reported by Ruben and coworkers in a Eu(III)/picoline-N-oxide dimer.[42] The incorporation of a single NO_2-group has shown to drastically affect the optical and magnetic properties of Ln/Tp compounds, thus there is a lot of potential in systematically studying how different types of functional groups will affect the optical and/or magnetic properties of new functionalized Ln/Tp-based compounds.

Diversification of Tp^- and Derived Complexes*.* As previously discussed, the introduction of different types of functional groups to the all-pyrazole heteroscorpionate ligand platform has the potential to significantly impact the physical (solubility), optical and magnetic properties of *f*-element Tp^- complexes. The precedent set by *n*-NO_2Tp^- complexes of sensitization of Ln^{3+} emission (Ln = Pr – Yb, except Pm and Tm), high stability and variable solubility suggests that future Ln/R-Tp^- complexes may find application as functional Ln-based materials. White light emission is possible owing to efficient sensitization of multiple lanthanide in mixed-metal compounds,[43] as well as chemotherapeutics, as highly luminescent Ln^{3+} complexes are indicative of efficient intersystem crossing ($S_n \rightarrow T_n$) and subsequent singlet oxygen generation.[44] Sensitive microthermometers/cellular temperature probes are feasible with water-soluble Ln/R-Tp^- complexes,[45] and other bioresponsive agents capable of optical- and/or magnetic resonance-contrast imaging.[46] Developing functionalized Ln/Tp compounds into such materials is dependent on the synthesis and characterization of panoply of new lanthanide complexes. In that respect, functionalized Tp^- are ideal ligands that offer the potential for either subtle or drastic changes in properties, associated with a change of functional groups.

A natural continuation after the NO_2-group, would be the introduction of strongly electron-donating amino (NH_2) groups, whether *via* the synthesis of the *n*-NH_2Tp^- ligand or reduction of preformed [Ln(*n*-$NO_2Tp)_x$] complexes (*n* = 3 or 4).[17] Unlike the nitro-group, electron-donating groups such as amino-functionalized antenna ligands can result in an increase in the energy of the T_1 state, as demonstrated by Boros and coworkers with pyridyl-functionalized, macrocyclic lanthanide complexes.[47-48] Thus, [Ln(NH_2Tp)$_x$] complexes have the potential to display enhanced quantum yields over the NO_2- or non-functionalized analogues. The information on which types of groups, e.g. NO_2-(withdrawing) vs NH_2-(donating), increase quantum yields in Ln/Tp compounds, can be used to design more efficient optical materials such as candidate LED-materials, luminescence sensors for pollutants and radiation. Additionally, the comparison among [LnTp$_3$], [Ln(4-NO_2Tp)$_3$] and [Ln(NH_2Tp)$_x$] would shed light on the impact that modulating the electronic structure Tp$^-$ ligands has on the optical and magnetic properties of Ln/Tp compounds and which property is best suited for a more electron-rich or electron-poor ligand environment; a useful design parameter for light-emitting Ln/Tp compounds.[49] This type of analysis of the primary coordination sphere and metal-ligand interaction is also critical to the development of LnTp-based single molecule magnets as well as AnTp-based materials (*discussed in the next section*).

Post-Synthetic Modifications of Ln/R-Tp$^-$ Complexes. Select functional groups such as NH_2-, and X- (X = Cl, Br, I) can facilitate additional functionalization *via* post-synthetic modifications. Taking inspiration from MOF(metal-organic framework)-chemistry, the structure and subsequent properties of hybrid materials can be *modified* after their initial synthesis.[50-52] As a consequence of post-synthetic modifications, MOFs can now access a wide variety of applications such as: gas adsorption, catalysis, chemical sensors and magnetism, dependent on the specific type of modification.[50] The application of this methodology to *f*-element Tp$^-$ complexes would aid in the development of robust structure-property relationships that informs the future design of *f*-element materials for a specific application, as well as open the door to the preparation of multifunctional materials. Using pendant, non-coordinating functional groups, e.g.: the NO_2-group in [Ln(4-NO_2Tp)$_3$], a host of new functional groups can be accessed. Both the amino- and halo-Tp$^-$ ligands can facilitate post-synthetic modifications (Figure 5) via orthogonal amine/diazonium and Pd cross-coupling chemistries respectively.[17, 53] This method will facilitate the generation of an expansive library of functionalized Ln/Tp compounds that span a wide range of steric requirements and electron-donating and withdrawing effects and consequently ligand field strengths.

Scheme 1: Amine/Diazonium Route



Scheme 2: Pd Cross-Coupling Route

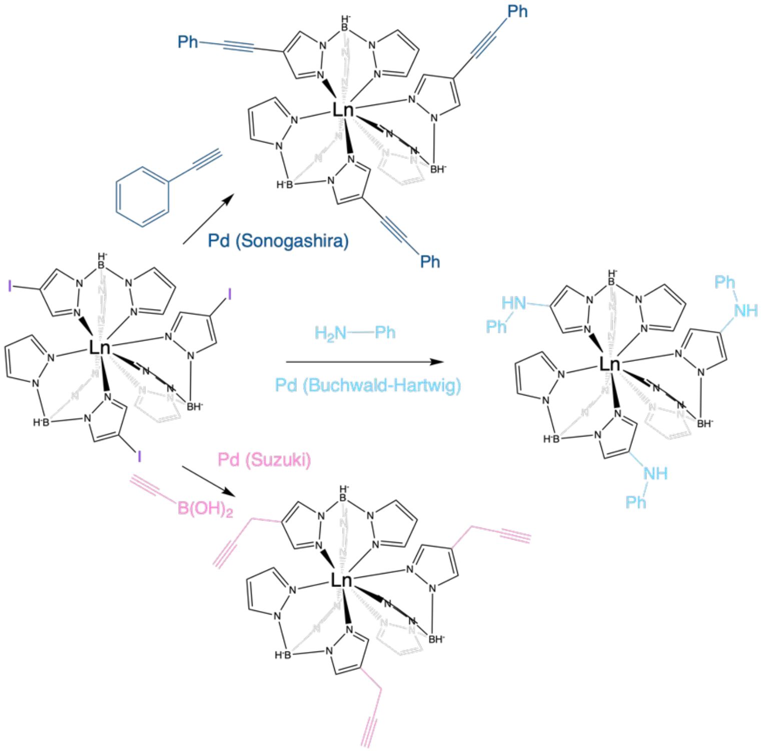


Figure 5: Schematic of the post-synthesis functionalization of: i) amino-substituted Ln/Tp complexes *via* amide, imine and diazonium chemistry and ii) iodo-substituted Ln/Tp complexes *via* Sonogashira, Buchwald-Hartwig and Suzuki Pd-cross coupling chemistry.

Actinide Tp$^-$ Complexes. The actinides (An), as a product of their 5*f*-valency, possess unique electronic properties including large spin-orbit coupling and large single-ion anisotropy, that make them good candidates for incorporation in future (magnetic) technology such as quantum computers and high-density data storage. Currently, the use of actinides in candidate magnetic materials for data processors is aspirational and require extensive materials' synthesis and screening. The combination of the actinides with all-pyrazole heteroscorpionates has the potential to address these challenges. Previous work with the actinides (Th – Cm) with Tp$^-$ or Tp^{Me2-}, has established that An/Tp complexes are highly stable in the solid state. This stability, combined with the diverse library of functional groups made available by post-synthetic modifications (Figure 5), facilitates the generation of actinide compounds that can be screened for desirable magnetic properties. The assertion of greater covalency in actinide complexes has been suggested to negatively affect magnetic anisotropy and slow magnetic relaxation,[30, 54] however, functionalization could offset this detriment, as NO$_2$-functionalization enhanced the SMM properties of [NdTp$_3$].

In addition to magnetic applications, the optical properties of the actinides can be harnessed to study the effect of the electronic structure of these under-studied elements. Since optical spectroscopy includes information on metal-centered excited states, ligand field splitting of those states, charge transfer states (between the metal and ligand) etc., it contains detailed information on the behavior of 5*f*-electrons (in case of the actinides), which is very difficult to predict using current theoretical models. The comprehensive analysis of the photophysical properties of the *n*-NO$_2$Tp$^-$ (*n* = 3 or 4) ligands by optical and computational methods,[24-25] makes them ideal ligands to study the optical properties of An^{3+} ions (An = U – Cm) as the demarcation between ligand vs An features will be straightforward. Of particular interest will be the polynuclear actinide complexes, and whether or not the same enhanced M^{3+}-to-M^{3+} interactions are observable in either the intra-electronic interactions or even magnetic coupling, given the higher degree of 5*f*-orbital overlap (covalency) in actinide complexes, as was the case for [{Ln(3-NO$_2$Tp)}$_4$(μ$_2$-OMe)$_6$(μ$_4$-O)] (Ln = Pr, Eu, Sm).[25]

The potential for variable denticity of functionalized trispyrazolylborates when coordinated to *f*-elements affords these ligands another application with the actinides, i.e. lanthanide/actinide separation within spent nuclear fuel. Owing to the intense heat load generated by Am-241 in spent nuclear fuel and the difficult in transmuting said Am when in the presence of lanthanide ions, considerable effort has been put forth in developing efficient methods for the separating lanthanides from transplutonium elements.[55-56] Given that 3-NO$_2$Tp$^-$ is flexidentate, it and other 3-substituted ligands, e.g. 3-COOHTp$^-$, have the potential to discriminate ions based on size. Potentially, this effect may be enhanced by adding more substituents in the 3-position, e.g. poly-nitrated Tp⁻ ligands, e.g. di-3-NO_2Tp^- [HB(3-$NO_2Pz)_2Pz$)] or tri-3-NO_2Tp^- [HB(3-$NO_2Pz)_3$].

Conclusion

Asymmetrically functionalized Tp^- ligands have the potential to be a highly diverse and tunable class of ligands with applications in optical and magnetic technologies; they represent the next step in the development of Tp^- chemistry first developed by Trofimenko in 1966 as the first example of all-pyrazole heteroscorpionates. Functionalization of Tp^- with a single NO_2-group has yielded a wide array of lanthanide materials displaying structural diversity, control over intermolecular interactions and crystal packing, charge transfer mediated optical properties and enhanced magnetic relaxation. As such, the inclusion of different types of functional groups could yield similar results of a drastic change in the optical and magnetic properties, compared to [$LnTp_3$].

Ongoing challenges involves synthesis and characterization of more asymmetric *n*-R-Tp^- (*n* = 3 or 4; R = NH_2, Cl, Br, I) ligands and derivative lanthanide complexes. Pendant amino- and halo-groups can be used to generate a library of [Ln(R-Tp)$_3$] compounds *via* post-synthetic modifications (amine/diazonium and Pd-cross coupling chemistries), structure-property relationships can be established to inform the design of multi-functional [Ln(R-Tp)$_3$] compounds and/or Ln-materials designed for a specific application. Additionally, this lanthanide work will inform the synthesis of [An(R-Tp)$_3$] compounds, where insights into 5*f*-electronic properties we can gleamed, aiding with the development of actinide spectroscopy and magnetic behavior. This field holds a lot of promise as the stability, and now tunability of [MTp_x] compounds, with the advent of all-pyrazole heteroscorpionates, allows for the facile study of isoelectronic *f*-element materials and delineation of the properties of 4*f* vs 5*f*-systems.

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The manuscript was written through contributions of all authors. CHH drafted the manuscript, which was edited by all authors.

Notes

The authors declare no competing financial interests.

Conflicts of Interest

The authors have no conflicts to declare.

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