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# Near-infrared Emitting Heterobimetallic Zn-4f Schiff Base Complexes with Visible Excitation Wavelength

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**Abstract:** Herein, we report the synthesis and characterization of heterobimetallic Zn-4f complexes formed by the 'valnap' ligand (**L**<sup>1</sup>) with extended aromaticity, thereby acting as visibly absorbing antenna for generating the near-infrared (NIR) luminescence of three different lanthanide(III) ions (Ln<sup>3+</sup>). The series of new Zn(py)L<sup>1</sup>Ln(NO<sub>3</sub>)<sub>3</sub> complexes [Ln = Yb (**1**), Nd (**2**), Er (**3**)] have been characterized by single crystal X-ray diffraction and were found to be isotypic, with a variation in the Ln<sup>3+</sup> coordination number (CN = 9 – 11) in line with increasing atomic radius. Absorption spectra recorded for **L**<sup>1</sup>, ZnL<sup>1</sup>, and complexes **1** – **3** display ligand-based absorption bands in the UV ( $\lambda_{\text{max}} \sim 320$  nm) and visible regions ( $\lambda_{\text{max}} \sim 430$  nm) with molar absorption coefficients up to  $6.3 \cdot 10^4$  and  $3.9 \cdot 10^4$  M<sup>-1</sup>cm<sup>-1</sup>, respectively. Upon excitation into ligand-centered absorption bands in the visible range, characteristic NIR emission signals of Yb<sup>3+</sup> (**1**), Nd<sup>3+</sup> (**2**), and Er<sup>3+</sup> (**3**) have been obtained. Quantum yields measured under visible excitation at 430 nm ( $Q_{\text{Ln}}$ ) and observed luminescence lifetimes ( $\tau_{\text{obs}}$ ) reflecting the excited states attributed to the <sup>2</sup>F<sub>5/2</sub> (Yb<sup>3+</sup>), <sup>4</sup>F<sub>3/2</sub> (Nd<sup>3+</sup>) and <sup>4</sup>I<sub>13/2</sub> (Er<sup>3+</sup>) levels have been determined. These data quantifying the luminescence properties of this family of complexes and absorption bands in the visible range with large molar absorption coefficients make complexes **1-3** of potential interest for biological applications where UV light is inappropriate.

## Introduction

There is a rich chemistry surrounding the tetradentate dianionic salen ligand platform (**Figure 1**) due, in part, to its modular and facile synthesis from a wide variety of diamines and aldehydes. Monometallic salen complexes have attracted attention for their catalytic activity in a number of transformations,<sup>[1]</sup> and particularly as enzyme model complexes.<sup>[2]</sup> The reaction, perhaps most celebrated, is the enantioselective Jacobsen-Katsuki epoxidation of olefins with a chiral manganese salen complex.<sup>[3]</sup> The rapid growth of the field in the mid-1990's has led Costes and co-workers to the discovery that the valen ligand (**Figure 1**) is capable of forming heterobimetallic 3d-4f complexes.<sup>[4]</sup>

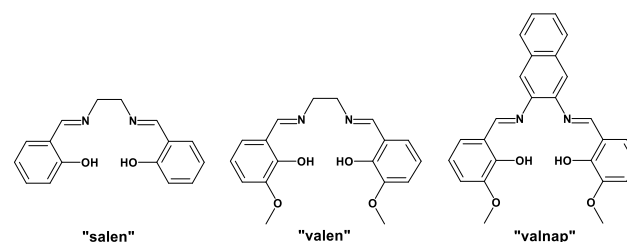
Condensation of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) with ethylenediamine produces a ligand with the traditional  $\kappa^2$ -N<sub>2</sub>O<sub>2</sub> metal binding site, as well as a peripheral  $\kappa^2$ -O<sub>2</sub>O<sub>2</sub> binding site.

The potential coordination chemistry of this ligand type has been reviewed extensively,<sup>[5]</sup> and many have taken advantage of the 3d-4f metal proximity to develop magnetic materials.<sup>[6]</sup> The  $\pi$ -conjugated ligand system also lends itself to act as an antenna for the sensitization of characteristic luminescence of lanthanide(III) ions (Ln<sup>3+</sup>). The Ln<sup>3+</sup> exhibit metal-based luminescence from *f-f* transitions, but as most of these electronic transitions are forbidden, free Ln<sup>3+</sup> absorb weakly. In order to generate a sufficient luminescence signal, a well-adopted strategy is based on the presence of a highly absorbing antenna that can transfer energy to the accepting electronic levels of Ln<sup>3+</sup>.<sup>[7]</sup> Particularly relevant to this work, *d-f* hybrid complexes have been shown to sensitize lanthanide luminescence,<sup>[8]</sup> taking advantage of a metal to ligand charge transfer (MLCT),<sup>[9]</sup> from *d<sup>6</sup>* metals (M = Ru<sup>2+</sup>, Os<sup>2+</sup>, Re<sup>2+</sup>).<sup>[10]</sup> As discussed below, we have selected *d<sup>10</sup>* Zn<sup>2+</sup> for our antenna, which will not participate in such charge transfer states.

Salen type ligands have been established as efficient antennae for NIR luminescence in the absence of a transition metal, with Ln<sup>3+</sup> coordinated in the traditional  $\kappa^2$ -N<sub>2</sub>O<sub>2</sub> metal binding site, in which case a dimeric [Nd<sup>3+</sup>(L)]<sub>2</sub> is formed.<sup>[11]</sup> Zinc(II) complexes of the valen ligand, monomeric [Zn<sup>2+</sup>(L)Ln<sup>3+</sup>], have been proven to be suitable antennae, and shown to sensitize NIR luminescence from Yb<sup>3+</sup>, Nd<sup>3+</sup>, and Er<sup>3+</sup>.<sup>[12]</sup> Subsequently, this modular multidentate ligand platform has allowed for the synthesis of coordination complexes with varying ligand to metal ratios,<sup>[13]</sup> high-nuclearity clusters,<sup>[14]</sup> and infinite coordination polymers,<sup>[15]</sup> all of which retain their NIR luminescence. The optical properties of the antenna can be controlled by the generation of a bathochromic shift by extending the aromatic system,<sup>[16]</sup> or by introducing electron withdrawing heavy-atoms (Br).<sup>[17]</sup> The photophysical tunability of this ligand platform has prompted us to explore antennae with low-energy visible excitation for potential biological applications, where high-energy UV excitation is inappropriate. Herein, we report a series of NIR-emitting Schiff base complexes with visible excitation, utilizing the extended aromatic valnap ligand antenna (**Figure 1**).

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Supporting information and the ORCID identification number(s) for the author(s) for this article is given via a link at the end of the document.

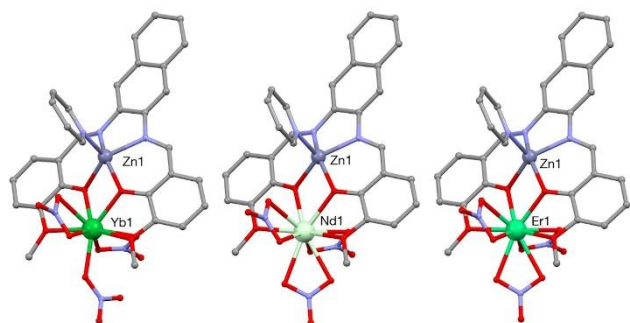


**Figure 1.** Schiff base ligand platforms of interest.

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## Results and Discussion

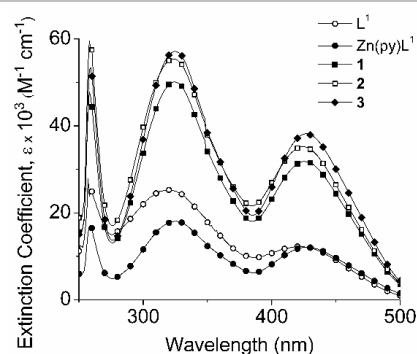
Condensation of 2,3-diaminonaphthalene with *o*-vanillin yielded the valnap ligand (**L**<sup>1</sup>); subsequent treatment with zinc(II) nitrate produced the **ZnL**<sup>1</sup> complex in moderate yield (ca. 50%, two steps).<sup>[18]</sup> Reflux with the appropriate Ln<sup>3+</sup> nitrate salt followed by vapor diffusion of tetrahydrofuran into pyridine (py) gave the series of **Zn(py)L**<sup>1</sup>Ln(NO<sub>3</sub>)<sub>3</sub> complexes [Ln = Yb (**1**), Nd (**2**), Er (**3**)] as crystalline products (ca. 10 – 25% isolated yield), suitable for single crystal X-ray diffraction analyses, with the Zn(py) bound to the κ<sup>2</sup>-N<sub>2</sub>O<sub>2</sub> pocket and the Ln(NO<sub>3</sub>)<sub>3</sub> bound to the κ<sup>2</sup>-O<sub>2</sub>O<sub>2</sub> pocket of **L**<sup>1</sup>.



**Figure 2.** X-ray crystal structures of **1** – **3** viewed along the *a*-axis.

X-ray crystal structure refinement data for complexes **1** – **3** are summarized in **Supporting Information** (CCDC # 1947963 – 1947965). The structures reported here are isotopic (**Figure 2**), but with variations in coordination number around the Ln<sup>3+</sup> ion, in line with the lanthanide contraction. The largest La<sup>3+</sup> ion, reported previously and crystallizing in a different setting but with very similar molecular structure, has a coordination number of 11 (η<sup>4</sup>-valnap/[η<sup>2</sup>-NO<sub>3</sub>]<sub>3</sub>/H<sub>2</sub>O) by coordination of an additional water molecule which is not present in Yb, Nd and Er complexes **1** – **3**.<sup>[18]</sup> Slightly smaller sized Nd<sup>3+</sup> and Er<sup>3+</sup> have coordination numbers of 10 (η<sup>4</sup>-valnap/[η<sup>2</sup>-NO<sub>3</sub>]<sub>3</sub>), and the smallest Yb<sup>3+</sup> ion studied has a coordination number of 9 (η<sup>4</sup>-valnap/[η<sup>2</sup>-NO<sub>3</sub>]<sub>2</sub>/[η<sup>1</sup>-NO<sub>3</sub>]), through detachment of one nitrate oxygen atom. In each case, the Ln(NO<sub>3</sub>)<sub>3</sub> moiety lies below the ligand plane, with distances between Ln<sup>3+</sup> and the ligand plane ranging from 0.32 Å for the smallest Yb<sup>3+</sup> to 0.86 Å for the largest La<sup>3+</sup>. The Zn<sup>2+</sup> ion adopts a distorted square pyramidal geometry, with the axial pyridine ligand pulling the Zn<sup>2+</sup> above the ligand plane. Unsurprisingly, it is observed that the smaller the Ln<sup>3+</sup> and the closer it sits to the ligand plane, the further the Zn<sup>2+</sup> is from the same calculated plane (0.63 Å, Yb<sup>3+</sup>; 0.52 Å, La<sup>3+</sup>). One important parameter for the design of NIR-emitting molecular complexes is the distance between the Ln<sup>3+</sup> and any high energy oscillators in the form of –CH, –NH, or –OH bonds; the overtones of these oscillators have a propensity for quenching NIR luminescence. The closest –CH bond in this antenna system lies ca. 3.5 Å from the Ln ion. Some of the most efficient NIR emitting, lanthanide molecular complexes in the literature have Ln ions sequestered from these types of oscillators by ca. 4.3 – 7.0 Å.<sup>[19]</sup>

Electronic absorption spectra in solution (DMSO) recorded for valnap ligand **L**<sup>1</sup> and associated metal complexes displayed two conserved features in the UV and visible/near-visible ranges with apparent maxima at ~320 and 430 nm; no absorption features were observed beyond 500 nm (**Figure 3**). The extinction coefficients are all on the same order of magnitude and consistent



**Figure 3.** Electronic absorption spectra of **L**<sup>1</sup> and metal complexes in DMSO (5 μM) at room temperature.

with allowed ligand-based transitions (**Table 1**). Zn<sup>2+</sup> does not participate in ligand to metal charge transfer (LMCT) and any Zn<sup>2+</sup> metal to ligand charge transfer (MLCT) transitions are expected to be located at much higher energy (< 250 nm),<sup>[20]</sup> further confirming the ligand-based nature of these electronic transitions.

In the solid state, upon excitation into the lowest energy electronic absorption feature (λ<sub>ex</sub> = 430 nm), characteristic NIR luminescence was observed arising from the <sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub>, <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>J</sub> (J = 9/2, 11/2, 13/2), and <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions, for Yb<sup>3+</sup> (**1**), Nd<sup>3+</sup> (**2**), and Er<sup>3+</sup> (**3**), respectively (**Figure 4**). Quantitative luminescence parameters, such as total quantum yield under ligands excitation (Q<sub>Ln</sub><sup>L</sup>) and observed luminescence lifetime (τ<sub>obs</sub>), reflect the efficiency of energy transfer from the **ZnL**<sup>1</sup> antenna to the Ln<sup>3+</sup> ion and the level of protection of the latter from non-radiative deactivations. Reported here for **1** – **3** (**Table 1**), Q<sub>Ln</sub><sup>L</sup> and τ<sub>obs</sub> were found to be on the same order of magnitude as those in the literature for molecular complexes in the solid state.<sup>[21]</sup>

**Table 1.** Quantitative photophysical parameters for **L**<sup>1</sup>, **ZnL**<sup>1</sup> and complexes **1-3** in the solid state or in DMSO solution at room temperature.

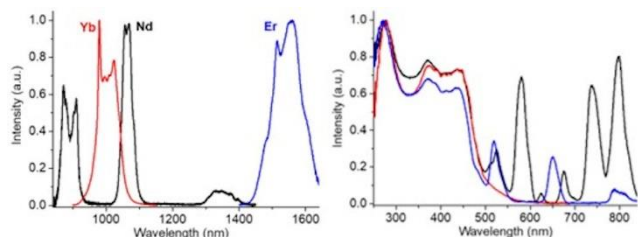
Compound	λ <sub>max</sub> (nm); log(ε) M <sup>-1</sup> cm <sup>-1</sup> [a]	NIR Q <sub>Ln</sub> <sup>L</sup> (%) <sup>[b, c]</sup>	τ <sub>obs</sub> (μs) <sup>[b, d]</sup>
<b>L</b> <sup>1</sup>	318; 4.4 438; 4.1	-	-
<b>ZnL</b> <sup>1</sup>	327; 4.3 427; 4.1	-	-
<b>1</b>	323; 4.7 423; 4.5	1.07(3)	13.7(4)
<b>2</b>	326; 4.7 423; 4.6	0.36(1)	1.43(5)
<b>3</b>	323; 4.8 425; 4.6	2.86(9) × 10 <sup>-2</sup>	3.56(5)

[a] For solutions in DMSO (λ<sub>max</sub> @ 5 μM). [b] For samples in the solid state; 2σ values are given between parentheses. [c] λ<sub>ex</sub> = 430 nm. [d] λ<sub>ex</sub> = 355 nm.

Solid state excitation spectra for **1** – **3** upon monitoring Yb<sup>3+</sup>, Nd<sup>3+</sup> or Er<sup>3+</sup> transitions at 980, 1064 or 1525 nm, respectively (**Figure 4**), exhibit broad ligand-centered peaks, trailing to 550 nm, being in alignment with solution phase absorption spectra (**Figure 3**). Such observation confirms the efficient sensitization of these NIR-emitting lanthanide(III) ions through ‘antenna effect’. In addition to broad ligand-centered bands, excitation spectra of Nd<sup>3+</sup> (**2**) and Er<sup>3+</sup> (**3**) complexes exhibit a series of narrower characteristic intraconfigurational f-f transitions with comparable

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(Nd<sup>3+</sup>) or lower (Er<sup>3+</sup>) intensities. These data prove the ability of direct sensitization of Nd<sup>3+</sup> and Er<sup>3+</sup> NIR emission in such heterobimetallic Schiff base complexes in the solid state.



**Figure 4.** Solid state NIR emission spectra (left) ( $\lambda_{\text{ex}} = 430$  nm) and excitation spectra (right) (Yb<sup>3+</sup>  $\lambda_{\text{ex}} = 980$  nm; Nd<sup>3+</sup>  $\lambda_{\text{ex}} = 1064$  nm; Er<sup>3+</sup>  $\lambda_{\text{ex}} = 1525$  nm) of complexes 1-3 at room temperature.

### Conclusion

We have shown that the modularity of the 'valen' type ligand platform allows for an attractive level of synthetic tunability of antenna photophysical properties for the sensitization of NIR Ln<sup>3+</sup> luminescence. The series of Zn(py)L<sup>1</sup>Ln(NO<sub>3</sub>)<sub>3</sub> complexes [Ln = Yb (1), Nd (2), Er (3)] exhibit characteristic NIR luminescence upon excitation in the visible range.

This work represents the first quantitative determination of NIR luminescence parameters for this type of Schiff base antenna platform, thereby serving as a benchmark for future design strategies. The variation of transition metal within the valnap scaffold and the development of new ligands with additional aromaticity or functional groups will allow us to design efficient Ln<sup>3+</sup>-based NIR-emitting probes suitable for biological applications.

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**Keywords:** heterobimetallic • lanthanide • luminescence • near-infrared • Schiff base

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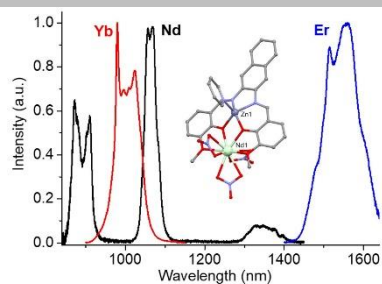
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Entry for the Table of Contents (Please choose one layout)

**Key Topic:** Lanthanide Luminescence

## COMMUNICATION

Heterobimetallic Zn-4f complexes have been synthesized with the 'valnap' salen type ligand. These complexes exhibit characteristic near-IR lanthanide luminescence from Yb<sup>3+</sup>, Nd<sup>3+</sup>, and Er<sup>3+</sup>, with sensitization occurring with visible excitation ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ). Shown here is a representative X-ray structure (Zn<sup>2+</sup>/Nd<sup>3+</sup>) and solid state near-IR emission spectra.



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