

Aryl-Bridged 1-Hydroxypyridin-2-one: Sensitizer Ligands for Eu(III)

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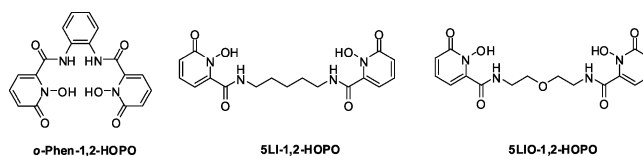
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The synthesis, crystal structure, solution stability, and photophysical properties of an aryl group bridging two 1-hydroxypyridin-2-one units complexed to Eu(III) are reported. The results show that this backbone unit increases the rigidity of the ensuing complex, and also the conjugation of the ligand. As a result of the latter, the singlet absorption energy is decreased, along with the energy of the lowest excited triplet state. The resulting efficiency of sensitization for the Eu(III) ion is influenced by these phenomena, yielding an overall quantum yield of 6.2% in aqueous solution. The kinetic parameters arising from the luminescence data reveal an enhanced nonradiative decay rate for this compound when compared to previously reported aliphatic bridges.

Due to the Laporte forbidden character and intraconfigurational nature of the $4f$ transitions,¹ luminescence from lanthanide cations is typically highly monochromatic, exhibits long-lived excited-state lifetimes when compared to organic compounds, and is usually insensitive to quenching by molecular oxygen, making these metal ions ideal for applications as fluorescent probes,² optical signal amplifiers,³ or light-emitting diodes.⁴ Unfortunately, for the same reason, the molar absorption coefficient of lanthanide transitions is very small (less than $10 \text{ M}^{-1} \text{ cm}^{-1}$).⁵ To obviate this problem, organic ligands having a large molar absorption coefficient can be coordinated to the lanthanide ion, resulting in sensitized emission through the so-called antenna effect. The mechanism of antenna sensitization can be approximated by three differing steps: the initial excitation of the ligand, followed by intersystem crossing to give an excited triplet state, and then subsequent energy transfer to yield the metal-centered excited state, which emits light.^{1,5–7} For this

Chart 1. Chemical Structures of the *o*-Phen-1,2-HOPO Ligand and Its Parent Derivatives (5LI-1,2-HOPO and 5LIO-1,2-HOPO)



mechanism, the energy of the sensitizing triplet state relative to the $^5\text{D}_0$ or $^5\text{D}_1$ excited states of Eu(III) is one of the critical parameters which can be tuned in order to optimize the system. Furthermore, the rate of intersystem crossing, energy transfer, and radiative versus nonradiative decay of the metal must be considered, and these rates may all be influenced by the geometry and chemical structure of the sensitizing ligand. We report here the synthesis, crystal structure, solution stability, and photophysical properties of a new 1-hydroxypyridin-2-one (1,2-HOPO)-based chelator, *o*-Phen-1,2-HOPO (Chart 1), acting as a tetradentate ligand to form an ML_2 complex with Eu(III). This ligand bridges two 1,2-HOPO units *via* an aryl group, yielding a higher degree of conjugation when compared to previously reported alkyl linkages.^{8,9} The resultant stability constants and optical properties of this new ligand architecture are compared to the parent 5LIO-⁹ and 5LI-1,2-HOPO⁸ compounds.

The *o*-Phen-1,2-HOPO ligand is readily prepared by reaction of the benzyl-protected 1,2-HOPO-6-carboxylic acid intermediate prepared¹⁰ from commercially available 6-bromopicolinic acid with the terminal primary aryl amines of *o*-aminoaniline (*o*-Phen), yielding the protected ligand (Scheme S1, Supporting Information). Deprotection under strongly acidic conditions gave the desired ligand, and complexation under standard conditions with Eu(III) furnished the desired complex in reasonable yield. X-ray-quality

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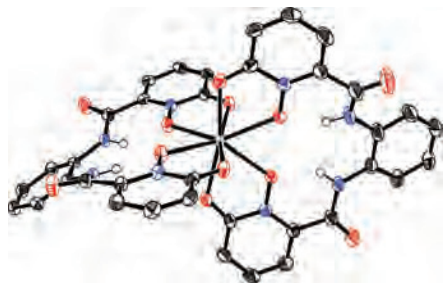


Figure 1. X-ray structure of the $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ complex ($^+\text{NMe}_4$ counteranion, selected H atoms and solvent molecules omitted for clarity). Non-H atoms are drawn at the 50% probability level.

crystals of the ligand and of the Eu(III) complex were grown by vapor diffusion of ether into methanol solutions. Further characterizations of the ligand and complexes with Eu(III) and Gd(III) are reported in the Supporting Information. Full crystallographic data in CIF format and the ligand crystal structure are given in the Supporting Information.

The X-ray structure of the EuL_2 complex is shown in Figure 1, wherein a significant difference between previously reported structures with alkyl linkages becomes readily apparent. For the *o*-Phen complex, while the coordination number remains the same ($\text{CN} = 8$), complexation to the metal forms a structure such that each ligand strand is oriented almost orthogonally, whereas previous structures had each ligand arranged in a pseudoparallel “sandwich”-type fashion. The geometry adopted can be attributed to the more rigid aromatic linker in the present case, and the significantly shorter (two atom) linkage between the 1,2-HOPO units within the *o*-Phen ligand backbone. Despite this obvious structural difference, the coordination polyhedron, as determined by shape analysis,⁸ remains closest to the bicapped trigonal prismatic (C_{2v}) geometry, and the observed coordinate bondlengths ($\text{Eu}-\text{O} = 2.393 \text{ \AA}$) are similar to those in previous reports.^{8,9}

Solution thermodynamic experiments assessed the stability of the $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ complex. The free ligand is quite acidic, with $\log K_a$ values of 3.88(3) and 5.35(2) attributed to the N-hydroxyl groups. Competition titrations with DTPA at variable pH determined the stability of the $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ chelate yielding $\beta_{120} = 22.73(5)$.¹¹ Six titrations at a low pH (2.4–1.55) with different Eu/L ratios (1:2.5 to 1.5:1) determined $\beta_{110} = 11.76(5)$ and $\beta_{121} = 25.26(3)$, which were then used to calculate a pEu of 18.58(3). The excellent stability of the $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ complex, as determined by its pEu, can be partially attributed to the 1,2-HOPO chelate which forms stable complexes with lanthanide ions.¹⁰ However, when compared to the complexes linked by an aliphatic linear spacer (5LIO-1,2-HOPO, pEu \sim 18.64(10),⁹ and 5LI-1,2-HOPO, pEu \sim 18.35(5)⁸), these data do not follow the usual trend that more acidic ligands (of the same chelate group) will form weaker metal complexes.¹² Instead, while the most acidic ligand is *o*-Phen-1,2-HOPO, it is evident that the 5LI-1,2-HOPO ligand forms the weakest ML_2 chelate. For the

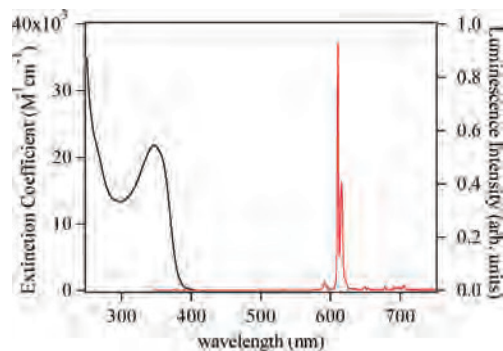


Figure 2. Absorption and luminescence spectra of $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ in a 0.1 M Tris buffer (pH 7.4) containing 0.3% (v/v) DMSO.

Table 1. Photophysical Data Obtained for $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ in a 0.1 M Tris Buffer (pH 7.4) Containing 0.3% (v/v) DMSO

$\lambda_{\text{max}}(\epsilon_{\text{max}})$	342 nm ($21\,020 \text{ M}^{-1} \text{ cm}^{-1}$)	k_{rad}	680 s^{-1}
$\tau_{\text{obs}}/\text{H}_2\text{O}$	536 μs	k_{nonrad}	1186 s^{-1}
$\tau_{\text{obs}}/\text{D}_2\text{O}$	734 μs		
$\Phi_{\text{tot}}/\text{H}_2\text{O}$	0.062 ± 0.009	Φ_{Eu}	0.365
τ_{rad}	1470 μs	η_{sens}	0.170

5LIO-1,2-HOPO derivative, it was suggested⁹ that the improved stability was a result of intermolecular hydrogen bonding involving the amide protons and the central oxygen of the bridge, which rigidifies the ligand, providing an improved chelate effect. Clearly, a similar argument applies in the present case, explaining the improved complex stability over 5LI-1,2-HOPO when using the *o*-Phen scaffold.

Electronic structure calculations using TD-DFT were performed using Gaussian 03.¹³ As a simplified model, only the Na^+ complex of a 6-phenylamide of the 1,2-HOPO anion (Figure S1, Supporting Information) was used as the input structure, and this was first geometry optimized to yield the relaxed output geometry with no symmetry constraints.^{8,14} The first excited-state can be described principally by a $\text{HOMO} \rightarrow \text{LUMO}+1$ excitation, with a smaller contribution from the $\text{HOMO}-2 \rightarrow \text{LUMO}+2$ excitation, yielding mixed $\pi-\pi^*$ and $n-\pi^*$ character, respectively, for this transition, with a predicted energy of $28\,950 \text{ cm}^{-1}$ (345.5 nm).

The experimentally determined absorption and luminescence spectra for $[\text{Eu}(\text{o-Phen-1,2-HOPO})_2]^-$ are shown in Figure 2, and the relevant photophysical parameters determined experimentally (and calculated from the emission spectrum as discussed elsewhere^{15,16}) are summarized in Table 1. The absorption spectrum is typical of the 1,2-HOPO chromophore^{8,9} and is red-shifted upon deprotonation or complexation to the metal. The maximum absorption, at *ca.* 342 nm, is significantly red-shifted compared to aliphatic-bridged analogs^{8,9} and is in excellent agreement with the time-dependent density-functional theory (TD-DFT) calculation. This is consistent with the expectation that the aryl-bridged ligand, compared with the previously reported

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aliphatic-bridged complexes, has a more delocalized electronic excited state.^{8,9} The luminescence spectrum is typical of those for the Eu(III) complexes. Notably, the $^5D_0 \rightarrow ^7F_2$ hypersensitive transition is very intense (83% of the Eu(III) spectral intensity), resulting in almost pure red luminescence ($\lambda_{em} = 612$ nm). The Gd(III) complex was prepared in order to determine the ligand-centered triplet-state energy. This metal cation has a similar size and atomic weight when compared to Eu(III), yet lacks an appropriately positioned electronic acceptor level, so luminescence measurements in a solid matrix (1:3 (v/v) MeOH/EtOH) performed at 77 K enable the observation of phosphorescence of the ligand (T_{0-0} state). For $[Gd(o\text{-Phen-1,2-HOPO})_2]^-$, upon cooling to 77 K, an intense unstructured emission band appeared from 450 to 600 nm (Figure S2, Supporting Information), which can be attributed to phosphorescence from the ligand T_{0-0} state. As detailed elsewhere, the lowest T_{0-0} energy was estimated by spectral deconvolution of the 77 K luminescence signal into several overlapping Gaussian functions (Figure S2, Supporting Information).⁸ The resulting T_{0-0} energy was evaluated to be *ca.* 20 964 cm^{-1} , which is notably in excellent agreement with the value estimated by TD-DFT methods for the $[Na(6\text{-phenyl-amide-1,2-HOPO})]$ complex ($T_{0-0} \sim 20\,700\,cm^{-1}$). The energetic position of this triplet state is *ca.* 300 cm^{-1} lower in energy, when compared to the values obtained *via* an identical analysis for 5LIO- and 5LI-1,2-HOPO. In the latter cases, the energy gap between T_{0-0} and the 5D_1 accepting state is optimal, at 2230 cm^{-1} .^{8,9} Hence, the decrease of this energy gap can be expected to decrease the sensitization efficiency for the *o*-Phen ligand.

A corresponding time-resolved analysis of the luminescence for $[Eu(o\text{-Phen-1,2-HOPO})_2]^-$ measured at 612 nm in H_2O and D_2O gave monoexponential decays with decay times of *ca.* 536 μs and *ca.* 734 μs , respectively, slightly shorter than those determined for the aliphatic spacer ligands. Application of the improved Horrocks equation¹⁷ to determine q , the number of inner-sphere water molecules, gives a value of 0.2 ± 0.1 . While essentially zero, the value suggests that the metal center may be slightly more accessible to solvent OH oscillators, which quench Eu(III)-centered luminescence. The luminescence quantum yield, Φ_{tot} , is 6.2% in aqueous solution. Given the moderate decrease in T_{0-0} for the *o*-Phen-1,2-HOPO (20 964 cm^{-1} *vs* 21 260 cm^{-1} for 5LIO-) complexes, the striking difference between the overall quantum yield data reported herein and that described previously for alkyl-linked 1,2-HOPO ligands (6.2% for *o*-Phen *vs* 20.7% and 21.5% for 5LI- and 5LIO-, respectively) warrants further investigation. While the difference in T_{0-0} energy and solvent accessibility are no doubt important, additional quenching pathways may be operant, affecting the efficiency of the antenna effect, due to differences in the chemical structure between $[Eu(o\text{-Phen-1,2-HOPO})_2]^-$, $[Eu(5LI-1,2-HOPO)_2]^-$, and $[Eu(5LIO-1,2-HOPO)_2]^-$.

In order to understand these differences, the kinetic parameters of the sensitization phenomenon were determined by calculating the nonradiative decay rate, k_{nonrad} .^{15,16} The sensitization efficiency, η_{sens} , defined as the product of the efficiency of

the energy transfer, η_{ET} , by the efficiency of the InterSystem Crossing (ISC), η_{ISC} was determined using the equation

$$\Phi_{tot} = \eta_{ISC} \times \eta_{ET} \times \Phi_{Eu} \quad (1)$$

with the resultant photophysical parameters summarized in Table 1. For $[Eu(o\text{-Phen-1,2-HOPO})_2]^-$, the radiative decay rate, k_{rad} , is slightly higher than that of either the 5LIO- or 5LI- derivatives (680 s^{-1} *vs* 620 s^{-1} and 609 s^{-1} , respectively). While each of the complexes has no water molecule in the inner-sphere, k_{nonrad} is much higher for $[Eu(o\text{-Phen-1,2-HOPO})_2]^-$, yielding a value as large as 1186 s^{-1} versus 810 s^{-1} and 740 s^{-1} respectively for the 5LIO- and 5LI-complexes. As a result, the quantum yield of metal-centered luminescence, Φ_{Eu} , is lower for the *o*-Phen bridge than for the 5LI- and 5LIO- (36.5% *vs* 45.7% and 43.3%, respectively). Applying this result to eq 1, we can see that the sensitization efficiency, η_{sens} ($\eta_{ISC} \times \eta_{ET} \sim 17\%$ *vs ca.* 48%), is much lower for the *o*-Phen bridge than for the 5LI- or 5LIO-1,2-HOPO derivatives. This indicates that the intersystem crossing and the energy transfer are affected in the *o*-Phen complex, resulting in a less efficient sensitization process. While this may be a result of the lower triplet-state energy, which facilitates enhanced nonradiative decay of the Eu(III) excited state by back energy transfer, we note that the difference in zero-phonon energy between the S_1 and T_{0-0} excited states is significantly larger for the alkyl-linked 5LI- and 5LIO- systems compared to the *o*-Phen complex (*i.e.*, $\Delta E = 8800\,cm^{-1}$ *vs* $\Delta E = 8280\,cm^{-1}$). We attribute the change in rate of intersystem crossing and decrease in η_{sens} to this difference in the singlet–triplet energy gap.

To summarize, this EuL_2 complex ($L =$ two 1,2-HOPO units connected by an aryl group) is very stable and soluble in aqueous solution. Despite the fact that the sensitization of the lanthanide ion is not as good as that observed for systems connected by an aliphatic chain, this ligand is interesting due to its alternate structure and photophysical properties, inducing a change in the intersystem crossing and energy-transfer rates. These factors have been shown to influence the luminescence in such a way that, while k_{rad} is slightly improved, k_{nonrad} is made significantly worse in terms of the overall quantum yield.

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Supporting Information Available: Detailed synthesis of *o*-Phen-1,2-HOPO and Ln(III) complexes, experimental data for titrations, additional photophysical data, and X-ray crystallographic files (in CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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