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

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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 non-radiative decay rate for this compound when compared to previously reported aliphatic bridges.

Due to the Laporte forbidden character and intraconfigurational nature of the 4*f* 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 $M^{-1}.cm^{-1}$).[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 is comprised of three differing steps: the initial excitation of the ligand, followed by intersystem crossing to give an excited triplet state, then subsequent energy transfer to yield the metal centered excited state which emits light.[1, 5-7] For this mechanism, the energy of the sensitizing triplet state relative to the $^5D_0$ or $^5D_1$ 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 *vs.* non-radiative 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 5LI-[8] and 5LIO-1,2-HOPO[9] compounds.

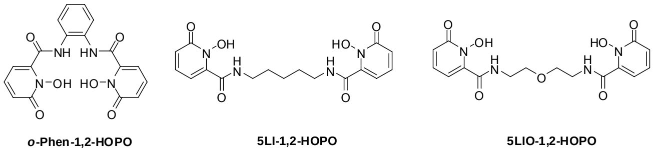

Chart 1. Chemical structures of the *o*-Phen-1,2-HOPO ligand and its parent derivatives (5LI-1,2-HOPO and 5LIO-1,2-HOPO).

The *o*-Phen-1,2-HOPO ligand is readily prepared by reaction of the benzyl-protected 1,2-HOPO-6-carboxylic acid intermediate prepared[10] from commercially available 6-bromopicolinic acid with the terminal primary aryl amines of *o*-aminoaniline (*o*-Phen), yielding the protected ligand (Scheme S1, Supp. Info). 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 crystals of the ligand and of the Eu(III) complex were grown by vapor diffusion of ether into methanol solutions. Further complete characterization of the ligand and complexes with Eu(III) and Gd(III) are reported in the supporting information.

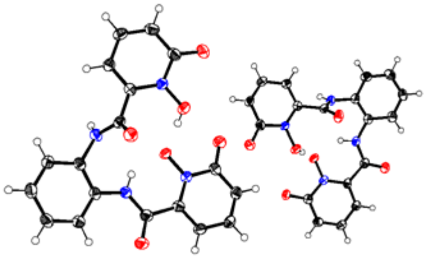

Figure 1. Structure of the *o*-Phen-1,2-HOPO ligand ($^+NH_2Me_2$ counter cations omitted for clarity). Non-H atoms are drawn at the 50% probability level.

The structure of the ligand was obtained by single crystal X-ray diffraction of the singly deprotonated dimethylammonium salt. Full crystallographic data in cif format are given in the supporting

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information. The ligand structure is typical of that observed for 1,2-HOPO type ligands, with a characteristic short keto-oxygen bond length of *ca.* 1.26 Å. The most striking feature is the presence of an intermolecular H-bonding contact between the adjacent protonated and deprotonated N-hydroxyl oxygen atoms, which arranges each of the crystallographically unique ligands into self complementary dimers (Fig. 1).

X-ray structure of the EuL_2 complex is shown in Fig. 2, 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 (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 pseudo-parallel '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 (Eu-O = 2.393 Å) are similar to previous reports.[8, 9]

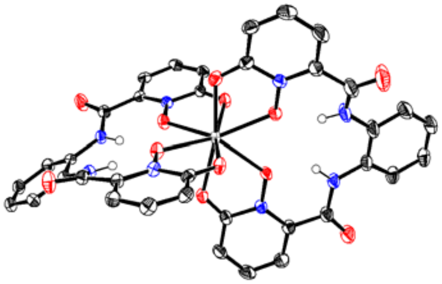

Figure 2. X-ray structure of the [Eu(*o*-Phen-1,2-HOPO)$_2$]$^-$ complex ($^+NMe_4$ counter cation, selected H atoms and solvent molecules omitted for clarity). Non-H atoms are drawn at the 50 % probability level.

Solution thermodynamic experiments assessed the stability of the [Eu(*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 [Eu(*o*-Phen-1,2-HOPO)$_2$]$^-$ chelate yielding β_{120} = 22.73 (5).[11] Six titrations at low pH (2.4 to 1.55) with different Eu:L ratios (1:2.5 to 1.5:1) determined β_{110} = 11.76 (5) and β_{121} = 25.26 (3), which were then used to calculate a pEu of 18.58 (3). The excellent stability of the [Eu(*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 ~ 18.64 (10)[8] and 5LI-1,2-HOPO, pEu ~ 18.35(5)[9]), 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 5LIO-1,2-HOPO derivative, it was suggested[9] 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] in order to further characterize the excited state. As a simplified model, only the Na^+ complex of a 6-phenylamide of the 1,2-HOPO anion (Fig. S1, Supp. Info) 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 HOMO → LUMO+1 excitation, with a smaller contribution from the HOMO-2 → LUMO+2 excitation, yielding mixed π-π^* and n-π^* character respectively for this transition, with a predicted energy of 28,950 cm^{-1} (345.5 nm).

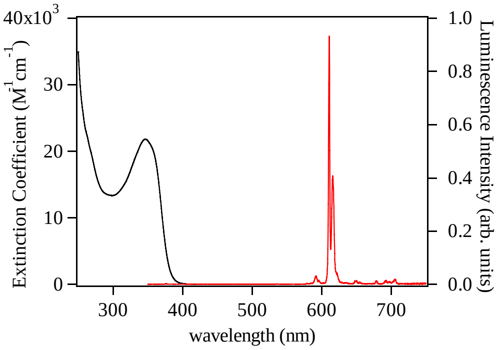

Figure 3. Absorption and luminescence spectra of [Eu(*o*-Phen-1,2-HOPO)$_2$]– in 0.1 M TRIS buffer (pH 7.4) containing 0.3 % (v/v) DMSO.

The experimentally determined absorption and luminescence spectra for [Eu(*o*-Phen-1,2-HOPO)$_2$]$^-$ are shown in Fig. 3 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 TD-DFT calculation. This is consistent with the expectation that the aryl bridged ligand, compared with the previously reported 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 (λ_{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 observation of phosphorescence of the ligand (T_{0-0} state). For [Gd(*o*-Phen-1,2-HOPO)$_2$]$^-$, upon cooling to 77 K, an intense unstructured emission band appeared from 450 to 600 nm (Fig. S2, Supp. Info), which can be attributed to phosphorescence from the ligand T_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 (Fig. S2, Supp. Info).[8] The resulting T_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-PhenylAmide-1,2-HOPO)] complex (T_{0-0} ~ 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 and the $^5D_1$ accepting state is optimal, at 2,230 cm^{-1}.[8, 9] Hence, the decrease of this energy gap can be expected to decrease the sensitization efficiency for the *o*-Phen ligand.

Corresponding time resolved analysis of the luminescence for [Eu(*o*-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 equation[17] 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 $T_{0\text{-}0}$ for the *o*-Phen-1,2-HOPO (20,964cm^{-1} vs. 21,260cm^{-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 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*-Phen-1,2-HOPO)$_2$]$^-$, [Eu(5LI-1,2-HOPO)$_2$]$^-$ and [Eu(5LIO-1,2-HOPO)$_2$]$^-$.

Table 1. Photophysical data obtained for [Eu(*o*-Phen-1,2-HOPO)$_2$]$^-$ in 0.1 M TRIS buffer (pH 7.4) containing 0.3% (v/v) DMSO.

$\lambda_{max}(\varepsilon_{max})$	342nm (21,020 M^{-1}.cm^{-1})	k_{rad}	680 s^{-1}
τ_{obs} / H_2O	536 µs	k_{nonrad}	1186 s^{-1}
τ_{obs} / D_2O	734 µs		
Φ_{tot}/ H_2O	0.062 ± 0.009	Φ_{Eu}	0.365
τ_{rad}	1470 µs	η_{sens}	0.170

In order to understand these differences, the kinetic parameters of the sensitization phenomenon were determined by calculating the non-radiative 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: $\Phi_{tot} = \eta_{ISC} \times \eta_{ET} \times \Phi_{Eu}$ (Eq1) with the resultant photophysical parameters summarized in Table 1. For [Eu(*o*-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). Significantly, while each of the complexes has no water molecule in the inner sphere, k_{nonrad} is much higher for [Eu(*o*-Phen-1,2-HOPO)$_2$]$^-$ yielding a value as large as 1186 s^{-1} *vs.* 810 s^{-1} and 740 s^{-1} respectively for the 5LIO- and 5LI- complexes. As a result, the quantum yield of metal centred 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 Eq1, we can see that the sensitization efficiency, η_{sens}, ($\Phi_{antenna} \times \eta_{ET}$ ~ 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/or the energy transfer are affected in the *o*-Phen complex resulting in a much less efficient sensitization process. While this may be a result of the lower triplet state energy, which facilitates enhanced non-radiative 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 $T_{0\text{-}0}$ excited states is significantly larger for the alkyl linked 5LI- and 5LIO- systems compared to the *o*-Phen complex (*i.e.* ΔE = 8,800 cm^{-1} *vs.* ΔE = 8,280 cm^{-1}). We attribute the change in rate of intersystem crossing and decrease in η_{sens}. to this difference in 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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