Near-Infrared Emitter

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3-Hydroxypyridin-2-one Complexes of Near-Infrared (NIR) Emitting Lanthanides: Sensitization of Holmium(III) and Praseodymium(III) in Aqueous Solution**

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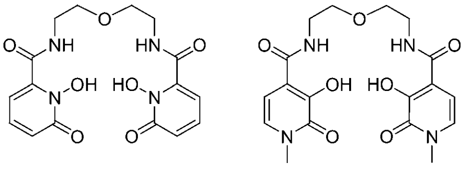
The near-infrared (NIR) emission originating from organic complexes of lanthanide (Ln^{III}) ions has received growing interest.[1,2] As a major impetus, biological tissues are considerably more transparent at these low-energy wavelengths than at visible wavelengths, which facilitates deeper penetration of incident and emitted light.[3] Furthermore, the luminescence lifetimes of Ln^{III} complexes (eg., Yb^{III}, $\tau_{rad} \approx 1$ ms), which are longer than typical organic molecules, can be utilized to vastly improve signal-to-noise ratios by employing time-gating techniques. While the quantum yield of Yb^{III} complexes, which is improved compared to other NIR emitters, favors their use in bioimaging applications, there has also been significant interest[4–6] in the sensitized emission from other 4f metals such as Ln = Nd, Ho, Pr, and Er which have well-recognized applications as solid-state laser materials[7] (e.g., Nd ≈ 1.06 μm, Ho ≈ 2.09 μm), and in telecommunications (e.g., Er ≈ 1.54 μm) where they can be used for the amplification of optical signals.[8]

As a result of their weak (Laporte forbidden) f–f absorptions, the direct excitation of Ln^{III} ions is inefficient, and sensitization of the metal emission is more effectively achieved using the so-called antenna effect.[1] We have previously examined[9] the properties of several Eu^{III} complexes which feature 1-hydroxypyridin-2-one (hopo) (Scheme 1) as the light-harvesting chromophore. While the 1,2-hopo isomer was found to strongly sensitize Eu^{III}, we noted that the analogous Me-3,2-hopo isomer does not, which prompted further investigation of the properties of this chromophore when complexed with other metals.



Scheme 1. Chemical structure of 5LIO-1,2-hopo (left) and 5LIO-Me-3,2-hopo (right) tetradentate ligands.

The synthesis of the 5LIO-Me-3,2-hopo ligand was previously reported by us.[10,11] Our initial in situ screening of this ligand with Pr^{III}, Ho^{III}, and Er^{III} revealed sensitized emission in the NIR region only for the former two metal ions. The corresponding Ln^{III} complexes for these two ions (Ln = Pr, Ho) were then prepared by using well-established methodologies (see the Experimental Section) and the desired compounds were obtained in analytically pure form as the charge-neutral ML_2H complexes. Single crystals[12] of $Na[Ho(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]$ suitable for X-ray analysis were grown by diffusion of diethyl ether into a 5% aqueous DMF/MeOH 1:1 (v/v) solution of the complex. The resulting X-ray structure is shown in Figure 1.

$Na[Ho(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]$ crystallizes in the triclinic space group $P\bar{1}$ with a single independent complex molecule in the asymmetric unit, together with one molecule of cocrystallized solvent (DMF). Notably, the crystal structure of $Na[Ho(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]$ is very similar to that

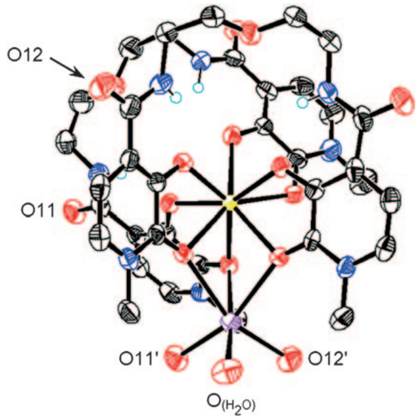


Figure 1. A view of the X-ray crystal structure for $Na[Ho(5LIO\text{-}3,2\text{-}hopo)_2]$. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level (black C, red O, blue N, yellow Ho, purple Na). Cocrystallized DMF and selected hydrogen atoms have been omitted for clarity.

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reported for the analogous Ce^{IV} complex,[11] and also the Ln^{III} complexes formed with the 5LIO-1,2-hopo ligand.[9] As expected, the Ho^{III} atom is coordinated by eight oxygen atoms of the two 5LIO-Me-3,2-hopo ligands in a sandwichlike structure (Figure 1), the average Ho–O bond lengths are 2.36 Å. The Ho–O (hydroxyl) bonds are significantly shorter than the corresponding Ho–O (keto) bonds, with average bond lengths of 2.30 and 2.41 Å respectively. Another structural parameter which can be obtained from the crystallographic data is the shape measure SM,[13,14] which is a measure of the agreement between the observed coordination polyhedron and the idealized cases. For a coordination number of eight, the three most common polyhedra are the bicapped trigonal prism (C_{2v}), square antiprism (D_{4d}), and trigonal dodecahedron (D_{2d}). Analysis of the Ho^{III} ion reveals that, in this case, the metal is best described as having an Archimedian antiprismatic (D_{4d}) geometry (SM = 4.49 (D_{4d}), 11.16 (C_{2v}) and 12.75 (D_{2d})). The counterion is Na^+, which is approximately 3.58 Å from the Ho^{III}, with its own hexadentate coordination geometry formed by a bridging interaction with three of the four Me-3,2-hopo chelates through the keto oxygen atoms and a single coordinated water molecule. The remaining two oxygen donors for the Na^+ ion originate from adjacent ligand amide carbonyl oxygen atoms, O11′ and O12′, which link two complexes together to form dimers. The Na^+ counterion has another interesting effect—each of the tetradentate ligand strands are in similar orientations with respect to each other unlike the structures in our previous reports,[15] which used noncoordinating alkyl amine counterions, wherein the least-square faces of the top and bottom ligands were offset by approximately 120°. Nonetheless, upon dissolution in water, we anticipate the Na^+ ion will dissociate to form the solvated ion, $Na^+_{(aq)}$, allowing each of the ligand strands to freely rotate.

The electronic absorption spectra of the Pr^{III} and Ho^{III} complexes are essentially identical, and display a broad ligand-centered absorption band (with poorly resolved vibrational structure) at 346 nm ($\varepsilon_{max} \approx 31250\,\text{M}^{-1}\text{cm}^{-1}$) as shown in Figure 2 for Pr^{III}. The emission spectra in the visible region for the two $[Ln(L)_2]^-$ complexes in buffered aqueous solution (tris(hydroxymethyl)aminomethane (TRIS), 0.1 M, pH 7.4) are also shown in Figure 2. These show the predominance of residual ligand emission common to both the complexes, centered at approximately 412 nm for Ho^{III} and 420 nm for Pr^{III}, which indicates incomplete energy transfer to the metal ion. The emission spectra in the visible region are of particular interest since these two Ln^{III} ions are known[16] to sometimes display metal-centered emission bands in the visible region (see below).

The corresponding spectra for both complexes in the NIR region are shown in Figure 3. Both display emission peaks which, when combined with the results from the visible region, are distinctive. For example, on the basis of the observed visible emission bands, we can unequivocally assign the observed 980 nm band in the NIR region (and the weaker shoulder at 1018 nm) to the $^5F_5 \rightarrow {}^5I_7$ transition of the Ho^{III} complex, since the corresponding band for the $^5F_5 \rightarrow {}^5I_8$ transition is clearly evident at approximately 650 nm (Figure 2). To the best of our knowledge, only two other examples of sensitized Ho^{III} emission in solution have been previously reported. The first example, which was measured in aqueous solution, was reported by Quici et al.[17] in 2005, the second, recorded in DMSO solution, was reported shortly thereafter by Petoud and co-workers.[18] In both these cases, the authors did not report the presence (or absence) of visible emission bands from the complexes. Interestingly, the corresponding $^5F_5 \rightarrow {}^5I_6$ transition, which is anticipated at approximately 1445 nm for Ho^{III}, was not observed in the spectra of our complex. The intensity of this band has been reported to be much weaker than the $^5F_5 \rightarrow {}^5I_7$ transition (e.g., in DMSO),[18] and was notably absent in the aqueous emission spectra reported by Quici et al.[17] This suggests the absence of this band may arise from strong reabsorption of the weakly emitted NIR radiation by the solvent, which has an absorption coefficient nearly two orders of magnitude higher at 1.5 µM versus 1 µM (ca. 21.6 cm^{-1} versus 0.41 cm^{-1}).[19]

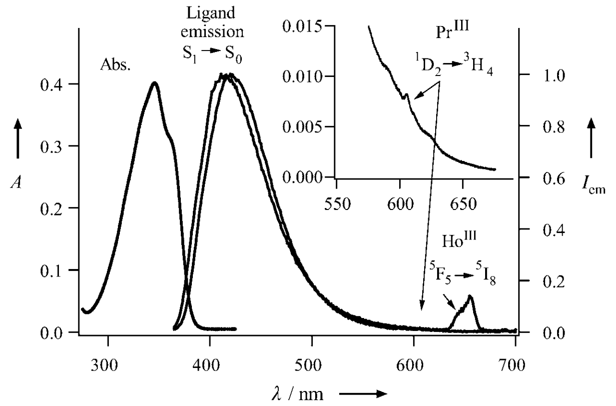

Figure 2. The absorption spectrum (Abs., left axis) of $[Pr(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]^-$ in buffered aqueous solution (0.1 M, TRIS, pH 7.4). Emission spectra (right axis) of the $[Ln(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]^-$ complexes ($\lambda_{ex} = 345$ nm) with Ln = Pr^{III} and Ho^{III} in buffered aqueous solution (TRIS, 0.1 M, pH 7.4) Inset: Expansion of the $Pr^{III}\ {}^1D_2 \rightarrow {}^3H_4$ transition at ca. 605 nm (see text).

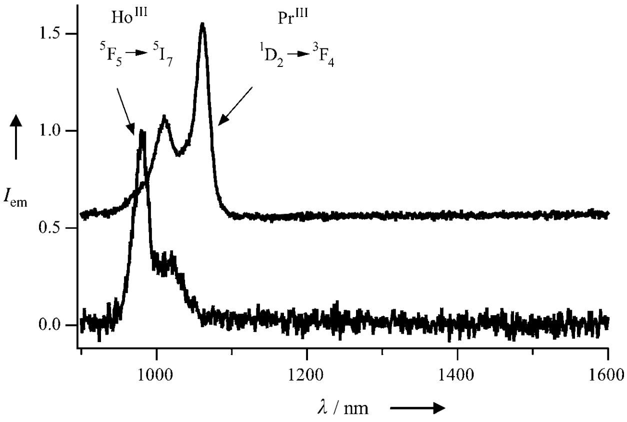

Figure 3. The NIR emission spectra ($\lambda_{ex} = 345$ nm) of the $[Ln(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]^-$ complexes in buffered aqueous solution (TRIS, 0.1 M, pH 7.4) with Ln = Pr^{III} and Ho^{III}. The emission spectra of the Pr^{III} complex is vertically offset for clarity.

The assignment of the emission observed from the Pr^{III} complex was less straightforward, since this metal can, in principle, emit from three excited states, namely the $^3P_0$, $^1D_2$, or $^1G_4$ levels. From a closer analysis of the visible emission, a weak faintly structured band at approximately 605 nm is apparent (Figure 2, inset), which can be attributed to the $^1D_2 \rightarrow ^3H_4$ transition. Notably, other expected peaks originating from the $^3P_0$ excited level (e.g., $^3P_0 \rightarrow ^3H_4 \approx 490$ nm, $^3P_0 \rightarrow ^3F_2 \approx 645$ nm) are absent, which suggests that the sensitizing triplet level of the Me-3,2-hopo ligand is too low to effectively populate this excited state. Assuming a common excited state origin, the observed NIR emission from the Pr^{III} complex at 1030 nm can then be assigned to the $^1D_2 \rightarrow ^3F_4$ transition; this agrees well with other reports.[16,20] By analogy with the case with Ho^{III}, the absence of the expected $^1D_2 \rightarrow ^1G_4$ transition for Pr^{III} in the NIR region at approximately 1440 nm probably arises from reabsorption by the aqueous solvent. As was the case with Ho^{III}, examples of sensitized emission from Pr^{III} complexes in the NIR region are quite rare.

Finally, in addition to the steady-state emission, we also performed time-resolved measurements in the visible and NIR region by using the time-correlated single photon counting (TCSPC) technique.[21] For the Ho^{III} complex, the emission of the $^5F_5 \rightarrow ^5I_8$ band was monitored at 650 nm and gave a satisfactory fit to a monoexponential lifetime with $\tau_{obs} = (6.4 \pm 0.1)$ ns. For the Pr^{III} complex, the $^1D_2 \rightarrow ^3H_4$ band was monitored at 605 nm and the corresponding lifetime decay data required fitting to a biexponential decay function, with $\tau_1 = (2.7 \pm 0.2)$ ns (99%) and $\tau_2 = (8.8 \pm 0.6)$ ns (1%). Given the very weak intensity of the Pr^{III}-centered emission at approximately 605 nm compared to the residual ligand singlet emission, we assigned the longer lifetime component to the metal center and the shorter lifetime component to the ligand. These assignments were then independently confirmed by lifetime measurements in the NIR region. Since the NIR emission band observed for the Pr^{III} complex at 1010–1060 nm originates from the same $^1D_2$ excited state, the lifetime should theoretically be the same as that observed in the visible region; the resulting lifetime obtained was monoexponential (see the Supporting Information) with a τ_{obs} value of (8.0 ± 0.4) ns, which is identical within experimental error. This value is in good general agreement with the previously reported value of $\tau_{obs} = 13$ ns for the $^1D_2$ excited state of a Pr^{III} complex, determined in CH_3OH solution at 1030 nm.[20] Similarly, for the $[Ho(5LIO\text{-}Me\text{-}3,2\text{-}hopo)_2]^-$ complex, the luminescence lifetime obtained in the NIR region was again monoexponential with $\tau_{obs} = (6.5 \pm 0.3)$ ns, which is consistent with measurements performed in the visible region by measuring the $^5F_5 \rightarrow ^5I_8$ band at 650 nm. To the best of our knowledge, this observation represents the first ever NIR lifetime determination in solution for a Ho^{III} complex, which are rarely emissive since their electronic structure facilitates highly competitive nonradiative deactivation.

Experimental Section

All chemicals and solvents were used as received unless otherwise noted. The Ln^{III} salts utilized were of the highest possible purity (>99.99%). The synthesis of 5LIO-Me-3,2-hopo has been previously reported.[10,11] Elemental analyses were performed by the Microanalytical Laboratory at University of California, Berkeley, CA.

A solution of $LnX_3 \cdot 6H_2O$ (0.026 mmol; Ln = Ho X = Cl, Ln = Pr X = Br) in methanol (1 mL) was added to a stirred solution of 5LIO-Me-3,2-hopo (ca. 20 mg, 0.05 mmol) in methanol (5 mL). An excess of pyridine (20 μL) was added and the suspension was heated to assist dissolution, then heated at reflux for approximately 4 h. After cooling to room temperature, slow addition of diethyl ether induced precipitation of the $[Ln(L)_2]^-$ complexes in their protonated charge-neutral form, which were collected by filtration and air dried to yield 10–15 mg of the desired products (ca. 60–85%). Elemental analysis calcd (%) for $H^+[Pr(C_{18}H_{20}N_4O_7)_2]^- \cdot 2H_2O$ (986.71 g mol^{-1}): C 43.97, H, 5.04, N 11.26; found C 43.66, H 4.92, N 11.11. Elemental analysis calcd (%) for $H^+[Ho(C_{18}H_{20}N_4O_7)_2]^- \cdot 5H_2O$ (1064.78 g mol^{-1}): C 40.61, H 4.83, N 10.52; found: C 40.14, H 4.65, N 10.25.

Crystals suitable for X-ray analysis were grown by vapor diffusion of diethyl ether into a 5% aqueous DMF solution of the isolated complex and data collection was performed at the Advanced Light Source (ALS), Beamline 11.3.1, Lawrence Berkeley National Laboratory (LBNL), by using well-established protocols. Resulting drawings of molecules were produced with ORTEP-3 for Windows.[22] CCDC 688308 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

UV/Visible spectra were recorded on a Varian Cary 300 double beam spectrometer using quartz cells of 1 cm path length. Emission spectra were measured using a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer equipped with an IBH TBX-04-D detector for the visible domain and a Hamamatsu H9170-75 detector for the NIR domain. Spectra were reference corrected for both excitation light source variation (lamp and grating) and emission spectral response (detector and grating). Time-resolved measurements were performed by using the TCSPC technique, further details are given in the Supporting Information.

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$a = 10.6416(6)$, $b = 12.9722(7)$, $c = 17.6879(10)$ Å, $\alpha = 74.467(1)$, $\beta = 80.512\ (1)$, $\gamma = 74.316(1)°$, $V = 2253.7(2)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.603\ \text{g cm}^{-3}$, $\mu = 2.303\ \text{mm}^{-1}$, synchrotron X-ray radiation source $\lambda = 0.77490$ Å, $T = 150\ (2)$ K, 28531 measured reflections, 11352 independent reflections ($8227 > 2\sigma(I)$), R_1 ($I > 2\sigma(I)$]) = 0.0531, wR_2 (all data) = 0.1224, GOF = 0.969.

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