

Long-Lived Near-Infrared Luminescent Lanthanide Complexes of Imidodiphosphate “Shell” Ligands

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Received December 14, 2004

Near-infrared emitting complexes of Nd(III), Er(III), and Yb(III) based on hexacoordinate lanthanide ions with an aryl functionalized imidodiphosphate ligand, tpip, have been synthesized and fully characterized. Three tpip ligands form a shell around the lanthanide with the ligand coordinating via the two oxygens leading to neutral complexes, Ln(tpip)₃. In the X-ray crystal structures of Er(III) and Nd(III) complexes there is evidence of CH– π interactions between the phenyl groups. Photophysical investigations of solution samples of the complexes demonstrate that all complexes exhibit relatively long luminescence lifetimes in nondeuterated solvents. Luminescence studies of powder samples have also been recorded for examination of the properties of NIR complexes in the solid state for potential material applications. The results underline the effective shielding of the lanthanide by the twelve phenyl groups of the tpip ligands and the reduction of high-energy vibrations in close proximity to the lanthanide, both features important in the design of NIR emitting lanthanide complexes.

Near-infrared light emitting lanthanides exhibit characteristic emission wavelengths with large Stokes shifts. These properties coupled with the advantages of signal transmittance of NIR radiation make them attractive for potential use in a number of applications from biomolecule labeling in luminescent bioassays¹ to materials for optical telecommunication networks^{2,3} and laser systems.⁴ To optimize complex stability and luminescence signal output for these applications, recent ligand design strategies involve two approaches: (i) design of cage-type structures to optimize

complex stability based on calixarenes,⁵ podands,^{6,7} and macrocycles^{8–11} and (ii) employment of fully fluorinated diketone or sulfonylamine ligands,^{4,12,13} or fully deuterated podand¹⁴ ligand architectures, to eliminate radiationless decay quenching pathways of *f–f* luminescence associated with the close proximity of high-energy C–H, N–H, or O–H oscillators to the luminescent center.

We have been interested in using sterically bulky didentate ligands based on imidodiphosphates to form lanthanide complexes stabilized by the ligand “hydrophobic shell” around the ion.^{15,16} We have chosen a tetraphenyl imidodiphosphate ligand, Htpip, due to its ideal framework structure for minimization of radiationless decay pathways of NIR *f–f* luminescence. This is based on the elimination of solvent molecules by the formation of a shell around the ion and the lack of any high-energy C–H, N–H, O–H oscillators within close proximity to the lanthanide ion. In this manuscript we wish to introduce Htpip as an efficient sensitizer for NIR light emitting complexes of Nd^{III}, Er^{III}, and Yb^{III}.

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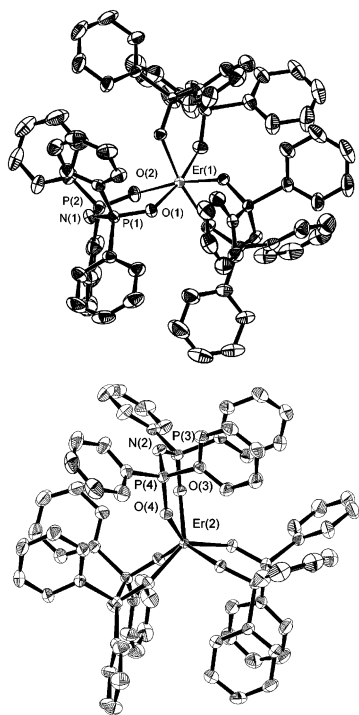
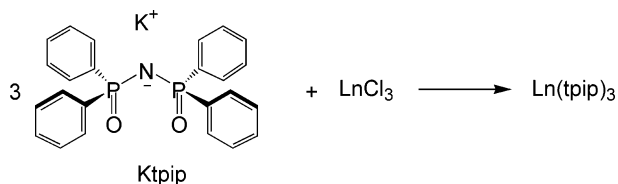


Figure 1. The X-ray single-crystal structure of $\text{Er}(\text{tpip})_3$ showing two geometries, a distorted octahedron (top) and a distorted trigonal prism (bottom).

One equivalent of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$) was reacted with three equivalents of Ktpip^{15} to produce the complexes $\text{Ln}(\text{tpip})_3$ in good yields (Scheme 1).

Scheme 1



Single crystals of $\text{Er}(\text{tpip})_3$ and $\text{Nd}(\text{tpip})_3$ were obtained by slow evaporation of acetonitrile solutions. The X-ray crystal structure of $\text{Er}(\text{tpip})_3$ was obtained and confirmed the complex formulation (Figure 1).¹⁷ There are two crystallographically independent complex positions in the structure ($\text{Er}(1)$ and $\text{Er}(2)$). In both, the Er^{III} ion is hexacoordinated by the oxygens of the three imidodiphosphinate ligands. The geometry of one Er^{III} ion is a distorted octahedron [with $\text{O}-\text{Er}(1)-\text{O}$ angles $169.32(6)^\circ$ and $82.71(6)-96.96(6)^\circ$], and the other is a distorted trigonal prism [with $\text{O}-\text{Er}(2)-\text{O}$ $136.61(6)^\circ$, $133.03(6)^\circ$, and $79.63(5)-83.58(6)^\circ$]. In both cases, the three ligands are symmetrically equivalent around the ion. However, in the trigonal prism case, the slightly more open complex allows space disordered “solvent”, refined as water, to occupy two sites at distances 4.09 and 3.88 Å from the lanthanide. The $\text{Er}-\text{O}$ distances in the complex are 2.238-

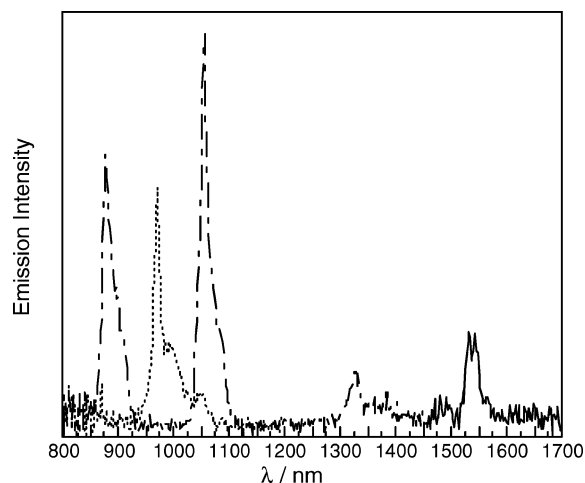


Figure 2. Emission spectra of $[\text{Nd}(\text{tpip})_3]$ (---), $[\text{Er}(\text{tpip})_3]$ (—), and $[\text{Yb}(\text{tpip})_3]$ (···), in CH_3CN (spectra not to scale).

(2) and 2.213(2) Å, and 2.243(2) Å for $\text{Er}(1)$ and 2.255(2) Å for $\text{Er}(2)$. These distances are shorter than those reported for Tb and Eu , as expected, due to the nature of the lanthanide ion. Intramolecular $\text{CH}-\pi$ interactions between the phenyl rings of the same ligand with $\text{C}(\text{H})$ to centroid distances of ca. 3.8 Å are observed. These interactions may stabilize the hydrophobic shell formation from the twelve phenyl groups around the lanthanide ion. The structure of $\text{Nd}(\text{tpip})_3$ complex (see Supporting Information) contains only one Nd complex in the asymmetric unit, with the geometry around the Nd ion as a slightly distorted trigonal prism.

The ^{31}P NMR spectra of the complexes in d_6 -acetone demonstrate the chemical equivalence of the ligand environment around the central lanthanide ion and high symmetry of the complex. Each spectrum of $\text{Nd}(\text{tpip})_3$, $\text{Er}(\text{tpip})_3$, and $\text{Yb}(\text{tpip})_3$ shows a single peak at values of 20.8, 19.1, and 18.8 ppm, respectively. In the same conditions, the chemical shift value for Ktpip is 11.0 ppm. The ^1H NMR spectra of the complexes in d_6 -acetone show signals in the range 6.5–8.5 ppm, assigned as the aromatic protons of the aryl group of the tpip ligand. These proton signals undergo the characteristic line broadening associated with paramagnetic complexes. This is more pronounced for the spectra of Er^{III} and Yb^{III} complexes, in which the signals appear as a single broad band. In the Nd^{III} complex three distinct signals in a 2:2:1 ratio are observed corresponding to the ortho, meta, and para protons of the aryl ring. The signal corresponding to the para proton at δ 7.25–7.33 (which is farthest away from the paramagnetic $\text{Nd}(\text{III})$ ion) shows less dramatic line broadening in comparison with the ortho and meta signals, which are in closer proximity to the lanthanide ion. For all three complexes the characteristic stretching vibrations of the PNP and PO bonds are observed in the IR spectra.

All complexes displayed characteristic NIR luminescence in solution (Figure 2) and in the solid state upon excitation at the ligand band around 265 nm. Solution samples showed strong luminescence in nondeuterated acetonitrile, in contrast with most previous lanthanide NIR luminescence studies where the samples are dissolved in deuterated solvents to avoid quenching effects. The Nd^{III} complex exhibits characteristic emission bands at 878, 1056, and 1329 nm,

(17) Single-crystal X-ray diffraction data for $\text{Er}(\text{tpip})_3$ and $\text{Nd}(\text{tpip})_3$ are detailed in the Supporting Information. CCDC 278872 and 278665 contain the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EK, UK; fax: +44-1233-336033.

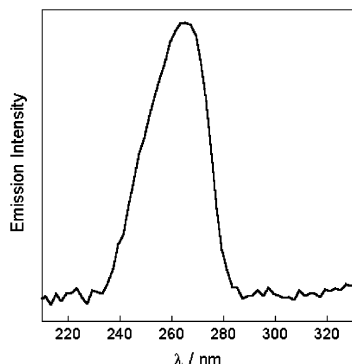


Figure 3. Excitation spectrum of [Nd(tpip)₃] in CH₃CN, $\lambda_{\text{em}} = 1054$ nm.

Table 1. Luminescence Lifetimes of the Nd³⁺ (⁴F_{3/2}), Er³⁺ (⁴I_{13/2}), and Yb³⁺ (²F_{5/2}) Levels in Ln(tpip)₃ (Ln = Nd, Er, Yb) ($\lambda_{\text{exc}} = 266$ nm)

	conditions ^a	τ μ s
Nd(tpip) ₃	dry CH ₃ CN solution	2.7
	dry CH ₃ CN solution + H ₂ O ^b	0.5
Er(tpip) ₃	dry CH ₃ CN solution	6.5
	dry CH ₃ CN solution + H ₂ O ^b	5.4
Yb(tpip) ₃	dry CH ₃ CN solution	52.8
	dry CH ₃ CN solution + H ₂ O ^b	40.2

^a Lifetimes measured at room temperature. ^b [H₂O] = 10 mol dm⁻³.

attributed to luminescent transitions ⁴F_{3/2} → ⁴I_J ($J = 9/2, 11/2, 13/2$). The Yb^{III} complex displays one luminescence band at 970 nm assigned to ²F_{5/2} → ²F_{7/2} whereas the Er^{III} complex luminescence is observed at around 1538 nm assigned to ⁴I_{13/2} → ⁴I_{15/2}. Excitation spectra provided a signature of the energy transfer process. When the emission of Nd^{III} was monitored at 1054 nm, an excitation profile was obtained that matched the absorption spectrum of the complex (Figure 3). These results suggested that the aromatic phenyl groups act as sensitizers of the Nd^{III}, Er^{III}, and Yb^{III} luminescence.

The complexes display long luminescence lifetimes in solutions of CH₃CN (Table 1). The observed lifetimes of all the Ln(tpip)₃ (Ln = Nd, Er, Yb) complexes are longer than the corresponding ones reported for other cage-type ligands and relate well with the range of lifetimes obtained for complexes of fully fluorinated diketonate ligands. These results indicate the absence of any deactivating, nonradiative pathways in solution due to solvent coordination and that deactivation pathways from the high-energy vibrations of the ligand framework structure are minimized. The effect of coordinated solvent molecules was examined by addition of excess water in a dry acetonitrile solution. A decrease in luminescence lifetimes for all the Ln(tpip)₃ complexes is observed. This is not surprising due to the expected coordination of H₂O in the lanthanide coordination sphere. In the crystal structure of Er(tpip)₃ there is evidence of two water molecules being in close proximity to the lanthanide. It is expected that in solution there will be rotational freedom around the lanthanide ion leading to empty coordination sites for the water to coordinate. In tpip complexes of Eu^{III} and Tb^{III}, it was calculated that only one water molecule coordinates in solution to the lanthanide.¹⁵ From the results in Table 1, it is interesting to note that Nd(tpip)₃ experiences the largest decrease in emission lifetime upon water coordination, of a magnitude of 81%, whereas the decreases for

Table 2. Luminescence Lifetimes of Powder Samples of [Ln(tpip)₃] (Ln = Nd, Er, Yb), $\lambda_{\text{exc}} = 266$ nm

	τ μ s
Nd(tpip) ₃	1.2
Er(tpip) ₃	2.3
Yb(tpip) ₃	17.8

Er(tpip)₃ and Yb(tpip)₃ amount to 17% and 24%, respectively. Even though the sizes of Er^{III} and Yb^{III} ions are smaller than the Nd^{III} ion, the latter is similar in size to Eu^{III} and is expected to have one water molecule coordinated in solution. This decrease is attributed to the higher quenching efficiency of O–H oscillators for Nd luminescence, probably due to better matching of the Nd energy levels to the O–H vibrational levels.

The luminescence lifetimes of powder samples (Table 2) were recorded to compare the effect of deactivating pathways in NIR lanthanide emission in solution and the solid state. It was found that the luminescence lifetimes of the powder samples were shorter than the solution lifetimes. The effect is more pronounced in the cases of Er(tpip)₃ and Yb(tpip)₃. This may be attributed to crystal lattice vibrations or cross-relaxation mechanisms between the closely positioned lanthanide ions in the solid state. Although these mechanisms were not previously shown to be operational in solid-state samples of visible emitting Eu and Tb complexes of tpip, it is reasonable to expect that they are efficient mechanisms in NIR luminescence due to the low energy of the NIR radiation. The suppression of energy migration between Nd^{III} ions was recently shown in a zeolite structure.¹⁸

We have demonstrated that long-lived NIR luminescent lanthanide complexes are formed by the assembly of three tpip ligands around Nd, Yb, and Er ions.¹⁹ The absence of any N–H or O–H and presence of few C–H vibrations in close proximity to the lanthanide, as well as the effective shielding of the twelve phenyl groups from solvent molecules, suggest that the tpip ligand acts as an efficient sensitizer for NIR luminescence.

Acknowledgment. We wish to thank EPSRC (A.P.B., P.B.G.) and the University of Birmingham for support. R.V.D. and P.N. acknowledge support from the EU CSG Programme, Project No. G5RD-CT-2001-00577 OPAMD (Optical Amplification in Polymer Based Materials and Devices). R.V.D. is a postdoctoral fellow of the FWO Flanders.

Supporting Information Available: Full characterization data for the complexes and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0482436

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- (19) A paper published during examination of this manuscript (Mancino, G.; et al. *J. Am. Chem. Soc.* **2005**, *127*, 524) reports two components for the luminescence lifetime of Er(tpip)₃ in solution and powder samples which we do not observe. The presence of two components is unusual for lanthanide complexes and may be attributed to the presence of more than one species perhaps due to water coordination. A fluorinated version of tpip reported in that paper and also developed in our group (P. B. Glover, Ph.D. Thesis, University of Birmingham, 2004) is shown to lead to even longer luminescence lifetimes for the Er complex.