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COMMUNICATIONS

Dramatic Increases in the Lifetime of the Er^{3+} Ion in a Molecular Complex Using a Perfluorinated Imidodiphosphinate Sensitizing Ligand

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There is a growing demand for low cost near infrared (NIR) light sources for communications, sensing, and analytical detection. Organic semiconductors are especially attractive due to their potential for low-cost fabrication and their proven capabilities as visible light sources. However, progress toward efficient NIR-emitting organic light-emitting devices (OLEDs) has, to date, been limited due to the relative scarcity of organic lumophores with efficient NIR emission. Several rare-earth ions do exist that emit in the NIR region, in particular, Er^{3+}, Nd^{3+}, and Yb^{3+}, and there have been several attempts to utilize the emission from these ions in organolanthanide complexes.[1]

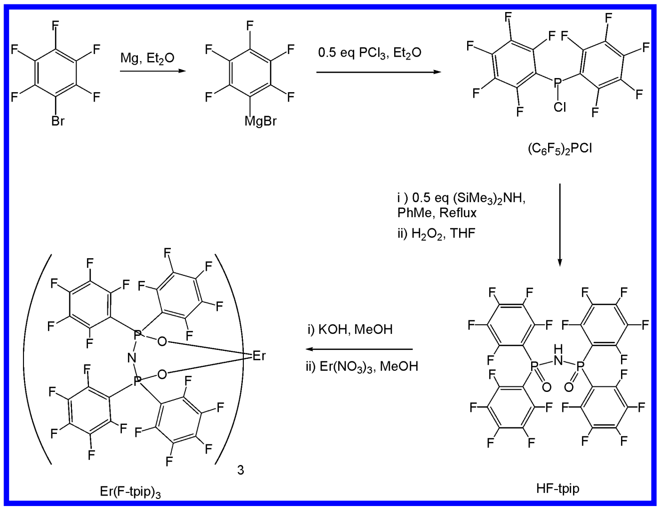
Luminescence from trivalent lanthanide ions (Ln^{3+}) arises from electronic transitions between the 4f orbitals. These transitions are forbidden on symmetry grounds, leading to poor absorption cross sections and relatively long-lived excited states.[2] Consequently, population of the emitting levels of the Ln^{3+} ion is best achieved by employing light-harvesting ligands (antenna chromophores) that can sensitize the metal ion by intramolecular energy transfer.[2,3]

It is well established that NIR-emitting Ln^{3+} ions are particularly prone to vibrational deactivation. Species containing high-energy oscillators, such as C−H and O−H bonds (typically found in the ligand, coordinated solvent and moisture), are able to quench the metal excited states nonradiatively, leading to decreased luminescence intensities and shorter excited-state lifetimes.[4] For example, photoluminescent (PL) studies of erbium tris(8-hydroxyquinolate), ErQ_3, shows lifetimes in the region of 0.2−2 μs depending on the ErQ_3 environment.[5] These observed lifetimes are much shorter than the natural radiative lifetime of the Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, implying that the quinolate ligand is unable to protect the metal ion from deleterious solvent/moisture coordination. This problem can be reduced by using sterically demanding ligands that encapsulate the metal within a hydrophobic shield. One such ligand is tetraphenylimidodiphosphinate (tpip)[6] and its *O*-methylated analogue, Metpip, which have been used as the basis for several Ln(tpip)$_3$ complexes (Ln = Dy, Eu, Sm, and Tb).[7,8]

Hasegawa et al. have shown that replacement of C−H bonds in β-diketonate ligands with lower-energy C−F oscillators leads to longer luminescence lifetimes for the Nd^{3+} ion in solution.[9] These studies have mainly focused on direct excitation into the metal excited states and describe only one example where a pentafluorophenyl moiety is used as an antenna chromophore.[10] Similar work has also been performed by Zheng et al., who report increased luminescent intensities for Tb^{3+}-based OLEDs when the metal ion is coordinated by fluorinated β-diketonate ligands.[11]

In this communication, we show how the encapsulation properties of the tpip moiety coupled with the advantages afforded by fluorination lead to dramatic improvements in the PL properties of Er^{3+}-based organolanthanide complexes. A new bidentate chelating ligand, tetrapentafluorophenylimidodiphosphinate (HF-tpip), has been synthesized, first by preparing the appropriate fluorinated phosphine precursor, $(C_6F_5)_2PCl$,[12] followed by coupling this to hexamethyldisilazane in a method analogous to that of Pikramenou et al.[8] The full synthetic scheme for HF-tpip is shown in Scheme 1. After formation of the potassium salt of the ligand (KF-tpip), the metal complex, Er(F-tpip)$_3$, was formed and purified by vacuum sublimation between 260 and 280 °C at 10^{-6} mBar, which is approximately 50−60 °C lower than the temperature required to sublime the nonfluorinated Er(tpip)$_3$ derivative. Fluorination increases the volatility of this material, and the lower sublimation temperature is advantageous with respect to fabricating films and devices using vapor deposition techniques.

Scheme 1. Synthesis of HF-tpip and Er(F-tpip)$_3$



Time-resolved PL[13] measurements were carried out on the Er(F-tpip)$_3$ complex as a powder, a 500 nm evaporated thin film on quartz, and in $CDCl_3$ solution. These were compared with similar measurements performed on the Er(tpip)$_3$ complex.

For each sample, the characteristic emission around 1530 nm, due to the intraconfigurational $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, is observed upon excitation at 266 nm into the phenyl absorption band of the ligand. A representative PL spectrum and decay profile (shown as inset) for Er(F-tpip)$_3$ in $CDCl_3$ are shown in Figure 1.

The Er^{3+} emission observed for the Er(F-tpip)$_3$ complexes is sharp and shows distinct fine structure, which is in contrast to many reported emission spectra of other erbium chelates, notably, ErQ_3.[5]

The time-dependence of the Er^{3+} emission was examined, following excitation at 266 nm, and the results are summarized in Table 1, along with a comparison between the decay kinetics of Er(F-tpip)$_3$ and the nonfluorinated analogue, Er(tpip)$_3$.

For both complexes and all different sample types, the decay is best described by a biexponential process and a nanosecond-scale rise-time component, both of which have been observed for other

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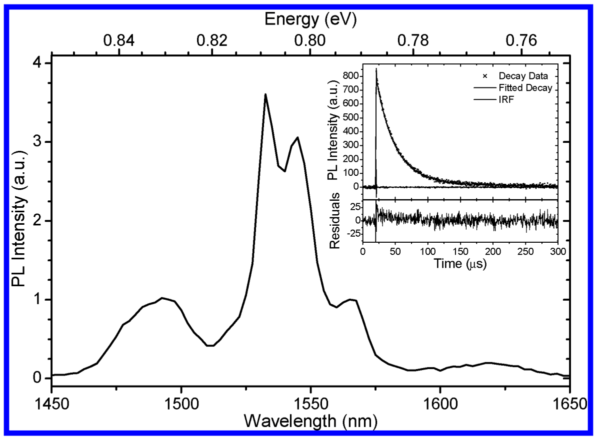

Figure 1. PL spectrum of Er(F-tpip)$_3$ in CDCl$_3$ (~10^{-4} M) (decay profile shown as inset).

Table 1. PL Lifetime Data for Er(tpip)$_3$ and Er(F-tpip)$_3$ as a Powder, in Solution, and as a Thin Film

Sample type and complex[a]	Lifetimes (μs)[b] τ_1	τ_2	PLQY[c]
powder			
Er(tpip)$_3$	6.0 (77%)	1.5 (23%)	0.05%
Er(F-tpip)$_3$	164 (95%)	46 (5%)	1.8%
CDCl$_3$ solution			
Er(tpip)$_3$	5.0 (87%)	2.4 (13%)	0.06%
Er(F-tpip)$_3$	145 (27%)	28 (73%)	0.4%
500 nm film			
Er(tpip)$_3$	4.8 (84%)	1.0 (16%)	0.04%
Er(F-tpip)$_3$	224 (92%)	27 (8%)	1.71%

[a] Excitation wavelength = 266 nm. [b] Fractional intensities in parentheses. [c] Photoluminescent quantum yield (PLQY) calculated by using the equation: $(A_1\tau_1 + A_2\tau_2)/\tau_r$, where A_1 and A_2 are the pre-exponential factors, normalized such that $A_1 + A_2 = 1$, and τ_r is the average radiative lifetime (8 ms) of the Er^{3+} ion.[5]

Er^{3+} complexes.[5] As can be seen in Table 1, the lifetimes of the Er^{3+} ion are substantially longer in the perfluorinated complex relative to those of the nonfluorinated analogue. The solution-state kinetic behavior of Er(F-tpip)$_3$ shows some deviation relative to the solid-state; specifically, the short-lived species dominates. This result suggests that the C−D bond on the solvent molecule may provide the dominant nonradiative pathway from the Er^{3+} excited state. This implies that the ligand system is sufficiently mobile in solution to allow solvent molecules to occupy gaps between the F-tpip ligands. On average, we observe a 10-fold increase in lifetime in solution, a 30-fold increase for the powder, and a remarkable 50-fold increase for the evaporated thin films.

It would appear that eliminating all of the C−H bonds serves to significantly reduce the degree of vibrational quenching, which in turn leads to longer lived Er^{3+} excited states and enhanced emission intensity. Structural studies are currently being performed in order to determine if perfluorination serves to increase the degree of shielding afforded to the Er^{3+} ion. Furthermore, studies are also being directed at understanding the specific energy transfer processes that are operational in the Er(F-tpip)$_3$ complex and whether fluorination serves to improve the degree of energy transfer between the ligand and metal ion.

While it is clear that the lifetimes observed for Er(F-tpip)$_3$ still fall some way short of the natural radiative lifetimes of Er^{3+} in inorganic glass matrices (typically on the order of milliseconds),[14] our results demonstrate that striking improvements in luminescence efficiency can be achieved by relatively straightforward synthetic tuning of the ligand, that is, perfluorination of all the aromatic antenna chromophores. Further work in this area will be geared toward gaining a better understanding of the decay channels operating in this perfluorinated system and, in turn, lead to further developments in the design of NIR-emitting devices for communications, sensing, and analytical detection.

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Supporting Information Available: Experimental procedure for the synthesis of the ligand and complex, the UV−vis absorption spectrum of Er(F-tpip)$_3$ in solution, and the procedure for the vapor deposition of thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Time-resolved PL measurements were made by illuminating the samples with a circular beam of ~5 mm using the 266 nm Q-switched output of an Nd:YAG laser (Spectra Physics) operating at 10 Hz. Pulse energies were typically in the region of 3−4 mJ with a pulse fwhm of 8 ns. The PL was collected at right angles and focused onto the entrance slit of a Jobin−Yvon Triax 320 monochromator with a grating blazed at 1 μm. The emitted light was detected with a nitrogen-cooled germanium photodiode/amplifier (North Coast EO-817P) operating in high-sensitivity mode. The signal was captured and averaged by a digital storage oscilloscope (Tektronix TDS320) and transferred to a PC for data analysis. The PL decays were analyzed by iterative reconvolution and nonlinear least-squares analysis of the instrument response profile with biexponential functions. The quality of the fits was assessed by the randomness of the residuals and a satisfactory reduced χ-squared. The fractional intensities given in Table 1 for each lifetime (f_i) were determined from the values of pre-exponential factors (A_i) and the lifetimes (τ_i) as follows: $f_1 = A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$ and $f_2 = A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$. PL spectra were generated by measuring the decay of the luminescence intensity at 2.5 nm wavelength intervals followed by integration of the area under the decay to give the total emission intensity at each wavelength.

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