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Quenching of Er(III) luminescence by ligand C–H vibrations: Implications for the use of erbium complexes in telecommunications

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The authors have quantified the quenching of the luminescence lifetime of Er³⁺ ions in organic complexes due to the presence of CH vibrational oscillators as a function of their distance from the ion. They have shown that any hydrogen atoms within a sphere of at least 20 Å from an erbium ion will cause sufficient quenching to prohibit its use in telecommunications applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345909]

Erbium-doped glasses are widely used for telecommunications due to the sharp intra-atomic $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in the 4f orbital which result in an emission at $\sim 1.5 \mu\text{m}$, which is the low loss window for silica optical fiber. If erbium is incorporated into organic hosts then the organic ligands can act as photosensitizers, resulting in much higher absorption cross sections, with broader absorption bands than for the free Er³⁺ ion.^{1–4} However, ligands and coordinated solvent molecules usually contain C–H and O–H bonds that can cause vibrational quenching of electronically excited erbium; this limits any application of such complexes in infrared emitting devices. Deuteration or fluorination of hydrogen-containing ligands, together with exclusion of coordinated water, can extend the lifetime of infrared luminescence from lanthanide complexes.⁵ Nd(III) has been a subject of particular study; however, there have been little data in actually quantifying the extent of the quenching. A recent paper by Quochi *et al.*⁶ has proposed a model for calculating the degree of quenching based on the assumption of a continuous distribution of CH oscillators which makes good predictions of the degree of quenching for systems where there are large amounts of CH or OH bonds present. As the authors state, the recent work by Mancino *et al.*⁷ where it has been shown that an evaporated thin film of Er(F-tpip)₃, where F-tpip is the perfluorinated imidodiphosphate [(C₆F₅)₂P(O)]₂N[−], having a luminescence lifetime of 224 μs does not fit with their model and they suggest that the discrepancy is probably due to residual hydrogen-containing impurities.

In order to quantify the effect of O–H and C–H bonds on the radiative lifetime of Er³⁺ ions and to determine the spatial distance over which deexcitation can occur we have used the tris complex Er(HFA)₃ and the tetrakis complex [Cs][Er(HFA)₄] (H-HFA = 1, 1, 1, 5, 5, 5-hexafluoro-2,4-pentanedione) to study the effect of removing water from the coordination sphere of the erbium ion. We have also investigated the effect of replacing the single hydrogen atom on the 3 position of the ligand with deuterium. We have shown that

by removing OH and CH bonds to increasing distances from an Er³⁺ ion we can obtain a three order of magnitude increase in the radiative lifetime and that the presence of a CH bond within a radius of $\sim 20 \text{ \AA}$ of an Er³⁺ ion can still be an effective deexcitation site for the Er³⁺ ion. These studies provide vital data for the future design of efficient lanthanide emitters using organic ligands.

[Er(HFA)₃(H₂O)₂] was prepared according to Ref. 8 and recrystallized from toluene to give large pink needles, mp (118–121) °C which were characterized by CH analysis, high resolution mass spectrometry, IR spectroscopy and single crystal x-ray diffraction (XRD). [Cs][Er(HFA)₄] was prepared by mixing aqueous CsHFA with the calculated amount of aqueous erbium(III) chloride; the pink precipitate was recrystallized from aqueous methanol to give pink needles which sublimed on heating above 200 °C and were characterized by CH analysis, high resolution mass spectrometry, IR spectroscopy, and single crystal x-ray diffraction and were found to be isomorphous with [Cs][Eu(HFA)₄].⁹ H-HFA was deuterated according to Ogoshi and Nakamoto,¹⁰ then used to prepare deuterated [Cs][Er(HFA)₄] in D₂O solution; the precipitated product was then recrystallized from CH₃OD–D₂O. Laser desorption/ionization mass spectroscopy (Bruker Daltonics Autoflex) on the resultant material showed that we had achieved 98% ± 1% deuteration.

Photoluminescence from the complexes was excited using ~ 7 ns pulses, at an excitation wavelength of 520 nm, from a Continuum Panther optical parametric oscillator pumped with a Surelite I laser. This wavelength was chosen to provide direct excitation into the $^4S_{3/2}$ level of the erbium ion which rapidly decays to the $^4I_{13/2}$ level with a measured decay time of the order of 25 ns. The luminescence was dispersed in a Triax 550 spectrometer and detected using a Hamamatsu R5509-72 infrared photomultiplier tube.

Lifetime data for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition were recorded at the peak of the photoluminescence spectra (1542 nm) at a temperature of 300 K and fitted with either a one or two exponential decay model using a Marquardt-Levenberg algorithm to find the best fit. Table I shows the results of the lifetime fits to five samples. Three samples

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TABLE I. Measured lifetimes of the 1542 nm emission from the Er^{3+} $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. The figures in parentheses are the percentage contribution from each component.

	τ_1	τ_2
$[\text{Er}(\text{HFA})_3(\text{H}_2\text{O})_2]$ dried	132 ns (17%)	1.8 μs (83%)
$[\text{Er}(\text{HFA})_3(\text{H}_2\text{O})_2]$ hydrated	100 ns (100%)	
$[\text{Cs}][\text{Er}(\text{HFA})_4]$	1.8 μs (100%)	
$[\text{Cs}][\text{Er}(\text{HFA})_4]$ in CD_3OD	1.6 μs (100%)	
$[\text{Cs}][\text{Er}(\text{HFA})_4]$ 98% deuterated	11 μs (96.4%)	106 μs (3.6%)

show single exponential decay, the $[\text{Er}(\text{HFA})_3(\text{H}_2\text{O})_2]$, the $[\text{Cs}][\text{Er}(\text{HFA})_4]$, and the $[\text{Cs}][\text{Er}(\text{HFA})_4]$ dissolved in methanol- d_4 . The presence of a single exponential decay suggests that all the Er^{3+} ions are in identical local environments.

For the $[\text{Er}(\text{HFA})_3(\text{H}_2\text{O})_2]$ sample that had been dried *in vacuo* at 1 mbar over P_2O_5 there are two lifetime components, a major one with a lifetime of 1.8 μs (83%) and a minor one with a lifetime of 132 ns (17%). The 132 ns component is due to the dramatic deexcitation effect of the water molecules in the erbium coordination sphere, where each hydrogen is only ~ 2.9 Å (determined from the XRD data) from the Er^{3+} ion. The 1.8 μs component is probably due to the presence of some anhydrous tris salt being formed during recrystallization and drying. Samples of this material were left next to an open beaker of water for 24 h in a sealed container. This was sufficient to fully hydrate the material so that only a pure 100 ns lifetime was observed. The slightly higher lifetime for the fast component in the anhydrous sample is probably due to some of the ions having only one water molecule in their coordination sphere as opposed to the two found in the hydrated sample. This hydrated sample was sublimed under a 10^{-7} mbar vacuum in a Kurt J. Lesker SPECTROS deposition system and the resulting material was found to be very similar to the hydrated sample with $\sim 85\%$ with a lifetime of 100 ns and $\sim 15\%$ with a lifetime of 0.5 μs . The 0.5 μs lifetime is probably shorter than that seen in the original “anhydrous” salt due to the low number of ions in this environment resulting in even the erbium ions in an anhydrous environment having water molecules in next nearest neighbor positions. This demonstrates that the coordinated water is difficult to entirely remove by sublimation which is in agreement with the findings of Richardson and Sievers.¹¹

The $[\text{Cs}][\text{Er}(\text{HFA})_4]$ sample was measured both before and after sublimation and no difference in the measured lifetime was observed. The lifetime of 1.8 μs , although more than an order of magnitude greater than for the $[\text{Er}(\text{HFA})_3(\text{H}_2\text{O})_2]$, demonstrates that even four CH bonds at a distance of ~ 4.7 Å (determined from the XRD data) from the Er^{3+} ion will have a dramatic effect of the deexcitation of the ion. For the $[\text{Cs}][\text{Er}(\text{HFA})_4]$ the sample was measured within 5 min of dissolving in order to reduce the probability of significant exchange of the hydrogen on the ligands. The very small decrease in the lifetime from the solid $[\text{Cs}][\text{Er}(\text{HFA})_4]$ sample to that dissolved in methanol- d_4 suggests that the lifetime of the Er^{3+} ions in the $[\text{Er}(\text{HFA})_4]^-$ anion is primarily affected by the CH bonds in each of the coordinated HFA ligands with only a small contribution from CH bond in the surrounding HFA ligands. From the x-ray crystallography these hydrogen atoms are at ~ 4.7 Å from

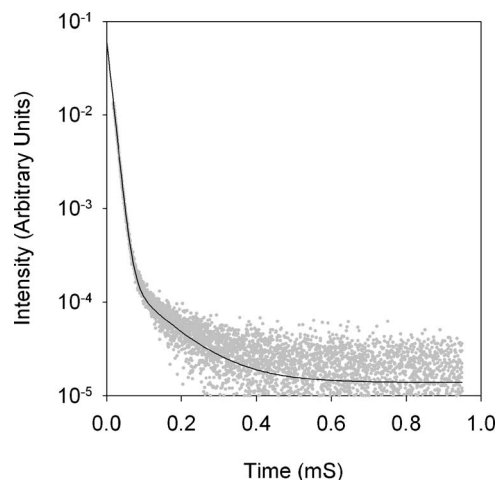


FIG. 1. Lifetime data for the 98% deuterated $[\text{Cs}][\text{Er}(\text{HFA})_4]$ sample recorded at a wavelength of 1542 nm.

the Er^{3+} ion. To investigate the role of these hydrogen atoms more fully we examined our 98% deuterated $[\text{Cs}][\text{Er}(\text{HFA})_4]$. The luminescence for this material showed two lifetimes with the major component (96.4%) having a lifetime of 11 μs and with 3.6% having a lifetime of ~ 106 μs (Fig. 1). It should be stressed that the low intensity of this component results in a significant error on the value of this lifetime. The fact that one component has a lifetime of ~ 106 μs implies that some of the Er^{3+} ions are in an environment with only a relatively weak deexcitation process occurring. If we assume that this is due to Er^{3+} ions that are in positions with no hydrogen in their nearest neighbor positions we can calculate that with 98% deuteration 3.6% of the Er^{3+} ions will be in sites where the ~ 160 nearest hydrogen sites are all fully deuterated. From the crystallographic data it can be seen that this corresponds to a sphere of radius ~ 20 Å around the Er^{3+} ion and is approximately equivalent to each of the 40 next nearest $[\text{Er}(\text{HFA})_4]^-$ anions being fully deuterated. Given the 98% deuteration level in this sample there is a 92% probability of an erbium being in a fully deuterated anion and a 7% probability of an anion having three deuteriums and one hydrogen. As we could only resolve one other lifetime component at 11 μs it suggests that in both of these environments the lifetime is dominated by the presence of hydrogen atoms in the next nearest neighbor sites.

As the natural radiative lifetime τ_R of the erbium will be of the order of milliseconds we can take the measured lifetime τ_M to be a good approximation of the sum of the rate

$$\frac{1}{\tau_M} = \frac{1}{\tau_R} + \sum k,$$

constants, k , for all the quenching mechanisms present.

As there is a Förster energy transfer¹² between the vibrational oscillator and the erbium the transfer will be inversely proportional to the sixth power of the distance between them. For molecules with a short lifetime we can therefore, to a first order approximation, consider the quenching to be dominated by the nearest neighbor oscillators. From the $[\text{Cs}][\text{Er}(\text{HFA})_4]$ lifetime this allows us to place an upper limit on the rate constant per CH bond on the anion (i.e., at a distance of 4.7 Å from the Er^{3+} ion) of $\sim 140\,000$ s^{-1} . This would give a lifetime for an Er^{3+} ion with one hydrogen and

three deuterium atoms in the nearest neighbor positions of $\sim 7 \mu\text{s}$, which is of the correct order; the actual value of $11 \mu\text{s}$ shows that the presence of CH bonds in the second nearest neighbor shell does play some role in the quenching and that the actual rate constant for a CH bond in the anion is probably less than $91\,000 \text{ s}^{-1}$. This should be compared to the maximum value for a CD bond in the same position which is $\sim 2400 \text{ s}^{-1}$ determined from the $106 \mu\text{s}$ lifetime. It should be stressed that it is not clear whether the $106 \mu\text{s}$ lifetime is dominated by the quenching to the CD oscillators in the nearest neighbor positions or due to more distant CH oscillators.

These results demonstrate that the nearest neighbor CH oscillators are by far the biggest contributor to the quenching of erbium ions in organic hosts which corresponds to the R_{min} value in the theory proposed by Quochi *et al.*,⁶ the role of the more distant oscillators is only of secondary importance. These results also show that to produce erbium-containing molecules where the lifetime of the erbium is not being dominated by quenching to hydrogen-related vibrational modes in the surrounding ligands requires the removal of all hydrogen from a distance of at least 20 \AA from the Er^{3+} ions, for a $100 \mu\text{s}$ lifetime. This is still far below the expected radiative recombination lifetime for the ion despite the average CH concentration in this sample ($\sim 10^3 \text{ \AA}^{-1}$) which is too low for us to observe by IR absorption. The results also demonstrate that although deuterating ligands can dramatically improve the Er^{3+} luminescence lifetime, the quenching due to any CH bonds which are still present is so strong that deuteration is not a viable solution and this means that fully halogenated ligands will have to be used. It also

shows that it will be necessary to produce molecules where there is no hydrogen-containing solvent within the crystal structure which suggests that solution processing as a means of producing devices may be problematic without the use of purely halogenated solvents. Furthermore due to the extreme sensitivity to hydrogen it is also probable that even in fully halogenated systems repeated vacuum sublimation as a purification step may well be necessary to obtain optimized lifetimes.

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