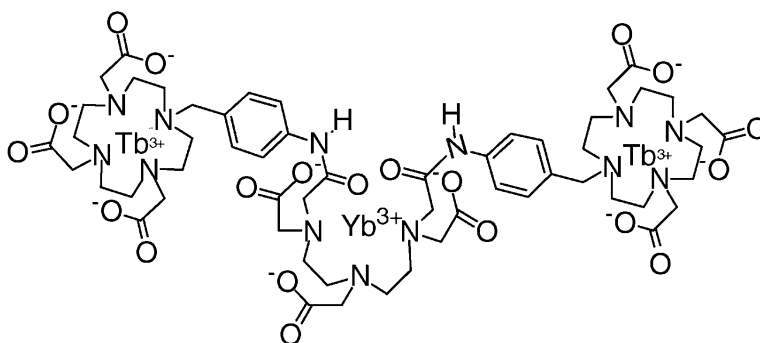## Communication

Lanthanide-Sensitized Lanthanide Luminescence:
Terbium-Sensitized Ytterbium Luminescence in a Trinuclear Complex

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Lanthanide-Sensitized Lanthanide Luminescence: Terbium-Sensitized Ytterbium Luminescence in a Trinuclear Complex

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Luminescence from lanthanide complexes has been of interest for many years.[1] The long luminescence lifetimes of certain lanthanide complexes (particularly europium and terbium complexes) have been applied widely, particularly in the fields of bioassay,[2] microscopy,[3] and sensor development.[4] More recently, interest has developed in lanthanide complexes that luminesce in the near-IR.[5-7] Such complexes contain lanthanide ions with relatively small energy gaps between the emissive state and the ground state, including neodymium,[5] erbium,[6] and ytterbium[7] complexes. These near-IR emissive complexes have begun to be applied in bioassay applications.[7c] Such complexes can be used with a much wider range of sensitizing chromophores than conventional complexes; these include metal complexes[8,9] as well a broad range of organic dye molecules.[10] Such species have tended to be d−f hybrids, since f−f mixed metal complexes are hard to prepare selectively.

We now report the results of a synthetic and luminescence study on a hetero-trimetallic lanthanide complex containing two terbium ions and one ytterbium ion (**1**). The synthetic strategy used (Scheme 1) allows the incorporation of a DTPA-like binding site as a bridge between two kinetically stable terbium complexes. Such binding sites are already used for imaging applications in vivo and have been shown to have high stability in the presence of endogenous metal ions.[1] Our strategy is based on functionalization of the widely used *tert*-butyl ester **2**,[11] prepared by reaction of 1,4,7,10-tetraazycylododecane with *tert*-butyl bromoacetate. Reaction of **2** with 4-nitrobenzylbromide yielded the nitrobenzyl-substituted derivative

3, which was reduced to the aminobenzyl derivative **4** by catalytic hydrogenation. Cleavage of the *tert*-butyl esters was accomplished using trifluoroacetic acid in dichloromethane, yielding the heptadentate ligand **5** which formed the terbium complex **6** on reaction with terbium trifluoromethanesulfonate. This complex also contains an amino group that is well placed to react further; reaction of 2 molar equiv of **6** with DTPA anhydride yielded the dinuclear complex **7**. At this stage, it was deemed necessary to assess the luminescence properties of the terbium complexes **6** and **7** with a view to ensuring that there was no migration of terbium to the central DTPA-like binding site. Differences in the efficiency of nonradiative quenching of lanthanide luminescence by O−H and O−D oscillators can be used to calculate of the inner sphere hydration state, q, using the equation

$$q = A_{Ln} (k_H - k_D - B)$$

where k_H and k_D are the observed rate constants for the luminescence in H_2O and D_2O, respectively, A_{Ln} is a constant for a given lanthanide, and B is a correction factor for outer sphere solvent contributions (this is also unique to a given lanthanide).[12] For terbium complexes, $A = 5.0$ ms and $B = 0.06$ ms^{-1}). Since such measurements give information about the local environment, they are an ideal tool to identify the nature of the binding site, particularly as the DO3A-derived binding site is heptadentate, while the DTPA-like site is octadentate. Both **6** and **7** gave classical terbium-centered luminescence spectra, and there is no change in the relative

Scheme 1: Synthesis of **1** and Its Precursors[a]
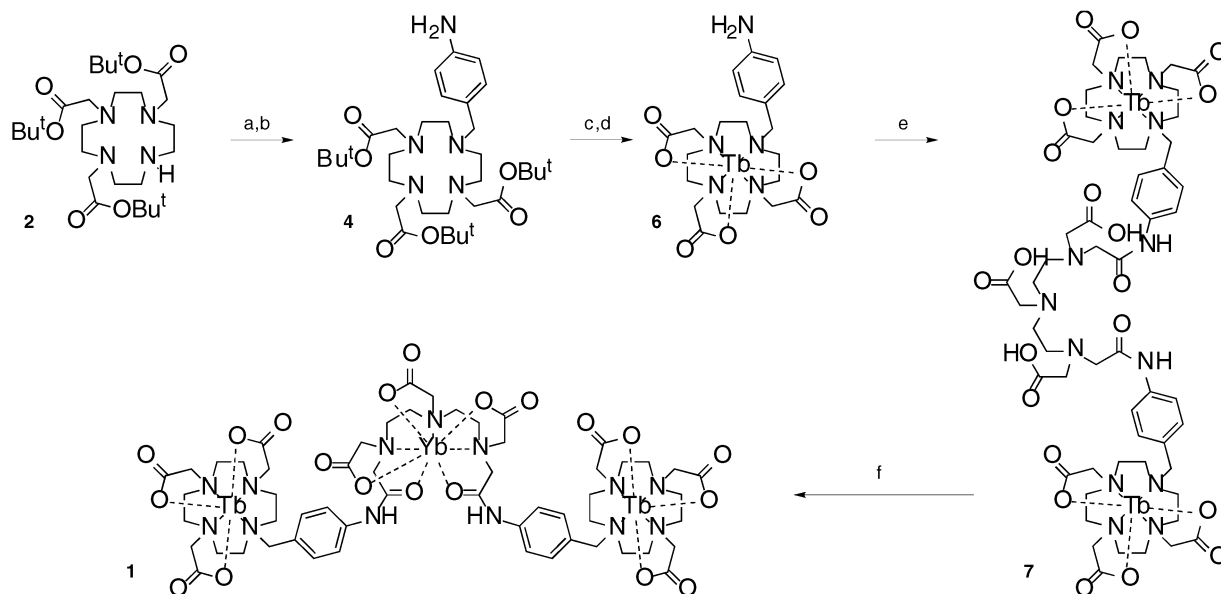
[a] Reagents and conditions: (a) BrCH$_2$C$_6$H$_4$NO$_2$,NaHCO$_3$, CH$_3$CN; (b) Pd/C, H$_2$, CH$_3$OH; (c) CF$_3$CO$_2$H, CH$_2$Cl$_2$; (d) Tb(OTf)$_3$, CH$_3$OH; (e) diethylenetriamine pentaacetic dianhydride, NEt$_3$, DMF; (f) Yb(Tf)$_3$, CH$_3$OH.

Table 1. Luminescence Lifetimes for the Complexes Studied

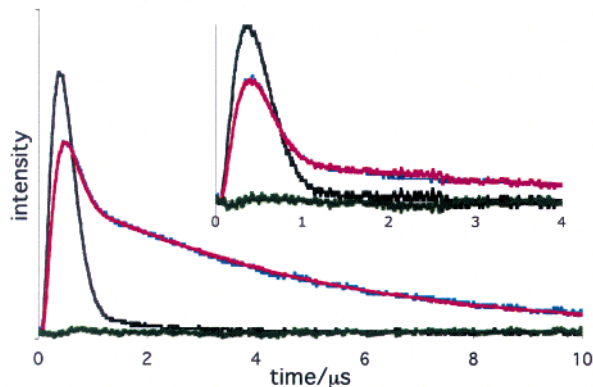| compd	Ln[a]	λ_{ex}/nm	λ_{em}/nm	τ_{H_2O}/μs	τ_{D_2O}/μs	q
6	Tb	266	545	860	1180	1.3
7	Tb	266	545	1140	1840	1.4
1	Yb	337	980	1.83	4.22	0.2
1	Yb	488	980		4.22	

[a] Lanthanide ion under examination.

Figure 1. Fitted luminescence decays for ligand-sensitized (main graph) and terbium-sensitized emission (inset) from ytterbium in compound **1** dissolved in D_2O. Both fit to a lifetime of 4.2 μs. The observed decay (blue) and fitted curve (red), superimpose almost exactly, as can be seen from the residual (dark green). The detector response (black) is also shown.

intensities of the emission maxima, with the strongest transition at 545 nm, when probed directly (λ_{ex} = 366 nm) or through the aryl chromophore of the aminobenzyl group (λ_{ex} = 266 nm). This suggests that the binding site is the same in both cases. Furthermore, the luminescence lifetimes obtained for **6** and **7** (Table 1) give similar hydration numbers, showing that the metal environment is almost certainly the same in both cases. Having thus ascertained that the terbium remains in a DO3A-like binding site through the course of the synthesis of **7**, it is reasonable to assume that the complex is kinetically robust. Reaction of **7** with ytterbium trifluoromethanesulfonate yielded the trinuclear complex **1**. Ytterbium has been shown to reduce the luminescence intensity of terbium in kinetically unstable systems.[13] In our system the metals are held in close proximity with one another throughout the experiment, and the luminescence from the ytterbium center can be studied without difficulty. Excitation at 337 nm using a nitrogen laser gave rise to emission from both metal centers. The emission from the terbium center was reduced in intensity relative to the terbium-centered luminescence in **7**, and a new emission at 980 nm was now observed, corresponding to the $^2F_{7/2}-^2F_{5/2}$ transition in the ytterbium ion.

The luminescence lifetime of the ytterbium center in **1** was determined using established reconvolution procedures. A typical fitted decay is shown in Figure 1. The luminescence lifetimes in H_2O and D_2O are recorded in Table 1, together with an inner sphere hydration number of 0.2 obtained by using A and B factors of 1.0 μs and 0.1 μs^{-1}, respectively.[12] This is consistent with the binding of the ytterbium ion in the DTPA binding site, essentially with no bound water molecules present as a result of the small size of

ytterbium and the steric demands of the amide substituents—the residual hydration probably results from outer sphere effects. We then studied the interaction between the terbium and ytterbium ions for a solution of **1** in D_2O. Direct excitation of the terbium absorption band at 488 nm resulted in the observation of ytterbium-centered emission at 980 nm. Stray light was rejected using a cutoff filter in front of the monochromator to remove signals below 850 nm and obviate the possibility of 2λ artifacts appearing close to 980 nm. The decay of the emission band at 980 nm fitted to a lifetime identical to that measured for the ytterbium complex in D_2O when excited at 337 nm. The fitted time-resolved decay is shown as an inset to Figure 1. It is reasonable to infer energy transfer from the terbium center, since neither ytterbium nor the ligand-centered chromophore have any absorption bands at 488 nm.

To our knowledge this represents the first report of lanthanide-centered near-IR emission sensitized by a lanthanide ion. We are currently investigating the use of different pairs of lanthanide ions and more complex arrays with a view to performing a thorough study of the energy transfer processes involved.

Supporting Information Available: Synthetic routes to **1** and its precursors; experimental procedures for luminescence spectroscopy and deconvolution; energy level diagram showing excited states for terbium and ytterbium. This material is available free of charge via the Internet at http://pubs.acs.org.

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