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Highly Luminescent, Neutral, Nine-Coordinate Lanthanide(III) Complexes

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Using a simple ligand design, we have prepared neutral, nine-coordinate lanthanide complexes that exclude water from the inner coordination sphere, thus leading to high emission quantum yields and long excited-state lifetimes. The complexes form in high synthetic yields (49–87 %) by simply mixing the ligand and the lanthanide. Visible luminescence from Eu^{III} (Φ = 60 %, τ = 2.2 ms) and Tb^{III} (Φ = 7 %, τ = 0.2 ms) and near-infrared luminescence from Yb^{III} (Φ = 0.7 %), Nd^{III} and Er^{III} were observed in acetonitrile and CH_2Cl_2 at room temperature. In addition, the Gd^{III} complex was prepared to gain information about the triplet state of the ligand.

Introduction

Lanthanide (Ln) complexes[1] that emit in the visible region of the electromagnetic spectrum (Tb, Eu) are important in light-emitting diodes (LEDs),[2] and near-infrared (NIR) emitting Ln^{III} complexes (Yb, Nd, Er) have potential applications in fiber-optic technologies[3] and biomedical imaging.[4] Because Ln^{III} salts have intrinsically low extinction coefficients ($\varepsilon \approx 1$–$10\ \text{M}^{-1}\,\text{cm}^{-1}$),[5] direct excitation is difficult without high intensity sources. The low absorption coefficients are due to intra-4f transitions, which are parity-forbidden. Therefore, it is common to indirectly excite lanthanide ions through an antenna chromophore – a molecule with a high absorption cross section that can readily transfer its energy to the lanthanide ion.[5,6] The advantages of lanthanide luminescence are their narrow emission bands, large Stokes' shifts and long lifetimes (µs to ms). Because the 4f orbitals are shielded by the outer 5s and 5p orbitals, these properties are mostly insensitive to chemical environment. Ln complex emission quantum yields and excited-state lifetimes decrease dramatically upon coordination of solvents (especially water) through vibronic coupling[6c] – a problem compounded for NIR-emitting Ln complexes due to the energy gap law.[7] In addition, lanthanide ions have coordination numbers between 6 and 12, although for bulky ligands it is effectively 8–10,[8] making full coordination somewhat difficult (remaining coordination sites are usually occupied by available solvent). Many lanthanide complexes reported in the literature are charged, rendering them unusable for many applications that require evaporation, such as in the fabrication of small-molecule light-emitting diodes (SMOLEDS).[2,9]

Here we report neutral, nine-coordinate lanthanide complexes with a simple tridentate ligand, which display high emission quantum yields due to the exclusion of solvent molecules from the first coordination sphere.

Results and Discussion

The syntheses of the complexes are shown in Scheme 1. Dropwise addition of the corresponding Ln^{III} salt, dissolved in water, to a mixture of readily available precursor **1** in EtOH/H_2O at 0 °C gave sparingly soluble complexes **2a**–**2g** in 49–87 % yield (see Supporting Information). After filtration of the resulting precipitated solid, the complexes were crystallized by slow evaporation of CH_2Cl_2 from a CH_2Cl_2/MeOH solution. All compounds were characterized by elemental analysis and mass spectrometry, and the diamagnetic lanthanum complex **2g** was also characterized by NMR spectroscopy (Figures S4 and S5).

To the best of our knowledge, the only report of similar systems is that of Comby et al.,[10] but these authors investigated the complexation of the ligand **3** with Ln^{III} ions in situ, without isolation of the products (Scheme 1). Ziessel and co-workers have developed a number of macrocyclic ligands based on the bipyridine carboxylate architecture.[11] Multinuclear complexes using a tridentate ligand containing a bipyridine moiety and a carboxylate group have recently been reported by Mamula and co-workers[12] and nonalanthanide cluster based on a derivative of **3** by Comby et al.[13]

The Eu and La complexes **2b** and **2g** formed crystals suitable for X-ray diffraction, and the resulting molecular structure of **2b** is shown in Figure 1 (**2g** is shown in Figure S1).

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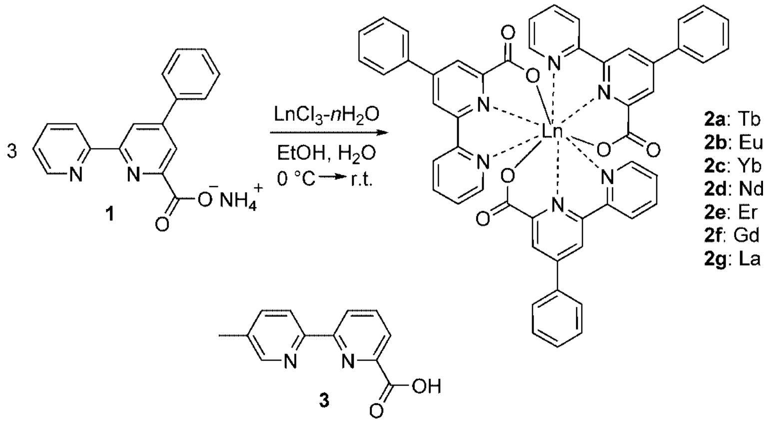

Scheme 1. Synthesis of the lanthanide complexes **2a**–**2g** and previously studied ligand **3**.[10]

The unit cell of **2b** contains one molecule each of MeOH and CH_2Cl_2 and that of **2g** contains three molecules of MeOH that are *not coordinated* to the Ln ions (i.e., the ligands fully saturate the inner coordination sphere of the Ln ions).

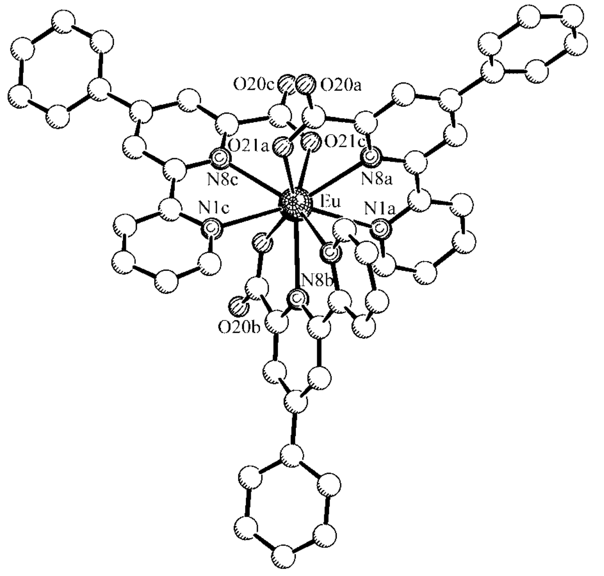

Figure 1. Molecular structure of complex **2b**. The hydrogen atoms and solvent molecules are omitted for clarity.

In **2g**, two La–O bonds have nearly the same length (2.44 Å), while the third is slightly longer (2.47 Å). In addition, the La–N distances range from 2.64 to 2.81 Å, where the longest La–O distance corresponds to the carbonyl group on the pyridine ring containing the longest La–N distance, indicating that there is steric hindrance around the La ion causing one ligand to be slightly crowded out. In **2b**, all distances are slightly shorter, but the same pattern exists: Eu–N distances range from 2.54–2.65 Å for two ligands, while the third has the longest Eu–N bond at 2.72 Å. Likewise, this third ligand has a slightly longer Eu–O distance (2.37 Å) than the other two (2.36 and 2.35 Å). In all cases, the pyridine ring containing the carbonyl group has the shorter of the two Ln–N distances. A table of selected crystal properties is given in the Supporting Information (Table S1).

It should be noted that different isomers of the complexes are possible, based on whether the carboxylate groups are up or down [up-up-up (*fac*) or up-up-down (*mer*)].[14] In the molecular structures isolated, the up-up-down (*mer*) isomer was exclusively observed. However, isomerization in solution is likely as indicated by the broad signals in the NMR spectrum of lanthanum complex **2g** (Figures S4 and S5) and the excited-state lifetime of terbium complex **2a**.[15] We attempted variable-temperature NMR experiments in order to observe the isomerization, but solubility problems prevented us from obtaining reliable measurements.

The complexes do not show absorption bands at energies lower than 340 nm, as can be expected for a simple ligand structure, and the bands can be assigned to π-π^* transitions in the ligand with the highest energy transitions localized on the bipyridine units and the shoulder at 320 nm on the carboxylate moieties. Molar extinction coefficient values for the peak maximum at 276 nm are ca. 70000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, and all the complexes show the same features (Figure S2).[16] The transitions in the absorption spectrum of ligand **1** (not shown) are slightly blueshifted vs. those in the complexes, but the features are similar.

The terbium (**2a**) and europium (**2b**) complexes emit brightly at room temperature in acetonitrile and CH_2Cl_2 solutions, showing the typical narrow spectra of Ln^{III} cations (Figure 2). For **2a**, excitation of the antenna at 315 nm leads to the characteristic green emission from Tb^{3+} arising from ${}^5D_4{\to}{}^7F_j$ transitions, with the most intense band at 545 nm corresponding to the ${}^5D_4{\to}{}^7F_5$ transition. Likewise, for **2b**, excitation of the ligand at 315 nm populates the Eu^{3+} excited state, leading to ${}^5D_0{\to}{}^7F_j$ transitions, with the most intense at 617 nm (${}^5D_0{\to}{}^7F_2$). The nondegenerate ${}^7F_0$ (579 nm) level is not split, giving evidence that complex **2b** exists as a single (time-averaged) luminescent species in solution.[7b] Due to the exclusion of solvent from the inner coordination sphere of the lanthanide, relatively long excited-state lifetimes (0.2 ms for **2a** and 2.2 ms for **2b**) and high emission quantum yields (7% for **2a**[17] and 60% for **2b**[18]) were found. This is in contrast to the estimated values found by Comby et al.[10] for ligand **3** (7% for Eu^{III}

complexes and 55% for the Tb^{III} derivatives), but this can be explained by the relative ordering of the energy levels (vide infra).

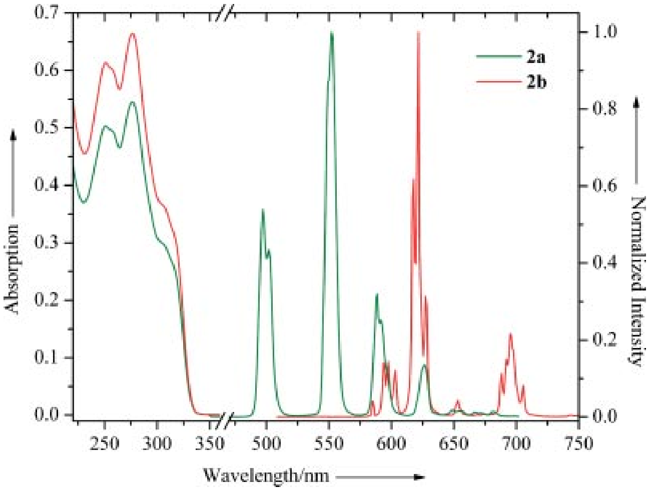

Figure 2. Absorption and normalized emission spectra of complexes **2a** (1×10^{-5} M) and **2b** (0.8×10^{-5} M) in aerated CH_3CN at room temperature ($\lambda_{exc.}$ = 315 nm).

The infrared emitters were likewise measured and found to give intense emission in the NIR region. Figure 3 shows the absorption and normalized emission spectra of complexes **2c**–**2e**, where the spectra shown are recorded for samples with identical absorbance values at the excitation wavelength and constant bandpass for emission. Excitation of **2c** at 315 nm led to infrared emission with a maximum at 980 nm, corresponding to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition for Yb^{3+}. The quantum yield of **2c** was found to be 0.7%,[19] which is quite remarkable for NIR emitters when taking into consideration the energy gap law.[7] Complex **2d** has two emission peaks at 1060 nm ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) and 1333 nm ($^4F_{3/2}\rightarrow{}^4I_{9/2}$) typical of Nd^{III} complexes.[20] Complex **2e** shows the typical broad emission of Er^{III} complexes, with a maximum at 1523 nm corresponding to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition. The spectra shown in Figure 3 are scaled due to the relatively low luminescence of **2d** and **2e** compared to Yb^{III} complex **2c**, showing the dramatic effect of the energy gap law on the emission properties of the complexes.

All complexes showed identical photophysical properties in acetonitrile and CH_2Cl_2 solutions.[15,21] In addition to the emitting lanthanides, gadolinium complex **2f** was prepared to ascertain the level of the ligand triplet state ($^3\pi$-π^*). Because the excited state of Gd^{III} ($^6P_{7/2}$) lies at 32150 cm^{-1} (≈ 311 nm),[7] it is very difficult to populate it through organic excited ligand triplet states. Therefore, Gd^{III} complexes offer the possibility to probe the ligand excited-state properties in systems nearly identical to the luminescent lanthanide complexes, including the enhanced intersystem crossing offered by the heavy gadolinium ion itself.

At room temperature, gadolinium complex **2f** shows a broad emission with a maximum at 350 nm (not shown), which corresponds to fluorescence of the ligand. Upon cooling to 77 K, a small amount of residual singlet emission is observed, but the emission spectrum is dominated by the phosphorescent triplet emission from the ligand (Figure S3). When a delay of 100 µs after the excitation pulse was applied, the singlet emission disappeared. The $^3\pi$-π state of the ligand was determined to be 22700 cm^{-1} (2.82 eV) from the 0-0 transition in the phosphorescence spectrum (440 nm) at 77 K. At room temperature, **2f** has a fluorescence lifetime <1 ns, while at 77 K, the lifetime of the phosphorescent triplet state is 5.4 ms.

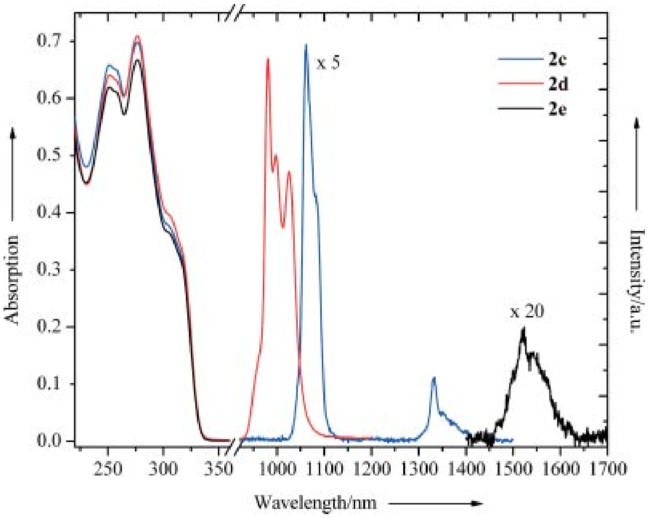

Figure 3. Absorption and emission spectra of complexes **2c**–**2e** in aerated CH_3CN (1×10^{-5} M) at room temperature. The emission spectra were recorded for samples having the same absorption at the excitation wavelength (315 nm) and identical conditions for emission and scaled [**2c** (1×), **2d** (5×), and **2e** (20×)].

The emitting levels of Eu^{III} ($^5D_0$) and Tb^{III} ($^5D_4$) lie at 17500 cm^{-1} and 20430 cm^{-1}, respectively, and therefore below the triplet state of the ligand (22700 cm^{-1}). However, the $^3\pi$-π state of the ligand should be sufficiently higher than the emitting level of the lanthanides such that energy transfer is fast and irreversible (i.e., no back energy transfer can occur). Experimental results have previously shown that triplet states of the ligand should be between 2000 cm^{-1}[6b] and 3500 cm^{-1}[22] above the emitting state of the Ln^{III} ion (ΔE). In the systems reported here, ΔE is 2270 cm^{-1} for **2a** and 5200 cm^{-1} for **2b**. Although the emission quantum yield of **2a** is still relatively high (5%), it is clear that the $^3\pi$-π state of the ligand and the $^5D_4$ state on Tb^{III} are not well matched. Although the $^5D_0$ state of Eu^{III} and the triplet state of the ligand have a high ΔE value, an emission quantum yield of 60% is obtained. This indicates that ΔE of 2000 cm^{-1} may allow, for these complexes at room temperature, back energy transfer into the triplet manifold of the ligand in complex **2a**. For the related complexes based on ligand **3**,[10] the quantum yields for the Eu^{III} and Tb^{III} complexes are reversed. Ligand **3** lacks a phenyl ring on the bipyridine ligand and the increased conjugation offered in the ligand reported here would serve to lower the triplet state and improve the energy match between the ligand and the Eu^{III} emitting state. Conversely, ligand **3**, with its higher triplet state, would favor energy matching the Tb^{III} emitting state, which shows the higher emission quantum yield in the previous study.

The gap between the ligand state in **2c** and that of the Yb^{III} $^2F_{5/2}$ state is quite high (ca. 12000 cm^{-1}), but still leads to a relatively high emission quantum yield (0.7%). Presumably, this can be increased by better energy matching of the $^3\pi$-π state of the ligand and the $^2F_{5/2}$ level of Yb^{III} (i.e., lowering the triplet level of the ligand by redshifting the absorption), although other processes may play a role.[23]

Conclusions

We have synthesized a series of neutral lanthanide (Ln) complexes based on simple ligand structures that effectively serve as antennae for energy transfer to the Ln^{III} ion, giving the typical narrow emission spectra, large Stokes' shifts and long luminescence lifetimes typical of Ln^{III} ions. In addition, the red- and near-infrared-emitting complexes have high emission quantum yields, which is likely due to the exclusion of vibronically deactivating solvent molecules from the inner coordination sphere of the complex. Another advantage of the present complexes is their neutrality, making them amenable to applications where charged lanthanide complexes are not, such as in the fabrication of SMOLEDs. We are currently investigating the volatility of the complexes.

Furthermore, functionalization of the ligand allows for the synthesis of more soluble derivatives in solvents of different polarity. Finally, more highly conjugated systems will shift the absorption into the visible region, potentially making the complexes more suitable for biological imaging, where ultraviolet excitation light can cause severe damage to biological tissue. The aforementioned derivatives will be presented in a forthcoming full paper.

Supporting Information (see footnote on the first page of this article): Synthetic, photophysical and X-ray methods, characterization data for the products, absorption spectra of all complexes, emission spectra of complex **2f**, crystal structure of **2g**, and NMR spectra of **1** and **2g**.

Acknowledgments

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[15] Terbium complex **2a** has a much longer excited state lifetime (1.6 ms) in CH_2Cl_2 (vs. 0.2 ms in acetonitrile). We have no concrete explanation for this dramatic change, but experiments are currently underway to understand it. One possible explanation is an isomerization in solution leading to different isomers with different properties, as discussed in the text.

[16] Due to the low solubility of the complexes, we do not feel confident quoting exact molar absorptivity values.

[17] Measured vs. quinine bisulfate in 1 N H_2SO_4 (Φ = 0.546).

[18] Measured vs. rhodamine 101 in ethanol (Φ = 1.0).

[19] Measured vs. $Yb(TTA)_3$ in toluene (Φ = 0.0035; TTA = thenoyltrifluoroacetylacetonat e). See: S. B. Meshkova, Z. M. Topilova, D. V. Bolshov, S. V. Beltyukova, M. P. Tsvirko, V. Y. Venchikov, *Acta Phys. Pol. A* **1999**, *95*, 983.

[20] Due to the effective range of our NIR photomultiplier tube, we could not observe the band at ca. 880 nm ($^4F_{3/2}\rightarrow{}^4I_{13/2}$).

[21] For the absorption spectra in CH_2Cl_2, see Figure S3.

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