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Lanthanide Luminescence

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Bright Blue-Emitting Ce^{3+} Complexes with Encapsulating Polybenzimidazole Tripodal Ligands as Potential Electroluminescent Devices**

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The versatile photophysical properties of lanthanide ions[1] have inspired vigorous research activities owing to a wide range of potential applications in the fields of bioassays,[2] sensor systems,[3] and optical materials.[4] The Eu^{3+} and Tb^{3+} ions are of particular interest owing to their long luminescence lifetime and narrow emission bands in the visible region. Some other lanthanide ions were also investigated for their near-infrared luminescence or diagnostic properties.[5] Recently, the electroluminescence of lanthanide ions has attracted increasing attention as potential light-emitting materials in light-emitting diodes (LEDs), and a number of Eu^{3+} and Tb^{3+} complexes have been incorporated into LED devices.[6] Compared with other lanthanide ions, the Ce^{3+} ion is unique, characteristic of parity-allowed electric-dipole $4f \rightarrow 5d$ transitions, which lead to fast decay times and high light outputs.[7] Great endeavors have been devoted to doping Ce^{3+} ions into inorganic crystals to serve as metal phosphors with possible applications in solid-state lasers, quantum cutters, inorganic scintillators, and fluorescent lamps and displays.[7] By contrast, investigations of the luminescence properties of Ce^{3+} ion in organic coordination environments remain rather rare, although that of the free Ce^{3+} ion has been thoroughly studied[8] and its luminescence in Ce^{3+} halides, organometallics, and polymer films has been studied.[9]

It is well known that although the inner 4f orbitals of Ce^{3+} are well shielded, their 5d orbitals are very sensitive to the ligand sphere. Many organic ligands have been found to quench Ce^{3+} luminescence upon complexation, and contact of Ce^{3+} ions with solvent molecules may engender nonradiative transitions to diminish the luminescence.[8] Nevertheless, studies have indicated that diazapolyoxabicyclic ligands (cryptands) could well shield the Ce^{3+} ions and result in efficient luminescence in the ultraviolet region.[10] Some Ce^{3+} complexes containing halide anions and certain carboxylate groups were also found to be luminescent, and the emission bands were remarkably red-shifted into the visible region up to 630 nm depending on the interactions of the 5d energy levels with the crystal field.[9,11] These findings suggest that, in principle, highly luminescent Ce^{3+} complexes are achievable provided that a suitable organic ligand is designed to encapsulate the Ce^{3+} ion. More important, as the ligand can be readily modified and decorated to provide an adjustable crystal field, the use of the Ce^{3+} chromophore in luminescent materials can potentially offer tunable emission wavelength and strength, covering the UV and Vis regions.[7–11] Taking into account the well-studied red-emitting Eu^{3+} complexes and green-emitting Tb^{3+} complexes in LEDs, luminescent Ce^{3+} complexes may provide an alternative as light-emitters in LED devices, in contrast with the commonly studied inorganic systems.[12]

We and others[13] have studied lanthanide complexes with tripodal ligands incorporating pyridyl (Py) and benzimidazolyl (Bim) units and found that these types of ligands could host lanthanide ions with the three arms effectively encapsulating the metal center. Herein, we report the preparation of the *N*-substituted tris(*N*-alkylbenzimidazol-2-ylmethyl)amine (NTB) ligands, triRNTB, as shown in Scheme 1 (R = ethyl: triEtNTB; R = *n*Pr: triPrNTB; and R = allyl: triAllNTB). A family of efficiently blue-emitting Ce^{3+} complexes, namely, $[Ce(triRNTB)_2](CF_3SO_3)_3$ (**1**–**3**), was obtained. Preliminary photoluminescence investigations were carried out in both the solution and solid state, and electroluminescence was studied in LED-based solid-state lighting devices.

The ligands were prepared according to a reported method by decorating the NTB ligand through NH group substitutions (see Supporting Information for experimental and analytical details). The complexes were readily obtained in satisfactory yields (about 80%) by reaction of $Ce(SO_3CF_3)_3{\cdot}6H_2O$ with the ligands in MeCN/EtOH. The crystalline products of complexes **1** and **2** obtained from diffusion of diethyl ether into the reaction mixture contained solvent molecules which partially escaped when the products were kept in air, while complex **3** crystallized without solvated molecules. The following compositions were obtained from the elemental analyses: $[Ce(triEtNTB)_2](CF_3SO_3)_3{\cdot}2H_2O$ ($\mathbf{1}{\cdot}2H_2O$), $[Ce(triPrNTB)_2](SO_3CF_3)_3{\cdot}2H_2O$ ($\mathbf{2}{\cdot}2H_2O$), and $[Ce(triAllNTB)_2](SO_3CF_3)_3$ (**3**). Water-free samples of **1** and **2** could be obtained by drying the solids in a dessicator. Thermogravimetric analyses indicated that the dried com-

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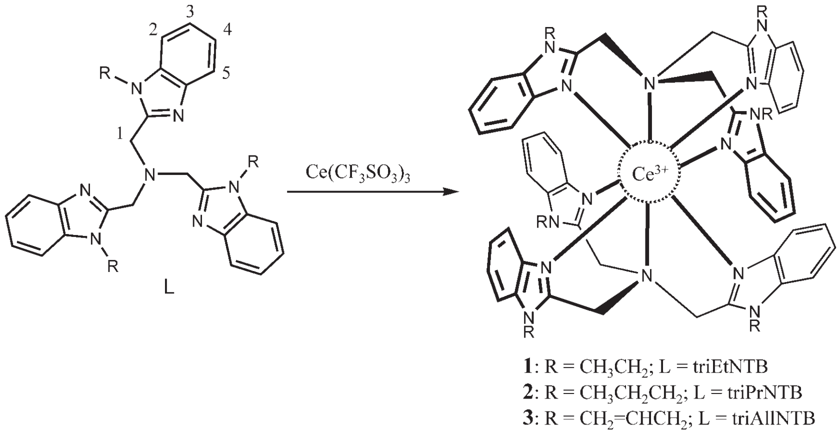

Scheme 1. Structures of the three NTB ligands and formation of the complexes **1**–**3**.

plexes are stable up to 300 °C, showing no further weight losses due to solvated molecules (Figure S1 in the Supporting Information). The molecular structures of the complexes were unambiguously established by X-ray single-crystal diffraction (Supporting Information), which confirmed that crystals of **1** and **2** contain solvated molecules with the formula [Ce(triEtNTB)$_2$](CF$_3$SO$_3$)$_3$·MeCN·2 EtOH (**1**·MeCN·2 EtOH) and [Ce(triPrNTB)$_2$](SO$_3$CF$_3$)$_3$·MeCN·4 H$_2$O (**2**·MeCN·4 H$_2$O), respectively.

The structural feature common to the three complexes is the **ML$_2$** cationic motif [Ce(triRNTB)$_2$]$^{3+}$, in which the central Ce^{3+} ion is hosted in the cavity formed by two face-to-face arranged tripodal ligands (Figure 1). Three imino N atoms and the apical tertiary N atom of each ligand participate in coordination of the metal ion, giving rise to a CeN$_8$ coordination sphere with Ce–N bond distances in the range of 2.546(3)–2.743(3) Å for **1** and 2.547(6)–2.742(6) Å for **2**. The six benzimidazole (Bim) arms wrap around the Ce^{3+} ion alternately to result in pseudo-C_3 symmetry with the axis passing through the two apical tertiary N atoms and the central Ce^{3+} ion. The coordination geometry of the Ce^{3+} ion may be best described as a slightly distorted cube in which the eight ligating N atoms occupy the corners as shown in Figure 1. The CF$_3$SO$_3^-$ counteranions and solvated MeCN, EtOH, or H$_2$O molecules are present in the crystal lattice but have no direct interactions with the central Ce^{3+} ion. Such an ability of the two tripods to shield the Ce^{3+} ion completely through the N donors of the bulky Bim rings without additional bound solvent molecules, especially water or ethanol, is important for the design of lanthanide supramolecular optical devices because the coordinating solvent molecules are frequently efficient quenchers of the lanthanide luminescence.[1–4,6] To clarify the solution structures of the complexes, ESI-MS spectroscopy was utilized to detect the solution species by dissolving the fresh crystals of **2** and **3** in MeCN. Salient peaks corresponding to the ML$_2$ motifs with charge-balancing ions were observed (Figures S2 and S3 in the Supporting Information), indicating that the [Ce(triRNTB)$_2$]$^{3+}$ motif similar to that observed in the solid state is retained to a significant extent in solution. The appearance of peaks corresponding to the ML species more or less suggested dissociation of the complexes in solution, in accord with NMR spectroscopy results[13b] that the ML$_2$ complex of the NTB-type tripodal ligand is strongly favored in solution.

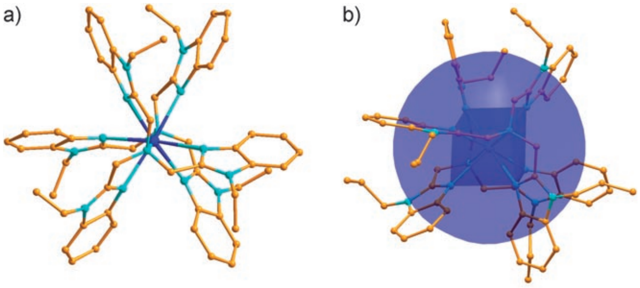

Figure 1. a) Structure of the complex cation of **1** (Ce dark blue, N light blue, C yellow), and b) structure of the complex cation of **2** showing the distorted cubic coordination geometry around the Ce^{3+} ion.

The absorption spectra of the free salt Ce(CF$_3$SO$_3$)$_3$, the ligand triPrNTB, and complex **2** were measured in ethanol (Figure 2). It is clear that the major absorption bands of the complex are rather similar to those of the ligands, displaying slight shifts and intensity changes indicative of the metal–ligand interaction. A significant difference was found between the spectra of the free Ce^{3+} ion and the complex. In EtOH, the Ce^{3+} ion exhibits two weak bands around 244 and 299 nm attributed to 4f→5d transitions.[8] Upon complexation, the low-wavelength band shifts to 383 nm with other potential metal-centered bands overlapped with the intraligand absorptions. Nevertheless, it is evident that the 4f→5d transitions in the complex are remarkably red-shifted compared with those of the free Ce^{3+} ion. This shift indicates a significant crystal-field effect on the 5d orbitals of the Ce^{3+}

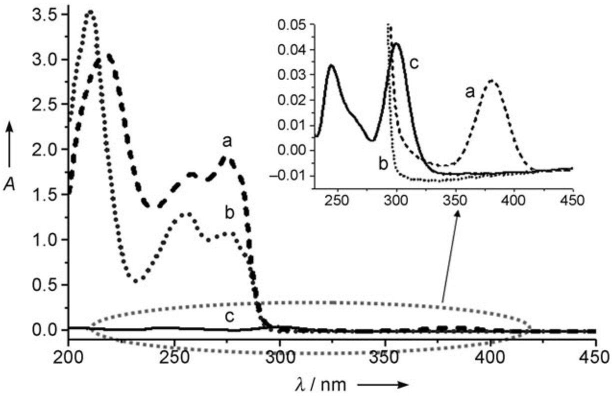

Figure 2. Absorption spectra in EtOH of a) **2** (5×10^{-5} M), b) triPrNTB (5×10^{-5} M), and c) Ce(CF$_3$SO$_3$)$_3$ (2×10^{-4} M). The inset shows an enlargement of the weak absorption bands marked with a gray dotted ellipse in the main plot.

ion,[7] which may consequently cause a red shift of the emission band into the visible region. This is important for the utilization of the cerium complexes in lighting devices.

Figure 3 shows the excitation and emission spectra of the free salt $Ce(CF_3SO_3)_3$, the ligand triPrNTB, and complex **2** measured in ethanol at room temperature (see Figures S4 and S5 in the Supporting Information for the spectra of complexes **1** and **3**). As expected, the emission band of the Ce^{3+} salt in ethanol appears in the UV region around 350 nm (λ_{ex} = 301 nm), the ligand triPrNTB exhibits an emission centered at 300 nm (λ_{ex} = 288 nm), while the sensitized emission of the Ce^{3+} ion in complex **2** is red-shifted into the visible region at about 441 nm. The band shape rather resembles that of the Ce^{3+} salt, which can be fitted to two Gaussian peaks with maxima at 429 and 468 nm (Figure 3 h). The energy difference between these two peaks is close to 2000 cm^{-1}, in good agreement with the characteristic splitting of the two Ce^{3+} 4f ground levels $^2F_{5/2}$ and $^2F_{7/2}$ induced by spin–orbit interaction. Therefore, these two emission bands can be attributed to the two electric-dipole 4d→5f transitions of Ce^{3+} from the lowest excited state ($^2D_{3/2}$) to the ground state $^2F_{5/2}$ and $^2F_{7/2}$.[7] To further confirm the nature of the blue emission, we measured the decay time of this band which gave a decay constant of about 50 ns. This value is comparable with those previously reported[8,9b,10] and larger than that of the ligand (1.5 ns), strongly pointing to the Ce^{3+} ion as being responsible for the blue emission band. The excitation spectrum corresponding to the blue emission shows two broad bands centered at 284 and 379 nm. Referring to the excitation and absorption spectra of the free Ce^{3+} ion and the ligand, the band at 284 nm can be tentatively assigned to the intraligand transition while the band at 379 nm is attributable to the Ce^{3+} 4f→5d transition. The selective excitations based on these two bands resulted in similar blue emission bands, but the emission that results from excitation at 284 nm is relatively less intense than that observed upon excitation at 379 nm, indicative of distinct energy-transfer procedures but similar emissions. In addition, excitation at 284 nm only offered a significantly diminished ligand-centered emission, suggesting effective energy transfer from the intraligand absorption to the Ce^{3+} 4d→5f emission. These results indicate that the energy transfer responsible for the blue emission can occur not only from the metal-based 4f→5d transition, but also from the ligand-based transition. Therefore, the ligands could act as "antennae" in the absorption of light and transfer of energy to enable Ce^{3+} emission, similar to the "antenna effect" in Eu^{3+} and Tb^{3+} complexes.[1]

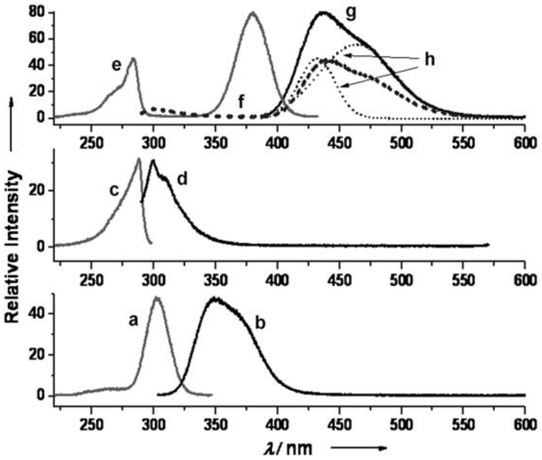

Figure 3. Luminescence spectra measured in EtOH at 298 K. a) Excitation and b) emission spectra of $Ce(CF_3SO_3)_3$ (2×10^{-4} M). c) Excitation and d) emission spectra of triPrNTB (5×10^{-5} M). e) Excitation and f, g) emission spectra (λ_{ex} = 284 nm (f); λ_{ex} = 379 nm (g)) of complex **2** (5×10^{-5} M). h) Gaussian fits for the emission of **2** at 441 nm.

Figure 4 shows the excitation and emission spectra of complexes **1**–**3** measured in the solid state at room temperature. The spectral profiles are similar to those observed in solution, however, the relative band intensity and position exhibit differences depending on the ligands. The *n*-propyl-substituted ligand (triPrNTB) results in a slightly intense emission, while the allyl-substituted ligand (triAllNTB) leads to a red shift of the emission maximum by 10 nm. As functionalization of the NTB ligand with different alkyl groups will slightly alter the electronic nature of the ligands, these observations demonstrate a ligand effect on the luminescence of complexes. Taking into account the environmental sensitivity of the 5d orbitals to the ligand crystal field,[7–9,11] such a ligand effect is of interest to enable regulation of the emission wavelength and strength by rational design and modification of the ligands.

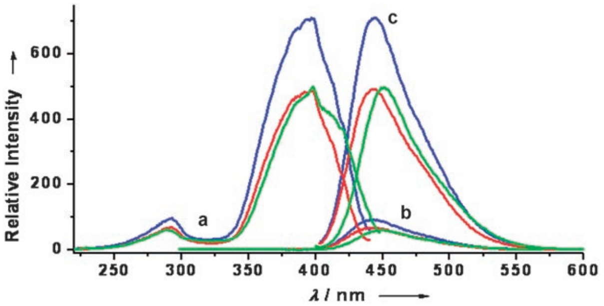

Figure 4. Luminescence spectra of complexes in the solid state at 298 K (**1** blue; **2** red; **3** green). a) Excitation spectra for **1** and **2** (λ_{em} = 442 nm) and for **3** (λ_{em} = 452 nm). b, c) Emission spectra for **1**–**3** (λ_{ex} = 293 nm (b); λ_{ex} = 397 nm (c)).

The emission quantum yield (ϕ) of complex **2** was determined with reference to quinine sulfate as the standard (std) with excitation at 389 nm in ethanol at 5×10^{-5} M according to Equation (1),[14] where *n* is the refractive index and *F* refers to the area of the emission peaks of the complex and the standard.

$$\phi_2 = \frac{n_2^2}{n_{std}^2}\frac{F_2}{F_{std}}\phi_{std} \qquad (1)$$

The calculated quantum yield, $\phi_2 = 0.55$, is relatively high compared with those of Eu^{3+} and Tb^{3+} complexes[1–3] and accounts for the observation of blue luminescence at rather low concentrations (10^{-5} M). This high quantum yield confirms that the Ce^{3+} ion is well protected by the encapsulating tripodal ligands against quenching by water and ethanol molecules, thus avoiding nonradiative transitions that consequently decrease the luminescence quantum yield. However, according to the solution equilibrium, dissociation of the complexes will become more significant as the concentration is lowered, leading to quenching of the luminescence in extremely dilute solutions (< 10 ppm).

The electroluminescent (EL) properties of the complexes were investigated by incorporating complex **2** as the emitter in LED devices. Two devices (A and B) were fabricated on indium tin oxide (ITO) using 1,4-bis[*N*-(1-naphthyl)-*N'*-phenylamino]biphenyl (NPB) and tris(8-quinolinolato)aluminum (AlQ3) as the hole-transport and electron-transport materials, respectively, and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN), doped with **2**, as the emitting layer to give the structure ITO/NPB(60 nm)/MADN:sample **2**(x%) (40 nm)/ALQ_3(20 nm)/LiF (1 nm)/Al(100 nm) (device A $x=5\%$, device B $x=7\%$). Figure 5 shows the detailed EL performances of the devices with voltages, luminescence yields, as well as power efficiencies measured at 20 mA cm^{-2}. The EL efficiency was significantly influenced by the concentration of the complex used to dope the MADN layer (Figure 5 a). Device A with 5% dopant gave a reasonable EL spectrum (Figure 5 c), providing an EL efficiency of 1.5 cd A^{-1} and 0.52 Lm/W at 9.1 V with CIE $x,y = 0.18, 0.21$ (Commission internationale de l'éclairage coordinates). This indicates that the carrier recombination zone is well confined in the doped layer and the complex emits efficiently.[6] However, when the dopant concentration increased to 7% (device B), the efficiency of the device dropped quickly compared with that of device A. This phenomenon suggests considerable self-quenching of the dopant at higher concentrations upon excitation. The higher efficiency achieved by device A may be attributed to the observation that the same current density is obtained at relatively lower voltage in device A than in device B as shown in Figure 5 b. From Figure 5 c, we can see that device B, compared with device A, displays a wider EL band that is red-shifted, indicative of contaminated AlQ_3 emission in device B.[6a,c]

These preliminary results demonstrate the potential of organic Ce^{3+} complexes for use as light-emitting materials in LEDs. Although narrow emissions are not usually characteristic of Ce^{3+} complexes, although they are associated with Eu^{3+} and Tb^{3+} complexes,[6] the highly efficient Ce^{3+} 5d→4f emission has the advantages of easy tunability and regulation as a result of the sensitivity of the 5d orbitals to the ligand crystal field.[7–9] Compared to the vigorously studied inorganic system,[7,12] such advantages can be fully realized thanks to the versatility of the organic ligands, which can be judiciously designed and functionalized. In addition, the possibility of energy transfer to the metal center following ligand-based excitation may endow more options for regulating the emission.

In summary, three Ce^{3+} complexes with tripodal encapsulating ligands were prepared for the study of their photoluminescence and electroluminescence properties. All complexes are highly blue-luminescent in both the solid state and solution, displaying efficient metal- and ligand-based excitation, energy transfer, and characteristic Ce^{3+} emission. Functionalization of the ligands through N substitution with different alkyl groups leads to a noticeable influence on the emission wavelength and intensity. The electroluminescence study confirms the possibility of using Ce^{3+} complexes as light-emitting materials in LEDs, implying a great potential for the design and syntheses of cerium complexes aiming at tunable light-emitters.

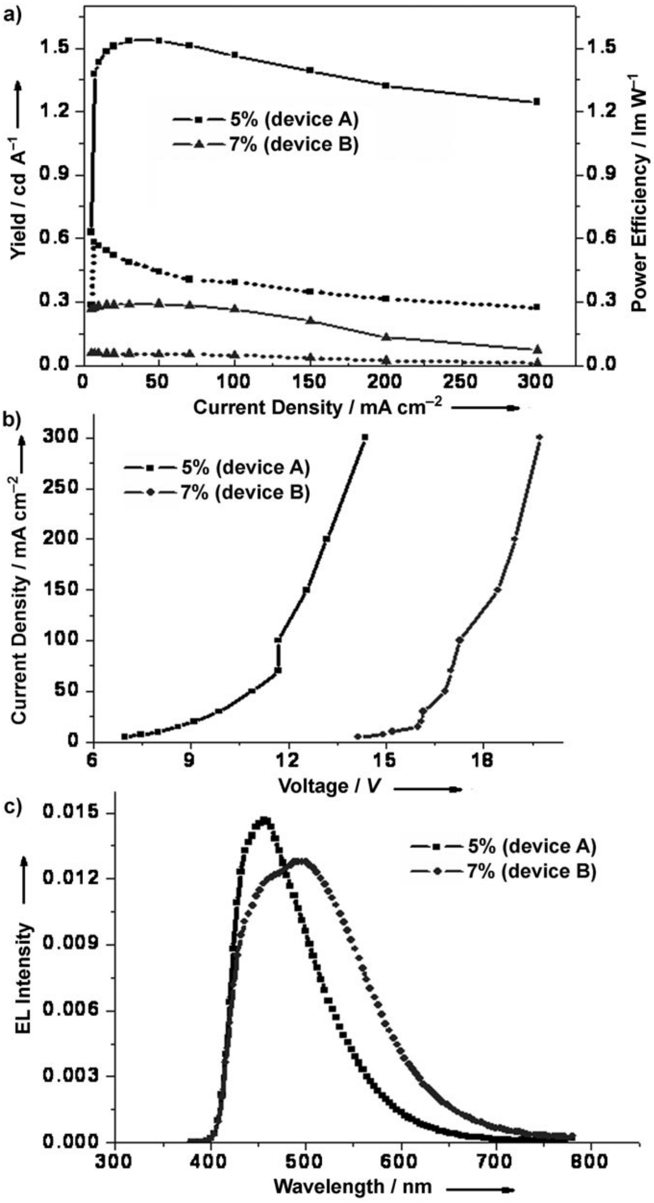

Figure 5. Electroluminescence (EL) performances of device A (5% complex **2**) and device B (7% complex **2**). a) Plots of luminescence yield (solid lines) and power efficiency (dotted lines), respectively, versus current density. b) Current density versus voltage curves. c) EL spectra of devices A and B.

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