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Highly Luminescent Homoleptic Europium Chelates

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The need for efficient and photostable lanthanide luminescent materials is dramatically increasing, in particular with respect to their growing application in lighting devices and biosciences. To this end, we have developed a facile synthesis of benzimidazole-substituted pyridine-2-carboxylic acids that efficiently sensitize europium luminescence in homoleptic neutral nine-coordinate complexes with overall quantum yields of 56−61% and lifetimes of 2.1−2.6 ms in the solid state at ambient conditions. The complexes reported here are potential synthons for the design of a variety of luminescent materials.

Practical applications for europium luminescence have burgeoned since the first phosphor material with bright-red emission, Y_2O_3:Eu with a quantum yield of 95%,[1] was discovered by Urbain at the beginning of the 20th century. Although fluorescent lamps, displays (cathode ray tubes, liquid crystal displays, and plasma displays), and X-ray detectors still benefit from its luminescence today, a wealth of other Eu-activated luminescent materials and molecular compounds have been synthesized and tested.[2] Their applications range from electroluminescent devices[3] to security inks, plastic films for agriculture, analytical probes, as well as bioprobes for immunoassays[4] or for imaging live cells in the context of cancer diagnostics and follow-up of corresponding therapy.[5]

Owing to the small dipole strengths of the f−f transitions,[6] a sensitization process of the metal-ion luminescence has to be designed, which requires energy harvesting by its environment followed by efficient energy transfer onto the metal-ion excited states. The entire process is intricate because diverse mechanisms and several ligand and metal-ion states are involved.[7] However, a preferred energy migration path often goes through a long-lived ligand triplet state (T_1), so that chemists frequently try to optimize the energy gap between T_1 and the emissive level of a lanthanide ion to obtain high sensitization efficiencies, η_{sens}, and quantum yields:[8,9]

$$Q^{\mathrm{Ln}}{}_{\mathrm{L}} = \eta_{\mathrm{sens}} \times Q^{\mathrm{Ln}}{}_{\mathrm{Ln}} = \eta_{\mathrm{sens}} \times (\tau_{\mathrm{obs}}/\tau_{\mathrm{rad}}) \qquad (1)$$

in which $Q_{\mathrm{L}}^{\mathrm{Ln}}$ and $Q_{\mathrm{Ln}}^{\mathrm{Ln}}$ are the overall and intrinsic quantum yields of the lanthanide luminescence obtained upon ligand excitation and direct f−f excitation, respectively.[2] Optimization of the intrinsic quantum yield is achieved by the design of a tight, rigid, and fully coordinative environment around the metal ion, devoid of high-energy vibrations. Despite extensive attempts aimed at producing luminescent Eu molecular compounds, reported quantum yields above 40% are rare.[9] Several ligand classes have been tested for this purpose, with the most studied ones being β-diketonates,[7,10,11] with $Q_{\mathrm{L}}^{\mathrm{Eu}}$ reaching 85% for [europium tris(thenoyltrifluoroacetonate)bis(dibenzylsulfoxide)].[7] However, β-diketonates are monoanionic bidentate ligands and cannot provide neutral homoleptic lanthanide complexes with a saturated coordination sphere (with common coordination numbers for $\mathrm{Ln^{III}}$ being 8−9). In addition, they undergo photobleaching under UV light,[10] and thus the search for other ligands is ongoing[12] with a recent example of $Q_{\mathrm{L}}^{\mathrm{Eu}}$ = 60% for [europium tris(4-phenyl-6-(2′-pyridyl)pyridine-2-carboxylate)].[13]

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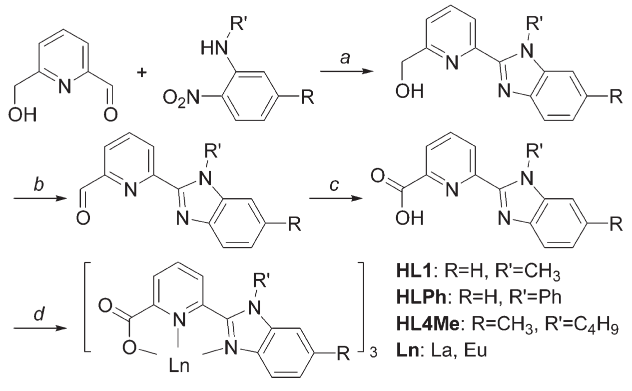
Scheme 1. Synthesis and Structures of Ligands and Complexes[a]



[a] Reaction conditions: (a) $Na_2S_2O_4$, 2-methoxyethanol/H_2O, under N_2, 100 °C, 53−72%; (b) SeO_2, dioxane, under N_2, 110 °C, 80−90%; (c) H_2O_2, formic acid, under air, 0 °C, 76−88%; (d) $LnCl_3 \cdot nH_2O$, NaOH, ethanol/H_2O, under air, heating, 55−75%.

Here, we describe highly luminescent homoleptic europium chelates with benzimidazole-substituted pyridine-2-carboxylic acids[14] (Scheme 1). The wrapping of three of these tridentate ligands around the Ln^{III} ion provides a saturated N_6O_3 nine-coordination environment,[15] while the benzimidazole−pyridine group acts as an efficient antenna for sensitizing Ln^{III} luminescence.[16]

The ligands were prepared by a new facile synthesis starting from 2-pyridinecarboxaldehyde-6-methanol and a substituted *o*-nitroaniline (see Scheme 1 and the Supporting Information). The initial formation of a benzimidazole ring[17] was followed by the stepwise oxidation[18] of a pyridine-2-methanol moiety to the corresponding carboxylic acid via carboxaldehyde.

The ligands react with lanthanide chlorides in a 3:1 molar ratio in ethanol/H_2O in the presence of NaOH as a base to yield neutral complexes $[Ln(ligand)_3] \cdot nH_2O$ (n = 1−3; Ln = La, Eu) as white solids that are sparingly soluble in dimethyl sulfoxide (DMSO; Supporting Information). X-ray-quality crystals of [Eu(**LPh**)$_3$] could be obtained (Figure 1). Europium is nine-coordinated by three ligands; its coordination polyhedron can be described as a distorted tricapped trigonal prism (TCTP), with N(pyridine) atoms in capping positions (these atoms are in-plane with Eu^{III}). Each of the three ligands spans both triangular faces of TCTP via a capping position. However, the complex lacks C_3 symmetry because the ligands are arranged in an up−up−down fashion around the metal. The bond lengths are in the range Eu−O = 2.345−2.422 Å, Eu−N(py) = 2.563−2.597 Å, and Eu−N(benzimidazole) = 2.594−2.745 Å, with N(benzimidazole) being the most weakly coordinated of the donor atoms (Table S2 in the Supporting Information). Within the ligand, the dihedral angles between pyridine and benzimidazole are in the range 12−23°, while phenyl rings are nearly orthogonal to the benzimidazole, with angles of 63−68°. The shortest Eu−Eu distance in the structure is 9.036 Å, which is likely to prevent interaction between metal centers. We note that *N*-aryl-substituted benzimidazole−pyridines have been rarely used in coordination chemistry,[19] and [Eu(**LPh**)$_3$] is the first example of a lanthanide complex with these types of ligands.

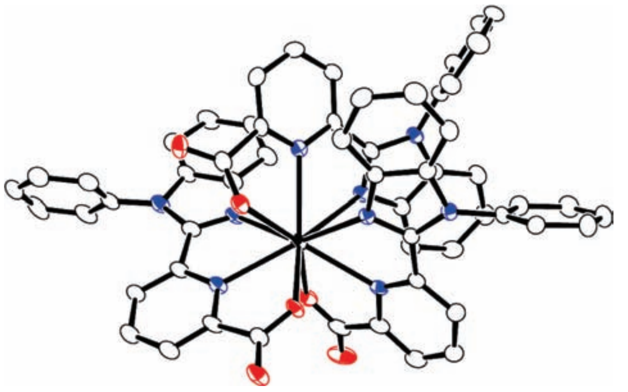


Figure 1. Molecular structure of [Eu(**LPh**)$_3$] viewed down the triangular face of the TCTP (50% probability ellipsoids; H atoms and cocrystallized solvent molecules are omitted). Heteroatoms: O, red; N, blue; Eu, black.

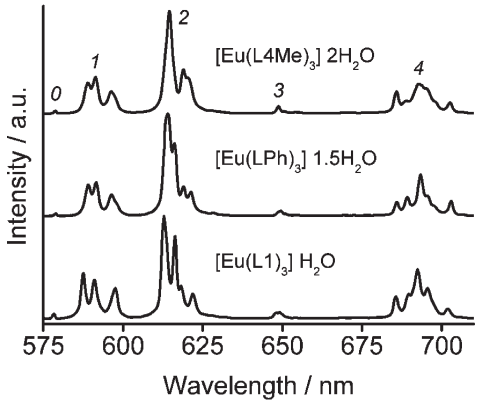


Figure 2. Corrected and normalized luminescence spectra of Eu complexes at room temperature (emission slit = 0.2 nm), displaying the $^5D_0 \rightarrow {}^7F_J$, J = 0−4, transitions; λ_{exc} = 320 nm.

In a DMSO solution, the ligands display broad absorption bands with maxima at 314 (**HL1**), 304 (**HLPh**), and 321 nm (**HL4Me**) and ε_{max} in the range $(1.8-2.4) \times 10^4$ M^{-1} cm^{-1}. Upon complex formation, this absorption band is red-shifted by 1−6 nm for **L1**$^-$ and **L4Me**$^-$ and by 14−18 nm for **LPh**$^-$ chelates (Figures S4−S6 and Table S3 in the Supporting Information). Because of the presence of three ligands around the metal, the molar absorption coefficient is substantial (Table S3 in the Supporting Information), a favorable situation for the pumping of electromagnetic energy into these complexes. At 77 K, solid-state samples of the La^{III} complexes emit a broad phosphorescence band with zero phonon transition at 20160 (**L1**$^-$), 19840 (**LPh**$^-$), and 20410 cm^{-1} (**L4Me**$^-$) (Figure S7 and Table S4 in the Supporting Information). Hence, the triplet-state energy in the new ligands is ideally suited for sensitization of the Eu^{III} luminescence.

Indeed, excitation of solid-state samples of the corresponding Eu^{III} complexes into the ligand results in emission spectra entirely dominated by the Eu($^5D_0 \rightarrow {}^7F_J$) transitions (Figure 2). Excitation spectra display ligand-centered bands, thus confirming the ligand-to-metal energy transfer (Figure S8 in the Supporting Information). In the emission spectra, a single,

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Table 1. Photophysical Parameters of Eu^{III} Complexes[a]

	τ_{obs}/ms	Q_L^{Eu}/%	τ_{rad}/ms	Q_{Eu}^{Eu}/%	η_{sens}/%
1[b]	2.47(3)	61(2)	4.7	53	≈100
2[b]	2.14(1)	58(1)	4.2	51	≈100
3[b]	2.58(1)	56(2)	4.4	58	96

[a] In the solid state at room temperature; λ_{exc} = 320 nm. Standard deviations (2σ) between parentheses; estimated relative errors = τ_{obs}, ±2%; Q_L^{Eu}, ±5%; τ_{rad}, ±10%; Q_{Eu}^{Eu}, ±12%; η_{sens}, ±17%. [b] Complexes: **1** = [Eu(**L1**)$_3$]·H_2O, **2** = [Eu(**LPh**)$_3$]·1.5H_2O, **3** = [Eu(**L4Me**)$_3$]·2H_2O.

weak $^5D_0 \rightarrow {}^7F_0$ transition is observed, while the $^5D_0 \rightarrow {}^7F_1$ transition is split into three components. The pattern of the $^7F_1$ crystal-field splitting in the case of [Eu(**LPh**)$_3$]·1.5H_2O with two closely spaced components at 305 and 375 cm^{-1} and a third at 510 cm^{-1} is characteristic of the pseudotrigonal symmetry, in line with the crystal structure analysis (a similar situation occurs for the other two complexes). The hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition dominates the overall emission spectrum (Table S5 in the Supporting Information).

Absolute quantum yields have been determined with an integration sphere.[20] They are reported in the Table 1, together with the Eu($^5D_0$) lifetimes and other relevant photophysical parameters. As is expected from the similar energies of the triplet states of the ligands, these quantum yields are comparable but, most importantly, they are high, reaching 56−61%. The luminescence decays are single-exponential functions pointing to the presence of only one emissive center in the solid samples. The corresponding lifetimes are long, 2.1−2.6 ms, suggesting the absence of water molecules in the inner coordination sphere of Eu. The radiative lifetime can be estimated with the following equation:[21]

$$1/\tau_{rad} = A_{MD,0} \times n^3 \times (I_{tot}/I_{MD}) \qquad (2)$$

where $A_{MD,0}$ is the emission probability of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ (14.65 s^{-1}), n is the refractive index (assumed to be 1.5 for solid-state coordination compounds), and I_{tot} and I_{MD} are the corrected, integrated total emission intensity and the intensity of the magnetic dipole transition, respectively. The calculated radiative lifetimes are in the range 4.2−4.7 ms [compared to 6.2−6.9 ms for similar, but more symmetric, N_6O_3 environments (C_3), in dinuclear helicates[16]]. The calculated intrinsic quantum yields, equal to τ_{obs}/τ_{rad}, are in the range 51−58% and are diagnostic of an environment with minimized nonradiative deactivation. Finally, the sensitization efficiency (i.e., the efficacy with which energy is transferred from the ligand onto the Eu^{III} ion) is estimated from eq 1 to be quantitative. It appears that the photophysical parameters of Eu complexes are not sensitive to the *N*-alkyl or *N*-aryl substitution at the benzimidazole ring, providing a convenient attachment point for functional groups.

In summary, monoanionic benzimidazole-substituted pyridine-2-carboxylates are ideal tridentate chelating units for the design of highly luminescent neutral homoleptic Eu complexes. The facile synthesis of the ligands (Scheme 1) opens the way for incorporation of their complexes in luminescent and electroluminescent polymers,[22] nanoparticles,[23] and liquid crystals.[24] Presently, we are exploring these possibilities, as well as the influence of substituents on the sensitization ability of this class of ligands.

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Supporting Information Available: Synthesis and characterization of ligands and complexes; crystallographic data; CIF, CCDC 731483; absorption, emission, and excitation spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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