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 synths 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, Y2O3:Eu, with a quantum yield of 95%, 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. Their applications range from electroluminescent devices to security inks, plastic films for agriculture, analytical probes, as well as bioprobes for immunoassays or for imaging live cells in the context of cancer diagnostics and follow-up of corresponding therapies.

Owing to the small dipole strengths of the f–f transitions, 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. 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 sensitzation efficiencies, $\eta_{\text{sens}}$, and quantum yields $Q_{\text{Ln}}$ in which $Q_{\text{Ln}}$ and $Q_{\text{Ln}}^\text{L}$ are the overall and intrinsic quantum yields of the lanthanide luminescence obtained upon ligand excitation and direct f–f excitation, respectively. 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. Several ligand classes have been tested for this purpose, with the most studied ones being $\beta$-diketones, with $Q_{\text{Ln}}^\text{L}$ reaching 85% for [europium tris(thenoyltrifluoroacetone)(bis(dibenzyl-sulfoxide))]. However, $\beta$-diketones are monoanionic bidentate ligands and cannot provide neutral homoleptic lanthanide complexes with a saturated coordination sphere (with common coordination numbers for Ln being 8–9). In addition, they undergo photobleaching under UV light, and thus the search for other ligands is ongoing with a recent example of $Q_{\text{Ln}}^\text{L} = 60\%$ for [europium tris(4-phenyl-6-[2'-pyridyl]pyridine-2-carboxylate)]

$Q_{\text{Ln}}^\text{L} = \eta_{\text{sens}} \times Q_{\text{Ln}}^\text{L} = \eta_{\text{sens}} \times (\tau_{\text{obs}}/\tau_{\text{rad}})$ (1)

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(3) de Bettencourt-Dias, A. Dalton Trans. 2007, 7229.
angles between pyridine and benzimidazole are in the range
Supporting Information). Within the ligand, the dihedral
NaOH, ethanol/H2O, under air, heating, 55°C.

Here, we describe highly luminescent homoleptic europium chelates with benzimidazole-substituted pyridine-2-carboxylic acids14 (Scheme 1). The wrapping of three of these tridentate ligands around the LnIII ion provides a saturated N2O3 nine-coordination environment,15 while the benzimidazole-pyridine group acts as an efficient antenna for sensitizing LnIII 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 ring17 was followed by the stepwise oxidation18 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/H2O in the presence of NaOH as a base to yield neutral complexes [Ln(ligand)3]–nH2O (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. However, the complex lacks C3 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.

In a DMSO solution, the ligands display broad absorption bands with maxima at 314 (HL1), 304 (HLPh), and 321 nm (HL4Me) and εmax in the range (1.8–2.4) × 104 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 LPht-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 LaIII complexes emit a broad phosphorescence band with zero phonon transition at 20160 (L1−), 19840 (LPht−), 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 EuIII luminescence.

Indeed, excitation of solid-state samples of the corresponding EuIII complexes into the ligand results in emission spectra entirely dominated by the Eu(5D0−7FJ) 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,

![Figure 1. Molecular structure of [Eu(LPh)3] viewed down the triangular face of the TCTP (50% probability ellipsoids; H atoms and co-crystallized solvent molecules are omitted). Heteroatoms: O, red; N, blue; Eu, black.](image)

![Figure 2. Corrected and normalized luminescence spectra of Eu complexes at room temperature (emission slit = 0.2 nm), displaying the 5D0−7FJ transitions; λexc = 320 nm.](image)
Table 1. Photophysical Parameters of EuIII Complexes*  

<table>
<thead>
<tr>
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<th>τ_{obs}/ms</th>
<th>Φ_{L}^{rad}/%</th>
<th>τ_{rad}/ms</th>
<th>Φ_{L}^{rad}/%</th>
<th>η_{sens}/%</th>
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<tr>
<td>1^b</td>
<td>2.47(3)</td>
<td>61(2)</td>
<td>4.7</td>
<td>53</td>
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</tr>
<tr>
<td>2^b</td>
<td>2.14(1)</td>
<td>58(1)</td>
<td>4.2</td>
<td>51</td>
<td>≈100</td>
</tr>
<tr>
<td>3^b</td>
<td>2.58(1)</td>
<td>56(2)</td>
<td>4.4</td>
<td>58</td>
<td>96</td>
</tr>
</tbody>
</table>

*a In the solid state at room temperature; λ_{exc} = 320 nm. Standard deviations (20) between parentheses; estimated relative errors = τ_{obs}±2%; Φ_{L}^{rad}±5%; τ_{rad}±10%; Φ_{L}^{rad}±12%; η_{sens}±17%. ^b Complexes: 1 = [Eu(L)3]·H2O, 2 = [Eu(LPh)3]·1.5H2O, 3 = [Eu(L4Me)3]·2H2O.

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 $^3\!D_0 \to ^7\!F_2$ transition dominates the overall emission spectrum (Table S5 in the Supporting Information).

Absolute quantum yields have been determined with an integration sphere. They are reported in the Table 1, together with the Eu($^3\!D_0$) 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

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

(2)

where $A_{MD,0}$ is the emission probability of the magnetic dipole transition $^3\!D_0 \to ^7\!F_1$ (14.65 s$^{-1}$), $n$ is the refractive index (assumed to be 1.5 for solid-state coordination).