Rational Design, Exploratory Synthesis and Lanthanide Emission Efficiency Comparison of Lanthanide(III)-cored Complexes Based on Naphthalene Acid Ligands for Efficient Energy Transfer Pathways

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The development of luminescent lanthanide complexes has been attracted considerable attention because of a wide variety of applications, such as planar waveguide amplifiers, light-emitting diodes, and MRI contrast agent. The complexation of luminescent Ln³⁺ ion with organic ligand can lead to a system capable of overcoming intrinsically low molar absorption coefficients (typically 1-10 M⁻¹ cm⁻¹) of Ln³⁺ ions and effectively transferring excited energy from the light-absorbing ligand to central Ln³⁺ ion. This sensitization process is much more effective than the direct excitation of Ln³⁺ ions. To date, it is well-believed that only energy transfer from the triplet state of luminescent ligands to Ln³⁺ ion is the most dominant mechanism. Therefore, most researches toward lanthanide ion sensitizers have been focused on developing the luminescent lanthanide ions with a triplet state matching the receiving lanthanide ion energy levels. Interestingly, however, several reports mentioned the energy transfer from the excited singlet state to Ln³⁺ ion. Very recently, we also reported all possible ET pathways using Pt-porphyrin (ETt) and anthracene ligand (ETs), and additionally, demonstrated the unusual ET pathway through the intramolecular charge transfer (ICT) state of the naphthalene ligand to Ln³⁺ ion (ETc) for the first time (see Scheme 1). For finding out the most dominant ET pathway toward the highly efficient Ln³⁺ emission, the Ln³⁺ emission efficiency comparison for all three ET pathways should necessarily be explored under similar ET conditions.

Here, to investigate all three possible ET pathways and compare the lanthanide emission efficiency for the various ET pathways in Er(III)-cored complexes, we have rationally designed and synthesized the structurally and UV-absorbingly similar ligands of 1-naphthoic acid (NA-0), 4-bromo-4-naphthalen-1-yl-benzoic acid (NA-1), 4-naphthalen-1-yl-benzoic acid (NA-2) and 4-phenyl-naphthalene-1-carboxylic acid ligand (NA-3) and their stable 9-coordinated Ln(III) complexes (Scheme 2) (see Supporting Information).

The nature of excited states of all four ligands was investigated by measuring the absorption and fluorescence spectra in various solvents (see Figure S4). In the previous report, we reported the large Stokes’ shifted emission of NA-2 in polar solvent which is due to the formation of an ICT state in the excited state. We could not observe the phosphorescence even in the Gd(III) complex based on NA-2. These results indicate that the ISC process is not dominant in NA-2 and the energy transfer takes places from the ICT state to Ln³⁺ ion in the Er(III) complex based on NA-2.

On the other hand, our photophysical results suggest that the Ln(III) complexes based on NA-0 and NA-1 ligands have the ET mechanism via the excited triplet state (see Figure S5-S7). Bromine-substituted NA-1 ligand, as compared with NA-0 ligand, increases the rate of intersystem crossing (ISC) and decreases the fluorescence quantum yield, due to the internal heavy atom effect. The luminescence spectra of Gd³⁺-[NA-0](tpy) and Gd³⁺-[NA-1](tpy) in deoxygenated m-THF at 77 K exhibit a strong phosphorescence band in the green region (see Figure S5). The phosphorescence lifetime was reduced from 50 μs for Gd³⁺-[NA-0](tpy) to 20 μs for Er³⁺-[NA-1](tpy) (see Figure S6). These results provide the direct evidence of an energy transfer from the triplet state of the ligand to the Er³⁺ ion. It
Table 1. Photophysical properties of naphthalene-typed ligands and their Er(III) complexes

<table>
<thead>
<tr>
<th>UV (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; of ligand</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; of Er&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Lifetime (µs)</th>
<th>φ&lt;sup&gt;f&lt;/sup&gt;</th>
<th>φ&lt;sup&gt;d&lt;/sup&gt;</th>
<th>φ&lt;sup&gt;4f&lt;/sup&gt;</th>
<th>φ&lt;sup&gt;4f&lt;/sup&gt; (×10&lt;sup&gt;-4&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-0</a></td>
<td>303</td>
<td>–</td>
<td>20</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-0</a></td>
<td>303</td>
<td>0.034 (0.11)</td>
<td>ND</td>
<td>2.13 (1.91)</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-1</a></td>
<td>305</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-1</a></td>
<td>305</td>
<td>0.0037 (0.0038)</td>
<td>20</td>
<td>2.22 (1.71)</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-2</a></td>
<td>298</td>
<td>–</td>
<td>ND</td>
<td>ND (1.12)</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;-<a href="tpy">Na-3</a></td>
<td>314</td>
<td>0.056 (0.15)</td>
<td>ND</td>
<td>1.97 (1.38)</td>
<td>2.5</td>
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*2-aminopyridine as a standard with φ = 0.60 in 1 N H<sub>2</sub>SO<sub>4</sub> (quantum yield of ligand in parentheses). λ<sub>em</sub> [nm] = 520 nm in degassed chlorobenzene. λ<sub>em</sub> [nm] = 1530 nm (lifetime of Er ion in solid state given in parentheses). Calculated from φ<sub>4f</sub> = φ<sub>α</sub>φ<sub>τ</sub>, where the radiative lifetimes were taken from the literature, with typical lifetimes of 8 ms for Er<sup>3+</sup> ion. ND: Not detected.

Figure 1. Emission spectra of the Er<sup>3+</sup>-[Na-X](tpy) in degassed chlorobenzene (a, λ<sub>em</sub> = 300 nm) and solid state (b, λ<sub>em</sub> = 350 nm). The NIR emission intensity has been corrected by the sample absorbance.

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Supporting Information Available: Experimental procedures for the synthesis of the ligands and their complexes and spectroscopic data (PDF). This material is available via http://www.kscnet.or.kr/kbcs.

References and Notes