The First Inert and Photostable Encapsulated Lanthanide(III) Complexes Based on Dendritic 9,10-Diphenylanthracene Ligands: Synthesis, Strong Near-Infrared Emission Enhancement, and Photophysical Studies**

By Nam Seob Baek, Yong Hee Kim, Soo-Gyun Roh, Bong Kyu Kwak, and Hwan Kyu Kim*

A series of inert and photostable encapsulated lanthanide(III) complexes—based on dendritic anthracene ligands—is shown for the first time to exhibit strong near-IR emission bands via efficient energy transfer from the excited states of the peripheral antenna to the Ln3+ ions (Er3+, Yb3+, and Nd3+). A significant decrease in the fluorescence of the anthracene ligand is accompanied by a strong increase in the near-IR emission of the Ln3+ ions. The near-IR emission intensities of Ln3+ ions in the encapsulated Ln3+-dendrimer complexes are dramatically enhanced on increasing the generation number (n) of dendrons, owing to site-isolation and light-harvesting effects. Furthermore, a first attempt is made to distinguish between the site-isolation and light-harvesting effects in the present complexes. Photophysical studies indicate the sensitization of Ln3+ luminescence by energy transfer through the excited singlet state of the anthracene ligands, and the energy-transfer efficiency between the dendritic anthracene ligands and the Ln3+ ion is evaluated to be in the range of 90 to 97%. Their energy-transfer efficiency is in good agreement with the result that the biexponential decays contain a radiative decay of anthracene units (< ca. 10%) and an energy-transfer component (> ca. 90%) from the excited state of anthracene ligands to the Ln3+ ions. Time-resolved luminescence spectra show monoeponential decays with a lifetime of 2 μs for the Er3+ ion 11 μs for the Yb3+ ion and 0.7 μs for the Nd3+ ion in thin films, and calculated intrinsic quantum yields of the Ln3+ ions are in the range of ca. 0.025 to 0.55%.

1. Introduction

Recently, luminescent lanthanide complexes have attracted much attention because of their academic interest and potential utility in a wide variety of photonic applications, such as planar waveguide amplifiers, plastic lasers, light-emitting diodes, and luminescent probes.[1–5] Lanthanide (Ln3+) ions have much attention because of their academic interest and potential utility in a wide variety of photonic applications, such as planar waveguide amplifiers, plastic lasers, light-emitting diodes, and luminescent probes.[1–5] Lanthanide (Ln3+) ions have an incompletely filled f-subshell, in which the f-electrons are shielded by the outer 5s and 5p electrons. These 4f electrons are slightly perturbed by the effects of lattice phonons and static strain fields in the coordination environment of the ions, leading to sharp spectral, linelike emission bands. Also, the 4f0–4f8 electronic transitions are forbidden because the energy levels of 4f0 electron shells in lanthanide ions have an equal parity. Thus, the absorption and emission cross section of lanthanide ions is small in absorption and photoluminescence (PL), whereas the luminescent lifetime is relatively long. To overcome these shortcomings, recently, luminescent ligands have been used to excite Ln3+ ions via an energy transfer from the luminescent ligands to the Ln3+ ions. In most cases,[2–17] the luminescent Ln3+ ions are usually coordinated to the organic luminescent ligands, which act as sensitizers or antenna chromophores, efficiently absorbing and transferring the energy of light to excite the Ln3+ ions via an energy-transfer process.[6,7] This sensitization process is much more effective than the direct excitation of Ln3+ ions, since the absorption coefficients of organic chromophores are many orders of magnitude larger than the intrinsically low molar-absorption coefficients (typically 1–10 m<sup>−1</sup> cm<sup>−1</sup>) of Ln3+ ions.

Very recently, several research groups have focused on developing efficient artificial light-harvesting lanthanide complexes, in which the use of dendrimers as the light-harvesting systems has been widely demonstrated.[8–16] The encapsulation of luminescent Ln3+ ions in luminescent dendrimers can lead to a system capable of shielding a central Ln3+ ion from a non-radiative environment, and efficiently transferring excited energy from the peripheral chromophores to the focal point of the dendrimer. For example, Fréchet and co-workers and Kawa and Takahagi have reported the site-isolation and antenna effects on the luminescent properties of spherical lanthanide(III)-cored dendrimer complexes based on Eu3+, Tb3+, or Er3+ ions.[8,11,16] To achieve the site isolation of a Ln3+ ion, the ion was surrounded by a dendritic shell of aryl-ether-type dendrons. They found that the enhanced luminescent intensities

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2. Results and Discussion

2.1. Chemical Structures and Synthesis of Encapsulated Lanthanide(III) Complexes Based on Dendritic 9,10-Diphenylanthracene Ligands

We demonstrated that the encapsulated Ln\textsuperscript{3+} complexes exhibit strong near-IR emission bands via efficient energy transfer from the excited states of the peripheral antenna to the Ln\textsuperscript{3+} ions (Er\textsuperscript{3+}, Nd\textsuperscript{3+}, and Yb\textsuperscript{3+} ions). To enhance the sensitization process in the Ln\textsuperscript{3+} complexes, we chose 9,10-diphenylanthracene (9,10-DPA or di-meso-substituted anthracene) as the luminescent ligand, because the quantum yield of 9,10-DPA is close to unity in solution and in the crystalline state.\cite{19} Fluorescence quantum yields of most organic chromophores are only observed in a dilute solution because of concentration quenching. In the case of 9,10-DPA, the dihedral angle between the phenyl group and the anthracene unit is estimated as 68°, owing to high steric hindrance between the phenyl group and the anthracene (An) unit (see Scheme 1). This hindrance causes there to be no effect of concentration on the quantum yield of the ligand’s derivatives. In line with this, the 9,10-DPA derivatives, which are in close proximity to the lanthanide ion, were synthesized to provide sufficient coordination sites, according to the novel synthetic methods developed previously by our group.\cite{18,20,21}

In our previous reports, some of the key parameters governing the enhancement of the near-IR emission in luminescent lanthanide complexes are i) the type of luminescent lanthanide complex, such as a directly chelated complex or an indirectly chelated complex, and ii) the coordination number of lanthanide ions with the complexed ligands. In case (i), the directly luminescent Ln\textsuperscript{3+} chelated complexes have much a higher PL efficiency than the indirectly luminescent Ln\textsuperscript{3+} chelated complexes,
owing to the much higher intersystem crossing (ISC) efficiency in the directly chelated complex.\[18a\] Directly chelated complexes possess a luminescent group directly coordinated to the Ln\(^{3+}\) ions. Indirectly chelated complexes have a luminescent group indirectly coordinated to the Ln\(^{3+}\) ions. As a result, the indirectly chelated complex does not have an external heavy-atom effect induced by the heavy and paramagnetic lanthanide ion. In case (ii), highly coordinated lanthanide-cored complexes (at least eight to nine coordinate) have much higher PL efficiencies than unsaturated six-coordinated complexes.\[20a\] Therefore, the 2,2′:6′:2″-terpyridine (terpy) unit used in this paper may be expected to effectively block luminescent deactivating molecules, leading to the formation of nine-coordinate, directly chelated Ln\(^{3+}\) complexes. The chemical structures of dendritic anthracene ligands and their stable, inert, and direct encapsulated lanthanide(III) complexes are shown in Scheme 2.

The aryl-ether-dendron-functionalized anthracene ligands ([G\(_n\)-An]-CO\(_2\)H; G: dendrimer generation) were synthesized in five steps, starting from 9,10-dibromoanthracene and [G\(_n\)]-Br.\[22\] In the Fourier transform IR (FTIR) spectra, the C=O stretching band of the carboxylic acid group of all the dendritic ligands is approximately 1690 cm\(^{-1}\). In comparison with these ligands, all the FTIR spectra of the Ln\(^{3+}\)-cored dendrimer complexes are very similar, with two characteristic bands of asymmetric (ca. 1600 cm\(^{-1}\)) and symmetric (ca. 1400 cm\(^{-1}\)) stretching vibration modes of the carboxylate group. This indicates that the carboxylic acid group was converted into a carboxylate anion as a result of the formation of the stable Ln\(^{3+}\)-cored complexes.\[21\] Unfortunately, the paramagnetic properties of the lanthanide ion do not permit NMR studies of Ln\(^{3+}\)-cored dendrimer complexes. Elemental analysis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and electrospray ionization (ESI) MS confirmed that the terpyridine units were coordinated directly to Ln\(^{3+}\) ions to form nine-coordinated, direct Ln\(^{3+}\)-cored complexes (see Supporting Information).

### 2.2. Absorption and Luminescence Properties of the Dendritic Anthracene Ligands and Their Encapsulated Ln\(^{3+}\) Complexes

UV-vis absorption and PL spectra of a series of dendritic anthracene ligands ([G\(_n\)-An]-CO\(_2\)H) are shown in Figure 1. The absorbance (or molar-extinction coefficient) of the aryl-ether-type dendrons in the dendritic anthracene ligands—at 285 nm, where the aryl-ether dendrons and the anthracene units absorb simultaneously—increased with the G\(_n\) of the dendrons. This phenomenon is in excellent agreement with previous literature results, and is due to the increasing number of dimethoxybenzene units in the dendrons.\[10\] The introduction of the aryl-ether dendron into di-meso-substituted anthracene also does not influence the restricted rotation barrier between the adjacent phenyl-ring and anthracene-ring hydrogen atoms (see Scheme 1). This restricted rotation barrier results in the di-
Standard. As summarized in Table 1, all dendritic anthracene ligands were determined by comparison with 9,10-DPA as a standard. The absorption spectra of all dendritic ligands, [(Gn-An)-CO2H], exhibited no red-shift in the ligand absorption bands on increasing n from 0 to 3, indicating that there is no \( \pi \)-electron interaction between the aryl-ether dendron and the anthracene unit. The fluorescence of the aryl-ether dendrons—at a maximum wavelength of 345 nm—was totally quenched when they were excited at 285 nm, in the dendron absorption band, but the significant decrease in the fluorescence of the aryl-ether dendron was accompanied by a strong increase in the fluorescence intensity of the anthracene moiety, in accordance with the growing number of generations in the dendritic anthracene ligands. These results show that a highly efficient energy transfer from the aryl-ether dendron to the anthracene moiety takes place.

Instead of using an excitation wavelength of 285 nm—at which the aryl-ether dendrons mainly absorbed—and in order to evaluate the fluorescent quantum efficiency of the anthracene units in the dendritic anthracene ligands, we selected another excitation wavelength, 357 nm, since only the anthracene unit is excited at 357 nm. Upon excitation of [Gn-An]-CO2H at 357 nm the fluorescence intensity of the 9,10-DPA unit in the dendritic ligands increases with \( n \), as shown in Figure 2.

The fluorescence quantum efficiencies of dendritic anthracene ligands were determined by comparison with 9,10-DPA as a standard.

### Table 1. Relative fluorescence quantum efficiencies of dendritic anthracene ligands and a Fréchet aryl-ether-type dendron of the third generation.

<table>
<thead>
<tr>
<th>[Gn-An]-CO2H</th>
<th>PL efficiency (( \Phi_f ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[G3]-OH [b]</td>
<td>0.02</td>
</tr>
<tr>
<td>[G0-An]-CO2H</td>
<td>0.55</td>
</tr>
<tr>
<td>[G1-An]-CO2H</td>
<td>0.62</td>
</tr>
<tr>
<td>[G2-An]-CO2H</td>
<td>0.77</td>
</tr>
<tr>
<td>[G3-An]-CO2H</td>
<td>0.80</td>
</tr>
</tbody>
</table>

[a] 9,10-DPA as a standard with \( \Phi_f = 0.90 \) in cyclohexane at 298 K [19].
[b] Indole as a standard with \( \Phi_f = 0.32 \) in methanol, 298 K.

Figure 2. PL spectra of a series of dendritic anthracene ligands ([(Gn-An)-CO2H]) in THF \( (2.0 \times 10^{-5} \text{ M}, \lambda_{ex} = 357 \text{ nm}) \) for the photoexcitation of the anthracene units.

Surprisingly, the quantitative quantum yield of a Fréchet aryl-ether dendron is relatively low (\( \Phi_f = 0.02 \)) in [G3]-OH, although Fréchet aryl-ether-type dendrons are widely used as light-harvesting antennae in many light-harvesting systems—widely demonstrated with porphyrins, metalloporphyrins, or azobenzene. We also observed that the excitation spectra of [Gn-An]-CO2H, monitored at 450 nm, are very similar to the absorption spectra of the dendritic ligands, which suggests that the ground state and the excited state of [Gn-An]-CO2H have the same chemical structure.

A series of the Er\(^{3+}\)-cored dendrimer complexes, Er\(^{3+}\)-[Gn-An]\(_n\) (terpy), shows UV-vis absorption behavior that is similar to the corresponding series of [Gn-An]-CO2H ligands, in which the absorbance of the aryl-ether-type dendrons increased with the \( n \) of the dendrons at 285 nm, and the absorbance of the anthracene moiety remained constant at each generation, as shown in Figure 3a. This indicates that there is no \( \pi \)-electron interaction between the aryl-ether dendron and the anthracene unit. All Er\(^{3+}\)-cored dendrimer complexes showed strong near-IR emission bands at 1530 nm, originating from the 4f–4f electronic transition from the first excited state \( ^1I_{13/2} \) to the ground state \( ^1I_{5/2} \) of the partially filled 4f shell. As shown in Figure 3b, a much stronger emission intensity of Er\(^{3+}\)-[G3-An]\(_n\) (terpy) in a thin film was obtained by indirect excitation of the dendritic ligand—3.8 \times 10^4 times or 1.82 \times 10^5 times, for \( \lambda_{ex} = 290 \) or 395 nm, respectively—than by the direct excitation of Er\(^{3+}\) ions (\( \lambda_{ex} = 488 \) nm \( (^2F_{7/2}) \) or 523 nm \( (^2H_{11/2}) \)), which supports the fact that an efficient energy transfer from the dendritic anthracene ligands to the Er\(^{3+}\) ions takes place, associated with site-isolation and light-harvesting effects. As a result, this sensitization process is much more effective than the direct excitation of Er\(^{3+}\) ions. Thus, dendritic anthracene ligands could be promising candidates for antenna chromophores, for efficiently absorbing and transferring the energy of light to excite Er\(^{3+}\) ions via an energy-transfer process.

### 2.3. Distinguishing the Site-Isolation Effect from the Light-Harvesting Effect

To enable a quantitative comparison among the sensitizing efficiencies of the Er\(^{3+}\) complexes, the emission intensities were
corrected for the absorbances of the samples. As depicted in Figure 4a, the near-IR emission intensities of the Er\textsuperscript{3+} complexes were dramatically enhanced with increasing \( n \) of the dendrons, upon excitation at a wavelength of 290 nm, at which wavelength the aryl-ether dendrons mainly absorbed. For example, the emission intensity of Er\textsuperscript{3+}-[G\textsubscript{3}-An\textsubscript{3}](terpy) was quantitatively 70 times stronger than that of Er\textsuperscript{3+}-[G\textsubscript{0}-An\textsubscript{3}](terpy). As \( n \) of the dendrons increases, the number of dimethoxybenzene units in the dendrons increases. As a result, the emission intensities of Er\textsuperscript{3+} ions in the Er\textsuperscript{3+} complexes increase nonlinearly, as compared with the increasing number of dimethoxybenzene units in the dendrons, probably due to the light-harvesting and site-isolation effects. This is confirmed by the fact that the excitation spectra of the Er\textsuperscript{3+} complexes, monitored at 1530 nm, match the absorption spectra of the dendritic anthracene units at 290 nm very well. With our results, it is very important to note that the present Er\textsuperscript{3+}-cored dendrimer systems, consisting of Er\textsuperscript{3+}-cored supramolecular complexes and light-harvesting dendritic photon antennae, must maintain a proper cascade-type energy gradient within the light-harvesting dendrons through the luminescent ligands to the Er\textsuperscript{3+} ion (see Fig. 6), for efficient light harvesting. On the other hand, upon excitation at a wavelength of 357 nm, at which only the anthracene unit absorbs, the near-IR emission intensities of the Er\textsuperscript{3+} complexes were dramatically enhanced with increasing \( n \) of the dendrons (see Fig. 4b).

In order to distinguish the site-isolation effect from the light-harvesting effect (see Scheme 3), we compared the near-IR intensity of Er\textsuperscript{3+} ion upon excitation of anthracene unit at 395 nm or 357 nm with that of Er\textsuperscript{3+} ion upon excitation of aryl-ether dendron unit at 290 nm in Ln\textsuperscript{3+} complexes. The near-IR intensity of the Er\textsuperscript{3+} ion upon excitation of the anthracene unit was 4.8 times stronger than that upon excitation of aryl-ether dendron unit (see Fig. 3b). This clearly indicates that the aryl-ether dendrons are effective at not sensitizing Er\textsuperscript{3+} luminescence through the anthracene units, but are able to shield the Er\textsuperscript{3+} ion—the so-called site-isolation effect. This effect should be dominant over the light-harvesting effect in the series of Er\textsuperscript{3+}-[G\textsubscript{n}-An\textsubscript{3}](terpy) complexes. It is considered to be due to the intrinsically low quantum yield of aryl-ether dendron \((\Phi_{l} = 0.02)\) for exciting anthracene units. In other words, aryl-ether-type dendrons in dendritic ligands do not effectively sensitize the Er\textsuperscript{3+} luminescence through the anthracene units; rather, they provide sufficient site isolation to prevent intermolecular interactions between Er\textsuperscript{3+} ions, which limits the near-IR intensity.[1,8]
In order to confirm that the site-isolation effect dominates the light-harvesting effect in a series of dendritic anthracenes, we compared the PL intensity of the anthracene units upon excitation of anthracene units, with that upon excitation of the aryl-ether dendron units at 290 nm in dendritic anthracenes. The PL intensities of the anthracene units, upon excitation of the anthracene units at 357 nm and 395 nm, were stronger than that upon excitation of aryl-ether dendron unit at 290 nm in dendritic anthracenes by 5.6 and 10 times, respectively (see Fig. S4, Supporting Information). This clearly implies that the aryl-ether dendrons are not sensitizing the anthracene units, but tend to shield them from anthracene–anthracene interactions, leading to a lack of concentration quenching between anthracene units.

Hence, the Er³⁺ ions can be excited via the anthracene moiety more effectively. Thus, new light-harvesting dendrons with relatively high quantum efficiencies and effective energy-transfer efficiencies to the anthracene units can be designed and synthesized, in order to more effectively enhance the photo-physical properties of the encapsulated lanthanide dendritic systems by taking advantage of the light-harvesting effect of artificial light energy gathering and transfer. In these new systems, the accumulating photon energy from the excited state of the anthracene ligands can excite the lanthanide ions as much as possible. Such new dendritic light-harvesting systems are currently being designed and synthesized in our laboratory.

2.4. Fluorescence Quenching and Relative Quantum Yields of Anthracene Units in Encapsulated Ln³⁺ Dendrimer Complexes

The fluorescence of the anthracene moiety upon photoexcitation at 390 nm in a thin film, which is mainly absorbed by the anthracene units, is strongly quenched in the Ln³⁺ complexes. We chose a photoexcitation wavelength of 390 nm, because Er³⁺ ions do not have any significant absorbance at 390 nm, and thus the direct excitation of Er³⁺ ions should be negligible. The relative fluorescence intensities of the anthracene moieties in Ln³⁺ complexes are shown in Figure 5, where the fluorescence intensity of the anthracene moiety in [G3-An]-CO₂H and the fluorescence quantum yield (Φ_rel) of the anthracene moiety in [G3-An]-CO₂H as a free ligand is set to unity. The fluorescence intensity of the anthracene moiety was dramatically quenched in the Ln³⁺ complexes, owing to the efficient energy transfer from the anthracene ligand to the Ln³⁺ ion. In addition, the emission spectra also show the typical emission characteristics originating from the 4f–4f electronic transition of the Yb³⁺ ion (980 nm, 2F₅/₂ → 2F₇/₂) and the Nd³⁺ ion ((890 nm, 4I₉/₂ → 4I₁₁/₂), (1073 nm, 4F₅/₂ → 4I₁₁/₂), (1342 nm, 4F₇/₂ → 4I₁₁/₂)). The strongest emission of Nd³⁺ ion is centered at around 1073 nm, and the intense emission band constitutes approximately 60% of the total emission intensity.

Figure 5. Emission spectra of the anthracene moiety in [G3-An]-CO₂H and Ln³⁺ ions in Ln³⁺-[G3-An]₃(terpy) upon photoexcitation at a wavelength of 390 nm in a thin film. The [Nd³⁺] and [Er³⁺] spectra are multiplied by factors of 25 and 27, respectively.
As a result, the significant decrease in the fluorescence intensity of the anthracene moiety in the Ln\(^{3+}\) complexes is accompanied by a strong increase in the near-IR emission of the Ln\(^{3+}\) ions. This is not only the case for the Er\(^{3+}\) ion, but also with the Yb\(^{3+}\) and Nd\(^{3+}\) ions. With these results, the relative fluorescence quantum yields of the anthracene moiety in Ln\(^{3+}\) complexes were determined and summarized (Table 2). By quantitative comparison with the emission intensity in the visible region of the anthracene moiety in [G3-An]-CO\(_2\)H \((\Phi_{\text{rel}} = 1)\), the relative fluorescence quantum yield for the anthracene moiety in the Ln\(^{3+}\) complexes was determined to be 0.07 for Er\(^{3+}\)-[G3-An]\(_3\)(terpy), 0.14 for Yb\(^{3+}\)-[G3-An]\(_3\)(terpy), and 0.07 for Nd\(^{3+}\)-[G3-An]\(_3\)(terpy). These results imply that the energy-transfer process between the dendritic anthracene ligand and Er\(^{3+}\) ion takes place efficiently, since the spectral overlap integral between the emission band of the anthracene derivative and the absorption bands of the Er\(^{3+}\) ion is sufficiently large (Fig. 6).

2.5. Energy-Transfer Pathway via a Singlet Excited State Between an Anthracene Ligand and the Lanthanide Ion

Although a number of sensitized Ln\(^{3+}\) complexes have been reported, energy-transfer pathways are not still fully understood for the sensitization of the lanthanide ions. Efficient energy-transfer pathways are very important in advanced photonics technology, particularly in the development of useful luminescent lanthanide complexes with efficient lanthanide emission. To date, two possible energy-transfer pathways for the sensitized emission in luminescent lanthanide complexes have been proposed. The first is energy transfer through the triplet excited state of a luminescent ligand; and the second is the direct energy transfer from the singlet excited-state of the ligand to the Ln\(^{3+}\) ion. Generally, it is well known that energy transfer from the triplet state of luminescent ligands, converting from the excited singlet state via ISC, to the Ln\(^{3+}\) ion, is the dominant mechanism. This can be ascribed to the fact that the rate of ISC in luminescent lanthanide complexes is very fast, owing to the heavy-atom effect of the Ln\(^{3+}\) ion.\(^{[25]}\) The possibility of energy transfer from the singlet state of the luminescent ligand was thought to be very low, because this process is usually too slow to compete with other processes, such as luminescent ligand fluorescence and ISC.\(^{[6c,17b]}\) Therefore, most research in lanthanide-ion sensitzers has focused on developing luminescent ligands containing chromophores with a triplet state matching the receiving Ln\(^{3+}\) ion energy level, such that efficient energy-transfer takes place from the triplet state to the Ln\(^{3+}\) ion. However, a few articles have reported energy transfer from the excited singlet-state to the Ln\(^{3+}\) ion.\(^{[15,26]}\)

Unusually, and very recently, we observed that the sensitized emission of luminescent lanthanide complexes based on a 4-naphthalen-1-yl-benzoic acid ligand takes place through charge transfer to Ln\(^{3+}\) ions.\(^{[27]}\) Although the dendritic anthracene ligand is structurally similar to the 4-naphthalen-1-yl-benzoic acid ligand used in previous work, [G0-An]-CO\(_2\)H did not show a large Stokes’ shift according to solvent polarity in its absorption and emission spectra (Fig. 7a), which implies that the formation of the charge-transfer state in the complexes is not significant. It might be considered to be due to the restricted rotation between an anthracene unit and an adjacent phenylene unit, caused by the steric hindrance among the ortho-hydrogen atoms in the two units (see Scheme 1).

To investigate the triplet energy-transfer pathway, it is generally accepted that the emission spectra and decay-time measurements for Gd\(^{3+}\) complexes allow the identification of the lowest triplet state of a ligand, generated by ISC from the singlet excited state, because the Gd\(^{3+}\) ion has no energy level below 32 000 cm\(^{-1}\). Therefore, Gd\(^{3+}\) ions cannot accept any excited energy from the singlet and triplet states of dendritic anthracene ligands. Also, the fluorescence quenching of the ligand in Ln\(^{3+}\) complexes could imply that excited singlet energy is transferred to either the Ln\(^{3+}\) ion or the triplet state. In our system, no

### Table 2. Measured fluorescence lifetimes of dendritic anthracene ligands and their Ln\(^{3+}\) complexes.

<table>
<thead>
<tr>
<th>[Gn-An]-CO(_2)H ([a])</th>
<th>(\Phi_{\text{rel}} ) ([b])</th>
<th>Lifetimes</th>
<th>(k_{\text{et}} ) ([s^{-1}])</th>
<th>(\phi_{\text{rel}} ) ([%]) ([e])</th>
</tr>
</thead>
<tbody>
<tr>
<td>[G3-An]-CO(_2)H</td>
<td>1</td>
<td>1.5 ns</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Er(^{3+})-[G3-An](_3)(terpy)</td>
<td>0.07</td>
<td>200 ps (97%)</td>
<td>2</td>
<td>4.3×10(^9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3 ns (3%)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Yb(^{3+})-[G3-An](_3)(terpy)</td>
<td>0.14</td>
<td>270 ps (90%)</td>
<td>11</td>
<td>3.0×10(^9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 ns (10%)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nd(^{3+})-[G3-An](_3)(terpy)</td>
<td>0.07</td>
<td>300 ps (95%)</td>
<td>0.7</td>
<td>2.7×10(^9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6 ns (5%)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\([a]\) \(\lambda_{\text{ex}} = 390\) nm in thin film. \([b]\) Relative quantum yield of anthracene unit (450 nm). \([c]\) The detection wavelength was 450 nm (the fractional intensities of each decay component are given in parentheses). \([d]\) The detection wavelength was 1530 nm. \([e]\) Calculated from \(\Phi_{\text{rel}} = \tau_{\text{rel}}/\tau_{\text{f}}\), where \(\tau_{\text{f}}\) is the radiative lifetime of Ln\(^{3+}\) ions (8 ms for Er\(^{3+}\), 2 ms for Yb\(^{3+}\), and 0.25 ms for Nd\(^{3+}\)).

![Figure 6. UV-vis absorption and PL spectra of anthracene units in THF solution (solid) overlayed with the PL spectra of dendrons (dashed) and the UV-vis absorption spectrum of ErCl\(_3\) (dash–dot).](image-url)
phosphorescence of the Gd\textsuperscript{3+} complex was observed, even in deoxygenated solution at 77 K (Fig. 7b), and the emission spectra of Ln\textsuperscript{3+} ions in the near-IR region are independent of oxygen concentration. As a result, Gd\textsuperscript{3+} ions cannot provide the formation of a triplet state by a heavy-atom effect in Gd\textsuperscript{3+} free ligand and the corresponding complexes. The times-resolved luminescence spectra of the anthracene units in the visible region show monoexponential decay with a luminescence lifetime of 1.5 ns for [G3-An]-CO\textsubscript{2}H and a biexponential process with lifetimes of 200 ps (97 %) and 1.3 ns (3 %) for Er\textsuperscript{3+}:[G3-An]\textsubscript{3}(terpy), as depicted in Figure 8.

The biexponential decays in the visible region of the anthracene unit for all Ln\textsuperscript{3+} complexes contain a radiative decay of anthracene units (< ca. 10 %) and an energy-transfer component (> ca. 90 %) from the excited state of the anthracene units to the Ln\textsuperscript{3+} ions. Therefore, the decreased fluorescence quantum yields and lifetimes of the dendritic antennae in Ln\textsuperscript{3+} complexes indicate that the sensitization of Ln\textsuperscript{3+} luminescence by energy transfer takes place via the singlet state of the dendritic anthracene ligand, and the energy-transfer rate ($k_{ET}$) from the excited singlet state of the ligand to the Ln\textsuperscript{3+} ions can be estimated to be smaller than 10\textsuperscript{8} s\textsuperscript{-1}. This can also compete with the fluorescence rate. The energy-transfer pathway via the singlet excited state between the anthracene ligand and the Ln\textsuperscript{3+} ion in a series of the Ln\textsuperscript{3+}-cored dendritic complexes, Ln\textsuperscript{3+}:[Gn-An]\textsubscript{3}(terpy), is proposed in Scheme 4.

2.6. Radiative Lifetime and Quantum Yield of Lanthanide(III) Ions

The time-resolved luminescence spectra in the near-IR region show monoexponential decays with a luminescence lifetime of 2 μs for the Er\textsuperscript{3+} ion, 11 μs for the Yb\textsuperscript{3+} ion, and 0.7 μs for the Nd\textsuperscript{3+} ion in a thin film. The lifetime of the Nd\textsuperscript{3+} ion is substantially shorter in the dendritic complex relative to that of the other Ln\textsuperscript{3+} ions. This result suggests that C–H bonds in the complex may provide a non-radiative pathway from the Nd\textsuperscript{3+} excited state. The PL quantum yields ($\Phi_{PL} = \tau_{obs}/\tau_{rad}$) were calculated from the observed lifetimes ($\tau_{obs} = (k_{r}+k_{nr})$), where $k_{r}$ is the rate of the radiative process and $k_{nr}$ the rate of the non-radiative process and the radiative lifetimes ($\tau_{rad} = k_{r}^{-1}$) of the Ln\textsuperscript{3+} ions. The radiative lifetimes were taken from the literature,\cite{29} with typical lifetimes of 8 ms for Er\textsuperscript{3+}, 2 ms for Yb\textsuperscript{3+},...
and 0.25 ms for Nd3+. The radiative lifetime is a very important parameter in the photophysical properties of near-IR emission, because the overall rate of non-radiative deactivation, determined by both $\tau_{\text{obs}}$ and $\tau_{\text{R}}$ and nonradiative process ($k_{\text{nr}}$), influences the observed luminescence lifetime. Calculated intrinsic quantum yields of the near-IR Ln3+ ion emission were 2.5 × 10⁻⁴ for Er3⁺, 5.5 × 10⁻³ for Yb3⁺, and 2.8 × 10⁻⁴ for Nd3⁺. Compared to the Nd3⁺ and Er3⁺ complexes, the strongest emission intensity and the longest luminescence lifetime were obtained for the Yb3⁺ complexes; this is probably due to the well-established energy-gap law.[30] The smaller the number of vibrational quanta between the lowest luminescent excited state and the highest nonluminescent state of the Ln³⁺ ion, the more effective vibrational quenching can be. The energy gap between the lowest luminescence excited state and the highest ground state of Yb3⁺ ($2F_{5/2} \rightarrow 2F_{7/2}$, ca. 12 000 cm⁻¹) is much larger than that of Nd3⁺ ($2F_{3/2} \rightarrow 4I_{15/2}$, ca. 5 300 cm⁻¹) and Er3⁺ ($4I_{15/2} \rightarrow 4I_{13/2}$, ca. 6 500 cm⁻¹), which implies that the large energy gap makes Yb3⁺ ions less sensitive to the high-energy vibration of a complex environment such as O–H (ν(O–H) ca. 3400 cm⁻¹) and C–H (ν(C–H) ca. 2950 cm⁻¹) oscillators. These phenomena are commonly observed in organic complexes.

Surprisingly, after Er³⁺-[G₃-An]₃(terpy) was irradiated with a 5 ns, 10 Hz pulse laser, which had a power of 13 mJ per pulse, for 2 h, its PL intensity was constant, indicating the excellent photostability of the present Ln³⁺-cored dendrimer complexes. Also, they are thermally stable up to 250 °C. They have good solubility in common organic solvents, allowing thin films of them to be made directly by spin-coating from solution. In addition, Er³⁺-[G₃-An]₃(terpy) has a very broad near-IR emission band with a full width at half-maximum (FWHM) of 77 nm, which is very important for wavelength division multiplexing (WDM) applications[3,31] and shows high absorption (εₐ) and emission (γₐem; 1.5 × 10⁻¹⁸ cm²) cross sections of Er³⁺ compared to the inorganic matrices (ca. 10⁻²⁰ cm²).[32]

3. Conclusions

We have demonstrated that a series of the stable and inert encapsulated lanthanide(III) complexes based on dendritic anthracene ligands exhibit strong near-IR emission bands via highly efficient energy-transfer from the excited states of the peripheral antennae to the Ln³⁺ ions (Er³⁺, Nd³⁺, and Yb³⁺). The near-IR emission intensity of the lanthanide complexes was dramatically enhanced on increasing $n$ of the Fréchet aryl-ether dendrons, owing to site-isolation and light-harvesting effects. Surprisingly, the site-isolation effect could dominate the light-harvesting effect in the series of Er³⁺-[Gₙ-An]₃(terpy) complexes, owing to the low quantum yield of the aryl-ether dendron ($Φ₁ = 0.02$), even though the system consisted of a lanthanide(III)-cored supramolecular complex and light-harvesting dendritic photon antennae in which a proper cascade-type energy gradient is maintained within the light-harvesting dendrons through luminescent ligands to the Er³⁺ ion. In other words, the Fréchet aryl-ether dendrons are effective in not sensitizing Ln³⁺ luminescence, and are able to shield the Ln³⁺ ion. Photophysical studies indicate the sensitization of Ln³⁺ luminescence by energy transfer through the excited singlet state of the anthracene ligands, and the energy-transfer efficiency between the anthracene ligand in the dendritic anthracene ligands and the Ln³⁺ ion was evaluated to be in the range of 90 to 97 %. Their electron-transfer efficiency was in good agreement with the result that the biexponential decays contain a radiative decay of anthracene units (<ca. 10 %) and an energy-transfer component (>ca. 90 %) from the excited state of anthracene ligands to the Ln³⁺ ions. The time-resolved luminescence spectra show monoexponential decays with a lifetime of 2 μs for Er³⁺ ions, 11 μs for Yb³⁺ ions, and 0.7 μs for Nd³⁺ ions in thin films, and calculated intrinsic quantum yields of Ln³⁺ ions are in the range of ca. 0.025–0.55 %. All Er³⁺-cored dendrimer complexes have excellent thermal stability and photostability, good solubility in common organic solvents, and a very broad near-IR emission band with a FWHM of 77 nm.

4. Experimental

Aryl-ether dendrons were synthesized as reported in the literature [22]. The di-meso-substituted anthracene derivatives, which form complexes that are more stable, were synthesized by the well-known Suzuki cross-coupling reaction; its compound was treated with an appropriate aryl-ether dendron, yielding the new aryl-ether type dendritic anthracene ligands ([Gₙ-An]-CO₂H) [18]. A series of novel lanthanide-encapsulated complexes having Gₙ-aryl ether dendrons (n ca. 0–3) was synthesized by the ligand-exchange reaction developed in our laboratory, using ErCl₃ [18,20,21]. The detailed synthesis and measurements are described in the Supporting Information.

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