

# Self-Assembled Lanthanide-Cored Dendrimer Complexes: Enhancement of the Luminescence Properties of Lanthanide Ions through Site-Isolation and Antenna Effects

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The site isolation of lanthanide cations ( $\text{Er}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$ ) has been achieved through the self-assembly of three convergent polyether dendrons, each with a carboxylate anion focal point, around the central trivalent cation. Evidence for the self-assembly of the dendritic complexes can be obtained by a variety of spectroscopic and other analytical means both in solution and in the solid state. The luminescence properties of these new dendrimers measured both in solution and in the bulk show a dependence of luminescence activity on the size of the dendritic shell. The observed enhancement in luminescence properties can be attributed both to a large antenna effect, involving the nonconjugated phenyl benzyl ether dendrimer framework, and to a shell effect that results from the effective site isolation of each lanthanide cation within a dendritic sphere, preventing their mutual interaction and decreasing their rate of self-quenching. The site isolation afforded by self-assembly and the antenna effect provided by the polyether dendrimer may be of general applicability in the design of energy-harvesting devices and amplifiers for fiber optics.

## Introduction

Lanthanide elements (noted as Ln) are known for their unique luminescence properties such as long, millisecond-order lifetime and narrow-width emission band.<sup>1</sup> When the lanthanide luminescence occurs in the near-infrared region, these elements may be used as fluorophores in the design of signal amplifiers for optical fiber communications. For example, erbium is frequently used in optical signal amplifiers since its emission wavelength (i.e., 1530 nm) is coincident with the signal wavelength commonly used in glass fiber systems.<sup>2</sup> However, the poor solubility of Ln cations ( $\text{Ln}^{3+}$ ) in conventional inorganic media such as silica glass leads to clustered  $\text{Ln}^{3+}$  species, which in turn has limited the amplification achievable. This is because cooperative energy-transfer processes (i.e., self-quenching process) that occur between the clustered  $\text{Ln}^{3+}$  cause a reduction in the intensity of luminescence.<sup>2a,b</sup> Considerable effort has been devoted to the search for improvement in the areas of lanthanide cation solubility

and methods for achieving homogeneous dispersions in inorganic glass through the optimization in both the composition of the glass and the fiber fabrication technique.<sup>2b,3</sup> However, despite these developments, the solubility in current systems is still limited to about 0.1 wt %.<sup>2,3</sup>

An alternative approach used to circumvent the solubility problem was to select transparent organic polymers instead of inorganic glass to increase the  $\text{Ln}^{3+}$  concentration in the matrix.<sup>4b,5,6</sup> For example, dispersions of  $\text{Ln}^{3+}$  with organic ligands (e.g., triacetate salt  $\text{Ln}(\text{OAc})_3$ ) in organic polymers such as polystyrene have been reported.<sup>4,6</sup> Organic ligands have also been directly attached onto polymeric chains.<sup>4b,5,6</sup> Another approach is the dispersion of organic  $\text{Ln}^{3+}$  complexes in inorganic matrixes such as silica via a sol-gel method<sup>7</sup> involving the hydrolysis–condensation of alkoxy-silanes. Although the cation concentration was reported to reach several weight percent by these methods,

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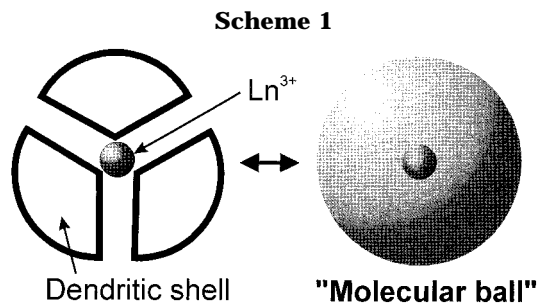
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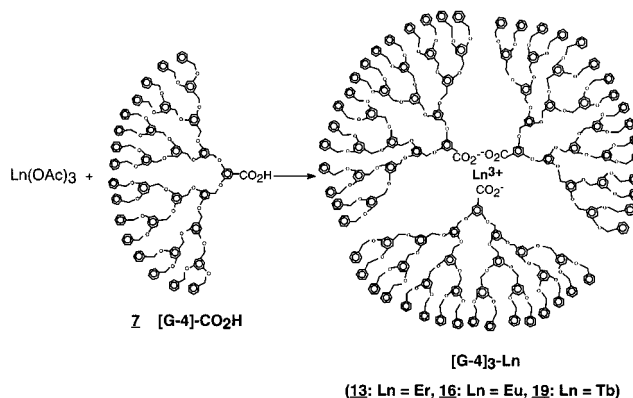
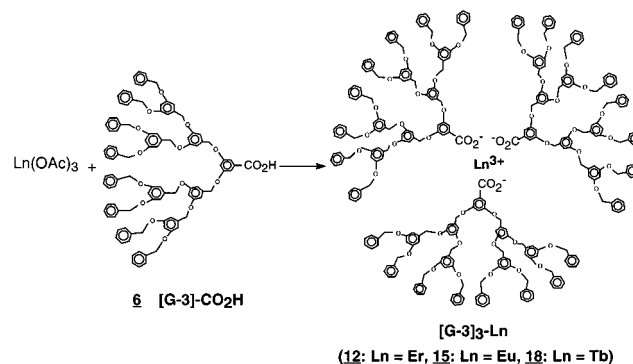
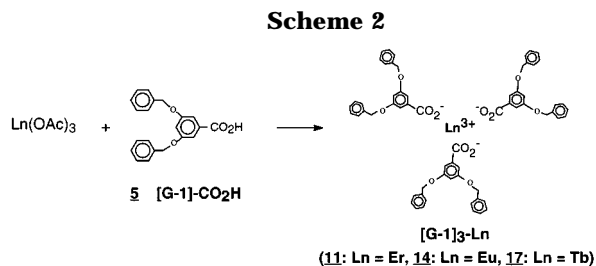


structural uncertainties still remain as ion clusters may form, even if macroscopic homogeneity appears to be realized.<sup>6</sup> Recently, a liquid-crystalline ligand featuring a nitrogen atom and a hydroxyl group coordinated to  $\text{Er}^{3+}$  has been reported<sup>8</sup> to produce a controlled smectic metallopolymer phase, a potential magneto-optical material. However, sources of hydroxyl ligands such as water or alcohols<sup>1</sup> are known to nonradiatively deactivate  $\text{Ln}^{3+}$  cations, a process that should be avoided in applications aimed at the enhancement of luminescence intensity.

To achieve site isolation of  $\text{Ln}^{3+}$  cations in a cluster-free environment<sup>9</sup> to maximize their luminescent characteristics, we have investigated the concept of surrounding the  $\text{Ln}^{3+}$  cations by a dendritic shell, thereby segregating the cations from each other and reducing the self-quenching process. The aim of this concept was to utilize self-assembly via ionic interactions between the carboxylate functionality at the focal point of a dendritic subunit and a single  $\text{Ln}^{3+}$  cation to create a dendritic  $\text{Ln}^{3+}$  "molecular ball" (Scheme 1) and to investigate the resultant luminescence behavior of this kind of self-assembled complex both in solutions and in the bulk state.

## Results and Discussion

**Synthesis of the Lanthanide-Cored Dendrimer Complexes.** The acid dendrons used as the "shell" components of the self-assembled  $\text{Ln}^{3+}$  molecular ball, were prepared as outlined below, where the various generation dendrons are designated by the notation  $[\text{G}-x]-F$ , in which  $[\text{G}-x]$  refers to generation number ( $x = 1, 2, 3, 4$ ) and  $F$  refers to the functional group located at the focal point of the dendrons. Ethyl 3,5-dihydroxybenzoate (**1**) was prepared in 86% yield from 3,5-dihydroxybenzoic acid. This ester **1**, used as the focal point component, was condensed with benzyl bromide, or the desired bromide dendrons<sup>10</sup>  $[\text{G}-2]-\text{Br}$  and  $[\text{G}-3]-\text{Br}$ , in excellent yield to form a series of ester dendrons,  $[\text{G}-1]-\text{CO}_2\text{Et}$  (**2**),  $[\text{G}-3]-\text{CO}_2\text{Et}$  (**3**), and  $[\text{G}-4]-\text{CO}_2\text{Et}$  (**4**), respectively. The ester dendrons were subsequently hydrolyzed in high yield to give the corresponding acid dendrons,  $[\text{G}-1]-\text{CO}_2\text{H}$  (**5**),  $[\text{G}-3]-\text{CO}_2\text{H}$  (**6**), and  $[\text{G}-4]-\text{CO}_2\text{H}$  (**7**), respectively. The Ln-cored dendrimer complexes were prepared via ligand-exchange reactions as



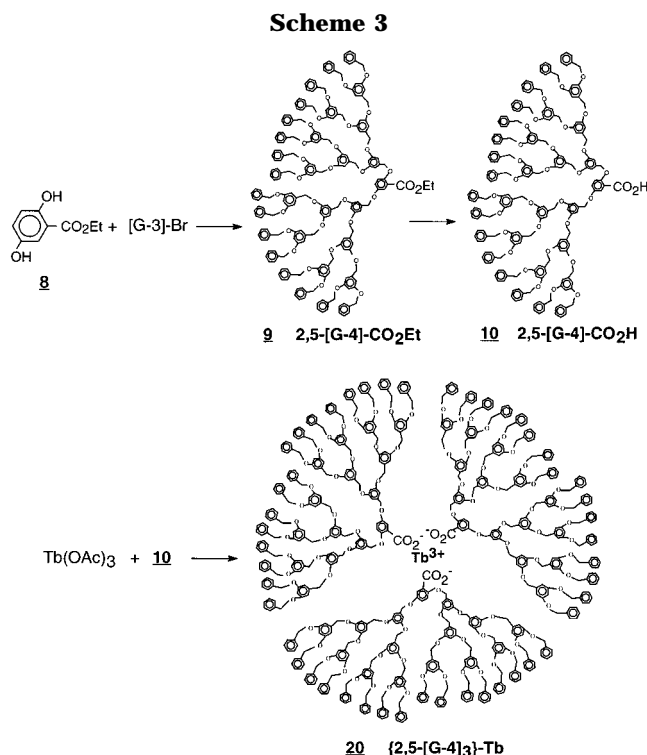
shown in Scheme 2. A stoichiometric mixture of an anhydrous lanthanide triacetate,  $\text{Ln}(\text{OAc})_3$ , and the appropriate acid dendron (1:3 molar ratio) were refluxed in chlorobenzene. The acetic acid generated by the exchange reaction was distilled off continuously with the solvent to afford the corresponding Ln-cored dendrimer complexes (**11–19**). Ethyl 2,5-dihydroxybenzoate (**8**) was also used as an alternate focal point component possessing different light absorption and emission characteristics. It was condensed with  $[\text{G}-3]-\text{Br}$  in 85% yield to form an isomer of the fourth generation ester dendron **4**, namely, 2,5- $[\text{G}-4]-\text{CO}_2\text{Et}$  (**9**). This fourth-generation ester dendron was then also hydrolyzed in high yield to afford the corresponding acid dendron, namely, 2,5- $[\text{G}-4]-\text{CO}_2\text{H}$  (**10**). In turn, this dendron **10** was converted into the corresponding terbium-cored complex **20** by reacting with anhydrous terbium triacetate (Scheme 3). In all of these systems, the higher generation dendrons, **3**, **4**, **6**, **7**, **9**, and **10** were successfully characterized by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry<sup>11</sup> to reveal single-peak spectra with the predicted mass (Figure 1).

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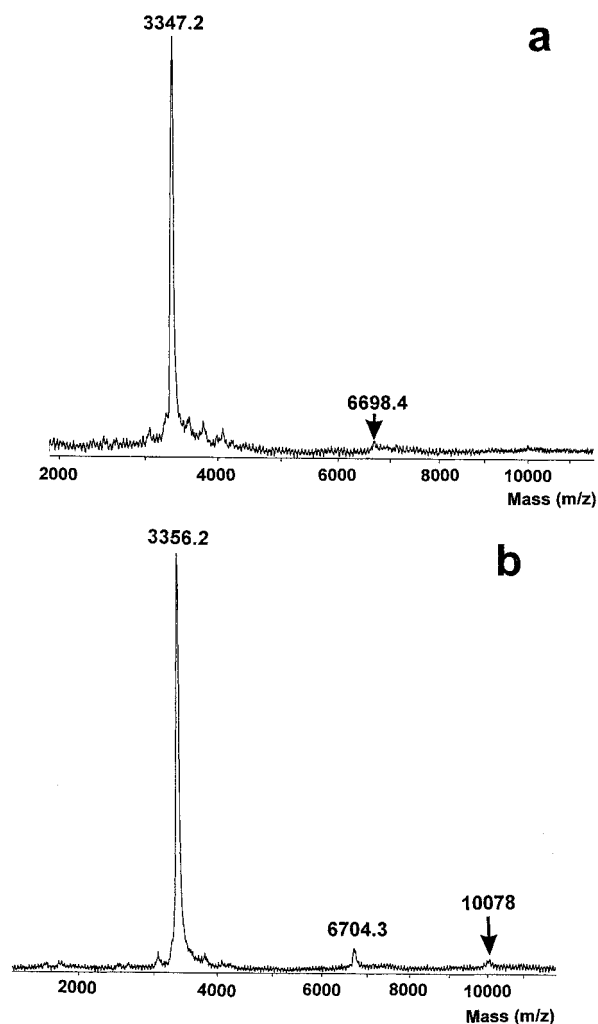
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The Ln-cored dendrimer complexes obtained were observed to possess enhanced solubility characteristics in common organic solvents (such as tetrahydrofuran (THF),  $\text{CH}_2\text{Cl}_2$ , acetone, and toluene) when compared to the corresponding dendritic acid starting materials. This observation supports the proposed self-assembled structure. It should be emphasized that  $\text{Ln(OAc)}_3$  is practically insoluble in common organic solvents, and hence coordination of large organic ligands to  $\text{Ln}^{3+}$  cation is required for the metal to be efficiently solubilized in a desired organic medium. However, further purification of the Ln-cored dendrimer complexes by silica gel column chromatography failed, yielding only the corresponding starting acid dendrons. This may be the result of a cation-exchange reaction between the self-assembled complex and the surface silanol groups ( $\text{Si-OH}$ ) of the silica gel, resulting in the adsorption of the  $\text{Ln}^{3+}$  cations onto the silica gel. This finding is not surprising given the relatively weak forces holding the dendrimer together and the dynamic equilibrium between dendrons and self-assembled dendrimers as a function of medium or temperature has also been observed by others.<sup>12</sup>

**Characterization.** As a result of their fragile nature resulting from the weak noncovalent ionic interaction between the  $\text{Ln}^{3+}$  cation and the dendritic carboxylate subunits, the self-assembled complexes could not be characterized as readily or thoroughly as covalent molecules using conventional spectroscopic techniques. Although FT-IR spectroscopy and elemental analysis gave reasonable results, both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy did not yield useful information because of extremely broad signals. For the purpose of the estimation of the assembly size, laser light-scattering technique



**Figure 1.** MALDI-TOF spectra of the fourth generation acid dendrons, (a)  $[\text{G-4}]\text{-CO}_2\text{H}$  and (b)  $2,5\text{-[G-4]}\text{-CO}_2\text{H}$ .

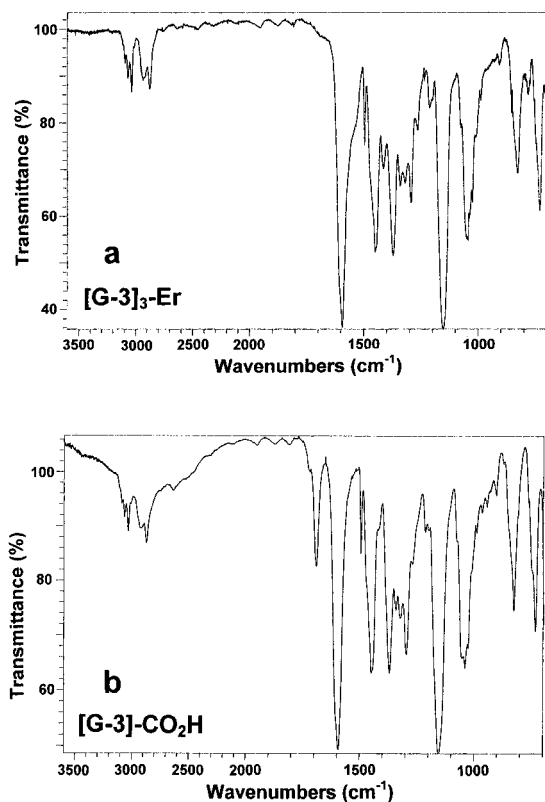
afforded satisfactory results, while size exclusion chromatography (SEC) and MALDI-TOF mass spectroscopy turned out to be inappropriate for these fragile complexes. Nonetheless, as will be seen below, luminescence measurements provided strong evidence for the assembly of the dendrons around the lanthanide ion.

**FT-IR Spectroscopy and Elemental Analysis.** The carbonyl absorption in FT-IR spectra associated with the acid dendrons,  $1692$  or  $1693\text{ cm}^{-1}$  for  $[\text{G-x}]\text{-CO}_2\text{H}$  (5–7) and  $1737\text{ cm}^{-1}$  for  $2,5\text{-[G-4]}\text{-CO}_2\text{H}$  (10), were absent in the spectra of corresponding Ln-cored dendrimer complexes. For example, a comparison of the spectra for the third generation dendrimer complex  $[\text{G-3}]_3\text{-Er}$  (12) and the corresponding acid dendron  $[\text{G-3}]\text{-CO}_2\text{H}$  (6) is shown in Figure 2: the carbonyl absorption at  $1693\text{ cm}^{-1}$  found in the acid dendron 6 is clearly absent in the corresponding Er-cored dendrimer complex 12. This may be interpreted as supporting evidence for the conversion of the carboxyl groups into carboxylate anions as a result of the self-assembly of the Ln-cored complex as recently reported in the literature for  $\text{Ln}^{3+}$  carboxylate salts.<sup>13</sup>

Additional experimental evidence for the proposed structure was provided by elemental analysis of the Ln-

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**Figure 2.** Comparison of the FT-IR spectra for (a) the dendrimer complex  $[G-3]_3\text{-Er}$  and (b) the corresponding dendritic carboxylic acid  $[G-3]\text{-CO}_2\text{H}$ .

**Table 1. Results of the Laser Light Scattering Experiments<sup>a</sup>**

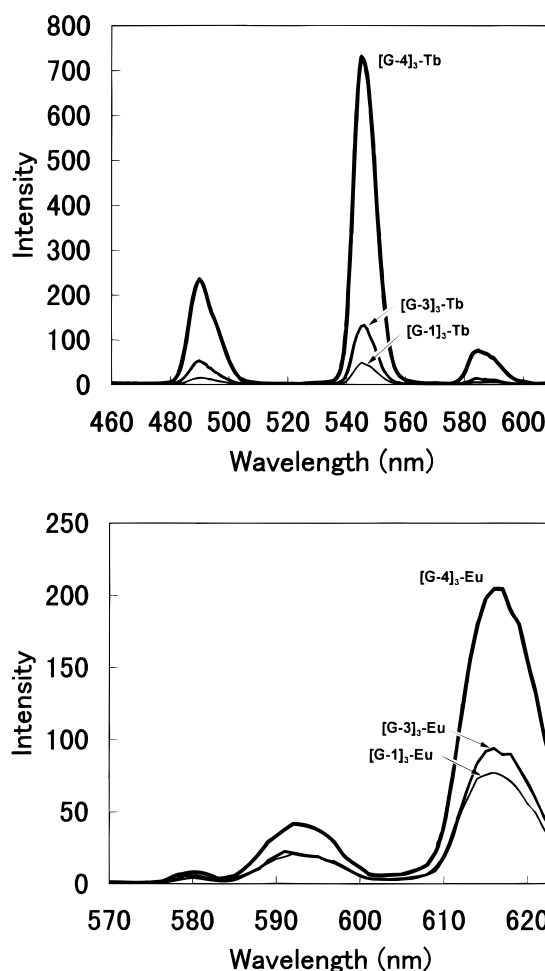
molecule	$M_{\text{calcd}}$	solvent	$dn/dc$ (mL/g)	$M_{\text{obsd}}$
$[G-4]\text{-CO}_2\text{H}$	3306	THF	0.259	4760
$[G-4]_3\text{-Tb}$	10073	THF	0.240	7520
$[G-4]_3\text{-Tb}$	10073	toluene	0.146	14900

<sup>a</sup>  $M_{\text{calcd}}$ , calculated molecular weight;  $n$ , refractive index of the solution;  $c$ , concentration in g/mL;  $M_{\text{obsd}}$ , observed molecular weight.

cored dendrimer complexes, including the ash values (as oxide:  $\text{Ln}_2\text{O}_3$ ), that were in good agreement with the calculated values. These cumulative data indicate that complete exchange of the acetate groups in the anhydrous Ln salt by the acid dendrons has occurred.

**Laser Light Scattering.** The technique of laser light scattering was applied to the acid dendron  $[G-4]\text{-CO}_2\text{H}$  (**7**) and the corresponding fourth generation terbium-cored dendrimer complex  $[G-4]_3\text{-Tb}$  (**19**) in various solvents (Table 1). The results obtained in THF with complex **19** show a molecular weight value higher than that measured for the corresponding acid dendron **7**, which provides some support for the self-assembly of the  $\text{Ln}^{3+}$  complex in the solution. The molecular weight value obtained by light-scattering technique for the dendrimer complex **19** in toluene is higher than that in THF. This finding is not unexpected since THF is a fairly polar solvent capable of solvating ions, a process that would unavoidably lead to partial dissociation<sup>12a</sup> of the dendrimer assembly. In contrast, toluene being nonpolar favors ionic association of the dendritic subunits with the  $\text{Tb}^{3+}$  core.

**Size Exclusion Chromatography (SEC) and MALDI-TOF.** SEC analysis using THF as the solvent

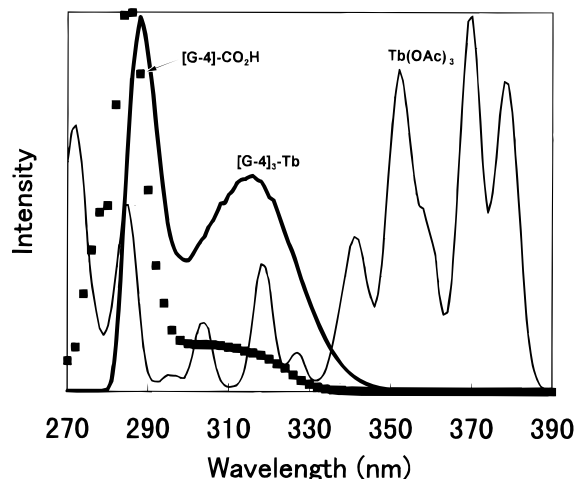


**Figure 3.** Emission spectra of the Ln-cored dendrimer complexes in toluene. (a, top)  $[G-x]_3\text{-Tb}$  ( $3 \times 10^{-5}$  mM), (b, bottom)  $[G-x]_3\text{-Eu}$  ( $3 \times 10^{-3}$  mM);  $x = 1, 3,$  and  $4$ . Excitation was performed at the wavelength with luminescence maximum in excitation spectra (315 nm for  $[G-1]_3\text{-Ln}$ , 289 nm for the others). In Figure 3b, the spectral region above 623 nm was removed, because of a large noise peak corresponding to double the wavelength of the excitation light.

applied to the erbium-cored dendrimer complexes (**11–13**) was unsuccessful probably as a result of a reversible dissociation related to the shear flow in the SEC column.

Similarly, MALDI-TOF spectroscopy did not afford a signal corresponding to the self-assembled complexes in a variety of matrixes, but instead complex spectra including the signal of the starting acid dendron were obtained. We believe that the structure of the complexes is too weak to withstand the conditions of the MALDI-TOF analysis. Fast atom bombardment mass spectrometry (FAB-MS) was also applied to the complex  $[G-3]_3\text{-Er}$  (**12**) as an alternative mass analysis providing for milder conditions; however, it yielded only a complex spectrum including the signal corresponding to the mass of the dimer of the acid dendron  $[G-3]\text{-CO}_2\text{H}$  (**6**).

**Luminescence in Solution.** The primary aim of the luminescence studies in solution was to obtain evidence for the self-assembled structure. It was anticipated that transfer of the excitation energy might occur from the aromatic dendritic ligand to the central  $\text{Ln}^{3+}$  cation in the self-assembled dendrimer complex (i.e., sensitization of  $\text{Ln}^{3+}$ ).<sup>4,13</sup> Low concentration of the complexes is favorable to minimize the possibility of intermolecular



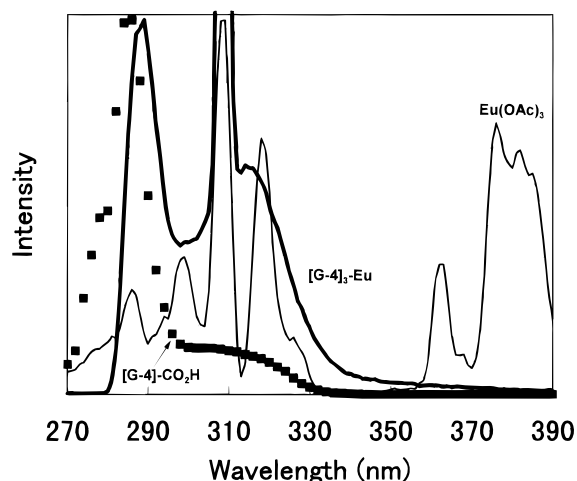
**Figure 4.** Excitation spectra of the Tb-cored complex  $[G-4]_3\text{-Tb}$  at  $3 \times 10^{-5}$  mM in toluene (bold line, emission at 545 nm) and of  $\text{Tb}(\text{OAc})_3$  in water (fine line) overlaid with the UV-vis absorption spectrum of the corresponding dendritic subunit  $[G-4]\text{-CO}_2\text{H}$  at  $1 \times 10^{-1}$  mM in toluene (dotted line). All spectra are normalized to a constant intensity at the maximum.

interactions occurring as a result of aggregation. Fortunately, the luminescence observed from two series of Ln-cored dendrimer complexes,  $[G-x]_3\text{-Eu}$  and  $[G-x]_3\text{-Tb}$  ( $x = 1, 3,$  and  $4$ ) in anhydrous toluene was of sufficient intensity to allow the quantitative studies to be performed in the range  $10^{-6}$ – $10^{-9}$  M concentration.

Figure 3 illustrates the emission spectra obtained for the Eu and Tb complexes in toluene excited at the wavelengths with maximum intensity in the corresponding excitation spectra around 290–315 nm. Three distinct observations can be made on these spectra: (i) the emission bands with relatively narrow widths are characteristic for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , (ii) the higher generation dendrimer complexes exhibit stronger luminescence, and (iii) the Tb complexes  $[G-x]_3\text{-Tb}$  exhibit much stronger emission than the Eu complexes  $[G-x]_3\text{-Eu}$  (note the difference in the concentrations).

The excitation spectra of  $\text{Ln}(\text{OAc})_3$  in water shown in Figures 4 and 5 show no relationships with those of the self-assembled complexes  $[G-4]_3\text{-Tb}$  and  $[G-4]_3\text{-Eu}$ . The overlap between the excitation spectra of the self-assembled complexes and the absorption spectrum of the corresponding dendritic subunit  $[G-4]\text{-CO}_2\text{H}$  are also shown in these figures. A similar spectral overlap is observed for all of the self-assembled complexes prepared. These observations clearly indicate the typical sensitization of the  $\text{Ln}^{3+}$  core by aromatic ligands, an "antenna effect",<sup>4b,14–16</sup> and thus confirm that the dendritic subunits are self-assembled around the  $\text{Ln}^{3+}$  core.

However, an explanation has to be proposed for the observed enhancement of the luminescence as a direct function of the generation of the dendritic subunits. It is well-known that an aromatic ligand effectively sensitizes a  $\text{Ln}^{3+}$  cation when the energy of the excited state of the ligand lies slightly higher<sup>14</sup> than the emission state of the  $\text{Ln}^{3+}$ . In the meantime, the Förster model,<sup>4b,17</sup> which considers the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, has been accepted for energy-transfer phenomena. Figure 6 overlays the emission spectrum of the dendritic subunits and the excitation spectra of  $\text{Ln}^{3+}$  cations, i.e.,  $\text{Ln}(\text{OAc})_3$  in water, sug-



**Figure 5.** Excitation spectra of the Eu-cored complex  $[G-4]_3\text{-Eu}$  at  $3 \times 10^{-3}$  mM in toluene (bold line, emission at 616 nm) and  $\text{Eu}(\text{OAc})_3$  in water (fine line). The UV-vis absorption spectrum of the corresponding dendritic subunit  $[G-4]\text{-CO}_2\text{H}$  at  $1 \times 10^{-1}$  mM in toluene (dotted line) is overlaid. All spectra are normalized to a constant intensity at the maximum. A large peak at 308 nm appearing in the excitation spectra corresponds to the overtone of the emission wavelength.

gesting that this overlap is better for  $\text{Tb}^{3+}$  than for  $\text{Eu}^{3+}$ . Note that the Tb complexes  $[G-x]_3\text{-Tb}$  exhibited luminescence intensities several hundred times stronger than those for the Eu complexes  $[G-x]_3\text{-Eu}$  in Figure 3. Thus the Förster model may well be operative in these systems.

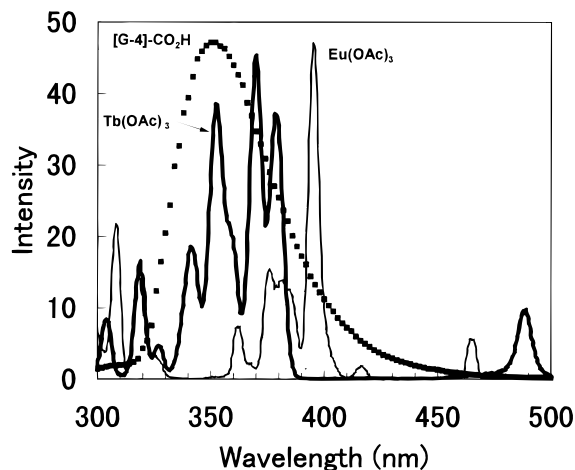
It is interesting to point out that the isomeric dendritic subunit 2,5- $[G-4]\text{-CO}_2\text{H}$  (**10**) exhibits a dramatically different antenna effect for  $\text{Tb}^{3+}$  when compared to that of  $[G-4]\text{-CO}_2\text{H}$  (**7**) as shown in Figure 7. The baseline emission shown in the emission spectrum of the complex  $\{2,5\text{-}[G-4]\}_3\text{-Tb}$  (Figure 7b) indicates insuf-

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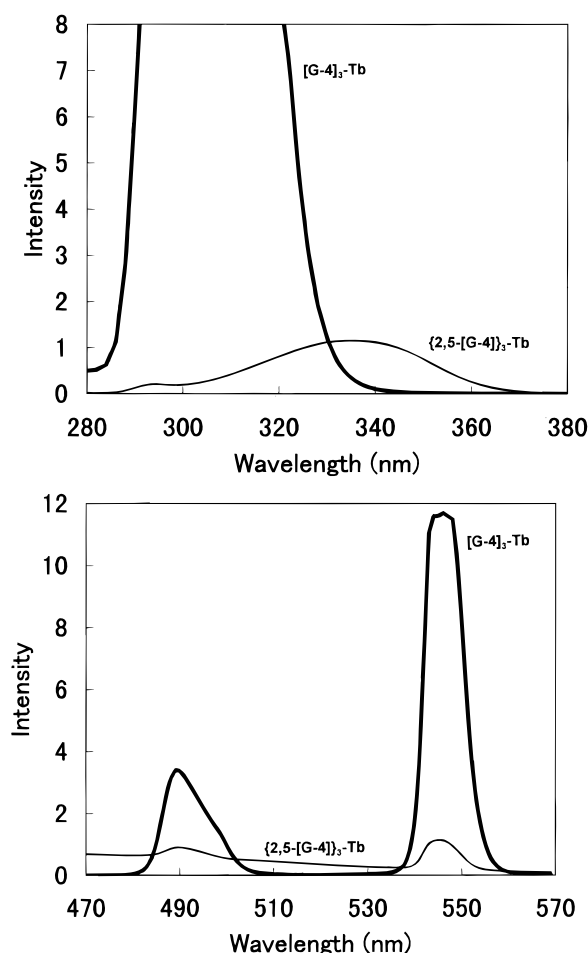
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**Figure 6.** Excitation spectra of Ln(OAc)<sub>3</sub> in water (Ln = Tb: bold line, Ln = Eu: fine line) and emission spectrum of the dendritic subunit [G-4]-CO<sub>2</sub>H (dotted line; excited at 289 nm in toluene, 1 × 10<sup>-4</sup> mM; normalized to a constant intensity set at the maximum of the spectrum of Er(OAc)<sub>3</sub>).



**Figure 7.** (a, top) Excitation spectrum and (b, bottom) emission spectrum of the isomeric complexes [G-4]<sub>3</sub>-Tb and {2,5-[G-4]}<sub>3</sub>-Tb at a concentration of 2.1 × 10<sup>-2</sup> mM in THF.

efficient energy transfer to the Tb<sup>3+</sup> core resulting in the direct broad luminescence from the dendritic subunit itself. It must be emphasized that these isomeric subunits differ only in the substitution pattern of their focal aromatic ring. Hence the focal aromatic structure is crucial for the antenna effect, although the individual aromatic rings within the subunits could be considered

as independent energy donors, transferring energy with an efficiency that decreases as the inverse sixth power of the interchromophore distance according to the Förster model. The origin of the very significant importance of the focal point moiety in these polyether dendrimers will require further study.

Although the polyether dendrimer structure is not a dendritic conjugated system specifically designed for an efficient energy transfer (e.g., conjugated dendritic systems as energy funnels<sup>15</sup>), a very distinct energy transfer from the dendritic shell to the Ln<sup>3+</sup> core is thought to be the dominant factor in the enhancement of the luminescence observed in dilute solutions of the self-assembled dendrimer complexes. The other proposed mechanism that could lead to this type of enhancement (i.e., the "shell effect") may be negligible in the dilute solutions used. However, the shell effect becomes evident for the Ln-cored complexes in the bulk state, as discussed in the text below.

**Hydration Experiments.** One might suspect that the enhanced luminescence of the self-assembled complexes as a function of the size of the dendritic subunits might result from a shielding effect of the larger subunits to effectively prevent the penetration of trace amounts of water in the solvent thereby decreasing the hydration of the Ln<sup>3+</sup> core. It is well-known that metallo-coordinated hydroxyl groups (and especially water molecules) are strong deactivators and reduce the luminescence intensity via a nonradiative vibronic deactivation pathway.<sup>1</sup> Therefore, an anhydrous environment around a Ln<sup>3+</sup> core would be favorable for the enhancement of its luminescence. To determine whether the presence of a dendritic shell around a Ln<sup>3+</sup> core would favor the exclusion of water from the vicinity of the metal cation, hydration experiments were carried out on the various generations of self-assembled complexes. The hydration of the Ln<sup>3+</sup> (Eu<sup>3+</sup> and Tb<sup>3+</sup>) core was carried out simply by the addition of water to the THF-mesitylene solution of the Ln-cored dendrimer complexes.

Horrocks and Sudnick<sup>18</sup> have shown that for Eu<sup>3+</sup> and Tb<sup>3+</sup>, the number of coordinated water molecules,  $q$ , to a Ln<sup>3+</sup> is given by eq 1, where  $A$  is a constant (1.05 for Eu<sup>3+</sup> and 4.2 for Tb<sup>3+</sup>),<sup>1</sup>  $\tau_h$  and  $\tau_d$  are the experimental excited-state lifetimes (in ms) in H<sub>2</sub>O and D<sub>2</sub>O solutions, respectively.

$$q = A(1/\tau_h - 1/\tau_d) \quad (1)$$

Horrocks and Sudnick have also reported an experimental relationship between the variation in the decay constant,  $\Delta k_{\text{obs}}$  ( $=1/\tau_h - 1/\tau_0$ ), and the value  $q$ , which may be expressed by eq 2, where  $B$  is a constant (0.958

$$\Delta k_{\text{obs}} = 1/\tau_h - 1/\tau_0 = Bq \quad (2)$$

$$q = q\tau_h(1/\tau_0)(1 - Bq\tau_h)^{-1} \quad (3)$$

for Eu<sup>3+</sup> and 0.237 for Tb<sup>3+</sup>),<sup>16</sup> and  $\tau_0$  is the experimental excited-state lifetime (in milliseconds) for the nonhydrated Ln<sup>3+</sup>. The value  $1/\tau_0$  was reported<sup>18</sup> as 0.77 ms<sup>-1</sup>

(18) (a) Horrocks, W. D.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334. (b) Horrocks, W. D.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384.

**Table 2. Evaluation of the Number of Coordinated Water Molecules<sup>a</sup>**

material	$q\tau_h$ (ms)	$q$
[G-1] <sub>3</sub> -Tb	1.69	2.34
[G-3] <sub>3</sub> -Tb	1.99	3.13
[G-4] <sub>3</sub> -Tb	2.28	4.10
[G-1] <sub>3</sub> -Eu	0.659	1.37
[G-3] <sub>3</sub> -Eu	0.735	1.91
[G-4] <sub>3</sub> -Eu	0.735	1.91

<sup>a</sup>  $q$ , number of water molecules coordinated to Ln-cored dendrimer complexes.  $\tau_h$ , fluorescence lifetime for the hydrated species.

for  $\text{Eu}^{3+}$  and  $0.83 \text{ ms}^{-1}$  for  $\text{Tb}^{3+}$ . Therefore eq 2 can be rewritten as eq 3.

Equation 4 is obtained from eq 1. As a first approximation, the fluorescence lifetime of  $\text{Ln}^{3+}$  may be considered to be proportional to the radiative deactivation intensity.  $I_h/I_d$  may thus be used instead of  $\tau_h/\tau_d$ , where  $I_h$  and  $I_d$  are the intensity of the strongest emission peak in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions, respectively. Thus eq 4 may be modified to eq 5.

$$q\tau_h = A(1 - \tau_h/\tau_d) \quad (4)$$

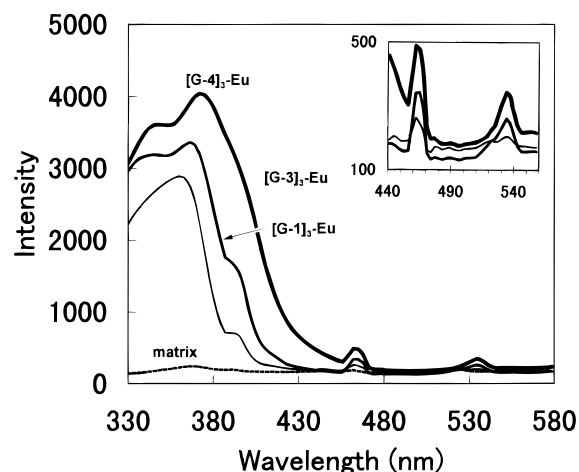
$$q\tau_h = A(1 - I_h/I_d) \quad (5)$$

Equation 5 allows the determination of  $q\tau_h$  using the experimental value  $I_h/I_d$  obtained from the luminescence intensity measurements, and then the hydration number  $q$  may be calculated from eq 3.

The 614–616 nm emission for the Eu-cored complexes (14–16; excitation at 352 nm) and the 544–546 nm emission for the Tb-cored complexes (17–19) (excitation at 328 nm) were used for the hydration experiments. The results obtained are summarized in Table 2.

Table 2 shows that the hydration number  $q$  increases with the generation of the dendritic subunits. This effect may be interpreted as follows: the higher the generation, the weaker the assembly, probably due to the increased steric requirement of the carboxylate focal point in the larger dendritic shells, thus leaving room for water molecules to coordinate the  $\text{Ln}^{3+}$  core.

Similar hydration experiments have also been described in the literature<sup>1</sup> for cyclic tertiary polyamines, which have been shown to efficiently exclude water molecules by chelation to  $\text{Ln}^{3+}$ . For example, a  $q$  value less than 0.5 was reported for a nine-membered ring polyamine.<sup>19</sup> This value is lower than that calculated for our system, although the molecular weight of the polyamine is significantly lower than that of the fourth-generation dendritic subunit used in this study. Thus, it appears that a rigid geometry of the ligands around the  $\text{Ln}^{3+}$  center is more important than the size of the ligand for the exclusion of water molecules. In fact, instead of “repelling” water of hydration, larger complexing dendritic subunits appear to make it easier for water to access the  $\text{Ln}^{3+}$  core, since the ion pairs formed between the  $\text{Ln}^{3+}$  center and the carboxylate functionalities are looser as a result of steric bulk around the carboxylate groups in large dendrons. Hence the observed enhanced luminescence as a function of the size of the dendritic subunits results from the antenna effect.



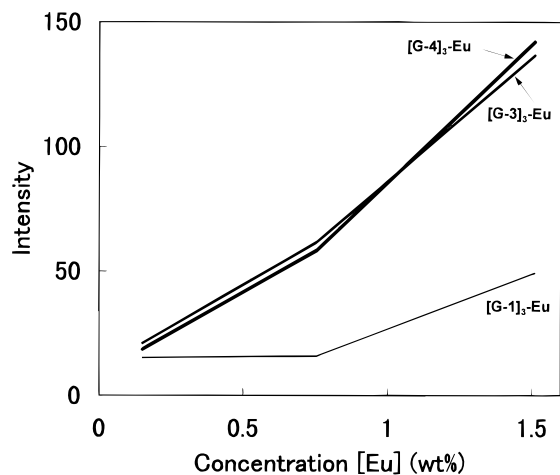
**Figure 8.** Excitation spectra of film samples of the Eu-cored complexes (emission at 612 nm,  $[\text{Eu}^{3+}] = 1.51 \text{ wt } \%$ ). The ester dendron 2,5-[G-4]- $\text{CO}_2\text{Et}$  was used as a matrix material to disperse the complexes. The spectrum of the matrix material itself is also shown as a dotted line in the figure. The inset shows the expanded spectra in the region 440–560 nm for the complexes.

**Bulk State Luminescence.** To investigate the possible use of the self-assembled  $\text{Ln}^{3+}$  complexes in amplifiers for optical fiber communications, the bulk state luminescence properties have to be investigated. While erbium has been identified as an important luminescer for this application, the erbium-cored dendrimer complexes did not reveal any significant emissions in the UV–vis excitation/emission experiments. We therefore concentrated our studies on the europium-cored complexes  $[\text{G}-x]_3\text{-Eu}$  ( $x = 1, 3, 4$ ) since these complexes, when excited at 462 nm in the bulk state, exhibit an emission band at 612 nm *without* the antenna effect.

The bulk state samples (films) were prepared by casting from a chlorobenzene solution of the Eu-cored complexes and the ester dendron 2,5-[G-4]- $\text{CO}_2\text{Et}$  (9) used as the matrix material miscible with the Eu-cored complexes, followed by heating in a press to a standardized film thickness (150  $\mu\text{m}$ ). To evaluate the distribution of  $\text{Eu}^{3+}$  in the matrix, the film samples were prepared at three different concentrations ( $[\text{Eu}^{3+}] = 1.51, 0.755, \text{ and } 0.151 \text{ wt } \%$ ; the highest concentration corresponding to the pure complex  $[\text{G}-4]_3\text{-Eu}$ ).

The excitation spectra (emission at 612 nm) recorded for the film samples prepared from the Eu-cored complexes (Figure 8) clearly show two distinct kinds of transitions: a broad band in the antenna effect region (below 460 nm), and small narrow bands located at 462 and 534 nm, respectively. The latter narrow transitions allow us to evaluate the luminescence in the absence of the antenna effect. The excitation band at 462 nm was selected for this evaluation because of its higher intensity in comparison to the 534 nm band. A slightly sloped baseline around the 462 nm band due to a residual antenna effect was subtracted. The intensity of the excitation band at 462 nm was recorded at four different sites on each film sample and was averaged after the baseline adjustment. Assuming that the film samples with the same concentration of  $\text{Eu}^{3+}$  (in wt %) contained the same number of  $\text{Eu}^{3+}$  per unit volume, i.e., the same density, we compared the averaged luminescence intensity. The results are summarized in Figure 9.

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**Figure 9.** Relationship between peak intensity (462 nm) in the excitation spectra of the Eu-cored complexes (emission at 612 nm) and the concentration of  $\text{Eu}^{3+}$  in film samples. The intensity was adjusted by baseline subtraction.

Figure 9 shows that the luminescence from the film samples is clearly enhanced in the higher generation dendrimer complexes  $[\text{G}-3]_3\text{-Eu}$  (**15**) and  $[\text{G}-4]_3\text{-Eu}$  (**16**) when compared to the luminescence of the first generation complex  $[\text{G}-1]_3\text{-Eu}$  (**14**). Since the residual antenna effect was removed by the baseline subtraction, this enhancement was attributed to a "shell effect": a site isolation effect originating from the forced dendrimer-induced increase in distance between the  $\text{Eu}^{3+}$  cores, that leads to a decrease in self-quenching. It should be noted that the lines for the higher generation complexes (**15** and **16**) are almost identical in Figure 9. This observation suggests that the size of the third-generation shell is sufficiently large to achieve maximum efficiency of the shell effect observed here. Furthermore, this enhancement behavior for the film samples is different from that for the dilute solutions shown in Figure 3: the enhancement observed in the dilute solutions between the fourth-generation complexes  $[\text{G}-4]_3\text{-Ln}$  ( $\text{Ln} = \text{Eu}, \text{Tb}$ ) and the corresponding third-generation complexes  $[\text{G}-3]_3\text{-Ln}$  was much larger than those observed between  $[\text{G}-3]_3\text{-Ln}$  and  $[\text{G}-1]_3\text{-Ln}$ . This difference in the enhancement of luminescence thus further supports that the mechanism of the enhancement observed for the bulk state samples was different from that observed for the dilute solutions.

In the context of applications to fiber optics, it is predicted that a similar effect will prevail for the 1530 nm emission of  $\text{Er}^{3+}$  for glass fiber amplifier applications, since the 980 nm excitation (which is typically used as the pumping wavelength)<sup>2</sup> is not likely to be absorbed by the dendritic organic shell, thereby ruling out any possible antenna effect.

### Conclusions

Lanthanide (Ln)-cored complexes consisting of  $\text{Ln}^{3+}$  ( $\text{Er}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$ ) cores and a surrounding dendritic carboxylate shell were prepared in good yield via a ligand-exchange reaction starting from the corresponding lanthanide triacetate. The products were characterized by FT-IR spectroscopy and elemental analysis. Light-scattering measurements and luminescence experiments also provided experimental evidence support-

ing the proposed self-assembled structure. This new class of dendrimers exhibits enhanced luminescence activity both in solution and in the bulk as the shell size increases. This enhancement is attributed to both an "antenna effect", the transfer of energy from the ligand to the core, and a "shell effect", the site isolation or steric exclusion phenomenon that keeps the  $\text{Ln}^{3+}$  cores apart from one another leading to a decrease in their rate of self-quenching.

The shell effect evident in the dendritic systems was identified as an efficient and general principle applicable to many lanthanide elements to improve their luminescence activity. This general approach involving sterically demanding dendritic "shells" may well be used with specially formulated dendrimers or hyperbranched polymers to develop improved laser-related devices such as optical amplifiers.<sup>2</sup> Finally, the very interesting ability of our nonconjugated polyether dendrimers<sup>10</sup> to act as antennas in energy-transfer processes,<sup>20</sup> as outlined above, may make them uniquely suited for the design of specially optical components or energy harvesting devices. We have already demonstrated that a different family of dye-labeled convergent dendrimers may be used to design efficient nanoscale systems for energy harvesting and transduction.<sup>21</sup>

### Experimental Section

**General Directions.** Melting points were determined on a Gallenkamp Melting Point Apparatus and are not corrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on solutions in  $\text{CDCl}_3$ , unless otherwise noted, on a Bruker WM 300 (at 300 and 75 MHz, respectively) spectrometer with the solvent signals used as the standard. FT infrared spectra (FT-IR) were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl crystal disk, unless otherwise noted. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Finnigan Mat LASER-MAT instrument equipped with 337 nm nitrogen laser, using *trans*-3-indoleacrylic acid as the matrix material, observing positive ions.<sup>11</sup> Fast atom bombardment mass spectra (FAB-MS) were obtained on a MS80RF instrument equipped with a krypton primary atom beam using 3-nitrobenzyl alcohol as the matrix material observing positive ions at a scan speed of 30 s/decade. Laser light-scattering experiments were performed on a Wyatt DAWN DSP multiangle light-scattering instrument (Wyatt Technology Co.) in macro batch mode at 632.8 nm wavelength. The  $dn/dc$  parameters of the dendrimers were measured with an Optilab 903 interferometric refractometer (Wyatt Technology Co.) at the same wavelength. Ultraviolet-visible (UV-vis) spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer using a quartz cell (10 mm light path). Luminescence spectra were recorded on a SLM Instruments AMINCO spectrofluorometer equipped with a xenon lamp, using a quartz cell (10 mm light path) for a solution sample. Size-exclusion chromatography (SEC) was performed (THF at 40 °C with nominal flow rate of 1 mL/min) on a liquid chromatograph consisting of a Waters 510 pump, a Waters U6K injector, a Milton Roy RefractoMonitor differential refractometer, and a Viscotek 110 differential viscometer connected in parallel; and four 5- $\mu\text{m}$  PL Gel columns (Polymer Laboratories) with porosities 100, 500, and 1000 Å and Mixed C. The system was calibrated with 16 monodisperse polystyrene samples.

**Materials.** Acetone, THF, methanol, and chlorobenzene (Fisher, Scientific Co.) and ethyl alcohol (Pharmco, dehydrated

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(21) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Polym. Mater. Sci. Eng.* **1997**, *77*, 91.



200 proof) were used as received. Anhydrous toluene and THF were freshly prepared by distillation over calcium hydride and Na/benzophenone. Anhydrous potassium carbonate (Fisher) was freshly ground just prior to use. Anhydrous lanthanide triacetate was prepared by heating the hydrate salt (Aldrich) under a nitrogen stream at 165 °C for 1 h. Analytical thin-layer chromatography (TLC) was performed on commercial Merck DC-Plastikfolien kieselgel 60 F<sub>254</sub> (0.2 mm thick). Silica gel used for flash column chromatography was Merck kieselgel 60 (230–400 mesh ASTM).

**Ethyl 3,5-Dihydroxybenzoate (1).** 3,5-Dihydroxybenzoic acid (60.0 g, 0.389 mol) and sulfuric acid (2.70 g, 0.0275 mol) were dissolved in absolute ethanol (700 mL) with stirring and refluxing. In the course of the reaction, generated water was removed by azeotropic distillation. After 2 days, the reaction reached completion as monitored by TLC (developed by 2:1 hexanes–ethyl acetate). The solvent was removed under reduced pressure to afford an oil, which was directly loaded onto a flash column, and eluted with 18% (v/v) diethyl ether in CH<sub>2</sub>Cl<sub>2</sub>. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to yield **1** as a white crystalline solid: yield 61 g (86%); mp 122 °C; FT-IR 3424 (broad), 3314 (broad), 2985, 1682, 1598, 1511, 1487, 1473, 1456, 1399, 1371, 1341, 1260, 1159, 1121, 1104, 1031, 1003, 963, 876, 856, 846, 778 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 1.32 (t, 3 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.27 (q, 2 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 6.57 (t, 1 H, *J* = 2.3 Hz, *p*-ArH to CO<sub>2</sub>Et), 7.00 (d, 2 H, *J* = 2.3 Hz, *o*-ArH to CO<sub>2</sub>Et), 8.59 (br s, 2 H, OH); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 14.48 (OCH<sub>2</sub>CH<sub>3</sub>), 61.27 (OCH<sub>2</sub>CH<sub>3</sub>), 107.77 (4-ArC), 108.53 (2- and 6-ArC), 133.37 (1-ArC), 159.36 (3- and 5-ArC), 166.58 (CO<sub>2</sub>H). Anal. Calcd for C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>: C, 59.34; H, 5.53. Found: C, 59.16; H, 5.67.

**General Procedure for the Etherification of 1 To Afford the Ester Dendrons (2–4).** The bromide dendron<sup>10</sup> (2.05 equiv), **1** (1.00 equiv), potassium carbonate (2.50 equiv), and 18-crown-6 (0.2 equiv) were dissolved in acetone or THF (the concentration of the phenol group was 0.2 M unless the reaction solution became too viscous) and heated at reflux and stirred vigorously under nitrogen until the bromide dendron was no longer seen on TLC. The mixture was then evaporated to dryness under reduced pressure. The residue was partitioned between water and CH<sub>2</sub>Cl<sub>2</sub> and the aqueous layer was subsequently extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated, and this crude product was purified.

**[G-1]-CO<sub>2</sub>Et (2).** This compound was prepared from benzyl bromide with acetone as a reaction solvent and purified by flash column chromatography eluting with 5:1 hexanes–ethyl acetate to afford **2** as a colorless viscous oil: yield 98%; FT-IR 2924, 2853, 1717, 1594, 1443, 1370, 1296, 1230, 1156, 1048, 766, 735 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.38 (t, 3 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.35 (q, 2 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 5.06 (s, 4 H, PhCH<sub>2</sub>O), 6.79 (t, 1 H, *J* = 2.3 Hz, *p*-ArH to CO<sub>2</sub>Et), 7.29 (d, 2 H, *J* = 2.3 Hz, *o*-ArH to CO<sub>2</sub>Et), 7.32–7.44 (m, 10 H, PhH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.15 (CH<sub>3</sub>), 60.96 (OCH<sub>2</sub>CH<sub>3</sub>), 70.06 (t, *J* = 3.5 Hz, PhCH<sub>2</sub>O), 106.78 (*p*-ArC to CO<sub>2</sub>Et), 108.24 (*o*-ArC to CO<sub>2</sub>Et), 127.42 (*o*-PhC to CH<sub>2</sub>O), 127.93 (*p*-PhC to CH<sub>2</sub>O), 128.44 (*m*-PhC to CH<sub>2</sub>O), 132.28 (ArC next to CO<sub>2</sub>Et), 136.37 (PhC next to CH<sub>2</sub>O), 159.61 (*m*-ArC to CO<sub>2</sub>Et), 166.04 (CO<sub>2</sub>Et). Anal. Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>: C, 76.22; H, 6.12. Found: C, 76.49; H, 6.32.

**[G-3]-CO<sub>2</sub>Et (3).** This compound was prepared from [G-2]-Br<sup>10</sup> with acetone as a reaction solvent and purified by flash column chromatography eluting with 1:1 to 3:1 CH<sub>2</sub>Cl<sub>2</sub>–hexanes to give **3** as a colorless glass: yield 94%; FT-IR 1720, 1595, 1450, 1373, 1297, 1156, 1047, 834, 737, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.35 (t, 3 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.34 (q, 2 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.94 (s, 8 H, ArCH<sub>2</sub>O), 4.97 (s, 4 H, ArCH<sub>2</sub>O), 4.99 (s, 16 H, PhCH<sub>2</sub>O), 6.51–6.55 (m, 6 H, ArH), 6.64–6.65 (m, 12 H, ArH), 6.76 (t, 1 H, *J* = 2.3 Hz, *p*-ArH to CO<sub>2</sub>Et), 7.26–7.45 (m, 42 H, PhH and ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.30 (CH<sub>3</sub>), 61.15 (OCH<sub>2</sub>CH<sub>3</sub>), 69.99 (PhCH<sub>2</sub>O), 70.03 (ArCH<sub>2</sub>O), 70.08 (ArCH<sub>2</sub>O), 101.58, 101.65, 106.35 and 106.46 (ArC), 106.87 (*p*-ArC to CO<sub>2</sub>Et), 108.41 (*o*-ArC to CO<sub>2</sub>Et), 127.53 (*o*-PhC to CH<sub>2</sub>O), 127.98 (*p*-PhC to CH<sub>2</sub>O), 128.56 (*m*-PhC to CH<sub>2</sub>O), 132.44 (ArC next to CO<sub>2</sub>Et), 136.73 (PhC next

to CH<sub>2</sub>O), 138.84 and 139.15 (ArC), 159.65 (*m*-ArC to CO<sub>2</sub>Et), 160.06 and 160.14 (ArC), 166.20 (CO<sub>2</sub>Et); MALDI-TOF calcd for C<sub>107</sub>H<sub>94</sub>O<sub>16</sub> *m/z* 1674.9 (M + K), found *m/z* 1666.8 as a single peak. Anal. Calcd for C<sub>107</sub>H<sub>94</sub>O<sub>16</sub>: C, 78.56; H, 5.79. Found: C, 78.73; H, 5.53.

**[G-4]-CO<sub>2</sub>Et (4).** This compound was prepared from [G-3]-Br<sup>10</sup> with THF as a reaction solvent and purified by flash column chromatography eluting with 10:3 CH<sub>2</sub>Cl<sub>2</sub>–hexanes to give **4** as a colorless glass: yield 97%; FT-IR 3033, 2874, 1716, 1595, 1498, 1450, 1373, 1297, 1156, 1048, 911, 833, 737 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.33 (t, 3 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.31 (q, 2 H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.92–5.03 (m, 60 H, PhCH<sub>2</sub>O and ArCH<sub>2</sub>O), 6.48–6.57 (m, 14 H, ArH), 6.60–6.68 (m, 28 H, ArH), 6.75 (t, 1 H, *J* = 2.2 Hz, *p*-ArH to CO<sub>2</sub>Et), 7.20–7.41 (m, 82 H, PhH and ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.28 (CH<sub>3</sub>), 61.12 (OCH<sub>2</sub>CH<sub>3</sub>), 69.92, 69.98 and 70.02 (PhCH<sub>2</sub>O and ArCH<sub>2</sub>O), 101.55, 106.34 and 106.38 (ArC), 106.80 (*p*-ArC to CO<sub>2</sub>Et), 108.45 (*o*-ArC to CO<sub>2</sub>Et), 127.52 (*o*-PhC to CH<sub>2</sub>O), 127.95 (*p*-PhC to CH<sub>2</sub>O), 128.53 (*m*-PhC to CH<sub>2</sub>O), 132.40 (ArC next to CO<sub>2</sub>Et), 136.73 (PhC next to CH<sub>2</sub>O), 138.91 and 139.17 (ArC), 159.62 (*m*-ArC to CO<sub>2</sub>Et), 160.01 and 160.10 (ArC), 166.15 (CO<sub>2</sub>Et); MALDI-TOF calcd for C<sub>219</sub>H<sub>190</sub>O<sub>32</sub> *m/z* 3372.9 (M + K), found *m/z* 3372.7 as a single peak. Anal. Calcd for C<sub>219</sub>H<sub>190</sub>O<sub>32</sub>: C, 78.90; H, 5.74. Found: C, 78.92; H, 5.86.

**Preparation of the Acid Dendrons (5–7).** **[G-1]-CO<sub>2</sub>H (5).** To a solution of the ester dendron **2** (18.0 g, 49.7 mmol, 1.00 equiv) in THF (200 mL) was added potassium hydroxide (3.84 g, 68.4 mmol, 1.38 equiv) dissolved in 30 mL of water. Methanol (80 mL) was then added to this two-phase system to produce a homogeneous solution. This mixture was heated at reflux for 20 min then poured into 1.3% acetic acid aqueous solution (1400 mL) dropwise with vigorous stirring to afford a white solid. The solid was filtered off and washed with water. The crude product was recrystallized from acetone to give **5** as a white crystalline solid: yield 15.6 g (94%); mp 198–201 °C; FT-IR (KBr disk) 3300–2100 (broad), 1693, 1596, 1446, 1423, 1379, 1346, 1302, 1217, 1166, 1059, 1030, 853, 769, 755, 738 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 5.17 (s, 4 H, PhCH<sub>2</sub>O), 6.92 (s, 1 H, *p*-ArH to CO<sub>2</sub>H), 7.25–7.49 (m, 12 H, PhH and ArH), 11.3 (br s, 1H, CO<sub>2</sub>H); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 70.84 (PhCH<sub>2</sub>O), 107.62 (*p*-ArC to CO<sub>2</sub>H), 109.38 (*o*-ArC to CO<sub>2</sub>H), 128.47 (*o*-PhC to CH<sub>2</sub>O), 128.73 (*p*-PhC to CH<sub>2</sub>O), 129.33 (*m*-PhC to CH<sub>2</sub>O), 133.50 (ArC next to CO<sub>2</sub>H), 138.03 (PhC next to CH<sub>2</sub>O), 160.94 (*m*-ArC to CO<sub>2</sub>H), 167.20 (CO<sub>2</sub>H). Anal. Calcd for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>: C, 75.43; H, 5.43. Found: C, 75.35; H, 5.60.

**[G-3]-CO<sub>2</sub>H (6).** To a solution of the ester dendron **3** (4.88 g, 2.98 mmol, 1.00 equiv) in THF (50 mL) was added potassium hydroxide (0.33 g, 5.88 mmol, 1.97 equiv) dissolved in 4.0 mL of water. Methanol (20 mL) was then added to this two-phase system to give a homogeneous solution. This was heated at reflux for 4 h then poured into 500 mL of dilute hydrochloric acid (containing 20 mmol of HCl) dropwise with vigorous stirring to give a viscous precipitate. The precipitated crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (70 mL), washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography eluting with 10:1 CH<sub>2</sub>Cl<sub>2</sub>–diethyl ether to afford **6** as a white crystalline solid: yield 4.6 g (96%); mp 150–151 °C; FT-IR (KBr) 2871, 1693, 1595, 1498, 1451, 1373, 1299, 1157, 1044, 831, 737 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.95 (s, 8 H, ArCH<sub>2</sub>O), 4.98 (s, 4 H, ArCH<sub>2</sub>O), 5.00 (s, 16 H, PhCH<sub>2</sub>O), 6.53–6.55 (m, 6 H, ArH), 6.64–6.66 (m, 12 H, ArH), 6.82 (t, 1 H, *J* = 2.6 Hz, *p*-ArH to CO<sub>2</sub>H), 7.23–7.40 (m, 42 H, PhH and ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 70.14 (PhCH<sub>2</sub>O and ArCH<sub>2</sub>O), 101.69, 101.82, 106.42 and 106.53 (ArH), 108.07 (*p*-ArC to CO<sub>2</sub>H), 108.99 (*o*-ArC to CO<sub>2</sub>H), 127.52 (*o*-PhC to CH<sub>2</sub>O), 127.97 (*p*-PhC to CH<sub>2</sub>O), 128.56 (*m*-PhC to CH<sub>2</sub>O), 130.91 (ArC next to CO<sub>2</sub>H), 136.81 (PhC next to CH<sub>2</sub>O), 138.79 and 139.22 (ArC), 159.79 (*m*-ArC to CO<sub>2</sub>H), 160.12 and 160.20 (ArC), 169.60 (CO<sub>2</sub>H); MALDI-TOF calcd for C<sub>105</sub>H<sub>90</sub>O<sub>16</sub> *m/z* 1630.8 (M + Na), found *m/z* 1632.4 as a single peak. Anal. Calcd for C<sub>105</sub>H<sub>90</sub>O<sub>16</sub>: C, 78.43; H, 5.64. Found: C, 78.26; H, 5.46.

**[G-4]-CO<sub>2</sub>H (7).** To a solution of the ester dendron **4** (2.13 g, 0.639 mmol, 1.00 equiv) in THF (60 mL) was added KOH

(0.12 g, 2.14 mmol, 3.35 equiv) dissolved in 1.9 mL of water. Then methanol (13 mL) was added to this two-phase system to produce a homogeneous solution. This was heated at reflux for 2 h and then poured into 500 mL of dilute hydrochloric acid (10 mmol of HCl) dropwise with vigorous stirring to yield a viscous precipitate. The precipitated product was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), washed (water), dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated to dryness under reduced pressure. The crude product purified by flash column chromatography (4:1 to 10:1  $\text{CH}_2\text{Cl}_2$ -diethyl ether) afforded **7** as a colorless glass: yield 1.9 g (90%); FT-IR 1692, 1595, 1499, 1453, 1375, 1296, 1157, 1053, 833, 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.89–5.00 (m, 60 H,  $\text{PhCH}_2\text{O}$  and  $\text{ArCH}_2\text{O}$ ), 6.49–6.51 (m, 14 H,  $\text{ArH}$ ), 6.62–6.63 (m, 28 H,  $\text{ArH}$ ), 6.76 (m, 1 H,  $p\text{-ArH}$  to  $\text{CO}_2\text{H}$ ), 7.24–7.36 (m, 82 H,  $\text{PhH}$  and  $\text{ArH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  69.68 and 69.98 ( $\text{PhCH}_2\text{O}$  and  $\text{ArCH}_2\text{O}$ ), 95.24, 96.63, 99.25, 101.53 and 106.32 ( $\text{ArC}$ ), 127.42 and 127.50 ( $o\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 127.73 and 127.93 ( $p\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 128.35 and 128.51 ( $m\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 136.72 ( $\text{PhC}$  next to  $\text{CH}_2\text{O}$ ), 138.82, 139.17, 159.73, 159.83, 159.99, 160.07 and 160.11 ( $\text{ArC}$ ), 169.60; MALDI-TOF calcd for  $\text{C}_{217}\text{H}_{186}\text{O}_{32}$   $m/z$  3344.8 (M + K), found  $m/z$  3347.2 as a single peak. Anal. Calcd for  $\text{C}_{217}\text{H}_{186}\text{O}_{32}$ : C, 78.84; H, 5.67. Found: C, 79.06; H, 5.49.

**Synthesis of the Dendron with 2,5-Disubstituted Benzoic Acid Focal Point Moiety. Ethyl 2,5-Dihydroxybenzoate (8).** 2,5-Dihydroxybenzoic acid (12.00 g, 86.9 mmol) was heated in absolute ethanol (600 mL) with sulfuric acid (1.66 g) at reflux for 24 h followed by the removal of the solvent (about 450 mL) by distillation with generated water as an azeotropic mixture, and the addition of absolute ethanol (450 mL). After an additional 48 h reflux the solvent was distilled off until the solution volume was approximately 20 mL. The resulting residue was then purified by flash column chromatography ( $\text{CH}_2\text{Cl}_2$ -hexanes 4:1) to afford **8** as a crystalline solid: yield 11.87 g (75%); mp 76–77 °C; FT-IR (KBr) 3405, 3240, 3000, 1674, 1608, 1326, 1227, 1017, 868, 837, 786, 663  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.38 (t, 3H,  $J = 7.1$  Hz,  $\text{CH}_3$ ), 4.37 (q, 2H,  $J = 7.1$  Hz,  $\text{CH}_2$ ), 4.80 (br s, 1H,  $\text{OH}$ ), 6.86 (d, 1H,  $J = 9.8$  Hz,  $\text{ArH}$ ), 7.00 (dd, 1H,  $J = 3.4$  and 9.8 Hz,  $\text{ArH}$ ), 7.29 (d, 1H,  $J = 3.4$  Hz,  $\text{ArH}$ ), 10.41 (s, 1H,  $\text{OH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.06 ( $\text{CH}_3$ ), 61.59 ( $\text{CH}_2$ ), 112.41, 114.83, 118.36, 123.95, 147.75 and 155.51 ( $\text{ArC}$ ), 169.81 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ). Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{O}_4$ : C, 59.34; H, 5.53. Found: C, 59.14; H, 5.65.

**2,5-[G-4]-CO<sub>2</sub>Et (9).** [G-3]-Br<sup>10</sup> (11.19 g, 6.75 mmol; 2.05 equiv), **8** (0.60 g, 3.3 mmol; 1.0 equiv), 18-crown-6 (0.43 g, 1.6 mmol; 0.50 equiv) and freshly ground  $\text{K}_2\text{CO}_3$  (2.27 g, 16.4 mmol; 5.00 equiv) were mixed and stirred vigorously in tetrahydrofuran (65 mL) at reflux for 22 h followed by the evaporation of the solvent. The resulting residue was partitioned between water (300 mL) and  $\text{CH}_2\text{Cl}_2$  (100 mL), and the aqueous layer was extracted by  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The combined organic layer was washed by water (100 mL) once and dried over  $\text{Na}_2\text{SO}_4$  followed by filtration and evaporation to dryness under reduced pressure. The obtained crude product was purified by flash column chromatography eluting with  $\text{CH}_2\text{Cl}_2$ -hexanes (4:1) to afford ester dendron **9** as a colorless glass: yield 9.31 g (85%); FT-IR (NaCl) 3032, 2873, 1723, 1595, 1498, 1451, 1374, 1295, 1205, 1158, 1047, 833, 737  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (t, 3 H,  $J = 7.1$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.27 (q, 2 H,  $J = 7.1$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.88–4.97 (m, 60 H,  $\text{CH}_2\text{O}$ ), 6.50–6.53 (m, 14 H,  $\text{ArH}$ ), 6.62–6.74 (m, 26 H,  $\text{ArH}$ ), 6.72 (d, 2 H,  $J = 1.8$  Hz,  $\text{ArH}$ ), 6.79 (d, 1 H,  $J = 9.2$  Hz,  $m\text{-ArH}$  to  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 6.92 (dd, 1 H,  $J = 3.2$  and 9.2 Hz,  $p\text{-ArH}$  to  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 7.23–7.43 (m, 81 H,  $\text{ArH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.28 ( $\text{OCH}_2\text{CH}_3$ ), 60.97 ( $\text{OCH}_2\text{CH}_3$ ), 69.91, 69.96, 70.01, 70.44 and 71.49 ( $\text{PhCH}_2\text{O}$  and  $\text{ArCH}_2\text{O}$ ), 101.34, 101.52, 105.89, 106.32, 116.06, 117.24, 119.84 and 121.86 ( $\text{ArC}$ ), 127.51 ( $o\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 127.95 ( $p\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 128.52 ( $m\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 136.70 ( $\text{PhC}$  next to  $\text{CH}_2\text{O}$ ), 139.15, 139.28, 139.59, 152.42, 159.94, 159.97, 160.00 and 160.09 ( $\text{ArC}$ ), 165.89 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ); MALDI-TOF calcd for  $\text{C}_{219}\text{H}_{190}\text{O}_{32}$   $m/z$  3371.89 (M + K), found  $m/z$  3383.7 as a single peak. Anal. Calcd for  $\text{C}_{219}\text{H}_{190}\text{O}_{32}$ : C, 78.90; H, 5.74. Found: C, 79.00; H, 6.00.

**2,5-[G-4]-CO<sub>2</sub>H (10).** To a solution of the ester dendron **9** (3.20 g, 0.960 mmol; 1.00 equiv) in tetrahydrofuran (33 mL)

and methanol (7.2 mL) was added potassium hydroxide (0.16 g, 2.85 mmol; 2.97 equiv) dissolved in 2.8 mL of water, and was then heated at reflux for 5 h with stirring. The solution was then poured into 200 mL of 5% hydrochloric acid dropwise with vigorous stirring to produce a viscous precipitate. The precipitated product was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography eluting with  $\text{CH}_2\text{Cl}_2$ -hexanes (4:1) to yield **10** as a colorless glass: yield 3.05 g (96%); FT-IR (NaCl) 3033, 2931, 2874, 1737, 1595, 1498, 1451, 1375, 1344, 1322, 1296, 1156, 1053, 833, 737  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.91–4.99 (m, 60 H,  $\text{CH}_2\text{O}$ ), 6.50–6.57 (m, 16 H,  $\text{ArH}$ ), 6.60–6.64 (m, 26 H,  $\text{ArH}$ ), 6.83 (d, 1 H,  $J = 9.2$  Hz,  $m\text{-ArH}$  to  $\text{CO}_2\text{H}$ ), 7.02 (dd, 1H,  $J = 3.1$  and 9.2 Hz,  $p\text{-ArH}$  to  $\text{CO}_2\text{H}$ ), 7.22–7.43 (m, 80 H,  $\text{PhH}$ ), 7.71 (d, 1H,  $J = 3.1$  Hz,  $o\text{-ArH}$  to  $\text{CO}_2\text{H}$ ), 10.95 (br s, 1H,  $\text{CO}_2\text{H}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  69.86, 69.96, 70.25 and 72.43 ( $\text{PhCH}_2\text{O}$  and  $\text{ArCH}_2\text{O}$ ), 101.48, 102.44, 106.29, 106.58, 114.61, 117.50, 118.40 and 122.49 ( $\text{ArC}$ ), 127.47 ( $o\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 127.91 ( $p\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 128.49 ( $m\text{-PhC}$  to  $\text{CH}_2\text{O}$ ), 136.67 ( $\text{PhC}$  next to  $\text{CH}_2\text{O}$ ), 136.76, 138.79, 138.87, 139.12, 139.15, 151.52, 153.39, 159.96, 159.98, 160.05 and 160.25 ( $\text{ArC}$ ), 164.91 ( $\text{CO}_2\text{H}$ ); MALDI-TOF calcd for  $\text{C}_{217}\text{H}_{186}\text{O}_{32}$   $m/z$  3343.84 (M + K), found  $m/z$  3356.2 as a single peak. Anal. Calcd for  $\text{C}_{217}\text{H}_{186}\text{O}_{32}$ : C, 78.84; H, 5.67. Found: C, 79.00; H, 5.83.

**General Procedure for the Preparation of the Lanthanide-Cored Dendrimer Complexes (11–20).** An appropriate acid dendron (in 0.5–1 g scale; 3.00 equiv) and anhydrous lanthanide triacetate (1.00 equiv) were stirred vigorously in chlorobenzene (20–30 mL) held at reflux. The generated acetic acid was distilled off with chlorobenzene continuously during the reaction for 1.5 h followed by final evaporation to dryness under reduced pressure. The product was stored in a vacuum desiccator over  $\text{CaSO}_4$  until use in the luminescence studies.

**[G-1]<sub>3</sub>-Er (11).** This compound was made from the acid dendron **5** and anhydrous erbium triacetate as a slightly pink glass: yield 99%; FT-IR 3034, 1528, 1499, 1455, 1440, 1417, 1377, 1213, 1160, 1056, 844, 786, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{63}\text{H}_{51}\text{ErO}_{12}$ : C, 64.82; H, 4.40; ash (as  $\text{Er}_2\text{O}_3$ ), 16.38. Found: C, 64.78; H, 4.60; ash, 16.60.

**[G-3]<sub>3</sub>-Er (12).** This compound was made from the acid dendron **6** and anhydrous erbium triacetate as a slightly pink glass: yield 97%; FT-IR 1596, 1498, 1451, 1374, 1214, 1156, 1053, 833, 787, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{315}\text{H}_{267}\text{ErO}_{48}$ : C, 75.85; H, 5.40; ash (as  $\text{Er}_2\text{O}_3$ ), 3.83. Found: C, 76.04; H, 5.33; ash, 4.01.

**[G-4]<sub>3</sub>-Er (13).** This compound was made from the acid dendron **7** and anhydrous erbium triacetate as a light amber glass: yield 99%; FT-IR 1597, 1497, 1453, 1375, 1296, 1157, 1053, 833, 735, 696  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{651}\text{H}_{555}\text{ErO}_{96}$ : C, 77.56; H, 5.55; ash (as  $\text{Er}_2\text{O}_3$ ), 1.90. Found: C, 77.39; H, 5.45; ash, 1.67.

**[G-1]<sub>3</sub>-Eu (14).** This compound was made from the acid dendron **5** and anhydrous europium triacetate as a slightly yellow glass: yield 98%; FT-IR 3033, 1534, 1455, 1440, 1413, 1376, 1289, 1213, 1157, 1055, 1028, 842, 786, 736  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{63}\text{H}_{51}\text{EuO}_{12}$ : C, 65.68; H, 4.46; ash (as  $\text{Eu}_2\text{O}_3$ ), 15.27. Found: C, 64.14; H, 4.65; ash, 16.24.

**[G-3]<sub>3</sub>-Eu (15).** This compound was made from the acid dendron **6** and anhydrous europium triacetate as a slightly yellow glass: yield 99%; FT-IR 3032, 2872, 1596, 1498, 1451, 1412, 1373, 1343, 1296, 1214, 1158, 1047, 832, 786, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{315}\text{H}_{267}\text{EuO}_{48}$ : C, 76.09; H, 5.41; ash (as  $\text{Eu}_2\text{O}_3$ ), 3.54. Found: C, 76.30; H, 5.46; ash, 3.60.

**[G-4]<sub>3</sub>-Eu (16).** This compound was made from the acid dendron **7** and anhydrous europium triacetate as a light amber glass: yield 97%; FT-IR 3032, 2873, 1596, 1498, 1453, 1374, 1322, 1296, 1214, 1157, 1054, 1046, 833, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{651}\text{H}_{555}\text{EuO}_{96}$ : C, 77.68; H, 5.56; ash (as  $\text{Eu}_2\text{O}_3$ ), 1.75. Found: C, 77.58; H, 5.38; ash, 1.89.

**[G-1]<sub>3</sub>-Tb (17).** This compound was made from the acid dendron **5** and anhydrous terbium triacetate as a slightly yellow glass: yield 99%; FT-IR 3032, 1534, 1455, 1414, 1376,

1212, 1157, 1047, 1028, 843, 786, 736  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{63}\text{H}_{51}\text{TbO}_{12}$ : C, 65.29; H, 4.43; ash (as  $\text{Tb}_2\text{O}_3$ ), 15.78. Found: C, 63.48; H, 4.45; ash, 17.85.

**[G-3]<sub>3</sub>-Tb (18).** This compound was made from the acid dendron **6** and anhydrous terbium triacetate as a slightly yellow glass: yield 99%; FT-IR 3032, 2873, 1596, 1498, 1453, 141, 1374, 1343, 1296, 1214, 1156, 1047, 832, 786, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{315}\text{H}_{267}\text{TbO}_{48}$ : C, 75.98; H, 5.40; ash (as  $\text{Tb}_2\text{O}_3$ ), 3.67. Found: C, 75.99; H, 5.57; ash, 3.90.

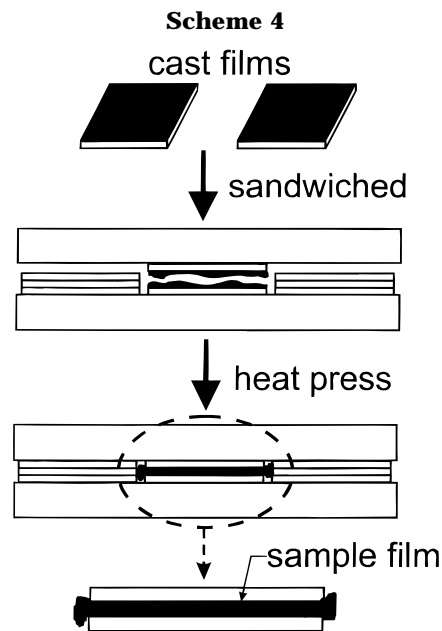
**[G-4]<sub>3</sub>-Tb (19).** This compound was made from the acid dendron **7** and anhydrous terbium triacetate as a light amber glass: yield 96%; FT-IR 3032, 2874, 1596, 1498, 1453, 1374, 1322, 1296, 1214, 1157, 1047, 833, 737  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{651}\text{H}_{555}\text{TbO}_{96}$ : C, 77.62; H, 5.55; ash (as  $\text{Tb}_2\text{O}_3$ ), 1.81. Found: C, 77.80; H, 5.72; ash, 1.66.

**{2,5-[G-4]<sub>3</sub>-Tb (20).** This compound was made from the acid dendron **10** and anhydrous terbium triacetate as a light amber glass: yield 100%; FT-IR 3032, 2872, 1595, 1498, 1452, 1374, 1296, 1213, 1156, 1054, 832, 737  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{651}\text{H}_{555}\text{TbO}_{96}$ : C, 77.62; H, 5.55; ash (as  $\text{Tb}_2\text{O}_3$ ), 1.81. Found: C, 77.48; H, 5.70; ash, 1.07.

**Luminescence Experiments. Solution Luminescence Study.** Initially a  $3 \times 10^{-3}$  mM solution in anhydrous toluene was prepared for both the terbium- and europium-cored dendrimer complexes (**14**–**19**). This stock solution was diluted with additional anhydrous toluene to afford  $3 \times 10^{-4}$ ,  $3 \times 10^{-5}$ , and  $3 \times 10^{-6}$  mM solutions. Excitation spectra were recorded (emission at 616 nm for the europium complex [G-4]<sub>3</sub>-Tb (**16**), and at 545 nm for the terbium complex [G-4]<sub>3</sub>-Tb (**19**)). Emission spectra were recorded with the excitation at the maximum intensity wavelength in the excitation spectra (315 nm for [G-1]<sub>3</sub>-Ln, 289 nm for the others). For the comparison of the isomeric structure, solutions of the isomeric complexes [G-4]<sub>3</sub>-Tb (**19**) and {2,5-[G-4]<sub>3</sub>-Tb (**20**) ( $2.1 \times 10^{-2}$  mM each) in anhydrous THF were prepared, and both excitation spectra (544 nm emission) and emission spectra (294 and 334 nm excitation, respectively, at which they gave maximum intensity in the excitation spectra) were recorded.

**Hydration Experiment.** The terbium-cored dendrimer complexes (**17**–**19**) were used in this experiment. Each compound (0.015 mmol) was put into a 5 mL volumetric flask and dissolved in about 3 mL of distilled mesitylene at reflux with a gentle bubbling of dry nitrogen to remove residual amount of water for 15 min. The solution was cooled to room temperature with nitrogen bubbling, and the volume was adjusted as 5 mL to afford a 3 mM solution. The 3 mM solution (0.50 mL) and anhydrous THF (2.00 mL) were combined and mixed well in the quartz cell just prior to the luminescence measurement. To obtain the spectra with  $\text{H}_2\text{O}$  coordination, THF (anhydrous)–water 70:30 by weight (3 drops, ca. 0.05 g) was added to the combined solution in the cell and was mixed thoroughly. To obtain the spectra with  $\text{D}_2\text{O}$  coordination, THF (anhydrous)– $\text{D}_2\text{O}$  70:30 by weight (3 drops, ca. 0.05 g) was added to a newly prepared combined solution and was mixed thoroughly in the cell. Emission spectra were taken (excitation at 324 nm), and the intensity of the main peak at 546 nm was used for the calculation of the number of the coordinated water molecules to  $\text{Tb}^{3+}$ . This procedure was also applied to the europium-cored dendrimer complexes (**14**–**16**), using an emission at 617 nm (excitation at 352 nm).

**Bulk State Luminescence Study.** [G-4]<sub>3</sub>-Eu (**16**) (0.3403 g, 0.0338 mmol) was weighed in a 5 mL volumetric flask and dissolved in chlorobenzene (about 3 mL) with gentle nitrogen bubbling. This mixture was allowed to boil in a oil bath for 3 min followed by cooling to room temperature with the continuous nitrogen bubbling. The volume was then adjusted as 5 mL (solution A). Two kinds of mixture, [G-1]<sub>3</sub>-Eu (**14**) (0.0389 g, 0.0338 mmol)/2,5-[G-4]-CO<sub>2</sub>Et (**9**) (0.3014 g) and [G-3]<sub>3</sub>-Er (**15**) (0.1681 g, 0.0338 mmol)/**9** (0.1722 g), were also handled in the same manner to afford solutions (solutions B and C, respectively). These three solutions contained the same weight of solute and had the same concentration of  $\text{Eu}^{3+}$ . The ester dendron **9** (0.6806 g) was also treated in the same manner except for using a 10 mL volumetric flask to afford a solution



(solution D). Solution D was used to dilute other solutions (A, B, and C) to afford 2 and 10 times diluted solutions for each, thereby obtaining three different concentrations for the complexes **14**, **15**, and **16**. Each solution (about 2 mL) was carefully spread onto two pieces of microscope cover glass ( $2.2 \times 2.2$  cm<sup>2</sup>, 0.015 cm thick) kept horizontally on a hot plate (about 150 °C) under a gentle nitrogen stream (using a funnel upside down connected with a dry nitrogen stream) to allow evaporation followed by intensive removal of the solvent in a vacuum oven at 65 °C for 16 h. The resulting two cast films on the cover glass were then sandwiched and gently pressed between glass plates on a hot plate (about 120 °C) with three stacked pieces of the cover glass as a spacer (150  $\mu\text{m}$  thick  $\times$  3) to ensure that the film thickness was the same as that of a piece of the cover glass (Scheme 4). Three series of transparent films with  $[\text{Eu}^{3+}] = 1.51, 0.755, \text{ and } 0.151$  wt % were obtained. The films were kept in a vacuum desiccator over  $\text{CaSO}_4$  until just prior to the measurement. Luminescence was measured using the film sample firmly held by a miniature vise, which allows the incident beam to enter through one of the cover glasses at exactly the same angle for all of the samples. Excitation spectra were taken (emission at 612 nm). Measurements were made at four different locations on a film, and the averaged intensity of a peak at 462 nm (after subtraction of the baseline intensity) was used for the comparison.

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