Improved Antenna Effect of Terbium(III)-Cored Dendrimer Complex and Green-Luminescent Hydrogel by Radical Copolymerization

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Received September 17, 2003. Revised Manuscript Received March 7, 2004

This study explored practical applications of the unique green fluorescence of terbium(III)-cored poly(benzyl ether) dendrimer complexes for luminescence polymeric materials. At first, to maximize the fluorescence ability, we examined the influence of the isomerism in the dendron skeleton, both at the focal point and the hyperbranch repeating unit. Next, a 4-vinylphenyl group was successfully introduced at the terminal of the dendron subunit for radical polymerization. A 3,4-dioxybenzoate moiety for the focal point of the dendron gave stronger fluorescence than the usual 3,5-isomer; however, the authentic 3,5-dioxybenzyl ether moiety appeared the best hyperbranch repeating unit for the fluorescence ability. The terminal vinyl groups enabled the copolymerization of the terbium(III)-cored dendrimer complex with *N*-isopropylacrylamide, resulting in a green-fluorescent, clear hydrogel. The hydrogel showed a gel phase transition at 33−35 °C to exhibit temperature-induced switching in the opacity.

Introduction

The aromatic dendritic scaffold is recognized to show a distinct light-harvesting function, which has been called energy funnels and/or antenna effects. The poly(benzyl ether) (PBE) dendron[1] has been recognized to have a remarkable antenna effect. For example, an organic photofunctional moiety such as poly(phenyleneethynylene)[2] was connected to the focal point of the PBE dendron and exhibited a concentration of photon energy absorbed by the PBE dendron. Antenna effects of metal complexes comprising PBE dendron subunits have been reported, e.g., lanthanides (Tb^{3+} and Eu^{3+}),[3] ruthenium (Ru^{2+}),[4,5] and copper.[6]

The Tb^{3+}-cored dendrimer complex (TbDC) has been one of the most successful fluorescence antenna system so far. TbDC is attractive for luminescence applications, because of its green-fluorescent, organic-soluble, film-forming, amorphous character. The essential advantages of TbDC for organic fluorescence dyes come from the intrinsic nature of the Tb^{3+} cation, which has a long fluorescence lifetime (millisecond order), large Stokes shift (more than 150 nm), and narrow emission bands (color purity).

The incorporation of TbDC in transparent, common, polymeric materials is the most practical method for wide applications, together with the basic improvement of the fluorescence ability of TbDC. Thus, we had two aims in this study. First, we tried to maximize the fluorescence ability of TbDC by the investigation of the variety of the chemical structure of PBE dendrons. Second, we tried to introduce radical polymerizing vinyl groups to the TbDC molecule for the copolymerization with common vinyl monomers (e.g., acrylic monomers and styrene derivatives).

The antenna effect of TbDC has been partly attributed to the space-occupying, shape-persistent nature (i.e., site-isolation) of dendron,[3] shielding the focal Tb^{3+} from the quenching interactions coming from the outer environment. However, dramatic changes in the efficiency of the antenna effects have been observed upon tiny structural modifications at the focal point of the PBE dendrons.[3,7] Only one isomeric difference on the focal benzene ring did harm the antenna effect of the whole macromolecule, even for a large PBE dendron (fourth-generation, $M_w > 3000$).[3] We believe that the difference at the focal point in the large dendritic skeleton is negligible in terms of the site-isolation ability of the whole macromolecule.

We examined the influence of local isomerism in PBE dendrons, both at the focal point and in the dendritic branching units, to improve the antenna effect of TbDC. Furthermore, we developed a radical copolymerizable TbDC, affording a green-fluorescent, temperature-

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10.1021/cm034873e CCC: $27.50

responding, *N*-isopropylacrylamide hydrogel as an example polymeric application.

Experimental Section

Notations of the Compounds. Two kinds of notations were used for the dendritic compounds prepared in this study. A general notation [G-*n*-*p*]-X stands for the series of poly(3,5-dihydroxybenzyl ether) dendrons bearing various substitutions on the focal benzene ring, where *p* (two- or three-digit number) refers to the number for the substitution positions on the focal benzene ring, *n* refers to the generation of the dendron, and X refers to the functional group located at the focal point of the dendron. Another notation [*q*/G-2]-X stands for the series of second generation poly(dihydroxybenzyl ether) dendrons bearing standard 3,5-substituted focal benzene ring and various substitutions on the branching benzene rings, where *q* (two-digit number) refers to the number for the substitution positions on the branching benzene ring and X refers to the functional group located at the focal point of the dendron.

Reagents and Materials. All the organic reagents used were purchased from Tokyo Kasei Co., except for 3,5-dihydroxybehzyl alcohol, which was from Aldrich Co. Anhydrous potassium carbonate was purchased from Kanto Kagaku Co. Chlorobenzene and dichloromethane were purchased from Kishida Kagaku Co. Acetone was purchased from Kokusan Kagaku Co. Potassium hydroxide and other organic solvents were purchased from Junsei Kagaku Co. All the reagents and solvents were used as supplied without further purification unless noted. Purified THF was obtained by the distillation from sodium hydride at ambient pressure. Purified dichloromethane was obtained by the distillation from P_2O_5 at ambient pressure. Anhydrous terbium(III) acetate was prepared from the corresponding hydrate salt (Aldrich Co.) by heating at 160 °C under a dry nitrogen stream for 30 min. Reactions were monitored by silica gel thin-layer chromatography (TLC, from Aldrich Co.). Silica gel column chromatography was performed using Woko Gel C-200 (Woko Junyaku Co.) for purification. Dried silica gel was prepared at 250 °C under nitrogen stream for 6 h for the purification of unstable bromide dendrons.

Synthesis. All the PBE dendron synthesis was essentially the same as the established etherification/bromination reaction.[1,3] Detailed synthetic procedure and characterization data are available as Supporting Information.

Measurement of Spectra. ^1H and ^{13}C NMR spectra (δ in ppm, 0 ppm was set at the signal from tetramethylsilane) were measured by a JNM-EX270 spectrometer (JEOL) at 270.05 and 67.80 MHz, respectively, using $CDCl_3$ as the solvent unless noted. FT infrared spectra (FTIR) were obtained using an FT/IR-8000 spectrometer (JASCO). MALDI-TOF mass spectra were measured by an Elite spectrometer (PerSeptive Biosystems) at the acceleration voltage of 20 000 V, using *trans*-3-indolacrylic acid as matrix material. Absorption spectra were taken by a UV-3100S UV−vis−NIR recording spectrophotometer (Shimadzu) with a 10-mm quartz cell at 23 °C.

Fluorescence Experiments. Fluorescence spectra were measured by an F-4500 spectrometer (Hitachi; 150 W Xe lamp) with a 10-mm quartz cell at 23 °C. All the samples for the fluorescence spectra were stored in a vacuum desiccator until just before the measurement so as not to be influenced by moisture. Except for the quantum yield measurement, the concentration of the solution used for the fluorescence observation was 3 μmol/L using purified solvents (THF and dichloromethane). The excitation wavelength of the emission spectra (emission wavelength: 542 nm) was set at the wavelength giving the maximum in the corresponding excitation spectra. The fluorescence lifetime was measured in tetrahydrofuran (0.1 mmol/L at 23 °C) using a 337 nm nitrogen laser pulse (5 ns pulse width with 100 ms interval) as the excitation light. Fluorescence quantum yields were evaluated as relative values based on the known value for quinine sulfate (0.55 in water).[2] Quinine sulfate was dissolved as the reference material in 0.5 mol/L H_2SO_4 aqueous solution at 4.0 μmol/L concentration. TbDCs were dissolved in purified dichloromethane at 1.3 μmol/L. All the solutions were freshly prepared just before the measurements. First of all, absorption data were taken. The absorption spectrum of the quinine sulfate solution was taken, affording an absorbance (A_r) at the maximum of the spectrum. Absorption spectra of the TbDCs were taken, and the absorbance (A_s) was recorded at the wavelength where the maximum was given in the corresponding excitation spectrum. Next, emission data were taken. Emission spectrum of the quinine sulfate solution was taken excited at the maximum wavelength of the absorption spectrum, affording the area of the emission band (E_r). Emission spectra of the TbDCs were taken excited at the wavelength where the maximum was given in the corresponding excitation spectrum, affording the area of the emission bands of Tb^{3+} (E_s). The calculation of the relative fluorescence quantum yield (f_s, %) was based on the following equation: $f_s = 0.55(A_r/A_s)(E_s/E_r)(n_s/n_r)^2 \times 100$, where n_s and n_r are the refractive indices of the solutions of the TbDCs and quinine sulfate, respectively.[2] Here we use the values of pure solvents ($n_s = 1.424$ and $n_r = 1.339$) because of the low concentrations.

Preparation of TbDC-Copolymerized Hydrogel. *N*-Isopropylacrylamide (6.79 g, 0.06 mol), methylenebisacrylamide (0.015 g, 97 μmol), and V-[G-1-34]$_3$–Tb (0.2328 g, 188 μmol) were dissolved in dimethyl sulfoxide (DMSO, 10 mL). The DMSO solution was degassed by nitrogen bubbling and kept at 60 °C for 10 min, followed by the addition of azobisisobutylonitrile (AIBN, 0.016 g, 97 μmol). About 10 min afforded a clear gel; however, several additional hours at 60 °C under nitrogen atmosphere completed the radical copolymerization. The resulting DMSO gel was then immersed in a large excess of water (continuous flow) at room temperature to complete the solvent exchange process, affording a clear colorless hydrogel.

Results and Discussion

1. Synthesis. We prepared a series of acid dendrons from bromide dendrons or benzyl bromide and the corresponding hydroxybenzoates by the reported etherification reaction[1] followed by an alkali hydrolysis/acidification to generate the focal carboxyl group.[3] The acid dendron was then reacted with anhydrous terbium(III) triacetate (1 equiv) in chlorobenzene at reflux to generate the corresponding TbDC by a reported ligand exchange reaction.[3]

The general synthesis of poly(benzyl ether) dendrimer (the etherification and the bromination reactions) was successfully employed for the preparation of the dendrons in this study, except for two bromide dendrons showing an unexpected instability against moisture ([G-1-24]-Br and [G-1-34]-Br, see the Experimental Section). The characterization of the dendrons prepared was successfully carried out by FTIR and NMR spectra. All of the NMR spectra for the isolated intermediate dendrons proved that they were pure enough for further synthesis. MALDI-TOF-MS and elemental analysis were performed only for the acid dendrons, the key precursors for the final TbDC, to ascertain the characterization and the purity. All TbDC prepared in this study showed the absence of infrared absorption bands corresponding to the COOH group, indicating the formation of the carboxylate complexes.[3]

The reduction reaction of the first-generation acid dendrons to the corresponding alcohol dendrons turned out to be tricky. At first we tried to reduce the acid dendrons with BH_3–THF complex in THF; however, this reduction turned out to be inappropriate due to side reactions affording a complex mixture. Thus, $LiAlH_4$, a stronger reducing agent, was used for the reduction of

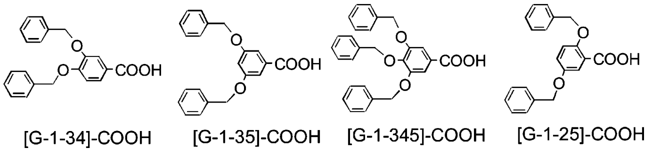


Figure 1. First-generation acid dendrons prepared.

the acid dendrons to afford the corresponding alcohol dendrons in good yields.

The bromination of the alcohol dendrons was hard for some isomers due to the instability against moisture. We failed to purify and used [G-1-24]-Br for the next synthetic step. [G-1-34]-Br was not pure enough (contamination of $CHBr_3$) for the next step.

2. Isomerism on the Focal Benzene Ring. Fluorescence spectra were taken in THF at the same concentration (3 μmol/L at 23 °C) for the first-generation TbDCs bearing various isomeric focal benzene rings (Figure 1). The emission bands characteristic for Tb^{3+} were observed for all the solutions, besides the obvious differences in the intensity for the complexes examined; i.e., $[G\text{-}1\text{-}34]_3-Tb$ (1.49) > $[G\text{-}1\text{-}345]_3-Tb$ (1.04) ≈ $[G\text{-}1\text{-}35]_3-Tb$ (1.00) > $[G\text{-}1\text{-}25]_3-Tb$ (0.68). Here the values indicated in parentheses are the relative intensity of the main fluorescence band at 542 nm. Dichloromethane solutions gave the same order of the fluorescence intensity (3 μmol/L at 23 °C), suggesting that the observed difference in the fluorescence ability originated from the intrinsic nature of TbDC, not from the solvent.

The 3,4-dioxybenzoate residue, the best focal moiety for Tb^{3+}, was then tested for higher generation TbDC. The fluorescence intensity of the third-generation TbDC $[G\text{-}3\text{-}34]_3-Tb$ was compared with the reported fourth-generation TbDC $[G\text{-}4\text{-}35]_3-Tb$ (original notation in the literature: $[G\text{-}4]_3-Tb$)[3] bearing a 3,5-dioxybenzoate focal moiety (Figure 2). As shown in Figure 3, the third-generation TbDC $[G\text{-}3\text{-}34]_3-Tb$ fluoresced 1.5 times stronger at 542 nm than the fourth-generation one $[G\text{-}4\text{-}35]_3-Tb$ in dichloromethane (3 μmol/L at 23 °C), again revealing the superiority of the 3,4-dioxybenzoate focal moiety. It should be noted that the third-generation acid dendron [G-3-34]-COOH (possessing 15 benzene rings) appeared to be a better “antenna” for the Tb^{3+} core than the fourth-generation acid dendron [G-4-35]-COOH (possessing 31 benzene rings).

Table 1. Fluorescence Lifetime (542-nm band) of the Tb^{3+}-Cored Dendrimer Complexes

complex	lifetime (ms)	complex	lifetime (ms)
$[G\text{-}1\text{-}34]_3-Tb$	1.1	$[G\text{-}1\text{-}25]_3-Tb$	1.1
$[G\text{-}1\text{-}345]_3-Tb$	1.1	$[G\text{-}4\text{-}35]_3-Tb$	1.5
$[G\text{-}1\text{-}35]_3-Tb$	1.7		

The fluorescence lifetime was measured to know if the various fluorescence abilities were attributed to any electronic transition property of the Tb^{3+} cation or the intrinsic property of the dendritic subunits. Table 1 summarizes the fluorescence lifetime of the 542-nm emission band. The similar lifetimes suggest that the Tb^{3+} cations are similar, and thus the variation comes from the property of the dendritic subunits.

3. Fluorescence Quantum Yield. *A. Comparison of Quantum Yield.* Table 2 summarizes the florescence quantum yield and the absorbance of the 1.3-μmol/L dichloromethane solution of TbDC. The relative emission intensity (peak intensity of the main band at 542 nm) is also shown. The excitation wavelengths were determined by the maximum wavelength in the excitation spectra.

Comparison between the isomeric first-generation TbDCs ($[G\text{-}1\text{-}34]_3-Tb$ and $[G\text{-}1\text{-}35]_3-Tb$) revealed relatively close quantum efficiency, despite a twice larger fluorescence intensity at the same concentration. The absorbance for $[G\text{-}1\text{-}34]_3-Tb$ is almost twice as much

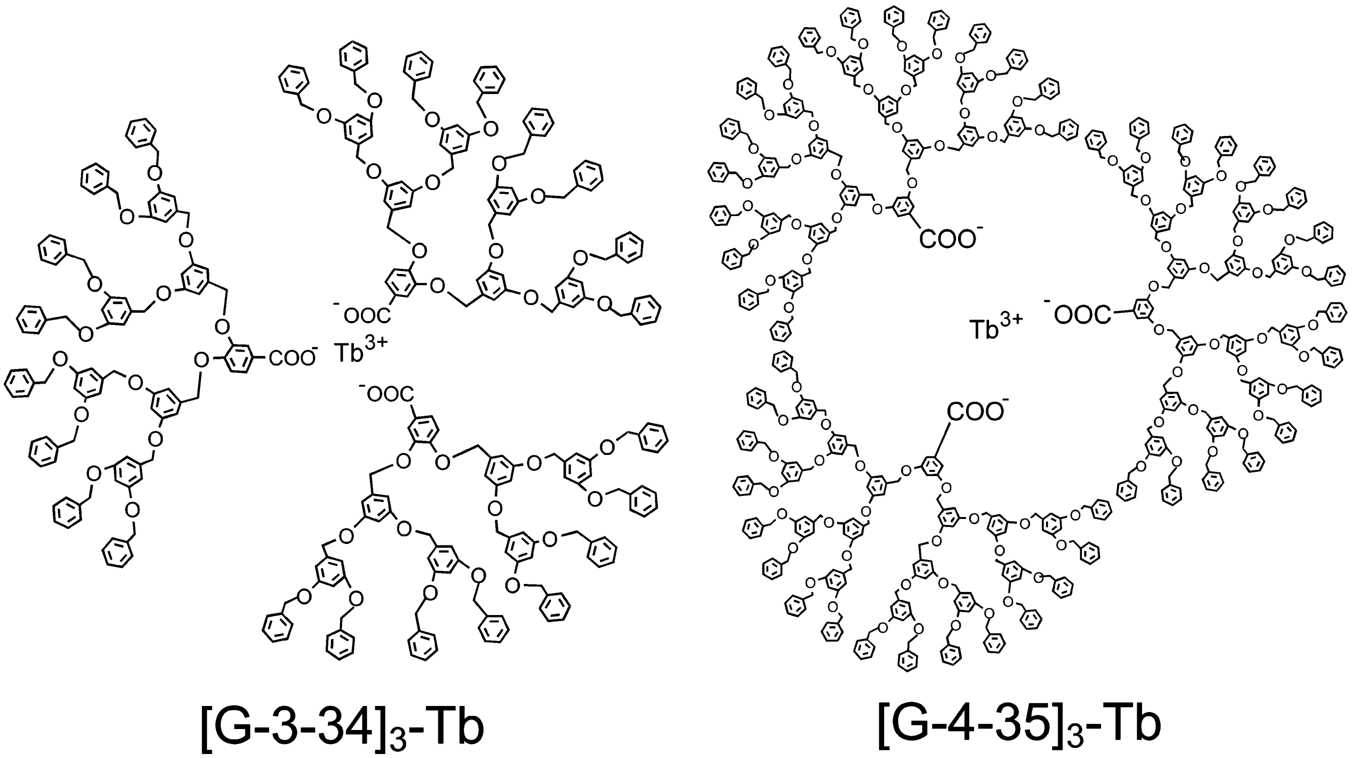


Figure 2. Third- and fourth-generation Tb^{3+}-cored dendrimer complexes prepared.

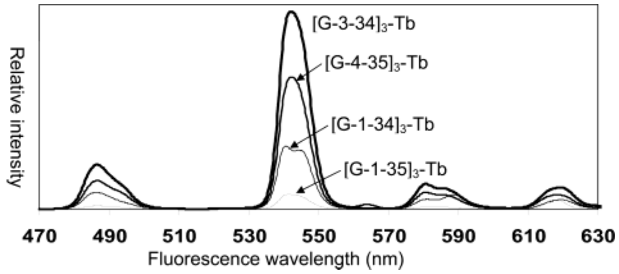


Figure 3. Emission spectra of the Tb^{3+}-cored dendrimer complexes in dichloromethane (3 μmol/L at 23 °C). Excitation was performed at 281 nm for [G-3-34]$_3$−Tb, 282 nm for [G-4-35]$_3$−Tb, 295 nm for [G-1-34]$_3$−Tb, and 309 nm for [G-1-35]$_3$−Tb.

Table 2. Fluorescence Quantum Yield (f_s) and Absorbance (A_s) of the Tb^{3+}-cored Dendrimer Complexes

dendrimer complex	λ_{ex}[a] (nm)	A_s (au)	f_s[b] (%) 486 nm	542 nm	579 nm	618 nm	rel emission intensity[c] (542 nm)
[G-1-35]$_3$−Tb	254	0.022	1.9	6.2	1.3	0.9	1.0
[G-1-34]$_3$−Tb	234	0.041	2.9	7.6	1.5	1.0	2.1
[35/G-2-35]$_3$−Tb	236	0.092	1.3	4.1	0.7	0.5	2.9
[34/G-2-35]$_3$−Tb	240	0.088	1.2	3.9	0.7	0.4	2.5
[25/G-2-35]$_3$−Tb	238	0.075	0.4	1.4	0.3	0.2	0.8
[G-3-34]$_3$−Tb	269	0.084	3.2	11.3	2.1	0.5	6.7

[a] λ_{ex} stands for the excitation wavelength. [b] f_s for the four emission bands of Tb^{3+} (indicated by the peak wavelengths) are shown. [c] Relative emission intensity was based on the peak intensity of the main emission band at 542 nm.

as for [G-1-35]$_3$−Tb, while the same numbers of aromatic rings are included.

Among the three second-generation isomers prepared (Figure 4), [35/G-2-35]$_3$−Tb indicated the highest fluorescence quantum efficiency. The difference among the three isomers, bearing the same 3,5-dioxybenzoate focal moiety, was the isomerism in the dendritic branching. Unfortunately, we did not succeed to prepare a 2,4-dendritic branching isomer; however, comparison of the three isomers seems to conclude that the authentic 3,5-dendritic branching is the best repeating unit in terms of the transfer of the excited electronic energy.

The third generation TbDC ([G-3-34]$_3$–Tb) exhibited fairly high fluorescence quantum yield. The sum of the quantum yield of the four bands reached 17%. Sato et al. reported the threshold size of the third-generation PBE dendron for the antenna effect of PBE-grafted poly(phenyleneethynylene).[2] The observed high quantum yield in this study for the third-generation complex might be interpreted by the similar size effect to maintain the excited electronic energy within the dendritic entity.

Despite of the variety of fluorescence ability, Figure 5 clearly proves the linear contribution of both the absorbance (A_s) and the quantum yield (f_s) to the fluorescence intensity for all TbDCs.

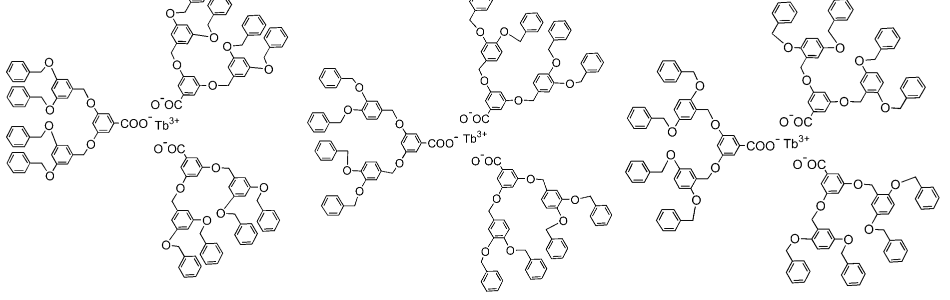
We point that A_s is not linear to the number of aromatic rings. For example, Table 2 tells that [G-3-34] $_3$-Tb has 45 benzene rings, affording only twice larger A_s than [G-1-34]$_3$−Tb, which has nine benzene rings with the same focal moiety. On the other hand, [35/G-2-35]$_3$−Tb has 21 benzene rings, resulting in more than 4 times larger A_s than [G-1-35]$_3$−Tb (nine benzene rings). A remarkable observation is, indeed, that the second-generation TbDC has larger A_s (0.092) than the third-generation one (0.084).

We propose a mechanism where terminal phenyl groups effectively shield the inner benzene rings for larger TbDC such like [G-3-34]$_3$−Tb, due to the increased density of the peripheral phenyl terminals. The peripheral shielding mechanism should be responsible not only for the ineffective absorption of photon energy by inner aromatic rings but also for the observed high quantum yield against quenching of absorbed energy.

B. Fluorescence Efficiency per Volume. From a practical point of view, fluorescence efficiency per volume is important for luminescence materials. We now compare fluorescence intensity per benzene ring to estimate the fluorescence efficiency per volume. We simply divided "relative emission intensity (542 nm)" in Table 2 by the total number of benzene rings for each TbDC; affording 2.1/9 = 0.23 for [G-1-34]$_3$−Tb, 2.9/21 = 0.14 for [35/G-2-35]$_3$−Tb, and 6.7/45 = 0.15 for [G-3-34]$_3$−Tb.

This comparison tells that the first-generation [G-1-34]$_3$−Tb is the best luminescer per volume, while [G-3-34]$_3$−Tb is the best per Tb^{3+} cation. We thus selected [G-1-34]−Tb as the fluorescence unit for the following hydrogel study.

4. Radical Copolymerizable TbDC and a Luminescence Hydrogel. We introduced vinyl groups onto the phenyl terminals of [G-1-34]$_3$−Tb (namely V-[G-1-34]$_3$−Tb), intending radical copolymerization with common monomers. For the vinyl-terminated dendron synthesis, commercial 4-vinylbenzyl chloride was used instead of benzyl bromide for the starting material of the PBE dendron synthesis. 4-Vinylbenzyl chloride (1.0 equiv) was reacted with ethyl 3,4-dihydroxybenzoate in the presence of tetraethylammonium bromide to activate less-reactive 4-vinylbenzyl chloride than the authentic benzyl bromide. After the consumption of 4-vinylbenzyl chloride, benzyl bromide (1.0 equiv) was then added, resulting in almost a one-spot reaction by TLC. The prepared vinyl-terminated dendron was then con-



[35/G-2-35]$_3$-Tb [34/G-2-35]$_3$-Tb [25/G-2-35]$_3$-Tb

Figure 4. Second-generation Tb^{3+}-cored dendrimer complexes bearing isomeric branching units.

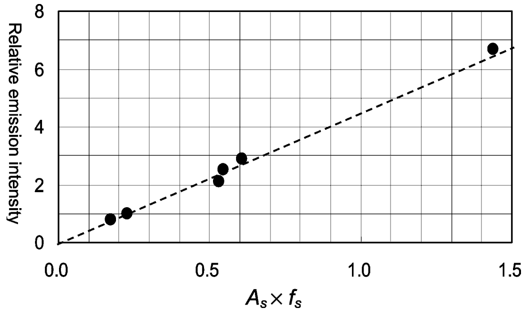


Figure 5. Relative emission intensity was plotted versus A_sf_s. The f_s value for this plot was the sum of the four emission bands.

verted to the vinyl-terminated TbDC by the same procedure for other TbDC preparation. V-[G-1-34]$_3$−Tb gave green fluorescence by the irradiation of 365-nm UV, at which usual phenyl-terminated TbDC is silent because of the absence of absorption. This observation supported the introduction of the terminal vinyl group.

We demonstrated a copolymerization of V-[G-1-34]$_3$−Tb with *N*-isopropylacrylamide (NIPA). NIPA has been known to give a temperature-responding hydrogel, exhibiting a thermal phase transition above 30 °C.[8] The phase transition occurs reversibly in millisecond order, changing the gel volume and the transparency. Therefore, if luminescence is added to the NIPA hydrogel, we might use it as a temperature-responding marker or a display material, etc., probably in the form of bulk articles, thin films, and micro- to nanoparticles. Less than 1 mol % of V-[G-1-34]$_3$−Tb was copolymerized with NIPA in the presence of methylenebisacrylamide as the cross-linking agent in DMSO. The polymerization gave a clear, colorless DMSO gel under a common condition (60 °C under nitrogen atmosphere), showing green fluorescence by 254-nm UV irradiation. DMSO was then substituted by large excess water thoroughly to give a clear colorless hydrogel.

The fluorescence ability of the hydrogel appeared almost the same as the DMSO gel by fluorescence measurement. The transparency and the preserved fluorescence ability of the hydrogel supported the fixation of V-[G-1-34]$_3$−Tb moiety in the gel network by the intended copolymerization. The preserved strong fluorescence even after the conversion to the hydrogel is a distinct phenomenon because the fluorescence of lanthanide cation is generally quenched remarkably by hydration. DMSO molecule(s) might strongly coordinate to the Tb^{3+} cation to inhibit the coordination of water molecules.

The Tb^{3+}-containing hydrogel showed a sharp gel phase transition between 33 and 35 °C, as reported for the pure NIPA hydrogel.[8] The hydrogel suddenly became opaque with obvious shrink when the temperature exceeded the transition temperature. The hydrogel once again became clear and swelled when cooled, proving the reversibility.

The fluorescence ability of the hydrogel was maintained both in the opaque and the clear state. At first we anticipated a reversible switching of the luminescence by the gel transition. That is, if the dendron subunits in a TbDC molecule were independently copolymerized in different linear chains in the gel network, the dimension jump by the gel transition might force a change in the distance between the Tb^{3+} core and the dendron subunits, switching the fluorescence intensity. However, the switching in luminescence was not observed in this study.

The fluorescence ability of the Tb^{3+}-contianing hydrogel was unchanged after immersion in saturated sodium chloride aqueous solution at room temperature at least for several weeks. This immersion was intended to test if the Tb^{3+} cation was exchanged by the large excess equivalent of Na$^+$ cation. The stability against electrolyte solution could be interpreted by the stability of the ionic bond of trivalent Tb^{3+} and the relatively hydrophobic environment at the focal point of the first-generation TbDC.

Conclusions

3,4-Dioxybenzoate moiety was the best focal point moiety for Tb^{3+}-cored poly(benzyl ether) dendrimer complexes (TbDC), showing 2.1 times higher fluorescence intensity than the authentic 3,5-focal point isomer, while the authentic 3,5-dioxybenzyl ether moiety appeared the best hyperbranching unit for the antenna effect of TbDC. A third-generation TbDC ([G-3-34]$_{3-}$Tb) bearing the 3,4-dioxybenzoate focal moiety showed the highest fluorescence quantum yield (17%) in this study, whereas relatively low absorbance per benzene ring was observed. A peripheral shielding mechanism by the terminal phenyl groups was proposed to interpret not only the ineffective absorption of photon energy but also the high quantum yield.

Radical copolymerizable TbDC was prepared by the introduction of vinyl groups to the phenyl terminal groups of [G-1-34]$_3$−Tb, which was successfully copolymerized with *N*-isopropylacrylamide to give a clear, green-fluorescent, temperature-responding hydrogel. The stability of the fluorescence was distinct against water, even in electrolyte solution, e.g., saturated NaCl solution. The polymerizable TbDC has been proved to afford transparent, luminescent, acrylic or styrenic copolymers with common monomers, which can be used as luminescence latex particles useful as fluoroimmunoassay reagents and for ink-jet printings, for example. The applications have been under development and will be reported elsewhere.

Acknowledgment. We thank Dr. Yutaka Sasaki in Mitsubishi Chemical Group Science and Technology Research Center, Inc. for the fluorescence lifetime measurement.

Supporting Information Available: Synthetic procedures and spectral data for the characterization of compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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