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Poly(benzyl ether) dendrimers with strongly fluorescent distyrylbenzene cores as the fluorophores for peroxyoxalate chemiluminescence: insulating effect of dendritic structures on fluorescent sites

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Abstract—Poly(benzyl ether) dendrimers containing strongly fluorescent distyrylbenzene cores were synthesized, and their fluorescence and electrochemical properties as well as the action as fluorophores in the chemiluminescence reactions were investigated. While all the dendrimers exhibited almost the same properties except for their intensities, a characteristic feature due to the dendritic structure was observed in the electrochemical behaviors. In the peroxyoxalate chemiluminescence reactions using these dendrimers as fluorophores, a bimolecular interaction between the high-energy intermediates and fluorophores was established, and a decrease in the chemiluminescence intensity with an increasing generation was observed, which was connected with the insulating effect of the dendritic structures on the core.

1. Introduction

Much attention has been paid to the architecture of multiform dendrimers,[1] that is, molecules with peculiar structures extending in certain directions from the core, and each branch radiates like a tree. Of the numerous number of dendrimers, the photoresponsive ones are of current interest for chemists because of their unique photochemical properties. For example, the photon-harvesting ability[2,3] and the insulating effect on some of the physical and chemical properties of the cores[4] are typical of their special functions due to their peculiar hyperbranched structures. While the photophysical properties of several dendrimers with fluorescent cores have been investigated and well characterized,[2c,3,5] only a few studies have described the chemiluminescent dendrimers[6] and there is little study using the fluorescent dendrimers during the chemiluminescence reactions.[7] Since an interaction between the high-energy intermediates, usually the cyclic peroxides, and the fluorophores is the crucial process in the peroxyoxalate chemiluminescence,[8] the use of fluorescent dendrimers is quite fascinating, because dendrimers would provide unusual reaction environments when they act as the activators in such reactions. In this paper, we describe the synthesis, fluorescence and electrochemical properties, and the use of Fréchet-type poly(benzyl ether) dendrimers having strongly fluorescent distyrylbenzene cores in peroxyoxalate chemiluminescence.[9]

2. Results and discussion

2.1. Synthesis of the distyrylbenzene core G0 and the dendrimers G1–G3

The synthetic procedure for the substituted distyrylbenzene **G0** and the dendrimers **G1–G3** is shown in Scheme 1. The fluorescent core, (*E*,*E*)-2,5-bis(2-ethylhexyloxy)-1,4-bis(4′-hydroxystyryl)benzene (**1**), was prepared by the Horner–Wadsworth–Emmons reaction[10,11] of 2,5-bis(2-ethylhexyloxy)-1,4-bis(ethylphosphonomethyl)benzene and 4-hydroxybenzaldehyde in the presence of *tert*-BuOK. The side chains, the 2-ethylhexyloxy groups attached at the 2 and 5 positions of the central benzene rings, were introduced for enhancing the solubility in organic solvents as well as the electron-donating ability of the fluorescent moiety.[11] The reaction of **1** and benzyl chloride in the

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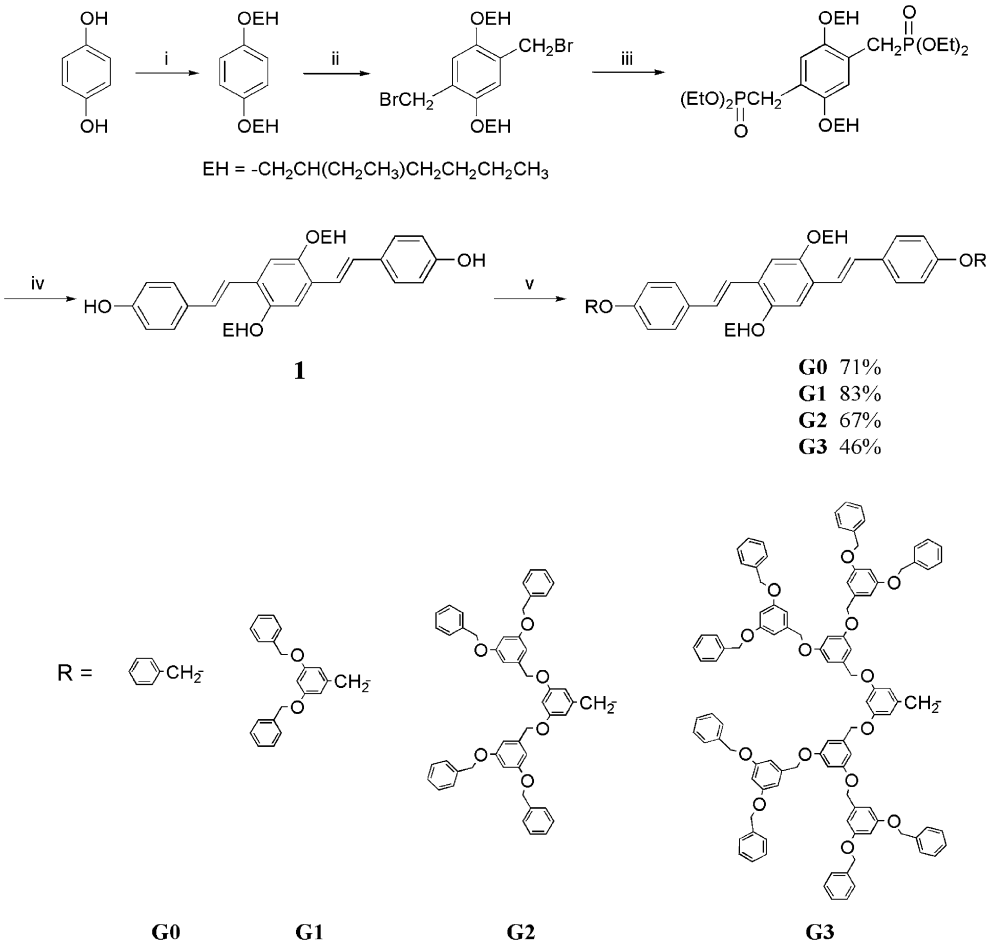


Scheme 1. Reagents and conditions: (i) EHBr, K_2CO_3, DMF, 95%; (ii) $(CH_2O)_n$, NaBr, H_2SO_4, CH_3COOH, 0 °C, 65%; (iii) $P(OEt)_3$, 100 °C, 99%; (iv) 4-hydroxybenzaldehyde, *tert*-BuOK, DMF, rt, 53%; (v) RBr, K_2CO_3, 18-crown-6, THF, reflux.

presence of K_2CO_3 and 18-crown-6 gave **G0**, and a similar procedure employing **1** and the corresponding dendritic benzyl bromides produced the dendrimers **G1**, **G2**, and **G3** with the first, second, and third generation of poly(benzyl ether) branches, respectively, at the peripheral rings, whose structures were confirmed by ^1H and ^{13}C NMR spectra as well as MALDI-TOF MS. Each fluorescent dendrimers showed a single peak in a HPLC by monitoring at 385 nm absorbed by the core.

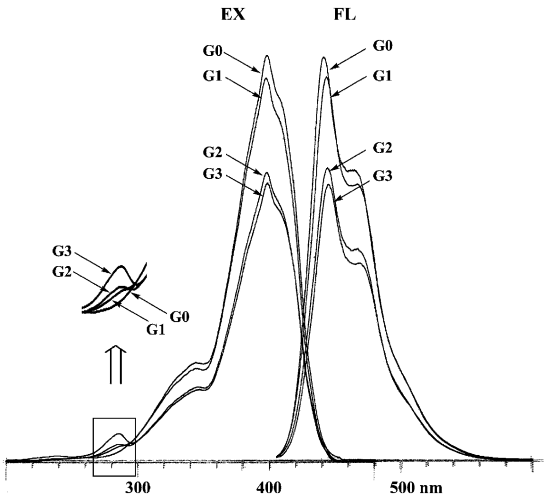


Figure 1. The excitation (EX) and fluorescence (FL) spectra of **G0–G3** in THF (1.0×10^{-6} M).

2.2. Fluorescence property

The fluorescence spectra of **G0–G3** are shown in Figure 1 and the selected spectral data are collected in Table 1. The excitation wavelengths were selected, at which the absorbance was 0.05 in the absorption spectra in THF. Upon excitation of the distyrylbenzene core at 386.5, 389, 396, and 387 nm for **G0**, **G1**, **G2**, and **G3**, respectively, all compounds showed a blue fluorescence at 442–444 nm with large fluorescence quantum yields (Φ_F), whereas the fluorescence intensity tends to decrease along with an increase in the generation. As a fluorescence intensity of each dendrimer was proportional to the concentration within

Table 1. Fluorescence properties for **G0–G3**

	EM λ_{max}	Φ_{Fl}[a]	τ (ns)[b]
G0	442	0.97	1.57
G1	442	0.93	1.57
G2	443	0.92	1.63
G3	444	0.89	1.59

Measured in THF (1.0×10^{-6} M).
[a] The measured Φ_{Fl}s are compared to 9,10-diphenylanthracene (Φ_{Fl}= 0.95).
[b] The lifetime measurements are carried out at a 392.57 nm irradiation.

a range of the measurements, a decrease in the intensity depending on the generation is not due to self-quenching or association, but to the properties of the dendrimers themselves. Although the reason is unclear at present, a variation in the fluorescence quantum yields with generation has been observed in another case of the Fréchet-type dendrimers with the fluorescent pyrrolopyrrole cores.[12] In the fluorescence excitation spectra, the small peaks in the shorter wavelength region at 285 nm increase with a generation increase (Fig. 1). This is due to the singlet energy transfer from the dendron moieties to the core,[2,3] and the efficiency of the energy transfer was estimated to be 0.16 for **G3** by comparing the fluorescence quantum yields with excitation at 285 and 387 nm.

The measurements of the fluorescence decays in THF under a nitrogen atmosphere revealed that all of them could be fitted to a mono-exponential model and all compounds **G0**–**G3** had almost the same fluorescence lifetimes ($\tau = 1.57$–1.63 ns) being much shorter than that for the poly(benzyl ether) dendrimers having the tristyrylbenzene cores,[3c] but comparable with those for the distyrylbenzene structurally close to **G0**[13] and the dendrimers with a stilbene core.[3a]

2.3. Electrochemical behavior

To investigate the electrochemical properties of these dendritically functionalized distyrylbenzenes, cyclic voltammetry (CV) measurements were carried out and the results are illustrated in Figure 2. All compounds **G0**–**G3** exhibited three-stage oxidation waves in dichloromethane. The first step, which might be due to oxidation of the distyrylbenzene core,[11] is almost reversible while the others are irreversible. Although the first half-wave potentials ($E_{1/2}$) for oxidation of the core are almost constant (0.88 V vs SCE) within the error range, the peak separation (ΔE_p) showed a slight increase with the increasing generation (ΔE_p: **G0**, 70; **G1**, 80; **G2**; 110, **G3**; 130 mV). It might be connected with retardation of the electron transfer due to encapsulation of the core by the dendritic moieties toward the electrode.[14] On the other hand, somewhat different electrochemical behaviors were observed in acetonitrile. While **G0** showed reversible redox waves, others showed a much decrease in reversibility. In the case of **G3**, no distinct peak was observable because of its low solubility. Consequently, these electrochemical behaviors indicate that the electron transfer from the

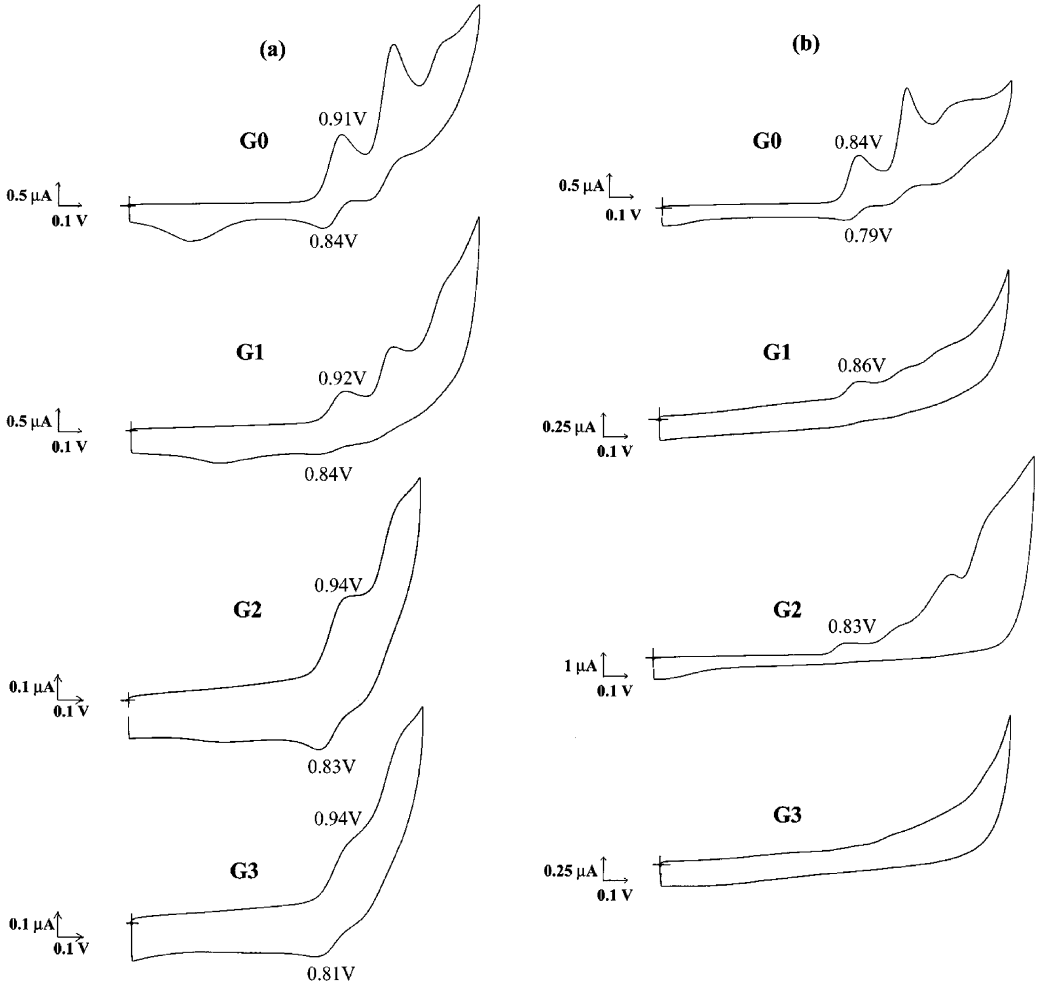


Figure 2. Cyclic voltammetry of **G0**–**G3**, (a) measured in CH_2Cl_2, (b) measured in CH_3CN.

distyrylbenzene core is affected by the insulating effect of the dendritic structures.[15]

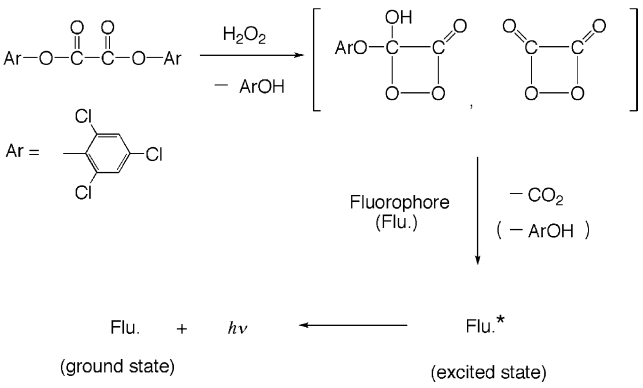
2.4. Use as the fluorophores during peroxyoxalate chemiluminescence

Among the many kinds of chemiluminescence reactions, the peroxyoxalate chemiluminescence reaction is the most convenient and efficient one,[16] where a molecular interaction between the fluorophores and the high-energy intermediates, usually the dioxetanones generated from the reactive oxalates and hydrogen peroxide, produces excited fluorophores that emit light corresponding to their fluorescence (Scheme 2).[8,17] Since the environments around the fluorophores would crucially influence the light forming efficiency,[18] a difference in the chemiluminescence behavior is expected to be presented between the prepared dendrimers having a common fluorescent core but different environments around the cores.

Employing bis(2,4,6-tricholorophenyl) oxalate (TCPO) as a typical luminophore and **G0–G3** as the fluorophores, the chemiluminescence reactions were carried out in the presence of hydrogen peroxide and potassium carbonate in aqueous THF to display a bright blue light emission. The good agreement of all the emission spectra (λ_{max} 443 nm) with the fluorescence spectra of the fluorophores indicates that the light emission was ascribed to the fluorescence from the excited distyrylbenzene cores. To explore the structural effect of the dendritic fluorophores, the chemiluminescence quantum yields of these chemiluminescence reactions were measured by varying the fluorophore concentration using the photon-counting method. According to the established kinetics of the peroxyoxalate chemiluminescence,[9b,17] the double reciprocal plot of Φ_S versus each fluorophore concentration should give a straight line if the high-energy intermediates and the fluorophores interact in a bimolecular reaction fashion. This relationship is expressed by the following equation:

$$\frac{1}{\Phi_s} = \frac{\Phi_{Fl}}{\Phi_{CL}} = \frac{1}{\Phi_r \Phi_S^{\infty}}\left(1 + \frac{k'}{k_{ss}}\frac{1}{[Flu]}\right)$$

where Φ_s is the singlet excitation state quantum yield of the chemiluminescence, Φ_{CL} is the total chemiluminescence quantum yield, Φ_r is the chemical reaction yield and can be regarded as unity because all TCPO was completely consumed during the reactions, Φ_s^{∞} is the singlet excitation state quantum yield at the infinitive fluorophore concentration, Φ_{Fl} is the fluorescence quantum yield of the fluorophores, k' is the rate of the unimolecular decomposition of the high-energy intermediates, k_{ss} is the rate of generation of the singlet excited state, and [Flu] is the concentration of the fluorophores. As shown in Figure 3A, the reciprocal of Φ_S estimated as Φ_{Fl}/Φ_{CL} is a linearly increasing function of the reciprocal of the concentration of **G0–G3**, demonstrating that this chemiluminescence reactions involve the bimolecular interaction process. Of key interest is a decrease in the Φ_{CL} when the dendritic fluorophores with the higher generation were employed at the higher concentration (Fig. 3B), namely, the Φ_Ss for **G0–G3** were almost same at the lower concentration of the dendrimers, while the difference in the Φ_S increased along



Scheme 2. Plausible reaction pathway of peroxyoxalate chemiluminescence.

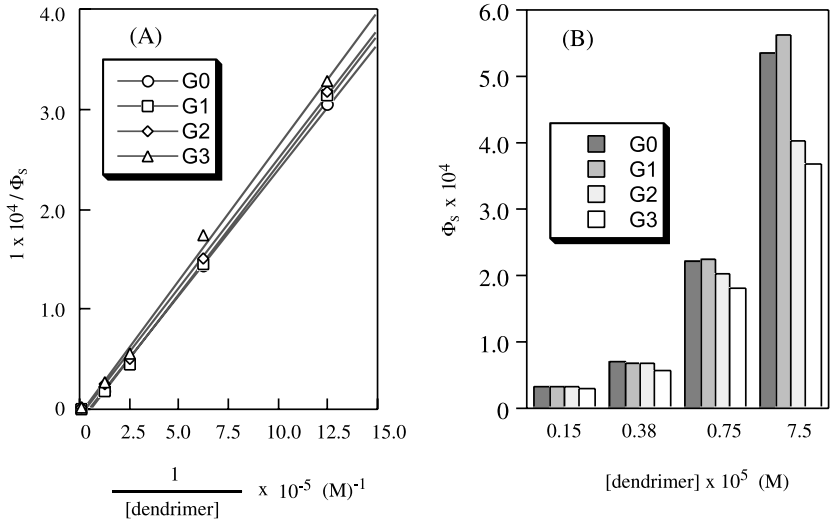


Figure 3. TCPO chemiluminescence in the presence of **G0–G3**. Double reciprocal plot of Φ_S versus [dendrimer] (A) and Φ_S at each [dendrimer] (B). The concentration of the reactants are as follows; [TCPO]=7.5×10^{-5} M, [K_2CO_3]=7.5×10^{-5} M, [H_2O_2]=7.5×10^{-3} M, [dendrimer]$\times10^6$=0.75, 1.5, 3.75, 7.5, 75 M. The slopes for the reciprocal plots are 0.31 M (R^2=0.998) for **G0**; 0.32 M (R^2=0.997) for **G1**; 0.32 M (R^2=0.998) for **G2**; 0.34 M (R^2=0.997) for **G3**.

with an increase in the dendrimer concentration. This indicates that the insulating effect of the dendritic structures with larger branches on the core allows the emission efficiency to decrease. Provided that this chemiluminescence reaction involves a CIEEL (chemically initiated electron exchange luminescence) or a CT (charge transfer) process,[17b,k,19] the rate of electron transfer or the CT interaction is significantly influenced by the electron-donating ability of the core as previously documented in the chemiluminescence using various distyrylbenzenes.[20] The observed variation of Φ_S depending on the structure of the dendrimers reflects the sensitive situation of the cores arising from the dendritic encapsulation because an excitation of the fluorophore needs two electronic process, an electron transfer from the fluorophore to the dioxetane intermediate and a back electron transfer from the radical anion generated by decomposition of the dioxetane to the fluorophore radical cation if the CIEEL mechanism is applied. Therefore, the observed decrease in Φ_S can be related with a decrease in the reversibility of an electron transfer observed in the CV measurements in the polar solvent.[14c] On the other hand, there is also another possible explanation by the site isolation, that is, the large dendritic moieties act as obstacles interrupting the approach of the high-energy intermediate to the fluorescent core, resulting in a decrease in Φ_S. However, differentiation of these effects, electronic or steric, is difficult at present, because the steric hindrance by the large branches retards an electronic interaction as observed in the CV study. Since the peroxyoxalate chemiluminescence is very sensitive to the electronic nature of the fluorophores, there should be much larger difference in Φ_S than observed if the decrease in Φ_S is ascribed to inhibition of an electron transfer. Furthermore, the steric shielding might be insufficient to prevent the interaction between the high-energy intermediate and the core in the case of these dendrimers, considering the ineffective penetration of small quenchers even in the fourth generation poly(aryl ether) dendrimer with the porphyrin core.[21] Identification of the crucial effect on the chemiluminescence efficiency might need architecturally well-designed dendritic fluorophores that provide much more definitive insulating effect. Nevertheless, observation of the structural effect of the fluorescent dendrimers on the chemiluminescence efficiency in this study is novel and provides a foothold of the molecular architecture for the fluorophores useful to control the environment where a light formation proceeds by a molecular interaction.

3. Conclusion

The poly(benzyl ether)dendrimers having strongly fluorescent distyrylbenzene cores were synthesized and their spectral and electrochemical properties were investigated. The dendron moieties hardly affected the spectral properties except for the slight difference in the fluorescence intensities, while retardation of the electron transfer due to encapsulation of the core by the dendritic moieties was detected in the CV measurements. The peroxyoxalate chemiluminescence of TCPO in the presence of **G0–G3** emitted light based on the fluorescent cores, and the decrease in the chemiluminescence efficiency was observed when the dendrimers were employed at the higher generation, which can be explained by the insulating effect of the dendritic structures on the core.

4. Experimental

Solvents and commercially available compounds were purchased from standard suppliers and purified by standard methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ as the solvent, and chemical shifts (δ) were given in ppm relative to tetramethylsilane (TMS) as the internal standard. Matrix-assisted laser desporption inonization time-of-flight mass spectral (MALDI-TOF-MS) measurements were taken on using dithranol (1,8,9-anthracentriol) as a matrix. Cyclic voltammetry was performed at room temperature with a three-compartment cell in dry dichloromethane or acetonitrile solution containing the substrate (ca. 10^{-4} M) and a supporting electrolyte (0.1 M tetrabutylammonium perchlorate). Pt disk, Pt wire, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The scan rate was 100 mV s^{-1}. Fluorescence lifetimes were measured in THF solution by means of a time-wavelength two-dimensional single photon-counting method coupled with a femtosecond Ti:sapphire regenerative amplifier system. The second harmonics of 392.5 nm of the laser system at the repetition rate of 3 kHz was used as an excitation source. Chemiluminescence quantum yields were measured by a photon-counting method using a Hamamatsu Photonics R456 photomultiplier connected with a photon-counting unit (C3866) and a photon-counting board M8784. The calibration was made by a standard method with the luminol chemiluminescence in the presence of potassium *tert*-butoxide in aerobic DMSO (vide infra).

4.1. Preparation of G0–G3

4.1.1. 2,5-Bis(2′-ethylhexyloxy)-1,4-bis(*p*-hydroxystyryl) benzene (1). To a suspension of *tert*-BuOK (4.59 g, 40.94 mmol) in DMF (15 mL) was added a solution (10 mL) of 2,5-bis(2′-ethylhexyloxy)-1,4-bis(diethylphosphonomethyl)benzene (3.12 g, 4.91 mmol) in DMF (10 mL) and stirred for 30 min. at room temperature. To the slurry was added dropwise a solution of *p*-hydroxybenzaldehyde (1.00 g, 8.19 mmol) in DMF (10 mL). After being stirred for 6 h at room temperature, the solvent was removed by distillation under a reduced pressure. The residue was acidified with 1 M HCl and extracted with ethyl acetate. The organic phase was washed with 1 M HCl twice and brine and then dried over anhydrous Na_2SO_4. After removal of the solvent, the product was recrystallized from ethyl acetate/hexane to give **1** (2.47 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (6H, t, J=7.3 Hz), 0.98 (6H, t, J=7.3 Hz), 1.32–1.62 (16H, m), 3.94 (4H, d, J=5.6 Hz), 6.83 (4H, d, J=8.8 Hz), 7.06 (2H, d, J=16.4 Hz), 7.09 (2H, s), 7.34 (2H, d, J=16.4 Hz), 7.41 (4H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.71, 14.49, 23.50, 24.63, 29.66, 31.34, 40.19, 72.24, 110.59, 115.98, 121.98, 127.14, 128.21, 128.35, 131.55, 151.44, 155.41. HRMS (EI) calcd for $C_{38}H_{50}O_4$ $[M]^+$: 570.3709, found 570.3693.

4.1.2. Compound G0. To a suspension of K_2CO_3 (0.194 g, 1.140 mmol) and 18-crown-6 (0.019 g, 0.07 mmol) in THF

(10 mL) was added benzyl chloride (0.089 g, 0.70 mmol) and a solution of **1** (0.20 g, 0.35 mmol) in THF (30 mL). After refluxing for 2 days, the solvent was removed under a reduced pressure. The residue was partitioned between benzene and saturated NH_4Cl solution. The organic phase was washed with satdurated Na_2CO_3 solution and brine and then dried over anhydrous Na_2SO_4. The solvent was removed under a reduced pressure. The crude product was recrystallized from methanol to give **G0** (0.24 g, 92%) as a yellow needle crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (6H, t, J=7.2 Hz), 0.98 (6H, t, J=7.2 Hz), 1.32–1.63 (16H, m), 1.78–1.84 (2H, m), 3.94 (4H, d, J=5.6 Hz), 5.10 (4H, s), 6.97 (4H, d, J=8.6 Hz), 7.08 (2H, d, J=16.4 Hz), 7.09 (s, 2H), 7.33–7.47 (16H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.34, 14.13, 23.13, 24.26, 29.29, 30.97, 39.82, 70.11, 71.84, 110.18, 115.11, 121.66, 126.78, 127.49, 127.65, 128.00, 128.61, 131.22, 137.01, 151.07, 158.36. MALDI-TOF-MS calcd for $C_{52}H_{62}O_4$ $[M]^+$: 750.46, found 750.05. Anal. Calcd for $C_{52}H_{62}O_4$: C, 83.16; H, 8.32. Found: C, 83.47; H, 8.52.

4.1.3. Compound G1. This compound was prepared from 3,5-bis(benzyloxy)benzyl bromide (0.108 g, 0.28 mmol), **1** (0.080 g, 0.14 mmol), K_2CO_3 (0.078 g, 5.6 mmol) and 18-crown-6 (7.4 mg, 0.028 mmol) in a manner similar to that describe above. Recrystallization from benzene/methanol gave **G1** (0.14 g, 83%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (6H, t, J=6.9 Hz), 0.99 (6H, t, J=7.4 Hz), 1.33–1.63 (16H, m), 1.79–1.84 (2H, m), 3.94 (4H, d, J=5.3 Hz), 5.03 (4H, s), 5.05 (8H, s), 6.58 (2H, t, J=2.0 Hz), 6.69 (4H, d, J=2.0 Hz), 6.94 (4H, d, J=8.6 Hz), 7.08 (2H, d, J=16.4 Hz), 7.09 (2H, s), 7.30–7.46 (26H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.34, 14.13, 23.12, 24.27, 29.29, 30.96, 39.82, 69.99, 70.17, 71.82, 101.61, 106.35, 110.17, 115.12, 121.67, 126.77, 127.57, 127.65, 128.02, 128.61, 128.75, 131.26, 136.81, 139.49, 160.22. MALDI-TOF-MS calcd for $C_{80}H_{86}O_8$ $[M]^+$: 1174.63, found 1174.33.

4.1.4. Compound G2. This compound was prepared from 3,5-bis[3′,5′-bis(benzyloxy)benzyloxy]benzyl bromide (0.130 g, 0.16 mmol), **1** (0.045 g, 0.08 mmol), K_2CO_3 (0.043 g, 0.32 mmol) and 18-crown-6 (4.2 mg, 0.016 mmol) in a manner similar to that describe above. Purification by silica gel column chromatography (eluent; benzene) gave **G2** (0.11 g, 67%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89–0.92 (6H, m), 0.96–0.99 (6H, m), 1.34–1.62 (16H, m), 1.77–1.83 (2H, m), 3.93 (4H, d, J=5.5 Hz), 4.98 (8H, s), 5.02 (4H, s), 5.03 (16H, s), 6.54–6.55 (2H, m), 6.57–6.58 (4H, m), 6.68 (12H, d, J=2.1 Hz), 6.95 (4H, d, J=8.8 Hz), 7.07 (2H, d, J=16.4 Hz), 7.08 (2H, s), 7.27–7.45 (46H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.33, 14.13, 23.12, 24.26, 29.28, 30.95, 39.81, 70.05, 70.16, 71.82, 101.60, 101.66, 106.43, 108.25, 110.19, 115.11, 121.68, 126.76, 127.56, 127.65, 128.01, 128.60, 131.27, 136.81, 139.24, 139.48, 151.07, 158.26, 160.12, 160.21. MALDI-TOF-MS calcd for $C_{136}H_{134}O_{16}$ $[M]^+$: 2022.97, found 2023.03.

4.1.5. Compound G3. This compound was prepared from 3,5-bis{3′,5′-Bis[3″,5″-bis(benzyloxy)benzyl-loxy]benzyl-oxy}benzyl bromide (57.7 mg, 0.035 mmol), 1 (9.0 mg, 0.016 mmol), K_2CO_3 (8.8 mg, 0.063 mmol) and 18-crown-6 (1.6 mg, 0.06 mmol) in a manner similar to that describe above. Reaction time was 5 days. Purification by silica gel column chromatography (eluent; ethyl acetate/hexane 1:1) gave **G3** (26.8 mg, 45%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87–0.91 (6H, m), 0.94–0.98 (6H, m), 1.26–1.42 (16H, m), 1.76–1.82 (2H, m), 3.91 (4H, d, J=5.4 Hz), 4.96 (24H, s), 4.98 (4H, s), 5.00 (32H, s), 6.53–6.57 (14H, m), 6.66–6.67 (24H, m), 6.68–6.69 (4H, m), 6.93 (4H, d, J=8.8 Hz), 7.06 (2H, d, J=16.0 Hz), 7.07 (2H, s), 7.29–7.44 (86H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.34, 14.14, 23.11, 24.25, 29.27, 30.94, 39.79, 70.03, 70.13, 71.81, 101.66, 106.41, 106.49, 110.19, 115.08, 121.67, 127.55, 127.65, 127.99, 128.58, 131.26, 136.80, 139.24, 151.07, 158.27, 160.10, 160.19. MALDI-TOF-MS calcd for $C_{248}H_{230}O_{32}$ $[M+H]^+$: 3720.64, found 3721.67.

4.2. Measurement of the CL quantum yields

The measurements were carried out according to the procedure reported previously using the luminol standard in DMSO for calibration of the photomultiplier tube.[22] For a typical run of **G0**-activated TCPO-CL, a solution (1.5 mL) containing TCPO (1.0×10^{-4} M) and **G0** (1.0×10^{-6} M) in distilled THF was place in a 1×1 cm quarts cell in front of the photomultiplier in exactly the same geometry. Photon-counting was initiated simultaneously with the injection of a solution (0.5 mL) containing H_2O_2 (3.0×10^{-4} M) and K_2CO_3 (3.0×10^{-2} M) into the cuvette, and the data collection was continued for 500 s. The similar measurements were carried out using the **G0** solution of different concentration, 2.0×10^{-6}, 5.0×10^{-6}, 1.0×10^{-5}, and 1.0×10^{-4} M in THF. The same procedure was applied to the measurements of the CL quantum yields for other dendrimers **G1**–**G3**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.108

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