

Synthesis of Poly(3,4,5-trihydroxybenzoate amide) and Poly(3,4,5-trihydroxybenzoate ester) Dendrimers from Polyphenols and Their Chemiluminescence

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Dendrimer chemistry is rapidly expanding for fundamental reasons as well as due to requirements in technological applications.¹ A recent interesting development in dendrimer chemistry concerns the coordination of metal ions by interior branches or exterior units.²⁻⁶

Dendrimers containing photoactive units⁷⁻¹⁷ are particularly interesting for two reasons: (1) cooperation among the photoactive components can allow the dendrimer to perform specific functions, and (2) changes in the properties of photoactive components can be exploited to monitor the participation of dendrimers in chemical processes.

Polyphenols such as pyrogallol and gallic acid (GA) produce a singlet oxygen in the presence of hydrogen peroxide in an alkaline medium and emit light. GA has also been utilized for selective Co²⁺ detection using a chemiluminescence (CL) flow injection system. The CL intensities of polyphenols are considerably weaker than those of luminal and acridinium ester, which are representative CL compounds. Hence, *trans*-4-(3-propionic acid) phenylboronic acid and 4-biphenylboronic acid in the presence of peroxidase or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide have been used as an enhancer for highly sensitive polyphenol CL determination. However, methods to derive polyphenols with strong CL intensity have not been reported yet.¹⁸

In recent times, after a new polymer, poly(amidoamine) dendrimer, was synthesized, dendrimers have been applied to material engineering based on optics in nanoscale science. The poly(propylene amine) family that was functionalized in the periphery with fluorescent dansyl units interacts with Co²⁺. More recently, acridinium dendrimers have been conjugated with bovine serum albumin, and its CL was estimated to be six times that of the acridinium salt.

In this paper, we report the design of new types of polyphenol dendrimers having an increased number of chemiluminophores for high CL intensity; they also have hydroxyl groups in their periphery to form hydrogen bonds with an analyte. Polyphenol dendrimers having GA in the periphery were synthesized, and their CL was measured. We synthesized first-generation polyphenol dendrimers with GA units in the periphery by employing a divergent method using phenol, pyrocatechol, resorcinol, hydroquinone, 1,2,4-tri-

hydroxybenzene, 3,4,5-trihydroxybenzene aniline, 1,2-diaminobenzene, and 1,3-diaminobenzene as the core molecules (Supporting information, Schemes 1 and 2).

Experimental methods and physical data from polyol **1a-f** to first-generation esters **5a-f** have been reported in our previous paper.¹⁹

The mass spectra of the zero-generation esters **3a-f** and first-generation esters **5a-5f** were obtained by matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI TOF MS) using 2,5-dihydroxybenzoic acid as the matrix. The amide group has a rigid, planer structure as a consequence of resonance interactions that give the amide bond ~40% double bond character. The planer conformation maximizes π -bonding overlap, which accounts for the amide group's rigidity.

From our standpoint about structural properties of the amide group, we designed new types of poly(3,4,5-trihydroxybenzoate amide) dendrimers having an increased number of chemiluminophores for high luminescence intensity and hydroxyl groups in the periphery to form hydrogen bonds with the analyte. The esterification of 3,4,5-trihydroxybenzoyl chloride with aniline yielded **2g** in 81.13%. After the debenzoylation of **2g**, we were able to separate **3g** and the by-product by chromatographic purification. Therefore, the designed zero-generation ester **3g** was not isolated. Compound **4g** and **5g** were synthesized by repeating this esterification and debenzoylation, respectively. But the yield of the first-generation ester **5g** was 69.20%. The esterification of 3,4,5-trihydroxybenzoyl chloride with 1,2-diaminobenzene **1h** and 3,4,5-trihydroxybenzoyl chloride with 1,3-diaminobenzene **1i** yielded **2h** (74.76%) and **2i** (69.6%) respectively. The zero-generation amides **3h** and **3i** and first-generation amides **5h** and **5i** were synthesized as described above. The yields of the poly(3,4,5-trihydroxybenzoate amide) dendrimers decreased with increasing dendrimer generation. Compounds **4g**, **4h** and **4i** were debenzoylated in high yield by catalytic reduction under hydrogen gas in the presence of palladium black at ambient temperature.

The mass spectra of the zero-generation amide **3g**, **3h**, and **3i** and first-generation amides **5g**, **5h**, and **5i** were obtained by matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI TOF MS) using 2,5-dihydroxy-

Table 1. Relative CL intensities of GA, **5a**, **5b**, **5e**, **5f**, **5g**, **5h** and **5i** in MeOH

Core	Compound ^a	NaOH (mM)	H ₂ O ₂ (mM)	Integral photon count ($\times 10^4$)	Relative CL intensity ^b
	GA	100	500	4.8	1.0
Phenol	5a	100	500	977.8	203.7
1,2-dihydroxybenzene	5b	100	500	2025.0	421.0
1,3,5-dihydroxybenzene ^c	5e	100	500	2986.0	622.0
1,2,4-dihydroxybenzene ^d	5f	100	500	123.1	25.6
aniline	5g	100	500	179.1	37.3
1,2-diaminobenzene	5h	100	500	31.7	6.6
1,3-diaminobenzene	5i	100	500	57.9	12.1

^aConcentration of each compound was 0.1 mM. ^bCL intensity of GA obtained in MeOH was taken as 1. ^cSymmetric dendrimer. ^dAsymmetric dendrimer

benzoic acid as the matrix.

The first-generation esters **5a-i** were very stable in MeOH. Compounds **5a**, **5b**, and **5e-i** showed maximum CL intensities when 100 mM sodium hydroxide and 500 mM hydrogen peroxide were added. Both the intensities of the maximum light emission and the length of the CL period of **5a**, **5b**, and **5e-i** were higher and longer than those of GA, respectively. The time of maximum light emission of **5a**, **5b**, and **5e-i** were 50 and 60 s after the injection of hydrogen peroxide. The CL intensities in 5 min after the injection of hydrogen peroxide were approximately half the maximum CL intensities. Such polyphenol compounds, which emit light for such a long CL life, have not been found. The CL intensities of **5b** and **5e** in MeOH were approximately 400- and 600-fold stronger than that of GA, respectively (Table 1).

The CL intensities per GA unit of **5b** and **5e** were approximately equal, which suggests that increasing the number of chemiluminophores was effective in increasing the CL intensity of polyphenol dendrimers. The increase in the CL intensity of GA was accomplished by the formation of a dendric structure. However, the CL intensity of **5f** as an asymmetric dendrimer in MeOH was weaker than that of **5e**, and it is suggested that the symmetry of chemiluminophores was effective in increasing the CL intensity of polyphenol dendrimers. And also the CL intensity of poly(3,4,5-trihydroxybenzoate amide) dendrimer in MeOH was weaker than that of poly(3,4,5-trihydroxybenzoate ester) dendrimer. This result proved that there is no effect of CL intensity by exchange of dendrimer's frame to amide.

In conclusion, polyphenol dendrimers were synthesized to obtain a strong CL compound, and their CL intensities were found to be considerably stronger than the CL intensity of GA. The esterification of the hydroxyl groups of GA in the dendrimer was very effective in developing a strong CL. Further, the relationship between the CL intensity and structure of polyphenol dendrimers must be clarified to understand the reason behind the strong light emission of high-per-branch compounds such as poly(3,4,5-trihydroxybenzoate ester) dendrimers. Polyphenol CL dendrimers can be used for a wide variety of CL assays by utilizing the hydroxyl groups of the polyphenol for forming a hydrogen bond with oxygen in the analyte structure.

Experimental Section

Melting points were determined using an electrothermal capillary melting point apparatus and uncorrected. Thin layer chromatography (TLC) was performed on glass plates coated with silicon oxide (silica gel 60F₂₅₄), and compounds were visualized using a UV lamp. ¹H and ¹³C NMR spectra were obtained with Bruker AC 2000 (200 MHz) and Varian Gemini (200 or 300 MHz) spectrometers. Mass spectra were measured with HP 5890 GC/Mass (70 eV, EI). The organic solvents and chemicals were obtained from commercial products and purified by the appropriate methods before use. Except where explicitly stated, all the starting materials were purchased from Aldrich, Fluka, Fisher, Lancaster, or TCI chemical companies and used as received.

Synthesis of 3,4,5-Tribenzyloxybenzoyl Chloride. 3,4,5-Tribenzyloxybenzoyl chloride was prepared as follows. To a stirred solution of methyl-3,4,5-trihydroxybenzoate (0.05 mol) and benzyl chloride (0.2 mol) in DMSO (150 mL) was added potassium carbonate (0.18 mol). The mixture was refluxed for 2 h, and then H₂O (300 mL) was added. The reaction solution was cooled in ice and then filtered. The crude product was dried and then re-crystallized by *n*-hexane/benzene (1:2, v/v) to give methyl-3,4,5-tribenzyloxybenzoate as a colorless powder (64.5%). To a stirred solution of methyl 3,4,5-tribenzyloxybenzoate (0.03 mol) and NaOH (0.13 mol) in MeOH (250 mL) was added H₂O (15 mL). The mixture was refluxed for 1 h, and then H₂O (250 mL) was added. The reaction solution was acidified by 36% HCl. The crude product was washed with H₂O, dried, and then re-crystallized by EtOH to give 3,4,5-tribenzyloxybenzoic acid as a colorless powder (86.8%). To a stirred solution of 3,4,5-tribenzyloxybenzoic acid (0.027 mol) and 95% thionyl chloride (0.56 mol) in benzene (200 mL) was added pyridine (0.5 mL). The mixture was refluxed for 1.5 h. To the resulting solution was added petroleum ether (150 mL) and then cooled in ice. The crude precipitate was re-crystallized by *n*-hexane to give 3,4,5-tribenzyloxybenzoyl chloride as a colorless powder (96% yield, mp 112–113 °C).

General Procedure for the Synthesis of 2-5. To a stirred solution of 4-dimethylaminopyridine (DMAP, 5 mmol), phenol (or polyphenol) **1** (5 mmol), and pyridine (0.7 mL) in CHCl₃ (60 mL) was added 3,4,5-tribenzyloxybenzoyl

chloride (5 mmol). After the mixture was refluxed under N₂ for 5 h, the organic layer was filtered, concentrated, and dried. A white solid product **2** was obtained by flash column chromatography on silica gel (CH₂Cl₂). To obtain **3**, a mixture of synthesized **2** (3.25 mmol) and activated carbon (0.15 g) in CHCl₃ (24 mL) and MeOH (12 mL) was stirred under hydrogen gas for 3 h at room temperature. After the reaction mixture was stirred for 3 h, the organic layer was filtered, concentrated, and dried. A light yellow solid product was then collected. After the debenzoylation of **2**, we were not able to separate **3** and the byproduct by chromatographic purification. Therefore, the desired zero-generation ester **3** was not isolated. Compounds **4** and **5** were synthesized in high yield by repeating this esterification and debenzoylation. The synthesis of polyphenol dendrimers by using the corresponding polyphenol was attempted using similar methods.

5-(Phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5a): Yield: 91%; mp 202-204 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.36 (s, 3H), 9.30 (s, 3H), 9.19 (s, 3H), 7.48 (m, 13H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.55 (m, 13H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 163.5, 163.4, 162.4, 150.6, 145.8, 145.7, 140.4, 139.9, 129.7, 127.1, 126.3, 122.7, 118.9, 116.9, 116.2, 115.3, 109.3, 109.2; MALDI-TOF MS 702.54 [M+Na]⁺; Anal. Calcd. for C₃₄H₂₂O₁₇: C, 58.13; H, 3.16. Found: C, 58.11; H, 3.20.

1,2-Di-5-(phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5b): Yield: 47%; mp 180-182 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.33 (s, 12H), 9.19 (s, 6H), 7.48 (m, 20H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.55 (m, 20H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 163.5, 163.5, 162.4, 150.6, 145.8, 145.7, 140.4, 139.9, 129.7, 127.1, 126.3, 122.7, 118.9, 116.9, 116.2, 115.3, 109.3, 109.2; MALDI-TOF MS 1350.27 [M+Na]⁺; Anal. Calcd. for C₆₂H₃₈O₃₄: C, 56.12; H, 2.89. Found: C, 56.17; H, 2.85.

1,3-Di-5-(phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5c): Yield: 64%; mp 199-201 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.11 (m, 18H), 7.49 (m, 20H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.48 (m, 20H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 167.5, 164.2, 163.6, 163.4, 145.7, 145.4, 140.0, 137.9, 123.0, 122.7, 120.4, 118.0, 117.3, 116.9, 109.5, 109.3, 108.7; MALDI-TOF MS 1350.27 [M+Na]⁺; Anal. Calcd. for C₆₂H₃₈O₃₄: C, 56.12; H, 2.89. Found: C, 56.09; H, 2.84.

1,4-Di-5-(phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5d): Yield: 23%; mp 222-224 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.30 (m, 18H), 7.49 (m, 20H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.47 (m, 20H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 167.9, 163.9, 145.9, 145.6, 144.6, 138.2, 123.5, 120.8, 118.5, 117.7, 117.4, 109.8, 109.2, 108.9; MALDI-TOF MS 1350.27 [M+Na]⁺; Anal. Calcd. for C₆₂H₃₈O₃₄: C, 56.12; H, 2.89. Found: C, 56.15; H, 2.83.

1,3,5-Tri-5-(phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5e): Yield: 21%; mp 238-239 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.34 (m, 18H),

9.17 (s, 9H), 7.48 (m, 27H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.45 (m, 27H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 163.9, 145.9, 144.7, 139.9, 118.6, 109.6; MALDI-TOF MS 1974.41 [M+Na]⁺; Anal. Calcd. for C₆₂H₃₈O₃₄: C, 56.12; H, 2.89. Found: C, 56.10; H, 2.93.

1,2,4-Tri-5-(phenoxycarbonyl)benzene-1,2,3-triyl tris-(3,4,5-trihydroxybenzoate) (5f): Yield: 54%; mp 234-235 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.54 (s, 18H), 9.41 (s, 9H), 7.01 (s, 27H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.01 (s, 27H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 167.5, 162.7, 145.9, 145.4, 140.4, 137.9, 120.5, 117.5, 109.5, 109.3; MALDI-TOF MS 1974.32 [M+Na]⁺; Anal. Calcd. for C₆₂H₃₈O₃₄: C, 56.12; H, 2.89. Found: C, 56.08; H, 2.95.

3,4,5-Tris(benzyloxy)-N-phenylbenzamide (2g): Yield: 81%; mp 182.5-184 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.75-7.12 (m, 23H), 5.12 (s, 6H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 164.42, 152.80, 137.88-136.55, 130.31-119.79, 107.04-106.86, 75.53-75.17, 71.73-71.05; Anal. Calcd. For C₉₉H₈₉N₃O₁₉: C, 73.18; H, 5.52. Found: C, 73.16; H, 5.55.

5-(Phenylcarbamoyl)benzene-1,2,3-triyl tris(3,4,5-tris(benzyloxy)benzoate) (4g): Yield: 4%; mp 91-93 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 8.04-7.15 (m, 58H), 5.03-4.78 (m, 18H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 163.46, 152.65, 144.26, 137.22, 136.12-135.91, 133.54, 128.17-119.74, 109.75-109.38, 75.40-74.82, 71.15-70.94; Anal. Calcd. for C₉₇H₇₇NO₁₆: C, 77.02; H, 5.13. Found: C, 77.05; H, 5.15.

5-(Phenylcarbamoyl)benzene-1,2,3-triyl tris(3,4,5-trihydroxybenzoate) (5g): Yield: 69%; mp 205-207 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 10.34 (s, 9H), 7.93-6.88 (m, 13H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 7.91-6.86 (m, 27H); ¹³C NMR (125 MHz, DMSO) δ (ppm) 163.45, 162.42, 145.73, 143.84, 139.81-138.33, 132.62, 128.68, 124.01, 120.58, 116.97, 109.19; MALDI-TOF: 724.77 [M+Na]⁺; Anal. Calcd. for C₃₄H₂₃O₁₆: C, 58.21; H, 3.30. Found: C, 58.18; H, 3.25.

N,N'-(1,2-Phenylene)bis(3,4,5-tris(benzyloxy)benzamide) (2h): Yield: 75%; mp 195-196 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 9.32 (s, 2H), 7.39-7.25 (m, 3H), 5.11 (s, 12H); ¹³C NMR (50 MHz, DMSO) δ (ppm) 165.74, 152.73, 137.42, 136.50, 130.32, 128.69-127.57, 126.03, 125.37, 107.12, 75.12, 75.22; Anal. Calcd. for C₆₂H₅₂N₂O₈: C, 78.13; H, 5.50. Found: C, 78.16; H, 5.47.

Poly(3,4,5-trihydroxybenzoate amide) dendrimer (4h): Yield: 9%; mp 190-191 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.44-7.18 (m, 112H), 5.15 (s, 36H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 170.81, 152.57, 136.54, 128.55-124.08, 109.67, 75.15, 71.36; Anal. Calcd. for C₁₈₈H₁₄₈N₂O₃₂: C, 76.62; H, 5.06. Found: C, 76.60; H, 5.07.

Poly(3,4,5-trihydroxybenzoate amide) dendrimer (5h): Yield: 75%; mp 244-245 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.20 (s, 12H), 8.80 (s, 6H), 6.88 (s, 20H); ¹H NMR (200 MHz, DMSO+D₂O) δ (ppm) 6.88 (s, 20H); ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 167.46, 145.40, 137.97, 120.44, 108.71; MALDI-TOF: 1348.37 [M+Na]⁺; Anal. Calcd. for C₆₂H₄₀N₂O₃₂: C, 56.20; H, 3.04. Found: C, 56.18; H, 3.02.

***N,N'*-(1,3-Phenylene)bis(3,4,5-tris(benzyloxy)benzamide) (2i)**: Yield: 70%; mp 163.5-164.5 °C; ¹H NMR (200 MHz, DMSO) δ (ppm) 10.18 (s, 2H), 8.23 (s, 1H), 7.50-7.24 (m, 37H), 5.20 (s, 8H), 5.01 (s, 4H); ¹³C NMR (50 MHz, DMSO) δ (ppm) 164.67, 152.00, 139.92, 139.21-127.70, 116.40, 113.43, 106.96, 74.28, 70.44; Anal. Calcd. for C₆₂H₅₂N₂O₈: C, 78.13; H, 5.50. Found: C, 78.10; H, 5.52.

Poly(3,4,5-trihydroxybenzoate amide) dendrimer (4i): Yield: 53%, mp 163-164 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.40-7.27 (m, 112H), 4.9-5.19 (m, 36H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 162.15, 152.76, 136.26, 128.60-123.45, 110.11, 75.20, 71.39; Anal. Calcd. for C₁₈₈H₁₄₈N₂O₃₂: C, 76.62; H, 5.06. Found: C, 76.59; H, 5.04.

Poly(3,4,5-trihydroxybenzoate amide) dendrimer (5i): Yield: 21%; mp 163-164 °C; ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.15 (s, 18H), 6.87 (s, 20H); ¹H NMR (200 MHz, DMSO-D₂O) δ (ppm) 6.88 (s, 20H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 167.47, 145.40, 137.96, 120.46, 108.70; MALDI-TOF: 1348.27 [M+Na]⁺; Anal. Calcd. for C₆₂H₄₀N₂O₃₂: C, 56.20; H, 3.04. Found: C, 56.22; H, 3.01.

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