Supplementary Information

Electron-transfer through potential gradient based on a dendrimer architecture

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Supplementary Information

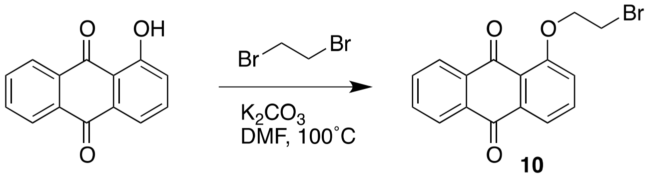
Experimental Section

General Method. A preparative recycling HPLC (Japan Analytical Industry: LC908) was used for the purification of the dendrimers using THF as the eluent at the flow rate of 3.5 ml/min. The NMR spectra were recorded using a FT-NMR spectrometer (JEOL, JNM-GX 400) operating at 400 MHz (^{1}H) or 100 MHz (^{13}C) at room temperature (25 ˚C). The ^{1}H NMR chemical shifts were referenced to tetramethoxysilane (TMS : 0 ppm) as the internal standard. The ^{13}C NMR chemical shifts were referenced to the solvent peak. The MALDI-TOF-mass spectra were obtained using a mass spectrometer (BRUKER, Ultra flex: Positive mode). Dithranol (1,8-dihydroxy-9[10H]- anthracenone) was used as the matrix for the MALDI-TOF-mass measurements. Analytical size-exclusion chromatography (SEC) was performed using an HPLC (Shimadzu, LC-10AP) equipped with two tandem SEC columns (Tosoh, TSK-GEL CMHXL and G3000HXL) at 40°C. Tetrahydrofuran (THF) was used as the eluent at the flow rate of 1 ml/min. The detection line was connected to a triple detector (Viscotek, TriSEC Model 302) operated at 30 ˚C. The molecular weights of the dendrimers were calculated from the SEC data using the Universal Calibration method.[1]

The UV-vis absorption spectra were recorded using an UV-3100PC (Shimadzu) with a sealed quartz cell (*d* = 1 cm). The fluorescence spectra were measured using a FP-6500 spectrophotometer (JASCO). Cyclic voltammograms were recorded using a 660A electrochemical analyzer (ALS). A glassy carbon electrode (ϕ = 3 mm) was used as the working electrode, which was polished with 0.05 mm alumina paste before the analysis. A coiled platinum wire was used as the counter electrode. A silver wire electrode dipped in a 0.01 M $AgNO_3$ + 0.1 M Bu_4NPF_6 / CH_3CN solution was used as the potential reference (Ag/Ag^+). The redox potential was then referenced to the in ferrocene / ferrocenium (Fc/Fc^+) standard by the half-wave potential of 0.2 mM ferrocene measured in 0.1 M Bu_4NPF_6 / CH_3CN.[2] The UV-vis absorption spectra of the electrochemically-oxidized species were measured using the same setup along with a custom-made quartz cell (*d* = 1 mm). A platinum mesh inserted into the optical path was used as the working electrode.

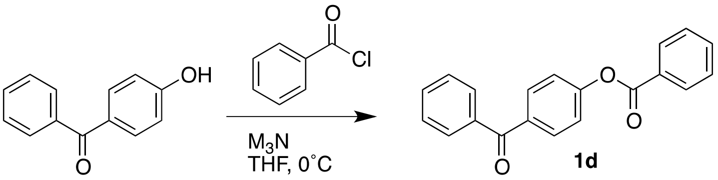
Synthesis of terminal-modified phenylazomethine dendrimers: Dendritic phenylazomethines with four terminal modifications were synthesized via stepwise-convergent approach. To control the number of modifications the dendrons (precursors) with only one terminal modification were synthesized.

Synthesis of 10.



5-hydroxy-1,4-anthraquinone (0.50 g, 2.2 mmol), dibromoethane (1 ml, 11.5 mmol) and potassium carbonate (1.0 g, 7.2 mmol) were dissolved in dimethylformamide (10 ml). The mixture was stirred at 100 ˚C for 4 hours. The resulting solution was concentrated and the fraction of product **10** was isolated by a silica gel column chromatography with chloroform used as the eluent. The solution was precipitated to afford **10** (70 % yield, 0.51 g, 1.5 mmol) as a pale yellow solid. ^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) = 8.28 (1H, dd, *J* = 7.2, 1.6 Hz), 8.24 (1H, dd, *J* = 7.2, 1.6 Hz), 8.03 (1H, dd, *J* = 8.0, 1.2 Hz), 7.81-7.70 (3H, m), 7.36 (1H, d, *J* = 8.4, 1.2 Hz), 4.49 (2H, dd, *J* = 7.2, 6.0 Hz), 3.81 (2H, dd, *J* = 7.2, 6.0 Hz); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 183.40, 182.28, 159.06, 136.05, 135.13, 135.07, 134.45, 133.51, 132.70, 127.41, 126.83, 121.25, 121.02, 70.24, 28.60; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 330.99 $[M+H]^+$, Found: 330.72; Anal. calcd for $C_{16}H_{11}BrO_3$: C 58.03, H 3.35, found: C 57.92, H 3.24, N 0.00.

Synthesis of benzoyl-protected dendron (1d).

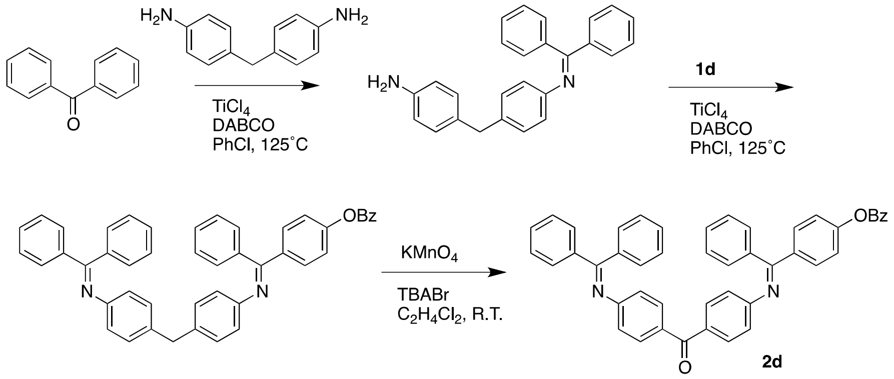


To the solution of 4-hydroxybenzophenone (5.0g, 25 mmol) in THF, trimethylamine (3.5 ml, 25 mmol) was slowly added and then stirred for 20 minutes at 0 ˚C. Then, benzoyl chloride (2.93 ml, 25 mmol) was added to the solution followed by stirring for 1 hour at 0 ˚C. The product **1d** (84 % yield, 6.4 g) was obtained by the recrystallization from chloroform/methanol.

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, 30 °C, TMS) δ 8.23 (2H, dd, *J* = 10.1, 3.0 Hz), 7.92 (2H, dd, *J* = 5.2, 6.0 Hz), 7.82 (2H, dd, *J* = 8.1, 4.2 Hz), 7.65 (1H, m), 7.6 (1H, m) 7.55 - 7.48 (4H, m) 7.36 (2H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 195.02, 168.67, 155.11, 139.00, 135.62, 132.53, 131.03, 130.92, 129.40, 129.27, 128.88, 128.20, 127.99, 120.27; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 302.32 $[M+H]^+$, Found: 303.1; Anal. calcd for $C_{20}H_{14}O_3$: C 79.46, H 4.67, found: C 79.25, H 4.77, N 0.00.

Supplementary Information

Synthesis of benzoyl-protected dendron (2d).



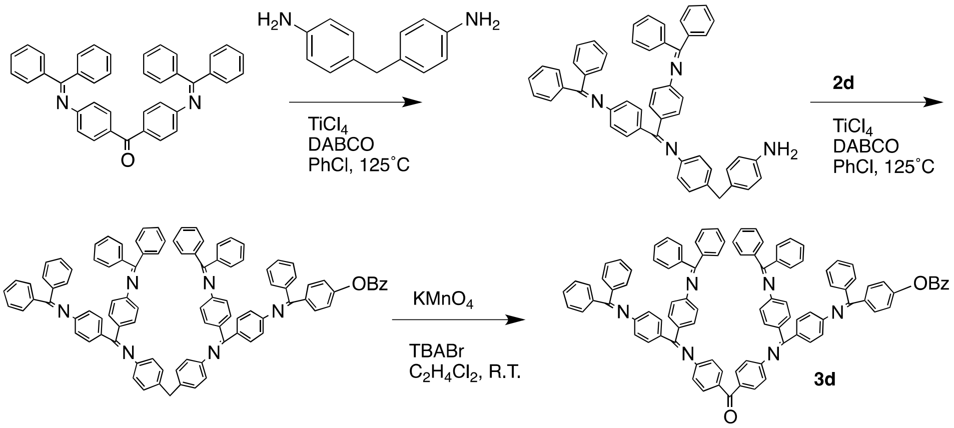
Benzophenone (5.0 g, 27 mmol), methylenedianiline (8.2 g, 42 mmol) and 1,4-diazabicyclo[2,2,2]octane (DABCO, 10 g, 89 mmol) was dissolved in chlorobenzene (100 ml) under nitrogen atmosphere. Titanium tetrachloride (3.0 ml, 9.3 mmol) dissolved in chlorobenzene (10 ml) was then added through a dropping funnel. The resulting solution was stirred at 125 ˚C for 3 hours to afford the crude intermediate product (9.4 g) after isolation using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 2 : 1 containing 0.5 wt% triethylamine).

The crude product (5.4 g, 14 mmol), **1d** (4.3 g, 14.3 mmol) and DABCO (10.0 g, 89 mmol) were again dissolved in chlorobenzene (100 ml), and then $TiCl_4$ (3.0 ml, 9.3 mmol) was added as described above. After the reaction for 3 hours at 125 ˚C, the second intermediate product (9.0 g, 13.9 mmol) was isolated using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 3 : 1 containing 0.5 wt% triethylamine).

Finally, **2d** (8.9 g, 97 % yield) was produced after oxidation of the intermediate product by potassium permanganate (6.0 g, 38 mmol) with tetra-n-butylammonium bromide (6.0 g, 19 mmol) in 1,2-dichloroethane at room temperature for 24 hours. The final product was purified by silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 3 : 1 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.16 - 8.23 (2H, m), 7.75 - 7.86 (4H, m), 7.40 - 7.62 (13H, m), 7.26 - 7.32 (10H, m), 7.11 - 7.16 (4H, m) 6.76 - 6.78 (4H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 155.21, 155.02, 133.81, 132.58, 131.43, 130.09, 130.25, 129.50, 129.40, 129.10, 128.99, 128.65, 128.37, 128.30, 128.18, 128.08, 121.63, 120.37; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 661.76 $[M+H]^+$, Found: 661.41; Anal. calcd for $C_{46}H_{32}N_2O_3$: C 83.61, H 4.88, N 4.24, found: C 83.44, H 4.95, N 4.09.

Synthesis of benzoyl-protected dendron (3d).



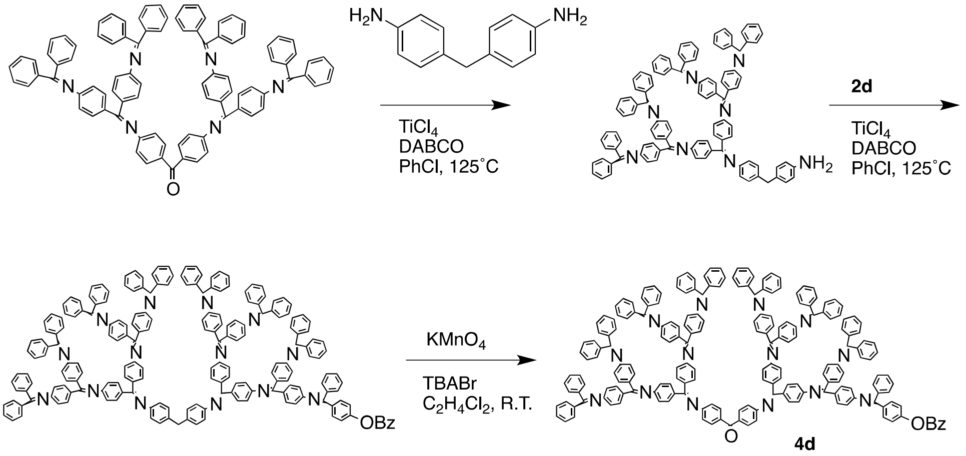
DPAG2 dendron (2.0 g, 3.7 mmol),[3] methylenedianiline (1.5 g, 7.6 mmol) and 1,4-diazabicyclo[2,2,2]octane (DABCO, 5.0 g, 45 mmol) was dissolved in chlorobenzene (60 ml) under nitrogen atmosphere. Titanium tetrachloride (1.0 ml, 3.1 mmol) dissolved in chlorobenzene (3 ml) was then added through a dropping funnel. The resulting solution was stirred at 125 ˚C for 3 hours to afford the crude intermediate product (1.9 g, 2.6 mmol) after isolation using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 1 : 1 containing 0.5 wt% triethylamine).

The crude product (1.9 g, 2.6 mmol), **2d** (2.1 g, 3.2 mmol) and DABCO (5.0 g, 45 mmol) were again dissolved in chlorobenzene (100 ml), and then $TiCl_4$ (1.0 ml, 3.1 mmol) was added as described above. After the reaction for 3 hours at 125 ˚C, the second intermediate product (3.2 g, 2.3 mmol) was isolated using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 3 : 1 containing 0.5 wt% triethylamine).

Finally, **3d** (3.0 g, 99 % yield) was produced after oxidation of the intermediate product by potassium permanganate (5.0 g, 32 mmol) with tetra-n-butylammonium bromide (5.0 g, 16 mmol) in 1,2-dichloroethane at room temperature for 48 hours. The final product was purified by silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 3 : 1 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.17 - 8.23 (4H, m), 7.75 - 7.86(9H, m), 7.41 - 7.66 (25H, m), 7.26 - 7.32 (14H, m), 7.11 - 7.16 (8H, m) 6.76 - 6.78 (8H, m); ^{13}C NMR (ppm, 100 MHz, CDCl3, TMS) δ 168.94, 168.43, 164.70, 164.65, 155.49, 153.90, 153.79, 153.73, 153.05, 151.99, 151.06, 139.20, 139.15, 139.01, 135.78, 135.55, 133.95, 133.68, 132.17, 131.01, 130.93, 130.73, 130.43, 130.35, 130.33, 130,28, 130.23, 130.14, 130.04, 129.61, 129.35, 129.21, 128.94, 128.90, 128.77, 128.54, 128.15, 127.99, 127.89, 127.80, 121.48, 120.66, 120.52, 120.27 ; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 1378.63 $[M+H]^+$, Found: 1378.51; Anal. calcd for $C_{98}H_{68}N_6O_3$: C 85.44, H 4.98, N 6.10, found: C 85.27, H 4.85, N 5.96.

Synthesis of benzoyl-protected dendron (4d).



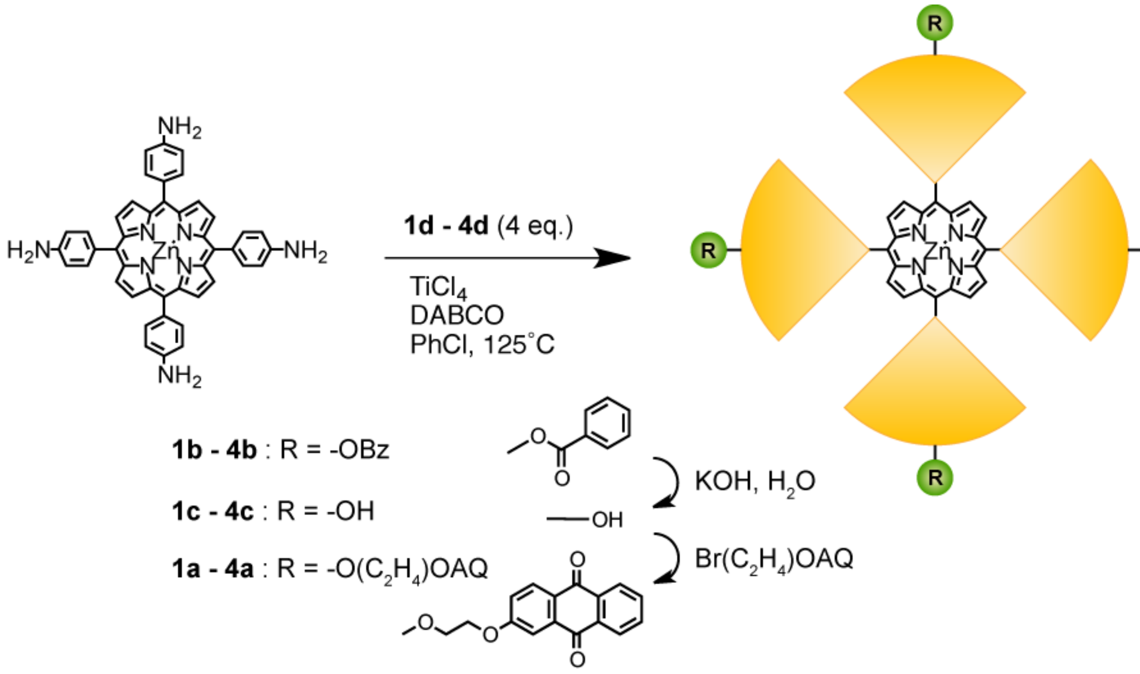
DPAG3 dendron (3.0 g, 2.2 mmol),[3] methylenedianiline (1.0 g, 5.0 mmol) and 1,4-diazabicyclo[2,2,2]octane (DABCO, 5.0 g, 45 mmol) was dissolved in chlorobenzene (60 ml) under nitrogen atmosphere. Titanium tetrachloride (1.0 ml, 3.1 mmol) dissolved in chlorobenzene (3 ml) was then added through a dropping funnel. The resulting solution was stirred at 125 ˚C for 3 hours to afford the crude intermediate product (1.5 g, 1.0 mmol) after isolation using silica gel column chromatography eluted by a mixed solvent (chloroform : ethylacetate = 6 : 1 containing 0.5 wt% triethylamine).

The crude product (1.5 g, 1.0 mmol), **3d** (1.4 g, 1.0 mmol) and DABCO (5.0 g, 45 mmol) were again dissolved in chlorobenzene (50 ml), and then $TiCl_4$ (1.0 ml, 3.1 mmol) was added as described above. After the reaction for 3 hours at 125 ˚C, the second intermediate product (2.1 g, 0.75 mmol) was isolated using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 6 : 3 : 2 containing 0.5 wt% triethylamine).

Finally, **3d** (2.1 g, 99 % yield) was produced after oxidation of the intermediate product by potassium permanganate (5.0 g, 32 mmol) with tetra-n-butylammonium bromide (5.0 g, 16 mmol) in 1,2-dichloroethane at room temperature for 48 hours. The final product was purified by silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 6 : 3 : 2 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, CDCl3, TMS) δ 8.21 (8H, br), 7.72 - 6.53 (132H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 194.51, 179.99, 168.78, 168.29, 168.19, 168.10, 167.98, 164.63, 164.56, 155.35, 154.27, 153.66, 152.97, 152.00, 151.87, 139.17, 138,94, 135.72, 135.55, 134.31, 134.10, 133.63, 132.26, 130.9, 130.81, 130.47, 130.12, 130.09, 130.00, 129.59, 129.54, 129.28, 128.96, 128.72, 128.49, 128.31, 128.09, 127.92, 127.73, 121.42, 120.81, 120.67, 120.41, 120.19, 119.94; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 2812.37 $[M+H]^+$, Found: 2812.53; Anal. calcd for $C_{202}H_{140}N_{14}O_3$: C 86.30, H 5.02, N 6.98, found: C 86.23, H 4.99, N 6.81.

Synthesis of the terminal modified dendrimers (1a – 4a).



Synthesis of 1b. tetrakis(4-aminophenyl)porphyrin (180 mg, 0.25 mmol), **1d** (300 mg, 1.0 mmol), DABCO (5.0g, 45 mmol) was dissolved in chlorobenzene (50 ml) at 90 °C. To the solution, titanium tetrachloride (1.0 ml, 9.0 mmol) was slowly added through a dropping funnel, and then stirred for 3 hours at 125 °C. The resulting solution was filtrated through a silica gel pad to remove insoluble part and DABCO. The product **1b** (40 % yield, 180 mg, 0.096 mmol) was obtained after purification using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 3 : 1 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, CDCl$_3$, TMS) δ 8.17 - 8.23 (4H, m), 7.75 - 7.86 (9H, m), 7.41 - 7.66 (25H, m), 7.26 - 7.32 (14H, m), 7.11 - 7.16 (8H, m) 6.76 - 6.78 (8H, m); ^{13}C NMR (ppm, 100 MHz, CDCl$_3$, TMS) δ 167.57, 164.20, 153.45, 151.53, 151.17, 150.07, 149.57, 138.22, 137.12, 136.43, 134.50, 134.30, 133.64, 131.39, 130.92, 130.78, 130.51, 130.00, 129.96, 129.70, 129.32, 128.87, 128.77, 128.62, 128.17, 128.09, 121.57, 120.14, 118.74, 118.63; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 1875.40 $[M+H]^+$, Found: 1876.22

Synthesis of 1a. To a solution of **1b** (28 mg, 15 μmol) in THF (2 ml), a methanol solution (2 ml) of potassium hydroxide (20 mg, 0.36 mmol) was added. After stirring for 10 minutes, the solution was evaporated to dryness followed by isolation of the crude product **1c** using silica gel column chromatography eluted by a mixed solvent (chloroform : ethylacetate = 3 : 1 containing 0.5 wt% triethylamine).

Then, **1c** was dissolved in dimethylformamide (10 ml) with **10** (100 mg, 0.30 mmol) and potassium carbonate (300 mg, 2.2 mmol). The mixture was reacted at 120 ˚C for 5 hours. The final product **1a** (40 % yield, 20 mg, 5.8 μmol) was produced after purification by silica gel column chromatography (chloroform : ethylacetate = 3 : 1) and preparative HPLC with size-exclusion columns (SEC).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.86 - 8.79 (8H, br), 8.31 - 8.20 (6H, br), 8.03 - 7.89 (20H, br), 7.82 - 7.70 (8H, br), 7.58 - 7.23 (44H, br), 7.18 - 7.04 (16H, br), 4.62 - 4.53 (16H, br) ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 186.26, 182.07, 167.92, 160.77, 159.33, 151.12, 151.07, 150.12, 150.07, 150.05, 137.39, 135.65, 34.90, 134.80, 134.61, 134.56, 134.43, 134.38, 134.20, 133.79, 133.21, 132.66, 132.41, 131.78, 131.58, 131.24, 131.19, 129.78, 129.57, 128.27, 127.95, 127.15, 126.57, 122.43, 120.73, 120.70, 120.39, 119.2, 114.48, 114.44, 114.33 MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 2460.97 $[M+H]^+$, Found: 2460.21; Anal. calcd for $C_{160}H_{104}N_8O_{16}Zn$: C 78.12, H 4.26, N 4.56, found: C 77.99, H 4.08, N 4.43.

Synthesis of 2b. tetrakis(4-aminophenyl)porphyrin (112 mg, 0.15 mmol), **2d** (200 mg, 0.61 mmol), DABCO (5.0g, 45 mmol) was dissolved in chlorobenzene (50 ml) at 90 ˚C. To the solution, titanium tetrachloride (1.0 ml, 9.0 mmol) was slowly added through a dropping funnel, and then stirred for 3 hours at 125 ˚C. The resulting solution was filtrated through a silica gel pad to remove insoluble part and DABCO. The product **2b** (73 % yield, 350 mg, 0.11 mmol) was obtained after purification using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 6 : 3 : 2 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, CDCl3, TMS) δ 8.91 - 8.76 (8H, m), 8.25 - 8.17 (6H, br), 7.97 - 6.77 (154H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 172.98, 168.04, 164.80, 164.80, 153.58, 152.18, 144.12, 139.12, 138.87, 135.81, 134.59, 133.79, 130.86, 130.67, 130.24, 129.48, 129.40, 128.65, 128.26, 128.13, 127.70, 121.58, 120.67, 120.32, 119.58; MALDI-TOF-Mass (Matrix: Dithranol) Calcd: 3309.14 $[M+H]^+$, Found: 3309.89

Synthesis of 2a. To a solution of **2b** (30 mg, 8.9 μmol) in THF (2 ml), a methanol solution (2 ml) of potassium hydroxide (20 mg, 0.36 mmol) was added. After stirring for 10 minutes, the solution was evaporated to dryness followed by isolation of the crude product **2c** using silica gel column chromatography eluted by a mixed solvent (chloroform : ethylacetate = 3 : 1 containing 0.5 wt% triethylamine).

Then, **2c** was dissolved in dimethylformamide (10 ml) with **10** (80 mg, 0.24 mmol) and potassium carbonate (300 mg, 2.2 mmol). The mixture was reacted at 120 ˚C for 5 hours. The final product **2a** (38 % yield, 12 mg, 3.4 μmol) was produced after purification by silica gel column chromatography (chloroform : ethylacetate = 4 : 1) and preparative HPLC with size-exclusion columns (SEC).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.90-8.65 (8H, br), 8.25-8.19 (6H, br), 8.01 - 6.74 (20H, br), 7.19 - 7.17 (142H, br), 4.58 - 4.45 (16H, br) ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 179.27, 168.55, 153.72, 150.09, 139.09, 137.23, 135.75, 134.89, 134.61, 134.29, 133.30, 131.74, 131.25, 130.97, 130.27, 129.47, 128.25, 128.11, 127.66, 127.20, 126.62, 126.12, 120.66, 119.57, 114.38, 113.58 MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 3894.71.$[M+H]^+$, Found: 3894.22 Elemental Analysis: C, 81.43; H, 4.56; N, 5.76; O, 6.57; Zn, 1.68; Anal. calcd for $C_{264}H_{176}N_{16}O_{16}Zn$: C 81.43, H 4.56, N 5.76, found: C 81.17, H 4.42, N 5.50.

Synthesis of 3b. tetrakis(4-aminophenyl)porphyrin (53 mg, 0.071 mmol), **3d** (400 mg, 0.29 mmol), DABCO (5.0g, 45 mmol) was dissolved in chlorobenzene (50 ml) at 90 ˚C. To the solution, titanium tetrachloride (1.0 ml, 9.0 mmol) was slowly added through a dropping funnel, and then stirred for 3 hours at 125 ˚C. The resulting solution was filtrated through a silica gel pad to remove insoluble part and DABCO. The product **3b** (70 % yield, 310 mg, 0.050 mmol) was obtained after purification using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 6 : 3 : 2 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$,TMS) δ 8.90 (8H, s), 8.24 - 6.29 (288H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 169.04, 168.35, 168.09, 164.78, 154.13, 153.78, 152.63, 152.02, 151.63, 150.05, 139.29, 137.56, 135.68, 135.41, 134.52, 133.72, 131.76, 130.91, 130.17, 129.46, 128.97, 128.60, 128.43, 128.22, 128.09, 127.59, 127.28, 121.56, 120.94, 120.80, 120.58, 120.36, 120.05, 119.72; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 6177.62 $[M+H]^+$, Found: 6177.23.

Synthesis of 3a. To a solution of **3b** (29 mg, 4.4 µmol) in THF (2 ml), a methanol solution (2 ml) of potassium hydroxide (20 mg, 0.36 mmol) was added. After stirring for 10 minutes, the solution was evaporated to dryness followed by isolation of the crude product **3c** using silica gel column chromatography eluted by a mixed solvent (chloroform : ethylacetate = 3 : 1 containing 0.5 wt% triethylamine).

Then, **3c** was dissolved in dimethylformamide (10 ml) with **10** (80 mg, 0.24 mmol) and potassium carbonate (300 mg, 2.2 mmol). The mixture was reacted at 120 ˚C for 5 hours. The final product **3a** (43 % yield, 12 mg, 1.9 µmol) was produced after purification by silica gel column chromatography (chloroform : ethylacetate = 5 : 1) and preparative HPLC with size-exclusion columns (SEC).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.90-8.75 (8H, br), 8.27 - 8.14 (6H, br), 8.03 - 6.30

(290H, m), 4.58 - 4.08 (16H, br) ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 169.06, 168.37, 154.16, 153.84, 152.03, 139.17, 135.71, 134.86, 134.26, 133.26, 130.93, 130.69, 130.18, 129.48, 128.92, 128.24, 128.08, 127.66, 127.18, 126.65, 120.95, 120.74, 120.58, 120.38, 120.09, 119.69, 114.37, 68.55, 66.56; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 6761.19.$[M+H]^+$, Found: 6762.32; Anal. calcd for $C_{472}H_{320}N_{32}O_{16}Zn$: C 83.85, H 4.77, N 6.63, found: C 83.63, H 4.66, N 6.57.

Synthesis of 4b. tetrakis(4-aminophenyl)porphyrin (33 mg, 0.045 mmol), **4d** (500 mg, 0.18 mmol), DABCO (5.0g, 45 mmol) was dissolved in chlorobenzene (50 ml) at 90 ˚C. To the solution, titanium tetrachloride (1.0 ml, 9.0 mmol) was slowly added through a dropping funnel, and then stirred for 3 hours at 125 ˚C. The resulting solution was filtrated through a silica gel pad to remove insoluble part and DABCO. The product **4b** (60 % yield, 320 mg, 0.027 mmol) was obtained after purification using silica gel column chromatography eluted by a mixed solvent (chloroform : hexane : ethylacetate = 3 : 1 : 1 containing 0.5 wt% triethylamine).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.77 (8H, s), 8.19 - 5.85 (576H, m); ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 169.05, 168.90, 168.42, 168.23, 167.91, 164.80, 160.80, 154.14, 153.70, 153.47, 152.40, 151.94, 151.58, 150.79, 150.15, 141.59, 139.35, 139.01, 137.36, 135.84, 135.67, 134.84, 134.36, 133.72, 132.79, 131.86, 130.83, 130.61, 130.44, 130.16, 129.44, 128.89, 128.62, 128.26, 128.18, 128.07, 127.96, 127.65, 121.51, 121.17, 120.54, 120.32, 119.67; MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 11911.57 $[M+H]^+$, Found: 11913.21

Synthesis of 4a. To a solution of **4b** (45 mg, 3.7 μmol) in THF (2 ml), a methanol solution (2 ml) of potassium hydroxide (20 mg, 0.36 mmol) was added. After stirring for 10 minutes, the solution was evaporated to dryness followed by isolation of the crude product **4c** using silica gel column chromatography eluted by a mixed solvent (chloroform : ethylacetate = 3 : 1 containing 0.5 wt% triethylamine).

Then, **4c** was dissolved in dimethylformamide (10 ml) with **10** (80 mg, 0.24 mmol) and potassium carbonate (300 mg, 2.2 mmol). The mixture was reacted at 120 ˚C for 5 hours. The final product **4a** (45 % yield, 20 mg, 1.7 μmol) was produced after purification by silica gel column chromatography (chloroform : ethylacetate = 6 : 1) and preparative HPLC with size-exclusion columns (SEC).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$, TMS) δ 8.80 - 8.66 (8H, br), 8.40 - 8.12 (6H, br), 8.00 - 5.89 (578H, m), 4.58 - 3.51 (16H, br) ^{13}C NMR (ppm, 100 MHz, $CDCl_3$, TMS) δ 168.89, 168.23, 154.16, 153.72, 151.96, 150.09, 139.35, 135.83, 134.91, 134.25, 132.50, 130.87, 130.63, 130.16, 129.43, 128.89, 128.19, 128.07, 127.20, 125.52, 120.55, 120.31, 119.72, 114.33, 68.60, 66.63 MALDI-TOF-Mass (Matrix : Dithranol) Calcd: 12497.14 $[M+H]^+$, Found: 12498.28; Anal. calcd for $C_{888}H_{608}N_{64}O_{16}Zn$: C 85.35, H 4.90 N 7.17, found: C 85.09, H 4.97, N 7.03.

Other Materials: Zinc tetraphenylporphyrin (**ZnTPP**) was purchased from Aldrich. 3,5-Di-tert-butyl-phenyl-naphthalenediimide (**BuPh-NDI**) was synthesized by a reported procedure.[4] 2,6-Dichlorobenzoquinone (**DCBQ**) was purchased from Tokyo Kasei Industry (TCI). All solvents and other reagents for the syntheses were purchased from Kantoh Kagaku Co. and used without further purification as reagent grade. The spectroscopic measurement-grade of THF without any stabilizer used for the transient absorption measurements was purchased from Kantoh Kagaku Co..

Measurements of transient absorption spectra. The transient absorption spectrum was measured by the typical pump and probe system. A pump light (532 nm, 3 mJ, 10 Hz) was generated on a Q switch Nd:YAG laser (Minilite, Continuum, Ltd.) as second harmonics. It was directed into a quartz cell (1 cm × 1 cm) filtered with a 2 mL sample solution. A probe light was generated by a CW 150 W Xe lamp (L8004, Hamamatsu) which was directed to the sample cell by a quartz optical fiber. The two beams crossed in the sample solution with an orthogonal orientation. The detection line was assembled using a CCD camera (C4742-98-24NR, Hamamatsu Photonics), a streak unit (C7700-01, Hamamatsu), a single polychromator (C5094, Hamamatsu) and a notch filter (532 nm). The sample solution was degassed by repeating the process of “freeze – vacuum – N_2 substitution – melting” three times. Both the YAG laser oscillation and streak camera gating were triggered by a four-channel digital delay/pulse generator (DG535, Oxford Research Systems, Inc.). The obtained data were processed by PC-based software (HPD-TA 7.1.0, Hamamatsu) on a PC.

Calculation of the quantum yields. The transient absorption of the triplet-excited state of **ZnTPP** (zinc tetraphenylporphyrin) in toluene (0.1 mM) was used as the reference sample for the quantum yield calculation. [5,6] The quantum yield and the molar absorptivity value in the literature $\Delta\varepsilon$□□□(470 nm) = 7.4×10^4 M^{-1} cm^{-1}, Φ_{ref} = 0.88, respectively were used for the calculation.

The static UV-vis absorbance spectrum of **ZnTPP**, which is the same solution used for the transient absorption measurement in a quartz cell (optical length 1 mm), was measured using a UV-vis spectrometer. At every wavelength (λ), $Abs_{ref}(\lambda)$ and $\Delta Abs_{ref}(\lambda)$ were obtained from the spectral data as the steady-state absorbance and transient absorbance of the reference sample, respectively. Similarly, the spectral data of a test sample produced $\mathrm{Abs}_{\mathrm{sample}}(\lambda)$ and $\Delta\mathrm{Abs}_{\mathrm{sample}}(\lambda)$. If the reference and the test samples were measured using the same setup, the quantum yields of the transient state of the test sample could be calculated using the following equation

$$\frac{\Delta\mathrm{Abs}_{\mathrm{ref}}(\lambda)}{\Delta\varepsilon_{\mathrm{ref}}(\lambda)\times\mathrm{Abs}_{\mathrm{ref}}(532\mathrm{nm})\times C_{\mathrm{ref}}\times\Phi_{\mathrm{ref}}}=\frac{\Delta\mathrm{Abs}_{\mathrm{sample}}(\lambda)}{\Delta\varepsilon_{\mathrm{sample}}(\lambda)\times A_{\mathrm{sample}}(532\mathrm{nm})\times C_{\mathrm{sample}}\times\Phi_{\mathrm{sample}}}=I \quad \text{(S1)}$$

□□□□□□$\varepsilon_{\mathrm{ref}}(\lambda)$ and □$_{\mathrm{sample}}(\lambda)$ are the absorption coefficient of the reference and test sample at the given wavelength (λ), respectively. C_{ref} and C_{sample} are the concentration of the reference and sample solution, respectively. The constant I is the instrumental value containing the effective optical path length and the laser intensity for excitation.

Bi-molecular rate constants of the charge separation (k_f). The charge separating reaction could be traced as the decay of the triplet-excited state, which has a characteristic transient absorption peak at 500 nm. This decay was completed within 100 ~ 300 ns (for **DCBQ**) or 1~3 □s (for **BuPh-NDI**). It was applied to the quasi-1st order kinetics with a residual absorption because an excess amount of the electron acceptors (**DCBQ** and **BuPh-NDI**) was added to the dendrimer solution. The decay lifetimes for various concentration of the acceptor were measured and applied to the Stern-Volmer equation [Eq. (S4)].

$$\frac{1}{\tau}-\frac{1}{\tau^{\circ}}=k_f[\mathrm{A}] \qquad \text{(S5)}$$

τ : apparent lifetime of the triplet-excited state in the presence of the electron acceptor.
τ_0 : lifetime of the triplet-excited state in the absence of the electron acceptor.
[A] : concentration of the electron acceptor.

Bi-molecular rate constants of the charge recombination (k_b). The charge recombination can be traced to the decay of the radical ion pair. This decay can be observed on a much longer timescale (100 ~ 1000 □s) than that of the charge separation (1 ~ 10 □s). Because these decays did not overlap each other on the timeline, no deconvolution analysis was needed. In principle, the recombination is the reaction between the anion and cation radicals of the same concentration. Therefore, it should obey 2nd order kinetics if the ion pair was dissociated into free ions. The decay curve of the **DPAG4-ZnTPP / BuPh-NDI** system actually followed the fitting line of the 2nd order kinetics (inverse function versus time). In contrast, application of the experimental curve for the 1st order kinetics (mono-exponential decay) failed. We also applied these experimental results to a multi-exponential decay curve. Although this application succeeded, the apparent lifetime was dependent on the initial concentration of the radical ion pair. This fact means that the recombination should be regarded as a bimolecular reaction. The bimolecular rate constants of the charge recombination were calculated as the slope of the linear approximation, which was obtained in a plot of the inverse concentration and the time after the excitation.

The concentration-time profile was obtained from the differential absorbance decay at 680 nm based on the Lambert-Beer law. The profile was normalized to the initial concentration of the radical ion pair calculated from their quantum yields. The other wavelength (e.g., 500 nm) also provided the same decay profiles under the normalization. When the excitation laser intensity is high enough to reach the saturation, the concentration of the radical ion pair is given by the following equation using the different absorbance values before the decay (ΔAbs.$^{\circ}$), and the concentration (C_{sample}) of the sensitizer (zinc porphyrin) using the following equation.

$$\begin{aligned} C_{\text{RIP}} &= C^{\circ}\frac{\Delta\text{Abs.}}{\Delta\text{Abs.}^{\circ}} \\ C^{\circ} &= \Phi_{\text{RIP}} \times C_{\text{sample}} \end{aligned} \qquad \text{(S5)}$$

Results

UV-vis spectra during electrochemical oxidation and reduction. Redox couples between the neutral and mono-reduced anion radicals were observed at –0.62 V (**DCBQ**) and –0.83 V (**BuPh-NDI**) in the THF solution. A similar redox was also observed at –0.56 V in benzene / acetonitrile (1:1). The oxidation of a zinc porphyrin core in the dendrimers was observed around +0.35 ~ 0.40 V as shown in a previous report.[7] The excitation energy of the triplet-excited state of the zinc porphyrin in the DPAs is 1.57 eV, which was characterized by a phosphorescence wavelength (789 nm).

The UV-vis absorption changes accompanying the reduction (**DCBQ** and **BuPh-NDI**) and oxidation (**DPVGX-ZnTPP**) were measured (**Fig. S5**). The obtained values of the absorption peak wavelength and its molar absorptivity of these radical ions are listed in **Table S1**.

Table S1. UV-vis absorption data of radical ions

Radical ion species	λ_{max} [nm] ($\varepsilon \times 10^{-3}$ [M^{-1} cm^{-1}])
DCBQ^{-}	328 (8.78), 442 (5.54)
BuPh-NDI^{-}	473 (20.8), 607 (5.82), 703 (1.84), 783 (3.25)
DPAG1-ZnTPP^{+}	426 (154), 674 (24.0)
DPAG2-ZnTPP^{+}	433 (151), 687 (23.1)
DPAG3-ZnTPP^{+}	434 (161), 686 (22.1)
DPAG4-ZnTPP^{+}	435 (168), 690 (18.5)

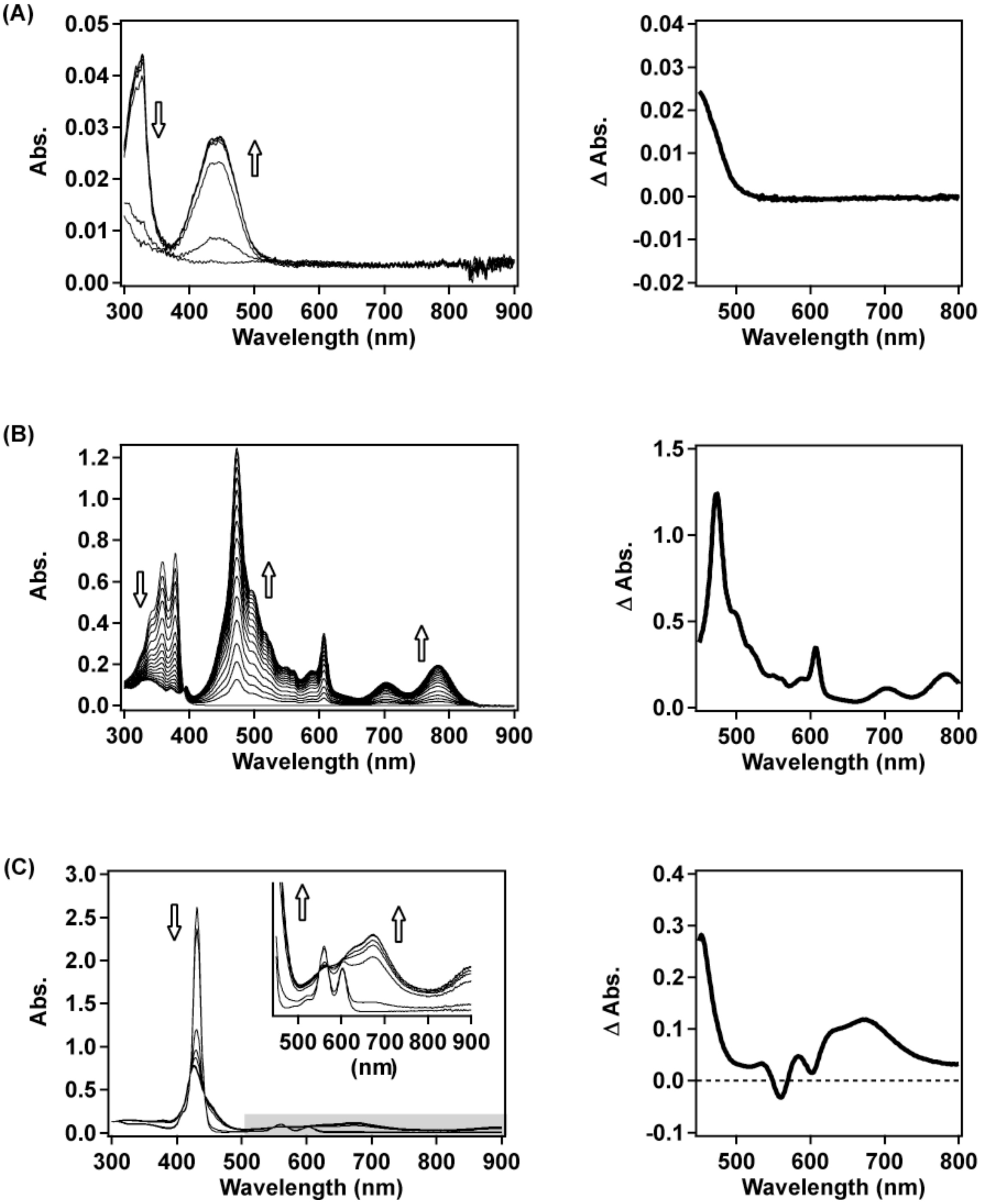


Figure S1. UV-vis spectral changes during the electrochemical reduction (A, B) and oxidation (C ~ F). Figures on the right side are the differential spectra of the electrolyzed species from the neutral one. (A) 0.1 mM **DCBQ** in benzene / acetonitrile (1:1) with 0.1 M tetrabutylammonium perchlorate electrolyzed at –0.8 V vs. Fc/Fc$^+$, (B) 0.3 mM **BuPh-NDI** in THF with 0.1 M tetrabutylammonium perchlorate electrolyzed at –1.2 V vs. Fc/Fc$^+$ under an N_2 atmosphere, (C) 0.05 mM **DPAG1-ZnTPP** in THF with 0.1 M tetrabutylammonium perchlorate electrolyzed at +0.6 V vs. Fc/Fc$^+$. The optical path length (*d*) is 1 mm (A and C) and 2 mm (B).

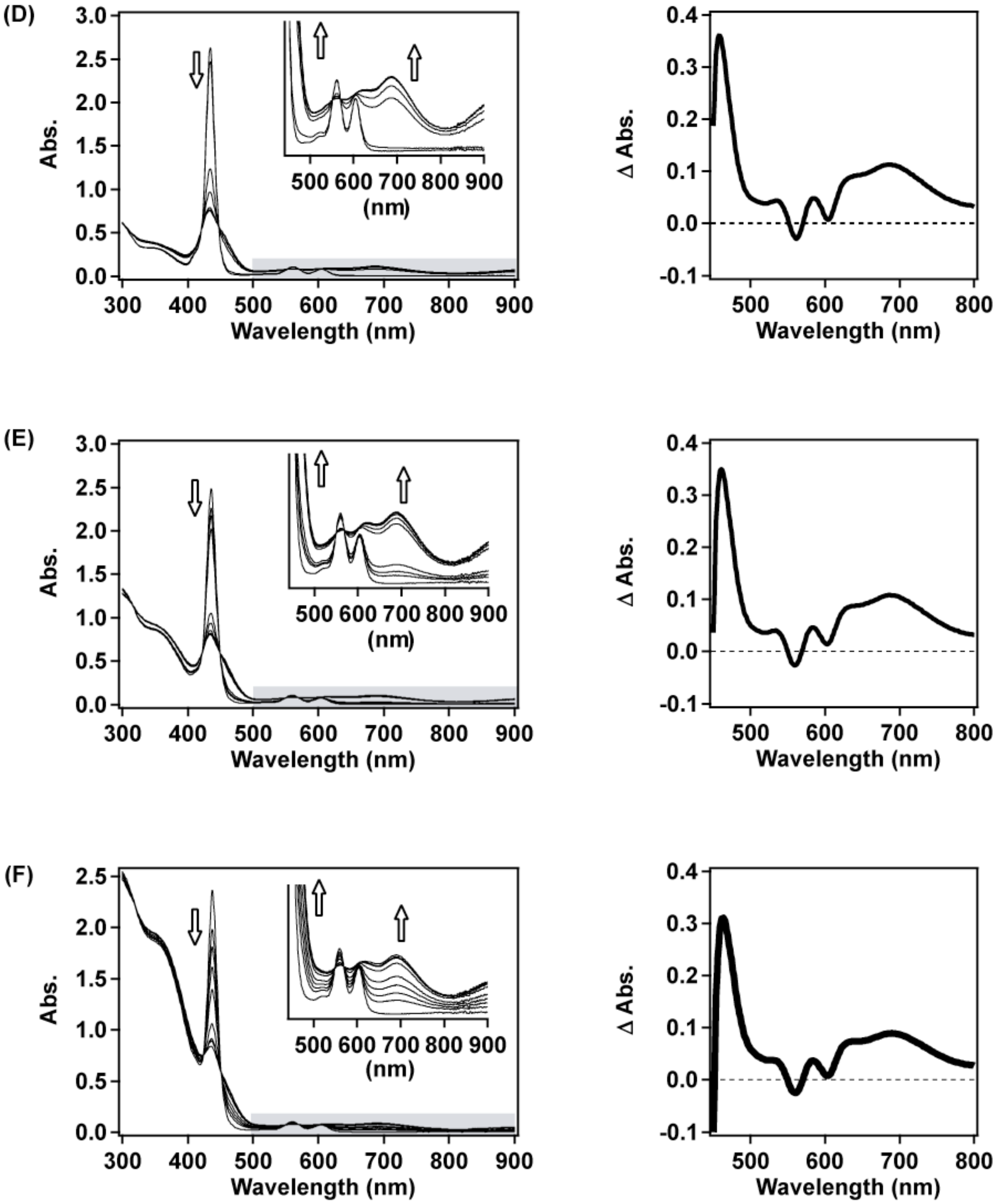


Figure S1 (continue). UV-vis spectral changes during the electrochemical reduction (A, B) and oxidation (C ~ F). Figures on the right side are the differential spectra of the electrolyzed species from the neutral one. (D) 0.05 mM **DPAG2-ZnTPP** in THF with 0.1 M tetrabutylammonium perchlorate electrolyzed at +0.6 V vs. Fc/Fc$^+$. (E) 0.05 mM **DPAG3-ZnTPP** in THF with 0.1 M tetrabutylammonium perchlorate electrolyzed at +0.6 V vs. Fc/Fc$^+$. (F) 0.05 mM **DPAG4-ZnTPP** in THF with 0.1 M tetrabutylammonium perchlorate electrolyzed at +0.6 V vs. Fc/Fc$^+$. The optical path length (*d*) is 1 mm.

Photochemical properties of dendrimers 1 - 4. The excitation of the Q band (zinc porphyrin core) results in the formation of a singlet-excited state (S_1) which shows a strong fluorescence at 600 ~ 610 nm. The lifetime of S_1 was determined to be 1.8 ns (G1), 2.1 ns (G2), 2.2 ns (G3) and 2.3 ns (G4) from the decay of the fluorescence (**Fig. S7**).

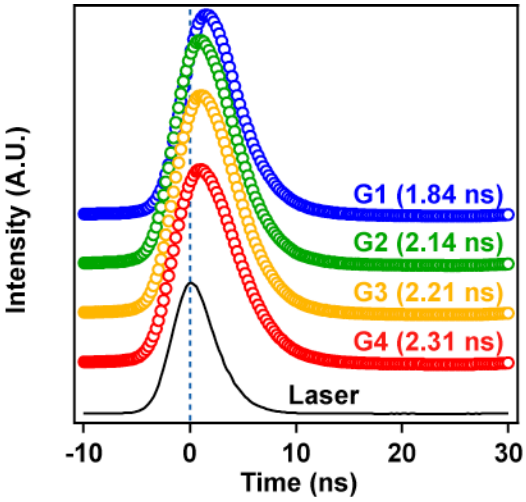


Figure S2. Fluorescence decays at 600 nm upon the excitation of **DPAGX-ZnTPP (X = 1 - 4)** by a 532 nm laser flash in THF (containing TBABr). The lifetimes were calculated by fitting of a mono-exponential decay with deconvolution of the laser profile into the experimental line.

The S_1 state is followed by the T_1 state through the intersystem crossing. The transient absorption spectra were measured 50 ns after the excitation (**Figure S8**). These spectra around the Q band bleaching (530 ~ 630 nm) were applied to the curve fitting by **Eq. S3, S4** using the parameters obtained from the steady state UV-vis absorption spectra. The fitting results were used in the calculation of these quantum yields.

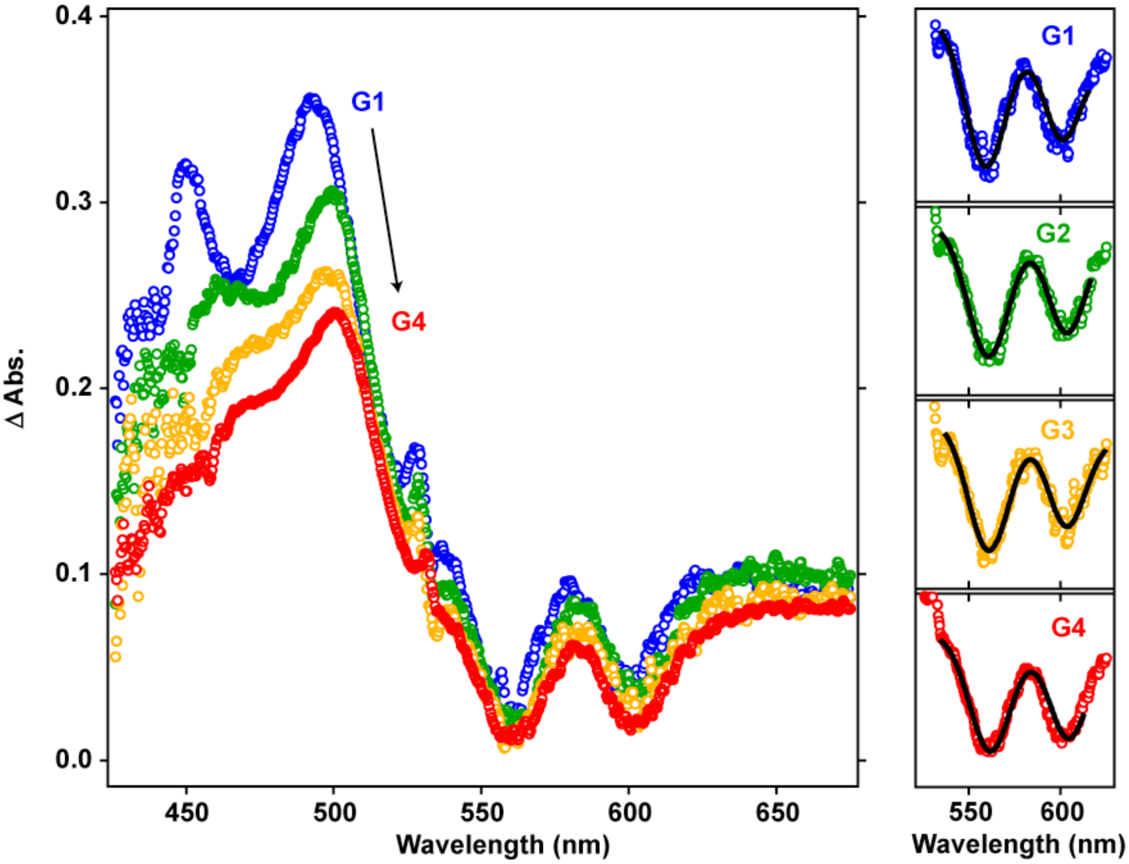


Figure S3. Transient absorption spectra of **DPAGX-ZnTPP (X = 1 - 4)** (50 μM) obtained 50 ns after the excitation (532 nm) in THF containing TBABr (0.05 M) under an N_2 atmosphere. The figures shown on the right side are the fitting results of these spectra using **Eq. S3, S4**.

Radical ion formation between dendrimers 1 - 4 and DCBQ in THF. The addition of the electron acceptor (**DCBQ**) results in the formation of the radical ion pair from the T_1 state that can be observed in the transient absorption spectra. The spectra and time-course are shown in **Figure S9** and **Figure S10**. The decay of the radical ion pair obeys the kinetics of a 2nd order reaction that shows an inverse functional decay. The displayed concentration profile in **Figure S11** was calculated from the differential absorbance profiles.

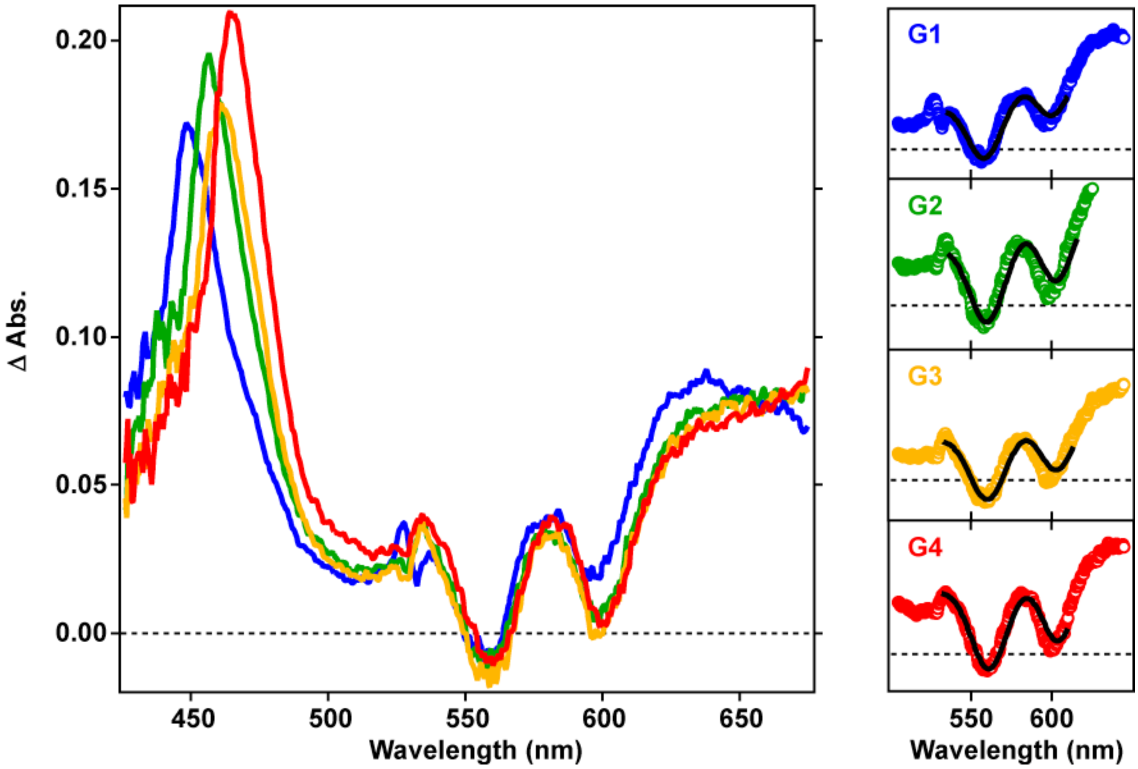


Figure S4. Transient absorption spectra of **DPAGX-ZnTPP** (50 μM) at 1 μs in the presence of **DCBQ** (2.5 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere. The figures shown on the right side are the fitting results of these spectra using **Eq. S3, S4**.

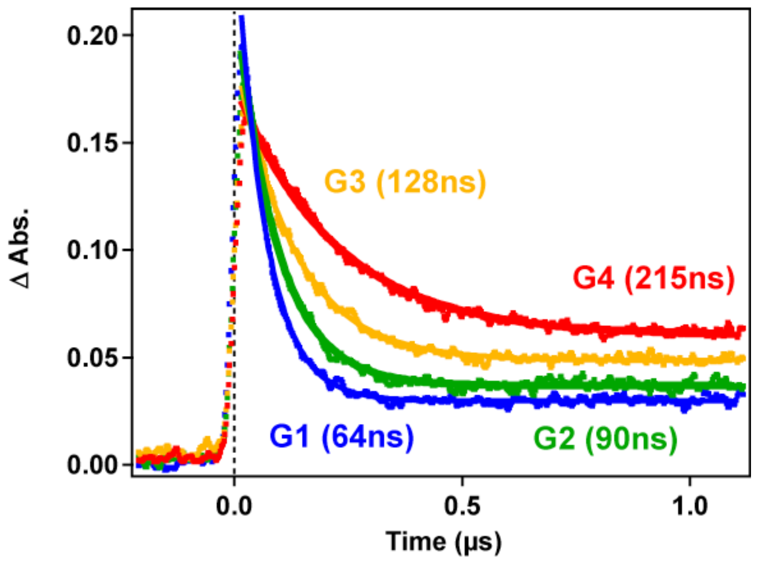


Figure S5. Time-profiles of the transient absorption (500 nm) of **DPAGX-ZnP (X = 1 - 4)** (50 μM) in the presence of **DCBQ** (2.5 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere. The decays correspond to the transitions from the T_1 state to the radical ions.

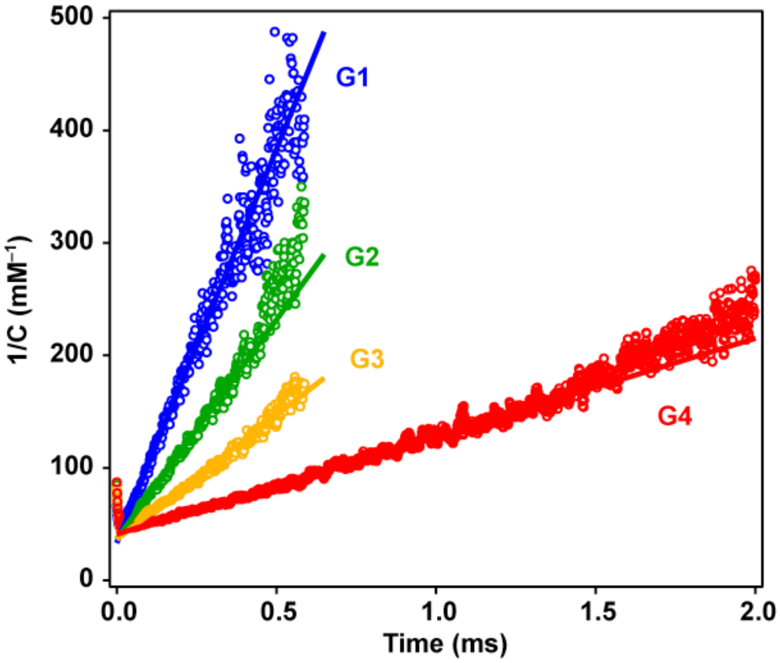


Figure S6. Inverse plots of radical ion pair (**DPAGX-ZnP$^+$ – DCBQ$^-$**) concentrations obtained from the analysis of the transient absorption decay versus time. These data were measured with **DPAGX-ZnP (X = 1 - 4)** (50 μM) in the presence of **DCBQ** (2.5 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere.

Table S2. Kinetic parameters of photochemical reactions (23 ˚C) of dendrimers **DPAGX-ZnTPP (X = 1 - 4)** with **DCBQ** in THF (TBABr).

X	**DCBQ**		
	k_f (mol^{-1} l s^{-1})[a]	Φ_{CS}[b]	k_b (mol^{-1} l s^{-1})[c]
1	5.9×10^9	0.52	7.5×10^8
2	3.8×10^8	0.57	4.2×10^8
3	2.7×10^8	0.74	2.7×10^8
4	1.6×10^8	0.86	8.6×10^7

[a] Second-order rate constant [mol^{-1} l s^{-1}] of the charge-separation. [b] Quantum yields of the radical ion pair formation from the triplet excited states. [c] Second-order rate constant [mol^{-1} l s^{-1}] of the charge-recombination.

Radical ion formation between dendrimer 1 - 4 and BuPh-NDI in THF. The data collection and processing were done similar to that for **BuPh-NDI** in THF. The spectral data are shown in the figures (**Figure S12, S13, S14**).

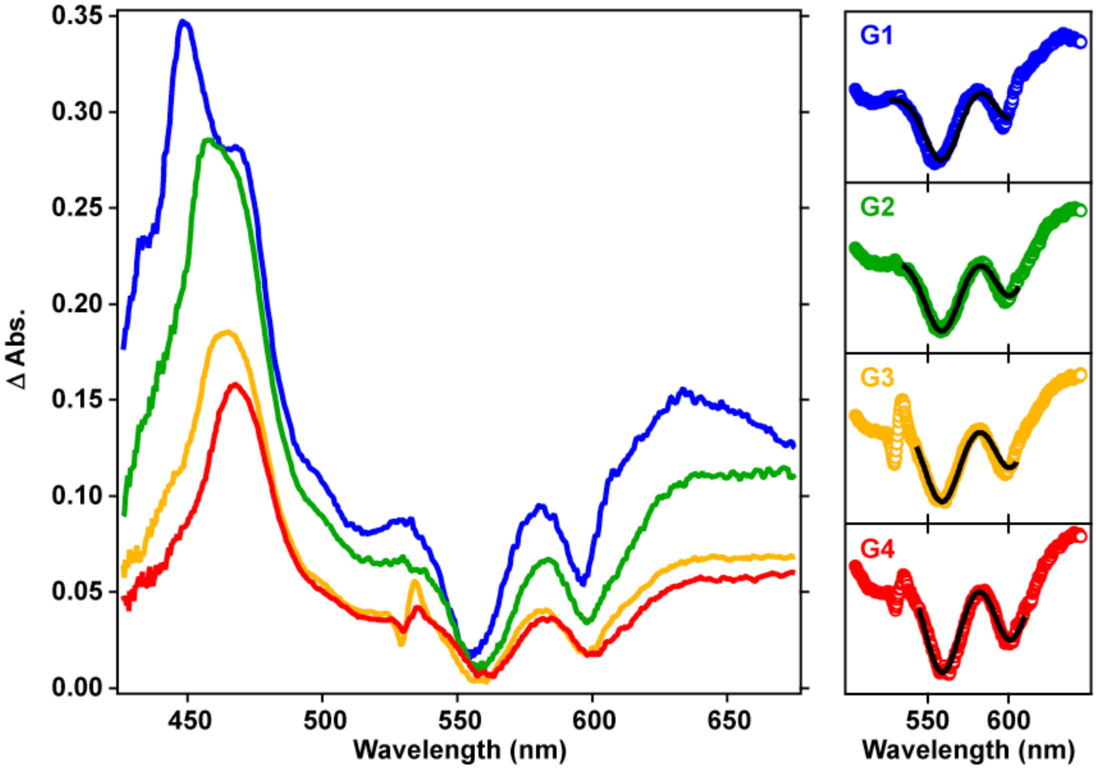


Figure S7. Transient absorption spectra of **DPAGX-ZnTPP (X = 1 - 4)** (50 μM) at 1 μs in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere. The figures shown on the right side are the fitting results of these spectra using **Eq. S3, S4**.

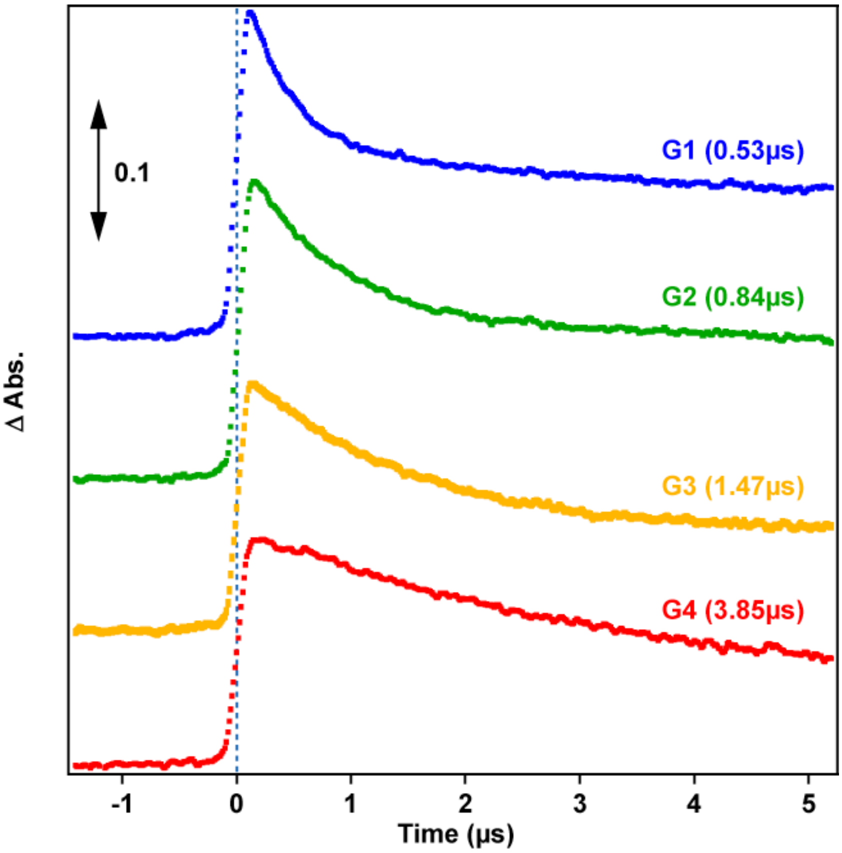


Figure S8. Time-profiles of the transient absorption (500 nm) of **DPAGX-ZnTPP (X = 1 - 4)** (50 μM) in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere. The decays correspond to the transitions from the T_1 state to the radical ions.

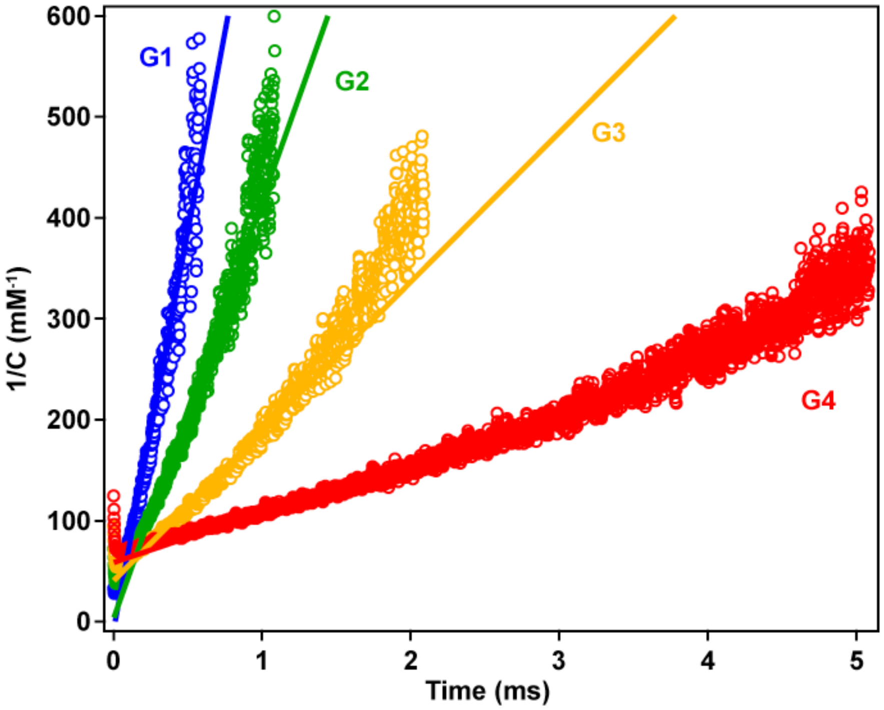


Figure S9. Inverse plots of radical ion pair (**DPAGX-ZnTPP^{+} – BuPh-NDI $^{-}$**) concentrations obtained from the analysis of the transient absorption decay versus time. These data were measured using **DPAGX-ZnTPP (X = 1 - 4)** (50 μM) in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 M) under an N_2 atmosphere.

Table S3. Kinetic parameters of photochemical reactions (23 ˚C) of dendrimers **DPAGX-ZnTPP (X = 1 - 4)** with **BuPh-NDI** in THF (TBABr).

X	**BuPh-NDI**		
	k_f (mol^{-1} l s^{-1})[a]	Φ_{CS}[b]	k_b (mol^{-1} l s^{-1})[c]
1	5.1×10^{8}	1.00	8.7×10^{8}
2	3.9×10^{8}	0.74	5.0×10^{8}
3	2.2×10^{8}	0.55	2.4×10^{8}
4	9.9×10^{7}	0.65	5.5×10^{7}

[a] Second-order rate constant [mol^{-1} l s^{-1}] of the charge-separation. [b] Quantum yields of the radical ion pair formation from the triplet excited states. [c] Second-order rate constant [mol^{-1} l s^{-1}] of the charge-recombination.

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