Supplemental Information

A Potential Gradient along the Layer-by-Layer Architecture for Electron Transfer Rectification

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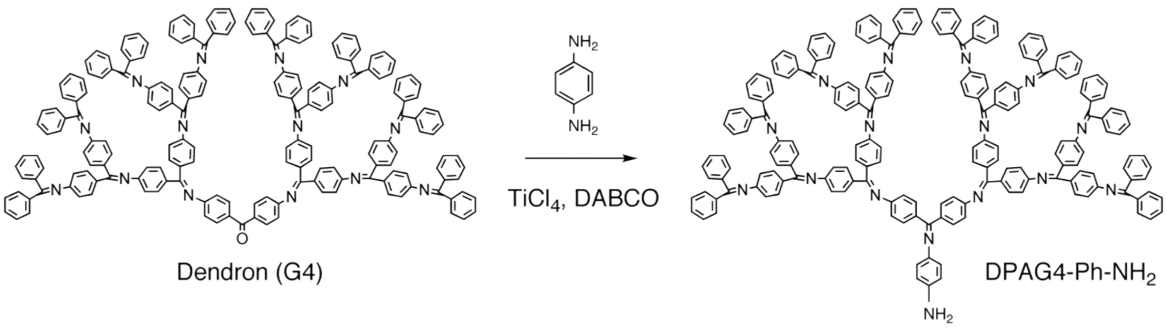
Experimental

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_4NClO_4 / 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_4NClO_4 / 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. Nanosecond transient absorptions were measured at room temperature (23°C) with an excitation at 532 nm. Their data analyses were carried out as previously reported.

Synthesis of DPAGX-NDI: DPAs having a naphthalenediimine core were prepared by the following procedure. First, the precursor materials (**DPAG*X*-Ph-NH$_2$**) were synthesized from the corresponding dendrons and 1,4-phenylenediamine with $TiCl_4$ as the dehydrating reagent.

Scheme S1



DPAG1-Ph-NH$_2$: Phenylenediamine (2.7 g, 25 mmol), benzophenone (0.91 g, 5 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 3.37 g, 30 mmol) were dissolved in monochlorobenzene (100 mL) under an N_2 atmosphere. Titanium tetrachloride ($TiCl_4$, 0.4 mL, 3.6 mmol) was slowly added to the solution through a dropping funnel. The resulting solution was heated at 125˚C for 3 hours. It was filtered after cooling and the solution was then evaporated to dryness. The product was isolated by silica gel column chromatography (neutral) with hexane / chloroform / ethylacetate (1:1:1) as the eluent. **DPAG1-Ph-NH$_2$**: 0.6 g (2.2 mmol), yield 44 %, ^{1}H NMR ($CDCl_3$, 30 ℃, TMS) $\delta =$ 7.71 (d, 2H, J = 8.0Hz), 7.46 – 7.26 (m, 6H), 7.13 (dd, 2H, J = 8.0, 2.0 Hz), 6.58 (d, 2H, J = 8.0 Hz), 6.49 (d, 2H, J = 8.0 Hz), 3.48 ppm (s, 2H); MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd 273.14 $[M+H]^+$, found 272.76.

DPAG2-Ph-NH$_2$: Phenylenediamine (2.16 g, 20 mmol), dendron (**DPAG2-dendron:** 2.16 g, 4 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.79 g, 16 mmol) were dissolved in monochlorobenzene (50 mL) under an N_2 atmosphere. Titanium tetrachloride ($TiCl_4$, 0.4 mL, 3.6 mmol) was slowly added to the solution through a dropping funnel. The resulting solution was heated at 125˚C for 3 hours. It was filtered after cooling and the solution was then evaporated to dryness. The product was isolated by silica gel column chromatography (neutral) with hexane / chloroform / ethylacetate (1:1:1) as the eluent. **DPAG2-Ph-NH$_2$**: 1.74 g (2.76 mmol), yield 69 %,

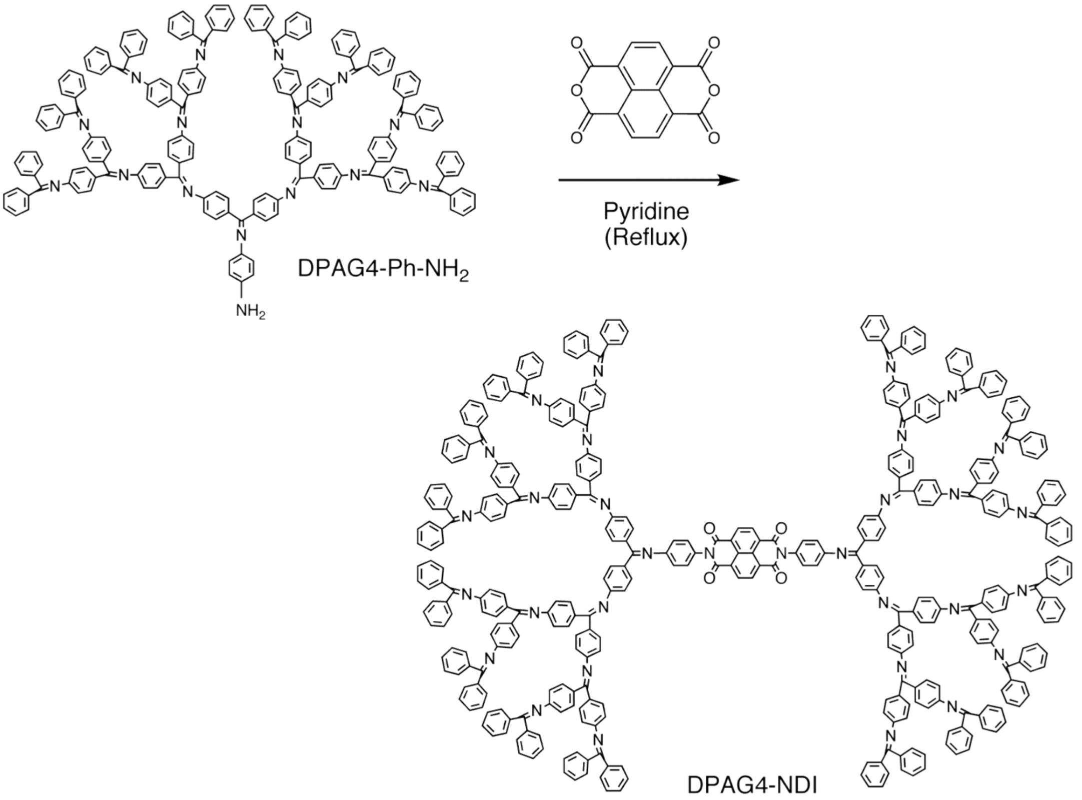
^{1}H NMR ($CDCl_3$, 30 ℃, TMS) $\delta =$ 7.74 (d, 4H, J = 8.0 Hz), 7.50 – 7.39 (m, 10H), 7.30 – 7.26 (m, 4H), 7.14 (dd, 2H, J = 8.0, 2.0 Hz), 7.08 (d, 2H, J = 8.0 Hz), 6.86 (d, 2H, J = 8.0 Hz), 6.70 (d, 2H, J = 8.0 Hz), 6.59 (d, 2H, J = 8.0 Hz), 6.50 (d, 2H, J = 8.0 Hz), 6.44 (d, 2H, J = 8.0 Hz), 3.48 ppm (s, 2H); MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd 631.29 $[M+H]^+$, found 631.32.

DPAG3-Ph-NH$_2$: Phenylenediamine (0.54 g, 5 mmol), dendron (**DPAG3-dendron:** 1.26 g, 1 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.45 g, 4 mmol) were dissolved in monochlorobenzene (50 mL) under an N_2 atmosphere. Titanium tetrachloride ($TiCl_4$, 0.1 mL, 0.8 mmol) was slowly added to the solution through a dropping funnel. The resulting solution was heated at 125˚C for 3 hours. It was filtered after cooling and the solution was then evaporated to dryness. The product was isolated using a silica gel column chromatograph (neutral) with hexane / chloroform / ethylacetate (1:1:1) as the eluent. **DPAG3-Ph-NH$_2$**: 0.8 g (0.59 mmol), yield 59 %; ^{1}H NMR ($CDCl_3$, 30 ℃, TMS) $\delta =$ 7.76 – 6.44 (m, 68H), 3.59 ppm (s, 2H); MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd 1348.59 $[M+H]^+$, found 1349.01.

DPAG4-Ph-NH$_2$: Phenylenediamine (1.08 g, 10 mmol), dendron (**DPAG4-dendron:** 5.37 g, 2 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.90 g, 8 mmol) were dissolved in monochlorobenzene (50 mL) under an N_2 atmosphere. Titanium tetrachloride ($TiCl_4$, 0.1 mL, 0.8 mmol) was slowly added to the solution through a dropping funnel. The resulted solution was heated at 125˚C for 3 hours. It was filtered after cooling and the solution was then evaporated to dryness. The product was isolated by silica gel column chromatograph (neutral) with hexane / chloroform / ethylacetate (1:1:1) as the eluent. **DPAG4-Ph-NH$_2$**: 4.4 g (1.58 mmol), yield 80 %; ^{1}H NMR ($CDCl_3$, 30 ℃, TMS) $\delta =$ 7.76 – 6.25 (m, 140H), 3.28 ppm (s, 2H); MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd 2782.18 $[M+H]^+$, found 2782.28.

These precursors were treated with naphthalene-tetracarboxylicanhydrate (from Aldrich) affording **DPAGX-NDI**. The products were isolated by silica gel column chromatography and preparative HPLC (Japan Analytical Industry, LC-908) equipped with an SEC column (Japan Analytical Industry, JAI-GEL 2H & 2.5 H).

Scheme S2



DPAG1-NDI: **DPAG1-Ph-NH$_2$** (0.6 g, 2.2 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.27 g, 1 mmol) were dissolved in pyridine (50 mL) under an N_2 atmosphere and heated at 110 ˚C (reflux) for 24 hours. The solution was then cooled and evaporated to dryness. The product was isolated using a column chromatograph with chloroform / ethyl acetate (1:1) as the eluent and further purified by a preparative HPLC (GPC column) which produced 125 mg of **DPAG1-NDI** (0.16 mmol, 16 %). Characterization data of **DPAG1-NDI:** ^{1}H NMR (CDCl$_3$, 30 ℃, TMS) δ = 8.80 (s, 4H), 7.79 (d, 4H, J = 8.0 Hz), 7.50 (t, 2H, J = 6.4 Hz), 7.38 (t, 2H, J = 6.4 Hz), 7.35 (m, 8H), 7.21 (dd, 4H, J = 6.4, 2.0 Hz), 7.10 (d, 4H, J = 6.4 Hz), 6.91 ppm (d, 4H, J = 8,0Hz); ^{13}C NMR (100 MHz, CDCl$_3$, 30˚C, TMS) δ = 168.85, 162.88, 151.70, 139.41, 135.65, 131.26, 130.89, 129.60, 129.42, 129.30, 128.99, 128.49, 128.19, 128.02, 127.07, 126.93, 121.92 ppm; IR (KBr) 1718, 1681, 1606, 1579, 1450, 1340, 1245, 1197, 1151 cm^{-1}; MALDI-TOF-Mass (Matrix: Dithranol) m/z calcd 776.24 [M + H]$^+$, found 776.66; UV-vis (CHCl$_3$) λ_{max} ($\varepsilon \times 10^{-3}$) = 362 (29), 381 nm (30 M^{-1} cm^{-1}).

DPAG2-NDI: **DPAG2-Ph-NH$_2$** (0.85 g, 1.35 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.20 g, 0.74 mmol) were dissolved in pyridine (50 mL) under an N_2 atmosphere and heated at 110 ˚C (reflux) for 24 hours. The solution was then cooled and evaporated to dryness. The product was isolated using a column chromatograph with hexane / chloroform / ethyl acetate (1:1:1) as the eluent and further purified by preparative HPLC (GPC column) which produced 478 mg of **DPAG2-NDI** (0.32 mmol, 48 %). Characterization data of **DPAG2-NDI:** ^{1}H NMR (400 MHz, $CDCl_3$, 30 ˚C, TMS) δ = 8.83 (s, 4H), 7.74 (d, 8H, J = 6.4 Hz), 7.50 – 7.07 (m, 40H), 6.94 (d, 4H), 6.82 (d, 4H), 6.75 (d, 4H), 6.65 ppm (d, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30℃, TMS) δ = 168.81, 168.40, 168.34, 162.84, 153.67, 151.95, 151.92, 139.26, 139.09, 135.75, 134.47, 131.26, 130.87, 130.37, 130.33, 129.50, 129.39, 129.36, 129.31, 128.96, 128.81, 128.56, 128.42, 128.16, 128.01, 127.73, 127.11, 126.98, 122.18, 120.48, 120.37 ppm; IR (KBr) 1716, 1679, 1587, 1500, 1444, 1407, 1342, 1311, 1247, 1222, 1133 cm^{-1}; MALDI-TOF-Mass (Matrix: Dithranol) *m/z* calcd 1493.54 $[M+H]^+$, found 1493.95; UV-vis ($CHCl_3$) λ_{max} ($\varepsilon \times 10^{-3}$) = 289 (66), 362 (60), 381 nm (61 M^{-1} cm^{-1}).

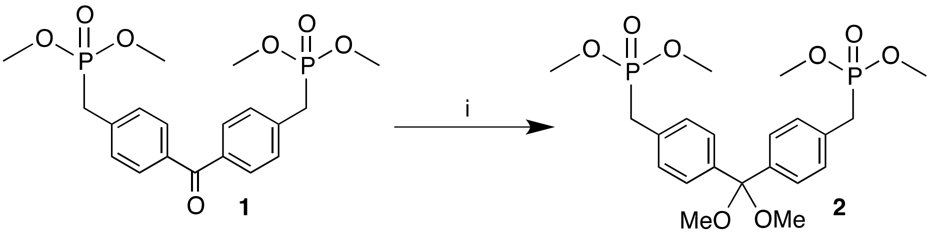
DPAG3-NDI: **DPAG3-Ph-NH$_2$** (0.80 g, 0.59 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (80 mg, 0.30 mmol) were dissolved in pyridine (50 mL) under an N_2 atmosphere and heated at 110 ˚C (reflux) for 24 hours. The solution was then cooled and evaporated to dryness. The product was isolated by a column chromatograph using hexane / chloroform / ethyl acetate (1:1:1) with the eluent and further purified by preparative HPLC (GPC column) which produced 263 mg of **DPAG3-NDI** (0.09 mmol, 30 %). Characterization data of **DPAG3-NIM:** ^{1}H NMR (400 MHz, $CDCl_3$, 30 ˚C, TMS) δ = 8.65 (s, 4H), 7.75 – 6.60 ppm (m, 204H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 ˚C, TMS) δ = 206.68, 168.85, 168.45, 168.33, 168.17, 168.09, 162.69, 154.08, 153.62, 152.31, 151.86, 151.67, 139.16, 139.00, 138.57, 138.54, 135.70, 135.53, 135.50, 134.11, 134.04, 133.89, 130.80, 130.52, 130.39, 130.31, 130.14, 129.99, 129.28, 129.06, 129.01, 128.82, 128.73, 128.54, 128.42, 128.08, 127.93, 127.75, 127.64, 126.78, 126.75, 122.22, 120.77, 120.65, 120.38, 120.18, 119.87 ppm; IR (KBr) 1716, 1680, 1581, 1498, 1444, 1408, 1342, 1309, 1290, 1248, 1224, 1176, 1132 cm^{-1}; MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd 2927.12 $[M+H]^+$, found 2928.53; UV-vis ($CHCl_3$) λ_{max} ($\varepsilon \times 10^{-3}$) = 290 (140), 362 (116), 382 nm (106 M^{-1} cm^{-1}).

DPAG4-NDI: **DPAG4-Ph-NH$_2$** (2.78 g, 1.0 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (201 mg, 0.75 mmol) were dissolved in pyridine (50 mL) under an N_2 atmosphere and heated at 110 ˚C (reflux) for 24 hours. The solution was then cooled and evaporated to dryness. The product was isolated using a column chromatograph with hexane / chloroform / ethylacetate (1:1:1) as the eluent and further purified by preparative HPLC (GPC column) which produced 790 mg of **DPAG4-NDI** (0.14 mmol, 20 %). Characterization data of **DPAG4-NDI:** ^{1}H NMR (400 MHz, $CDCl_3$, 30 ˚C, TMS) δ = 8.57 (s, 4H), 7.74 – 6.39 ppm (m, 280H); ^{13}C NMR (100 MHz, $CDCl_3$, 30˚C, TMS) δ = 168.45, 168.07, 162.73, 154.11, 151.94, 140.06, 139.25, 138.89, 138.39, 137.67, 135.78, 134.22, 130.87, 130.41, 130.06, 129.50, 129.36, 128.80, 128.61, 128.52, 128.25, 128.16, 128.00, 127.83, 121.80, 120.99, 120.84, 120.78, 120.50, 120.27, 120.12 ppm; IR (KBr) 1716, 1680, 1579, 1496, 1444, 1408, 1342, 1309, 1224, 1174, 1132 cm^{-1}; MALDI-TOF-Mass (Matrix : Dithranol) *m/z* calcd: 5794.92 $[M+H]^+$, found: 5795.18; UV-vis ($CHCl_3$) λ_{max} ($\varepsilon \times 10^{-3}$) = 290 (294), 361 (239), 380 nm (209 M^{-1} cm^{-1}).

Synthesis of DPVGX-ZnTPP: Dendritic phenylenevinylenes (DPV) were synthesized by a modified method based on a previously reported[5] convergent approach employing the Horner-Wadsworth-Emmons reaction.

Benzophenone bis-phosphonate and its protected compound. Benzophenone bis-phosphonate (**1**) was synthesized from 4,4'-dibromomethyl benzophenone with trimethyl phosphite according the previous method.[5] The ketone moiety of this product should be protected in order to prohibit the polymerization of (**1**). This product (**1**) was protected with methanol. **1** (1.0 g, 2.34 mmol), trimethyl orthoformate (1 ml, 9.14 mmol) and p-toluenesulfonic acid (60 mg) was dissolved in methanol (10 mL) and the reaction mixture was refluxed for 48 hours. To the resulting solution, $CHCl_3$ and water were added, and the product was extracted two times with $CHCl_3$. Finally, isolation by silica gel column chromatography ($CHCl_3/CH_3OH$ = 50/1) afforded 319 mg (yield 29 %) of **2**. ^1H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 7.43 (4H, d, J = 8.1 Hz), 7.22 (4H, d, J = 8.2 Hz), 3.63 (12H, d, J = 10.5Hz), 3.12 (4H, d, J = 22Hz), 3.10 (6H, s); MALDI-TOF-Mass: calcd: 473.4 $[M+H]^+$, found: 472.6 $[M+H]^+$, 440.7 $[M-OMe+H]^+$.

Scheme S3. (i) *p*-toluenesulfonic, trimethyl orthoformate in MeOH under reflux conditions.

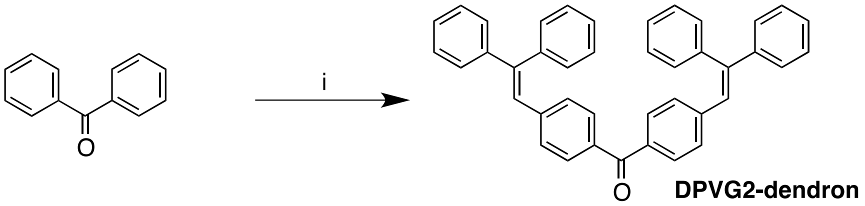


Synthesis of DPVG2-dendron. **1** (1.5. g, 3.5 mmol) and an excess amount of benzophenone (12.8 g, 70.4 mmol) was dissolved in dimethylformamide (40 ml). To a stirred solution of the mixture, potassium *tert*-butoxide 1.59 g (4.2 mmol) was slowly added at 0 ˚C. The deep orange mixture of the reaction was then stirred at room temperature for 16 hours. The resulting solution was slowly added to 200 mL of methanol to give the product as a precipitate. Silica gel column chromatography ($CHCl_3$/hexane = 1/1) and preparative HPLC using a size exclusion column (SEC,

$CHCl_3$) were carried out to isolate the pure **DPVG2-dendron** (807 mg, 43 %).

^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 7.53 (4H, d, J = 8.3 Hz), 7.34-7.29 (16H, m), 7.22-7.18 (4H, m), 7.08 (4H, d, J = 8.3 Hz), 6.99 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 195.56, 145.07, 142.97, 141.62, 139.90, 135.61, 130.28, 129.82, 129.27, 128.82, 128.33, 128.02, 127.85, 127.77, 127.07; MALDI-TOF-Mass calcd: 539.2 $[M+H]^+$, found: 539.6; Anal. calcd for $C_{41}H_{30}O$: C 91.42, H 5.61, O 2.97, found: C, 91.28, H, 5.46.

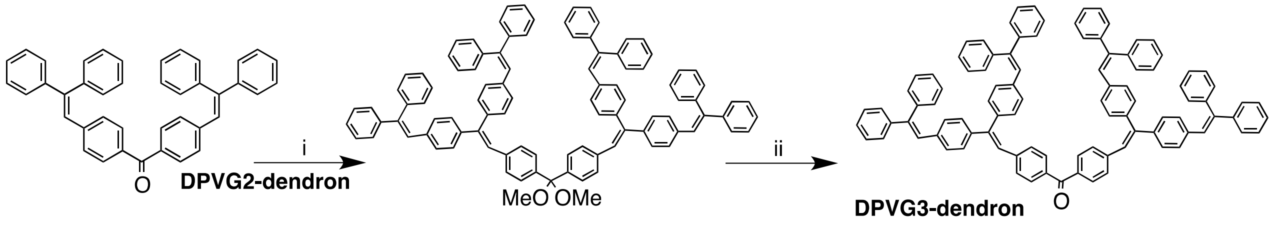
Scheme S4. (i) **1**, ^{t}BuOK in DMF at R.T. for 16 hr.



Synthesis of DPVG3-dendron. 2 (419 mg, 0.884 mmol) and **DPVG2-dendron** (1.00 g, 1.86 mmol) was dissolved in tetrahydrofuran (20 ml). To the stirred solution of the mixture, potassium tert-butoxide 397 mg (3.54 mmol) was slowly added at 0 ˚C. The orange mixture of the reaction was then stirred at room temperature for 21 hours. The resulting solution was slowly added to 100 mL of methanol to give the product as a precipitate. The crude product was then dissolved in tetrahydrofuran (13 mL) with p-toluenesulfonic acid (170 mg, 0.894 mmol) and water (0.07 mL), and stirred for 17 hours to remove the protecting group to give the ketone form. Silica gel column chromatography ($CHCl_3$/hexane = 1.4) and preparative HPLC with SEC ($CHCl_3$) were carried out to isolate the pure **DPVG3-dendron** (570 mg, 50 %).

^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 7.50 (4H, d, J = 8.5 Hz), 7.38-7.18 (40H, m), 7.06 (8H, dd, J = 11.5, 8.5 Hz), 6.97-6.89 (18H, m); ^{13}C NMR ($CDCl_3$) δ = 195.46, 144.41, 143.34, 143.30, 143.22, 143.00, 141.68, 141.68, 140.98, 140.43, 140.30, 138.07, 137.23, 137.17, 135.59, 130.36, 130.33, 129.99, 129.91, 129.79, 129.48, 129.27, 128.81, 128.66, 128.27, 127.72, 127.65, 127.60, 127.55, 127.38, 126.75; MALDI-TOF-Mass: calcd: 1252.5 $[M+H]^+$, found: 1251.6; Anal. calcd for $C_{97}H_{70}O$: C 93.08, H 5.64, O 1.28, found: C 93.31, H 5.59.

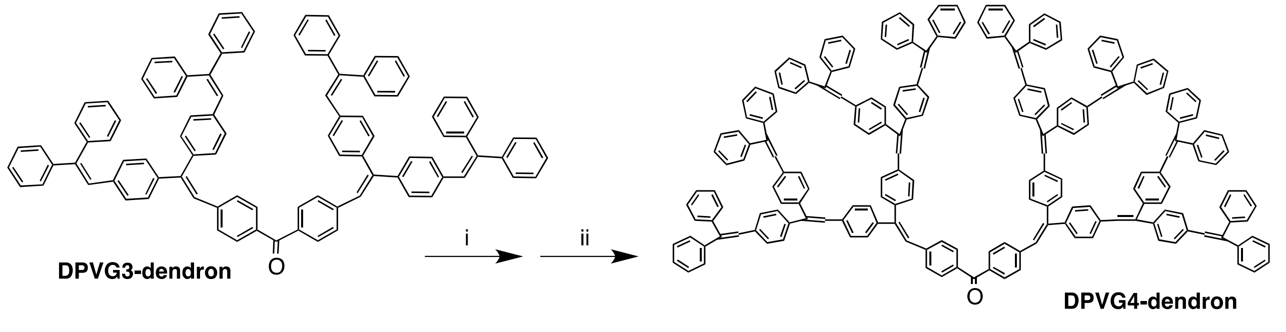
Scheme S6. (i) **2**, ^{t}BuOK in THF at R.T. for 21 hr. (ii) *p*-toluenesulfonic acid, H_2O at R.T. for 17hr.



Synthesis of DPVG4-dendron. 2 (57 mg, 0.121 mmol) and **DPVG3-dendron** (320 mg, 0.256 mmol) was dissolved in THF (20 ml). To the stirred solution of the mixture, potassium tert-butoxide 397 mg (3.54 mmol) was slowly added at 0 ˚C. The orange mixture of the reaction was then stirred at room temperature for 21 hours. The resulting solution was slowly added to 100 mL of methanol to give the product as a precipitate. The crude product was then dissolved in THF (13 mL) with p-toluenesulfonic acid (170 mg, 0.894 mmol) and water (0.07 mL), and stirred for 17 hours to remove the protecting group to give the ketone form. Silica gel column chromatography ($CHCl_3$/hexane = 1.4/1.0) and preparative HPLC with SEC ($CHCl_3$) were carried out to isolate the pure **DPVG4-dendron** (570 mg, 50 %).

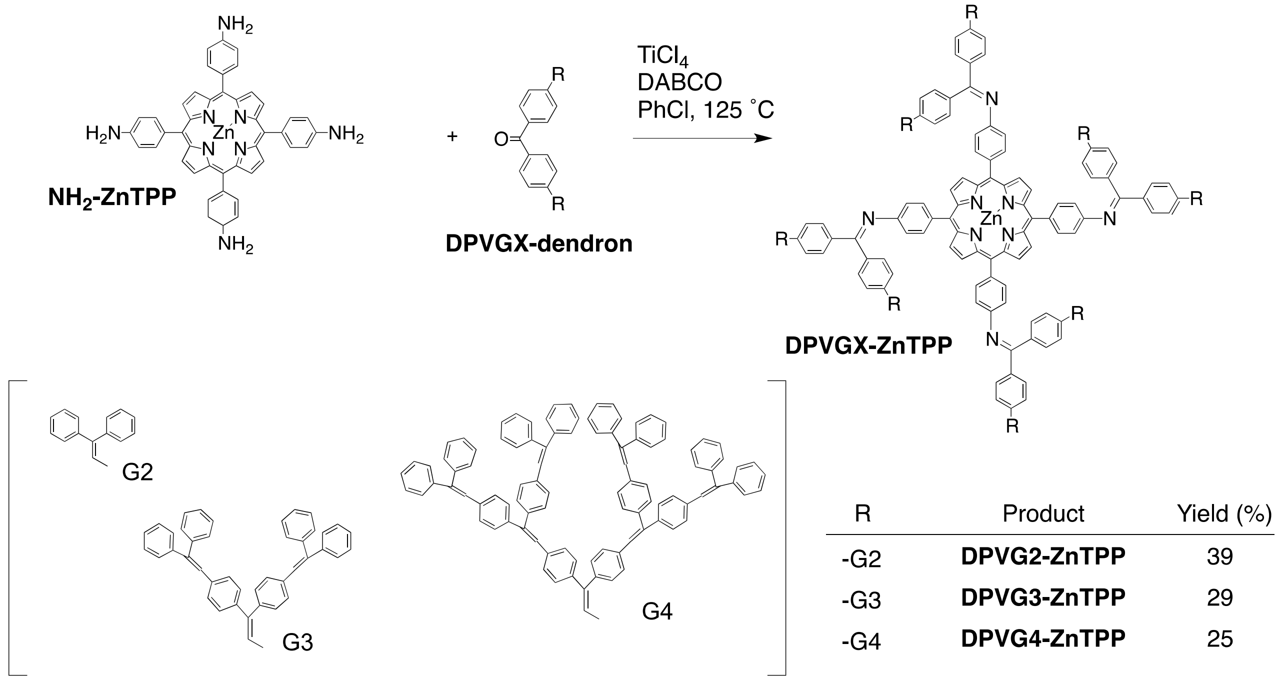
^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 7.49 (4H, d, *J* =8.5 Hz), 7.39-6.91 (142H, m), 6.85 (4H, d, *J* = 8.0Hz); ^{13}C NMR ($CDCl_3$) δ = 195.24, 144.46, 143.40, 143.34, 143.29, 143.03, 1 42.97, 142.73, 142.70, 142.38, 142.30, 141.62, 141.38, 141.32, 140.96, 140.47, 140.33, 140.2 9, 138.60, 138.52, 138.07, 137.26, 137.10, 136.87, 136.80, 136.77, 135.56, 130.41, 130.34, 1 29.99, 129.93, 129.85, 129.50, 129.43, 129.28, 128.80, 128.61, 128.54, 128.26, 128.22, 127.8 8, 127.83, 127.72, 127.64, 127.58, 127.53, 127.48, 127.37, 127.18, 126.82; MALDI-TOF-Mass: calcd: 2678.4 $[M+H]^+$, found:2679.5; Anal. calcd for $C_{209}H_{150}O$: C 93.76, H 5.65 O 0.60, found: C 93.76 H 5.28.

Scheme S5. (i) **2**, ^{t}BuOK in THF at R.T. for 21 hr. (ii) *p*-toluenesulfonic acid, H_2O at R.T. for 17hr.



The dendrimers (**DPVG*X*-ZnTPP:** *X* = 2 - 4) were synthesized from zinc *meso*-tetrakis(4-aminophenyl)porphyrin (**NH_2-ZnTPP**) and the dendron (**DPVGX-dendron**) with the corresponding generation number. **NH_2-ZnTPP**, dendron (**DPVGX-dendron: X = 2 - 4**) and 1,4-diazabicyclo[2,2,2]octane (DABCO) were dissolved in monochlorobenzene under an N_2 atmosphere (The amounts of reagents were different based on the generation number as shown below). Titanium tetrachloride ($TiCl_4$) diluted by chlorobenzene was slowly added to the solution through a dropping funnel. The resulting solution was heated at 125˚C for 3 hours. After cooling, it was passed through a silica gel column to remove any excess DABCO and titanium compounds. A solution containing the product was eluted using a mixed solvent of chlorobenzene and ethylacetate, and then concentrated to dryness. The isolation by preparative recycling HPLC (Japan Analytical Industry: LC908) with SEC columns (Japan Analytical Industry: 2H + 2.5H) eluted by THF afforded the pure dendrimer product (**DPVGX-ZnTPP: X = 2 - 4**). The details and characterization of the product are shown below.

Scheme S8. Synthesis of the dendrimer (**DPVGX-ZnTPP: X = 2 - 4**)



R	Product	Yield (%)
-G2	**DPVG2-ZnTPP**	39
-G3	**DPVG3-ZnTPP**	29
-G4	**DPVG4-ZnTPP**	25

DPVG2-ZnTPP. NH$_2$-ZnTPP (28 mg, 0.036 mmol), dendron (**DPVG2-dendron:** 65 mg, 0.125 mmol), DABCO (1.57 g, 14.0 mmol), TiCl$_4$ (300 μl, 2.7 mmol) and chlorobenzene (9 mL) were used for the synthesis. Silica gel column chromatography was conducted with the mixed solvent (CHCl$_3$ + hexane + EtOAc = 7:7:1 containing 0.8 wt% Et$_3$N). The product **DPVG2-ZnTPP** (34 mg) was finally obtained. Yield 39 %. ^{1}H NMR (ppm, 400MHz, CDCl$_3$, TMS) δ = 8.89 (8H, s), 7.94 (8H, d, J = 8.3 Hz), 7.65 (8H, d, J = 8.3 Hz), 7.38-6.96 (H, m); ^{13}C NMR (CDCl$_3$) δ = 168.3, 150.89, 150.33, 144.21, 143.99, 143.23, 143.14, 140.25, 140.11, 140.05, 138.17, 137.88, 137.74, 134.62, 134.54, 131.91, 130. 41, 130.31, 129.66, 129.47, 129.25, 129.07, 128.88, 128.64, 128.33, 128.29, 127.85, 127.75, 127.69, 127.64, 127.56, 127.4, 121.03, 119.45; MALDI-TOF-Mass: calcd 2821.8 [M+H]$^+$, found 2822.8; Anal. calcd for $C_{208}H_{144}N_8Zn$: C 88.56, H 5.15, N 3.97, found: C 88.33, H 5.0 3, N 3.97.

DPVG3-ZnTPP. NH$_2$-ZnTPP (14 mg, 0.017 mmol), dendron (**DPVG3-dendron:** 71 mg, 0.057 mmol), DABCO (1.06 g, 9.44 mmol), TiCl$_4$ (200 μl, 1.8 mmol) and chlorobenzene (8 mL) were used for the synthesis. Silica gel column chromatography was conducted with the mixed solvent ($CHCl_3$ + hexane = 4:1 containing 0.8 wt% Et_3N). The product **DPVG3-ZnTPP** (23 mg) was finally obtained. Yield 29 %. ^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 8.83 (8H, s), 7.89 (8H, d, *J* = 7.8Hz), 7.68 (8H, d, *J* = 8.0Hz), 7.38-6.82 (H, m), 6.70 (6H, s); ^{13}C NMR ($CDCl_3$) δ = 168.28, 150.25, 143.37, 143.29, 143.13,142.94, 142.85, 142.76, 142.67, 141.27, 141.21, 140.49, 140.39, 140.33, 140.11, 138.36, 138.25, 138.2, 137.71, 137.01, 136.84, 134.49, 131.78, 130.42, 130.36, 130.25, 130.1 4, 130.06, 129.94, 129.74, 129.66, 129.46, 129.2, 129.04, 128.82, 128.77, 128.69, 128.42, 12 8.27, 128.22,127.95, 127.86, 127.69, 127.61, 127.55, 127.48, 127.31, 127.11, 120.9, 119.31; MALDI-TOF-Mass: calcd 5673.5[M+H]$^+$, found 5674.0; Anal. calcd for $C_{432}H_{304}N_8Zn$: C 91.47, H 5.40, N 1.98, found: C 91.16, H 5.19, N 1.91.

DPVG4-ZnTPP. NH_2-ZnTPP (11 mg, 0.013 mmol), dendron (**DPVG4-dendron:** 96 mg, 0.035 mmol), DABCO (1.59 g, 14.2 mmol), $TiCl_4$ (300 μl, 2.7 mmol) and chlorobenzene (8 mL) were used for the synthesis. Silica gel column chromatography was conducted with the mixed solvent ($CHCl_3$ + hexane = 5:2 containing 0.8 wt% Et_3N). The product **DPVG4-ZnTPP** (25 mg) was finally obtained. Yield 25 %. ^{1}H NMR (ppm, 400MHz, $CDCl_3$, TMS) δ = 8.76 (8H, s), 7.78 (8H, d, *J* = 7.8Hz), 7.61 (8H, d, *J* = 8.0Hz), 7.37-6.55 (H, m); ^{13}C NMR ($CDCl_3$) δ = 168.01, 150.92, 150.14, 143.46, 143.4, 143.35, 143.29, 143.12, 143.02, 142.84, 142.78, 142.69, 142.59 142.57, 142.44, 142.24, 142. 08, 142.01, 141.92, 141.46, 141.33, 141.27, 141.19, 141.09, 140.5, 140.43, 140.33, 140.26, 1 40.17, 140.1, 140.03, 138.64, 138.56, 138.36, 138.26, 138.11, 136.99, 136.91, 136.84, 136.73, 136.67, 136.6, 136.43, 134.48, 134.38, 131.73, 131.68, 130.39, 130.34, 130.27, 130.16, 129. 99, 129.88, 129.64, 129.4, 129.15, 129.03, 128.74, 128.64, 128.59, 128.53, 128.46, 128.42, 1 28.23, 128.2, 128.05, 127.88, 127.83, 127.73, 127.62, 127.54, 127.47, 127.37, 127.32, 127.2, 127.16, 126.94, 120.89, 119.26; MALDI-TOF-Mass: calcd 11376.8[M+H]$^+$, found 11377.1; Anal. calcd for $C_{880}H_{624}N_8Zn$: C 92.91, H 5.53, N 0.99, found: C 92.91; H 5.46, N 1.11.

Other Materials: Zinc tetraphenylporphyrin (**ZnTPP**) was purchased from Aldrich. 3,5-Di-tert-butyl-phenyl-naphthalenediimide (**BuPh-NDI**) was synthesized by a reported procedure.[6] 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..

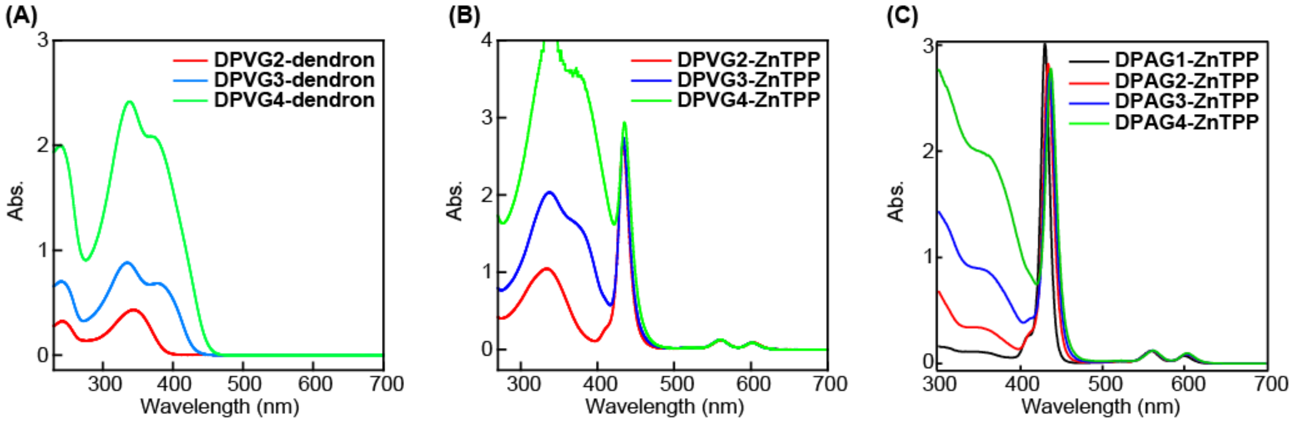


Figure S1 (a) UV-vis absorption spectra of **DPVGX-dendron** (10 μmol L^{-1}) in THF, (b) **DPVGX-ZnTPP** (50 μmol L^{-1}) in THF containing TBABr (0.05 mol L^{-1}) and (c) **DPAGX-ZnTPP** (50 μmol L^{-1}) in THF containing TBABr (0.05 mol L^{-1}). The UV-vis absorption spectra of **DPVGX-dendron** and **DPVGX-ZnTPP** were measured in THF solvent. Characteristic absorption of the dendritic phenylenevinylenes was observed in the wavelength range between 300 and 400 nm. Although the generation number increased from 2 to 3 providing a significant red shift in the absorption, the absorption edge and peaks were almost the same between 3 and 4.

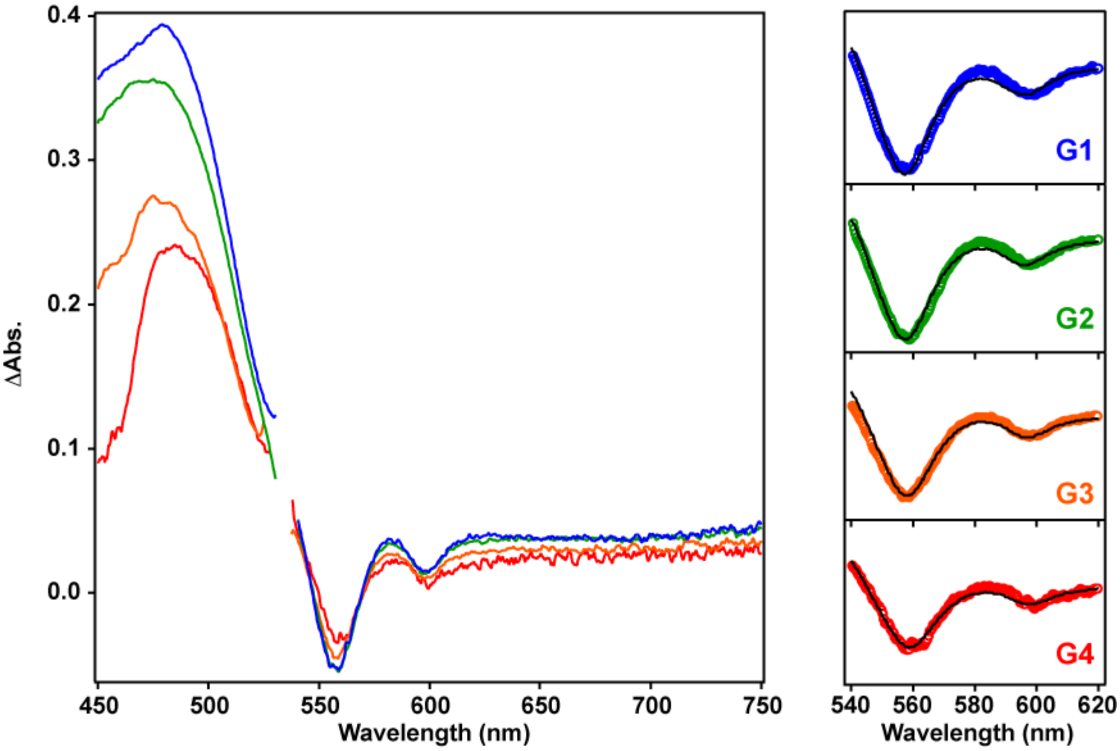


Figure S2. Transient absorption spectra of **BzEGX-ZnTPP (X = 1 - 4)** (50 µM) obtained 50 ns after the excitation (532 nm) in THF containing TBABr (0.05 M) under an N_2 atmosphere at room temperature (23°C). The figures shown on the right side are enlargements of the bleaching with fitting results based on the static UV-vis absorption spectra.

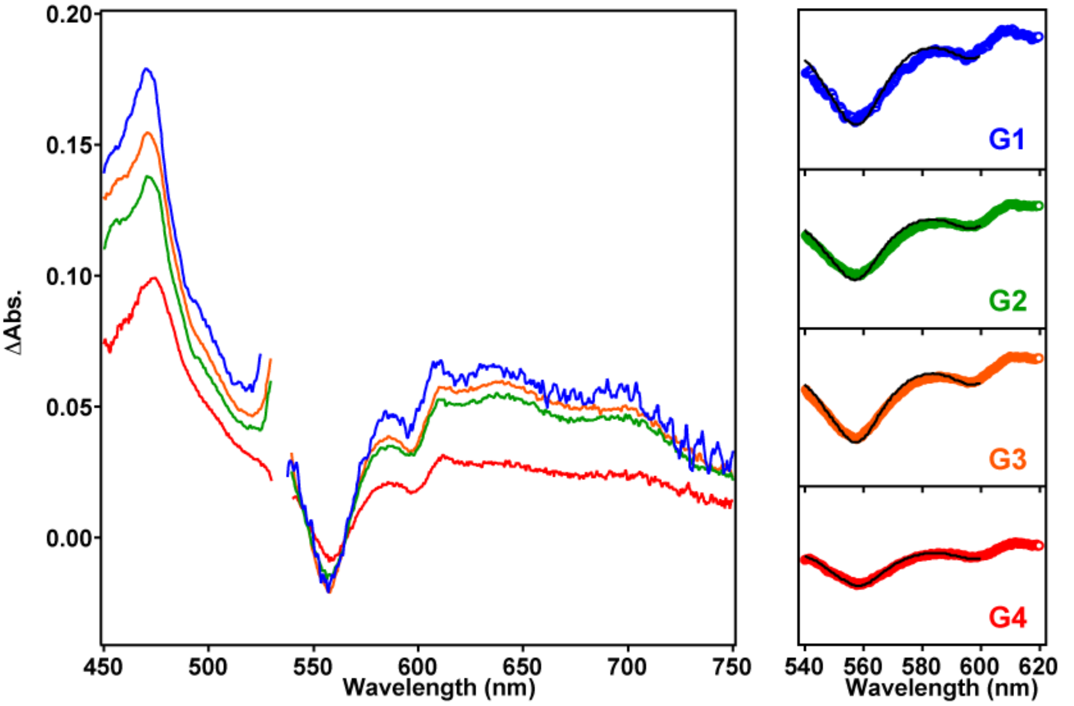


Figure S3. Transient absorption spectra of **BzEX-ZnTPP (X = 1 - 4)** (50 µM) at 1 µs in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere.

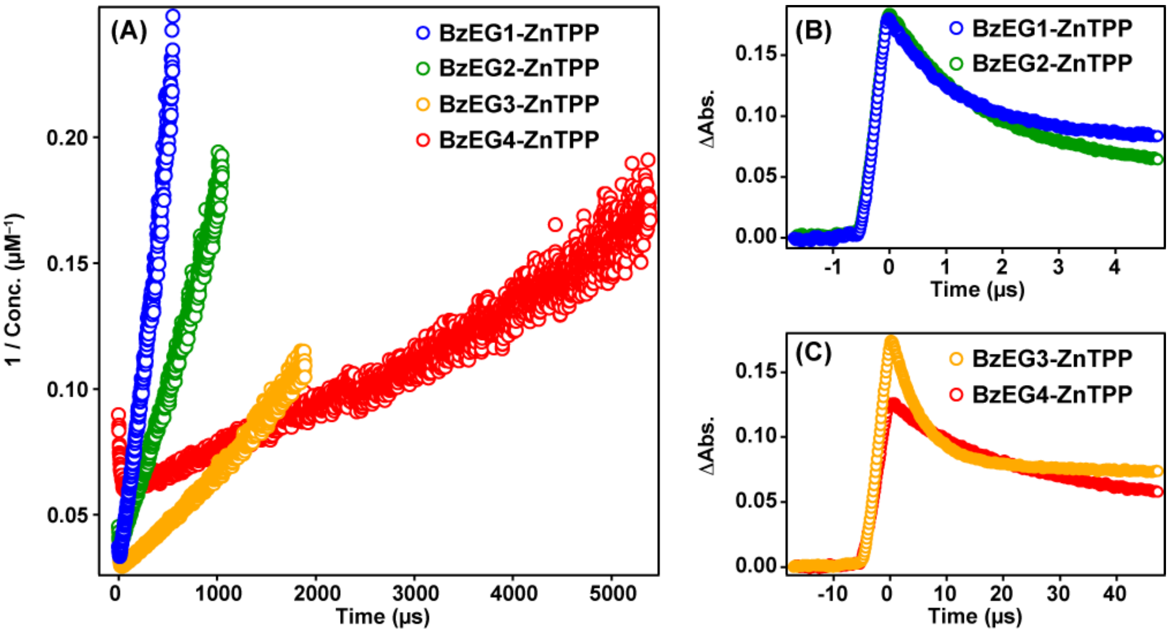


Figure S4. (A) Inverse plots of radical ion pair (**BzEGX-ZnTPP**$^{+}$ – **BuPh-NDI** $^{-}$) concentrations obtained from the analysis of the transient absorption decay versus time. These data were measured using **BzEGX-ZnTPP (X = 1 - 4)** (50 μM) in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 M) under an N_2 atmosphere. (B, C) Time-profiles of the transient absorption (500 nm) of **BzEGX-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.

Table S1. Kinetic parameters of photochemical reactions (23 ˚C) of dendrimers **BzEGX-ZnTPP (X = 1 - 4)** with **BuPh-NDI** in THF (TBABr).

X	**BzEGX-ZnTPP - BuPh-NDI**		
	k_f (mol^{-1} l s^{-1})[a]	Φ_CS[b]	k_b (mol^{-1} l s^{-1})[c]
1	2.9×10^{8}	0.73	3.5×10^{8}
2	1.6×10^{8}	0.63	1.4×10^{8}
3	5.0×10^{7}	0.83	4.2×10^{7}
4	1.5×10^{7}	0.52	2.0×10^{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.

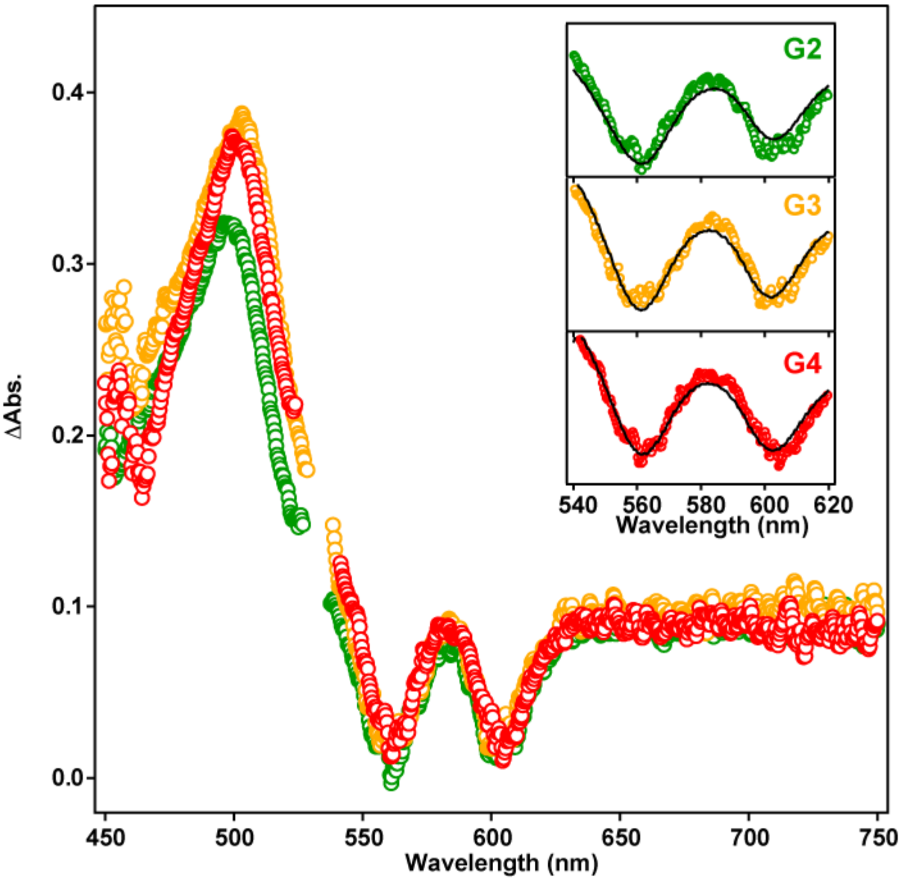


Figure S5. Transient absorption spectra of **DPVGX-ZnTPP (X = 2 - 4)** (50 μM) obtained 50 ns after the excitation (532 nm) in THF containing TBABr (0.05 M) under an N_2 atmosphere.

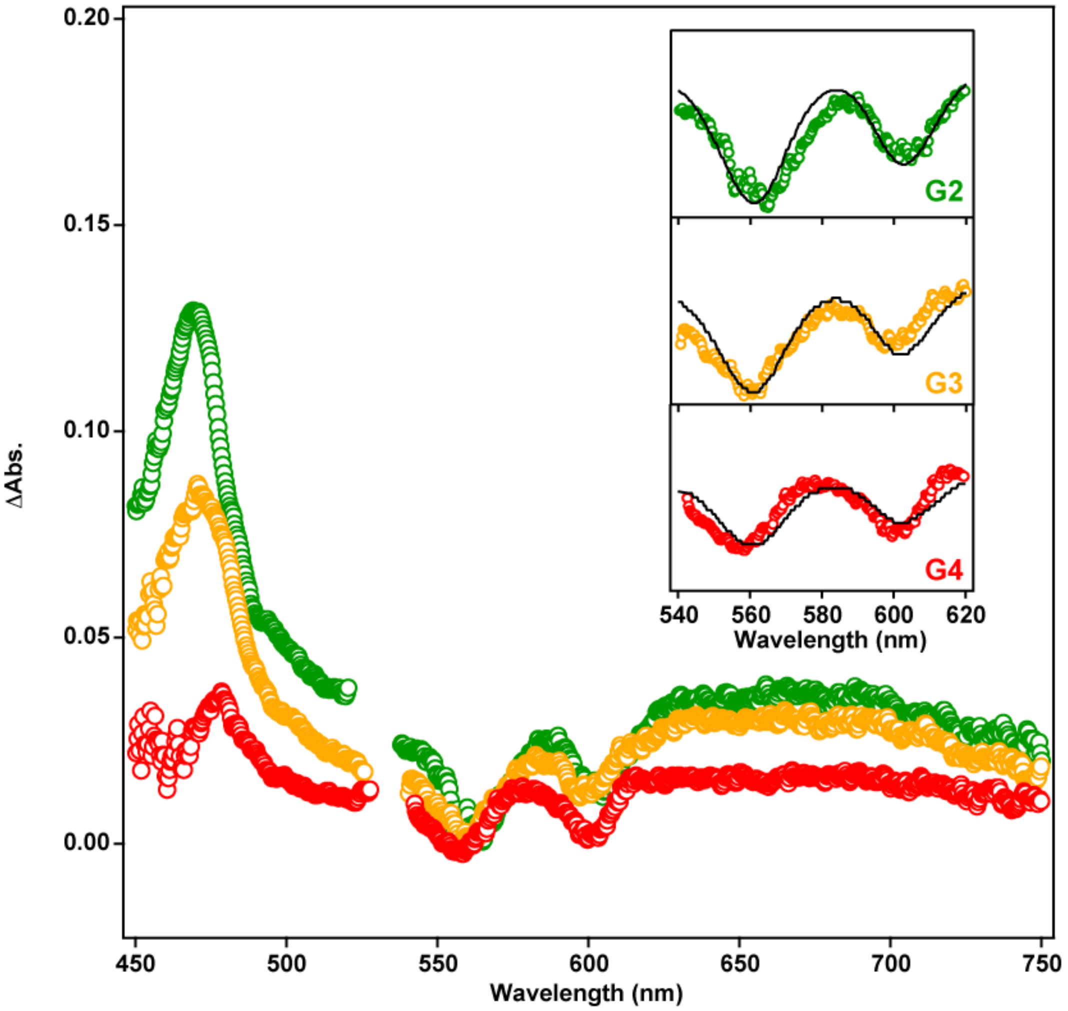


Figure S6. Transient absorption spectra of **DPVX-ZnTPP (X = 2 - 4)** (50 μM) at 1 μs in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 mM) under an N_2 atmosphere.

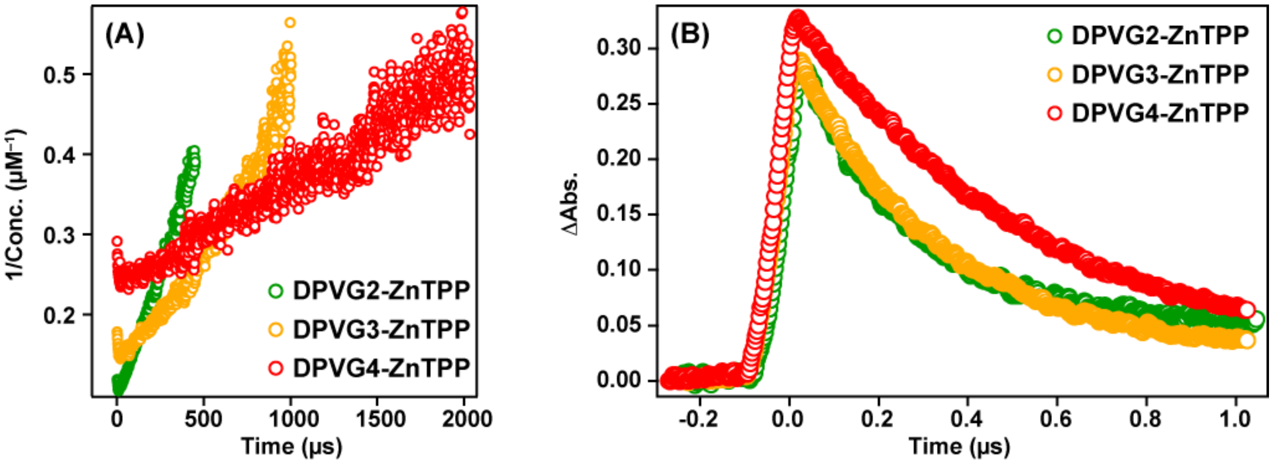


Figure S7. (A) Inverse plots of radical ion pair (**DPVGX-ZnTPP**$^{+}$ – **BuPh-NDI**$^{-}$) concentrations obtained from the analysis of the transient absorption decay versus time. These data were measured using **DPVGX -ZnTPP (X = 2 - 4)** (50 μM) in the presence of **BuPh-NDI** (3 mM) in THF containing TBABr (0.05 M) under an N_2 atmosphere. (B) Time-profiles of the transient absorption (500 nm) of **DPVGX -ZnTPP (X = 2 - 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.

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

X	**DPVGX-ZnTPP - BuPh-NDI**		
	k_f (mol^{-1} l s^{-1})[a]	Φ_{CS}[b]	k_b (mol^{-1} l s^{-1})[c]
2	3.4×10^8	0.35	7.8×10^8
3	1.4×10^8	0.26	3.4×10^8
4	4.1×10^7	0.16	1.3×10^8

[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.

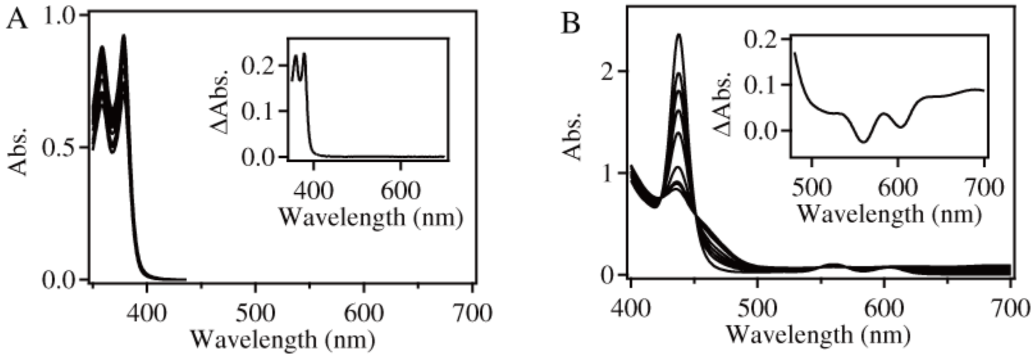


Figure S8. In-situ UV-vis spectral changes upon the electrolysis in THF under N_2 atomosphere. (A) **DPAG4-NDI** (0.25 mM) at –1.2 V vs. Fc/Fc^+. (B) **ZnTPP** (0.05 mM) at 0.6 V vs. Fc/Fc^+.

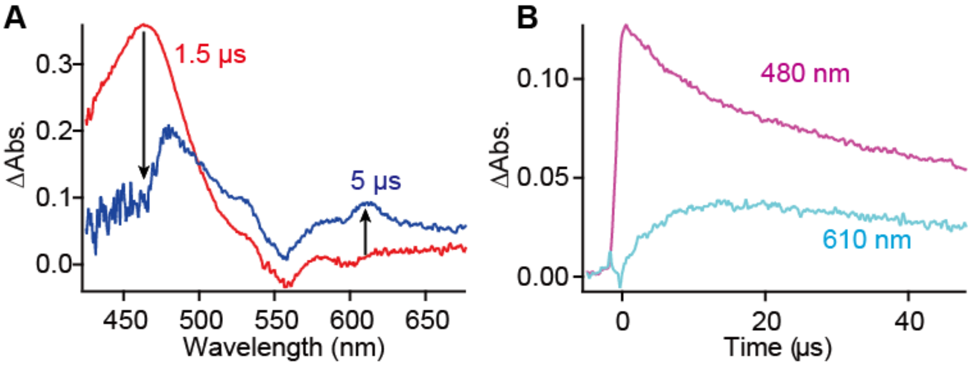


Figure S9. (A) Transient absorption spectra of **ZnTPP** (0.05 mM) in the presence of **DPAG4-NDI** (2.5 mM) at 1.5 μs and 5.0 μs after the excitation (532 nm). The red line (1.5 μs) corresponds to the triplet excited state of **ZnTPP**, and the blue line corresponds to the radical ion pair. (B) The transient absorption time-profiles at 480 nm and 610 nm.

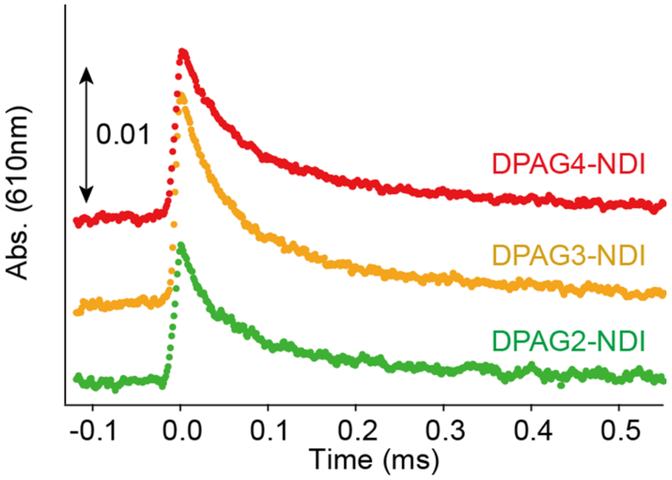


Figure S10. (A) Transient absorption decays of **ZnTPP** (0.05 mM) in the presence of **DPAG*X*-NDI** (2.5 mM). The decays correspond to the charge recombination to the ground state.

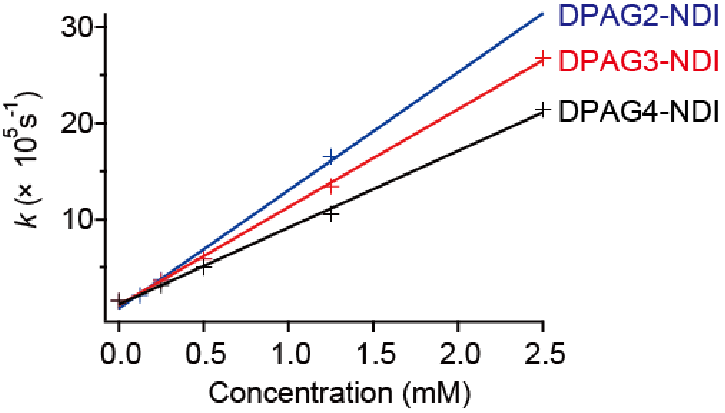


Figure S11. Apparent rate constants of the initial decays of **ZnTPP** (0.05 mM) in the presence of **DPAG*X*-NDI** at different concentrations. These rates correspond to the charge separation reactions.

Table S3. Kinetic parameters of photochemical reactions (23 ˚C) of dendrimers **DPAGX-NDI (X = 2 - 4)** with **ZnTPP** in THF (TBABr).

X	**ZnTPP - DPAGX-NDI (X = 2 - 4)**		
	k_f (mol^{-1} l s^{-1})[a]	Φ_{CS}[b]	k_b (mol^{-1} l s^{-1})[c]
2	1.2×10^9	0.38	1.6×10^9
3	1.0×10^9	0.34	1.5×10^9
4	0.8×10^9	0.36	1.4×10^9

[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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