Supporting Information

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69451 Weinheim, Germany

Wei–Shi Li, Dong–Lin Jiang, and Takuzo Aida

1. Materials and Methods

(1) Synthesis of G3–1 and G1[sBu]–1

G3–DEB: A THF solution (20 mL) of a mixture of G3–Br (0.65 mmol), 2,5-trimethylsilyl ethynyl-1,4-hydroquinone (0.26 mmol), K2CO3 (2.72 mmol), and 18-crown-6 ether (0.26
mmol) was refluxed under Ar overnight in the dark and evaporated to dryness.\textsuperscript{[1]} The residue was poured into water (100 mL) and extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined extract was dried over anhydrous MgSO$_4$ and subjected to preparative GPC with CHCl$_3$ as eluent. The first fraction was collected and evaporated to dryness, to give G$_3$–DEB (0.22 mmol) as white solid in 84% yield. MALDI–TOF–MS for C$_{252}$H$_{218}$O$_{62}$ (Calcd. 4238.39), $m/z = 4259.81$ [M + Na$^+$], 4276.49 [M + K$^+$]. \textsuperscript{1}$H$ NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.97 (d, 32 H; m-H in C$_6$H$_4$(CO$_2$Me)), 7.40 (d, 32 H; o-H in C$_6$H$_4$(CO$_2$Me)), 6.89 (s, 2 H, o-H in C$_6$H$_2$(C≡CH)$_2$), 6.64 (d, 4 H; o-H in inner C$_6$H$_3$), 6.61 (d, 16 H; o-H in outer C$_6$H$_3$), 6.59 (d, 8 H; o-H in mid C$_6$H$_3$), 6.47 (b, 10 H; p-H in inner and outer C$_6$H$_3$), 6.45 (t, 4 H; p-H in mid C$_6$H$_3$), 5.01 (s, 32 H, OC$_2$H$_2$C$_6$H$_4$(CO$_2$Me)), 4.90 (t, 4 H; mid ArOC$_2$H$_2$Ar'), 3.86 (s, 48 H; CO$_2$C$_3$), 3.29 (s, 2 H; C≡CH).

UV–Vis (THF; $\lambda_{max}$): 276.0, 335.0 nm.

G$_1$–DEB: A THF solution (20 mL) of a mixture of G$_1$–Br (2.49 mmol), 2,5-trimethylsilyl ethynyl-1,4-hydroquinone (1.00 mmol), K$_2$CO$_3$ (10 mmol), and 18-crown-6 ether (1.00 mmol) was refluxed under Ar overnight in the dark. The reaction mixture was treated in a manner similar to that for the preparation of G$_3$–DEB, to give G$_1$–DEB (0.78 mmol) as white solid in 78% yield. MALDI–TOF–MS for C$_{60}$H$_{50}$O$_{14}$ (Calcd. 995.03), $m/z = 1017.58$ [M + Na$^+$], 1033.56 [M + K$^+$]. \textsuperscript{1}$H$ NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.02 (d, 8 H; m-H in C$_6$H$_4$(CO$_2$Me)), 7.45 (d, 8 H; o-H in C$_6$H$_4$(CO$_2$Me)), 6.95 (s, 2 H, o-H in C$_6$H$_2$(C≡CH)$_2$), 6.68 (d, 4 H; o-H in C$_6$H$_3$), 6.50 (t, 2 H; p-H in C$_6$H$_3$), 5.08 (s, 8 H, OCH$_2$C$_6$H$_4$(CO$_2$Me)), 5.03 (s, 4 H; inner ArOCH$_2$Ar'), 3.90 (s, 12 H; CO$_2$C$_3$), 3.32 (s, 2 H; C≡CH). UV–Vis (THF; $\lambda_{max}$): 276.0, 335.0 nm.

G$_1$[sBu]–DEB: A toluene/2-butanol (15 mL/15 mL) solution of a mixture of G$_1$–DEB (0.20 mmol) and Ti(OEt)$_4$ (0.10 mL) was refluxed for 2 h under Ar, in a 50 mL two–necked flask equipped with a 5 mL Barratte–type distilling receiver to trap volatile fractions. Then, a mixture of toluene (5 mL) and 2-butanol (5 mL) was again added to the flask, and refluxing was continued for 2 h. This process was repeated 6 times, and the reaction mixture, finally obtained, was poured into dilute hydrochloric acid (1 M, 200 mL) and extracted with CHCl$_3$ (200 mL × 3). The combined extract was dried over anhydrous MgSO$_4$ and

chromatographed on silica gel with CHCl₃ as eluent. The first fraction was collected and evaporated to dryness, to give G₁[SBu]–DEB (0.16 mmol) as white solid in 80% yield.

MALDI–TOF–MS for C₇₂H₇₄O₁₄ (Calcd. 1163.35), m/z = 1185.92 [M + Na⁺]. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.03 (d, 8 H; m-H in C₆H₄(CO₂SBu)), 7.45 (d, 8 H; o-H in C₆H₄(CO₂SBu)), 6.97 (s, 2 H, o-H in C₆H₂(C=CH₂)), 6.68 (d, 4 H; o-H in C₆H₃), 6.51 (t, 2 H; p-H in C₆H₃), 5.08 (m, 12 H; ArOC₆H₂Ar'), 3.34 (s, 2 H; C≡C), 1.69 (m, 8 H; CO₂CH(CH₃)C₆H₂), 1.32 (d, 12 H; CO₂CH(C₆H₃)CH₂CH₃), 0.95 (t, 12 H; CO₂CH(CH₃)CH₂C₆H₃). UV–Vis (THF; λₘₚₐₓ): 276.0, 335.0 nm.

G₃–1: A THF solution of a mixture of G₃–DEB (0.32 mmol), 1-iodo-4-trimethylsilylethynylbenzene (0.85 mmol), Pd(PPh₃)₄ (0.09 mmol), and CuI (0.19 mmol) in the presence of tPr₂NH (2 mL) was degassed by four freeze–pump–thaw cycles, purged with Ar, and then stirred at 55 °C overnight in the dark. The reaction mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (50 mL × 3). The combined extract was dried over anhydrous MgSO₄ and subjected to recycling preparative GPC with CHCl₃ as eluent. The first fraction was collected and evaporated to dryness, to give TMS–protected G₃–1 (0.26 mmol) as yellow solid in 81% yield. The solid (0.26 mmol) was treated with Bu₄NF (0.52 mmol) in THF (20 mL) at 25 °C for 1 h. Then, the reaction mixture was evaporated, and the residue was subjected to recycling preparative GPC with CHCl₃ as eluent. The first fraction was collected and evaporated to dryness, to give G₃–1 (0.23 mmol) as yellow solid in 87% yield. MALDI–TOF–MS for C₂₆₈H₂₂₆O₆₂ (Calcd. 4438.62), m/z = 4461.65 [M + Na⁺], 4478.27 [M + K⁺]. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.97 (d, 32 H; m-H in C₆H₄(CO₂Me)), 7.40 (d, 36 H; o-H in C₆H₄(CO₂Me) and o-H in outer (C≡C)C₆H₄(C≡C)), 7.19 (d, 4 H; m-H in outer (C≡C)C₆H₄(C≡C)), 6.98 (s, 2 H, o-H in inner C₆H₂(C=CH₂)), 6.77 (b, 4 H; o-H in inner C₆H₃), 6.61 (b, 16 H; o-H in outer C₆H₃), 6.58 (b, 8 H; o-H in mid C₆H₃), 6.52 (b, 2 H, p-H in inner C₆H₃), 6.47 (b, 12 H, p-H in mid and outer C₆H₃), 5.00 (s, 36 H, outer and inner ArOCH₂Ar’), 4.89 (s, 24 H; mid ArOCH₂Ar’), 3.85 (s, 48 H; CO₂CH₃), 3.04 (s, 2 H; C≡CH). UV–Vis (THF; λₘₚₐₓ): 276.0, 379.8 nm.

G₁[SBu]–1: A THF solution (30 mL) of a mixture of G₁[SBu]–DEB (0.16 mmol), 1-iodo-4-trimethylsilylethynylbenzene (0.40 mmol), Pd(PPh₃)₃ (0.04 mmol), and CuI (0.08 mmol) in the presence of tPr₂NH (2 mL) was degassed by four freeze–pump–thaw cycles,
purged with Ar, and stirred at 55 °C overnight in the dark. The reaction mixture was treated in a manner similar to that for the preparation of TMS–protected G3–1, to give TMS–protected G1[sBu]–1 (0.12 mmol) as yellow solid in 72% yield. The solid (0.12 mmol) was treated in a manner similar to that for the preparation of G3–1, to give G1[sBu]–1 (0.08 mmol) as yellow solid in 70% yield. MALDI–TOF–MS for C88H82O14 (Calcd. 1363.58), m/z = 1364.52 [M +H+] 1385.45 [M + Na+], 1402.47 [M + K+]. 1H NMR (500 MHz, CDCl3): δ (ppm) 8.02 (d, 8 H; m-H in C6H4(CO2sBu)), 7.45 (d, 4 H: o-H in outer (C≡C)C6H4(C≡C)), 7.39 (d, 8 H; o-H in C6H4(CO2sBu)), 7.30 (d, 4 H; m-H in outer (C≡C)C6H4(C≡C)), 7.08 (s, 2 H, o-H in C6H2(C≡CH)2), 6.78 (d, 4 H; m-H in C6H3), 6.52 (t, 2 H; p-H in C6H3), 5.08 (m, 8 H; inner ArOCH2Ar’ and CO2CH(CH3)CH2CH3), 5.02 (s, 8 H; outer ArOCH2Ar’), 3.13 (s, 2 H; C≡CH), 1.69 (m, 8 H; CO2CH(CH3)CH2CH3), 1.32 (d, 12 H; CO2CH(CH3)CH2CH3), 0.95 (t, 12 H; CO2CH(CH3)CH2CH3). UV–Vis (THF; λmax): 276.0, 376.0 nm.
Oligomerization of G₃–1: A THF solution (180 mL) of a mixture of G₃–1 (0.06 mmol), Cu(OAc)₂ (3.97 mmol), and TMEDA (1.99 mmol) was stirred at 55 °C under Ar for 10 min. The reaction mixture was poured into dilute aqueous H₂SO₄ (0.1 M, 200 mL) and extracted with CH₂Cl₂ (200 mL × 3). The combined extract was washed with water (200 mL × 3), dried over anhydrous MgSO₄, and subjected to recycling preparative GPC using CHCl₃ as eluent. After three cycles of GPC, G₃–2 (6.53 µmol, 23%), G₃–3 (2.85 µmol, 15%), G₃–4 (1.40 µmol, 10%), and G₃–5 (0.76 µmol, 7%) were separated as yellow powdery substances.
G3–2: MALDI–TOF–MS for C_{536}H_{450}O_{124} (Calcd. 8874.91), m/z = 8914 [M + K^+]. \( M_{\text{GPC}} = 8865 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 404.7 nm.

G3–3: MALDI–TOF–MS for C_{804}H_{674}O_{186} (Calcd. 13310.36), m/z = 13332 [M + Na^+]. \( M_{\text{GPC}} = 12513 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 415.1 nm.

G3–4: MALDI–TOF–MS for C_{1072}H_{898}O_{248} (Calcd. 17746.80), m/z = 17785 [M + K^+]. \( M_{\text{GPC}} = 16519 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 418.6 nm.

G3–5: MALDI–TOF–MS for C_{1340}H_{1122}O_{310} (Calcd. 22183.25), m/z = 22237. \( M_{\text{GPC}} = 20513 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 422.0 nm.

**Oligomerization of G3–2:** A THF solution (120 mL) of a mixture of G3–2 (3.52 \( \mu \)mol), Cu(OAc)\(_2\) (2.63 mmol), and TMEDA (1.32 mmol) was stirred at 55 °C under Ar for 15 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G3–1, to isolate G3–4 (3.90 \( \mu \)mol, 22%), G3–6 (1.57 \( \mu \)mol, 13%), G3–8 (1.00 \( \mu \)mol, 11%), and G3–10 (0.34 \( \mu \)mol, 5%) as yellow powdery substances.

G3–6: MALDI–TOF–MS for C_{1608}H_{1346}O_{372} (Calcd. 26619.70), m/z = 26643 [M + Na^+]. \( M_{\text{GPC}} = 23920 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 423.8 nm.

G3–8: MALDI–TOF–MS for C_{2144}H_{1794}O_{496} (Calcd. 35493.60), m/z = 35429. \( M_{\text{GPC}} = 31881 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 426.8 nm.

G3–10: MALDI–TOF–MS for C_{2680}H_{2242}O_{620} (Calcd. 44367.49), m/z = 44474. \( M_{\text{GPC}} = 44075 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 427.0 nm.

**Oligomerization of G3–4:** A THF solution (35 mL) of a mixture of G3–4 (11.10 \( \mu \)mol), Cu(OAc)\(_2\) (0.78 mmol), and TMEDA (0.38 mmol) was stirred at 55 °C under Ar for 15 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G3–1, to isolate G3–8 (1.13 \( \mu \)mol, 20%), G3–12 (0.41 \( \mu \)mol, 11%), and G3–16 (0.24 \( \mu \)mol, 9%) as yellow powdery substances.

G3–12: MALDI–TOF–MS for C_{3216}H_{2688}O_{744} (Calcd. 53239.38), m/z = 53120. \( M_{\text{GPC}} = 50331 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 427.5 nm.

G3–16: MALDI–TOF–MS for C_{4288}H_{3586}O_{992} (Calcd. 70987.76), m/z = 70045. \( M_{\text{GPC}} = 67746 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 428.7 nm.

**Oligomerization of G3–8:** A THF solution (15 mL) of a mixture of G3–8 (4.58 \( \mu \)mol), Cu(OAc)\(_2\) (2.10 mmol), and TMEDA (1.06 mmol) was stirred at 55 °C under Ar for 15 min, and it was treated in a manner similar to that for the oligomerization of G3–1, to isolate G3–16...
(0.62 µmol, 27%) and G₃–24 (0.26 µmol, 17%) as yellow powdery substances.

**G₃–24:** MALDI–TOF–MS for C₅₄₃₂H₅₃₇₈O₁₄₈₈ (Calcd. 106480.83), m/z = 104966. \( M_{\text{GPC}} = 99619 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 428.7 nm.

**Oligomerization of G₃–16:** A THF solution (3.5 mL) of a mixture of G₃–16 (0.50 µmol), Cu(OAc)₂ (0.50 mmol), and TMEDA (0.25 mmol) was stirred at 55 °C under Ar for 30 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G₃–1, to isolate G₃–32 (0.07 µmol, 26%) as yellow solid.

**G₃–32:** MALDI–TOF–MS for C₈₅₇₆H₇₁₇₀O₁₉₈₄ (Calcd. 141973.50), m/z = 140004. \( M_{\text{GPC}} = 137687 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 428.7 nm.

**Oligomerization of G₃–32:** A THF solution (2.5 mL) of a mixture of G₃–32 (0.10 µmol), Cu(OAc)₂ (0.38 mmol), and TMEDA (0.19 mmol) was stirred at 55 °C under Ar for 2 h, and the reaction mixture was treated in a manner similar to that for the oligomerization of G₃–1, to isolate G₃–64 (0.01 µmol, 15%) as yellow solid.

**G₃–64:** GPC for C₁₇₁₅₂H₁₄₃₃₈O₃₉₆₈ (Calcd. 283944.99), \( M_{\text{GPC}} = 264714 \). UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 427.0 nm.

**G₃[sBu]–10:** A toluene/2-butanol (10 mL/5 mL) solution of a mixture of G₃–10 (0.03 µmol) and Ti(OEt)₄ (0.15 mL) was refluxed for 2 h under Ar, in a 50 mL two-necked flask equipped with a 5 mL Barratte–type distilling receiver to trap volatile fractions. Then, a mixture of toluene (5 mL) and 2-butanol (5 mL) was again added to the flask, and refluxing was continued for 2 h. This process was repeated 6 times, and the reaction mixture, finally obtained, was poured into dilute hydrochloric acid (1 M, 20 mL) and extracted with CHCl₃ (20 mL × 3). The combined extract was dried over anhydrous MgSO₄ and subjected to recycling preparative GPC with CHCl₃ as eluent. The first fraction was collected and evaporated to dryness, to give G₃[sBu]–10 (0.027 µmol) as yellow solid in 87% yield. MALDI–TOF–MS for C₃₁₆₀H₃₂₀₂O₆₂₀ (Calcd. 51101.03), m/z = 50852. UV–Vis (THF; \( \lambda_{\text{max}} \)): 276.0, 427.0 nm.

**Oligomerization of G₁[sBu]–1:** A THF solution (275 mL) of a mixture of G₁[sBu]–1 (0.08 mmol), Cu(OAc)₂ (6.12 mmol), and TMEDA (3.05 mmol) was stirred at 55 °C under Ar for 15 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G₃–1, to isolate G₁[sBu]–2 (13.21 µmol, 32%), G₁[sBu]–3 (4.40 µmol, 16%), G₁[sBu]–4 (2.20 µmol, 11%), and G₁[sBu]–5 (1.32 µmol, 8%) as yellow powdery substances.
substances.

**G1[sBu]–2:** MALDI–TOF–MS for C$_{176}$H$_{162}$O$_{28}$ (Calcd. 2725.13), $m/z = 2764$ [M + K$^+$].

$M_{GPC} = 4422$. UV–Vis (THF; $\lambda_{max}$): 276.0, 399.0 nm.

**G1[sBu]–3:** MALDI–TOF–MS for C$_{264}$H$_{242}$O$_{42}$ (Calcd. 4086.69), $m/z = 4126$ [M + K$^+$].

$M_{GPC} = 6847$. UV–Vis (THF; $\lambda_{max}$): 276.0, 408.0 nm.

**G1[sBu]–4:** MALDI–TOF–MS for C$_{352}$H$_{322}$O$_{56}$ (Calcd. 5448.29), $m/z = 5473$ [M + Na$^+$].

$M_{GPC} = 9467$. UV–Vis (THF; $\lambda_{max}$): 276.0, 410.0 nm.

**G1[sBu]–5:** MALDI–TOF–MS for C$_{440}$H$_{402}$O$_{70}$ (Calcd. 6808.80), $m/z = 6833$ [M + Na$^+$].

$M_{GPC} = 11297$. UV–Vis (THF; $\lambda_{max}$): 276.0, 412.6 nm.

**Oligomerization of G1[sBu]–2:** A THF solution (55 mL) of a mixture of G1[sBu]–2 (16.55 $\mu$mol), Cu(OAc)$_2$ (1.21 mmol), and TMEDA (0.60 mmol) was stirred at 55 °C under Ar for 15 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G3–1, to isolate G1[sBu]–4 (2.39 $\mu$mol, 29%), G1[sBu]–6 (0.61 $\mu$mol, 11%), G1[sBu]–8 (0.29 $\mu$mol, 7%), and G1[sBu]–10 (0.09 $\mu$mol, 2%) as yellow powdery substances.

**G1[sBu]–6:** MALDI–TOF–MS for C$_{528}$H$_{482}$O$_{84}$ (Calcd. 8170.36), $m/z = 8194$ [M + Na$^+$].

$M_{GPC} = 15127$. UV–Vis (THF; $\lambda_{max}$): 276.0, 414.0 nm.

**G1[sBu]–8:** MALDI–TOF–MS for C$_{704}$H$_{642}$O$_{112}$ (Calcd. 10893.48), $m/z = 10913$ [M + Na$^+$].

$M_{GPC} = 23523$. UV–Vis (THF; $\lambda_{max}$): 276.0, 416.0 nm.

**G1[sBu]–10:** MALDI–TOF–MS for C$_{880}$H$_{802}$O$_{140}$ (Calcd. 13616.59), $m/z = 13655$ [M + K$^+$].

$M_{GPC} = 27051$. UV–Vis (THF; $\lambda_{max}$): 276.0, 416.2 nm.

**Oligomerization of G1[sBu]–4:** A THF solution (12 mL) of a mixture of G1[sBu]–4 (3.52 $\mu$mol), Cu(OAc)$_2$ (0.27 mmol), and TMEDA (0.13 mmol) was stirred at 55 °C under Ar for 30 min, and the reaction mixture was treated in a manner similar to that for the oligomerization of G3–1, to isolate G1[sBu]–8 (0.44 $\mu$mol, 25%), G1[sBu]–12 (0.26 $\mu$mol, 22%), and G1[sBu]–16 (0.07 $\mu$mol, 8%) as yellow powdery substances.

**G1[sBu]–12:** MALDI–TOF–MS for C$_{1056}$H$_{962}$O$_{168}$ (Calcd. 16340.84), $m/z = 16374$. $M_{GPC} = 33702$. UV–Vis (THF; $\lambda_{max}$): 276.0, 416.9 nm.

**G1[sBu]–16:** MALDI–TOF–MS for C$_{1408}$H$_{1282}$O$_{224}$ (Calcd. 21787.11), $m/z = 20737$. $M_{GPC} = 47904$. UV–Vis (THF; $\lambda_{max}$): 276.0, 417.9 nm.
2. Measurements

$^1$H NMR spectroscopy was performed in CDCl$_3$ on a JEOL model 500 FT NMR Excalibur spectrometer operating at 500 MHz, where the chemical shifts were determined with respect to CHCl$_3$ ($\delta$ 7.24 ppm). $^1$H NMR spin–spin relaxation times ($T_2$) were measured in CDCl$_3$ at 30 °C. MALDI–TOF–MS spectra were recorded on an Applied Biosystems model BioSpectrometry Workstation$^{TM}$ Voyager–DE$^{TM}$ STR in a reflector or a linear mode using $\alpha$-cyano-4-hydroxycinnamic acid or dithranol as matrix. Electronic absorption spectra were recorded using a quartz cell of 1–cm path length on a JASCO model V–560 spectrophotometer equipped with a temperature controller. Fluorescence spectra were recorded using a quartz cell of 1–cm path length on a JASCO model FP–6500 spectrofluorometer equipped with a temperature controller, and corrected for wavelength–dependent detector sensitivity and excitation light source output. All samples were degassed by four freeze–pump–thaw cycles and purged with Ar. Polarized fluorescence spectra were measured at 25 °C in THF/polystyrene (DP = 1000–1400, 0.2 g/mL) as a viscous solvent, upon excitation at the absorption maxima of the conjugated backbone ($abs = 0.1$).

Recycling preparative gel permeation chromatography (GPC) was performed using JAIGEL 2.5H, 3H, and 4H columns on a JAI model LC–908 recycling HPLC equipped with a JASCO model MD–2020 multichannel detector. Analytical GPC was performed using JAIGEL 4H–A/5H–A columns and calibrated with polystyrene standards.
3. Spectral Data

Figure S1. Recycling preparative GPC profiles (2 cycles), monitored at 276.0 nm, of the oligomerization mixtures of G3–n, using JAIGEL 3H/4H columns with CHCl3 as eluent.
Figure S2. MALDI–TOF–MS spectral profiles of \( G_3^n \) and \( G_1^{[sBu]}_n \).  
a) \( G_3^1 \); b) \( G_3^2 \); c) \( G_3^4 \); d) \( G_3^8 \); e) \( G_3^{16} \); f) \( G_3^{32} \); g) \( G_1^{[sBu]}_1 \); h) \( G_1^{[sBu]}_2 \); i) \( G_1^{[sBu]}_4 \); j) \( G_1^{[sBu]}_8 \); k) \( G_1^{[sBu]}_{16} \).
Figure S3. $^1$H NMR spectra of $G_3$–$n$ in CDCl$_3$ at 25 °C.

Figure S4. $^1$H NMR spectra of $G_1$[sBu]–$n$ in CDCl$_3$ at 25 °C.
Figure S5. Energy differences (cm$^{-1}$) between $\text{G}_3-n$ and $\text{G}_{1}[\text{sBu}]-n$ at absorption (J) and emission (B) maxima of their conjugated backbones in THF at 25 °C.

Figure S6. a) Electronic absorption and b) emission spectra (normalized) of $\text{G}_{1}[\text{sBu}]-n$ ($n = 1$–6, 8, 10, 12, and 16; from left to right) in THF at 25 °C.
Figure S7. a) Electronic absorption maxima due to the conjugated backbones of G3–n (J) and G1[sBu]–n (E). b) Emission maxima of G3–n (E) and G1[sBu]–n (G) upon excitation at the conjugated backbones.

Figure S8. a) Electronic absorption spectra (normalized) and b) emission spectra of G3–DEB (black solid curves), G1–DEB (blue dashed curves), and G1[sBu]–DEB (red dotted curves) in THF at 25 °C. Emission spectra were recorded upon excitation at 335.0 nm.
Figure S9. a) Electronic absorption spectra (normalized) and b) emission spectra of $G_{3–10}$ (blue dotted curves) and $G_{3[3sBu]–10}$ (red solid curves) in THF at 25 °C. Emission spectra were recorded upon excitation at 427.0 nm.

Figure S10. $\Phi_{FL}$ values of $G_{3–16}$ (J) and $G_{1[3sBu]–16}$ (B), upon excitation at the absorption maxima of the conjugated backbones in THF at 25 °C.
Figure S11. $^1$H NMR spin–spin relaxation times $T_2$ of ortho–H in the most outer aromatic rings of the dendrimeric wedges of $G_{1}[sBu]_n$ in CDCl$_3$ at 30 °C. In contrast to the case of $G_{3–n}$, $^1$H NMR spectroscopy of $G_{1}[sBu]_n$ displays only one doublet signal (δ 8.02 ppm) due to ortho–H of the most outer aromatic rings in the dendrimeric wedges.