Conjugated molecular wires with discrete lengths are important for the exploration of physical properties related to the delocalization of π electrons, and have also attracted attention for their potential application in molecular electronics and photonics. Examples of discrete conjugated wires so far reported include derivatives of polyphenylene, polyacetylene, poly(phenylenevinylene), poly(phenylethynylene), polythiophene, and polyporphyrin. However, with the exception of only one example, those oligomers are limited in length to tens of nanometers, because of their low solubility and strong tendency to aggregate. From a photochemical point of view, such a strong tendency to aggregate is a major drawback of "naked" nanowires, which results in collisional deactivation of photoexcited states and hinders their potential utilities. A promising approach to solving this problem is to design "isolated" nanowires bearing "insulating" shells. However, such insulated nanowires with discrete molecular lengths are unprecedented.

We report herein the first example of discrete conjugated wires wrapped in dendrimeric envelopes (Scheme 1a, $G_m$-$n$; $m$ = generation number of dendrimeric wedges, $n$ = number of repeating monomer units). Incorporation of large G3 poly(benzyl ether) dendrimeric wedges into the repeating units allowed us to overcome the solubility problem and to synthesize conjugated wires with a molecular length of up to 147 nm. This dendrimeric core–shell strategy guarantees that only a single conjugated chain is integrated into the focal core, thereby representing a clear contrast to reported strategies with other nanoscopic architectures, such as zeolite channels, that incorporate bundles of conjugated polymers. Herein, we highlight "dendrimer effects" on the photoluminescence properties of the conjugated focal core, with an emphasis on a possible effect of intramolecular interactions between the large dendrimeric wedges on the π-electronic conjugation of the backbone.

[**] We thank Y. Suna for technical assistance and the Japan Analytical Industry Co., Ltd (JAI), for recycling preparative GPC.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
Monomer G_1-1 was synthesized by a Pd/IPr/Cu^I-catalyzed coupling of dendrimeric 1,4-diethynylbenzene with 1-iodo-1-trimethylsilyl ethynylbenzene in THF, followed by treatment with Bu_4NF.\(^8\) Coupling of G_1-1 in the presence of a mixture of Cu(OAc)_2 and TMEDA in THF at 55°C for 10 minutes\(^9\) afforded a mixture of dimer G_2-2 (23%), trimer G_3-3 (15%), tetramer G_4-4 (10%), and pentamer G_5-5 (7%), which were separated by recycling preparative gel permeation chromatography (GPC) with CHCl_3 as the eluent, and then further oligomerized to give higher oligomers (Scheme 1a). In contrast to the case with short-chain G_1-1–G_8-8, the coupling reaction of higher oligomers such as G_16 and G_2-32 proceeded rather sluggishly to afford only their dimerized products G_3-32 (26%) and G_6-64 (15%), respectively. Likewise, oligomers G_1-[sBu]-n were synthesized as lower-generation reference compounds (Scheme 1a; n = 2–6, 8, 10, 12, and 16) from G_1-[sBu]-1, which bears CO_2Me groups on its external surface, since the G1 monomer (G_1-1) with CO_2Me surface groups was barely soluble in common organic solvents. G_1-1 and G_1-[sBu]-n, thus prepared, were unambiguously characterized by analytical methods.\(^7\)

A computer-aided molecular modeling study suggested that higher oligomers G_1-[sBu]-n adopt a rodlike morphology with a diameter of roughly 4 nm (Scheme 1b; G_16). G_6-64, which contains 192 aromatic rings and 256 triple bonds at its focal core, was estimated to be 147 nm long,\(^9\) which is the longest discrete wire reported to date.\(^10\) The ^1H NMR spectrum of a solution of G_1-1 in CDCl_3 at 30°C displayed a set of signals at δ = 6.98, 7.19, and 3.04 ppm corresponding to the aromatic (H^2 and H^6) and acetylenic (H^3) protons, respectively, at the focal core. In contrast, the lower-generation G_1-[sBu]-1 showed the corresponding signals at slightly lower magnetic fields with δ values of 7.08 (H^6), 7.30 (H^2), and 3.13 ppm (H^3), respectively. Interestingly, the spin–spin relaxation times (T_2) of H^6 and H^2 in G_1-1 were 0.39 and 0.59 s, respectively, which were clearly smaller than those of G_1-[sBu]-1 (0.78 [H^2] and 1.20 s [H^6]). The relatively short T_2 values observed for the backbone of G_1-1 indicate that there are constrained conformational motions of the focal aromatic rings attached to the large G3 dendrimeric wedges.

Solutions of G_1-1 in THF at 25°C exhibited absorption bands in the visible region as a consequence of the conjugated backbone, as well as two absorption bands at 231 nm and 276 nm arising from the dendrimeric wedges (Figure 2a). As the number of repeating units n increased, this absorption band was red-shifted from 379.8 nm for G_1-1 to 428.7 nm for G_6-64, with saturation of the spectral change observed at around n = 8. Lower-generation G_1-[sBu]-n, under identical conditions to the above, showed a similar spectral change profile upon increment of n, again with a saturation point around n = 8.\(^7\) However, one may also note that the absorption bands of higher-generation G_1-[sBu]-n are located at a longer wavelength than those of G_1-[sBu]-1. For example, decamers G_10-10 and G_16-[sBu]-10 showed absorption bands at 427.0 and 416.2 nm, respectively, thus the energy difference is as large as 608 cm\(^{-1}\) (Table 1). It is unlikely that the observed spectral differences between G_1-[sBu]-1 and G_1-[sBu]-n are caused by their surface groups, since the transformation of the CO_2Me groups on the exterior surface of G_10 into CO_2Bu (G_16-[sBu]-10) resulted in no substantial
change in the absorption spectral profile. Furthermore, $G_{310}$ and $G_{[sBu]-10}$ showed only slight spectral changes when the THF solvent was replaced with 1,3-dimethoxybenzene, an analogue of the dendrimeric wedge building block. The shorter-chain oligomers also displayed smaller energy differences, as shown in Table 1. In relation to this observation, 1,4-diethynylbenzene derivatives bearing $G_1$ and $G_3$ dendrimeric wedges ($G_{1-DEB}$, $G_{[sBu]-DEB}$, and $G_{3-DEB}$; Scheme 1a), which are devoid of any conformational diversity at the focal cores, all showed an absorption maximum at 335.0 nm, irrespective of the surface group and generation number of the poly(benzyl ether) dendrimeric wedges.[7] Thus, the spectral differences between $G_{3-n}$ and $G_{[sBu]-n}$ are most likely related to conformational aspects of their conjugated backbones; namely, the conformation of the backbone of $G_{3-n}$ allows better conjugation between the chromophore units than that in $G_{[sBu]-n}$, although the effective conjugation lengths of $G_{3-n}$ and $G_{[sBu]-n}$ are almost identical to one another.

Dendrimeric compounds $G_{3-n}$ and $G_{[sBu]-n}$ emitted a blue fluorescence upon excitation of their conjugated backbones in THF at 25°C (Figure 2b). As we have already reported for a nondiscrete poly(phenyleneethynylene) with $G_3$ dendrimeric wedges,[3a] the fluorescence quantum yields ($\Phi_{FL}$) of $G_{3-n}$ were all high (80–90%), irrespective of the number of the repeating units $n$ (Figure 3).[11] In sharp contrast, the $\Phi_{FL}$ values of lower-generation $G_{[sBu]-n}$ displayed a tendency to drop when the $n$ value was $\geq 8$, possibly because of an enhanced probability of collisional quenching of the singlet excited state. Higher-generation $G_{3-n}$ are less-sensitive to concentration than $G_{[sBu]-n}$. For example, when the absorbance of the solution was increased from 0.01 up to 0.24, the $\Phi_{FL}$ value of $G_{3-16}$ was preserved in a range of 80–85%, whereas a notable decrease in the $\Phi_{FL}$ value from 65% to 45% was observed for $G_{[sBu]-16}$.[7] Thus, the large dendrimeric envelope of $G_{3-n}$ wraps around the conjugated backbone and prevents collisional deactivation of the excited...
Communications

A closer look at the luminescence properties of \(G_r\)-\(n\) and \(G_{sBu}\)-\(n\) showed a dependence of the luminescence maximum on the “dendrimer size” (Table 1), analogous to that observed for the absorption spectral profiles. For example, a solution of \(G_r\)-10 in THF at 25°C emitted a luminescence centered at 449.4 nm, which is red-shifted by 4.2 nm from that of lower-generation \(G_{sBu}\)-10 (445.2 nm), and the energy difference is calculated to be 210 cm\(^{-1}\).[12] In contrast, 1,4-diethynylbenzene derivatives \(G_r\)-DEB, \(G_{sBu}\)-DEB, and \(G_r\)-DEB, which had no conformational diversity at the focal cores, displayed virtually identical fluorescence spectra to one another. On the other hand, not only \(G_r\)-10 but also lower-generation \(G_{sBu}\)-10 showed only very small changes in the fluorescence spectra when the THF solvent was replaced by 1,3-dimethoxybenzene.

Since the conjugated backbone in \(G_r\)-\(n\) is spatially isolated by the thick G3 dendrimeric envelope, we investigated the fluorescence depolarization profiles of \(G_r\)-\(n\) (\(n = 4, 8, 12, 16, 24, 32,\) and 64), which are considered to reflect the photochemical events in the isolated wires. Suppression of Brownian motion in a viscous medium should result in the fluorescence depolarization occurring predominantly by excitor migration along the conjugated backbone.[13] Here the degree of fluorescence depolarization (\(p\)) is defined as \(p = (I_p - G) / (I_p + G)\), where \(I_p\) and \(I_o\) are the fluorescence intensities of parallel and perpendicular components relative to the polarity of the excitation light, respectively, while \(G\) is an instrumental correction factor. Excitation of the absorption maxima of viscous solutions of \(G_r\)-\(n\) in THF/polystyrene at 25°C gave fluorescence depolarization profiles (Figure 4) where the value of \(p\) gradually became smaller as the number of the repeating units \(n\) increased. For example, the \(p\) value for short-chain \(G_r\)-4 was 0.38, which dropped to 0.21 and further to 0.11 when the \(n\) value was increased to 16 (\(G_r\)-16) and then to 64 (\(G_r\)-64). The absence of a saturation tendency up to a molecular length of 147 nm (\(G_r\)-64) is quite interesting, since previous studies on conjugated polymers without dendrimeric side groups have shown that the exciton migration subsides within several nanometers.[13,14]

Taking all the above results into account, it is likely that \(G_r\)-\(n\) bearing the large G3 dendrimeric wedges prefers a planar conformation of the conjugated backbone, which is good for electronic conjugation (Table 1)[15] and may also allow preservation of fluorescence anisotropy in a long-range exciton migration (Figure 4). There are several examples of attractive van der Waals interactions between poly(benzyl ether) dendrimers in their self-organized structures.[16] We assume that the dendrimeric wedges in \(G_r\)-\(n\) could similarly interact with one another intramolecularly. To support this hypothesis we investigated the dynamics of the conformational change of the dendrimeric wedges of \(G_r\)-\(n\). The \(^1\)H NMR spectrum of a solution of \(G_r\)-1 in CDCl\(_3\) at 30°C exhibited a doublet at \(\delta = 7.97\) ppm which is attributed to the ortho-\(H\) of the outermost aromatic rings in the dendrimeric wedges.[7] Dimer \(G_r\)-2 showed, in addition to this signal, a new ortho-\(H\) doublet at a slightly higher magnetic field (\(\delta = 7.93\) ppm). Furthermore, trimer \(G_r\)-3 showed another new doublet at \(\delta = 7.92\) ppm. When the degree of polymerization \(n\) of \(G_r\)-\(n\) was larger, the signal at \(\delta = 7.92\) ppm was more intense. These characteristic signals were assigned as shown in Figure 5, where the signal at \(\delta = 7.97\) ppm originates from the...

**Figure 4.** Fluorescence depolarization \(p\) of \(G_r\)-\(n\) upon excitation with a polarized light at their absorption maxima (\(A = 0.1\)) in THF/polystyrene (degree of polymerization (DP) = 1000–1400; 0.2 g mL\(^{-1}\)) as a viscous solvent at 25°C.

**Figure 5.** \(^1\)H NMR spin–spin relaxation times \(T_2\) of ortho-\(H\) in the outermost aromatic rings of the dendrimeric wedges of \(G_r\)-\(n\) in CDCl\(_3\) at 30°C.
dendrimeric wedges located at both ends of the backbone (red), while the signals at \( \delta = 7.93 \) and 7.92 ppm are from the other dendrimeric substituents (blue). We measured spin–spin relaxation times (\( T_2 \)) of these characteristic signals (Figure 5), and found that the \( T_2 \) values of the signal at \( \delta = 7.92 \) ppm is smaller when the degree of polymerization \( n \) is larger, and reaches a plateau at \( n = 10 \) (blue bars; the \( T_2 \) value of the signal at \( \delta = 7.93 \) ppm is shown for \( G_3 \)-2). In sharp contrast, the \( T_2 \) value of the signal at \( \delta = 7.97 \) ppm, which arises from the dendron units at the edges of the backbone (red), is virtually unchanged by \( n \) (red bars). These contrasting results suggest that the molecular motions of the inner dendrimeric wedges, which are densely aligned along the rigid, conjugated backbone, are highly constrained as a consequence of intramolecular van der Waals interactions. In contrast, the \( T_2 \) values of the corresponding signals in lower-generation \( G_1 \)-[sBu]-\( n \) were only slightly dependent on \( n \).[7,17]

In summary, we have reported the first example of discrete conjugated wires \( G_x \)-[sBu]-\( n \) bearing large dendrimeric substituents. A great advantage of the dendrimeric architecture is that it allows for the synthesis and isolation of a 147-nm long discrete wire (\( G_6 \)-64), in which the conjugated backbone consisting of 192 aromatic rings and 256 triple bonds is wrapped in a thick dendrimeric envelope. Comparative photochemical studies with lower-generation \( G_x \)-[sBu]-\( n \) as reference compounds indicate that the conjugated backbone in \( G_x \)-[sBu]-\( n \) tends to adopt a planar conformation, most probably because of intramolecular van der Waals interactions between the large, densely aligned G3 dendrimeric wedges. The planar conformation of the backbone allows efficient electronic conjugation of the chromophores and low fluorescence depolarization in an exciton migration event. Application of such insulated nanowires to molecular electronics and photonics is one of the interesting subjects worthy of further investigations.

Received: December 12, 2003 [Z53519]

**Keywords:** conjugation · dendrimers · exciton migration · luminescence · molecular wires

---


[5] The coupling reaction of \( G_3 \)-DEB took place very sluggishly and gave only very small amounts of higher oligomers.


[7] See the Supporting Information.


[9] The molecular lengths of \( G_x \)-[sBu]-\( n \) as estimated by an MM2 module implemented in the Chem. 3D software package were \( n = 4 \), 18 (\( n = 8 \)), 27 (\( n = 12 \)), 36 (\( n = 16 \)), 55 (\( n = 24 \)), 74 (\( n = 32 \)), and 147 nm (\( n = 64 \)).


[17] The slow spin–spin relaxation of the focal aromatic rings in \( G_3 \)-1 (Figure 1) suggests the large G3 dendrimeric wedges could also affect the conformation of such a short-chain conjugated backbone on steric grounds.
Supporting Information

for

Angew. Chem. Int. Ed. Z53519

© Wiley-VCH 2004

69451 Weinheim, Germany
Photoluminescence Properties of Discrete Conjugated Wires Wrapped within Dendrimeric Envelopes: “Dendrimer Effects” on \(\pi\)-Electronic Conjugation

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

1. Materials and Methods

(1) Synthesis of \(G_3\)–1 and \(G_1[sBu]\)–1

\[G_3\text{-DEB}: \text{A THF solution (20 mL) of a mixture of } G_3\text{-Br (0.65 mmol), 2,5-trimethylsilyl ethynyl-1,4-hydroquinone (0.26 mmol), } K_2CO_3 (2.72 mmol), \text{and 18-crown-6 ether (0.26} \text{mmol) was treated with } Pd(PPh_3)_4, CuI, iPr_2NH, \text{and THF reflux.} \]
mmol) was refluxed under Ar overnight in the dark and evaporated to dryness.[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$^+$]. $^1$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$_5$), 6.61 (d, 16 H; o-H in outer C$_6$H$_5$), 6.59 (d, 8 H; o-H in mid C$_6$H$_5$), 6.47 (b, 10 H, p-H in inner and outer C$_6$H$_5$), 6.45 (t, 4 H, p-H in mid C$_6$H$_5$), 5.01 (s, 32 H, OC$_2$H$_2$C$_6$H$_4$(CO$_2$Me)), 4.92 (s, 4 H; inner ArOC$_2$H$_2$Ar$^+$), 4.90 (b, 24 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$^+$]. $^1$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$_5$), 6.50 (t, 2 H; p-H in C$_6$H$_5$), 5.08 (s, 8 H, OCH$_2$C$_6$H$_4$(CO$_2$Me)), 5.03 (s, 4 H; inner ArOC$_2$H$_2$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 $G_1\{sBu\}$–DEB (0.16 mmol) as white solid in 80% yield. MALDI–TOF–MS for $C_{72}H_{74}O_{14}$ (Calcd. 1163.35), $m/z = 1185.92$ [$M + Na^+$]. $^1$H NMR (500 MHz, CDC1₃): $\delta$ (ppm) 8.03 (d, 8 H; $m$-H in $C_6H_4(CO_2sBu)$), 7.45 (d, 8 H; $o$-H in $C_6H_4(CO_2sBu)$), 6.97 (s, 2 H; $o$-H in $C_6H_2(C=CH_2)$), 6.68 (d, 4 H; $o$-H in $C_6H_3$), 6.51 (t, 2 H; $p$-H in $C_6H_3$), 5.08 (m, 12 H; ArOC$_2$H$_2Ar'$), 3.34 (s, 2 H; C≡C), 1.69 (m, 8 H; CO$_2$CH(CH$_3$)C$_2$H$_5$), 1.32 (d, 12 H; CO$_2$CH(C$_3$)CH$_2$CH$_3$), 0.95 (t, 12 H; CO$_2$CH(CH$_3$)CH$_2$C$_3$). UV–Vis (THF; $\lambda_{max}$): 276.0, 335.0 nm.

**$G_3$–1:** A THF solution of a mixture of $G_3$–DEB (0.32 mmol), 1-iodo-4-trimethylsilylethynylbenzene (0.85 mmol), Pd(PPh$_3$)$_4$ (0.09 mmol), and CuI (0.19 mmol) in the presence of iPr$_2$NH (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 CH$_2$Cl$_2$ (50 mL × 3). The combined extract was dried over anhydrous MgSO$_4$ and subjected to recycling preparative GPC with CHCl$_3$ as eluent. The first fraction was collected and evaporated to dryness, to give TMS–protected $G_3$–1 (0.26 mmol) as yellow solid in 81% yield. The solid (0.26 mmol) was treated with Bu$_4$NF (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 CHCl$_3$ as eluent. The first fraction was collected and evaporated to dryness, to give $G_3$–1 (0.23 mmol) as yellow solid in 87% yield. MALDI–TOF–MS for $C_{268}H_{226}O_{62}$ (Calcd. 4438.62), $m/z = 4461.65$ [$M + Na^+$], 4478.27 [$M + K^+$]. $^1$H NMR (500 MHz, CDC1₃): $\delta$ (ppm) 7.97 (d, 32 H; $m$-H in $C_6H_4(CO_2Me)$), 7.40 (d, 36 H; $o$-H in $C_6H_4(CO_2Me)$ and $o$-H in outer (C≡C)C$_6H_4(C≡C)$), 7.19 (d, 4 H; $m$-H in outer (C≡C)C$_6H_4(C≡C)$), 6.98 (s, 2 H, $o$-H in inner $C_6H_2(C=CH_2)$), 6.77 (b, 4 H; $o$-H in inner $C_6H_3$), 6.61 (b, 16 H; $o$-H in outer $C_6H_3$), 6.58 (b, 8 H; $o$-H in mid $C_6H_3$), 6.52 (b, 2 H; $p$-H in inner $C_6H_3$), 6.47 (b, 12 H, $p$-H in mid and outer $C_6H_3$), 5.00 (s, 36 H, outer and inner ArOCH$_2$Ar’), 4.89 (s, 24 H; mid ArOCH$_2$Ar’), 3.85 (s, 48 H; CO$_2$CH$_3$), 3.04 (s, 2 H; C≡C). UV–Vis (THF; $\lambda_{max}$): 276.0, 379.8 nm.

**$G_1\{sBu\}$–1:** A THF solution (30 mL) of a mixture of $G_1\{sBu\}$–DEB (0.16 mmol), 1-iodo-4-trimethylsilylethynylbenzene (0.40 mmol), Pd(PPh$_3$)$_4$ (0.04 mmol), and CuI (0.08 mmol) in the presence of iPr$_2$NH (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–I, to give TMS–protected G₁[sBu]–I (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–I, to give G₁[sBu]–I (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)), 6.78 (d, 4 H; o-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.
(2) Synthesis of \( G_3-n \) and \( G_1[\text{sBu}]-n \)

\[
\begin{align*}
\text{G}_3-1 & \quad \text{a} \quad \text{H} \quad \text{G}_3-n
\end{align*}
\]

\( \text{G}_1[\text{sBu}]-1 \quad \text{G}_1[\text{sBu}]-n \)

| \( G_3-1 \) | \( a \) | \( G_3-2 \) | \( a \) | \( G_3-4 \) | \( a \) | \( G_3-16 \) | \( a \) | \( G_3-64 \)
| \( G_3-3 \) | \( a \) | \( G_3-6 \) | \( a \) | \( G_3-12 \) | \( a \) | \( G_3-24 \)
| \( G_3-4 \) | \( a \) | \( G_3-8 \) | \( a \) | \( G_3-16 \) | \( a \) | \( G_3-32 \) | \( a \) | \( G_3-64 \)

\( \text{G}_1[\text{sBu}]-1 \quad \text{a} \quad \text{G}_1[\text{sBu}]-2 \quad \text{a} \quad \text{G}_1[\text{sBu}]-4 \quad \text{a} \quad \text{G}_1[\text{sBu}]-8 \quad \text{a} \quad \text{G}_1[\text{sBu}]-16 \)

| \( G_1[\text{sBu}]-3 \) | \( a \) | \( G_1[\text{sBu}]-6 \) | \( a \) | \( G_1[\text{sBu}]-12 \) | \( a \) | \( G_1[\text{sBu}]-16 \)
| \( G_1[\text{sBu}]-4 \) | \( a \) | \( G_1[\text{sBu}]-8 \) | \( a \) | \( G_1[\text{sBu}]-10 \) | \( a \) | \( G_1[\text{sBu}]-16 \)

(a): \( \text{Cu(OAc)}_2, \text{TMEDA, THF, 55 °C} \)

---

**Oligomerization of \( G_3-1 \):** A THF solution (180 mL) of a mixture of \( G_3-1 \) (0.06 mmol), \( \text{Cu(OAc)}_2 \) (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 \( \text{H}_2\text{SO}_4 \) (0.1 M, 200 mL) and extracted with \( \text{CH}_2\text{Cl}_2 \) (200 mL \( \times \) 3). The combined extract was washed with water (200 mL \( \times \) 3), dried over anhydrous \( \text{MgSO}_4 \), and subjected to **recycling preparative GPC** using CHCl\(_3\) as eluent. After three cycles of GPC, \( G_3-2 \) (6.53 \( \mu \)mol, 23%), \( G_3-3 \) (2.85 \( \mu \)mol, 15%), \( G_3-4 \) (1.40 \( \mu \)mol, 10%), and \( G_3-5 \) (0.76 \( \mu \)mol, 7%) were separated as yellow powdery substances.
G₃–2: MALDI–TOF–MS for C₅₃₆H₄₅₀O₁₂₄ (Calcd. 8874.91), m/z = 8914 [M + K⁺]. MGPC = 8865. UV–Vis (THF; λmax): 276.0, 404.7 nm.


G₃–4: MALDI–TOF–MS for C₁₀₇₂H₈₉₈O₂₄₈ (Calcd. 17746.80), m/z = 17785 [M + K⁺]. MGPC = 16519. UV–Vis (THF; λmax): 276.0, 418.6 nm.

G₃–5: MALDI–TOF–MS for C₁₃₄₀H₁₁₂₂O₃₁₀ (Calcd. 22183.25), m/z = 22237. MGPC = 20513. UV–Vis (THF; λmax): 276.0, 422.0 nm.

Oligomerization of G₃–2: A THF solution (120 mL) of a mixture of G₃–2 (3.52 μmol), 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 μmol, 22%), G₃–6 (1.57 μmol, 13%), G₃–8 (1.00 μmol, 11%), and G₃–10 (0.34 μmol, 5%) as yellow powdery substances.

G₃–6: MALDI–TOF–MS for C₁₆₀₈H₁₃₄₆O₃₇₂ (Calcd. 26619.70), m/z = 26643 [M + Na⁺]. MGPC = 23920. UV–Vis (THF; λmax): 276.0, 423.8 nm.

G₃–8: MALDI–TOF–MS for C₂₁₄₄H₁₇₉₄O₄₉₆ (Calcd. 35493.60), m/z = 35429. MGPC = 31881. UV–Vis (THF; λmax): 276.0, 426.8 nm.

G₃–10: MALDI–TOF–MS for C₂₆₈₀H₂₂₄₂O₆₂₀ (Calcd. 44367.49), m/z = 44474. MGPC = 44075. UV–Vis (THF; λmax): 276.0, 427.0 nm.

Oligomerization of G₃–4: A THF solution (35 mL) of a mixture of G₃–4 (11.10 μmol), 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 μmol, 20%), G₃–12 (0.41 μmol, 11%), and G₃–16 (0.24 μmol, 9%) as yellow powdery substances.

G₃–12: MALDI–TOF–MS for C₃₂₁₆H₂₆₈₈O₇₄₄ (Calcd. 53239.38), m/z = 53120. MGPC = 50331. UV–Vis (THF; λmax): 276.0, 427.5 nm.

G₃–16: MALDI–TOF–MS for C₄₂₅₈H₃₅₈₆O₉₉₂ (Calcd. 70987.76), m/z = 70045. MGPC = 67746. UV–Vis (THF; λmax): 276.0, 428.7 nm.

Oligomerization of G₃–8: A THF solution (15 mL) of a mixture of G₃–8 (4.58 μmol), Cu(OAc)₂ (2.10 mmol), and TMEDA (1.06 mmol) was stirred at 55 °C under Ar for 15 min, and was treated in a manner similar to that for the oligomerization of G₃–1, to isolate G₃–16.
(0.62 µmol, 27%) and $\text{G}_3$–$\text{G}3$–24 (0.26 µmol, 17%) as yellow powdery substances.

**$\text{G}_3$–24:** MALDI–TOF–MS for $\text{C}_{6432}\text{H}_{5378}\text{O}_{1488}$ (Calcd. 106480.83), $m/z = 104966$. $M_{\text{GPC}} = 99619$. UV–Vis (THF; $\lambda_{\text{max}}$): 276.0, 428.7 nm.

**Oligomerization of $\text{G}_3$–16:** A THF solution (3.5 mL) of a mixture of $\text{G}_3$–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 $\text{G}_3$–1, to isolate $\text{G}_3$–32 (0.07 µmol, 26%) as yellow solid.

**$\text{G}_3$–32:** MALDI–TOF–MS for $\text{C}_{8576}\text{H}_{7170}\text{O}_{1984}$ (Calcd. 141973.50), $m/z = 140004$. $M_{\text{GPC}} = 137687$. UV–Vis (THF; $\lambda_{\text{max}}$): 276.0, 428.7 nm.

**Oligomerization of $\text{G}_3$–32:** A THF solution (2.5 mL) of a mixture of $\text{G}_3$–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 $\text{G}_3$–1, to isolate $\text{G}_3$–64 (0.01 µmol, 15%) as yellow solid.

**$\text{G}_3$–64:** GPC for $\text{C}_{17152}\text{H}_{14338}\text{O}_{3968}$ (Calcd. 283944.99), $M_{\text{GPC}} = 264714$. UV–Vis (THF; $\lambda_{\text{max}}$): 276.0, 427.0 nm.

**$\text{G}_3\{\text{sBu}\}$–10:** A toluene/2-butanol (10 mL/5 mL) solution of a mixture of $\text{G}_3$–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 CHCl$_3$ (20 mL $\times$ 3). The combined extract was dried over anhydrous MgSO$_4$ and subjected to recycling preparative GPC with CHCl$_3$ as eluent. The first fraction was collected and evaporated to dryness, to give $\text{G}_3\{\text{sBu}\}$–10 (0.027 µmol) as yellow solid in 87% yield. MALDI–TOF–MS for $\text{C}_{3160}\text{H}_{3202}\text{O}_{620}$ (Calcd. 51101.03), $m/z = 50852$. UV–Vis (THF; $\lambda_{\text{max}}$): 276.0, 427.0 nm.

**Oligomerization of $\text{G}_3\{\text{sBu}\}$–1:** A THF solution (275 mL) of a mixture of $\text{G}_1\{\text{sBu}\}$–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 $\text{G}_3$–1, to isolate $\text{G}_1\{\text{sBu}\}$–2 (13.21 µmol, 32%), $\text{G}_1\{\text{sBu}\}$–3 (4.40 µmol, 16%), $\text{G}_1\{\text{sBu}\}$–4 (2.20 µmol, 11%), and $\text{G}_1\{\text{sBu}\}$–5 (1.32 µmol, 8%) as yellow powdery
substances.

**G₁[sBu]–2:** MALDI–TOF–MS for C₁₇₆H₁₆₂O₂₈ (Calcd. 2725.13), \(m/z = 2764\) [M + K⁺].

\[M_{GPC} = 4422.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 399.0 nm.

**G₁[sBu]–3:** MALDI–TOF–MS for C₂₆₄H₂₄₂O₄₂ (Calcd. 4086.69), \(m/z = 4126\) [M + K⁺].

\[M_{GPC} = 6847.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 408.0 nm.

**G₁[sBu]–4:** MALDI–TOF–MS for C₃₅₂H₃₂₂O₅₆ (Calcd. 5448.29), \(m/z = 5473\) [M + Na⁺].

\[M_{GPC} = 9467.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 410.0 nm.

**G₁[sBu]–5:** MALDI–TOF–MS for C₄₄₀H₄₀₂O₇₀ (Calcd. 6808.80), \(m/z = 6833\) [M + Na⁺].

\[M_{GPC} = 11297.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 412.6 nm.

**Oligomerization of G₁[sBu]–2:** A THF solution (55 mL) of a mixture of G₁[sBu]–2 (16.55 μmol), 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 μmol, 29%), G₁[sBu]–6 (0.61 μmol, 11%), G₁[sBu]–8 (0.29 μmol, 7%), and G₁[sBu]–10 (0.09 μmol, 2%) as yellow powdery substances.

**G₁[sBu]–6:** MALDI–TOF–MS for C₅₂₈H₄₈₂O₈₄ (Calcd. 8170.36), \(m/z = 8194\) [M + Na⁺].

\[M_{GPC} = 15127.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 414.0 nm.

**G₁[sBu]–8:** MALDI–TOF–MS for C₇₀₄H₆₄₂O₁₁₂ (Calcd. 10893.48), \(m/z = 10913\) [M + Na⁺].

\[M_{GPC} = 23523.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 416.0 nm.

**G₁[sBu]–10:** MALDI–TOF–MS for C₈₈₀H₈₀₂O₁₄₀ (Calcd. 13616.59), \(m/z = 13655\) [M + K⁺].

\[M_{GPC} = 27051.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 416.2 nm.

**Oligomerization of G₁[sBu]–4:** A THF solution (12 mL) of a mixture of G₁[sBu]–4 (3.52 μmol), 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 μmol, 25%), G₁[sBu]–12 (0.26 μmol, 22%), and G₁[sBu]–16 (0.07 μmol, 8%) as yellow powdery substances.

**G₁[sBu]–12:** MALDI–TOF–MS for C₁₀₅₆H₉₆₂O₁₆₈ (Calcd. 16340.84), \(m/z = 16374\). 

\[M_{GPC} = 33702.\]

UV–Vis (THF; \(λ_{max}\)): 276.0, 416.9 nm.

**G₁[sBu]–16:** MALDI–TOF–MS for C₁₄₀₈H₁₂₈₂O₂₂₄ (Calcd. 21787.11), \(m/z = 20737\). 

\[M_{GPC} = 47904.\]

UV–Vis (THF; \(λ_{max}\)): 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$^{\text{TM}}$ Voyager–DE$^{\text{TM}}$ 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 G$_3$–$n$, using JAIGEL 3H/4H columns with CHCl$_3$ as eluent.
Figure S2. MALDI–TOF–MS spectral profiles of G₃⁻⁻ⁿ and G₁[SBu]⁻⁻ⁿ. a) G₃⁻⁻¹; b) G₃⁻⁻²; c) G₃⁻⁻⁴; d) G₃⁻⁻⁸; e) G₃⁻⁻¹₆; f) G₃⁻⁻₃₂; g) G₁[SBu]⁻⁻¹; h) G₁[SBu]⁻⁻₂; i) G₁[SBu]⁻⁻₄; j) G₁[SBu]⁻⁻₈; k) G₁[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.
Supporting Information
Photoluminescence Properties…
W. –S. Li, D. –L. Jiang, T. Aida
ERATO NANOSPACE PROJECT

Figure S5. Energy differences (cm$^{-1}$) between $G_3$–$n$ and $G_1$[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 $G_1$[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 $G_3\text{-}10$ (blue dotted curves) and $G_3[s\text{Bu}]\text{-}10$ (red solid curves) in THF at 25 °C. Emission spectra were recorded upon excitation at 427.0 nm.

Figure S10. $\Phi_{FL}$ values of $G_3\text{-}16$ (J) and $G_1[s\text{Bu}]\text{-}16$ (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 $G_1[\text{sBu}]-n$ in CDCl$_3$ at 30 °C. In contrast to the case of $G_3-n$, $^1$H NMR spectroscopy of $G_1[\text{sBu}]-n$ displays only one doublet signal ($\delta$ 8.02 ppm) due to ortho–H of the most outer aromatic rings in the dendrimeric wedges.