Dendrimeric Structures

Photoluminescence Properties of Discrete Conjugated Wires Wrapped within Dendrimeric Envelopes: "Dendrimer Effects" on π-Electronic Conjugation**

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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.[1] Examples of discrete conjugated wires so far reported include derivatives of polyphenylene, polyacetylene, poly(phenylenevinylene), poly(phenyleneethynylene), polythiophene, and polyporphyrin.[2] However, with the exception of only one example,[2c] 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.[3,4]

We report herein the first example of discrete conjugated wires wrapped in dendrimeric envelopes (Scheme 1a, $\mathbf{G}_m$-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[5] 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[6a] 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.[6b,c] 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.

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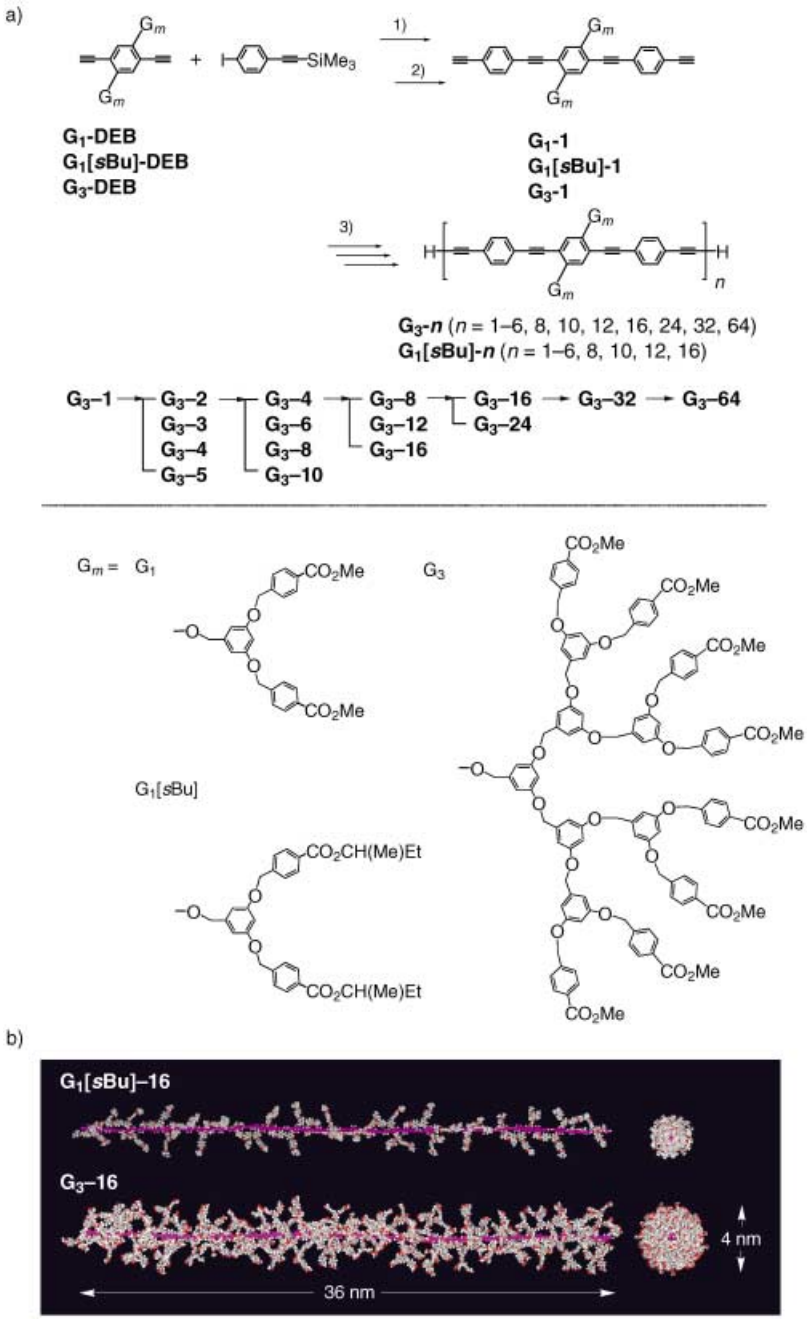

Scheme 1. a) Synthesis of **G_1-1**, **G_1[*s*Bu]-*n***, and **G_3-*n***. Conditions: 1) $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF, reflux; 2) Bu_4NF, THF, RT; 3) $Cu(OAc)_2$, TMEDA, THF, 55 °C. THF = tetrahydrofuran, TMEDA = tetramethylethylene diamine. b) Computer-generated images of the molecular structures of **G_1[*s*Bu]-16** and **G_3-16**.

Monomer **G_3-1** was synthesized by a Pd^0/Cu^I-catalyzed coupling of dendrimeric 1,4-diethynylbenzene with 1-iodo-4-trimethylsilylethynylbenzene in THF, followed by treatment with Bu_4NF.[7] Coupling of **G_3-1** in the presence of a mixture of $Cu(OAc)_2$ and TMEDA in THF at 55 °C for 10 minutes[8] afforded a mixture of dimer **G_3-2** (23 %), trimer **G_3-3** (15 %), tetramer **G_3-4** (10 %), and pentamer **G_3-5** (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 1 a). In contrast to the case with short-chain **G_3-1**–**G_3-8**, the coupling reaction of higher oligomers such as **G_3-16** and **G_3-32** proceeded rather sluggishly to afford only their dimerized products **G_3-32** (26 %) and **G_3-64** (15 %), respectively. Likewise, oligomers **G_1[*s*Bu]-*n*** were synthesized as lower-generation reference compounds (Scheme 1 a; $n = 2$–6, 8, 10, 12, and 16) from **G_1[*s*Bu]-1**, which bears CO_2*s*Bu 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_3-*n*** and **G_1[*s*Bu]-*n***, thus prepared, were unambiguously characterized by analytical methods.[7] A computer-aided molecular modeling study suggested that higher oligomers **G_3-*n*** ($n \geq 4$) adopt a rodlike morphology with a diameter of roughly 4 nm (Scheme 1 b; **G_3-16**). **G_3-64**, 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.[2] The ^1H NMR spectrum of a solution of **G_3-1** in $CDCl_3$ at 30 °C displayed a set of signals at $\delta = 6.98$, 7.19, and 3.04 ppm corresponding to the aromatic (H^a and H^b) and acetylenic (H^c) protons, respectively, at the focal core. In contrast, the lower-generation **G_1[*s*Bu]-1** showed the corresponding signals at slightly lower magnetic fields with δ values of 7.08 (H^a), 7.30 (H^b), and 3.13 ppm (H^c), respectively. Interestingly, the spin–spin relaxation times (T_2) of H^a and H^b, located in the proximity of the dendrimeric wedges, are dependent on the generation number m, whereas that of H^c is virtually unaffected (Figure 1):[10] The T_2 values of H^a and H^b in **G_3-1** were 0.39 and 0.59 s, respectively, which were clearly smaller than those of **G_1[*s*Bu]-1** (0.78 [H^a] and 1.20 s [H^b]). The relatively short T_2 values observed for the backbone of **G_3-1** indicate there are constrained conformational motions of the focal aromatic rings attached to the large G3 dendrimeric wedges.

Solutions of **G_3-*n*** 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 231.0 and 276.0 nm arising from the dendrimeric wedges (Figure 2 a). As the number of repeating units n increased, this absorption band was red-shifted from 379.8 nm for **G_3-1** to 428.7 nm for **G_3-64**, with saturation of the spectral change observed at around $n = 8$. Lower-generation **G_1[*s*Bu]-*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_3-*n*** are located at a longer wavelength than those of **G_1[*s*Bu]-*n***. For example, decamers **G_3-10** and **G_1[*s*Bu]-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_3-*n*** and **G_1[*s*Bu]-*n*** are caused by their surface groups, since the transformation of the CO_2Me groups on the exterior surface of **G_3-10** into CO_2*s*Bu (**G_3[*s*Bu]-10**) resulted in no substantial

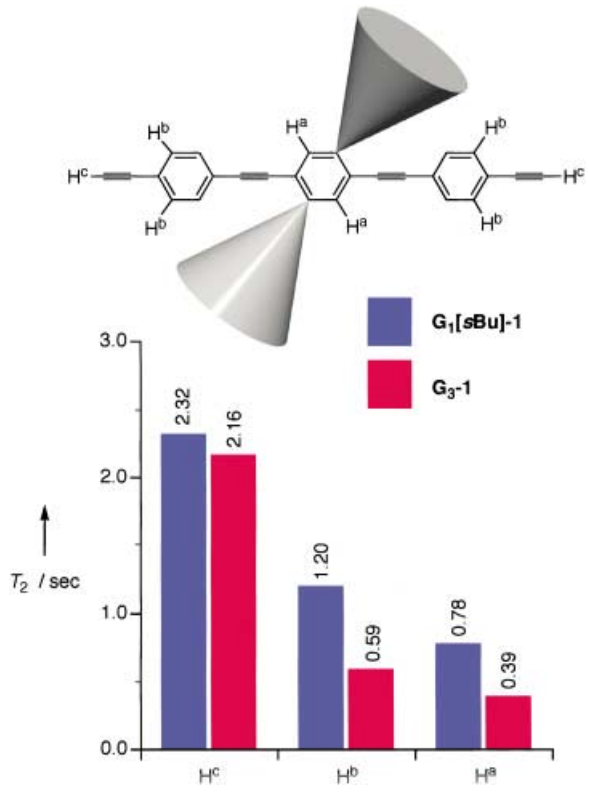

Figure 1. ^{1}H NMR spin–spin relaxation times T_2 of H^a, H^b, and H^c in **G_1[*s*Bu]-1** and **G_3-1** recorded in $CDCl_3$ at 30 °C.

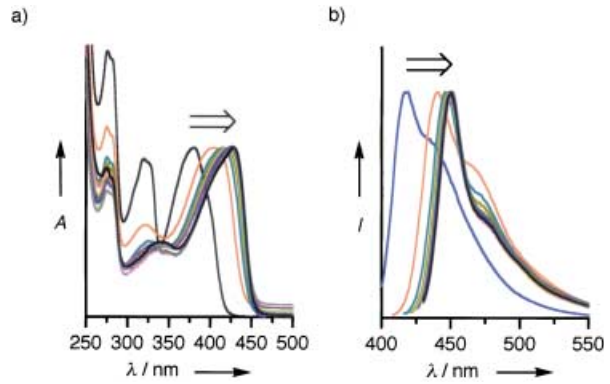

Figure 2. a) Electronic absorption and b) emission spectra (normalized) of **G_3-*n*** (n = 1–6, 8, 10, 12, 16, 24, 32, and 64; from left to right) in THF at 25 °C.

Table 1: Energy differences between **G_3-*n*** and **G_1[sBu]-*n*** at the absorption and emission maxima of their conjugated backbones in THF at 25 °C.

n	Energy differences [cm^{-1}] at absorption maxima	Energy differences [cm^{-1}] at emission maxima
1	266.1	155.6
2	353.0	182.5
4	501.1	201.5
6	558.6	200.2
8	608.3	200.0
10	607.7	209.9
12	594.8	214.4
16	602.8	209.6

change in the absorption spectral profile. Furthermore, **G_3-10** and **G_1[*s*Bu]-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 G1 and G3 dendrimeric wedges (**G_1-DEB**, **G_1[*s*Bu]-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_1[*s*Bu]-*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_1[*s*Bu]-*n***, although the effective conjugation lengths of **G_3-*n*** and **G_1[*s*Bu]-*n*** are almost identical to one another.

Dendrimeric compounds **G_3-*n*** and **G_1[*s*Bu]-*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 G3 dendrimeric wedges,[3a] the fluorescence quantum yields (Φ_{FL}) of **G_3-*n*** were all high (80–90 %), irrespective of the number of the repeating units n (Figure 3).[11] In sharp

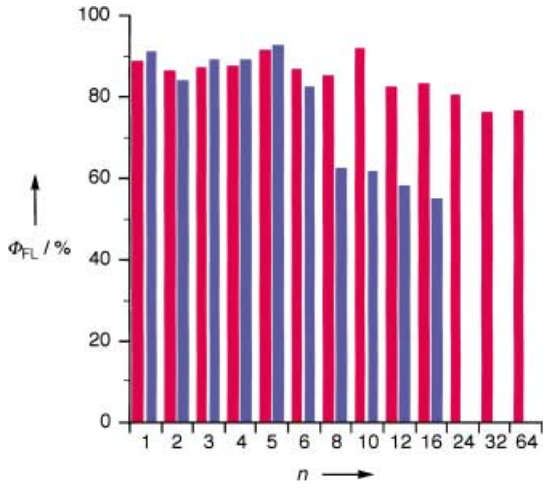

Figure 3. Fluorescence quantum yields (Φ_{FL}) of **G_3-*n*** (red bars) and **G_1[sBu]-*n*** (blue bars) upon excitation at their absorption maxima (A = 0.1) in THF at 25 °C.

contrast, the Φ_{FL} values of lower-generation **G_1[*s*Bu]-*n*** displayed a tendency to drop when the n value was ≥ 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_1[*s*Bu]-*n***. For example, when the absorbance of the solution was increased from 0.01 up to 0.24, the Φ_{FL} value of **G_3-16** was preserved in a range of 80–85 %, whereas a notable decrease in the Φ_{FL} value from 65 % to 45 % was observed for **G_1[*s*Bu]-16**.[7] Thus, the large dendrimeric envelope of **G_3-*n*** wraps around the conjugated backbone and prevents collisional deactivation of the excited

states.[3a] A closer look at the luminescence properties of **G_3-*n*** and **G_1[*s*Bu]-*n*** showed a dependence of the luminescence maximum on the "dendrimer size" (Table 1),[7] analogous to that observed for the absorption spectral profiles. For example, a solution of **G_3-10** 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_1[*s*Bu]-10** (445.2 nm), and the energy difference is calculated to be 210 cm^{-1}.[12] In contrast, 1,4-diethynylbenzene derivatives **G_1-DEB**, **G_1[*s*Bu]-DEB**, and **G_3-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_3-10** but also lower-generation **G_1[*s*Bu]-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_3-*n*** is spatially isolated by the thick G3 dendrimeric envelope, we investigated the fluorescence depolarization profiles of **G_3-*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 exciton migration along the conjugated backbone.[13] Here the degree of fluorescence depolarization (p) is defined as $p = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + GI_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ 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_3-*n*** in THF/polystyrene at 25 °C gave fluorescence depolarization profiles (Figure 4)

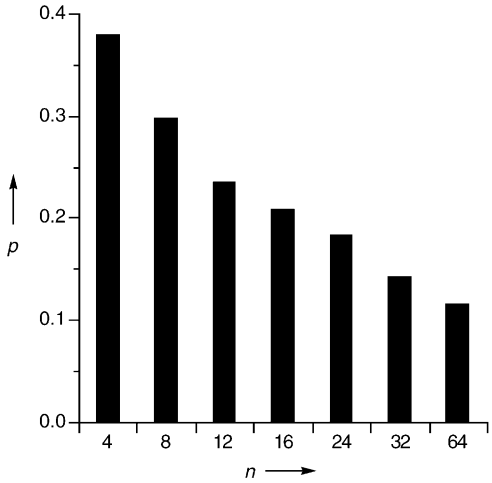

Figure 4. Fluorescence depolarization p of **G_3-*n*** upon excitation with a polarized light at their absorption maxima ($A = 0.1$) in THF/polystyrene (degree of polymerization (DP) = 1000–1400; 0.2 g mL^{-1}) as a viscous solvent at 25 °C.

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_3-4** was 0.38, which dropped to 0.21 and further to 0.11 when the n value was increased to 16 (**G_3-16**) and then to 64 (**G_3-64**). The absence of a saturation tendency up to a molecular length of 147 nm (**G_3-64**) 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_3-*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_3-*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_3-*n***. The ^{1}H NMR spectrum of a solution of **G_3-1** 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_3-2** showed, in addition to this signal, a new *ortho*-H doublet at a slightly higher magnetic field ($\delta =$ 7.93 ppm). Furthermore, trimer **G_3-3** showed another new doublet at $\delta = 7.92$ ppm. When the degree of polymerization (n) of **G_3-*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

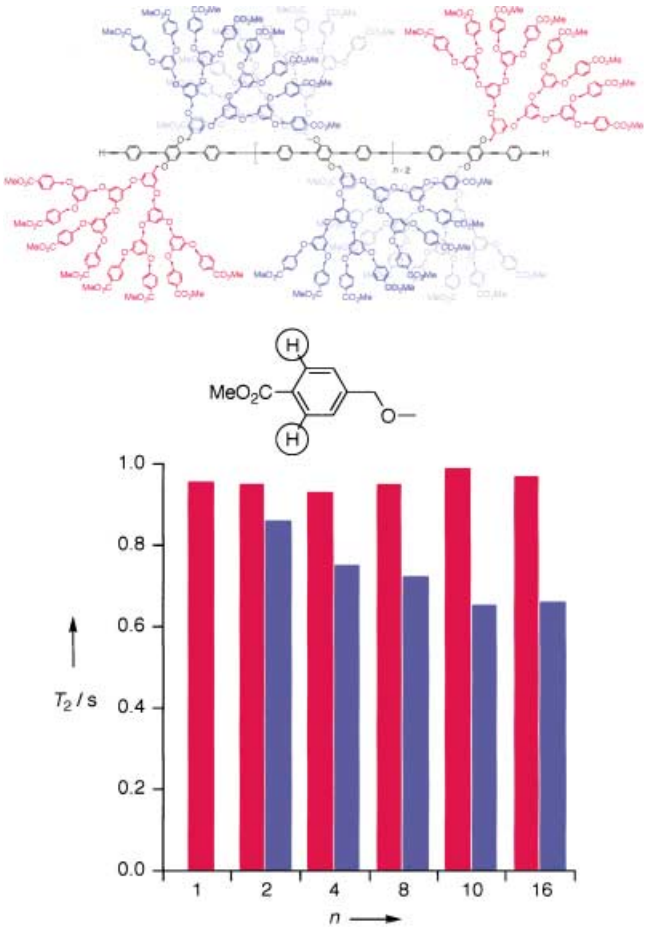

Figure 5. ^{1}H NMR spin–spin relaxation times T_2 of *ortho*-H in the outermost aromatic rings of the dendrimeric wedges of **G_3-*n*** in $CDCl_3$ at 30 °C.

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 value 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[*s*Bu]-*n*** were only slightly dependent on n.[7,17]

In summary, we have reported the first example of discrete conjugated wires **G_3-*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_3-64**), 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_1[*s*Bu]-*n*** as reference compounds indicate that the conjugated backbone in **G_3-*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.

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