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Synthesis and Optical Properties of Polyphenylene Dendrimers Based on Perylenes

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A series of polyphenylene-dendronized perylenes have been synthesized, and their physical and mesoscopic properties have been investigated. The attached polyphenylene dendrons have significant effects on the physical properties of the perylenes. They increase the solubility of perylenes in common organic solvents, suppress significantly the aggregation of the perylene core, and lead to red-shifted absorption and emission. The polyphenylene dendrons give rise to a strong absorption band in the UV region and exhibit efficient intramolecular energy transfer to the perylene moiety. The functionalization of perylenes with polyphenylene dendrons allows the preparation of films by spin-coating.

Introduction

Perylene and its derivatives, especially perylene-3,4,9,-10-tetracarboxdiimides, are well-known for their versatility as dyes and pigments because of their high fluorescence quantum yield and their high photostability and chemical stability.[1–6] Unsubstituted perylene **1** shows strong fluorescence (from 350 to ~ 450 nm) and is a key chromophore in fields such as dye lasers[7] and light emitting diodes (LEDs).[8] However, the poor solubility of unsubstituted perylene in organic solvents and the low fluorescence quantum yield in the solid state, attributable to its aggregation, limit the applications of perylene. Efforts have been made to attach solubilizing and shielding side chains to the molecules, thereby improving their performances.[9] Recently, Moore et al.[10] and Peng et al.[11]

have reported the synthesis of phenylacetylene-dendronized perylenes for the study of intramolecular energy transfer. In this paper, we describe a facile method to synthesize a series of polyphenylene-dendronized perylenes and investigate their properties.

Dendrimers are macromolecules with highly branched and regular structural units.[12–15] A dendritic shell could create a distinct microenvironment for the incorporated core and offer unique photochemical, photophysical, electrochemical, and catalytic properties.[16] The polyphenylene dendrons,[14,17] characterized by their shape-persistent structure[18,19] and out-of-plane twisted phenyl components, have been successfully attached to various functions. Moreover, they significantly suppress the aggregation of the incorporated perylenetetracarboxidi-imide chromophore.[20] These bulky moieties can also absorb light energy which is then funneled efficiently to the core.[21] In this paper, we describe the synthesis of a series of perylenes equipped with polyphenylene den-

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SCHEME 1. Synthesis of the Perylene Core[a]
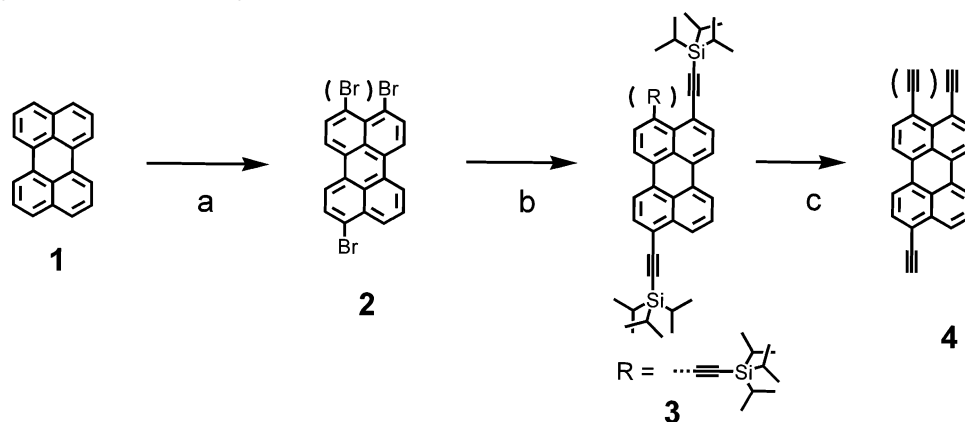
[a] (a) Br$_2$, AcOH, 50 °C, 5 h, 92%; (b) triisopropylsilylethyne, PdCl$_2$(PPh$_3$)$_2$, CuI, THF/Et$_3$N, rt, 15 h, 91%; (c) THF, *n*-Bu$_4$NF, 30 min, rt, 98%.

drons, which show that the polyphenylene dendrimers (1) increase the solubility of perylene in common organic solvents, (2) provide an additional absorption band allowing efficient intramolecular energy transfer, and (3) form good films on quartz by simple spin-coating of the dendrimer solution instead of vacuum deposition, and the resulting films show strong green fluorescence in the solid state.

Results and Discussion

The synthesis of polyphenylene-dendronized perylenes starts from a diethynyl-substituted perylene **4**, which is prepared in three steps from perylene **1** (Scheme 1). In the first step, the simple preparation of 3,9(10)-dibromoperylene **2** gives a high yield according to the literature.[9] The isomeric mixture of 3,9- and 3,10-substituted dibromoperylene cannot be separated by column chromatography or HPLC and results in isomers of poylphenylene-dendronized perylenes. The 3,9- and 3,10-substituted perylene isomers, however, do not show significant differences in their physical and chemical properties.[22] In particular, the molecular shapes of both isomers are very similar (see the later discussion of the molecular modeling) when two bulky dendrons are attached in the 3,9- or 3,10-position of perylene. The two bromo substituents in **2** are then replaced in the second step by triisopropylsilylethylnyl by a Hagihara–Sonogashira coupling at 80 °C.[23] The reaction is carried out in a mixture of THF and triethylamine (3:1) with a catalyst system consisting of di(triphenylphosphine)dichloropalladium [Pd(Ph$_3$)$_2$Cl$_2$] and copper iodide (CuI). The base and catalyst are easily removed by column chromatography, and the desired product (ditriisopropylsilylethylnyl)perylene **3** is obtained in 91% yield as a dark-yellow solid. The diethynyl-substituted perylene **4** is obtained after cleavage of the triisopropylsilyl (TIPS) groups with

tetrabutylammonium fluoride (Bu$_4$NF) in distilled THF. A series of perylene-core polyphenylene dendrimers is synthesized by means of the synthetic concept previously presented (Scheme 2).[14,17] The first-generation polyphenylene-dendronized perylene **6** results from the Diels–Alder cycloaddition of **4** with a 3-fold excess of cyclopentadienone **5** in *m*-xylene at 140 °C. The use of *m*-xylene as a solvent has the advantage that the product is easily isolated by precipitation from methanol. The growth of the second-generation dendrimers **10** or **14** with different degrees of branching is carried out by a Diels–Alder cycloaddition of **4** with the A$_2$B reagent 3,4-di[4-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone **7** or the A$_4$B-branching reagent 2,3,4,5-tetra[4-(triisopropylsilylethynyl)phenyl]cyclopenta-2,4-dienone **11**, followed by the quantitative cleavage of the protecting groups with Bu$_4$NF (which resulted in precursor **9** or **13** of the second-generation dendrimer) and the subsequent Diels–Alder cycloaddition with 6 or 12 equiv of **5**.

Polyphenylene-dendronized perylenes are soluble in common organic solvents such as dichloromethane, toluene, or THF, which allows for their purification by column chromatography and their full characterization by standard spectroscopic measurements such as ^{1}H and ^{13}C NMR spectroscopy as well as FD mass spectrometry, MALDI-TOF mass spectrometry, and elemental analysis (see the Experimental Section). The Diels–Alder reaction is monitored by FD and MALDI-TOF mass spectrometry. The experimentally determined and the calculated *m*/*z* ratios agree very well for all dendrimers **6**, **10**, and **14**. As an example, the MALDI-TOF mass spectrum of **14**, shown in Figure 1, clearly demonstrates its monodispersity. Characterization of dendronized perylenes and their precursors by ^{1}H NMR spectroscopy is performed in THF because of the good solubility of the compounds in this solvent. Well-separated and assignable signals of the perylene core **4** and intermediates **8**, **9**, **12**, and **13** are obtained for the aromatic protons on perylene as well as for the ethynyl groups or the TIPS groups. For the first-generation dendrimer **6** and second-generation dendrimer **10**, all perylene protons are clearly assignable and also show the corresponding signals of isomers. In the ^{13}C NMR spectrum, the precursors of dendrimers **4**, **5**, **8**, **9**, **12**, and **13** also show similar results, which indicates that

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SCHEME 2. Synthesis of the Polyphenylene-Dendronized Perylenes[a]
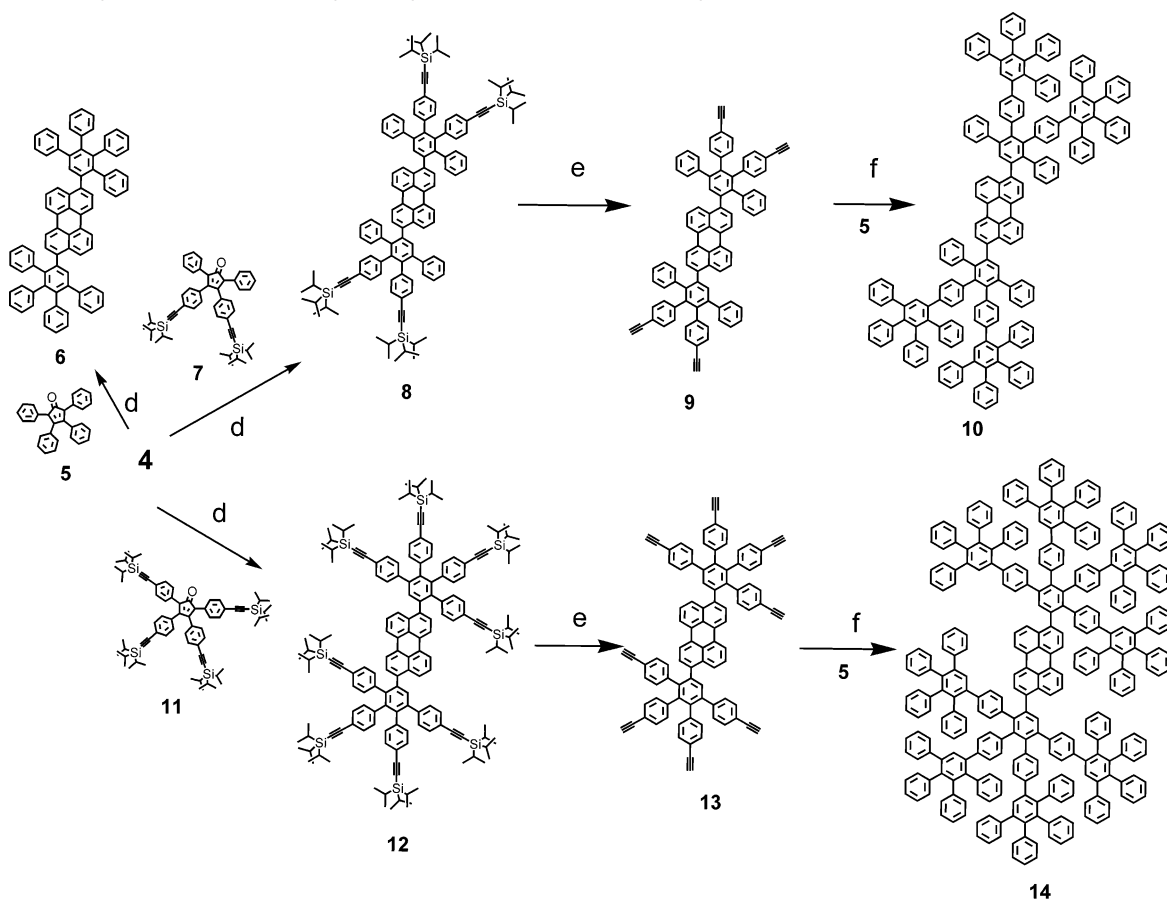
[a] (d) *m*-xylene, 15 h, reflux, 92%; (e) THF, *n*-Bu₄NF, 30 min., rt, 98%; (f) *m*-xylene, 2 d, reflux, 85%.
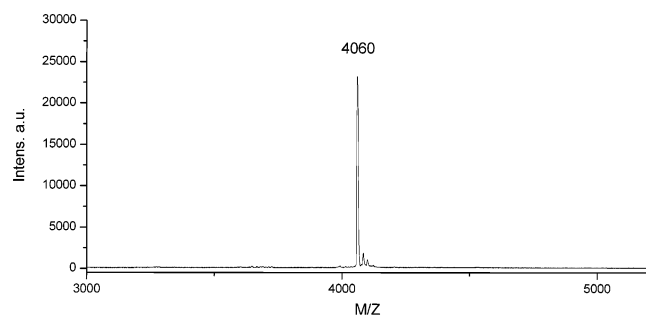

FIGURE 1. MALDI-TOF spectrum of the second-generation dendrimer **14**.

the dendrimers are isomers. For example, 3,9(10)-diethynylperylene **4** shows three signals for the alkyne carbon atom at 85.3, 85.1, and 82.5 ppm due to the presence of two regioisomers.

The structure of the polyphenylene dendrons is calculated using the MM2 (MM+) force field geometry optimization, and the conformation of the perylene core is calculated using the semiempirical PM3 method, as implemented in HyperChem 6.0 (Hypercube Inc.). Optimization of the dendritic system is performed by combining two polyphenylene dendrons to the 3,9- and 3,10-positions of perylene, respectively, and then minimizing the energy of the whole system. The calculated structures of polyphenylene-dendronized perylenes (Figure 2) demonstrate that dendrimers **6**, **10**, and **14** are three-

dimensional objects. Obviously, the results of the molecular modeling of the dendrimers show that the aggregation of two perylene cores that are surrounded by shape-persistent polyphenylene dendrons should be hindered, which is in agreement with the optical properties of dendrimers **6**, **10**, and **14** in the solid state (see the following section). The size of these dendrimers increases using the second-generation dendritic arms. The diameter of the sphere is determined to be 2.3 nm for the first-generation dendrimer **6** and 4.0 nm for the second-generation dendrimer **14**. Because of the bulky nature of the polyphenylene dendrons, the 3,9- and 3,10-dendronized perylenes have very similar structures and second-generation dendrimer **14** shows almost no difference between the two isomers.

As a result of the out-of-plane twisted polyphenylene dendrons, the dendronized perylenes have a high solubility in various organic solvents such as dichloromethane, chloroform, toluene, or THF. The absorption spectra of these dendrimers in THF are shown in Figure 3A. There are two distinct bands, one in the visible region (370–500 nm) and the other in the UV region (280–350 nm). The absorption in the visible region is due to the S_0–S_1 transition of the perylene core, which exhibits distinct vibronic fine structure. The absorption maximum shows a slight bathochromic shift upon increasing the attached polyphenylene dendron generation or degree of branching. The absorption at energy higher than 350 nm, which increases significantly with increasing dendrimer gen-
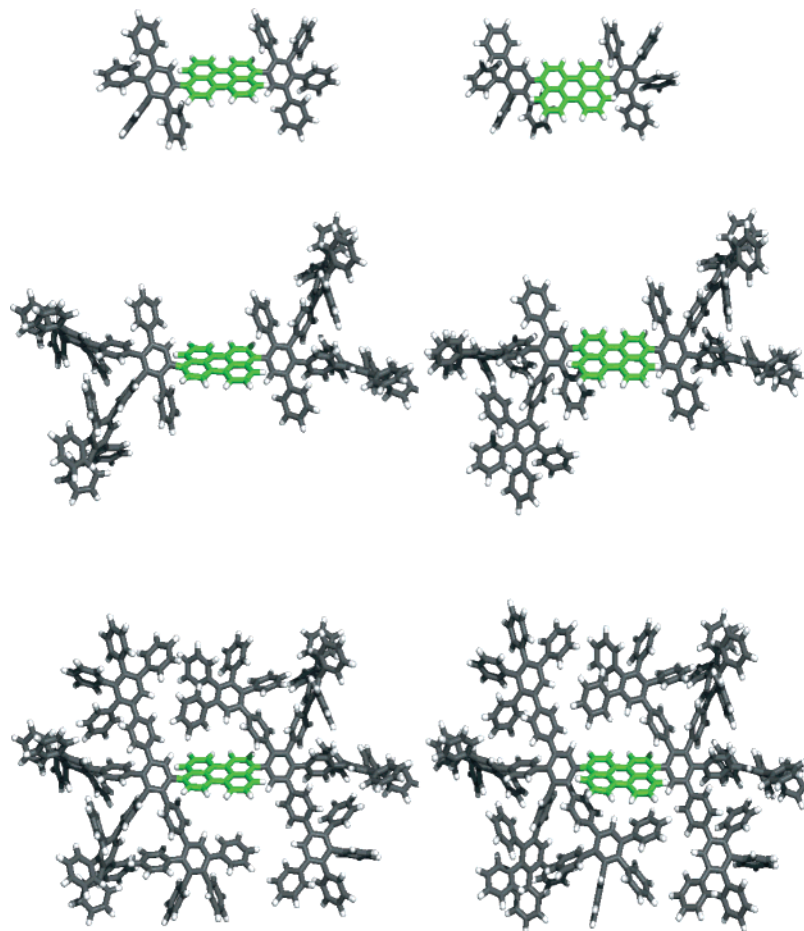
FIGURE 2. Molecular models for 3,10-substituted dendrimers **6** (top left), **10** (middle left), and **14** (bottom left) and 3,9-substituted dendrimers **6** (top right), **10** (middle right), and **14** (bottom right).

eration or degree of branching, is predominantly attributed to the polyphenylene dendritic arms.[21] Compared to the absorption spectrum of unsubstituted perylene (inset in Figure 3A), the absorption spectra of polyphenylene-dendronized perylenes show a substantial bathochromic shift. Absorption maxima for **6**, **10**, and **14** are at 460, 461, and 464 nm, respectively, whereas the absorption maximum for unsubstituted perylene is 437 nm, indicating increased conjugation with the phenyl groups of the polyphenylene dendrons. The direct substitution of perylene with phenyl and phenylacetylene groups has been shown to induce a bathochromic shift of the absorption maximum.[9–11]

The emission spectra of dendronized perylenes, obtained upon excitation of the perylene core at 436 nm, are normalized to the same absorbance at the excitation wavelength and are shown in Figure 3B. The fluorescence quantum yield of the perylene core, which is about 0.7 for dendrimers **6**, **10**, and **14**, does not show a decrease upon increasing the dendrimer generation or degree of branching. Again, the dendronized perylenes demonstrate a red-shifted emission compared to that of perylene (inset in Figure 3B). The emission maxima for **6**, **10**, and **14** in THF are at 478, 479, and 481 nm, respectively, whereas the emission maximum for perylene in THF is at 439 nm.

When **6**, **10**, and **14** are excited at 310 nm where most of the radiation is absorbed by the polyphenylene den-

drons as indicated by the absorption spectra in Figure 3A, predominant emission from the perylene core is observed, with a negligible residual fluorescence of polyphenylene dendrons at about 365 nm (Figure 3C). Furthermore, the fluorescence intensity increases as the absorption cross section of the dendritic arms increases as a result of increasing either the dendrimer generation or the degree of branching (Figure 3C). The fact that the excitation of polyphenylene dendrons leads to perylene-core fluorescence undoubtedly indicates that intramolecular energy transfer occurs in these dendrimers. The excitation spectra of these dendrimers are shown in the Figure 3D. These spectra are similar in shape to the corresponding absorption spectra, indicating that the dendritic branches are also responsible for the population of the emitting excited state of the perylene core. For polyphenylene-dendronized perylenes, almost complete intramolecular energy transfer is observed given the negligible residual fluorescence of the polyphenylene dendritic arms at about 365 nm. Within the framework of the Förster formulations, an effective radius (Förster radius) R_0 was estimated to be 2.5 nm for polyphenylene dendrimers containing a perylene core based on the spectral overlap, by assuming a quantum yield of fluorescence of polyphenylene dendrons of 0.25[21] and by setting the orientation factor to $^2/_3$. Therefore, the highly efficient intramolecular energy transfer within the polyphenylene-dendronized perylenes can be understood
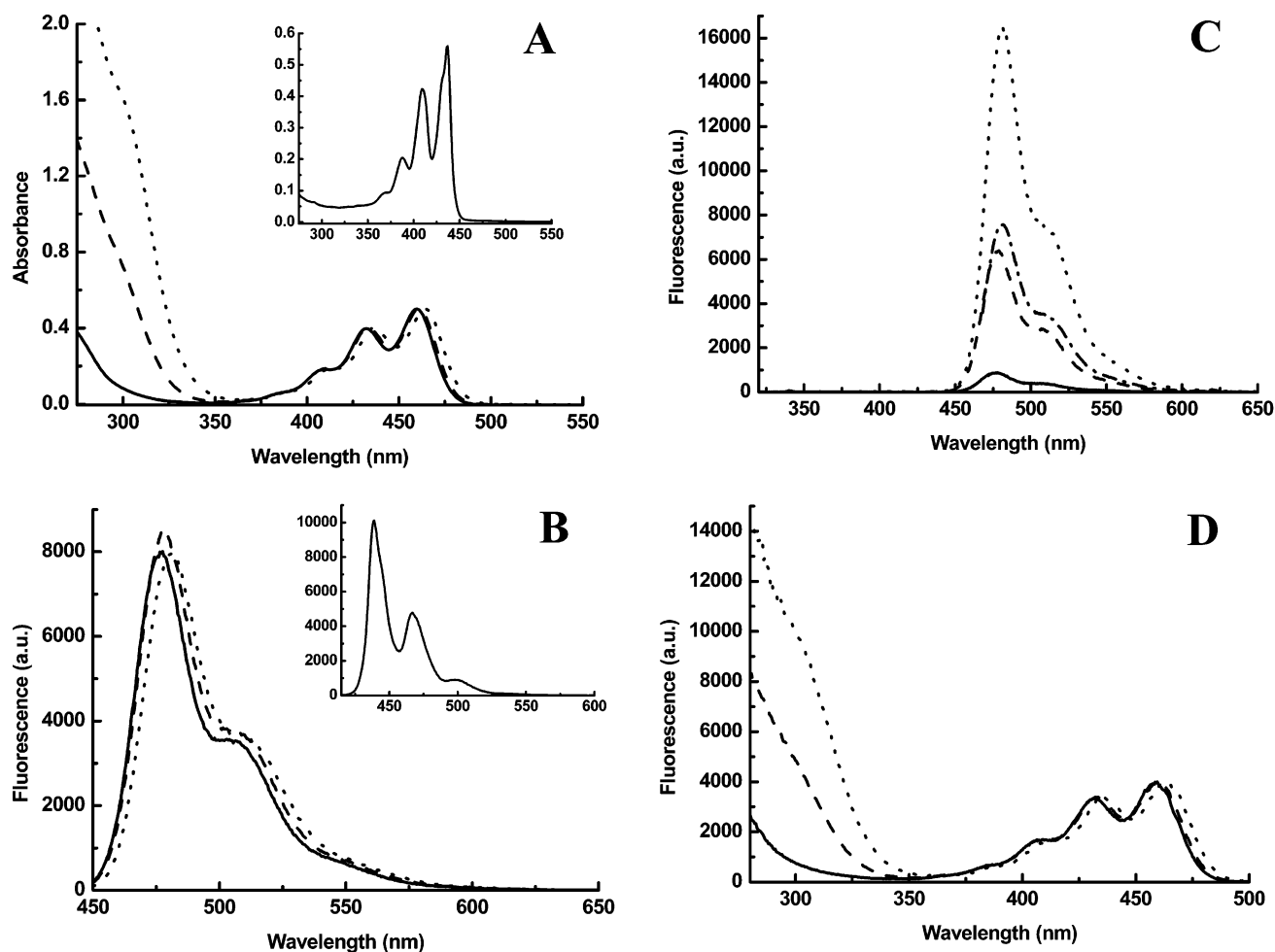
FIGURE 3. (A) Absoprtion spectra and (B) emission spectra of polyphenylene-dendronized perylenes **6** (solid line), **10** (dashed line), and **14** (dotted line) in THF. The absorption spectra are normalized at the perylene absorption maxima. The emission spectra are excited at 436 nm and are normalized to the same optical density at the excitation wavelength (436 nm). The absorption and emission spectra (excitation wavelength, 404 nm) of perylene **1** in THF are shown in the insets. (C) Fluorescence emission spectra of polyphenylene-dendronized perylenes **6** (solid line), **10** (dashed line), and **14** (dotted line) in THF excited at 310 nm. The spectra are normalized to the same concentration of perylene. The emission spectrum of second-generation dendrimer **14** (dash−dot−dash line), directly excited at the absorption maximum (464 nm) at the same concentration, is also shown. (D) Fluorescence excitation spectra of polyphenylene-dendronized perylenes **6** (solid line), **10** (dashed line), and **14** (dotted line) in THF. The spectra are normalized at the maximum around 460 nm. The detected emission wavelength is 510 nm.

because all polyphenylene dendrons are located within the space defined by the Förster radius, as indicated from their calculated structures shown in Figure 2.[24] The high extinction coefficients of polyphenylene dendrimers at short wavelength, together with the efficient intramolecular energy transfer from the polyphenylene dendritic arms to the perylene core, result in higher intensity emission from the perylene core by exciting polyphenylene dendritic arms in second-generation dendrimer **14**, as can be clearly seen from Figure 3C and the excitation spectra shown in Figure 3D.

The solid-state absorption and emission spectra of these polyphenylene-dendronized perylenes are shown in Figure 4. Dendrimers **6**, **10**, and **14** are spin-coated from a chloroform solution onto a quartz substrate and display good film-forming properties. The absorption spectra in Figure 4 exhibit similar maxima as those of dendrimers

in solution and also show distinct vibronic fine structure. The emission spectra of polyphenylene-dendronized perylenes, which have maxima at 519, 501, and 496 nm for **6**, **10**, and **14** respectively, display a difference in the bathochromic shift depending on the dendrimer generation and degree of branching. The emission spectrum of the first-generation dendrimer **6** is significantly shifted to the red by 1650 cm^{-1} compared with the emission spectrum in THF solution, indicating that emission occurs from trap sites which might be aggregated. However, a bathochromic shift of 1270 cm^{-1} is observed for the second-generation dendrimer **10**, suggesting a decreased interaction between the perylene cores for higher generation polyphenylene dendritic arms. Further increasing the degree of branching of the rigid dendritic arms can significantly suppress the perylene-core aggregation. For instance, the emission spectrum of second-generation dendrimer **14** in the solid state exhibits vibronic structures and is only 630 cm^{-1} red-shifted compared to its emission spectrum in THF solution. To

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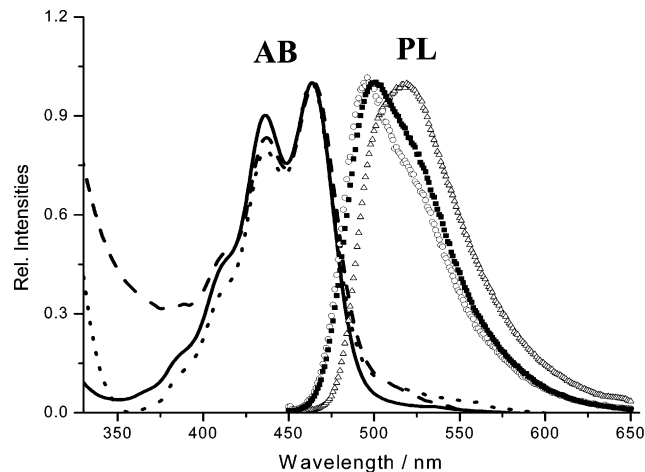
FIGURE 4. Normalized absorption spectra (AB) and emission spectra (PL, λ_{ex} = 435 nm) of polyphenylene-dendronized perylenes **6** (solid line), **10** (dashed line), and **14** (dotted line) in solid films.

observe a significant bathochromic shift in the solid-state emission spectra between the first-generation dendrimer **6** and the second-generation dendrimer **10**, **14** can be suggested to avoid the aggregation of the perylene unit by the second-dendrimer generation.

Conclusions

A series of polyphenylene-dendronized perylenes have been prepared with high yields under mild conditions. As a result of the out-of-plane twisted phenyl units within the polyphenylene dendrons, the dendronized perylenes exhibit high solubility in various common organic solvents. The results of the absorption and fluorescence spectra both in solution and in solid films on quartz show that the aggregation of the perylene core has been significantly suppressed by the higher generation and/or higher degree of branching of the rigid polyphenylene dendritic arms. The polyphenylene-dendronized perylenes show bathochromically shifted absorption and emission spectra relative to that of unsubstituted perylene. Efficient intramolecular energy transfer from the polyphenylene dendrons to the perylene core has been confirmed by steady-state spectroscopic measurements. The functionalization of perylene with polyphenylene dendrons allows film formation by spin-coating, and the resulting thin films show strong green fluorescence from the perylene core. This result suggests that the study of these dendrimers as LEDs is warranted, and their electroluminescence is under investigation.

Experimental Section

3,9(10)-Di(triisopropylsilylethynyl)perylene (3). 3,9-(10)-Dibromoperylene **2** (2.00 g, 4.87 mmol) was dissolved in a degassed mixture of triethylamine (50 mL) and absolute THF (150 mL) under argon. Bis(triphenylphosphine)palladium(II) dichloride (350 mg, 0.50 mmol) and copper(I) iodide (190 mg, 0.10 mmol) were then added under a flow of argon. After the flask was sealed with a septum, triisopropylsilylethyne (1.65 mL, 7.50 mmol) was injected. The reaction mixture was stirred at room temperature overnight and then poured into an equivalent volume of dichloromethane and filtered. Hydrochloric acid (6 M) was carefully added to the filtrate until the

aqueous phase became slightly acidic (pH < 5). After that, the organic phase was removed, washed twice with distilled water, extracted with a saturated solution of ammonium chloride, washed again several times with distilled water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel affording **3** (2.7 g, 91%). R_f = 0.96 (CH$_2$Cl$_2$); mp = 130.3 °C; ^{1}H NMR spectrum (250 MHz, THF, 300 K) δ [ppm] 8.40 (d, J = 7.5 Hz, 2H), 8.28 (m, 4H), 7.71 (dd, J = 8.0 Hz, 2H), 7.61 (t, J = 6.8 Hz, J = 7.5 Hz, 2H), 1.24 (s, 42H, isopropyl); ^{13}C NMR spectrum (j-modulated spin−echo, 62.5 MHz, THF, 300 K) δ [ppm] 135.8 (q), 132.8 (t), 132.7 (t), 132.4 (q), 128.5 (t), 127.6 (t), 127.2 (t), 122.9 (t), 122.5 (t), 122.0 (q), 121.7 (t), 121.2 (t), 106.8 (q), 97.9 (q), 97.7 (q), 19.3 (t), 12.5 (t); IR spectrum (KBr) ν = 2944, 2891, 2863, 2361, 2142, 2060, 1643, 1574, 1462, 1387, 1243, 1123, 1071, 1015, 993, 918, 882, 827, 804, 764, 731, 635, 538 cm^{-1}; UV−vis spectrum (chloroform) λ_{max} (M^{-1} cm^{-1}) = 426 (12 415), 453 (30 064), 484 nm (43 079); fluorescence spectrum (chloroform) λ_{max} = 497, 527, 565 nm (excitation at 450 nm); FD mass spectrum (8 kV) m/z = 612 (100%) [M$^+$] (Calcd 613). Anal. Calcd (%) for (C$_{42}$H$_{52}$-Si$_2$): C, 82.29; H, 8.55. Found: C, 82.51; H, 8.19.

3,9(10)-Diethynylperylene (4). Trialkylsilyl derivative **3** (1.00 g, 1.63 mmol) was dissolved in THF (50 mL) under argon. A THF solution of n-tetrabutylammonium fluoride (1.50 g, 4.89 mmol) was injected into a 100 mL Schlenk flask. The mixture was stirred for 30 min at room temperature. The solution was diluted with dichloromethane (200 mL) and then extracted with hydrochloric acid (100 mL, 6 M). The organic phase was removed, washed with distilled water (100 mL), and dried over magnesium sulfate. The solvents were removed in a vacuum, and the crude product was purified by column chromatography on silica gel to give the brown solid **4** (460 mg, 95%). R_f = 0.90 (CHCl$_3$); mp > 300 °C; ^{1}H NMR spectrum (250 MHz, THF, 300 K) δ [ppm] 7.69 (d, J = 7.5 Hz, 2H), 7.59 (dd, J = 8.0 Hz, 2H), 7.54 (dd, J = 8.0 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 6.90 (t, J = 7.5 Hz, 2H), 3.42 (s, 1H), 3.40 (s, 1H); ^{13}C NMR spectrum (62.5 MHz, THF, 300 K) δ [ppm] 135.7, 132.6, 132.5, 132.3, 129.0, 128.3, 127.3, 126.9, 122.6, 122.2, 121.4, 121.1, 121.0, 120.8. 85.2, 85.1, 82.5; IR spectrum (KBr) ν = 3292, 2927, 2865, 2361, 2336, 2095, 1645, 1567, 1499, 1463, 1385, 1191, 1050, 883, 831, 806, 762, 648, 601 cm^{-1}; UV−vis spectrum (chloroform) λ_{max} (M^{-1} cm^{-1}) = 417 (14 044), 442 (32 192), 472 nm (42 328); fluorescence spectrum (chloroform) λ_{max} = 486, 515, 551 nm (excitation at 440 nm); FD mass spectrum (8 kV) m/z = 300 (100%) [M$^+$] (Calcd 300). Anal. Calcd (%) for (C$_{24}$H$_{12}$): C, 95.97; H, 4.03. Found: C, 95.81; H, 4.11.

8-Cascade:perylene[2-3,9(10)]:(2,3,4,5-phenylene):benzene (6). A mixture of perylene derivative **4** (200 mg, 0.667 mmol) and tetraphenylcyclopentadienone **5** (770 mg, 2.0 mmol) in m-xylene (5 mL) was stirred at 140 °C for 15 h under argon. The cooled reaction mixture was added to 100 mL of methanol. The precipitated product was filtered under suction. The yellow solid **6** (630 mg, 93%) was obtained by reprecipitation several times in methanol until the red color of the tetraphenylcyclopentadienone disappeared. Mp > 300 °C; ^{1}H NMR spectrum (250 MHz, THF, 300 K) δ [ppm] 8.15 (m, 2H), 8.04 (m, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H), 7.36 (m, 2H), 7.23−7.07 (m, 12H), 6.91 (s, 12 H), 6.82 (m, 14H), 6.67 (m, 4H); ^{13}C NMR spectrum (j-modulated spin−echo, 62.5 MHz, THF, 300 K) δ [ppm] 143.0 (q), 142.7 (q), 141.7 (q), 141.5 (q), 141.3 (q), 141.1 (q), 140.5 (q), 140.3 (q), 140.2 (q), 140.1 (q), 134.5 (q), 132.9 (t), 132.8 (t), 132.5 (t), 132.4 (t), 132.2 (q), 132.1 (q), 132.0 (t), 131.1 (q), 131.0 (q), 130.8 (t), 129.2 (q), 128.3 (t), 127.7 (t), 127.4 (t), 127.3 (t), 127.0 (t), 126.9 (t), 126.3 (t), 126.0 (t), 120.9 (t), 120.8 (t), 120.3 (t), 120.2 (t); IR spectrum (KBr) ν = 3055, 2361, 2336, 1643, 1498, 1438, 1388, 1073, 810, 761, 699, 672, 533 cm^{-1}; UV−vis spectrum (chloroform) λ_{max} (M^{-1} cm^{-1}) = 264 (116 921), 421 (19 658), 443 (41 858), 470 nm (53 284); fluorescence spectrum (chloroform) λ_{max} = 484, 512 nm (excitation at 440 nm); MALDI-TOF mass spectrum

m/z = 1013 (100%) [M$^+$] (Calcd 1013). Anal. Calcd (%) for (C$_{80}$H$_{52}$): C, 94.83; H, 5.17. Found: C, 94.53; H, 5.46.

32-Cascade:perylene[2-3,9(10)]:(2,3,4,5-phenylene): (1,2,3,4,5-phenylene):benzene (14). A mixture of **13** (100 mg, 0.082 mmol) and tetraphenylcyclopentadienone **5** (510 mg, 1.32 mmol) in *m*-xylene (4 mL) was stirred at 170 °C for 48 h under argon. The cooled reaction mixture was added to 100 mL of methanol to give a precipitate. The product was purified by column chromatography to give a yellow solid (260 mg, 79%). R_f = 0.93 (CH$_2$Cl$_2$); mp = 317.2 °C; ^{1}H NMR spectrum (250 MHz, THF, 300 K) δ [ppm] 8.24 (m, 2H), 8.12 (m, 2H), 7.72–7.25 (m, 14H), 7.20–7.06 (m, 32H), 6.97 (m, 14H), 6.86–6.70 (m, 124H), 6.61–6.36 (m, 24H); ^{13}C NMR spectrum (j-modulated spin–echo, 62.5 MHz, THF, 300 K) δ [ppm] 142.9 (q), 142.8 (q), 142.7 (q), 142.5 (q), 141.9 (q), 141.8 (q), 141.5 (q), 141.4 (q), 141.3 (q), 141.2 (q), 141.0 (q), 140.9 (q), 140.7 (q), 140.5 (q), 140.3 (q), 140.2 (q), 140.1 (q), 140.0 (q), 139.7 (q), 139.0 (q), 138.6 (q), 134.4 (q), 132.6 (t), 132.4 (t), 132.2 (t), 131.9 (t), 131.0 (q), 130.7 (t), 130.6 (t), 130.3 (t), 130.0 (t), 129.2 (q), 128.3 (t), 127.7 (t), 127.3 (t), 126.9 (t), 126.4 (t), 126.0 (t); IR spectrum (KBr) ν = 3054, 3026, 2361, 2336, 1643, 1600, 1497, 1436, 1386, 1072, 1025, 903, 837, 762, 699, 672, 544 cm^{-1}; UV–vis spectrum (chloroform) λ_{max} (M^{-1} cm^{-1}) = 271 (323 355), 423 (18 170), 447 (39 561), 473 nm (49 446); fluo-rescence spectrum (chloroform) λ_{max} = 487, 515 nm (excitation at 440 nm); MALDI-TOF mass spectrum m/z = 4060 (100%) [M$^+$] (Calcd 4057). Anal. Calcd (%) for (C$_{320}$H$_{212}$): C, 94.73; H, 5.27. Found: C, 94.52; H, 5.49.

Supporting Information Available: Materials and analytical methods; data including full experimental details for **8**–**10**, **12**, and **13**; NMR peak assignments for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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