

Multichromophoric Polyphenylene Dendrimers: Toward Brilliant Light Emitters with an Increased Number of Fluorophores

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Abstract: Two routes for the introduction of highly fluorescent peryleneimide chromophores into the scaffolding of polyphenylene dendrimers via iterative Diels–Alder cycloadditions are presented. The key intermediates for the divergent dendrimer buildup were two cyclopentadienone branching units carrying two peryleneimides and two masked terminal alkynes. The difference between the two reagents is the mode of incorporation of the chromophores. In the first case, the chromophores were attached to the α -position of the tetraphenylcyclopentadienones. In the second case, peryleneimides are used as a “spacer” in the β -position of the cyclopentadienones giving rise to dendrimers with extended molecular diameters (up to 12 nm) and 24 chromophores within their scaffold. Absorption and emission characteristics of the new multichromophoric nanoparticles were investigated and compared to those of the parent dyes. Additionally, an asymmetrically substituted first-generation dendrimer with six perylene diimide chromophores and one ester functionality is reported. The ester serves as a potential anchor group, and this nanoemitter paves the way to a multichromophoric fluorescence label. All dendrimers have good solubility in common organic solvents, high fluorescence quantum yields, and defined distances between the chromophores, making them attractive candidates for single-molecule spectroscopy.

Introduction

In recent years, there has been an increasing interest in multichromophoric systems.¹ The concept of concentrating many chromophores in a confined volume is used by nature in light-harvesting complexes² and fluorescent proteins.³ Important representatives of artificial multichromophoric systems are supramolecular assemblies,⁴ fluorescent latex nanoparticles,⁵ and polymers, in which the chromophores are covalently attached to the polymer backbone or as a side chain.⁶ In many cases, the optical functions depend sensitively upon the distances and relative spatial orientations of the individual chromophore centers. In artificial multichromophoric dyads or triads, the vectorial energy transfer of natural light-harvesting complexes

to an active center has been imitated.⁷ Other examples are multichromophoric polymers used as active components in light-emitting diode (LED) materials.⁸ The increased fluorescence intensity of multichromophoric systems has been used to increase the sensitivity of biological labels.⁹ A group of macromolecules that is particularly qualified for the design of multichromophoric systems is that of dendrimers.¹⁰ Especially for biological labels and for molecular probes, where the sensitivity often correlates directly with the number of fluorophores, dendritic structures have distinct advantages over supramolecular or polymeric multichromophores. As dendrimers are monodisperse molecules, it is possible to tailor the number of chromophores within these nanoobjects and thus to quantify the concentration of the analyte. In the case of flexible dendrimers, intramolecular aggregation of the dyes is not always suppressed and can result in excimer formation with the

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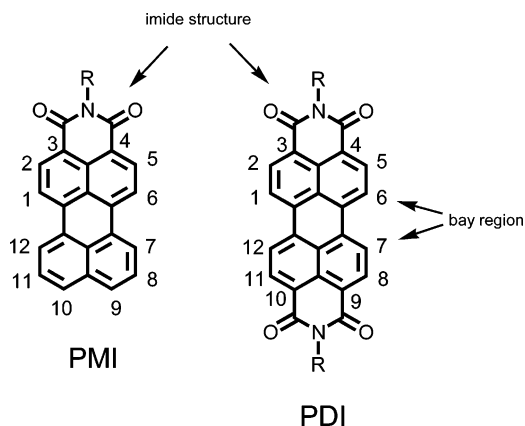


Figure 1. Chemical structures of unsubstituted peryleneimide chromophores: perylene-3,4-dicarboximide (PMI) and perylene-3,4,9,10-tetracarboxdiimide (PDI).

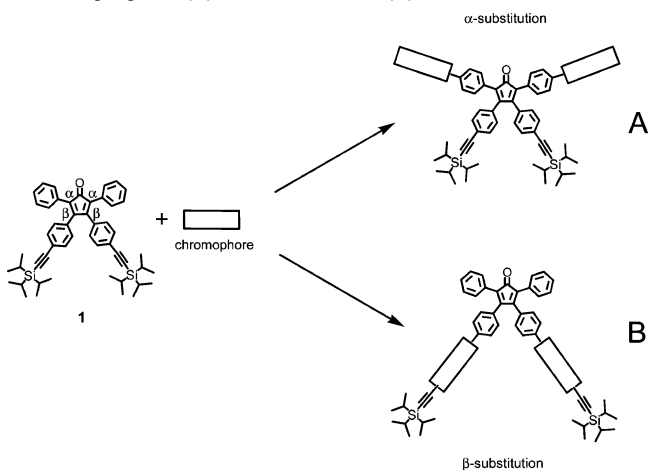
concomitant decrease in fluorescence intensity.¹¹ Hence, the chromophore interactions within these dendrimers are rather complex, and their study is further inhibited by the often low photostability and fluorescence quantum yields of the chosen chromophores.¹²

We have recently shown that the use of shape-persistent polyphenylene dendrimers as rigid dendritic scaffolds ensures the spatial separation of chromophores. Thus, after loading a polyphenylene dendrimer with perylenedicarboximide (PMI, see Figure 1), the chromophores on the surface do not show detectable intramolecular aggregation.¹³ Furthermore, the interchromophore distances are well defined, which makes them perfect candidates for investigating excitation energy transfer, especially at the single-molecule level.^{14,15}

Polyphenylene dendrimers are made by repetitive Diels–Alder reactions using an ethynyl-functionalized core and a tetraphenylcyclopentadienone derivative as the branching agent, leading to pentaphenylbenzene repeating units. The benzene rings are twisted out-of-plane, and the polyphenylene dendrimers show high thermal and photochemical stabilities as well as shape persistence.¹⁶

Besides the surface functionalization of polyphenylene dendrimers with PMI, a variety of polyphenylene dendrimers have been synthesized carrying perylenetetracarboxdiimide (PDI, see Figure 1) as the core.¹⁷ These dendronized dyes have excellent thermal, chemical, and photochemical stabilities, high extinction

Scheme 1. Variation of the Chromophore Location in the AB₂ Branching Agent: (A) Side Chains and (B) Backbone



coefficients, and a fluorescence quantum yield of ~ 1 .¹⁸ These properties render them attractive candidates for single-molecule spectroscopy.

The insertion of fluorescent dyes into the scaffold of a rigid dendrimer can lead to a variety of new and desirable properties: (i) the number of dyes within the nanoemitter is not restricted to the number of the possible surface functions; (ii) the distance between individual dyes in the same or different generations is defined by the design of the branching units; and (iii) as the number of chromophores increases within the dendrimer generations, the intensity of the overall absorption or emission increases, as does the sensitivity of molecular probes and biological labels as well. Accordingly, a large number of chromophores within a confined, well-defined volume is desirable.

Herein, we report two different methods of inserting peryleneimide dyes into the scaffolding of polyphenylene dendrimers. In each route, functionalization of the tetraphenylcyclopentadienone branching reagent with peryleneimides is the key step, resulting in a dendritic branching unit carrying two peryleneimides and two triisopropylsilyl (TIPS)-protected terminal alkynes for further dendritic growth. In the first case (route A, Scheme 1), a chromophore was attached to the phenylene rings at the α -position of the cyclopentadienone. In the second case (route B, Scheme 1), the dyes were inserted between the phenylene rings at the β -position and the alkyne. The dye units thereby act as stiff spacers between the diene and the dienophile, maintaining the rigid nature of the resulting dendrimer. The spacer extends the diameter of the resulting dendrimers compared to the parent polyphenylene dendrimer by approximately a pentaphenyl moiety per generation. This approach has been successfully carried out with a *p*-terphenyl spacer up to the fifth generation to yield a diameter above 20 nm (see Figure 2).¹⁹ Using PDI as a spacer, the buildup of even larger nanoparticles with an even higher number of generations should be possible. Furthermore, the insertion of the PDI as a “functional” spacer permits the material to be used in a number of applications not accessible to the dendrimer containing the *p*-terphenyl spacer,

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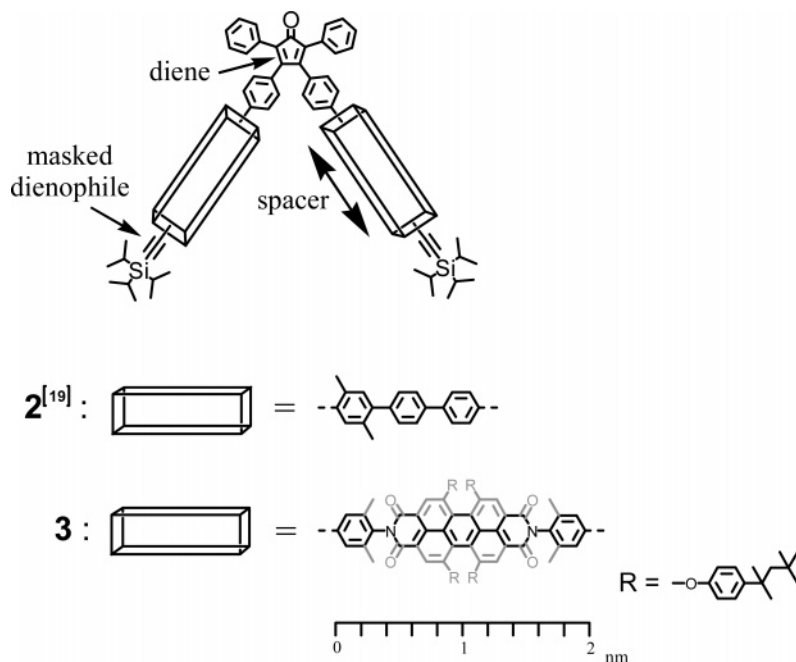


Figure 2. Introduction of different spacers into a tetraphenylcyclopentadienone branching agent.

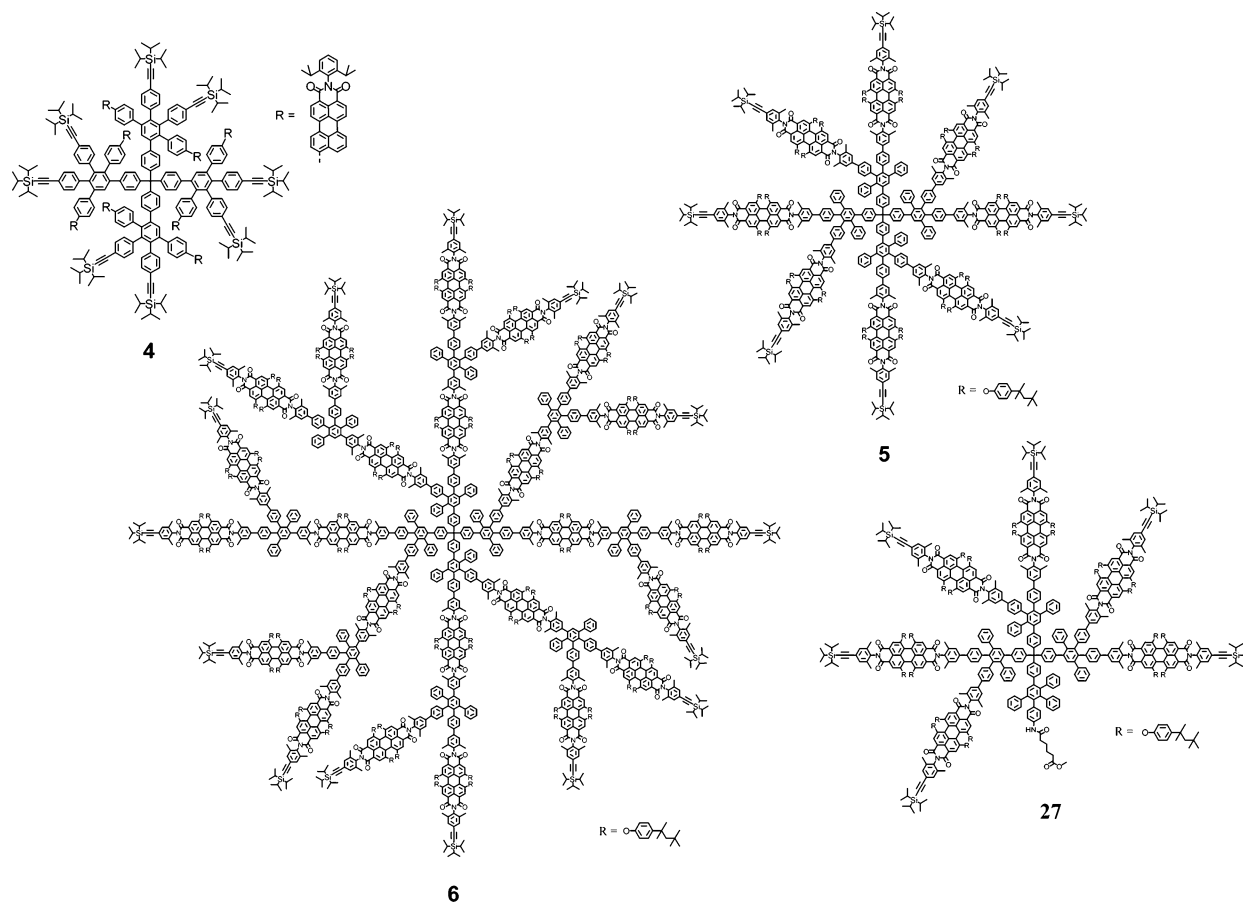
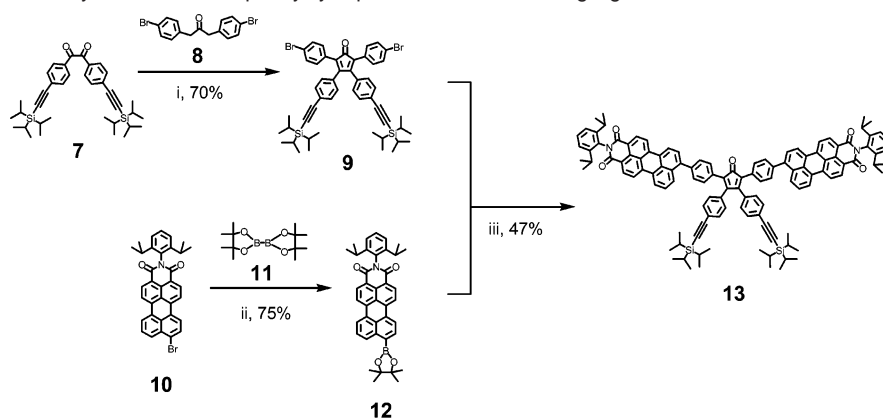


Figure 3. Multichromophoric polyphenylene dendrimers 4, 5, 6, and 27.

e.g., as high-fluorescence molecular probes and as single-photon sources at a single-molecular level.

The two peryleneimide-functionalized cyclopentadienones, **3** (Figure 2) and **13** (Scheme 2, below), are subsequently used to build up multichromophoric first-generation polyphenylene dendrimers **4** and **5** (Figure 3), each carrying eight peryleneimide

chromophores. Remarkably enough, in the case of the tetraphenylcyclopentadienone branching reagent **3**, the second-generation dendrimer **6** (Figure 3), containing 24 PDI chromophores and 16 terminal ethynyl functions, can be achieved. Branching agent **3** was also used for the construction of an asymmetric first-generation dendrimer (**27**, Figure 3 and Scheme 6, below)

Scheme 2. Synthesis of the “Dye-Loaded” Tetraphenylcyclopentadienone Branching Agent **13**^a

^a Reagents and conditions: (i) 1,3-bis(4-bromophenyl)acetone (**8**), KOH, ethanol, 20 min, 80 °C, 70%; (ii) bis(pinacolato)diboron (**11**), potassium acetate, [Pd(dddppf)], dioxane, 16 h, 70 °C, 75%;²⁴ (iii) compound **9**, PMI **12**, K₂CO₃, [Pd(PPh₃)₄], toluene/ethanol, 16 h, 80 °C, 47%.

with six PDI chromophores and one aliphatic ester. The ester function is a potential anchor group which could be attached to different kinds of substrates, e.g., surfaces, polymers, or biologically active moieties. With its multiplied fluorescence intensity, its use as a fluorescence label is anticipated.

Results and Discussion

We have already described the synthesis of tetraphenylcyclopentadienones bearing rylene chromophores as functional moieties.²⁰ There, the Pd-catalyzed Suzuki cross-coupling reaction²¹ appeared as a straightforward synthetic tool for introducing chromophores into the tetraphenylcyclopentadienone branching units, as it is easy to handle and results in good yields. Here we use this synthetic strategy of introducing peryleneimide chromophores into tetraphenylcyclopentadienones via the Suzuki coupling reaction for the substitution at both the α - and β -positions. Whereas in the case of the α -coupling the required chromophore carries only the boronic ester function needed for a Suzuki coupling, in the case of the β -linkage a chromophore with two different functions is needed: one aryl halide for the Suzuki coupling with the cyclopentadienone and one TIPS-protected ethynyl group to ensure further dendritic growth. The resulting dendrimers were synthesized using a divergent route, which we have used repeatedly in the past,²² starting from tetrakis(4-ethynylphenyl)methane (**24**).

Syntheses. The α -Substituted Tetraphenylcyclopentadienone Branching Unit **13.** Cyclopentadienone **9** was prepared via a Knoevenagel condensation of 4,4'-bis(triisopropylsilyl-ethynyl)benzil (**7**) and 1,3-bis(4-bromophenyl)acetone (**8**),²³ bearing two bromides in the para position of the phenyl ring in the α -position and two TIPS-protected ethylene functions at the phenyl ring in the β -position of the cyclopentadienone (Scheme 2). Cyclopentadienone **9** was then treated with the boronic ester-functionalized PMI derivative **12**²⁴ in a palladium-catalyzed

coupling reaction under Suzuki conditions^{21,25} to afford **13** in 47% yield. Chromatographic purification was performed after each step.

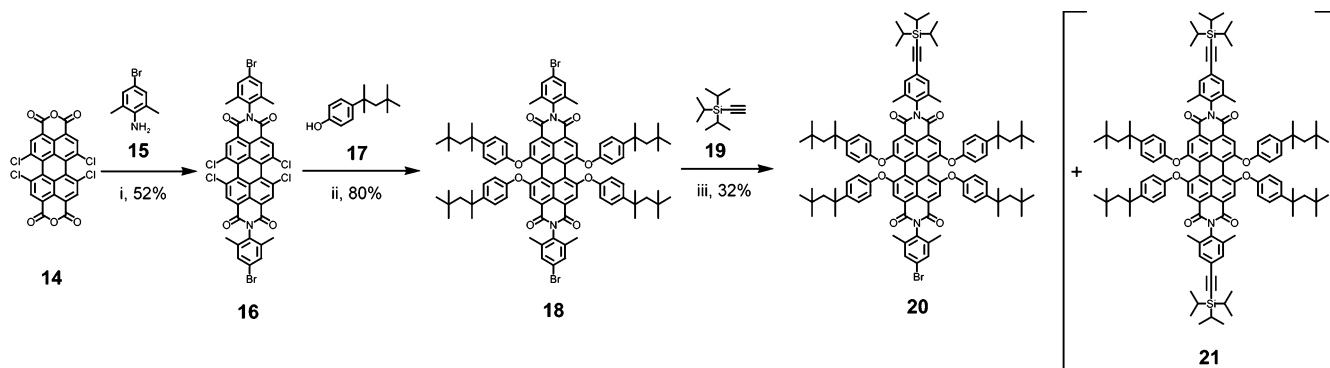
The “Extended” Tetraphenylcyclopentadienone Branching Unit **3.** To use PDI as a rigid spacer, the two functions were introduced into the imide structures of the PDI chromophore, whereby the inherent stiffness of the chromophore is retained. In an imidization reaction, 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxy dianhydride²⁶ (**14**) was reacted with 4-bromo-2,6-dimethylaniline (**15**) in propanoic acid for 16 h at 160 °C (Scheme 3). For characterization, **16** was purified by column chromatography using CH₂Cl₂ as an eluent, which, due to the low solubility, led to significant losses. In general, the crude product was used directly after precipitation from water. After subsequent substitution of the chlorides in the so-called “bay region” of the chromophore (see Figure 1) with an excess of the bulky *tert*-octyl-substituted phenol **17** in *N*-methylpyrrolidone (NMP) at 90 °C, the product was purified by column chromatography due to its increased solubility. Compound **18** was obtained as a red solid with a yield of 80%.

The desymmetrization of **18** was achieved via a statistical palladium-catalyzed Hagihara reaction²⁷ with 1.15 equiv of triisopropylsilylacetylene (**19**). This resulted in two products: the doubly substituted PDI **21** and the singly substituted PDI **20**. The two products were separated by column chromatography using petroleum ether/CH₂Cl₂ (3/2) as the eluent to obtain **21** and the desired desymmetrized PDI chromophore **20** in 11% and 32% yield, respectively, with recovery of the starting material.

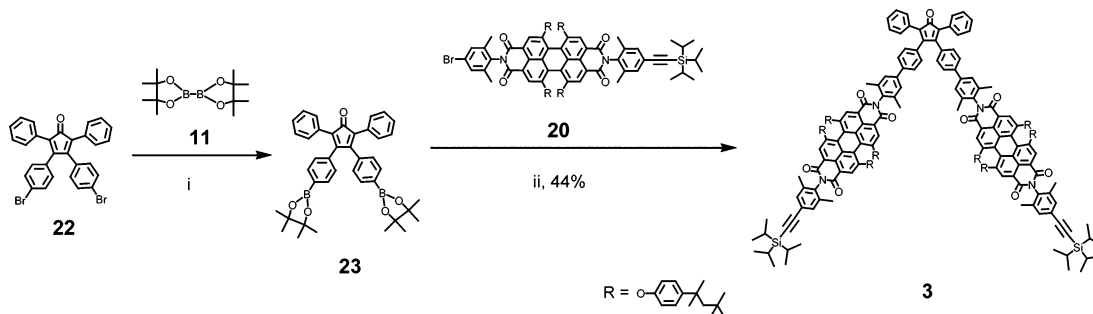
Cyclopentadienone **22** was prepared according to literature procedures.^{23,28} The cyclopentadienone derivative **23** was achieved by a palladium-catalyzed reaction of commercially available bis(pinacolato)diboron (**11**) and **22** in a modification of the Miyaura procedure²¹ (Scheme 4). The pure product could be obtained by using column chromatography with CH₂Cl₂ as eluent. However, since this purification leads to a loss of

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Scheme 3. Synthesis of the Desymmetrized PDI Chromophore **20**^a

^a Reagents and conditions: (i) 2,6-dimethyl-4-bromoaniline (**15**), propanoic acid, 16 h, 160 °C, 52%; (ii) 4-(1,1,1,3,3-tetramethylbutyl)phenol (**17**), K₂CO₃, NMP, 16 h, 90 °C, 80%; (iii) triisopropylsilylacetylene (**19**), CuI, PPh₃; [Pd(PPh₃)Cl₂], THF/triethylamine (1/1), 15 h, 80 °C, 14%.

Scheme 4. Synthesis of the Branching Agent **3**, Bearing a PDI Chromophore as a Spacer between Diene and Dienophile^a

^a Reagents and conditions: (i) bis(pinacolato)diboron (**11**), potassium acetate, [Pd(ddpf)], dioxane, 16 h, 75 °C; (ii) PDI chromophore **20**, K₂CO₃/H₂O, [Pd(PPh₃)₄], toluene/ethanol, 16 h, 80 °C, 44%.

product, crude **23** was used without further purification. The formation of the PDI-substituted cyclopentadienone derivative **3** was achieved by a palladium-catalyzed Suzuki coupling.²⁵ Purification by column chromatography with petroleum ether/CH₂Cl₂ (3/2 → 1/1) gave the branching agent **3** in 44% yield. To prevent the photooxidation of the branching unit, **3** was stored in the dark under an argon atmosphere at 4 °C.

The Multichromophoric Dendrimers 4, 5, and 6. For the synthesis of the multichromophore **4** with the chromophores in the side chain, the tetrahedral core molecule tetrakis(4-ethynylphenyl)methane (**24**) was treated with branching agent **3** in diphenyl ether at 180 °C (Scheme 5). After 2 days, the reaction mixture was precipitated into methanol and purified by column chromatography to give the first-generation multichromophore **4**, bearing eight PMI and eight protected alkynes, in 69% yield.

The first-generation dendrimer **5**, with the chromophores in the backbone, was formed by Diels–Alder reaction of the tetrahedral core **24** with an 8-fold excess of the branching unit **3** in *m*-xylene at 150 °C. Dendrimer **5** was isolated by column chromatography with petroleum ether/CH₂Cl₂ (1/1) as eluent in 86% yield. After facile deprotection of **5** with tetrabutylammonium fluoride, the ethynyl-functionalized dendrimer **25** was treated with 24 equiv of **3** to give the second-generation dendrimer **6**, bearing 24 PDI chromophores and 16 terminal TIPS-protected alkynes. Column chromatography on silica gel, as well as purification by dialysis (in dimethylformamide), failed to separate dendrimer **6** from branching agent **3**. Molecular mechanics calculations (see following section) suggest that the β -substituted dendrimers possess large cavities, so we assume that the branching unit **3** can penetrate into these cavities,

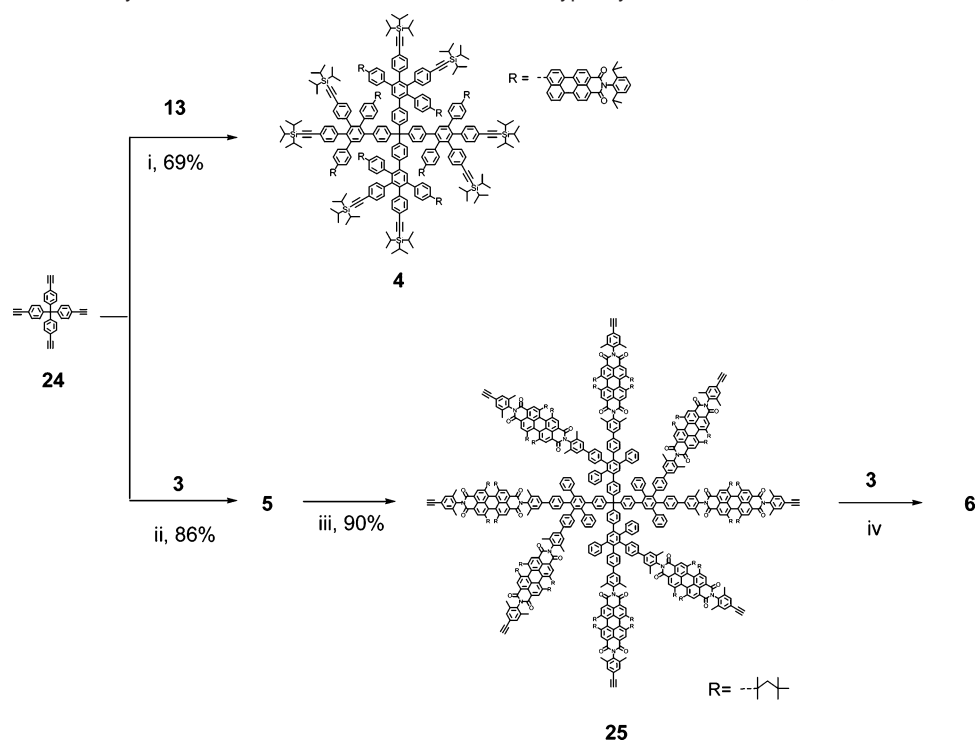
thereby inhibiting purification by column chromatography and dialysis. However, pure **6** was obtained by size exclusion chromatography with tetrahydrofuran (THF) as eluent.

All the dendrimers described in this paper are highly soluble in common organic solvents such as dichloromethane, toluene, and THF. Characterization by MALDI-TOF mass spectrometry, ¹H NMR, and ¹³C NMR spectroscopy was therefore easily accomplished.

The MALDI-TOF spectrum of **4** (Figure 4a) showed three peaks: one at *m/z* 7122, corresponding to the molecular ion mass, and two below the molecular ion peak. As they do not correspond to any potential growth imperfections and their intensities increase with increasing laser power (in comparison to the molecular ion peak), they are likely the result of fragmentation during ionization. The perfect agreement between the calculated and experimentally determined *m/z* ratios strongly supports the monodispersity of the dendrimer **4**.

The MALDI-TOF spectrum of **6** (Figure 4b) shows only one peak, at *m/z* 41 674. The broad appearance of the molecular ion peak results from the linear detection mode of the MALDI measurement, which, due to the high molecular mass of the molecule, is necessary for detection. However, the broad molecular ion peak does not overlap with the peak of any potential growth imperfection due to unreacted ethynyl groups during the Diels–Alder reaction. This side product would cause a mass difference of 3546 g/mol.

The ¹H NMR spectrum of **4** (see Supporting Information) indicates that the eight PMI chromophores are not identical. Due to the rigid nature of the dendrimer backbone, the two chromophores at one dendrimer arm are located in substantially different environments. The signals of the benzylic CH protons

Scheme 5. Synthesis of the “Dye-Loaded” First- and Second-Generation Polyphenylene Dendrimers **4**, **5**, and **6**^a

^a Reagents and conditions: (i) branching agent **13**, diphenyl ether, 180 °C, 2 d, 69%; (ii) branching agent **3**, *m*-xylene, 150 °C, 5 d, 86%; (iii) tetrabutylammonium fluoride, THF, 1 h, 90%; (iv) branching agent **3**, diphenyl ether, 200 °C, 18 d.

of the diisopropylphenyl group appear as two overlapping equally intense septets at 2.86–2.66 ppm. The signals of the corresponding methyl groups are also nonequivalent.

The ¹H NMR spectra of **5** and **6** (see Supporting Information) show well-separated and assignable signals for the protons of the bay region of the PDI chromophore at 8.11 ppm as well as for the aliphatic protons between 2.05 and 0.71 ppm. Further, the signals of the single proton on the central benzene ring of the pentaphenylbenzene units show generation-dependent chemical shifts.²² The relative intensities of aromatic and aliphatic signals correspond well with the expected values.

The Monofunctional “PDI-Loaded” Polyphenylene Dendrimer 27. For the design of a biological label, not only a high fluorescence quantum yield and a high absorption cross section but also one anchor group are needed. The β -substituted branching agent **22** was applied to the synthesis of a polyphenylene dendrimer decorated with six PDI chromophores and one aliphatic carboxylic acid group (**27**). The introduction of the aliphatic ester, which can serve as an anchor, succeeds by application of the monofunctional core building block **26**. This core was recently introduced by our group²⁹ and carries one protected carboxylic acid and three terminal ethyne functions, which are needed for Diels–Alder reaction during the dendritic growth. As a result of the [4+2] cycloaddition mechanism during the formation of **26**, this product exists in two chromatographically inseparable regioisomers (**26a** and **26b**).²⁹

In the synthesis of the monofunctional first-generation dendrimer **27**, the asymmetrically substituted core molecule **26** (the product of both isomers) was reacted with the cyclopentadienone branching agent **3** (Scheme 6). After removal of the

solvent, column chromatography with petroleum ether/CH₂Cl₂ (1/1) gave the mixture of **27a** and **27b** in 52% yield. Separation of these two isomers by column chromatography was not possible.

The presence of the regioisomers was verified by ¹H NMR (see Supporting Information). As the polar esters of the two isomers are localized in substantially different environments, the protons of the methoxy groups appear as two separate singlets at 3.64 and 3.63 ppm. The ratio of **27a**:**27b**, calculated from the intensities of these peaks, is about 1:1.

Visualization and Simulation. The structures of the three dendrimers **4**, **5**, and **6** (Figure 5) have been optimized by applying the MM+ force field and the Conjugate Gradient algorithm implemented in the HyperChem 6.0 program package.³⁰ Although all the dendrimers were built around the same core molecule, the two types of dendrimers have different appearances. Whereas the β -substituted dendrimers **5** and **6** show an overall tetrahedral structure, the α -substituted dendrimer **4** has a dense “pancake-like” shape with no large cavities. The calculated diameters of **5** and **6** are larger than those of **4** and the corresponding parent polyphenylene dendrimers, which are built up from core molecule **24** and branching agent **1** (see Table 1). The diameter of the second-generation dendrimer **6** is about 7 nm larger than that of the second generation of the parent polyphenylene dendrimer²² and about 2.5 nm larger than that

(30) The hypersurfaces of the dendrimer branches were first calculated separately by using the MM+ force field method and the “Fletcher–Reeves” algorithm until a global minimum was evaluated. In the next step, they were attached to the separately minimized core molecule, and the geometry of the complete molecule was calculated again with the MM+ force field and the “Fletcher–Reeves” algorithm. Because the hypersurfaces generally obtained for more complex dendrimers were fairly flat, the three-dimensional structures presented here are one of several possible local minima. However, these structures were found to be sufficient to evaluate the dimension of the molecules.

(29) Mihov, G.; Scheppelmann, I.; Müllen, K. *J. Org. Chem.* **2004**, *69*, 8029–8037.

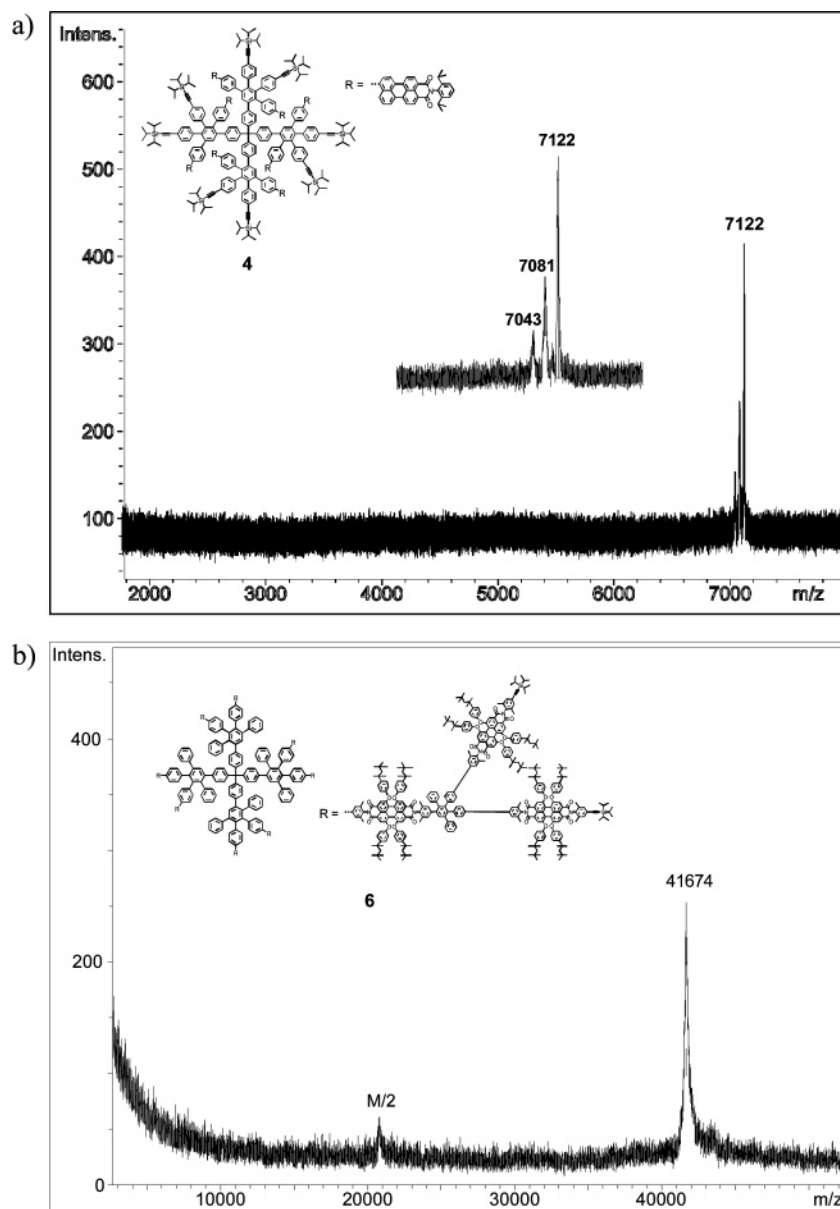


Figure 4. (a) MALDI-TOF mass spectrum of the first-generation dendrimer **4** (m/z 7122 $[M]^+$, calcd for **4** m/z 7121.78; dithranol matrix, reflector mode). (b) MALDI-TOF mass spectrum of second-generation dendrimer **6** in the presence of sodium triflate (m/z 41 715 $[M]^+$, calcd for **6** m/z 41 705; dithranol matrix, linear mode).

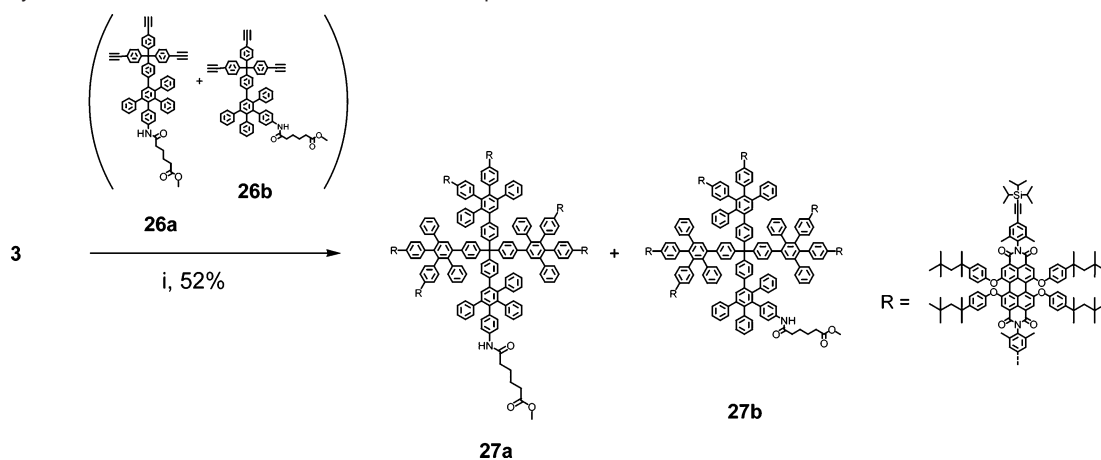
of the second generation of the previously presented “extended” dendrimer built from branching unit **2**.¹⁹ Calculations of the theoretical dendrimer density³¹ (Table 1) show significantly lower densities for the β -substituted dendrimers **5** and **6** than for **4** and the parent polyphenylene dendrimers.¹⁹ This suggests much higher porosities. Indeed, large cavities can be seen in the calculated structures. In selected cases of polyphenylene dendrimers, we have already verified the porosity by the uptake of guest molecules as measured by using an ultramicro balance.³² Due to the small diameter and the compact shape of **4**, several chromophores within this multichromophore are close together; distances between the “midpoints”³³ of the two

chromophores are less than 9 Å, making chromophore–chromophore interactions very likely (see the following section). The distances between chromophores within dendrimers **5** and **6** are larger. The smallest distance is that between the two chromophores within the same repeat unit. Here, the two PDI chromophores are almost face-to-face, and the distance between the “midpoints”³³ of the chromophores is larger than 14 Å.

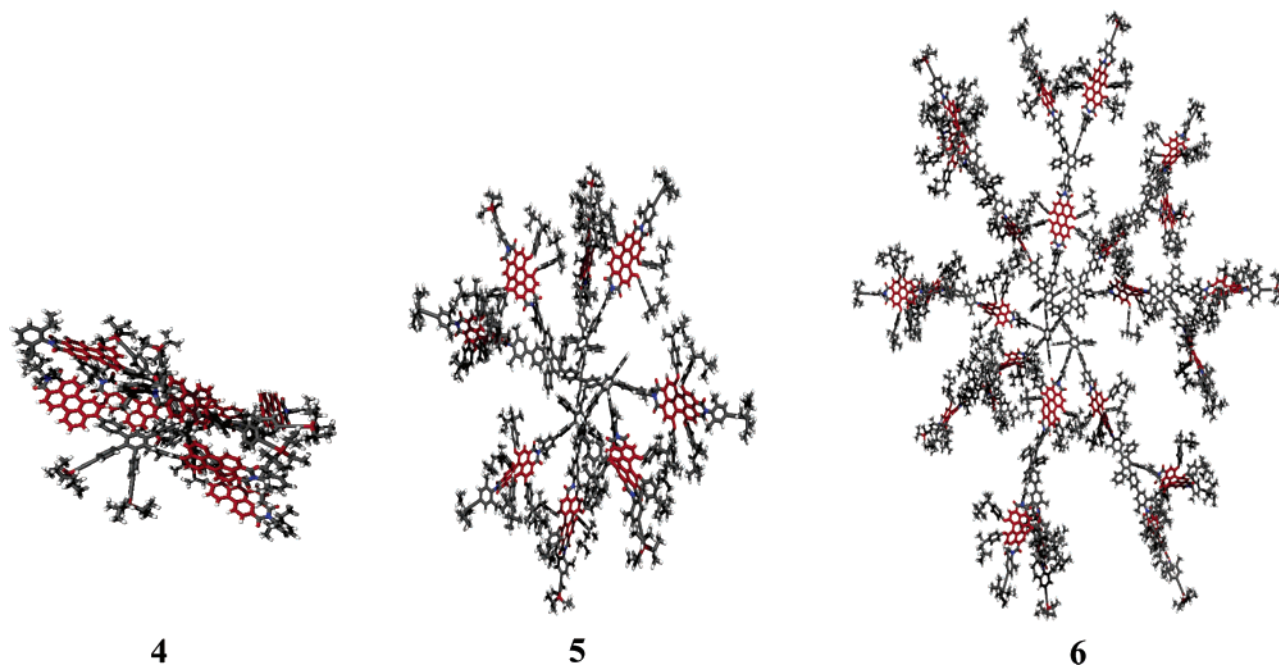
We showed for many examples that the results of molecular dynamics simulations provide a good first approximation of the three-dimensional structures of polyphenylene dendrimers. The results of these simulations are supported by experimental data such as fluorescence correlation spectroscopy (FCS),³⁴ dynamic light scattering (DLS),^{19,34} transmission electron microscopy (TEM),^{19,22} and atomic force microscopy (AFM).^{16,35} However,

(31) The dendrimer densities were calculated by dividing the molecular mass by the volume determined from the radius given by the molecular mechanics calculation.
 (32) Schlupp, M.; Weil, T.; Berresheim, A. J.; Wiesler, U. M.; Bargon, J.; Müllen, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4011–4015.
 (33) In this calculation, the center of gravity of the aromatic perylene system was chosen as the “midpoint” of the chromophore.

(34) Minard-Basquin, C.; Weil, T.; Hohner, A.; Rädler, J. O.; Müllen, K. *J. Am. Chem. Soc.* **2003**, *125*, 5832–5838.
 (35) Shifrina, Z. B.; Rajadurai, M. S.; Firsova, N. V.; Bronstein, L. M.; Huang, X. L.; Rusanov, A. L.; Müllen, K. *Macromolecules* **2005**, *38*, 9920–9932.

Scheme 6. Synthesis of the Ester-Functionalized Multichromophoric Dendrimer **27**^a

^a Reagents and conditions: (i) ester-functionalized core **26**, diphenyl ether, 170 °C, 5 d, 52%.

**Figure 5.** Calculated (MM+) 3D structures of first-generation dendrimer **4**, first-generation dendrimer **5**, and second-generation dendrimer **6**.**Table 1.** Molecular Mass, Theoretical Diameter, and Fluorescence Quantum Yields of **10**, **20**, **27**, **4**, **5**, and **6**

compd	molecular formula	no. of dyes	extinction coefficient ^a [L/(mol·cm)]	molecular mass [g/mol]	FD/MALDI-TOF MS ^b [g/mol]	SEC M _p (PS) ^c [g/mol]	SEC PD	theor radius ^d [nm]	theor dendrimer density ^e [g/mL]	Φ _f ^f
10	C ₃₄ H ₂₆ BrNO ₂	1	35 320	560						0.94
20	C ₁₀₇ H ₁₂₅ BrN ₂ O ₈ Si	1	45 970	1 675	1 676					0.98
27	C ₇₉₄ H ₈₅₅ N ₁₃ O ₅₁ Si ₆	6	201 600	11 565	11 588 (Na)					0.97
4	C ₅₀₅ H ₄₆₀ N ₈ O ₁₆ Si ₈	8	282 900	7 122	7 122			2.1	0.30	0.95
5	C ₁₀₀₁ H ₁₀₉₂ N ₁₆ O ₆₄ Si ₈	8	275 400	14 596	14 619 (Na)			3.2	0.18	0.96
6	C ₂₈₆₅ H ₃₀₇₆ N ₄₈ O ₁₉₂ Si ₁₆	24	1 090 000	41 705	41 674 (Na)	33633	1.04	6.7	0.09	0.95

^a Extinction coefficients were measured in CHCl₃. The extinction coefficient of **10** is known³⁶ and was measured in CH₂Cl₂. ^b All MALDI-TOF mass spectra were acquired by irradiating the 1:250 analyte/matrix mixture with a nitrogen laser (337 nm) using dithranol as matrix and, if specified, sodium trifluoroacetate salt as cationization agent. ^c SEC was performed at room temperature in THF using SEC columns with 500, 10⁴, and 10⁶ Å porosities and calibrated against narrowly disperse, linear polystyrene (PS) standards. ^d Theoretical radii were determined by using MM+ molecular mechanics calculations.³⁰ ^e The dendrimer densities were calculated by dividing the molecular mass by the volume determined by the radius given by the molecular mechanics calculation. ^f Fluorescence quantum yields were measured in chloroform by excitation at 540 nm with cresyl violet (in MeOH) as the reference chromophore.

to obtain insight into the dynamic behavior, a molecular dynamics conformational search is necessary, which is still under investigation.

Optical Characterization. The UV/vis absorption spectra of all dendrimers exhibit two components: an absorption between 400 and 650 nm due to the chromophores and one at much shorter wavelength arising from the dendritic framework, which consists of strongly twisted polyphenylene units. In order

(36) Geerts, Y.; Quante, H.; Platz, H.; Mahrt, R.; Hopmeier, M.; Böhm, A.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 2357–2369.

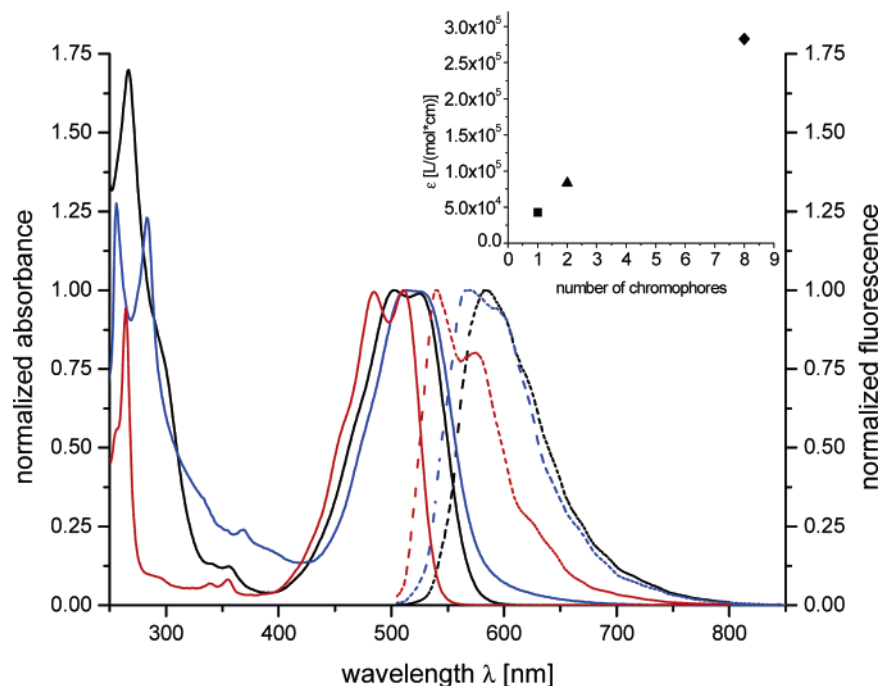


Figure 6. Normalized UV/vis (solid lines) and fluorescence spectra (dashed lines) of PMI **10** (red), dye-functionalized cyclopentadienone **13** (blue), and first-generation dendrimer **4** (black). Inset: Extinction coefficient of PMI chromophore **10** (■), branching agent **13** (▲), and first-generation dendrimer **4** (◆).

to determine the influence of the spatial arrangement of the chromophores within the dendrimers, the absorption and emission spectra of the dendrimers were compared with those of individual dyes.

In the case of the precursors to dendrimer **4**, substitution of the bromine atom of **10** with an aryl group (to give cyclopentadienone **13**) results in a red-shift of both the absorption and emission spectra of $\Delta\lambda_{\text{max}} = 23$ nm (Figure 6) and a loss of the fine structure of both spectra. Formation of the dendrimer **4** results in a small hypsochromic shift of the absorption maxima but a bathochromic shift of the emission maximum. In the emission spectra of **4**, nearly no fine structure is detectable. The loss of the fine structure and the bathochromic shift of the fluorescence maxima indicate interaction between neighboring chromophores. This was also suggested by the molecular mechanics calculations (see above). Due to the small distances between the chromophores in **4** (~ 0.9 Å), excimer formation becomes more likely. However, a direct correlation exists between the number of chromophores and the extinction coefficients at the absorption maximum (Figure 7, inset), and the dendrimer **4** shows a fluorescence quantum yield close to unity (see Table 1).

For dendrimers **5** and **6** (with the chromophores in the backbone), the absorption spectra show spectra comparable to that of the monomeric dye **20** (Figure 7). The emission spectra of the first-generation dendrimer **5** and the monomeric dye **20** are also nearly identical. The fluorescence maximum for both molecules is located at 628 nm. The fluorescence band of the second-generation dendrimer **6** is hypsochromically shifted, with an emission maximum at 623 nm. The retention of the fine structures for both the absorbance and the emission spectra indicates the absence of strong interactions of neighboring chromophores within the dendrimers **5** and **6**. The fluorescence quantum yields of **20** and **5** and **6** are nearly unity (Table 1). As in dendrimer **4**, a direct correlation exists between the

number of chromophores and the extinction coefficients at the absorption maximum (Figure 7, inset). Dendrimer **6**, with 24 chromophores, exhibits an extinction coefficient of $1\,090\,000$ $\text{M}^{-1} \text{cm}^{-1}$ and possesses almost the same absorption per chromophore as an isolated chromophore.

The absorption and emission spectra of the monofunctional first-generation dendrimer **27** (Figure 8) show signal patterns similar to those of the spectra of the monomeric chromophore **20** and the first-generation dendrimer with eight PDI chromophores, **5**. Compared to these latter spectra, the emission spectrum of **27** is slightly hypsochromically shifted. The fluorescence quantum yield of **27** is 0.97 (Table 1) and thus remains as high as those of the chromophore **20** and the first-generation dendrimer **5**. No quenching effect, with its associated reduction of the fluorescence quantum yield, is detected, and the fluorescence intensity of the dendrimer is 6 times higher than that of the single PDI dye **20**.

Conclusion

We have presented new ways to create multichromophoric nanomaterials that possess a large number of chromophores in a confined volume. In this process, peryleneimide chromophores were inserted into the scaffold of shape-persistent polyphenylene dendrimers **4**, **5**, and **6** using two novel tetraphenylcyclopentadienone branching agents, **13** and **3**. By linking the chromophores at different positions of the tetraphenylcyclopentadienone branching agent, dendrimers with diverse topologies were obtained. Thus, connecting the chromophores at the α -position of the tetraphenylcyclopentadienone branching agent **13** gave a densely packed dendrimer, **4**, in which the chromophores are in close proximity. Loss of the fine structure of the absorption and emission spectra indicates chromophore–chromophore interaction. In contrast, linking chromophores at the β -position of the branching unit **3** led to the drastically enlarged dendrimers **5** and **6**, which are distinguished by

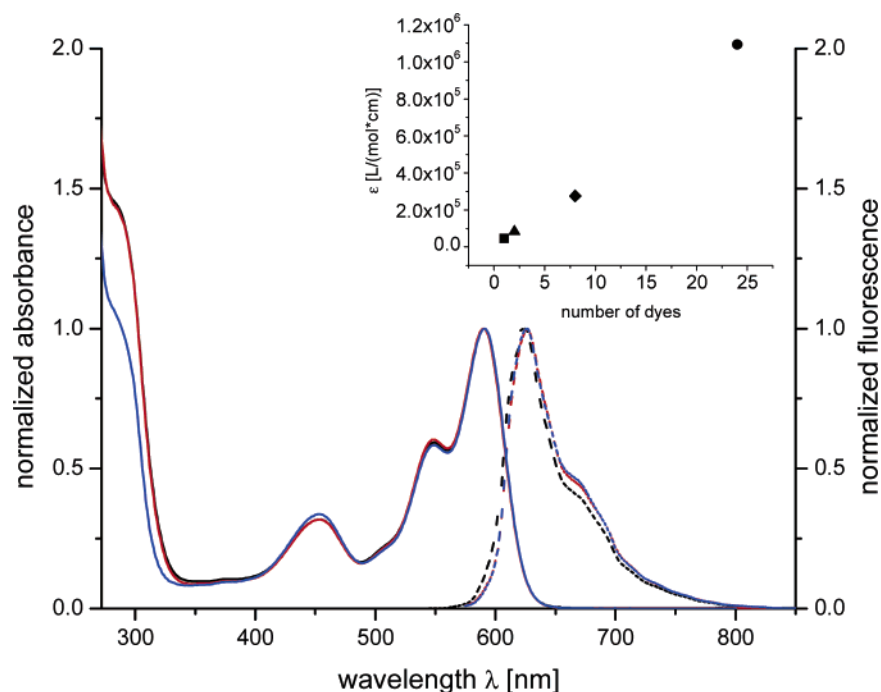


Figure 7. Normalized UV/vis (solid lines) and fluorescence spectra (dashed lines) of PDI **20** (blue), first-generation dendrimer **5** (red), and second-generation dendrimer **6** (black). Inset: Extinction coefficient of PDI chromophore **20** (■), branching agent **3** (▲), first-generation dendrimer **5** (◆), and second-generation dendrimer **6** (●).

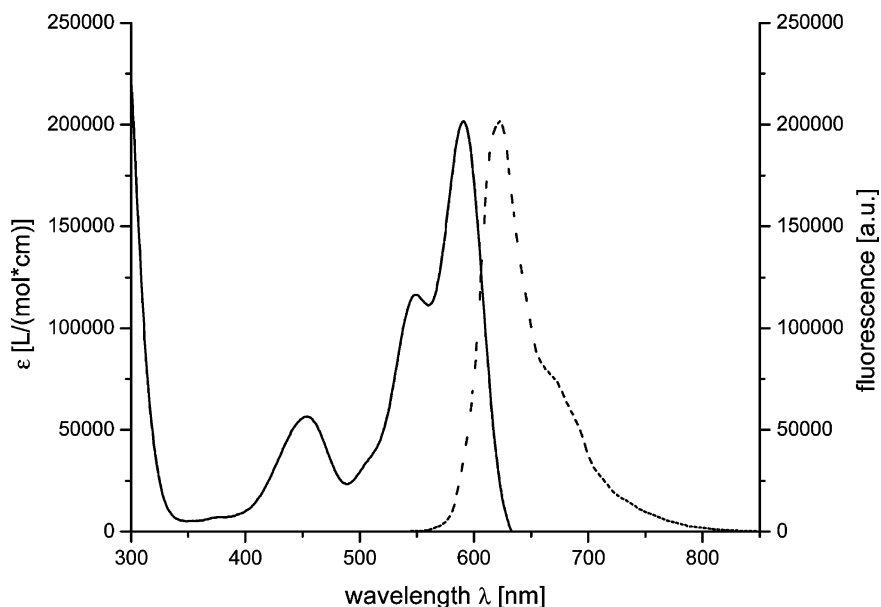


Figure 8. Absorption (solid line) and emission spectrum (dashed line) of the monofunctional multichromophore **27** in chloroform (excitation at 540 nm).

increased interchromophore distances. Thus, both dendrimers show no loss of the fine structure of the absorption and emission spectra compared to the single dye **20**.

All dendrimers possess fluorescence quantum yields near unity. Due to the high photochemical stability of the chromophore units and their incorporation into well-defined positions within the dendrimers, the dendritic multichromophores reported herein can be used for single-molecule spectroscopy, leading to a better insight into interactions between chromophores in close proximity. In addition, peryleneimide-functionalized dendrimers have high potential as single-photon sources, as several single-molecule studies have already shown.^{15,37}

By using the core molecule **26**, it was possible to build up the first-generation dendrimer **27**, bearing six PDI chromophores and one aliphatic ester. The ester represents a potential anchor group which could potentially be attached to various substrates, such as surfaces, polymers, or biologically active moieties. The high extinction coefficient and a fluorescence quantum yield near unity make it an attractive candidate for use as a fluorescence label.

(37) (a) Vosch, T.; Cotlet, M.; Hofkens, J.; Van der Biest, K.; Lor, M.; Weston, K.; Tinnefeld, P.; Sauer, M.; Latterini, L.; Müllen, K.; De Schryver, F. C. *J. Phys. Chem. A* **2003**, *107*, 6920–6931. (b) Tinnefeld, P.; Weston, K. D.; Vosch, T.; Cotlet, M.; Weil, T.; Hofkens, J.; Müllen, K.; De Schryver, F. C.; Sauer, M. *J. Am. Chem. Soc.* **2002**, *124*, 14310–14311.

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Supporting Information Available: Experimental section and ^1H NMR spectra of **4**, **5**, **6**, **20**, and **27**. This material is available free of charge via the Internet at <http://pups.acs.org>.

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