Polyphenylene Dendrimers with Perylene Diimide as a Luminescent Core

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Abstract: A novel synthesis is presented of a fourfold ethynyl-substituted perylene diimide dye **4**, which acts as a core molecule for the buildup of polyphenylene dendrimers. Around the luminescent core **4**, a first-generation (**5**), a second-generation (**6**), and a third-generation (**7**) polyphenylene dendritic environment consisting of pentaphenylbenzene building blocks are constructed. The dendrimers **5** and **6** are synthesized by an exclusively divergent route, whereas for **7**, a combination of a divergent and convergent approaches is applied. Absorption and emission spectra of **5**–**7** in different solvents and in a film have been measured and compared to a nondendronized model compound **13**. In solution, the internal chromophore is scarcely influenced by the dendritic scaffold; however, in the solid state, aggregation of the perylene diimide is prevented very effectively by the four rigid dendrons. Additionally, fluorescence quantum yields in solution have been determined for **5**–**7** and **13**; they decrease as the number of generation increases.

Keywords: aggregation · cycloaddition · dendrimers · dyes/pigments · perylenes

Introduction

In recent years, the focus of interest in the field of dendrimers has switched from constructing new skeletons and higher generations to the search for new applications. In this context, the functionalization of dendrimers with dyes plays an important role.[1–3] In particular, the covalent incorporation of a chromophore into the center of these cascade molecules has produced new supramolecular systems. Azobenzene connected to a dendritic framework acts as a photoswitch,[4, 5] and central porphyrines within dendrimers are model compounds for heme-containing proteins[6, 7] and molecular antennae.[8] Monosubstituted perylenes connected to phenylacetylene dendrons of different sizes make effective energy funnels.[9]

In this contribution, we present the incorporation of a perylenetetracarboxylic diimide chromophore into the center of a dendrimer. This class of pigments and dyes exhibits outstanding chemical, thermal, and photochemical stability.[10–14] Therefore they are widely used in the fields of paints and lacquers; but they are also key chromophores for high-tech applications, such as photovoltaic cells,[15] optical switches,[16] lasers,[17, 18] and light emitting diodes.[19–21]

As a shape-persistent scaffold we selected polyphenylene dendrimers, which have recently been introduced by our group.[22–25] These dendrimers are made by repetitive Diels–Alder reactions by using an aromatic core bearing at least one ethynyl function and a tetraphenylcyclopentadienone derivative to form pentaphenylbenzene units. In this structural motif, the benzene rings are strongly twisted so that they do not serve as chromophores themselves. The unique features of the highly soluble, three-dimensional polyphenylenes are high thermal (>450 °C) and photochemical stability as well as shape persistence.[26]

Connecting dendrons of different generations to an internal chromphore the size of the resulting nanostructure can be controlled, and the dye is separated from the surrounding medium. As a consequence, aggregation, crystallization, and migration should be suppressed; this would result in a better solubility, better film forming properties, and hindering of the formation of excimers and exciplexes of the internal dye.

The above-mentioned changes in the physical properties of the incorporated dye suggest the use of these nanostructures in the emissive layer of LEDs. This objective has been pursued by Wang et al. and Pillow et al. by the construction of an energy- and electron-transport dendritic layer around small molecule emitters.[27, 28]

Apart from that, the generation of a covalently attached environment around a stable chromophore, which can be considered as a blend on the molecular level, makes these molecules potential candidates for single-molecule spectros-

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0947-6539/01/0722-4844 $ 17.50+.50/0

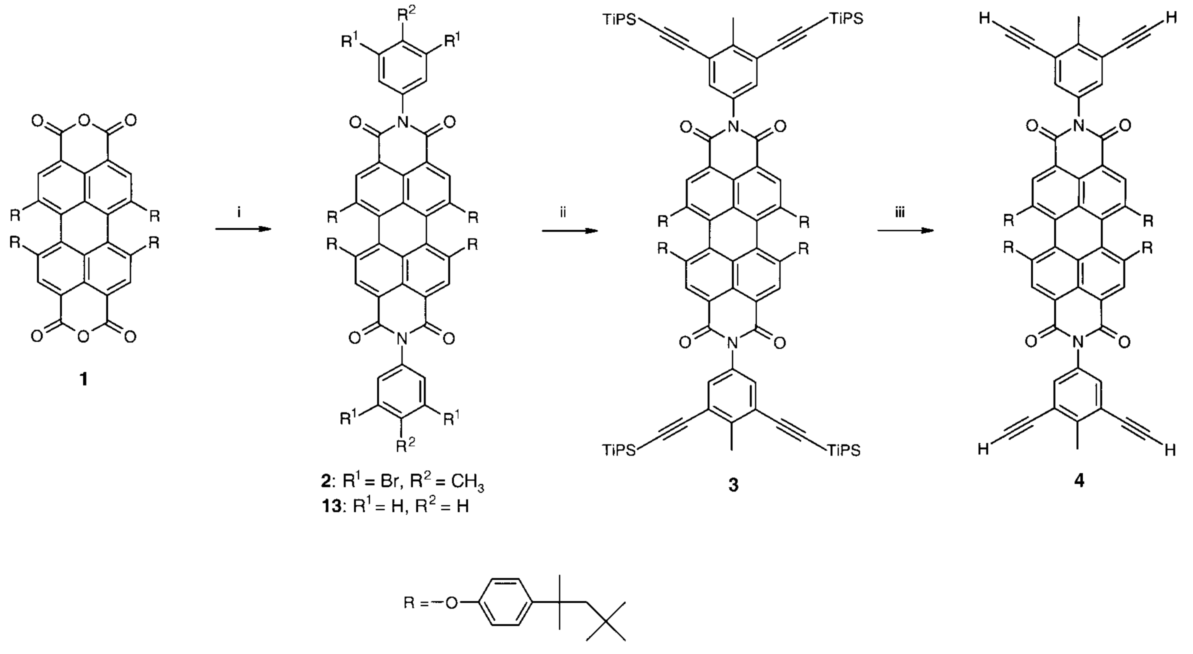
copy (SMS). With this technique it is possible to study the interaction of a fluorophore with the surrounding matrix with a very high spatial resolution and at cryogenic temperatures even with high frequency resolution. Observing only single molecules enables their characterization in complex condensed matter, and heterogeneities in a population of molecules can be identified and related to their molecular environment. In contrast to this technique, conventional methods generally give results averaged over many molecules.[29–31]

In this paper we describe the synthesis of a tetraethynyl-substituted perylenetetracarboxylic diimide derivative **4**, which is required as a core in this dendrimer type. Starting from this luminescent core, the preparation of a first (**5**), second (**6**), and third-generation dendrimer (**7**) is presented. In the last, a divergent and a convergent approach for the dendrimer growth are combined in a very efficient way. To compare the optical properties of these dendritic chromophores with a nondendronized chromophore, the model compound **13** has also been synthesized.

Results and Discussion

Synthesis of the perylene core molecule 4 and the model compound 13: The synthesis of the luminescent core **4** as well as that of the model compound **13** is shown in Scheme 1. It starts from tetrakis(tetramethylbutylphenoxy)-3,4,9,10-perylenetetracarboxylic dianhydride (**1**), which is readily available on the gram scale.[32] This class of perylene derivatives, which carry substituents in the 1, 12 and 6, 7 positions—the so called bay regions, show some remarkable features. By introducing two or four substituents into these bay regions, the two naphthalene units of the planar perylene core are twisted against each other because of the sterical demand of the substituents. This holds true for all perylene derivatives described herein, and can be seen in Figure 3, below. The nonplanarity of compound **1**, as well as the four bulky alkylaryloxy substituents, increases its solubility, which makes subsequent purification by column chromatography much easier. Moreover, the phenoxy substituents contribute to the shielding of the internal chromophore. Imidization of **1** with commercially available 3,5-dibromo-4-methylaniline leads to the perylenetetracarboxylic diimide **2**, which carries four bromo substituents (Scheme 1). In this imidization reaction, the standard procedures for aromatic amines (i.e., high boiling solvents like quinoline or imidazole in the presence of zinc salts at temperatures of about 200–220 °C) known for perylenetetracarboxylic dianhydride lead to a mixture of all possible isomers of debrominated derivatives of **2** due to the addition of an inorganic condensation catalyst such as zinc acetate or zinc chloride.[33, 34] The debromination reaction can be suppressed by using quinoline as a solvent, the more moderate temperature of 160 °C, and a reaction time of six hours. An eightfold excess of 3,5-dibromo-4-methylaniline and P_2O_5 as the catalyst are also used. Similar reaction conditions have been applied by Gregg et al., who have elaborated a straightforward synthesis for perylenetetracarboxylic diimides with enhanced solubilities (pyridine, 100–125 °C).[35] Acidic workup and subsequent purification with column chromatography on silica give the desired product **2** in 89 % yield. To synthesize the unsubstituted model compound **13**, from which no dendrimer growth is possible, the same reaction conditions were used as for the synthesis of **2**. The only difference consisted of the use of aniline as aromatic amine for imidization. Compound **13** was obtained as a purple material in 89 % yield.

By applying a fourfold Hagihara–Sonogashira coupling,[36–38] the four bromo substituents can be replaced by triisopropylsilylacetylene. The reaction is carried out in a

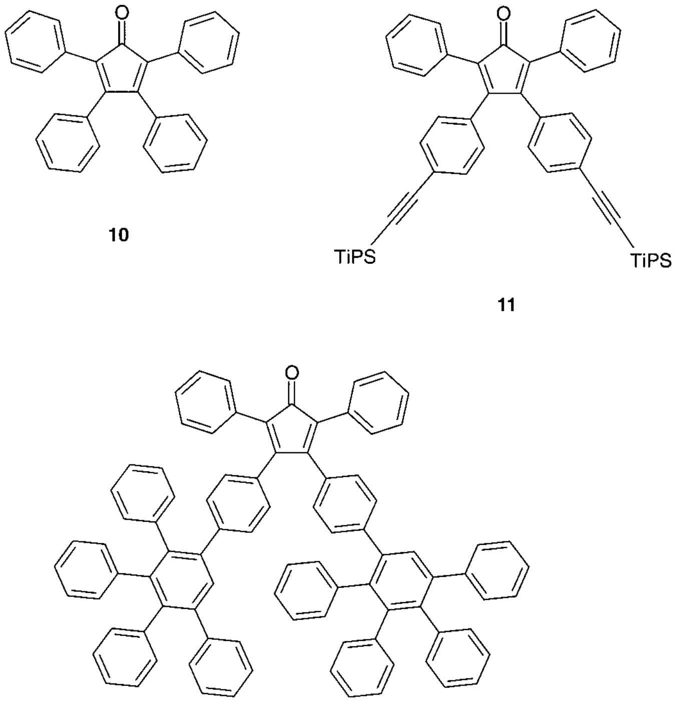


Scheme 1. Synthesis of the core molecule **4** and model compound **13**; i) 6 equiv 3,5-dibromo-4-methylaniline, P_2O_5, quinoline, 160 °C, 85 %; ii) 12 equiv triisopropysilylethyne, $Pd[PPh_3]_4$, CuI, THF/piperidine, 80 °C, 79 %. iii) 4 equiv $n\mathrm{Bu}_4\mathrm{NF}$, THF, RT, 81 %.

mixture of piperidine and THF (1:1) with a catalyst system consisting of tetrakis(triphenylphosphine)palladium and CuI at 65 °C. Traces of a threefold ethynylated debrominated species are detected as a side product, but can easily be separated from the title compound **3** by column chromatography. The desired product is obtained in 81 % yield as a purple solid. The tetraethynyl-substituted luminescent core molecule **4** is obtained after cleavage of the triisopropylsilyl (TiPS) groups with tetrabutylammonium fluoride (Bu_4NF) in THF.

Despite their extended rigid molecular structures, the solubilities of **1**–**4** and **13** in common organic solvents are high (70–80 mg mL^{-1} in chlorinated solvents like dichloromethane or chloroform); this allows full characterization. Additionally, their analysis by ^{1}H NMR spectroscopy is facilitated by the high degree of symmetry in the molecules (see Experimental Section).

Dendrimer formation: The key steps of the dendrimer synthesis consist of an iterative protocol of a Diels–Alder reaction followed by a deprotection step. In this way, an aromatic ethyne reacts with a cyclopentadienone of types **10**–**12** (Scheme 2) that acts as a building unit in the [2+4]cycloaddition. After the extrusion of carbon monoxide, a new benzene ring is formed. This leads to pentaphenylbenzene repeat units. With cyclopentadienone derivatives **10** and **12**, no further dendrimer growth is possible because they do not possess acetylene groups. In this respect cyclopentadienones **10** and **12** act as terminating reagents and produce one or two dendritic layers, respectively. In contrast, 3,4-bis[4′-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (**11**) contains, beside the diene function, two dienophile functions and can thus be regarded as an A_2B-branching reagent. Since the two ethyne groups are protected by the sterically demanding TiPS groups, compound **11** only acts as a diene. After realization of the Diels–Alder reaction, the protecting groups can be removed from the subsequent generation by employing Bu_4NF. Due to the inherent stiffness of the phenyl–phenyl array and the dense packing of the benzene rings, which has been proven by Atomic Force Microscopy measurements,[26] a shape persistent, nanosized (up to 6 nm), all-hydrocarbon dendritic framework is created.



10

11

12

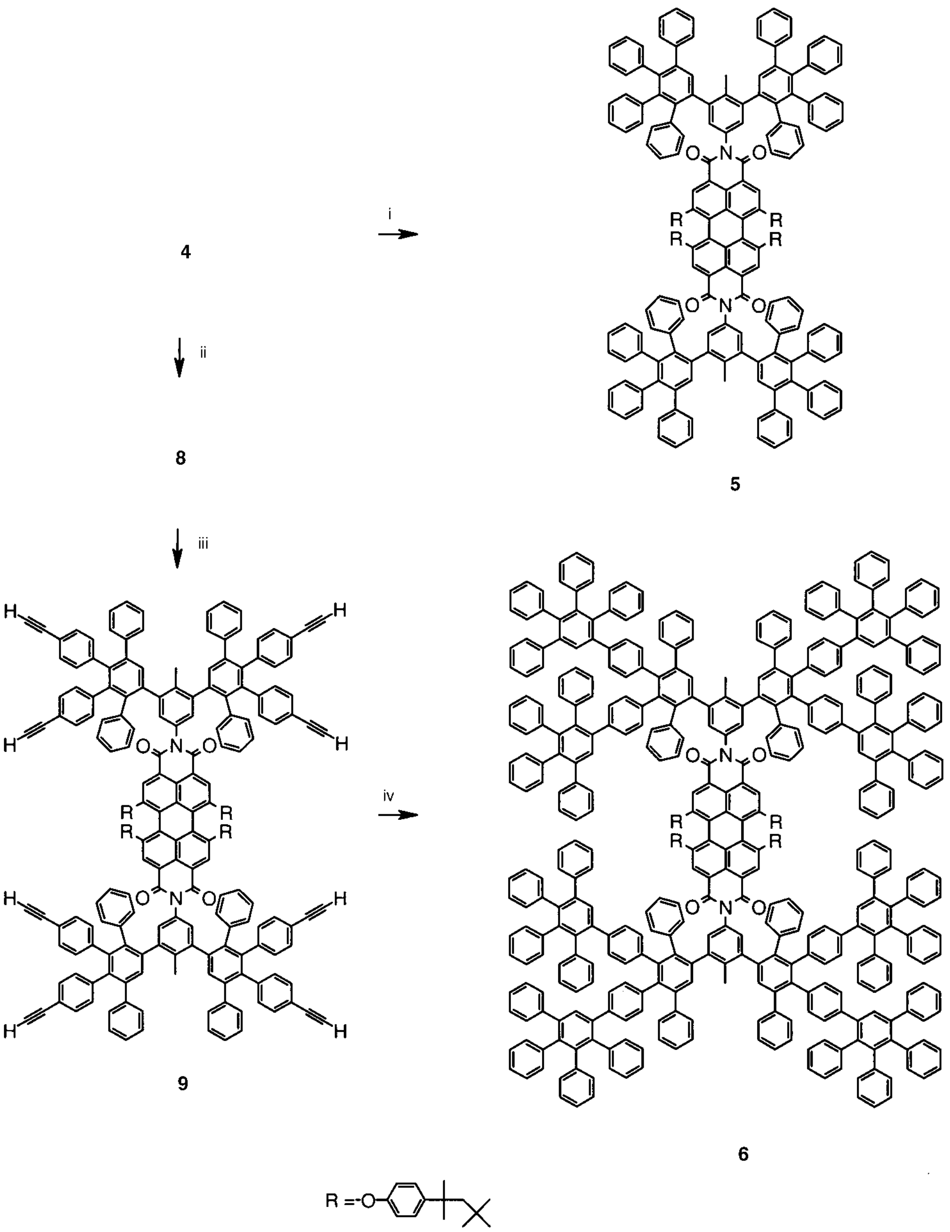
Scheme 2. Building blocks **10**, **11**, and **12** for the dendrimer sythesis.

In the synthesis of the first-generation dendrimer, core molecule **4** reacts with an eightfold excess of cyclopentadienone **10**. The reaction can be carried out either in a mixture of diphenyl ether and tetraethylene glycol at 195 °C or in *o*-xylene at 140 °C. Applying *o*-xylene as a solvent has the advantage that the product is easily obtained by precipitation in methanol after concentration. On the other hand, the use of the solvent mixture necessitates a further purification step, but leads to shorter reaction times. After filtration, the pure product **5** is obtained as a purple powder.

For the buildup of the second-generation dendrimer, the A_2B-building unit **11** and the terminating reagent **10** have to be employed. The Diels–Alder reaction of the core **4** with **11** leads to the octakis-TiPS-ethynyl-substituted first-generation dendrimer **8**. Thereafter the same solvents as for the formation of the first generation can be applied. Workup is different in this case; purification by column chromatography is necessary because a portion of the starting material **11** also precipitates from methanol. After an easy deprotection of **8** with Bu_4NF, compound **9** is used for an eightfold addition of **10**; this results in the second-generation dendritic chromophore **6** in a yield of 84 % (Scheme 3). The same reaction conditions as for the formation of the first generation are applied, but with a 20-fold excess of the diene.

In contrast to the formation of the first two generations, the third-generation dendritic chromophore is synthesized by an approach combining divergent and convergent growth. This has the advantage that, due to higher mass differences, in the case of incomplete reaction the product can be better purified. No conversion is observed when building block **12** is employed with the octaethynyl-substituted first-generation dendrimer **9** and *o*-xylene is used as solvent. The use of 20 equivalents of **12** at 195 °C in diphenyl ether/tetraethylene glycol leads, after 7 days' reaction time, to the desired product **7** in 58 % yield (Scheme 4).

The nonfunctionalized dendritic structures **5**, **6**, and **7**, as well as the triisopropylsilyl-protected first-generation dendrimer **8** and the octaethynyl-substituted unprotected first-generation dendrimer **9**, are all highly soluble in common solvents such as dichloromethane, toluene, or tetrahydrofuran. Therefore, characterization is performed by MALDI-TOF mass spectrometry as well as by ^{1}H and ^{13}C NMR spectroscopy. Experimentally determined and calculated *m/z* ratios agree perfectly for all title compounds within the range of accuracy of the instruments. The signals obtained for these macromolecules consist either of only the $[M]^+$ or of the

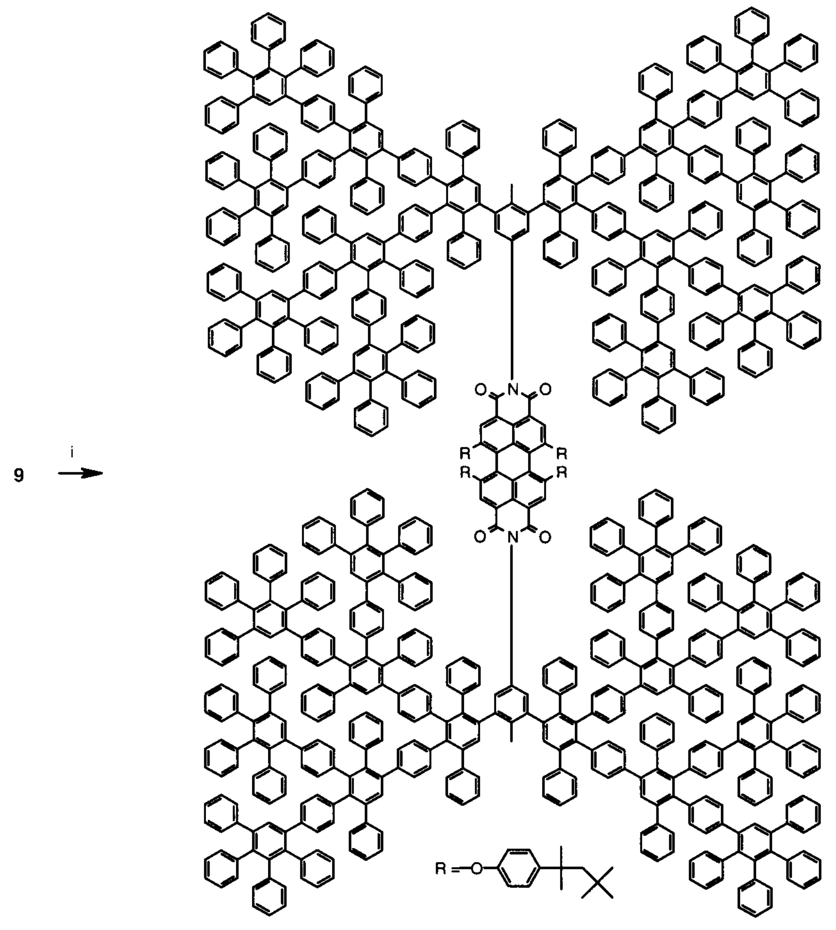


Scheme 3. Synthesis of the first-generation dendrimer **5** and the second-generation **6**; i) 8 equiv **10**, diphenyl ether/tetraethylene glycol, 195 °C, 88 %; ii) 8 equiv **11**, diphenyl ether/tetraethylene glycol, 195 °C, 82 %; iii) 8 equiv nBu$_4$NF, THF, RT, 87 %; iv) 20 equiv **10**, diphenyl ether/tetraethylene glycol, 195 °C, 85 %.

$[M{+}\mathrm{Na}]^+$ peak, and confirm their monodispersity (see Experimental Section). MALDI-TOF-MS measurements, moreover, allow the detection of potential growth imperfections resulting from unreacted ethynyl groups during the Diels–Alder reaction with the building blocks **10**, **11**, and **12**, even for the higher generations. Each unreacted ethynyl group would cause a mass difference of 356, 711, or 1117 g mol^{-1} (for **10**, **11**, or **12**, respectively, less CO) relative to the completely reacted product. Therefore MALDI-TOF-MS is used for both the characterization of the monodisperse dendritic macromolecules described herein and for controlling the dendrimer growth, especially for the synthesis of the third generation **7** with its long reaction time. An example MALDI-TOF spectrum of **7** is given in Figure 1 that clearly demonstrates the monodispersity of this compound.

Characterization of the perylene diimide core dendrimers by ^{1}H NMR spectroscopy is performed in tetrachloroethane because the signal of this solvent does not overlap with any signal of the characterized dendrimers. Well-separated and assignable signals are obtained for the aromatic perylene protons and the aliphatic protons consisting of C**H**$_3$, C**H**$_2$, (C**H**$_3$)$_2$, and (C**H**$_3$)$_3$ groups of the core molecule. For the dendritic environment, only the TiPS groups of **8** and the ethyne protons of **9** are clearly assignable. The aromatic protons of the core and the aromatic protons of the dendrons can not be distinguished due to a strong overlap of the signals. As the number of aromatic signals increases with the number of generations, the peaks become more unstructured in the range of the aromatic region between $\delta = 6.6$ and 7.4. However, the intensity ratios between all separated peaks and the absorptions of the aromatic region agree perfectly with the theoretically expected values. All dendrimers should exhibit a high degree of symmetry, but ^{1}H NMR spectroscopy reveals the formation of conformational isomers. This conclusion can be drawn from the spectra of **5** measured at 333 and 413 K, which are depicted in Figure 2.

At 333 K, the perylene protons and some aromatic protons as well as the CH$_2$ and the (CH$_3$)$_3$ protons show a larger number of signals than expected from the constitution. This outcome is due to dynamic exchange processes because, at 413 K, these signals exhibit coalescence behavior with formation of broadened singlets. Related findings are made for the homologous dendritic structures **6** and **7**, but not, however, for model compound **13**, which is without a dendritic shell. Hindered rotations around the O-phenyl bond and around the N-phenyl bond of the imide moiety are possible dynamic processes that could cause the line broadening, because both rotational interconversions are supposed to change the magnetic sites of the above-mentioned protons. The lack of line broadening for the nondendronized structure **13** suggests that only N-phenyl rotation or, more probably, both rotational processes with a mutual steric hindrance of dendron and alkylphenoxy units



7

Scheme 4. Synthesis of the third-generation dendrimer **7**; i) 20 equiv **12**, diphenyl ether/tetraethylene glycol, 195 °C, 58 %.

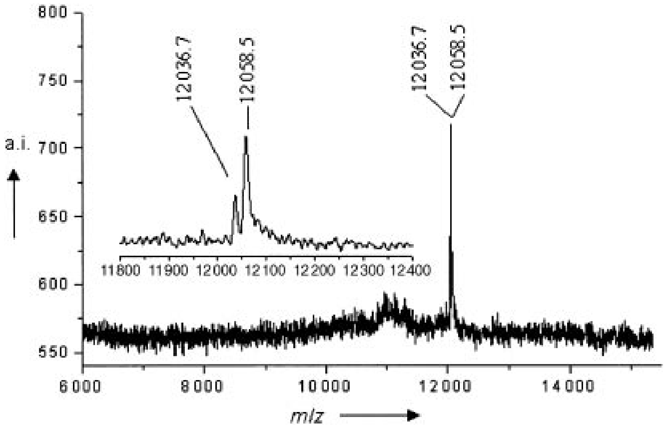


Figure 1. MALDI-TOF mass spectrum of the third-generation dendrimer **7** (12036.7 $[M]^+$, 12058.5 $[M+\mathrm{Na}]^+$).

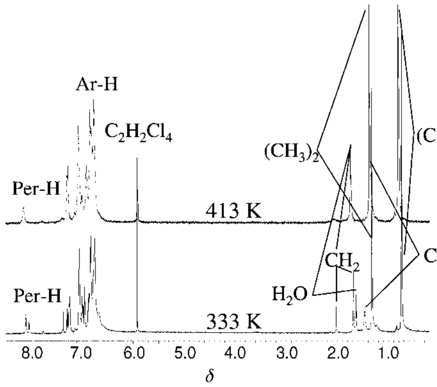


Figure 2. ^{1}H NMR spectra of **5** at 333 and 413 K (500 MHz, $C_2D_2Cl_4$).

are responsible for the observed spectra. Further NMR experiments and calculations of the energy hypersurface of **5** are under way and will be published elsewhere. What is also relevant for these considerations is the fact (see below) that, due to the strong hindrance of neighboring aryloxy groups, the perylene π-system strongly deviates from planarity.

^{13}C NMR resonances of the polyphenylene dendrons can not be assigned completely because of the many overlapping signals, and at high generations some of the resonances of the core carbons are to weak to be detected.

Visualization/simulation: The structures of the perylene core and of the model compound **13** have been optimized by using the semiempirical PM3 method, as implemented in HyperChem 5.1 (Hypercube Inc.). The resulting molecule is strongly twisted in the bay position with a torsion angle of 28° between the two naphthalene units. This calculation stands in very good agreement with the crystal structure of a similar molecule.[39] The dendrons from the first up to the third generation have been minimized separately by using MM2 (MM+) force field geometry optimization. Furthermore, optimization of the whole dendritic system was performed by combining four first-generation dendrons with the perylene core and minimizing the whole system. The conformer with the lowest energy for the first generation **5** shows dendrons arranged nearly perpendicular to the averaged perylene plane (Figure 3). The higher-generation dendronized perylene (second generation **6**) was obtained similarly by connecting an optimized second-generation dendron with the minimized perylene core and subsequent geometry optimization of the entire molecule. To get an idea of the molecular dimensions,

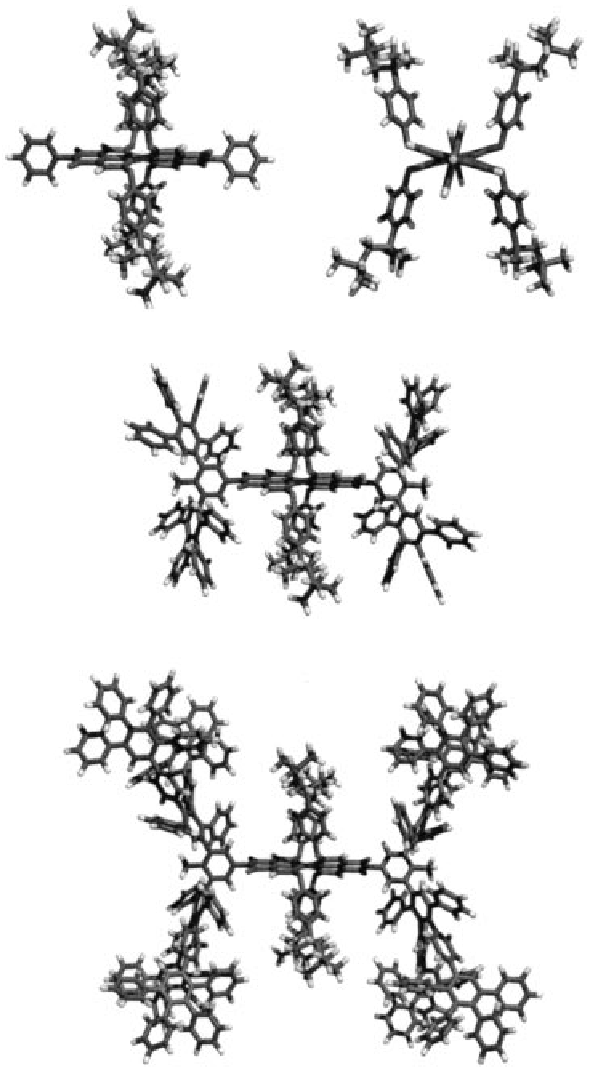


Figure 3. Visualization of model compound **13** (top), G1 dendrimer **5** (middle), and G2 dendrimer **6** (bottom).

the diameter of each generation can be determined from the optimized three-dimensional structures and amounts to 3.1 nm for the first, 4.7 nm for the second, and 6.1 nm for the third generation (whose optimized structure is not shown). These values indicate a successive increase in size on going from one generation to the next higher one. Obviously, the dendrons shield the perylene core so that aggregation of two perylene units should be hindered. This is in agreement with the optical behavior of compounds **5**–**7** and **13** in the solid-state (see following section).

In this case the simulation of the series of dendrimers **5**–**7** is a good first approximation of the three-dimensional structures; however, to obtain insight into the dynamic behavior described above, a molecular dynamics conformational search is necessary, which is still under investigation.

Optical characterization: For the application of the structures **5**–**7** and **13** as light emitting layers in LEDs or as probes for SMS it is necessary to study the influence of the dendritic shell on the optical behavior of the incorporated chromophore. Therefore, UV/Vis absorption and emission spectra of the dendrimers **5**, **6**, and **7** and of the model compound **13** were measured in solution and as a film, and their fluorescence quantum yields were determined.

The UV/Vis absorption spectra of all the dendrimers exhibit two components. One absorption is due to the central chromophore, the other absorption band at much shorter wavelengths is dominated by the dendritic framework, which consists of strongly twisted benzene units. The ratio of the dendron absorption to that of the core increases with the generation number, as can be seen from Figure 4, which shows the UV/Vis spectra of **5** and **6**. The dramatic increase in the relative intensities of the dendron absorption and the perylene diimide absorption with its maxima at 571, 529, and 443 nm can be explained by the different number of benzene rings present in the structures **5** and **6**. The G1 dendrimer **5** contains 26 benzene rings, whereas the G2 dendrimer **6** has 66 benzene rings per perylene chromophore.

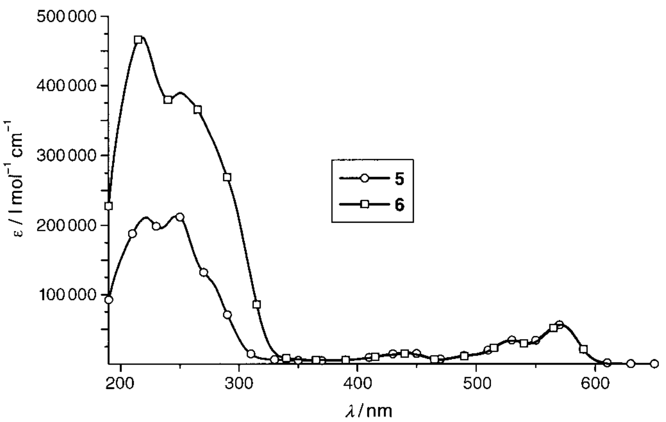


Figure 4. Absorption spectra of **5** and **6** in cyclohexane.

In order to determine the effect of the dendritic shell on the incorporated perylene diimide chromophore, the dendritic structures **5**–**7** can easily be compared with the unsubstituted model compound **13**. The absorption spectrum of perylene diimide **13** in toluene solution, which is structurally similar to the polyphenylene dendrons, exhibits three maxima at 577, 537, and 444 nm (Figure 5a). Between this spectrum and the spectra of the dendritic structures **5**–**7** virtually no difference can be observed.

This changes when chloroform is used as a solvent are shown in Figure 5b. In this more polar medium (as compared with toluene or the polyphenylene dendrons) the absorption spectrum of **13** differs from that of **5**–**7**. The main absorption maximum of **13**, which is located at 590 nm, is bathochromically shifted by 6 nm in contrast to the main absorption maxima at 584 nm of **5**–**7**.

The same trend, nearly identical spectra for the model compound **13** and for the dendrimers in toluene with maxima at 608 nm and a significantly red shifted spectrum of **13** relative to **5**–**7** in chloroform, is also observed for the emission spectra. In chloroform, **13** emits with a maximum at 622 nm while the dendrimers show a maximum emission at 618 nm. Additionally, excitation at the wavelengths of 287, 463, 549, and 589 nm leads to emission spectra of the same

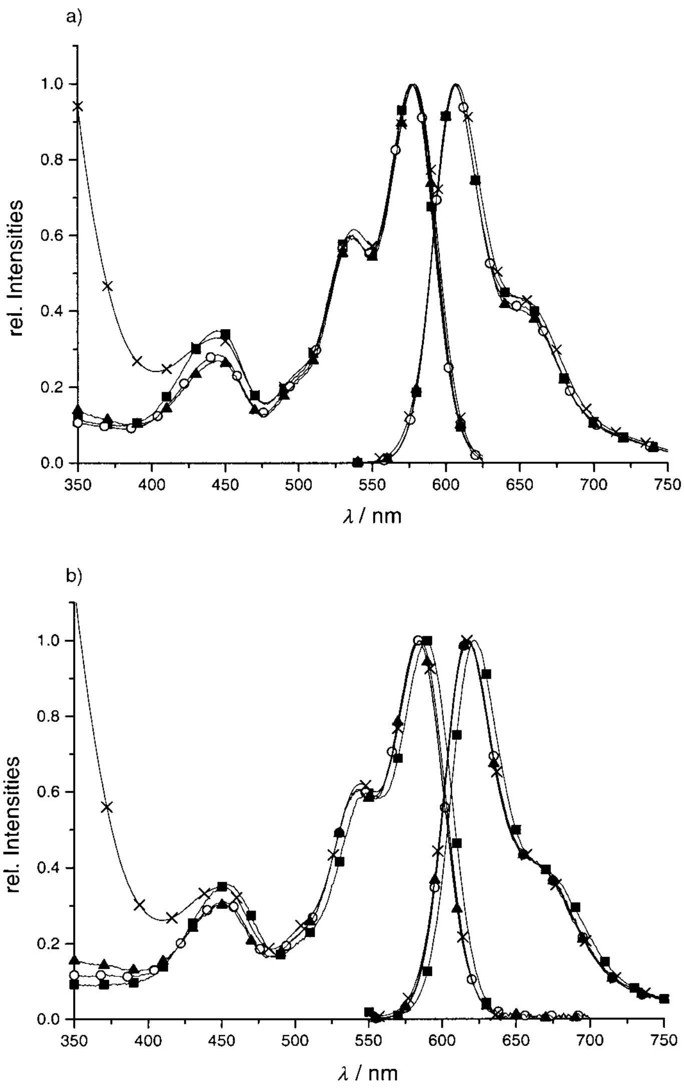


Figure 5. Absorption and emission spectra of **13** (■), **5** (○), **6** (▲), and **7** (×) a) in toluene and b) in chloroform (excitation at 543 nm).

shape as presented in Figure 5. The intensity of the emission is not influenced significantly by the dendritic framework.

Major differences between the model compound and dendrimers occur when considering the solid-state absorption behavior. These spectra have been recorded from films prepared by spin-coating from toluene solutions onto quartz substrates, and are depicted in Figure 6. Remarkably, the transparency of thin films of the dendritic structures **5**–**7** is higher in contrast to the model compound **13**; this is due to crystallization of the nondendronized chromophore. The spectra show typical broadening relative to solution spectra. In this case, the onset of the absorption bands of the model compound **13** is shifted by 20 nm to the red in comparison with the dendrimers **5**–**7**. The absorption maximum of **13** is located at 585 nm, whereas the maxima of G1 **5**, G2 **6**, and G3 **7** occur at 565, 565, and 566 nm, respectively. This shift in the homologous series of model, G1, G2, and G3 as observed for the solid-state absorption behavior is also visible in the fluorescence spectra of these compounds. The spectrum of the model compound **13** is also significantly shifted to the red by 20 nm (compare Figure 6b).

The fluorescence quantum yields of **5**–**7** and **13** were determined by using cresyl violet as a reference chromophore. Upon excitation with a wavelength of 540 nm, the quantum yields for **5**, **6**, **7**, and **13** were found to be 0.83, 0.81, 0.73, and 0.90 in chloroform and 0.95, 0.83, 0.78, and 0.99 in toluene, respectively. The fact that the fluorescence quantum yield decreases with the number of generations suggests that new nonradiative deactivation pathways are opened up by the polyphenelene dendrons. The observed significant red shift in the solid-state absorption and emission spectra of the model compound **13** relative to the spectra of the dendrimers **5**, **6**, and **7** can be ascribed to the avoidance of π-stacking of the perylene core even by the first dendrimer generation. Moreover, the results of the solution absorption and emission measurements suggest that the dendritic substituents dominate the microenvironment of the chromophore.

Conclusion

We have synthesized a fourfold ethynyl-substituted perylene diimide **4** that is a suitable core molecule for the buildup of polyphenylene dendrimers. Around this luminescent core, a first-generation (**5**), a second-generation (**6**), and a third-generation (**7**) polyphenylene dendritic environment consisting of pentaphenylbenzene building blocks have been constructed. A clear advantage of the combination of a divergent and a convergent approach is that few synthetic steps have to be carried out on the dendrimer for the synthesis of the third generation **7**. Only on the core molecule for the synthesis of the octaethynyl G1 **9** do many steps have to be performed, and here structural control is easy because the addition of the A_2B-building block is only fourfold, and additional purification is feasible. This helps to avoid the accumulation of impurities and growth imperfections for the higher generations, as might be the case in an exclusively divergent approach. Cyclopentadienone **12** is a powerful reagent for the synthesis of two polyphenylene dendritic layers and should be applied when very accurate structural control of the product is desired.

The photophysical investigation of the dendritic structures **5**, **6**, and **7** and the nondendronized model compound **13** shows that the four dendrons around the core only have a small influence on the optical behavior of the internal chromophore. On the other hand, the dendritic framework substantially improves the film-forming properties of these materials. The absorption and emission behavior of optical-quality films allow the conclusion that, from the first generation on, no aggregation of the perylene diimide chromophore occurs in the solid state. Accordingly, the optical properties of the internal chromophore, such as high quantum yield of fluorescence, absorption and emission properties, and high photostability, have been maintained to a large extend while processing and aggregation properties have been improved; this might be of especial interest for further applications in LEDs. The photophysical behavior and the formation of isomers, detected by NMR spectroscopy, are challenging starting points for SMS studies, which will be published separately.

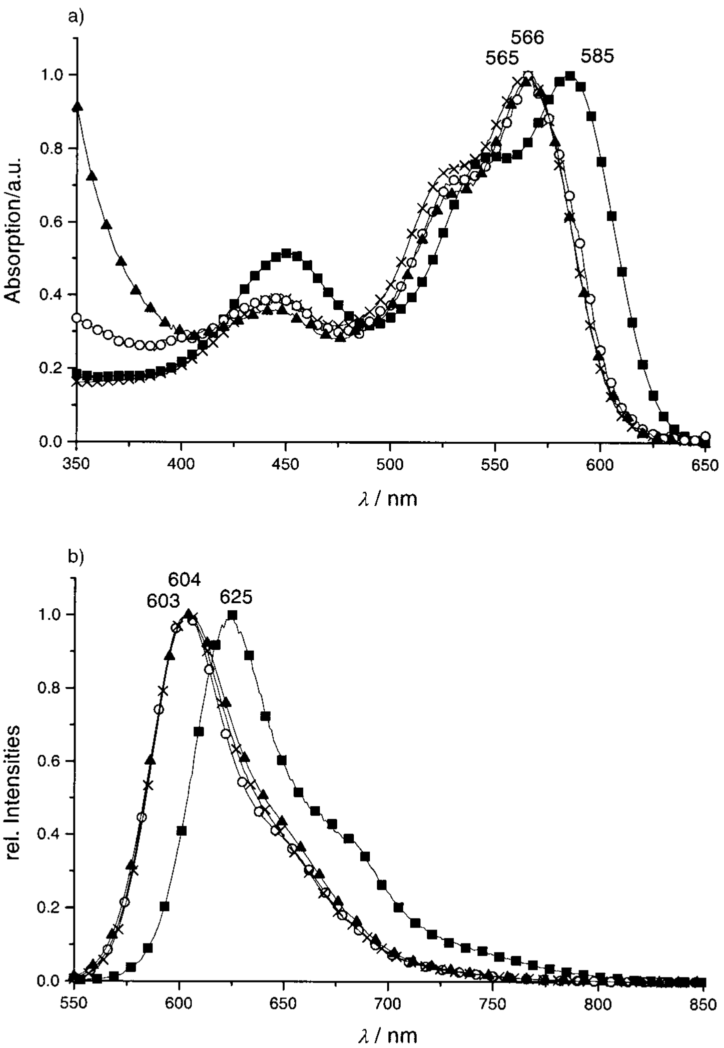


Figure 6. a) Absorption spectra of **13** (■), **5** (×), **6** (○), and **7** (▲) and b) emission spectra of **13** (■), **5** (○), **6** (×), and **7** (▲) in a film prepared from toluene solution (excitation at 543 nm).

Experimental Section

Materials: Tetrahydrofuran (Fluka) was distilled over sodium/benzophenone. Quinoline (Acros), P_2O_5 (Fluka), 3,5-dibromo-4-methylaniline (Aldrich), piperidine (99.5 + %, Aldrich), tetrabutylammmonium fluoride (Fluka), tetrakis(triphenylphosphine)palladium(0) (Strem), triisopropylsilylethyne (Aldrich), copper(I) iodide (Aldrich), 2,3,4,5-tetraphenylcyclopentadienone (Aldrich), diphenyl ether (Aldrich), aniline (Aldrich), and tetraethylene glycol (Aldrich) were used as obtained from the commercial sources. Column chromatography was performed with dichloromethane (chromasolv, Riedel) and light petroleum (p.a., 40–60 °C, Fluka) on silica gel (Geduran Si60, Merck). All the reported yields are isolated yields.

Physical and analytical methods: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX250, a Bruker AC300, and a Bruker AMX500 NMR spectrometer by using the residual proton resonance of the solvent or the carbon signal of the deuterated solvent as the internal standard. Chemical shifts are reported in parts per million. Infrared spectra were obtained on a Nicolet FT-IR320. For ^{13}C j-modulated spin-echo NMR measurements, the abbreviations q and t represent quaternary C atoms and CH_2 as well as CH_3 and CH groups, respectively. FD mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP. MALDI-TOF mass spectra were measured with a Bruker Reflex II with THF and dithranol as matrix (molar ratio dithranol/sample 250:1). The mass peaks with the lowest isotopic mass are reported. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer, fluorescence spectra on a SPEX Fluorolog 2 spectrometer. The elemental analyses were carried out by the Microanalytical Laboratory of the Universität Mainz (Germany).

1,6,7,12-Tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic dianhydride (1): *N,N′*-Dipropyl-1,6,7,12-tetra-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic diimide (7.5 g, 5.8 mmol), propan-2-ol (1 L), H_2O dest. (100 mL), and KOH (150 mL) were stirred for 12 h under reflux under an atmosphere of argon. After cooling down, the reaction mixture was poured into H_2O/HCL_{conc} (2.75 L, 10:1). This mixture was stirred for a further 30 min. After filtration, the precipitate was washed with water and dried. Recrystallization from CH_2Cl_2/MeOH gave **1** as a dark red powder. Yield: 5.74 g, 82 %; m.p. > 178 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 578 (33037), 544 (27803), 444 (16453), 286 nm (46854 $M^{-1}cm^{-1}$); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.07 (s, 4H), 7.30 (d, ^3J(H,H) = 8.8 Hz, 8H), 6.85 (d, ^3J(H,H) = 8.8 Hz, 8H), 1.72 (s, 8H), 1.36 (s, 24H), 0.75 (s, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $CDCl_3$, 20 °C): δ = 159.67, 156.70 (q), 151.89 (q), 147.42 (q), 133.20 (q), 127.94 (t), 120.74 (q), 120.65, 119.68(t), 119.54 (q), 118.55 (q), 57.03 (q), 38.34 (q), 32.35 (q), 31.75 (t), 31.42 (t); IR (KBr): $\tilde{\nu}$ = 2955, 2903, 2873, 1775(C=O), 1745(C=O), 1590, 1504, 1475, 1476, 1411, 1396, 1365, 1337, 1288, 1252, 1223, 1214, 1172, 1137, 1102, 1015, 994, 849, 837 cm^{-1}; MS (FD, 8 kV): m/z (%): 1208.9 (100) $[M]^+$; elemental analysis calc (%) for $C_{80}H_{88}O_{10}$: C 79.44, H 7.33; found C 78.75, H 7.19.

***N,N′*-Bis-(3,5-dibromo-4-methyl)phenyl-1,6,7,12-tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic diimide (2)**: 1,6,7,12-tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic dianhydride (**1**) (5.0 g, 4.13 mmol), 3,5-dibromo-4-methylaniline (6.57 g, 24.78 mmol), and P_2O_5 (500 mg) were dissolved in quinoline (150 mL), and the mixture was stirred for 6 h at 160 °C under an atmosphere of argon. After cooling, the reaction mixture was poured into HCl (1.5 L, 18 %). The precipitate was filtered and washed with water. The crude product was dried and chromatographed on silica with CH_2Cl_2/light petroleum (2:1) as eluent. Compound **2** was obtained as a purple solid. Yield: 5.98 g, 85 %; m.p. > 300 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 593 (38900), 551 (23100), 455 (13400), 288 (35200), 265 nm (53500 $M^{-1}cm^{-1}$); ^{1}H NMR (300 MHz, $[D_2]$ $C_2H_2Cl_4$, 20 °C): δ = 8.08 (s, 4H), 7.38 (s, 4H), 7.21 (d, ^3J(H,H) = 8.5 Hz, 8H), 6.83 (d, ^3J(H,H) = 8.5 Hz, 8H), 2.54 (s, 6H), 1.64 (s, 8H), 1.28 (s, 24H), 0.69 (s, 36H, CH_3); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): δ = 163.50 (q), 156.75 (q), 152.44 (q), 147.41 (q), 138.80 (q), 134.37 (q), 133.26 (q), 132.24 (t), 128.01 (t), 125.49 (q), 122.27 (q), 120.85 (q), 119.94 (t), 119.83 (t), 119.63 (q), 57.25 (q), 38.58 (q), 32.60 (q), 32.16 (t), 31.76 (t), 23.87 (t); IR (KBr): $\tilde{\nu}$ = 3039, 2953, 2900, 1710(C=O), 1678(C=O), 1586, 1553, 1503, 1459, 1404, 1364, 1337, 1318, 1287, 1249, 1214, 1171, 1098, 1013, 977, 879, 846, 802, 749, 580 cm^{-1}; MS (FD, 8 kV): m/z (%): 1703.4 (100) $[M]^+$; elemental analysis calcd (%) for $C_{94}H_{98}Br_4N_2O_8$: C 66.28, H 5.80, N 1.64; found C 66.36, H 5.84, N 1.58.

***N,N′*-Bis-[3,5-bis(triisopropylsilylethynyl)-4-methylphenyl]-1,6,7,12-tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic diimide (3)**: In a Schlenck flask under inert conditions **2** (5.0 g, 2.9 mmol), tetrakis(triphenylphosphine)palladium(0) (0.68 g, 0.59 mmol), and copper(I) iodide (60 mg, 0.32 mmol) were dissolved in a mixture of THF and piperidine (250 mL, 1:1). The reaction vessel was closed with a septum and heated to 70 °C. Then triisopropylsilylethyne (6.4 g, 35 mmol) was added with a syringe while keeping the reaction temperature constant. Afterwards the temperature was increased to 80 °C, and the reaction mixture was allowed to stir for 12 h. After cooling, the solution was diluted with CH_2Cl_2 (250 mL) and poured into HCl (1 L, 18 %). In a seperation funnel the organic phase was separated, dried with $NaSO_4$, and evaporated under reduced pressure. The crude product was chromatographed on silica with light petroleum/CH_2Cl_2 (2:1) as eluent. Compound **3** was obtained as a purple solid. Yield: 4.89 g, 79 %; m.p. = 105 °C; UV/Vis ($CDCl_3$): λ_{max} $(\varepsilon)=$ 583 (36562), 551 (21496), 451 (12142), 266 nm (73300 $M^{-1}cm^{-1}$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=8.08$ (s, 4H), 7.22 (s, 4H), 7.19 (d, $^3J(H,H)=8.5$ Hz, 8H), 6.82 (d, $^3J(H,H)=8.5$ Hz, 8H), 2.59 (s, 6H), 1.63 (s, 8H), 1.27 (s, 24H), 1.03 (s, 84H); 0.68 (s, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=163.75$ (q), 156.66 (q), 152.52 (q), 147.25 (q), 144.17 (q), 133.22 (q), 132.70 (q), 132.30 (t), 127.96 (t), 125.63 (q), 122.46 (q), 120.80 (q), 119.89 (t), 119.68 (q), 116.09 (t), 104.36 (q), 97.14 (q), 57.22 (q), 38.55 (q), 32.58 (q), 32.14 (t), 31.84 (t), 19.63 (t), 19.00 (t), 11.52 (t); IR (KBr): $\tilde{\nu}=2944$, 2865, 2723, 2150 ($C\equiv C$), 2062 ($C\equiv C$), 1711($C=O$), 1679($C=O$), 1586, 1502, 1463, 1407, 1336, 1365, 1338, 1277, 1214, 1173, 1074, 1015, 994, 919, 883, 848, 817, 802, 744, 711, 675, 632, 584, 552, 537 cm^{-1}; MS (FD, 8 kV): m/z (%): 2109.2 (100) $[M]^+$; elemental analysis calcd (%) for $C_{138}H_{182}N_2O_8Si_4$: C 78.58, H 8.70, N 1.33; found C 78.46, H 8.82, N 1.29.

***N,N′*-Bis[-3,5-diethynyl-4-methylphenyl)-1,6,7,12-tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic diimide (4)**: Compound **3** (0.90 g, 0.43 mmol) was dissolved in THF (60 mL), and subsequently tetrabutylammmoniumfluoride (0.45 g, 1.72 mmol) was added. The solution was stirred at room temperature while the conversion was monitored by TLC. Typical reaction times range from 0.5 to 1 h. Before full conversion occured, the reaction was stopped by adding CH_2Cl_2 (150 mL) and distilled H_2O (500 mL). The organic phase was separated, washed with HCl (400 mL, 18 %), and distilled H_2O. Afterwards, the organic phase was dried with $NaSO_4$, and the solvent was evaporated under vacuum. Purification of the product was carried out by column chromatography with light petroleum/CH_2Cl_2 (2:1) as eluent. The desired product **4** was obtained as a purple solid. Yield: 0.51 g, 81 %; m.p. >300 °C; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=591$ (50800), 550 (30200), 455 (17600), 293 nm (41800 $M^{-1}cm^{-1}$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=8.08$ (s, 4H), 7.28 (s, 4H); 7.20 (d, $^3J(H,H)=8.3$ Hz, 8H), 6.83 (d, $^3J(H,H)=8.3$ Hz), 3.30 (s, 4H), 2.55 (s, 6H), 1.64 (s, 8H), 1.28 (s, 24H), 0.69 (s, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=163.60$ (q), 156.71 (q), 152.45 (q), 147.33 (q), 144.51 (q), 136.85 (t), 133.27 (q), 133.22 (t), 132.71 (q), 128.01 (t), 124.16 (q), 122.41 (q), 120.78 (q), 119.96 (t), 119.63 (q), 83.28 (q), 69.23 (t), 57.25 (q), 38.58 (q), 32.60 (q), 32.16 (t), 31.78 (t), 18.06 (t); IR (KBr): $\tilde{\nu}=3303$, 3039, 2951, 2867, 2106($C\equiv CH$), 1710($C=O$), 1676($C=O$), 1586, 1502, 1451, 1406, 1364, 1337, 1284, 1211, 1172, 1129, 1114, 1079, 1014, 988, 887, 871, 834, 816, 800, 749, 647, 614, 586, 554 cm^{-1}; MS (FD, 8 kV): m/z (%): 1483.8 (100) $[M]^+$; elemental analysis calcd (%) for $C_{102}H_{102}N_2O_8$: C 82.56, H 6.93, N 1.89; found C 82.57, H 6.91, N 1.79.

G1 Dendrimer 5: In a Schlenck tube tetraphenylcyclopentadienone, **10** (208 mg, 0.54 mmol) was dissolved in a mixture of diphenyl ether (2 mL) and tetraethylene glycol (2 mL). After being degassed and flushed with argon, the reaction tube was closed with a septum and stirred at 195 °C. Over a period of 1 h, a solution of **4** (100 mg, 0.067 mmol) in diphenyl ether (3 mL) and tetraethylene glycol (2 mL) was injected with a syringe. The resulting solution was then allowed to stir for 8 h. After cooling, the reaction mixture was added dropwise to methanol (700 mL). The product **5** precipitated as a purple solid and was filtered. It was then taken up in CH_2Cl_2 (3 mL) and recrystallized from methanol (700 mL). The pure product was obtained as a purple solid. Yield: 172 mg, 88 %; m.p. = 264 °C; UV/Vis (cyclohexane): λ_{max} $(\varepsilon)=571$ (56100), 530 (34200), 443 (16100), 249 (212900), 222 nm (211200 $M^{-1}cm^{-1}$); ^1H NMR (500 MHz, $C_2D_2Cl_4$, 413 °C): $\delta=8.13$ (s, 4H), 7.35–6.60 (br, 104H); 1.73 (s, 8H); 1.36 (s, 30H); 0.80 (d, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=164.03$ (q), 153.15 (q), 147.11 (q), 142.70 (q), 140.74 (q), 140.48 (q), 140.00 (q), 139.71 (q), 139.52 (q), 131.88 (t), 130.27 (t), 129.91 (t), 127.86 (t), 127.48 (t), 126.91 (t), 126.61 (t), 126.18 (t), 125.55 (t), 125.27 (t), 123.36 (q), 119.82 (t), 119.20 (t), 57.54 (q), 38.66 (q), 32.53 (q), 32.11 (t), 31.66 (t), 23.91 (t); IR (KBr): $\tilde{\nu}=3055$, 3026, 2953, 2901, 1711($C=O$), 1678($C=O$), 1589, 1502, 1442, 1405, 1364, 1338, 1313, 1280, 1212, 1173, 1129, 1073, 1026, 1014, 902, 869, 840, 823, 803, 763, 752, 696, 645, 581, 541 cm^{-1}; MS (FD, 8 kV): m/z (%): 2909.0 (100) $[M]^+$; (FAB 8 kV): m/z (%): 2909.6 (100) $[M]^+$; (MALDI-TOF): m/z (%): 2909.1 (100) $[M]^+$; elemental analysis calcd (%) for $C_{214}H_{182}N_2O_8$: C 88.33, H 6.30, N 0.96; found C 88.03, H 6.26, N 0.92.

Octakistriisopropylsilylethynyl G1 Dendrimer (8): The Diels–Alder reaction was carried out as described for **5**. 3,4-Bis-[4-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone, **11** (402 mg, 0.54 mmol) and **4** (100 mg, 0.067 mmol) are utilized. In contrast to the preparation of **5**, the reaction time was increased to 12 h, and the workup also differs. After precipitation from methanol (700 mL), purification of the product **8** was carried out by column chromatography on silica with light petroleum/CH_2Cl_2 (2:1) as eluent. Compound **8** was obtained as a purple solid. Yield: 241 mg, 82 %; m.p. = 274 °C; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=583$ (48000), 543 (39500), 451 nm (19900 $M^{-1}cm^{-1}$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=8.13$ (s, 4H); 7.29–6.66 (br, 96H); 1.72 (s, 8H); 1.36 (s, 24H); 1.28 (s, 6H); 1.08 (d, $^3J(H,H)=1.9$ Hz, 168H); 0.80 (s, 36H) ; ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=$ 164.02 (q), 156.44 (q), 153.26 (q), 147.21 (q), 142.35 (q), 141.64 (q), 140.88 (q), 140.53 (q), 140.11 (q), 138.79 (q), 133.31 (q), 131.61 (t), 130.82 (t), 130.55 (t), 130.15 (t), 127.81 (t), 127.69 (t), 127.08 (t), 126.48 (t), 125.94 (t), 123.42 (q), 121.19 (q), 120.90 (q), 120.62 (q), 120.05 (t), 119.72 (t), 108.11 (q), 108.02 (q), 90.49 (q), 90.30 (q), 57.57 (q), 38.69 (q), 32.49 (q), 32.07 (t), 31.59 (t), 18.82 (t), 11.83 (t); IR (KBr): $\tilde{\nu}=3054$, 3025, 2953, 2152($C\equiv C$), 1711($C=O$), 1678($C=O$), 1567, 1501, 1461, 1403, 1365, 1337, 1311, 1278, 1214, 1174, 1073, 1015, 994, 882, 834, 752, 698, 675, 577, 546 cm^{-1}; MS (MALDI-TOF): m/z (%): 4353.2 (100) $[M]^+$, 4375.3 (50) $[M+Na]^+$; elemental analysis calcd (%) for $C_{302}H_{342}N_2O_8Si_8$: C 83.33, H 7.92, N 0.64; found C 83.26, H 7.95, N 0.59.

Octaethynyl G1 Dendrimer (9): Compound **3** (100 mg, 0.023 mmol) was dissolved in THF (20 mL), and subsequently tetrabutylammmoniumfluoride (48 mg, 0.183 mmol) was added. The solution was stirred at room temperature while the conversion was monitored by TLC (light petroleum/CH_2Cl_2 2:1). Typical reaction times range from 3 to 4 h. Before full conversion occured, the reaction was stopped by adding CH_2Cl_2 (100 mL) and distilled H_2O (300 mL). The organic phase was separated and washed with HCl (300 mL, 18 %) and distilled H_2O. Afterwards, the organic phase was dried with $NaSO_4$, and the solvent was evaporated under vacuum. Purification of the product was carried out by column chromatography with light petroleum/CH_2Cl_2 (1:1) as eluent. The desired product **9** was obtained as a purple solid. Yield: 62 mg, 87 %; m.p. = 116 °C; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=583$ (48200), 544 (39700), 452 nm (20000 $M^{-1}cm^{-1}$); ^1H NMR (250 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=8.04$ (s, 2H), 7.97 (s, 2H), 7.34–6.58 (br, 96H), 2.97 (s, 4H), 2.94 (s, 4H), 1,94 (s, 2H), 1,64 (s, 6H); 1,28 (s, 30H); 0.69 (s, 36H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100 °C): $\delta=163.08$, 153.09, 145.09, 142.13, 141.88, 141.24, 141.03, 140.74, 139.83, 139.42, 138.73, 137.92, 131.74, 131.62: 131.47, 131.26, 131.08, 131.05, 130.85, 130.35, 130.12, 129.02, 128.75, 128.41, 128.27, 128.16, 127.95, 127.92, 127.82, 127.67, 126.78, 126.68, 126.62, 126.02, 119.86, 119.57, 119.35, 84.51, 77.25, 77.09, 57.38, 38.66, 32.53, 32.08, 31.66, 22.80; IR (KBr): $\tilde{\nu}=2923$, 2864, 2104($C\equiv CH$), 1705($C=O$), 1678($C=O$), 1588, 1502, 1463, 1380, 1285, 1215, 1081, 1049, 1014, 883, 847, 792, 755, 700, 675 cm^{-1}; MS (MALDI-TOF): m/z (%): 3100.3 (100) $[M]^+$, 3122.3 (40) $[M+Na]^+$; elemental analysis calcd (%) for $C_{230}H_{182}N_2O_8$: C 89.06, H 5.91, N 0.90; found C 88.86, H 5.74, N 0.84.

G2 Dendrimer (6): The Diels–Alder reaction was carried out as described for **5** except that the reaction time was increased to 16 h. The tetraphenylcyclopentadienone **10** (156 mg, 0.406 mmol) and **9** (63 mg, 0.0203 mmol) were utilized. Compound **6** was obtained as a purple solid. Yield: 103 mg, 85 %; m.p. = 279 °C; UV/Vis (cyclohexane): λ_{max} $(\varepsilon)=572$ (56000), 530 (33300), 442 (14600), 251 (389600), 217 nm (469600 $M^{-1}cm^{-1}$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=8.01$ (s, 2H), 7.95 (s. 2H), 7.40–6.30 (br, 264H), 1.86 (s, 2H), 1.61 (s, 6H), 1.26 (s, 24H), 1.16 (s, 6H), 0.66 (s, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta=164.11$ (q), 156.47 (q), 152.70 (q), 146.93 (q), 142.13 (q), 141.91 (q), 140.46 (q), 140.28 (q), 139.31 (q), 139.20 (q), 138.70 (q), 138.07 (q), 133.21 (q), 131.79 (t), 131.37 (t), 130.39 (t), 130.22 (t), 128.64 (t), 127.79 (t), 127.06 (t), 126.76 (t), 126.34 (t), 125.65 (t), 125.34 (t), 122.98 (q), 120.31 (q), 119.98 (t), 57.35 (q), 38.55 (q), 32.61 (q), 32.15 (t), 31.81 (t), 18.82 (t), 164.11 (q), 156.47 (q), 152.70 (q), 146.93 (q), 142.13 (q), 141.91 (q), 140.46 (q), 140.28 (q), 139.31 (q), 139.20 (q), 138.70 (q), 138.07 (q), 133.21 (q), 131.79 (t), 131.37 (t), 130.39 (t), 130.22 (t), 128.64 (t), 127.79 (t), 127.06 (t), 126.76 (t), 126.34 (t), 125.65 (t), 125.34 (t), 122.98 (q), 120.31 (q), 119.98 (t), 57.35 (q), 38.55 (q), 32.61 (q), 32.15 (t), 31.81 (t), 18.82 (t); IR (KBr): $\tilde{\nu} = 3054$, 3025, 2953, 1711 (C=O), 1678 (C=O), 1596, 1501, 1441, 1428, 1403, 1365, 1337, 1311, 1278, 1211, 1174, 1073, 1025, 899, 845, 801, 761, 729, 698, 550 cm^{-1}; MS (MALDI-TOF): m/z (%): 5956.1 (100) $[M]^+$; elemental analysis calcd (%) for $C_{454}H_{342}N_2O_8$: C 91.59, H 5.80, N 0.47; found C 91.23, H 5.80, N 0.45.

G3 Dendrimer (7): The Diels–Alder reaction was carried out as described for **5**. G2 cyclopentadienone dendron **12** (220 mg, 0.192 mmol) and **9** (30 mg, 0.0097 mmol) were utilized. In contrast to the preparation of **5**, the reaction time was increased to 7 d and the workup also differed. After being precipitated from methanol (500 mL), the crude product was redissolved in CH_2Cl_2 (3 mL) and precipated again from methanol (500 mL). Subsequent purification consisted of column chromatography on silica first with light petroleum/CH_2Cl_2 (1:1) and then with pure CH_2Cl_2 as eluent. Compound **7** was obtained as a pink solid. Yield: 68 mg, 58%; m.p. >300 °C; UV/Vis (cyclohexane): λ_{max} (ε) = 571 (55900), 530 (33100), 442 (19300), 225 nm (926700 M^{-1} cm^{-1}); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 20 °C): $\delta = 8.09$ (s, 2H); 8.04 (s, 2H); 7,42–6,30 (br, 584H); 1,68 (s, 8H); 1,33 (s, 24H); 1.26 (s,6H); 0,75 (s,36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta = 154.76$ (q), 147.05 (q), 142.27 (q), 142.04 (q), 140.82 (q), 140.65 (q), 140.43 (q), 140.31 (q), 139.52 (q), 132.84 (t), 132.44 (t), 131.82 (t), 131.24 (t), 130.81 (t), 130.20 (t), 130.05 (t), 129.08 (t), 128.83 (t), 128.63 (t), 128.54 (t), 128.23 (t), 127.66 (t), 127.33 (t), 126.94 (t), 126.63 (t), 126.30 (t), 125.65 (t), 125.32 (t), 124.26 (q), 119.18 (t), 32.11 (t), 31.59 (t); IR (KBr): $\tilde{\nu} = 3054$, 3025, 2953, 1711(C=O), 1678(C=O), 1592, 1500, 1442, 1404, 1364, 1313, 1279, 1213, 1174, 1073, 1026, 1012, 900, 870, 843, 823, 799, 755, 713, 688, 664, 581, 560 cm^{-1}; MS (MALDI-TOF): m/z (%): 12036.7 (30) $[\text{M}]^+$, 12058.5 (100) $[M+\text{Na}]^+$; elemental analysis calcd (%) for $C_{934}H_{662}N_2O_8$: C 93.16, H 5.54, N 0.23; found C 92.89, H 5.37, N 0.11.

***N,N′*-diphenyl-1,6,7,12-tetrakis-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]-3,4,9,10-perylenetetracarboxylic diimide** (**13**). The preparation of **13** was analogous to that of **2** except for the amine component aniline. The crude product was chromatographed on silica with CH_2Cl_2 as eluent. Compound **13** was obtained as a purple solid. Yield: 290 mg, 86%; m.p. >300 °C; UV/Vis (cyclohexane): λ_{max} (ε) = 566 (34300), 526 (22900), 443 (12900), 287 nm (39100 M^{-1} cm^{-1}); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 20 °C): $\delta = 8.08$ (s, 4H), 7.44 (m, 6H), 7.20 (d, ^3J(H,H) = 8.5 Hz, 8H), 7.17 (d, ^3J(H,H) = 7.17 Hz, 4H), 6.82 (d, ^{3}J(H,H) = 8.5 Hz, 8H), 1.63 (s, 8H), 1.27 (s, 24H), 0.68 (s, 36H); ^{13}C j-modulated spin-echo NMR (75 MHz, $C_2D_2Cl_4$, 20 °C): $\delta =$ 163.35 (q), 156.16 (q), 152.05 (q), 146.78 (q), 134.90 (q), 132.78 (q), 129.24 (t), 128.62 (t), 128.34 (t), 127.47 (t), 122.18 (q), 120.16 (q), 119.43 (q), 119.25 (t), 119.20 (t), 56.74 (q), 38.08 (q), 32.10 (q), 31.66 (t), 31.27 (t); IR (KBr): $\tilde{\nu} = 3140$, 2952, 2902, 1706 (C=O), 1674 (C=O), 1591, 1503, 1404, 1364, 1340, 1316, 1282, 1213, 1174, 1127,1095, 1015, 957, 908, 877, 835, 803, 740, 691, 582, 551 cm^{-1}; MS (FD, 8 kV): m/z (%): 1359.7 (100) $[M]^+$; elemental analysis calcd (%) for $C_{92}H_{98}N_2O_8$: C 81.26, H 7.26, N 2.06; found C 81.18, H 7.28, N 1.91.

Acknowledgements

J.H. thanks the FWO for a post-doctoral fellowship. T.V. wishes to thank the IWT for a doctoral fellowship. The financial support of Fonds der Chemie, of BASF AG, of the DWTC through IUAP-4–11, of the EU through TMR program SISITOMAS, and of the VW Stiftung is gratefully acknowledged.

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Received: October 23, 2000
Revised: May 25, 2001 [F2815]