

Dendronized Perylenetetracarboxdiimides with Peripheral Triphenylamines for Intramolecular Energy and Electron Transfer

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Abstract: Novel perylene-3,4,9,10-tetracarboxdiimides (PDI) dyes functionalized with polyphenylene dendrimers attached at the bay region are reported. Derivatives of PDI bearing polyphenylene dendrimers up to the second generation, substituted with an increasing number of triphenylamine (TPA)

moieties at the periphery, as well as a related nondendronized model compound were prepared. Intramolecular

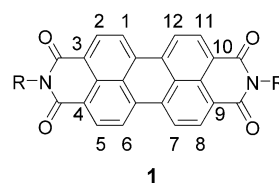
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energy transfer was demonstrated by the observation of PDI emission on excitation of the triphenylamines, and electron transfer was detected by comparing photoluminescence quenching in solvents of different polarity.

Introduction

In recent years, there has been growing interest in understanding the photophysical and photochemical properties of multicomponent dyads containing covalently linked electron donors and acceptors, especially as an approach to artificial photosynthesis.^[1] Incorporation of rigid spacing units into donor-linked acceptor molecular assemblies allows control of the distance and angles between the donor and acceptor sites, which govern the rate and efficiency of long-distance photoinduced electron-transfer and charge-recombination processes, which play important roles in potential applications such as photovoltaic and optoelectronic devices.^[2]

Chromophores based on perylene-3,4,9,10-tetracarboxdiimides (PDI, **1**) and derivatives thereof bearing substituents in the 1,12- and 6,7-positions (the so-called bay regions) are widely used as dyes and pigments in a variety of applications due to their outstanding chemical, thermal, and photochemical stability,^[3] for example, in paints, lacquers, reprographic processes,^[4] fluorescent solar collectors,^[5] optical switches,^[6] and dye lasers.^[7] The high electron mobility^[8] of PDI deriv-



atives was exploited by Friend, Müllen et al.^[9] in the fabrication of high-efficiency organic photovoltaic devices by using a blend of electron-accepting PDI and a hole-accepting hexabenzocoronene. Gregg et al.^[10] also reported solar cells based on a polymer/PDI blend.

To investigate whether the large difference in forward and backward electron-transfer rates in electron-donor/acceptor composites is a molecular or materials property, we explored photoinduced electron and energy transfer in molecular dyads of electron donors covalently linked to PDI (acceptor) through a rigid spacer. Redox-active triphenylamino (TPA) groups, which are widely used as hole-transport (HT) and electron-donor materials, were introduced into the bay region of PDI. Since photoluminescence (PL) self-quenching caused by aggregation,^[11] can influence the investigation of electron transfer from donor to acceptor, it would be beneficial to encapsulate PDI within a “protective” organic matrix, effectively isolating the dye and preventing self-quenching. Recently, we reported PDI derivatives bearing highly soluble, three-dimensional, shape-persistent, thermally stable (>450 °C), and photochemically stable polyphenylene dendrimers (PPD)^[12] on the imide ring, which showed no aggregation in solution and high photoluminescence efficiency.^[13] A polyphenylene dendrimer was therefore selected

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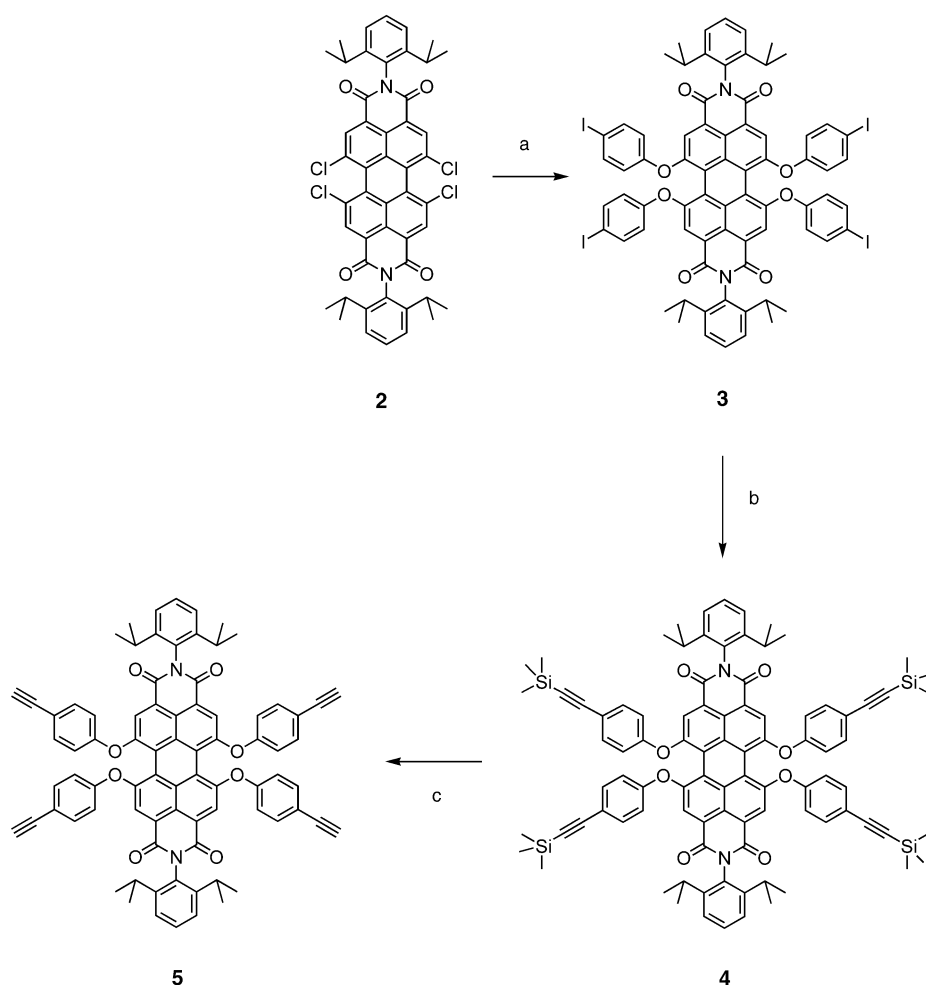
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as spacer and rigid shell, with the hole-transporting TPA moieties located on the periphery of the dendrimers. By using different solvents, it is possible to address the effect of the polarity of the medium on photoinduced charge separation and recombination.

Here we describe the synthesis and characterization of tetrakis(4-ethynylphenoxy)perylene-tetracarboxydiimide (**5**) as core, and tetrakis[4-(diphenylamino)phenoxy]perylene-tetracarboxydiimide (**12**) as a non-dendronized model compound. Starting from this luminescent core, first- and second-generation dendronized TPA-substituted PDI were prepared. We report on their photophysical properties in different solvents, and we demonstrate that both energy- and electron-transfer reactions occur upon photoexcitation of TPA-PPD-PDI by comparing the emission spectra at different excitation wavelengths and photoluminescence quantum yields in different polar solvents. The degree of discrimination between the energy- and electron-transfer processes strongly depends on the polarity of the medium, and we demonstrate complete energy transfer in nonpolar solvents.

Results and Discussion

Synthesis of tetrakis(4-ethynyl-*p*-phenoxy)perylene-tetracarboxydiimide (5**) as the core molecule:** The synthesis of the luminescent core **5** is shown in Scheme 1. It starts from tetrachloroperylene-tetracarboxydiimide **2**, which is readily available on a gram scale.^[14] Phenoxylation of **2** with an excess of iodophenol in 1-methyl-2-pyrrolidone (NMP) gives tetraphenoxypylene-tetracarboxydiimide **3** with four iodo groups. The iodo group was chosen as it is optimal for attachment of an alkynyl group in the next step. The temperature of phenoxylation, however, is important, as deiodination occurs if the reaction temperature is higher than 100 °C; in contrast, the yield decreases below 60 °C. The four iodo substituents were replaced by triisopropylsilyl ethynyl groups by fourfold Hagihara–Sonogashira coupling in high yield.^[15] The reaction was carried out in THF/NEt₃ (3/1) at room temperature with a [PdCl₂(PPh₃)₂]/CuI catalyst system. Base and catalyst are easily removed by column chromatog-

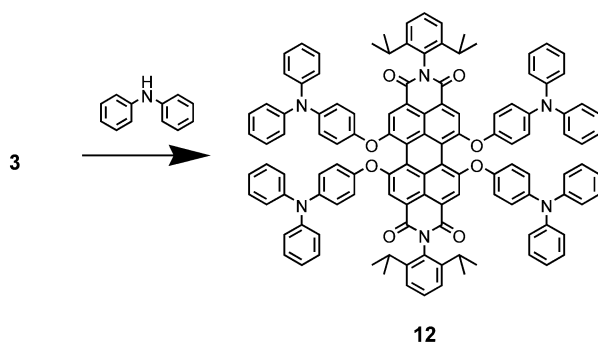


Scheme 1. Synthesis of the core molecule **5**: a) 4-Iodophenol, NMP, K₂CO₃, 80 °C, 15 h, 85 %; b) trimethylsilyl-ethyne, [PdCl₂(PPh₃)₂], CuI, THF/Et₃N, RT, 15 h, 91 %; c) *n*Bu₄NF, THF, RT, 30 min, 85 %.

raphy, and the desired product **4** is obtained in 91 % yield as a red solid. The tetraethynyl-substituted luminescent core molecule **5** was obtained after cleavage of the trimethylsilyl (TMS) groups with Bu₄NF in distilled THF. The high solubilities of **3**, **4**, and **5** in common organic solvents such as dichloromethane allows easy purification by column chromatography and full characterization by standard spectroscopic measurements.

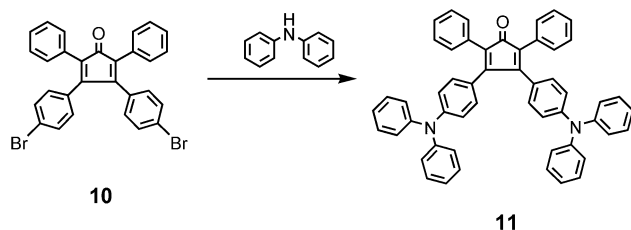
Synthesis of nondendronized model compound **12 and dendrimers **7** and **8**:** The synthesis of model compound 1,6,7,12-tetrakis[4-(diphenylamino)phenoxy]-*N,N'*-(2,6-diisopropylphenyl)-perylene-3,4,9,10-tetracarboxydiimide (**12**) is shown in Scheme 2. The four iodo substituents of **3** are easily replaced by diphenylamino groups in a fourfold Hartwig–Buchwald amination due to their high reactivity.^[16] Quantitative conversion was obtained when the reaction was carried out in a glove box. The yield is significantly lower and a deiodinated byproduct is formed if the reaction is performed outside of the glove box due to the high reactivity of tri-*tert*-butylphosphane.

The most important step of the dendrimer synthesis is the Diels–Alder cycloaddition, in which after extrusion of



Scheme 2. Synthesis of model compound **12**: $[\text{Pd}_2(\text{dba})_3]$, $t\text{Bu}_3\text{P}$, $t\text{BuONa}$, toluene, RT, 1 h, 98 %.

carbon monoxide a new benzene ring is formed and penta-phenylbenzene repeat units are obtained. The Diels–Alder cycloaddition requires an aromatic ethyne and a cyclopentadienone derivative. The synthesis of 3,4-bis[4-(diphenylamino)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (**11**) as functional cyclopentadienone derivative is shown in Scheme 3. It



Scheme 3. Synthesis of building block **11**: $[\text{Pd}_2(\text{dba})_3]$, $t\text{Bu}_3\text{P}$, $t\text{BuONa}$, toluene, RT, 1 h, 91 %.

starts from dibromocyclopentadienone **10**, prepared by basic condensation.^[12a] Cyclopentadienone derivative **11** was then obtained in high yield by Buchwald coupling, as described above for **12**. 3,4-Bis[4-(triisopropylsilylethynyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (**9**) contains two dienophile functions and can be regarded as an A_2B branching reagent, as the sterically demanding triisopropylsilyl (TIPS) groups protect the two ethynyl groups. After completion of the Diels–Alder reaction with **9**, the protecting groups can be removed with Bu_4NF to afford a first-generation dendrimer with eight ethynyl groups as precursor for the second-generation dendrimer. In contrast, if the cyclopentadienone with TPA functional groups **11** is used, triphenylamines can be attached to the dendrimer at the periphery.

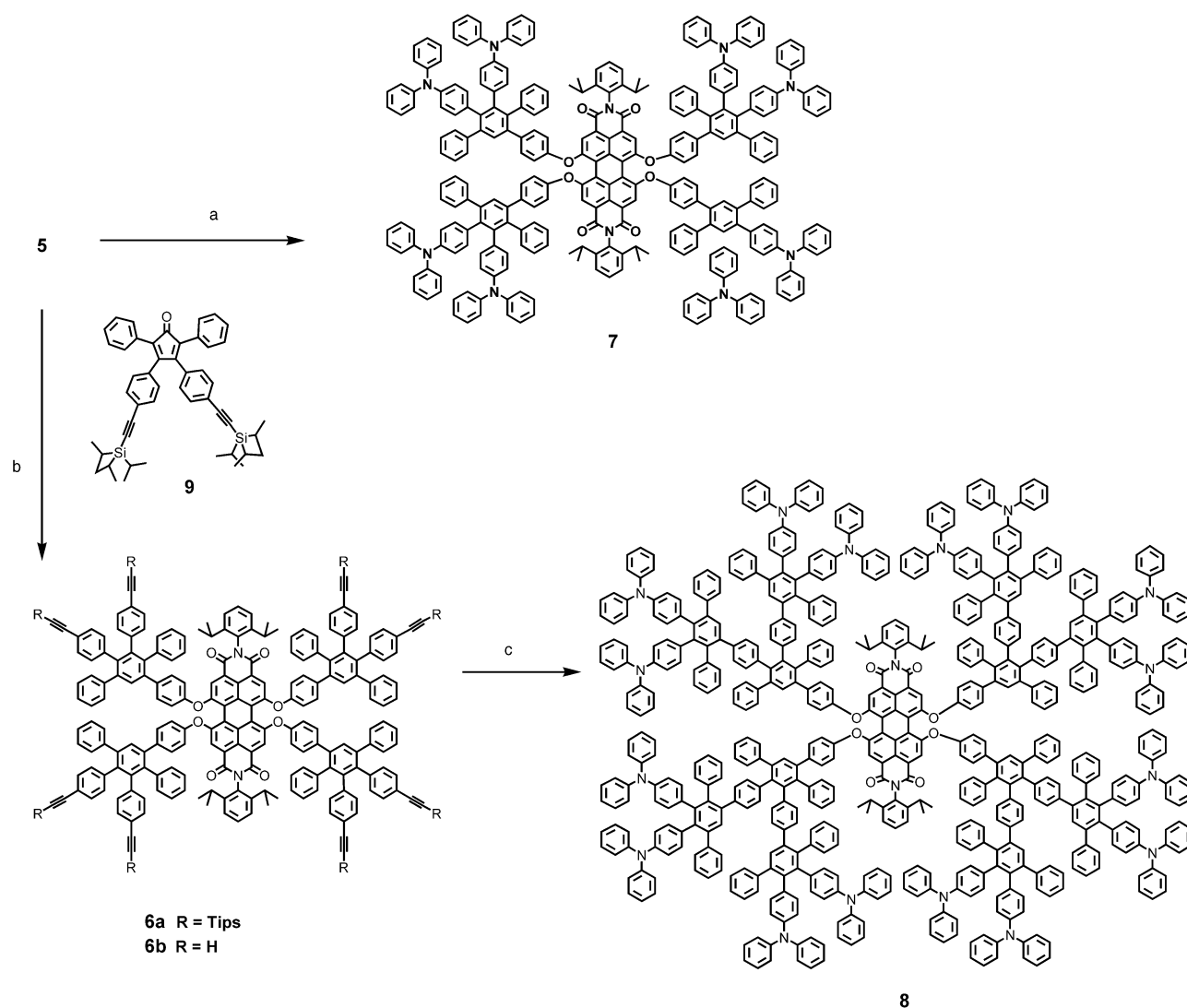
The syntheses of dendrimers **7** and **8** are shown in Scheme 4. The first-generation dendrimer was formed by Diels–Alder reaction of core molecule **5** with a sixfold excess of cyclopentadienone **11** in *m*-xylene at 140°C . Using *m*-xylene as solvent has the advantage that the product is easily isolated by precipitation with methanol. After filtration, the mixture of product **7** and excess **11** was obtained as a dark red powder. Compound **7** was isolated by column chromatography. To build up the second-generation dendrimer, A_2B building block **9** was employed. Diels–Alder reaction of core **5** with **9** afforded the first-generation den-

dimer **6a** with eight TIPS-protected ethynyl groups. After facile deprotection of **6a** with Bu_4NF , compound **6b** was obtained, which is easily purified by washing with methanol. First-generation ethynyl-bearing dendrimer **6b** was then treated with 12 equivalents of **11** to give second-generation dendritic chromophore **8** containing 16 triphenylamino groups in a yield of 79 % after column chromatography.

The functionalized dendritic structures **7** and **8**, as well as TIPS-protected first-generation dendrimer **6a** and octa-ethynyl-substituted unprotected first-generation dendrimer **6b**, are all highly soluble in common solvents such as dichloromethane, toluene, and THF. Characterization by MALDI-TOF mass spectrometry, elemental analysis, and ^1H and ^{13}C NMR spectroscopy is therefore easily accomplished. Experimentally determined and calculated m/z ratios agree perfectly for **6a**, **6b**, **7**, and **8** within the range of accuracy of the instrument. The signals obtained for these macromolecules not only show the $[M]^+$ peaks but also confirm their monodispersity (see Experimental Section). Moreover, MALDI-TOF MS measurements allow the detection of potential growth imperfections resulting from ethynyl groups that did not react during the Diels–Alder reaction with building blocks **9** and **11**. Therefore, MALDI-TOF MS was used both for the characterization of the monodisperse dendritic macromolecules described herein as well as for monitoring dendrimer growth, especially for the synthesis of second-generation dendrimer **8**, which requires a longer reaction time. As an example, the MALDI-TOF spectrum of **8** (Figure 1) clearly demonstrates the monodispersity of this compound.

Characterization of dendrimers **7**, **8** and their precursors by ^1H NMR spectroscopy was performed in tetrachloroethane or dichloromethane due to their good solubility in these solvents. Well-separated and assignable signals of non-dendronized intermediates and the model compound **12** were obtained. The TIPS groups of **6a** and the ethynyl protons of **6b** are clearly assignable. Dendrimers **7** and **8** also show well-separated signals (Figure 2) for the aromatic perylene protons and for the aliphatic protons of the CH and $(\text{CH}_3)_2$ groups on the imide structure. Most of the protons of triphenylamino groups and dendrons are located together between 6.4 and 7.2 ppm, but in the first generation, a single peak for the dendron can be distinguished, which corresponds to the only proton on the central benzene ring of the pentaphenylbenzene unit (Figure 2). In addition, 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 ^{13}C NMR resonances of the polyphenylene dendrons could not be assigned completely because of the many overlapping signals, and some of the resonances of the core carbon atoms are too weak to be detected for the second-generation dendrimer.

Visualization and simulation: The structure of the perylene core was optimized by using the semiempirical PM3 method, and the dendrons decorated with TPAs from the first and second generation were minimized separately by using MM2 (MM+) force-field geometry optimization as



Scheme 4. Synthesis of first-generation dendrimer **7** and second-generation dendrimer **8**: a) 6 equiv **11**, *m*-xylene, 140 °C, 15 h, 84%; b) i) 6 equiv **9**, *m*-xylene, 140 °C, 15 h, 89%; ii) 16 equiv *n*Bu₄NF, THF, RT, 30 min, 80%; c) 12 equiv **11**, *m*-xylene, 150 °C, 48 h, 79%.

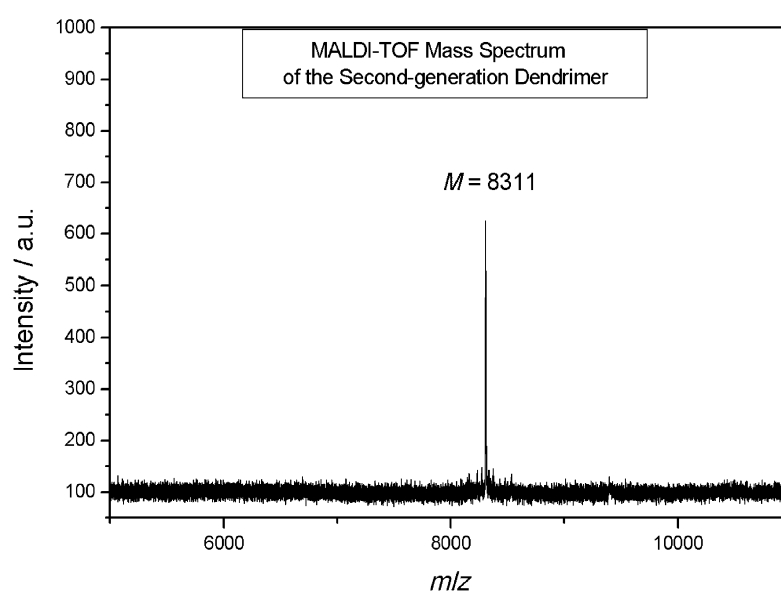


Figure 1. MALDI-TOF mass spectrum of second-generation dendrimer **8** (m/z : 8311 [M]⁺, dithranol matrix).

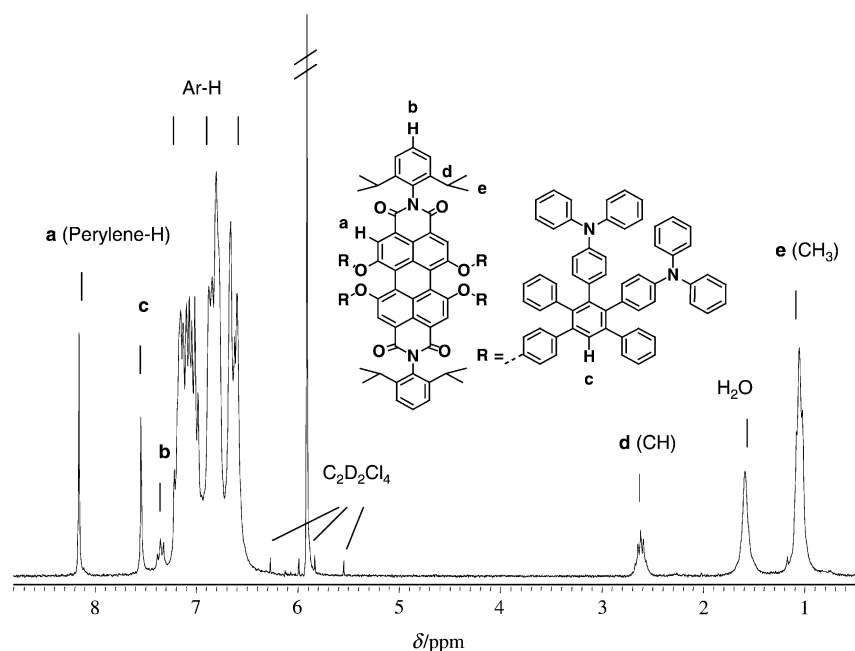


Figure 2. ^1H NMR spectrum of the first-generation dendrimer **7** at 300 K (500 MHz, CD_2Cl_2).

implemented in HyperChem 6.0 (Hypercube Inc.). Furthermore, the whole dendritic system was optimized by combining four first- and second-generation dendrons with the perylene core and minimizing the whole system. The nondendronized model compound **12** was obtained similarly by connecting four TPAs with the minimized perylene core and subsequent geometry optimization of the entire molecule. As shown in Figure 3, the two naphthalene rings of **12**, **7**, and **8** are strongly twisted at the bay positions with a torsional angle of around 28° between the two naphthalene units, which is in good agreement with the calculated structure^[13] and crystal structure of a similar molecule.^[17] In the simulated structure of model compound **12**, the phenoxy groups are nearly perpendicular to the perylene ring. The same considerations of torsion angles hold for the dendrimers (not shown in Figure 3). Molecular modeling shows that dendrimers **7** and **8** are three-dimensional structures, and the chromophores are surrounded by dendritic

shells with TPAs at the periphery. The size of the compounds increases with increasing dendrimer generation; the diameter is 3.7 nm for the first generation, and 5.3 nm for the second. Clearly, the perylene core is shielded by the dendrons, so that self-aggregation of perylene units is prohibited. The TPAs at the periphery have various torsional angles relative to PDI. In this case, the simulation of the series of compounds **12**, **7**, and **8** is a good approximation of the three-dimensional structures.

Steady-state spectroscopy: Dendrimers **7** and **8** are soluble in various solvents such as methylcyclohexane, toluene, and THF. Their absorption spectra in methylcyclohexane, together

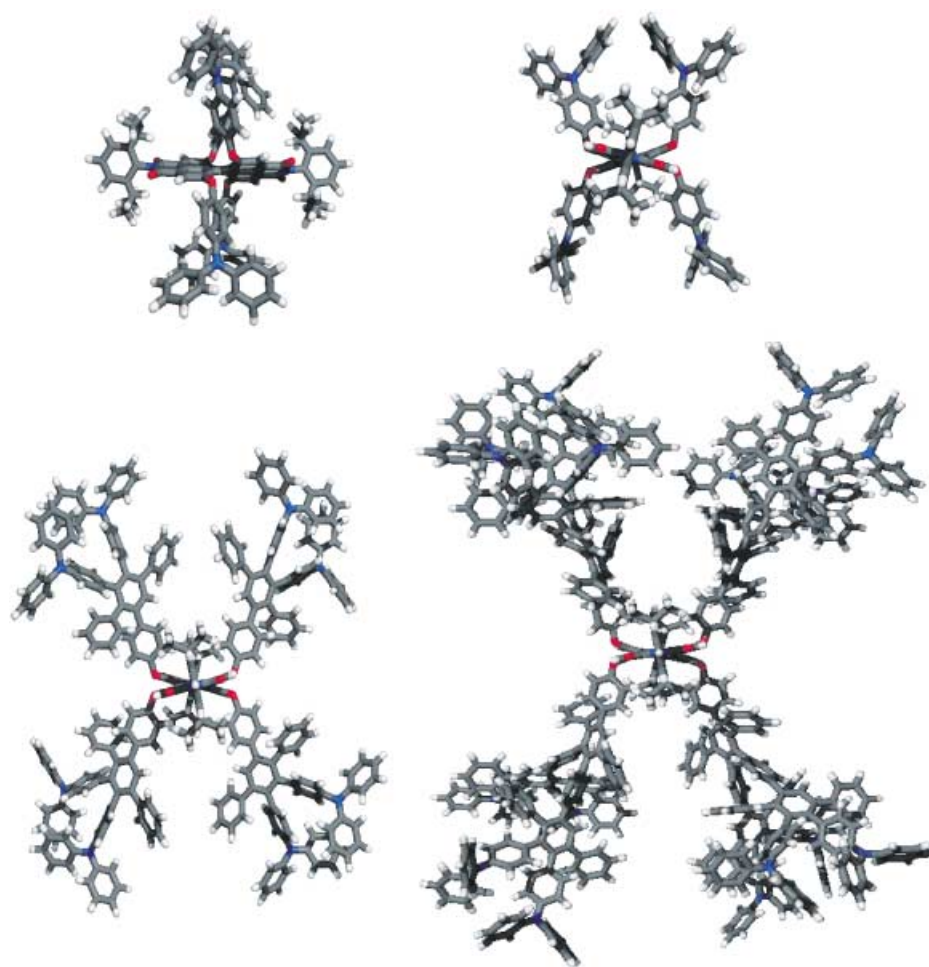


Figure 3. Visualization of nondendronized model compound **12** (top), first-generation dendrimer **7** (bottom left), and second-generation dendrimer **8** (bottom right).

with those of dendrimers **7*** and **8*** (Figure 4)^[18] with the same PDI core but without the peripheral TPA groups as model compounds for investigating optical properties of

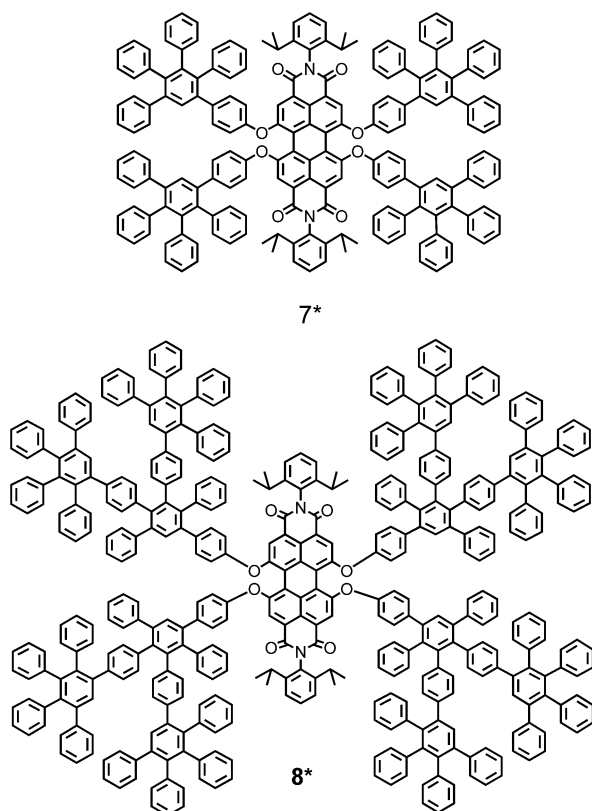


Figure 4. Model compounds without the functional group: first-generation dendrimer **7*** and second-generation dendrimer **8***.

dendrimers **7** and **8**, are shown in Figure 5. The absorption spectra of dendrimers **7** and **8** exhibit three absorption regions. Between 480 and 600 nm the absorption reflects the S_0 – S_1 electronic transition of PDI along the long axis. An

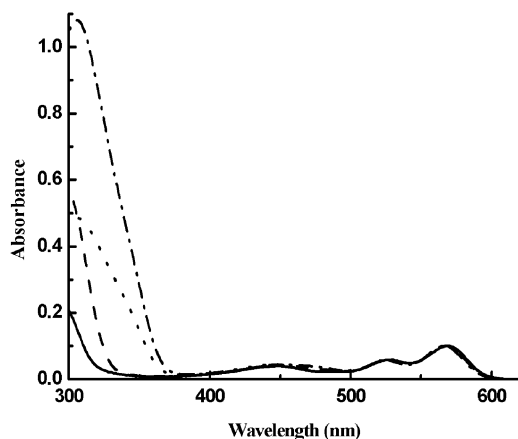


Figure 5. Absorption spectra of the first-generation dendrimer **7** (.....), the second-generation dendrimer **8** (–. –.), and their model compounds **7*** (—) and **8*** (---) in methylcyclohexane. The spectra are normalized at the PDI absorption maximum.

additional peak between 400 and 460 nm corresponds to the S_0 – S_2 transition, for which the transition dipole moment is along the short axis. The absorption between 300 and 380 nm is mainly due to the polyphenylene dendrons and the TPA groups.^[19] The difference in absorption in this region between **7**, **8** and **7***, **8*** is due to the presence of TPA. Figure 5 shows that the contribution of TPA to the absorption almost doubles with increasing generations, and this reflects the corresponding change in the number of TPA moieties at the dendrimer periphery.

The absorption and normalized emission spectra of dendrimers **7** and **8** when excited at the PDI core, measured in solvents of different polarity such as methylcyclohexane (MCH, $\epsilon=2.02$ ^[20]), toluene (TOL, $\epsilon=2.38$), and tetrahydrofuran (THF, $\epsilon=7.58$), are shown in Figure 6. Both dendrimers display similar absorption and emission bands, independent of the dendrimer generation or the solvent. However, the absorption and normalized emission spectra exhibit slight bathochromic shifts in polar solvents. The excitation spectra are identical to the absorption spectra (not shown in the figure).

The fluorescence quantum yields of dendrimers **7** and **8** (excited at 540 nm) and model compounds **7*** and **8*** were

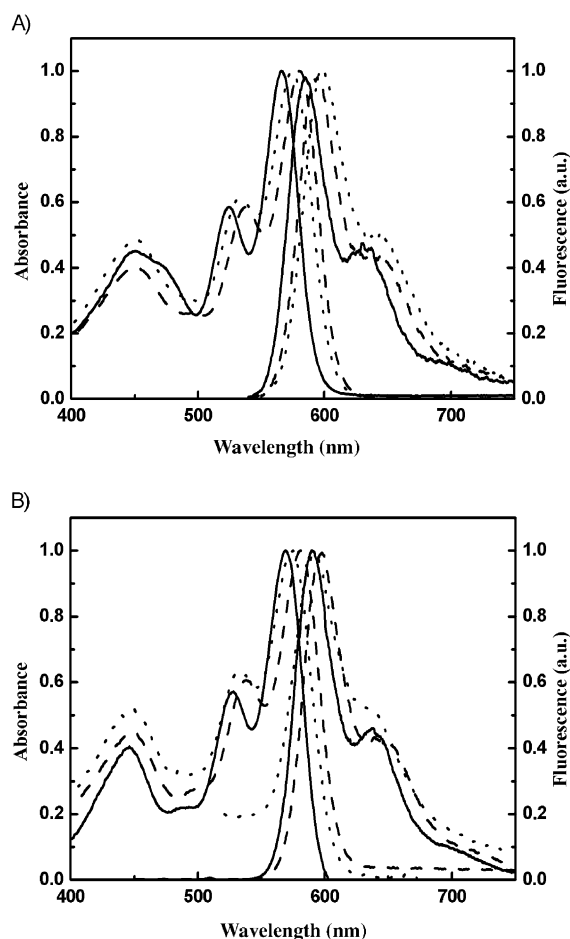


Figure 6. Normalized absorption and emission spectra (excitation at 530 nm) of the first-generation dendrimer **7** (A) and the second-generation dendrimer **8** (B) in methylcyclohexane (—), toluene (---) and THF (.....).

Table 1. Photoluminescence quantum yield (Φ_{PL}) in polar and nonpolar solvents at room temperature (reference chromophore: Cresyl Violet, excitation at 540 nm)

Solvent	7	8	7*	8*
methylcyclohexane	0.77	0.83	0.96	0.93
toluene	0.14	0.55	0.92	0.91
THF	0.001	0.02	0.77	0.76

measured in different solvents with cresyl violet as reference and are listed in Table 1.^[21] The presence of TPA at the periphery of dendronized perylenetetracarboxydiimides dramatically quenches the fluorescence of the PDI core in polar solvents such as THF. The fluorescence quenching can be explained by efficient intramolecular electron transfer induced by excitation of the electron acceptor PDI. To obtain experimental proof of this phenomenon, femtosecond transient absorption spectroscopy is presently being performed on these systems, and preliminary results indicate the presence of a broad absorption band above 700 nm that belongs to the anion of perylenetetracarboxydiimide. A full account of these results will be published elsewhere. In nonpolar solvents such as methylcyclohexane, only a slight decrease in quantum yield (540 nm excitation wavelength) was observed for dendrimer **8** relative to model compound **8***, and this indicates an absence or very low efficiency of intramolecular electron transfer. Earlier reports on intramolecular electron transfer in donor-spacer-acceptor dyads also demonstrated the dependence of the rate of electron transfer on the dielectric constant of the solvent.^[22] The intramolecular electron transfer efficiency is also dependent on the dendrimer generation (or the average distance between the electron donor and acceptor), as can be clearly seen in Table 1. Particularly in the case of toluene, an appreciable difference was observed for the quantum yields of dendrimers **7** and **8**, while **7*** and **8*** have the same quantum yield. For the first-generation dendrimer **7**, in which the distance between the electron donor and the electron acceptor is shorter, more efficient intramolecular electron transfer was observed, even in methylcyclohexane.

To investigate the possibility that energy transfer competes with electron transfer in these systems, **7** and **8** were also excited in the same solvents at 360 nm. The excitation wavelength of 360 nm was chosen on the basis of the absorption spectra in Figure 5, so that TPA can be selectively excited. The fluorescence emission spectra of dendrimers **7** and **8** in different solvents, normalized to the same optical density at 360 nm, are shown in Figure 7. Interestingly, the excitation of TPA in both **7** and **8** gives rise to a strong emission from the PDI core and no TPA emission in nonpolar methylcyclohexane. Compared to the emission intensity of **7** and **8** excited at 567 nm in methylcyclohexane (direct excitation of the PDI core), a decrease to 65% was observed when they are excited at 360 nm for identical optical density (Figure 7). The values of the quantum yield also decrease in the same ratio when **7** and **8** are excited at the same wavelength (Table 2).

Time-resolved measurements on **8** excited at 360 nm in methylcyclohexane indicate the presence of a rise compo-

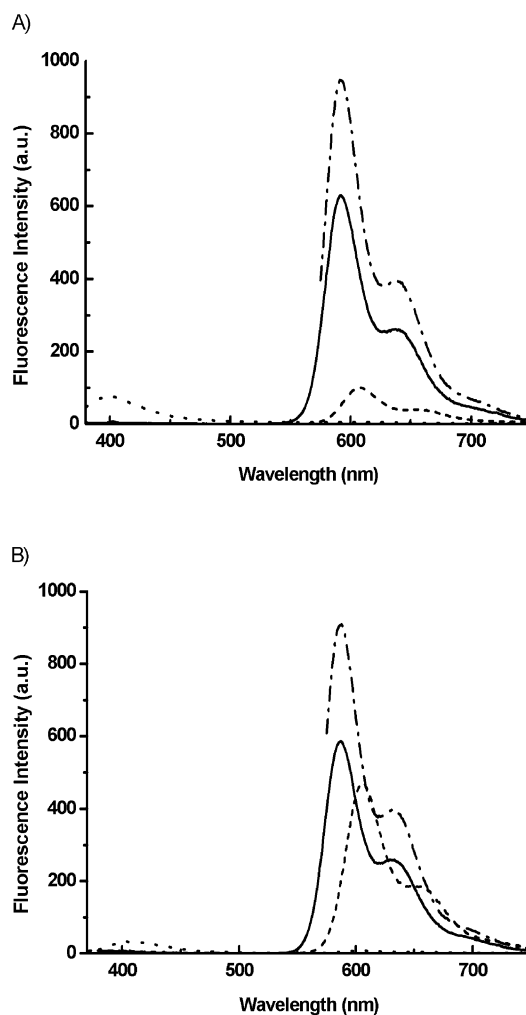


Figure 7. Fluorescence emission spectra of the first-generation dendrimer **7** (A) and the second-generation dendrimer **8** (B) in methylcyclohexane (—), toluene (----) and THF (.....). The spectra are normalized to the same absorbance at the excitation wavelength 360 nm. The emission spectra (— · —) of dendrimers **7** and **8** in methylcyclohexane excited around the PDI absorption maximum at the same absorbance are also shown.

Table 2. Fluorescence quantum yield at room temperature (reference compounds: perylene for **7** and **8**, excitation 360 nm; quinine sulfite for TPA, excitation 290 nm).

Solvent	7	8	TPA
methylcyclohexane	0.46	0.54	0.13
toluene	0.06	0.22	0.105

nent of 42 ps. This component does not appear in the analysis of the decay histograms obtained by excitation at 543 nm (direct excitation of PDI chromophore) of the same compound in the same solvent. All of these data point to a very efficient energy transfer process followed by electron transfer in methylcyclohexane. The higher rate of electron transfer for **7** and **8** in methylcyclohexane with excitation at 360 nm can be understood by the more exothermic process at this excitation wavelength. The negligible fluorescence emission from the PDI core observed in THF solution from

both **7** and **8** indicates the dominance of electron transfer. Excitation at 360 nm of **7** and **8** in toluene results in extensive quenching of electron transfer in **7** and enhanced electron transfer in **8**, which is also proved by the lower quantum yield compared with the values obtained on excitation at 540 nm (Tables 1 and). Since we have multiple donors and only one acceptor, and different distances between the donors and the acceptor, detailed quantitative analysis at the ensemble level of this system is not feasible. At the single-molecule level, however, compound **8** could be analyzed in a polystyrene matrix and showed, for a fraction of molecules, forward and backward electron transfer.^[23]

Conclusion

We have presented the synthesis of polyphenylene dendronized perylenetetracarboxdiimides bearing peripheral triphenylamino groups. Due to the shape-persistent properties of polyphenylene dendrons, the distance between the PDI core and TPA is well defined. Intramolecular electron and energy transfer in these donor–spacer–acceptor systems was confirmed by steady-state spectroscopy by exciting the acceptor and the donor in solvents with various polarities. While intramolecular energy transfer dominates in nonpolar solvents, intramolecular electron transfer suppresses energy transfer efficiently and becomes the dominant process in polar solvents. Furthermore, intramolecular electron transfer becomes more significant with decreasing dendrimer generation, that is, with shorter distance between TPA donor and PDI acceptor.

Experimental Section

Materials: THF (Fluka) was distilled over sodium/benzophenone. Bu₄NF (Fluka), [PdPdCl₂(PPh₃)₂] (Strem), trimethylsilylethyne (Aldrich), copper(I) iodide, *p*-iodophenol (Avocado), *m*-xylene (Aldrich), sodium *tert*-butoxide (Aldrich), *t*Bu₃P (Aldrich), [Pd₂(dba)₃] (Aldrich, dba = dibenzylideneacetone) were used as obtained from commercial sources. Column chromatography was performed with dichloromethane (chromasolv, Riedel) or toluene on silica gel (Geduran Si60, Merck). All yields are for isolated compounds.

Physical and analytical methods: ¹H and ¹³C NMR spectra were recorded on Bruker AMX 250 and AC 300 spectrometers by using the residual proton signals of the solvent or the carbon signal of the deuterated solvent as the internal standard. Chemical shifts are reported in parts per million. IR spectra were obtained on a Nicolet FT-IR 320. For ¹³C j-modulated spin-echo NMR measurements, the abbreviations q and t represent quaternary C atoms and CH₂, and CH₃ 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, and photoluminescence spectra on a SPEX Fluorolog 2 spectrometer. The correction for the wavelength-dependent intensity of the excitation source was performed by using the rhodamine quantum counter. The elemental analyses were carried out by the Microanalytical Laboratory of the Universität Mainz (Germany).

1,6,7,12-Tetrakis(4-iodophenoxy)-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (3): Tetrachloroperylene-tetracarboxdiimide **2** (5.0 g, 5.9 mmol) was stirred with *p*-iodophenol (8.0 g, 36 mmol) in NMP

(300 mL) at 80 °C in a 500 mL flask in the presence of powdered anhydrous K₂CO₃ (2.5 g, 18 mmol) under argon. The temperature was kept at 80 °C overnight. The reaction mixture was cooled to room temperature and poured into hydrochloric acid (800 mL, 2 N). The precipitated product was filtered under suction, washed three times with water (100 mL), and dried at 75 °C under vacuum. The crude product was purified by column chromatography (eluent: CH₂Cl₂, R_f=0.95) to give red solid **3** (7.9 g, 85 %). M.p. 381.4 °C; ¹H NMR (250 MHz, C₂D₂Cl₄, 300 K): δ = 8.12 (s, 4H), 7.54 (d, *J* = 8.7 Hz, 8H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 8H), 2.59 (m, 4H), 1.04 ppm (d, *J* = 6.7 Hz, 24H); ¹³C NMR (60 MHz, C₂D₂Cl₄, 300 K): δ = 164.5 (C=O), 156.5, 156.3, 146.6, 140.3, 134.3, 131.4, 130.6, 125.2, 124.2, 123.1, 121.9, 121.8, 121.6, 89.5 (CI), 30.2 (CH isopropyl), 25.4 ppm (CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ = 2960, 2867, 2361, 2336, 1706, 1671, 1592, 1508, 1478, 1408, 1339, 1310, 1281, 1201, 1006, 873, 673, 526 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ) = 573 (51 824), 536 (32 471), 455 nm (19 630 M⁻¹ cm⁻¹); photoluminescence spectrum (chloroform): λ_{max} = 610 nm; FD MS (8 kV): *m/z*: 1581.7 (100 %) [*M*]⁺ (calcd 1582.3); elemental analysis (%) calcd for C₇₂H₅₄I₄N₂O₈: C 54.63, H 3.44, N 1.77; found: C 54.25, H 3.71, N 1.63.

1,6,7,12-Tetrakis[4-(trimethylsilylethynyl)phenoxy]-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (4): Compound **3** (5.0 g, 3.1 mmol) was dissolved in a degassed mixture of triethylamine (50 mL) and absolute THF (150 mL) under argon. [PdCl₂(PPh₃)₂] (180 mg, 2 mol %), CuI (240 mg, 10 mol %), and PPh₃ were then added under a flow of argon. After the flask was sealed with a septum, trimethylsilylethyne (1.80 g, 18.6 mmol) was injected. The reaction mixture was stirred at room temperature overnight, and then poured into an equal volume of dichloromethane and filtered. Hydrochloric acid (6 M) was carefully added to the filtrate until the aqueous phase became slightly acidic (pH < 5). Then 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 purified by column chromatography on silica gel to afford **4** (4.2 g, 91 %). M.p. > 400 °C; ¹H NMR (250 MHz, C₂D₂Cl₄, 300 K): δ = 8.06 (s, 4H), 7.38 (m, 10H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 8H), 2.58 (m, 4H), 1.04 (d, *J* = 6.7 Hz, 24H), 0.16 ppm (s, 48H); ¹³C NMR (60 MHz, C₂D₂Cl₄, 300 K): δ = 163.4 (C=O), 156.0, 155.7, 146.3, 134.1, 133.3, 131.2, 129.9, 124.4, 123.6, 121.4, 121.3, 121.2, 120.0, 119.9, 104.3, 94.7, 29.5, 24.1, 0.0 ppm (CH₃Si); IR (KBr): $\tilde{\nu}$ = 2960, 2361, 2159, 1708, 1674, 1591, 1498, 1405, 1339, 1280, 1205, 864, 759, 546 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ) = 574 (45 278), 536 (28 290), 458 nm (18 907 M⁻¹ cm⁻¹); photoluminescence spectrum (chloroform): λ_{max} = 608 nm (excitation 540 nm); FD MS (8 kV): *m/z*: 1462.5 (100 %) [*M*]⁺ (calcd 1464.0); elemental analysis (%) calcd for C₉₂H₉₀N₂O₈Si₄: 75.47, H 6.20, N 1.91; found: C 75.08, H 6.36, N 1.84.

1,6,7,12-Tetrakis(4-ethynylphenoxy)-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (5): Compound **4** (1.0 g, 0.68 mmol) was dissolved in THF (50 mL) under argon. A solution of *n*BuNF (1.7 g, 5.4 mmol) in THF was added by injection. 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 vacuum, and the crude product was purified by column chromatography on silica gel (eluent: CH₂Cl₂, R_f=0.90) to give red solid **5** (677 mg, 85 %). M.p. > 400 °C; ¹H NMR (300 MHz, THF, 300 K): δ = 8.24 (s, 4H), 7.45 (d, *J* = 8.8 Hz, 8H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 8H), 3.54 (s, 4H), 2.73 (m, 4H; CH isopropyl), 1.09 ppm (d, 24H, *J* = 6.8 Hz; CH₃ isopropyl); ¹³C NMR (75 MHz, THF, 300 K): δ = 163.8 (C=O), 157.3, 156.6, 147.1, 135.2, 134.4, 132.3, 130.4, 125.1, 124.8, 122.3, 122.1, 122.0, 120.8, 120.3, 83.8 (C ethynyl), 79.3 (CH ethynyl), 30.4 (CH isopropyl), 24.7 ppm (CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ = 3296, 3073, 2963, 2923, 2871, 2361, 2336, 1708, 1672, 1591, 1497, 1407, 1338, 1308, 1281, 1205, 876, 671, 554 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ) = 573 (51 358), 536 (32 653), 455 nm (20 179 M⁻¹ cm⁻¹); photoluminescence spectrum (chloroform): λ_{max} = 600 nm (excitation 540 nm); FD MS (8 kV): *m/z*: 1175 (100 %) [*M*]⁺ (calcd 1175.0); elemental analysis (%) calcd for C₈₀H₅₈N₂O₈: 81.75, H 4.97, N 2.38; found: C 80.80, H 4.89, N 2.19.

First-generation dendrimer bearing 8 triisopropylsilylethynyl groups (6a): A mixture of **5** (200 mg, 0.17 mmol) and **9** (720 mg, 1.0 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 and reprecipitated several times in methanol until the red color of **9** disappeared. Finally, the product was dried under vacuum and purified by column chromatography on silica gel (eluent: CH₂Cl₂ R_f =0.95) to give red solid **6a** (610 mg, 89%). M.p. > 400 °C; ¹H NMR (250 MHz, CD₂Cl₂, 300 K): δ =8.11 (s, 4H), 7.49 (s, 4H), 7.35 (t, J =7.9 Hz, 2H), 7.22 (d, J =8.4 Hz, 4H), 7.8–6.65 (m, 116H), 2.63 (m, 4H), 1.18 (s, J =6.7 Hz, 24H; TIPS CH isopropyl), 1.00 ppm (m, 168H); ¹³C NMR (75 MHz, C₂D₂Cl₄, 300 K): δ =163.4 (q, C=O), 156.1 (q), 154.0 (q), 145.7 (q), 141.5 (q), 141.0 (q), 140.8 (q), 140.6 (q), 140.3 (q), 140.2 (q), 139.7 (q), 139.2 (q), 138.6 (q), 138.1 (q), 133.1 (q), 132.8 (t), 131.5 (t), 131.2 (t), 130.9 (t), 130.2 (t), 129.8 (t), 129.5 (t), 128.8 (t), 128.5 (t), 128.1 (t), 127.4 (t), 126.6 (t), 126.4 (t), 122.9 (q), 120.9 (q), 120.8 (q), 120.5 (q), 119.5 (t), 107.5 (q), 90.5 (q), 29.3 (t; CH isopropyl), 24.5 (p; CH₃ isopropyl), 18.9 (p; SiCH₃ isopropyl), 11.6 ppm (t; Si-CH isopropyl); IR (KBr): $\tilde{\nu}$ =3031, 2941, 2892, 2864, 2362, 2152, 1709, 1675, 1591, 1501, 1462, 1404, 1336, 1306, 1279, 1206, 1171, 1105, 1072, 1015, 994, 916, 881, 836, 759, 672, 562 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ)=584 (45287), 543 (27428), 466 nm (21325 M⁻¹cm⁻¹); photoluminescence spectrum (chloroform): λ_{max} =610 nm (excitation 540 nm); MALDI-TOF MS: m/z : 4041 (100%) [M]⁺ (calcd 4044); elemental analysis (%) calcd for C₂₈₀H₂₉₈N₂O₈Si₈: 83.16, H 7.43, N 0.69; found: C 82.47, H 7.07, N 0.64.

First-generation dendrimer bearing 8 ethynyl groups (6b): Trialkylsilyl derivative **6a** (600 mg, 0.15 mmol) was dissolved in THF (20 mL) under argon. A solution of *n*Bu₄F in THF (750 mg, 2.4 mmol, 1.0 M) was injected slowly into the flask. The mixture was stirred for 30 min at room temperature. After most of the THF was removed under vacuum to give a red solid, methanol (100 mL) was added to the solution to give a precipitate, which was collected by filtration and washed three times with methanol (100 mL). The product **6b** was dried under vacuum (340 mg, 80%). M.p. > 400 °C; ¹H NMR (250 MHz, CD₂Cl₂, 300 K): δ =8.13 (s, 4H), 7.58 (s, 4H), 7.93 (t, J =7.8 Hz, 2H), 7.32 (d, J =8.5 Hz, 4H), 7.14–6.65 (m, 88H), 3.03 (s, 4H), 3.01 (s, 4H), 2.68 (m, 4H), 1.09 ppm (d, J =6.6 Hz, 24H); ¹³C NMR (75 MHz, C₂D₂Cl₄, 300 K): δ =163.4 (q, C=O), 156.1 (q), 154.1 (q), 145.6 (q), 141.3 (q), 141.0 (q), 140.9 (q), 140.7 (q), 140.2 (q), 139.6 (q), 139.1 (q), 138.4 (q), 138.0 (q), 133.1 (q), 131.7 (t), 131.3 (t), 131.0 (t), 130.6 (q), 130.2 (t), 128.1 (t), 127.6 (t), 126.8 (t), 126.2 (t), 122.9 (q), 120.9 (q), 120.4 (q), 119.5 (t), 119.2 (q), 118.8 (q), 84.4 (q), 77.5 (q), 29.3 (t; CH isopropyl), 24.5 ppm (p; CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ =3294, 3030, 2963, 2927, 2869, 2361, 2336, 2106, 1708, 1673, 1591, 1501, 1440, 1404, 1336, 1307, 1279, 1205, 1170, 1105, 1016, 842, 700, 651, 558 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ)=583 (51645), 543 (31123), 462 nm (24006 M⁻¹cm⁻¹); photoluminescence spectrum (chloroform): λ_{max} =610 nm (excitation 540 nm); MALDI-TOF MS: m/z : 2793 (100%) [M]⁺ (calcd 2793); elemental analysis (%) calcd for C₂₀₈H₁₃₈N₂O₈: 89.44, H 4.98, N 1.00; found: C 88.45, H 5.06, N 0.91.

First-generation dendrimer bearing 8 diphenylamino groups (7): As for **6a**, **5** (100 mg, 0.085 mmol) and **11** (370 mg, 0.51 mmol) gave **9** (300 mg, 84%). M.p.: 292.5 °C; ¹H NMR (250 MHz, C₂D₂Cl₄, 300 K): δ =8.15 (s, 4H), 7.54 (s, 4H), 7.35 (t, J =7.8 Hz, 2H), 7.21–6.59 (m, 172H), 2.61 (m, 4H), 1.05 ppm (d, J =6.7 Hz, 24H); ¹³C NMR (60 MHz, CD₂Cl₂, 300 K): δ =163.5 (q, C=O), 156.2 (q), 154.0 (q), 147.9 (q), 147.9 (q), 145.7 (q), 145.3 (q), 145.0 (q), 141.9 (q), 141.7 (q), 140.9 (q), 140.3 (q), 139.6 (q), 139.4 (q), 139.3 (q), 138.4 (q), 136.0 (q), 135.4 (q), 133.2 (q), 132.8 (t), 131.8 (t), 131.3 (t), 130.7 (q), 130.4 (t), 129.3 (t), 127.8 (t), 127.3 (t), 126.5 (t), 125.9 (t), 124.2 (t), 123.8 (t), 123.5 (t), 123.0 (q), 122.5 (t), 122.3 (t), 121.1 (t), 121.0 (q), 120.4 (q), 119.5 (t), 29.3 (t; CH isopropyl), 24.4 ppm (p; CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ =3027, 2962, 2361, 1707, 1672, 1509, 1493, 1439, 1403, 1322, 1275, 1203, 1173, 1107, 1074, 1022, 839, 751, 696, 664, 562, 509 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ)=584 (45777), 543 (28197), 457 nm (21092 M⁻¹cm⁻¹); photoluminescence spectrum (chloroform) λ_{max} =607 nm (excitation 540 nm); MALDI-TOF MS: m/z : 3935 (100%) [M]⁺ (calcd 3935); elemental analysis (%) calcd for C₂₈₈H₂₁₀N₁₀O₈: C 87.82, H 5.37, N 3.56; found: C 86.89, H 5.06, N 3.44.

Second-generation dendrimer bearing 8 *N,N*-diphenylamino groups (8): A mixture of **6b** (150 mg, 0.050 mmol) and **11** (460 mg, 0.65 mmol) in *m*-xylene (5 mL) was stirred at 150 °C for 48 h under argon. The cooled reaction mixture was added to methanol (100 mL). The precipitated product was filtered under suction. The product **8** was dried under vacuum

and purified by column chromatography on silica gel (eluent: toluene, R_f =0.75) to give **8** (320 mg, 79%). M.p.: 317.2 °C; ¹H NMR (250 MHz, CD₂Cl₂, 300 K): δ =8.15 (s, 4H), 7.50 (s, 4H), 7.46 (s, 4H), 7.44 (s, 4H), 7.33 (t, J =7.8 Hz, 2H), 7.18–6.49 (m, 396H), 2.70 (m, 4H), 1.11 ppm (d, J =6.8 Hz, 24H); ¹³C NMR (60 MHz, CD₂Cl₂, 300 K): δ =163.6 (q, C=O), 156.0 (q), 154.3 (q), 148.1 (q), 148.1 (q), 146.3 (q), 145.7 (q), 145.3 (q), 142.1 (q), 142.0 (q), 141.6 (q), 141.2 (q), 141.0 (q), 140.6 (q), 140.4 (q), 140.3 (q), 140.2 (q), 139.6 (q), 139.4 (q), 139.2 (q), 138.9 (q), 138.5 (q), 138.2 (q), 136.2 (q), 135.6 (q), 132.9 (t), 132.0 (t), 131.8 (t), 131.4 (t), 130.3 (t), 129.4 (t), 129.3 (t), 127.9 (t), 127.2 (t), 126.6 (t), 125.8 (t), 123.9 (t), 123.7 (t), 123.6 (t), 123.3 (q), 122.6 (t), 122.5 (t), 121.3 (q), 120.8 (q), 29.4 (t; CH isopropyl), 24.1 ppm (p; CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ =3031, 2963, 2923, 2361, 1707, 1673, 1591, 1494, 1448, 1405, 1334, 1311, 1278, 1205, 1172, 1075, 1022, 878, 751, 697, 554, 510 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ)=583 (36771), 543 (21992), 468 nm (17286 M⁻¹cm⁻¹); photoluminescence spectrum (chloroform) λ_{max} =607 nm (excitation 540 nm); MALDI-TOF MS: m/z : 8311 (100%) [M]⁺ (calcd 8313); elemental analysis (%) calcd for C₆₂₄H₄₄₂N₁₈O₈: C 90.08, H 5.35, N 3.03; found: C 89.56, H 5.43, N 2.79.

3,4-Bis[4-(*N,N*-diphenylamino)phenyl]-2,5-diphenylcyclopenta-2,4-dien-one (11): Dibromocyclopentadienone **10** (2.2 g, 4.0 mmol), diphenylamine (1.8 g, 8.0 mmol), [Pd₂(dba)₃] (73 mg), and *t*BuONa (1.15 g, 12.0 mmol) were added to a 50 mL Schlenk flask in a glove box. Toluene (30 mL) was poured into the flask to dissolve the mixture, and tri-*tert*-butylphosphane toluene solution (1.2 mL, 20 mg mL⁻¹, prepared from pure tri-*tert*-butylphosphane and distilled toluene in the glove box) was added by injection. The mixture was stirred at room temperature for 1 h under argon. Then the solution was filtered under suction, and the filtrate extracted with water (500 mL). The organic phase was dried under vacuum to give a dark crude product. The product **11** (2.6 g, 99%) was purified by column chromatography on silica gel (eluent: CH₂Cl₂, R_f =0.95). M.p. 273.3 °C; ¹H NMR (250 MHz, CD₂Cl₂, 300 K): δ =7.18 (m, 18H), 7.00 (m, 12H), 6.74 ppm (m, 8H); ¹³C NMR (60 MHz, CD₂Cl₂, 300 K): δ =200.5 (C=O), 154.6, 148.4, 147.5, 131.9, 131.0, 130.5, 129.7, 128.2, 127.5, 126.7, 125.3, 124.9, 123.9, 121.5 ppm; IR (KBr): $\tilde{\nu}$ =3031, 2362, 1701, 1588, 1488, 1442, 1355, 1277, 1176, 1111, 1077, 1025, 894, 840, 752, 696, 618, 561 cm⁻¹; FD MS (8 kV): m/z : 718.2 (100%) [M]⁺ (calcd 718.8); elemental analysis (%) calcd for C₅₃H₃₈N₂O: C 88.55, H5.33, N 3.90; found: C 88.53, H 5.24, N 3.88.

1,6,7,12-Tetrakis[4-(*N,N*-diphenylamino)phenoxy]-*N,N*-(2,6-diisopropyl-phenyl)perylene-3,4,9,10-tetracarboxydiimide (12): Compound **3** (500 mg, 0.32 mmol), diphenylamine (20 mg, 1.3 mmol), [Pd₂(dba)₃] (12 mg), and *t*BuONa (180 mg, 2.0 mmol) were added to a 25 mL Schlenk flask in the glove box. Toluene (10 mL) was injected into the flask to dissolve the mixture. Tri-*tert*-butylphosphane in toluene (0.2 mL, 20 mg mL⁻¹) was then injected into the flask in the glove box. The mixture was stirred at room temperature for 4 h under argon. After 1 h, the solution was filtered under suction and the filtrate extracted with water (100 mL). The organic phase was dried under vacuum to obtain a purple crude product, which was purified by column chromatography (eluent: CH₂Cl₂, R_f =0.90) to give **12** (501 mg, 91%). M.p.: 234.6 °C; ¹H NMR (250 MHz, CD₂Cl₂, 300 K): δ =8.26 (s, 4H), 7.42 (t, J =7.9 Hz, 2H), 7.24 (d, J =8.8 Hz, 4H), 7.15 (t, J =8.2 Hz, 16H), 7.01–6.83 (d, J =8.8 Hz, 40H), 2.64 (m, 4H), 1.04 ppm (d, J =6.8 Hz, 24H); ¹³C NMR (60 MHz, CD₂Cl₂, 300 K): δ =163.7 (C=O), 156.3, 150.9, 148.1, 146.4, 145.0, 133.6, 131.5, 129.7, 125.2, 124.6, 124.4, 123.3, 123.1, 121.0, 120.7, 120.5, 29.4 (CH isopropyl), 24.1 ppm (CH₃ isopropyl); IR (KBr): $\tilde{\nu}$ =2962, 2361, 1706, 1673, 1589, 1493, 1405, 1335, 1309, 1275, 1202, 874, 752, 696, 511 cm⁻¹; UV/Vis (chloroform): λ_{max} (ϵ)=595 (25268), 537 (23696), 437 nm (13332 M⁻¹cm⁻¹); FD MS (8 kV): m/z : 1747.8 (100%) [M]⁺ (calcd 1748.0); elemental analysis (%) calcd for C₁₂₀H₉₄N₆O₈: C 82.45, H 5.427, N 4.81; found: C 82.40, H 5.43, N 4.81.

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