Synthesis and Characterization of Dendritic Multichromophores Based on Rylene Dyes for Vectorial Transduction of Excitation Energy

Tanja Weil, Erik Reuther, Cornelia Beer, and Klaus Müllen*[a]

Abstract: The synthesis of dendritic multichromophores based on a rigid polyphenylene scaffold is presented. Different rylene chromophores are incorporated into the core, the branches, and the surface of the dendrimer. In this way, two generations of dendritic dyads consisting of a terrylenediimide core, a stiff polyphenylene scaffold, and a perylenemonoimide periphery were obtained. Furthermore, the first synthetic approach to a dendritic triad is introduced. The outer sphere of this macromolecule is formed by naphthalenemonoimide chromophores, whereas perylenemonoimide groups are located in the dendritic scaffold, and the terrylenediimide chromophore serves as a core molecule. This multichromophore absorbs over the whole range of the visible spectrum and shows well-separated absorption envelopes. In the course of dendrimer synthesis new attempts towards a straightforward functionalization strategy for rylene dyes are also presented.

Keywords: chromophores • cycloaddition • dendrimers • energy transfer • rylene dyes

Introduction

In recent years different attempts towards the synthesis of organic,[1–3] supramolecular,[4] polymeric,[5] and dendritic[6] multichromophores have been reported. Among other reasons, these molecules have been of special interest for the investigation of interactions between chromophores and have been considered to be promising model compounds for multichromophore arrays and potential light-harvesting systems. In this context, the importance of dendrimers as model compounds for biopolymers such as proteins has been especially emphasized, which is due to their combination of high molecular weight and structural perfection (monodispersity).[6] Furthermore, dendrimers can be grown from a focal point and offer the unique possibility that functional groups can be introduced at three different positions[7]: The center,[8] the scaffold,[4,9,10] and the periphery.[11,12] This holds especially true for so-called rigid dendrimers, in which the branches show no backfolding[13,14] and the topology of the functionality is retained even in solution. Important examples of dendritic multichromophores bearing different types of chromophores have been reported by Moore et al.,[15–17] Fréchet et al.,[18–20] Aida et al.,[21] and Balzani et al.[10a,b] Moore et al. reported phenylacetylene dendrimers with a central perylene dye and a scaffold consisting of ethynyl groups with different conjugation lengths. Most of the other groups used an aryl ether scaffold introduced by Fréchet et al.[22,23] These dendrimers have been decorated with two kinds of coumarin dyes or porphyrins. In all cases, efficient energy transfer was observed,[24] and for the phenylacetylene dendrimers an energy gradient from the periphery towards the center has been proven.[16] However, the investigation of chromophore interactions in these dendrimers is often very complicated due to the flexible nature of the dendritic branches of most dendrimers and the low photostability and fluorescence quantum yields of the chosen chromophores.[24,25] Collective effects, quite well-known in biological systems, have been demonstrated in rigid polyphenylene dendrimers functionalized with very photostable perylenemonoimide chromophores at the periphery, for which an investigation at the single-molecule level could be achieved.[26]

Here, we present a new approach towards the synthesis of dendritic multichromophores in which the topology of the chromophores within the dendrimer is well defined due to a polyphenylene scaffold which serves as a stiff matrix. Since rylene dyes survive a temperature of 200 °C[27–29] and have excellent photostability, high extinction coefficients, and a fluorescence quantum yield of approximately one,[30] we were able to design an outstanding multichromophoric array by using a thermally and chemically stable polyphenylene dendrimer. For the buildup of multichromophores in which efficient energy transfer over long distances can take place,

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the optical properties of the individual chromophores and their spatial arrangement are crucial.[31] Nature has brought this principle to perfection, as can be seen from the crystal structure of the light-harvesting antenna complex (LH2) of the purple bacterium *Rhodopseudomonas acidophila*.[32] In a photosynthetic system light is collected by the antenna system and transferred to the reaction center. Therefore, chromophores absorbing short wavelengths are located at the outside and transfer their energy to longer-wavelength-absorbing acceptor chromophores. In this way, energy transfer is achieved over large distances. These very efficient systems inspired us to synthesize globular polyphenylene dendrimers bearing a long-wavelength-absorbing terrylenediimide (TDI) chromophore (Figure 1 a) in the center and shorter-wavelength-absorbing perylenemonoimide (PMI) chromophores (Figure 1 a) at the periphery. The spatial arrangement of PMI chromophores at the periphery and a TDI chromophore in the center was chosen with a view to the formation of an energy gradient from the periphery towards the center of the dendrimer.[35] The synthesis of a bichromophore as well as a dendrimer allowing very efficient energy transfer between perylene and terrylene chromophores has already been demonstrated in the literature, albeit based on a different structural concept to that presented here.[33,34]

Furthermore, the synthesis of the first dendritic triad consisting of terrylenetetracarboxdiimide, perylenedicarboxmonoimide, and naphthalenedicarboxmonoimide (NMI, Figure 1 a) chromophores is presented in detail.[35] Figure 1 b outlines the synthetic concept: **A** depicts a dendritic multichromophore consisting of one type of chromophore (e.g., PMI), whereas **B** and **C** represent two molecular dyads with increasing interchromophore distance, and **D** stands for an NMI-PMI-TDI-containing molecular triad. To contribute to the clarity of the molecular structure, the notation "dyad" (Figure 1 b, **B** and **C**) is used in the following for dendritic multichromophores bearing two, and "triad" for the respective multichromophores bearing three different types of chromophores (Figure 1 b, **D**).

Results and Discussion

We have already described the synthesis of polyphenylene dendrimers decorated with PMI chromophores.[34,36] Fluorescent first-generation polyphenylene dendrimers (**4**, Scheme 1) were obtained by Diels–Alder cycloaddition of a tetraphenylcyclopentadienone carrying one PMI chromophore **2** with a tetrahedral core molecule **1** bearing free ethynyl groups. This reaction proceeds at 170 °C in *o*-xylene with extrusion of CO. For the convergent buildup of second-generation polyphenylene dendrimer **5** a functionalized polyphenylene dendrimer branch **3** (dendron) is required (Scheme 1).[34,37,40a]

Here we describe the spatially defined introduction of chromophores into the center (Figure 2 a), the scaffold (Figure 2 b), and at the surface (Figure 2 c) of the dendrimer. For this purpose, the synthesis of a chromophore core building block and cyclopentadienone branching and terminating agents functionalized with different chromophores are crucial. In our case, a core building block bears more than one free ethynyl group, and this allows regular dendrimer growth by reaction with cyclopentadienones (Figure 2 a). Branching agents allow the introduction of functionalities within the dendritic scaffold and therefore bear at least one ethynyl group as well as the functional group, for example, a chromophore (Figure 2 b, **12** in Figure 4), whereas terminating agents are cyclopentadienones lacking ethynyl groups (Figure 2 c). After cyclo-

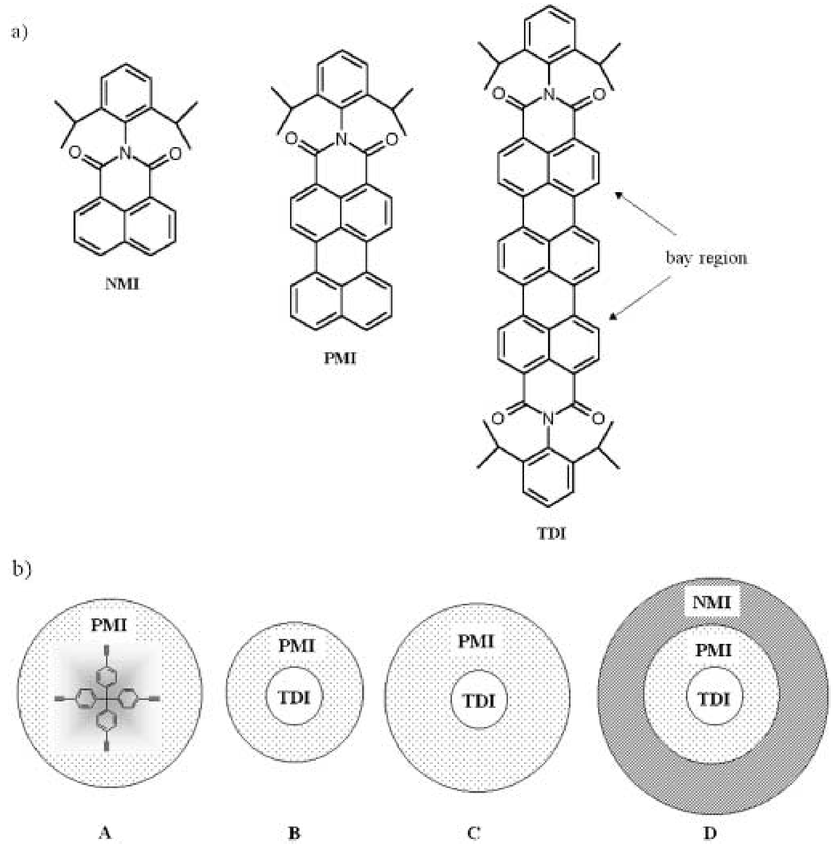
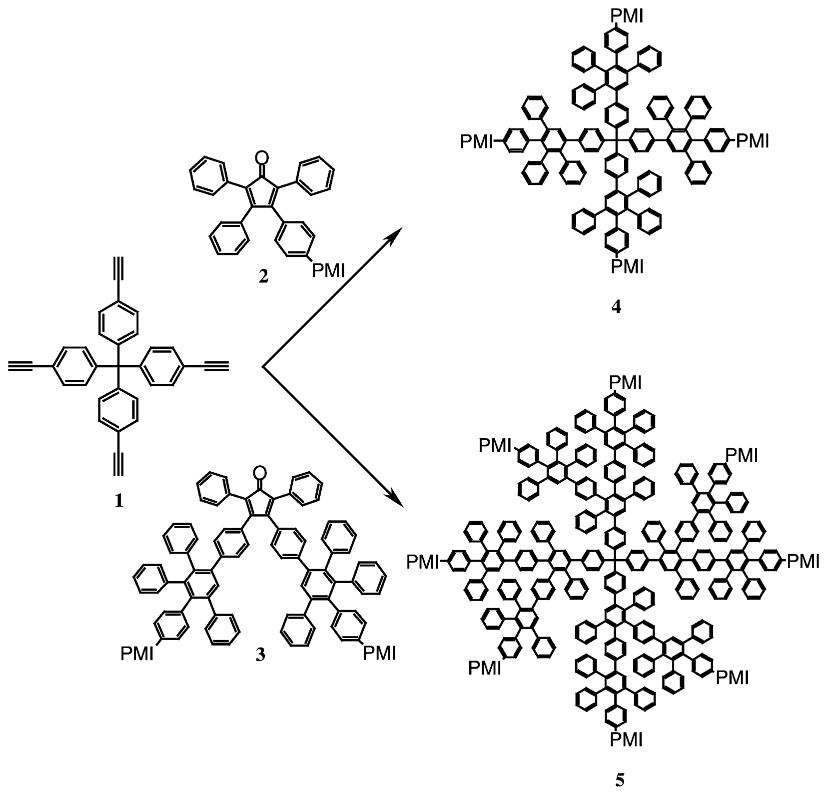


Figure 1. a) Chemical structures of unsubstituted rylenediimide chromophores: naphthalenedicarboximide (NMI), perylenedicarboximide (PMI), and terrylenetetracarboxdiimide (TDI); b) Sketch of the herein-reported synthetic approach. **A** represents a multichromophore carrying PMI substituents at the surface; **B** and **C** correspond to two molecular dyads, and **D** stands for an NMI-PMI-TDI triad.

addition with a terminating reagent further dendritic growth is no longer possible.

First, the synthesis of a TDI core molecule bearing free ethynyl groups is presented. This synthetic approach requires the introduction of bromine substituents in the so-called bay region of the TDI chromophore (Figure 1 a), which has not been described before. Furthermore, tetraphenylcyclopentadienones and polyphenylene dendrons functionalized with PMI and NMI dyes must be synthesized which will serve as terminating reagents for the introduction of chromophores exclusively in the outer sphere. Therefore, the synthesis of a dendritic triad requires a cyclopentadienone branching agent bearing a chromophore and a protected ethynyl group.



Scheme 1. Schematic overview of Diels–Alder cycloaddition of a tetraphenyltetraethynylmethane core **1** with a tetraphenylcyclopentadienone building block **2** or a dendrimer branch **3** decorated with PMI chromophores leading to first- and second-generation polyphenylene dendrimers **4** and **5**, respectively.[34,40a]

Synthesis of the terrylenetetracarboxdiimide core: As core molecule we chose a terrylenetetracarboxdiimide chromophore (TDI, **6**) because its absorption maximum is located at longer wavelength in the visible spectrum.[38,39] The synthesis of **6** was first published by us,[38] and a recent improvement to this synthetic approach has made larger quantities available.[40b] However, the functionalization of **6** has not been described before. Tetrabromoterrylenetetracarboxdiimide chromophore **7** was prepared by bromination of **6** with five equivalents of bromine in boiling trichloromethane (Scheme 2). Monitoring of the reaction by TLC or FD mass spectrometry is indispensable to avoid overbromination after extended reaction times. Purification was achieved by column chromatography with trichloromethane as eluent ($R_f = 0.9$). Sometimes, a further chromatographic step using toluene was required ($R_f = 0.15$) which gave pure **7** as a blue solid in 75 % yield. The introduction of substituents in the

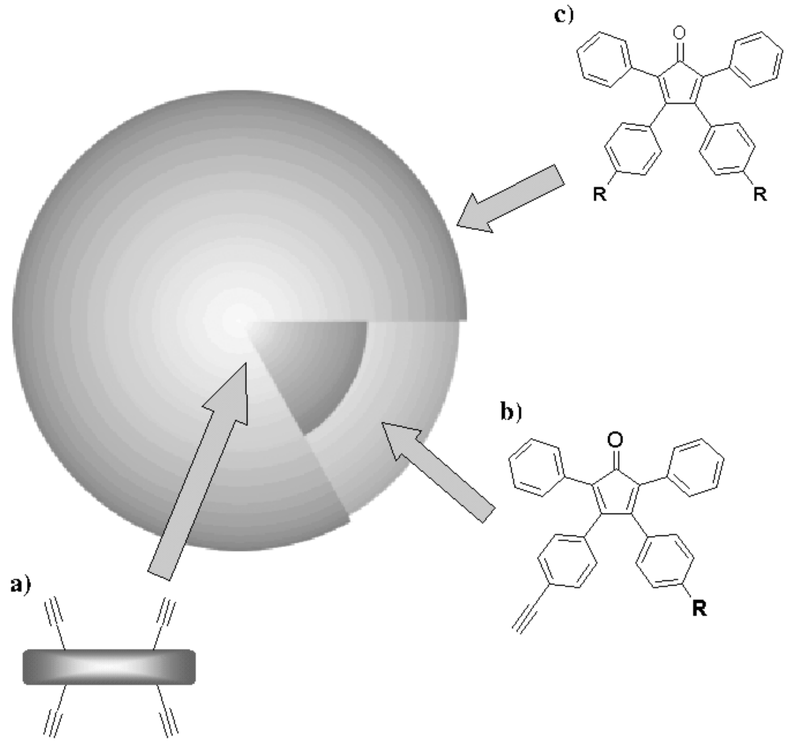
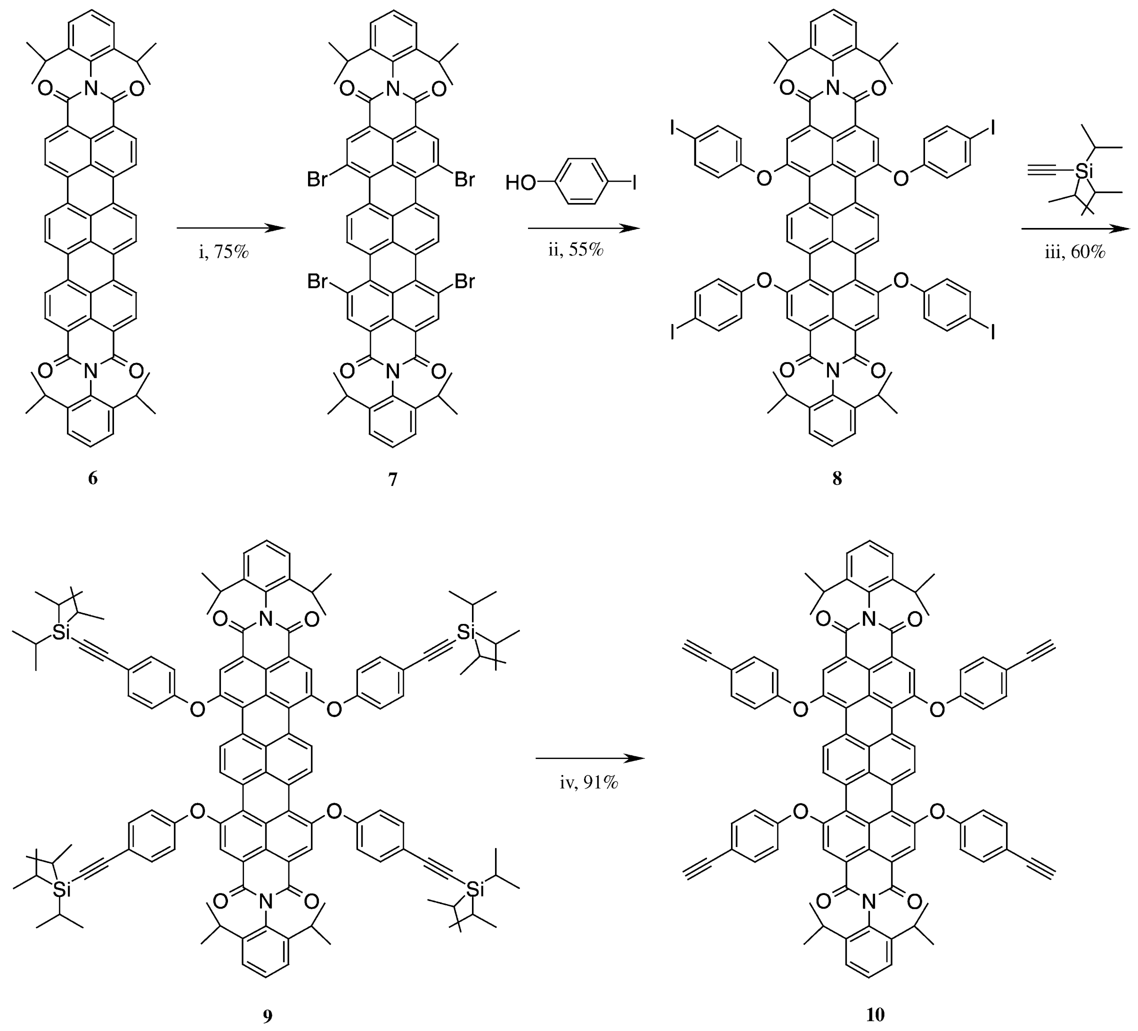


Figure 2. Introduction of functional groups at different locations of a polyphenylene dendrimer: core molecule (a), branching agent (b), and terminating agent (c).



Scheme 2. Introduction of functional groups into the bay region of the TDI chromophore **6**. i) 5 equiv Br_2, chloroform, 75 %; ii) 15 equiv 4-iodophenol (**18**), 7.5 equiv K_2CO_3, *N*-methylpyrrolidone, 12 h, 90 °C, 55 %; iii) 5 equiv triisopropylsilylacetylene, 0.4 equiv copper(I) iodide, 0.4 equiv PPh_3, 0.2 equiv $[Pd(PPh_2)Cl_2]$, THF/triethylamine (3/1), 60 %; iv) 1 equiv tetrabutylammonium fluoride, THF, 3 min, 91 %.

bay region of TDI chromophore **6** reduces the planarity of the aromatic terrylene chromophore and results in a significantly higher solubility of **7** in organic solvents such as dichloromethane, toluene, and THF. Consequently, purification and characterization are facilitated. In the next step, we achieved complete exchange of the four bromine groups of **7** by 4-iodophenol (10 equiv) in moderate yields (55 %). The reaction proceeded with eight equivalents of K_2CO_3 in *N*-methylpyrrolidone at 90 °C over 12 h. The crude mixture was poured into 2 N HCl, and a blue precipitate was formed. After filtration the product mixture was washed twice with water/dichloromethane and purified by column chromatography with dichloromethane as eluent ($R_f = 0.86$). Thus, **8** was obtained in 55 % yield.

Compound **8** was treated with triisopropylsilylacetylene (TiPS-acetylene) at room temperature over 20 h to give the corresponding TDI chromophore **9** carrying four triisopropylsilylethynyl groups in a procedure first reported by Sonogashira et al.[41] In some cases a mixture of tri- and tetrasubstituted derivatives was obtained even after extended reaction times and with an excess of the acetylene component. However, the byproduct could easily be separated by column chromatography with dichloromethane/petroleum ether (1/1, R_f(product) = 0.95, R_f(by-product) = 0.81), which gave **9** in 60 % yield. Cleavage of the four triisopropylsilyl protecting groups of **9** with one equivalent of $Bu_4NF\cdot 3H_2O$ was complete after 3 min in freshly distilled THF. Thereafter, the reaction was quenched with water and washed with water and dichloromethane. Longer reaction times led to a drastically reduced yield of **10**, and monitoring of he reaction by TLC (dichloromethane) is therefore indispensable. After column chromatography with dichloromethane the desired TDI core molecule **10** was obtained in 91 % yield as a dark blue solid. This core molecule possesses four ethynyl groups which can be subjected to Diels–Alder cycloaddition with tetraphenylcyclopentadienones to give a polyphenylene dendrimer with a TDI core.

Figure 3 shows the ^1H NMR spectrum of **10**. The assignment of the signals was based on H,H COSY and NOE experiments. The singlet at 9.30 ppm with a relative intensity of 4H corresponds to H-1 of the bay region of the TDI

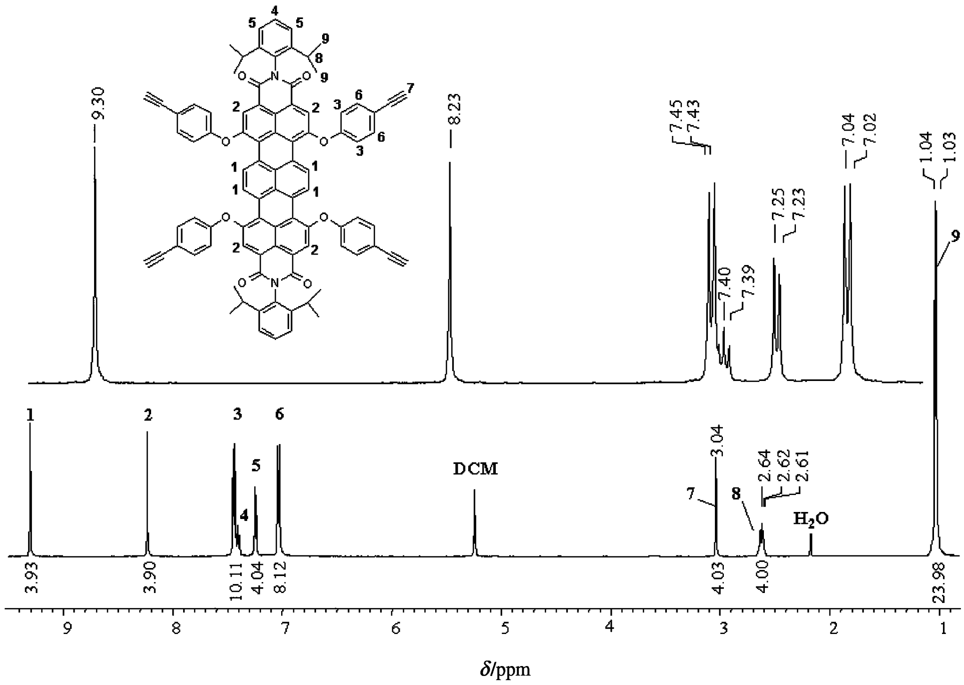
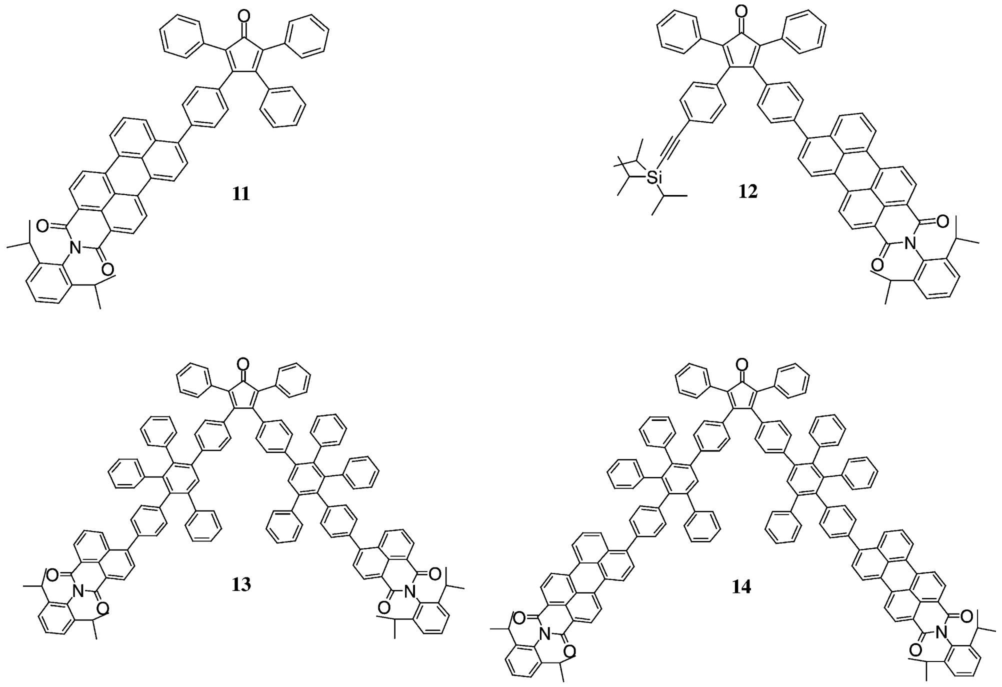


Figure 3. 500 MHz ^{1}H NMR spectrum of **10** in [D$_8$]THF at 298 K.

chromophore, and the four protons located near the imide structure H-2 are observed at 8.23 ppm.

Synthesis of the dendritic scaffold: The PMI dye shown in Figure 1 a has absorption maxima which are hypsochromically shifted relative to TDI. Therefore, PMI chromophores should be positioned in the dendritic scaffold or at the periphery, where they can pass on energy after excitation from the surface toward the TDI center. For the preparation of a dendritic triad, the NMI chromophore, which absorbs and emits at shorter wavelength than PMI and TDI, must be located exclusively at the periphery to generate an energy gradient between the periphery and the center. With regard to the characteristic spectral features of these chromophores, the following chromophore-labeled cyclopentadienone building blocks are required for the synthesis of dendritic dyads and triads (Scheme 3): A cyclopentadienone-based terminating agent **11** bearing a single PMI chromophore and a polyphenylene dendron **14** carrying two PMI chromophores, which will allow the synthesis of first- and second-generation dyads with varying PMI–TDI distances.

The synthesis of a dendritic triad requires a branching agent, namely, **12** bearing a PMI chromophore and an addi-



Scheme 3. Tetraphenylcyclopentadienone-based building blocks for introduction of chromophores into the dendritic scaffold and at the periphery. Compound **11** serves as a terminating agent for introduction of PMI chromophores at the periphery, **12** is a building block for introduction of PMI chromophores into the dendritic scaffold, and **13** and **14** are terminating building block for buildup of second-generation dendrimers bearing NMI or PMI chromophores.

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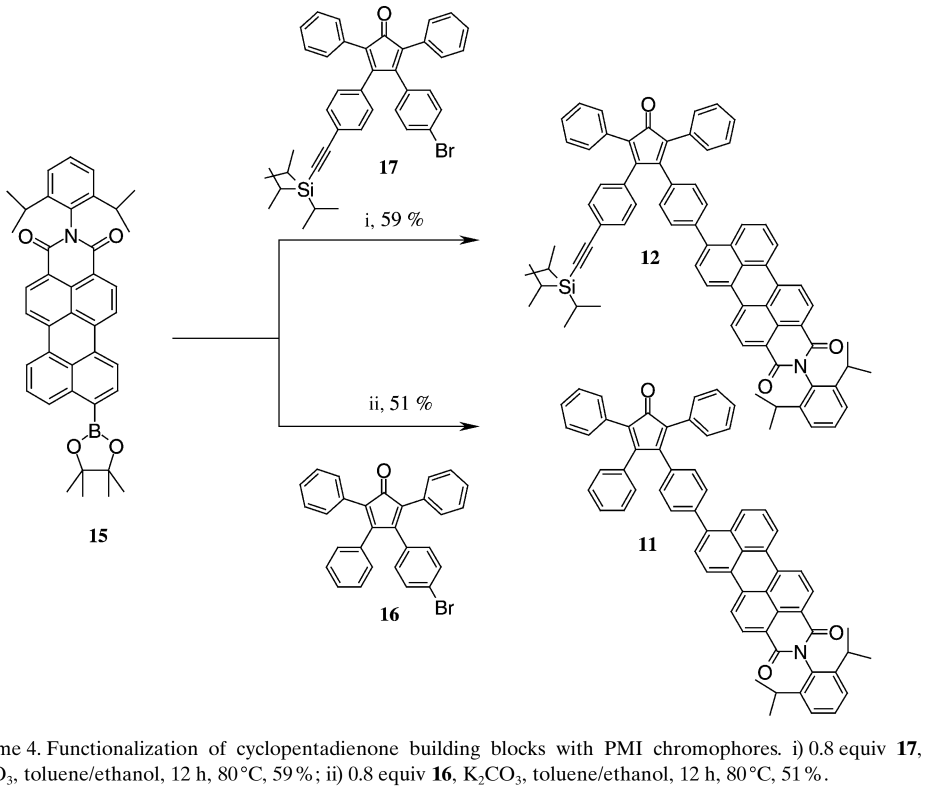
tional triisopropylsilyl-protected ethynyl unit which leads to further dendrimer growth. The NMI-substituted dendron **13** can also serve as terminating agent.

The synthesis of cyclopentadienones and dendrons carrying one PMI dye has already briefly been discussed in the literature.[34] The key building block is the boronic ester of a PMI chromophore (**15**), which is accessible by palladium-catalyzed coupling of commercially available bispinacolatodiboron and the corresponding bromo-substituted chromophore[42] in a modification of the Suzuki procedure[43] (Scheme 4).

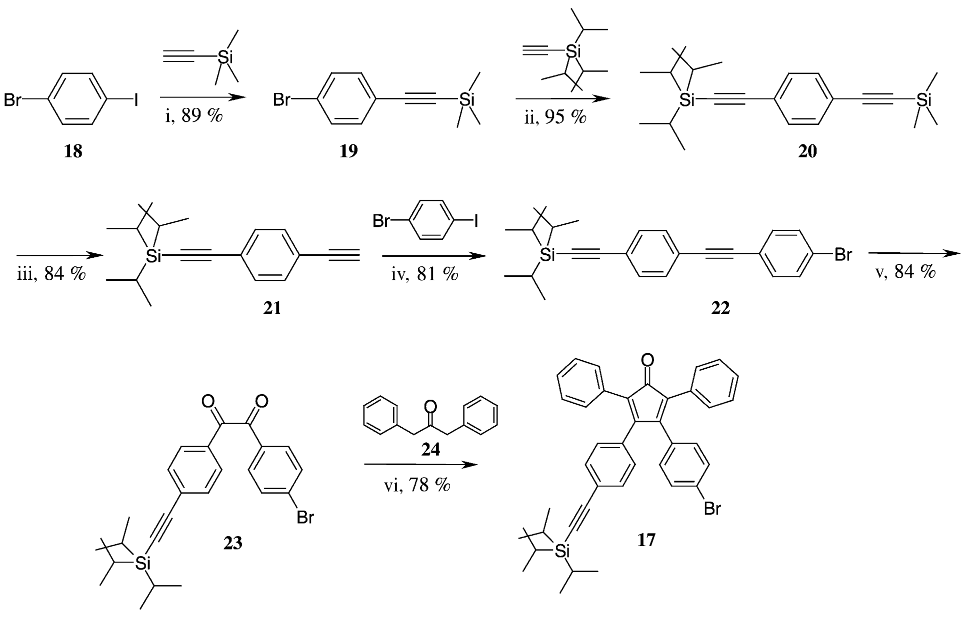
This mild procedure particularly tolerates already existing functional groups such as esters, ketones, and cyano or nitro substituents, in contrast to conventional methods involving lithiation reactions. The reaction proceeded in high yield in dioxane and potassium acetate at 80 °C with exclusion of light. In some cases homocoupling of two PMI chromophores can occur. However, by-products were separated by column chromatography with dichloromethane. Compound **15** was then treated with bromo-substituted tetraphenylcyclopentadienone **16** or **17** in a palladium-catalyzed coupling reaction under Suzuki conditions[44,45] (Scheme 4). By using a 1.5-fold excess of **15**, catalytic amounts of [Pd(PPh$_3$)$_4$], and caustic conditions (2 N K$_2$CO$_3$) in a two-phase system (toluene/ethanol) at 85 °C, both **11** and **12** were obtained in a single reaction step. Purification by column chromatography with dichloromethane gave the cyclopentadienones **11** and **12** in 51 and 59 % yield, respectively. A further chromatography step with dichloromethane/petroleum ether (1.5/1) was sometimes necessary to achieve sufficient purity. The synthesis of a cyclopentadienone branching agent such as **17** has not been described before. We achieved the synthesis of **17** in six steps and high yield (Scheme 5).

1-Bromo-4-iodobenzene (**18**) underwent selective coupling with trimethylsilylacetylene (TMS-acetylene) at room temperature in toluene/triethylamine (1/3) according to a literature procedure.[46] Thereafter, Sonogashira coupling of **19** with TiPS-acetylene proceeded under the same reaction conditions but at a temperature above 70 °C to give **20** in 95 % yield. Compound **20** bears two different ethynyl protecting groups, whereby only the TMS group is sensitive to caustic conditions. Thus, **20** could selectively be deprotected by using 1 M potassium hydroxide in THF, as already described.[46] Compound **21** could be subjected to a further Sonogashira coupling with 1-bromo-4-iodobenzene to give diphenylacetylene **22**. After purification by column chromatography with petroleum ether as eluent **22** was obtained as a colorless solid in 81 % yield. The next reaction step involved the oxidation of **22** with I$_2$ in DMSO at 190 °C over 12 h. This reaction proceeded in high yield, whereupon benzil derivative **23** was isolated as a bright yellow solid. The last step was based on a Knoevenagel condensation of **23** with 1.1 equivalents of 1,3-diphenylacetone (**24**) and tetrabutylamonium hydroxide in ethanol at 80 °C (15 min).[47] After cooling, a dark precipitate was formed, which was collected by filtration, washed with a small amount of cold ethanol, and purified by column chromatography with dichloromethane/petroleum ether (1/1) to give **17** as a dark purple solid in 78 % yield. A key feature is that the bromo substituent of **17** allows a wide variety of functional groups to be introduced by palladium-catalyzed coupling with, for example, boronic acid, as was shown above (Scheme 4).

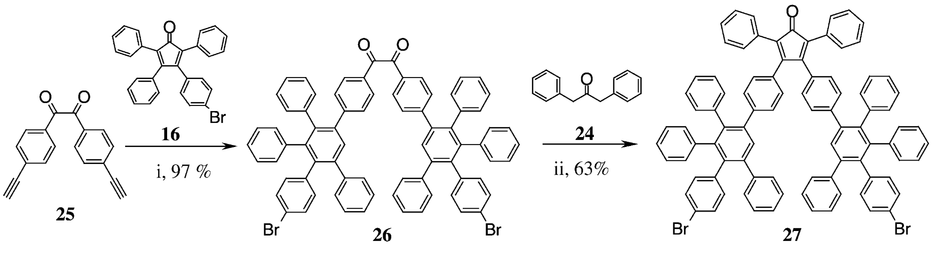
An important compound for the preparation of polyphenylene dendrons was 4,4′-diethynylbenzil (**25**), whose synthesis was previously published by our group.[34,37] Compound **25** was treated with an excess of 3-(4-bromophenyl)-2,4,5-triphenylcyclopentadienone (**16**) in a Diels–Alder cycloaddition in refluxing *o*-xylene (Scheme 6). Hereby, benzil **26** was formed as a pale yellow amorphous powder in high yield (97 %). Purification was achieved by column chromatography or simple precipitation from methanol. The latter method reduced the overall yield by about 10 %. Subsequent Knoevenagel condensation of **26** with 1,3-diphenylacetone (**24**) in toluene in the presence of tetrabutylammonium hydroxide at 100 °C (50 min) gave the corresponding dendron **27** in 63 % yield.



Scheme 4. Functionalization of cyclopentadienone building blocks with PMI chromophores. i) 0.8 equiv **17**, K$_2$CO$_3$, toluene/ethanol, 12 h, 80 °C, 59 %; ii) 0.8 equiv **16**, K$_2$CO$_3$, toluene/ethanol, 12 h, 80 °C, 51 %.



Scheme 5. Synthesis of a building block for the introduction of functionalities into the dendritic scaffold. i) 1.25 equiv trimethylsilylacetylene, 0.1 equiv triphenylphosphane, 0.1 equiv copper(I) iodide, 0.05 equiv $[PdCl_2(PPh_3)_2]$ toluene/triethylamine (1/3), 12 h, RT, 89 %; ii) 1.25 equiv triisopropylsilylacetylene, 0.1 equiv triphenylphosphane, 0.1 equiv cooper(I) iodide, 0.05 equiv $[PdCl_2(PPh_3)_2]$, toluene/triethylamine (1/3), 12 h, 80 °C, 95 %; iii) 2 N potassium hydroxide, ethanol, 3 h, RT, 84 %; iv) 1.25 equiv 4-bromoiodobenzene, 0.1 equiv triphenylphosphane, 0.1 equiv cooper(I)iodide, 0.05 equiv $[PdCl_2(PPh_3)_2]$ catalyst, toluene/triethylamine (1/3), 12 h, RT, 81 %; v) iodine, DMSO, 190 °C, 12 h, 84 %; vi) 1 equiv **24**, tetrabutylammonium hydroxide, toluene, 15 min, 90 °C, 78 %.



Scheme 6. Synthesis of a polyphenylene dendron carrying two bromo substituents. i) 3 equiv **16**, *o*-xylene, 12 h, 170 °C, 97 %; ii) 1.1 equiv **24**, tetrabutylammonium hydroxide, toluene, 50 min, 90 °C, 63 %.

Finally, the introduction of the chromophore units was achieved by Suzuki coupling of **27** and a 1.5-fold excess of the appropriate chromophore **15** or **28** with catalytic amounts of $[Pd(PPh_3)_4]$ under caustic conditions (2 N K_2CO_3), as described before (Scheme 7). After column chromatography with dichloromethane the twofold PMI- and NMI-substituted dendrons **13** and **14**, respectively, were isolated in moderate yields (42–43 %) as a dark red (PMI compound) and brownish solids (NMI dendron).

Synthesis of multichromophores: In the last step, TDI core **10** was treated with five equivalents of PMI-cyclopentadienone building block **11** in *o*-xylene at 170 °C (Scheme 8). After 12 h the crude product was purified by column chromatography with dichloromethane to give first-generation multichromophore **29** bearing four PMI substituents at the periphery. Second-generation multichromophore **30** was obtained by reaction of TDI core **10** with 10 equivalents of PMI-substituted dendron **14** in *o*-xylene at 170 °C over three days. Compound **30** was purified by column chromatography with acetone. After separation of the starting material, **30** was eluted with THF. Pure dyad **30** was obtained as a purple solid in 83 % yield. For the synthesis of the triad **32** a multistep reaction was necessary. First TDI core **10** was treated with five equivalents of PMI-labeled branching agent **12** at 170 °C over 12 h. Thereafter, the crude product was separated by column chromatography with dichloromethane to give **31a** in 90 % yield. Compound **31a** has nearly the same chemical structure as **29**, the only difference being four TiPS-protected ethynyl groups at the periphery of the dendrimer. These protecting groups could be cleaved by applying one equivalent of tetrabutylammonium fluoride in THF. After four minutes, the reaction was quenched by adding water, and the whole reaction mixture was washed with water and dichloromethane. Pure **31b** was obtained in nearly quantitative yield after filtration through a short pad of silica gel with dichloromethane as solvent. This first-generation polyphenylene dendrimer bearing two different types of chromophores can now undergo a further reaction with dendron **13** carrying two NMI substituents. This reaction proceeded in a *o*-xylene/diphenyl ether (1/1) at 195 °C over three days. Workup again required column chromatography, with acetone as an eluent. In this way, the multichromophore **32** was obtained as a dark purple solid in 63 % yield.

Typical MALDI-TOF mass spectra are shown in Figure 4. The MALDI-TOF spectra of **30** and **32** (matrix: dithranol, addition of silver triflate; Figure 4) show only one peak at *m*/*z* 9703 and *m*/*z* 12165, respectively, in accordance with the molecular mass of the $[M+Ag]^+$ cluster. The perfect agreement between the calculated and experimentally determined *m*/*z* ratios for different generations of dendrimers confirms their monodispersity.

Figure 5 shows the ^1H NMR spectrum of **29**. Well-separated and assignable signals are obtained for the aliphatic CH and $(CH_3)_2$ groups of PMI and the TDI core molecule, the aromatic protons of the bay region of the PMI and TDI chromophores, and the H-4 protons of the pentaphenyl groups of the dendrimer branches. The signals of the other aromatic protons of the chromophores and the polyphenylene dendrons can not be distinguished due to strong overlap. The number of aromatic signals is higher for high-generation dendrimers, and unstructured signals are obtained in the aromatic region between $\delta = 6.6$ and 7.4 ppm.

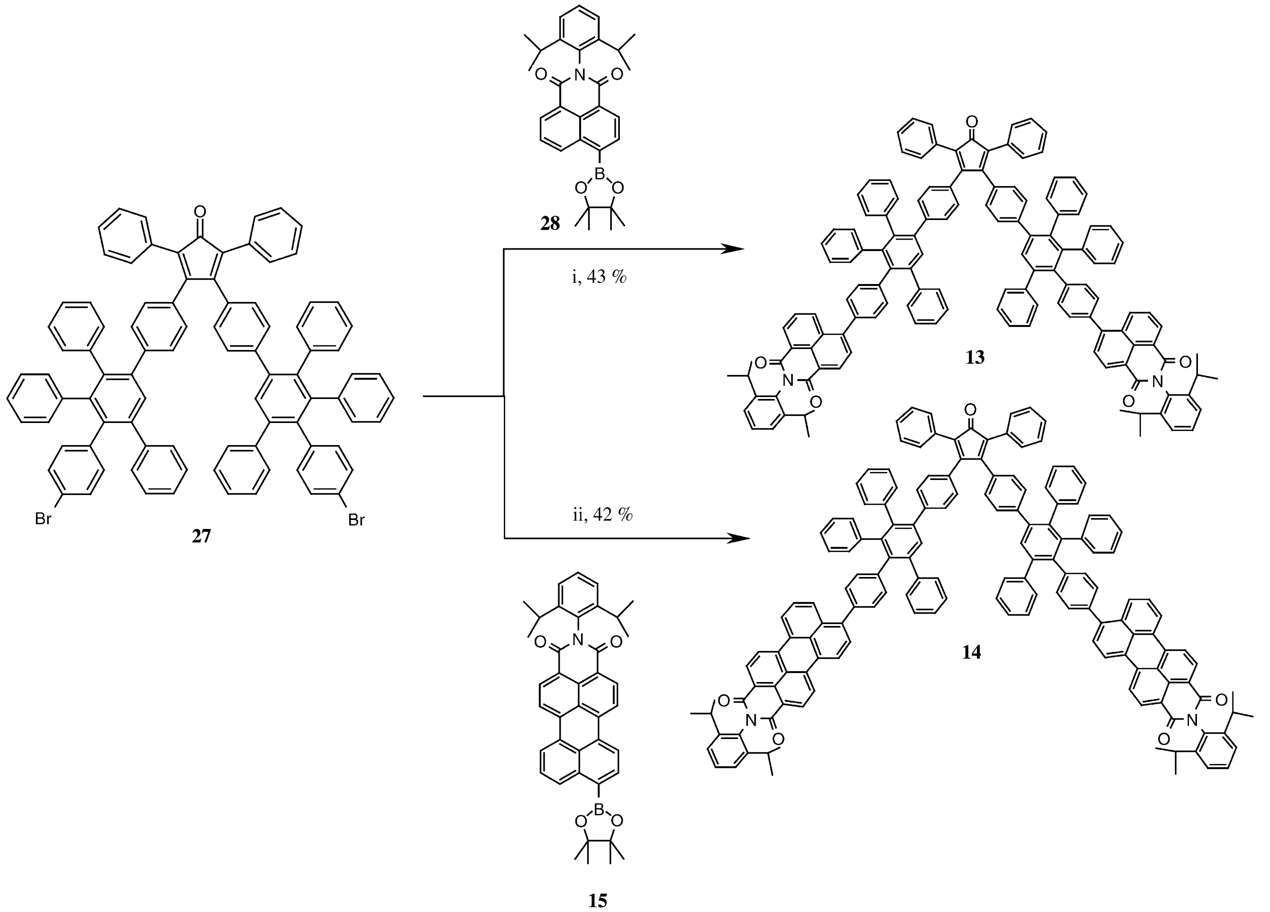
This is also true of the ^{1}H NMR spectrum of **32** (Figure 6). Here, the aforementioned characteristic signals of protons in the bay region of the PMI and TDI chromophores are still clearly assignable. Furthermore, additional signal groups at $\delta = 7.87$ and 7.79 ppm are detected, which could correspond to the protons of the NMI chromophores or to the protons of the pentaphenyl groups of the dendrimer branches. Although the dendritic triad **32** contains over 500 protons, characteristic signals of different chromophore substituents are still evident.

Isolation of chromophore sites at the periphery: Figure 7 shows the absorption spectra of dyads **29** and **30**, TDI chromophore **10**, and a series of polyphenylene dendrimers carrying a one, four (**4**, TdPMI$_4$, Scheme 1) and eight PMI chromophores (**5**, TdPMI$_8$, Scheme 1) at the periphery, whose synthesis has already been described by us.[34] TdPMI$_4$ absorbs at 502 ($\varepsilon = 119\,200$) and 526 nm ($\varepsilon = 119\,200\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), whereas TDI chromophore **10** absorbs at 667 nm ($\varepsilon = 87\,125\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$, Table 1). The dyad **29** displays

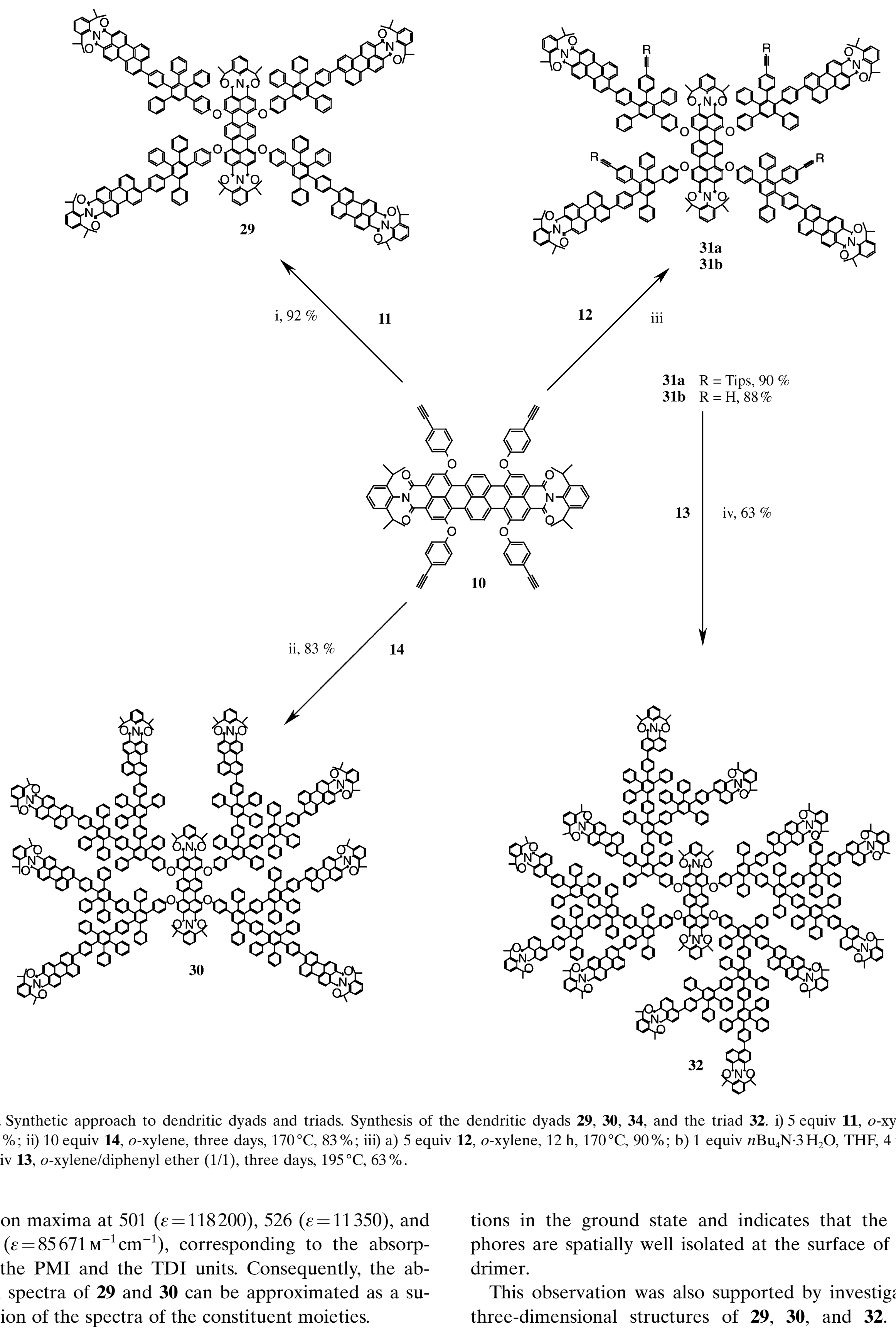
Table 1. λ_{max} [nm] and ε [$\mathrm{M}^{-1}\mathrm{cm}^{-1}$] of dendrimers **29**, **30**, **34, 32**, and the TDI core **10** in toluene.

Compound	Absorption λ_{max} [nm] (ε [$\mathrm{M}^{-1}\mathrm{cm}^{-1}$]) NMI	PMI	TDI	Emission λ_{max} [nm]
Td*G1*PMI$_1$		501 (42 200)		553 (PMI)[b,d]
		527 (41 400)		
4	–	502 (119 200)	–	556 (PMI)[b,d]
Td*G1*PMI$_4$		526 (119 200)		
5	-	501 (218 300)	–	557 (PMI)[b,d]
Td*G2*PMI$_8$		525 (216 500)		
10	–	–	667	698 (TDI)[c]
			(87 125)	
29	–	501 (118 200)	675	559w (PMI)[b]
		526 (111 350)	(85 671)	701s (TDI)
30	–	500 (227 270)	674	557w (PMI)[b]
		524 (222 680)	(89 990)	702s (TDI)
32	370 (178 854)	501 (134 576)	676	432w (NMI)[a]
		526 (136 565)	(98 462)	

[a] λ_{exc} at 370 nm. [b] $\lambda_{exc} = 488$ nm. [c] $\lambda_{exc} = 675$ nm. [d] Fluorescence quantum yield of 0.98 in toluene.



Scheme 7. Functionalization of a polyphenylene dendron with PMI and NMI substituents. i) 3 equiv **28**, K_2CO_3, toluene/ethanol, 12 h, 80 °C, 43 %; ii) 3 equiv **15**, K_2CO_3, toluene/ethanol, 12 h, 80 °C, 42 %.



Scheme 8. Synthetic approach to dendritic dyads and triads. Synthesis of the dendritic dyads **29**, **30**, **34**, and the triad **32**. i) 5 equiv **11**, *o*-xylene, 12 h, 170 °C, 92 %; ii) 10 equiv **14**, *o*-xylene, three days, 170 °C, 83 %; iii) a) 5 equiv **12**, *o*-xylene, 12 h, 170 °C, 90 %; b) 1 equiv $n\mathrm{Bu_4N{\cdot}3\,H_2O}$, THF, 4 min, 88 %; iv) 16 equiv **13**, *o*-xylene/diphenyl ether (1/1), three days, 195 °C, 63 %.

absorption maxima at 501 ($\varepsilon = 118200$), 526 ($\varepsilon = 11350$), and 675 nm ($\varepsilon = 85671\,\mathrm{M^{-1}cm^{-1}}$), corresponding to the absorption of the PMI and the TDI units. Consequently, the absorption spectra of **29** and **30** can be approximated as a superposition of the spectra of the constituent moieties.

A direct correlation exists between the number of chromophores and the extinction coefficients at the absorption maximum (inset to Figure 7). This behavior can be attributed to the absence of intramolecular chromophore interactions in the ground state and indicates that the chromophores are spatially well isolated at the surface of the dendrimer.

This observation was also supported by investigating the three-dimensional structures of **29**, **30**, and **32**. Figure 8 shows the minimized structure[51] of **30** with views of the imide structure (middle) and bay region (right) of the central TDI chromophore. It is evident that the terminal PMI chromophores are located exclusively at the periphery, spa-

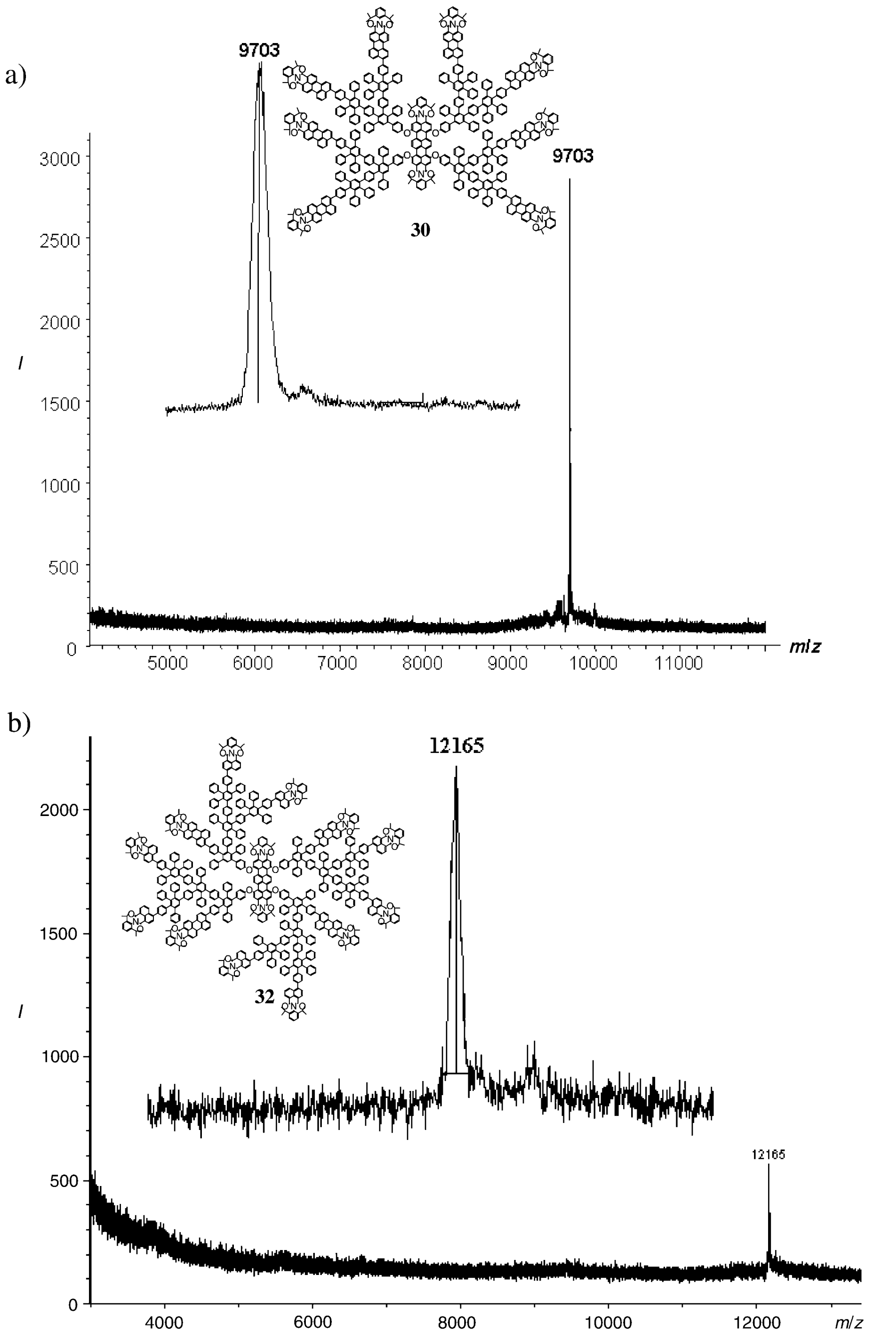


Figure 4. a) MALDI-TOF mass spectrum of second-generation polyphenylene dyad **30** in the presence of silver triflate (*m*/*z* 9703 $[M+\mathrm{Ag}]^+$; calcd for **30**: 9594). b) MALDI-TOF mass spectrum of triad **32** in the presence of silver triflate (*m*/*z* 12165 $[M+\mathrm{Ag}]^+$; calcd for **32**: 12053).

tially well-isolated from each other. Furthermore, it was reported previously that the dynamics of peripheral groups in high-generation polyphenylene dendrimers are strongly reduced due to the formation of a dense shell of phenyl rings at the outer sphere of the dendrimer.[52] Therefore, the probability that two chromophores come close enough to form excimerlike species is low. Consequently, even for polyphenylene dendrimers carrying a high number of terminal chromophores, nearly quantitative fluorescence quantum yields have been determined (Table 1), which makes these molecules highly fluorescent "superchromophores".

Vectorial energy transfer: The synthesis of multichromophores containing different types of chromophores enables the investigation of energy transfer processes between these chromophores. After exciting the PMI chromophores of dyad **29** at 488 nm a strong emission at 701 nm occurs (Figure 9), which is due to efficient energy transfer from the PMI chromophores towards the TDI center. The emission maxima of the dyads **29** and **30** are given in Table 1. This energy transfer proceeds by the Förster mechanism[48,49] and has already been investigated in solution[35] and at the single-molecule level.[50]

Triad **32** bears a TDI chromophore in the center, four PMI chromophores in the scaffold, and eight NMI chromophores at the periphery. The absorption spectrum of **32** was discussed before[35] and it was pointed out that this multichromophore absorbs over the whole visible spectrum with well-separated absorption envelopes. This fact is of special importance with regard to selective excitation of different chromophore units of the multichromophore. It was shown that excitation of the NMI chromophores at the periphery of the dendrimer results in weak emissions of the NMI and PMI groups but in strong emission from the TDI core[35] (Figure 9).

This behavior has been attributed to efficient vectorial energy transfer from the NMI donor chromophores at the periphery via the PMI chromophores in the scaffold towards the TDI center of **32**. For vectorial transduction of excitation energy, formation of an energy gradient is required, which has been achieved by spatial localization of the chromophore units by using a polyphenylene dendrimer scaffold as a stiff matrix.

The great importance of the PMI chromophores in the dendritic scaffold for energy transfer becomes obvious when the emission spectrum of an NMI chromophore is compared with the absorption spectrum of a TDI chromophore, since both spectra reveal only a small spectral overlap. However, an efficient energy transfer according to the Förster mecha-

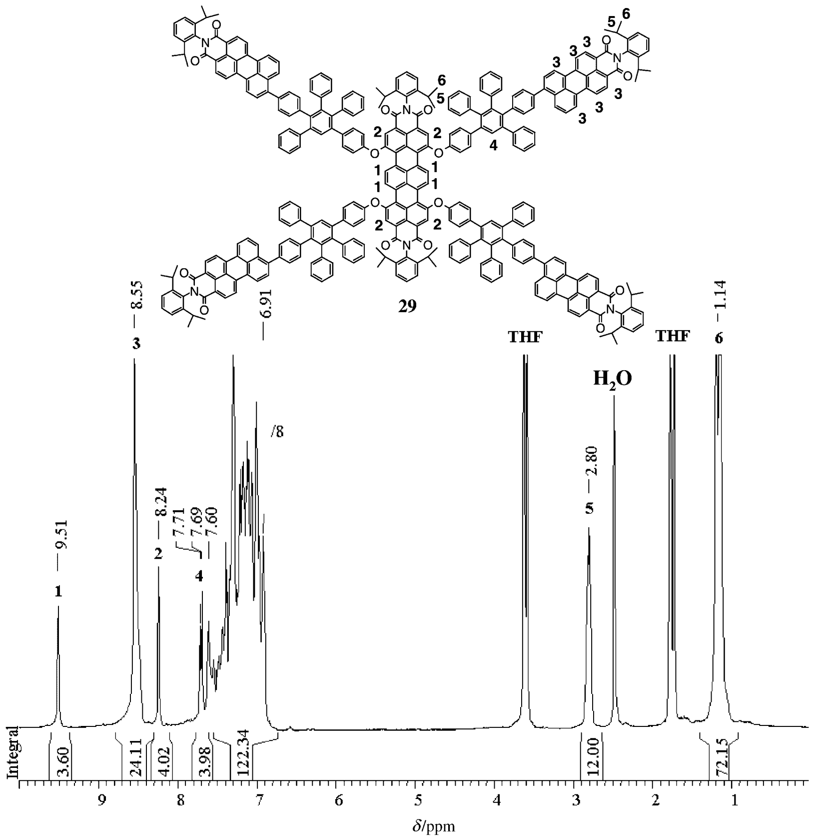


Figure 5. 500 MHz ^{1}H NMR spectrum of **29** in [D$_8$]THF at 298 K.

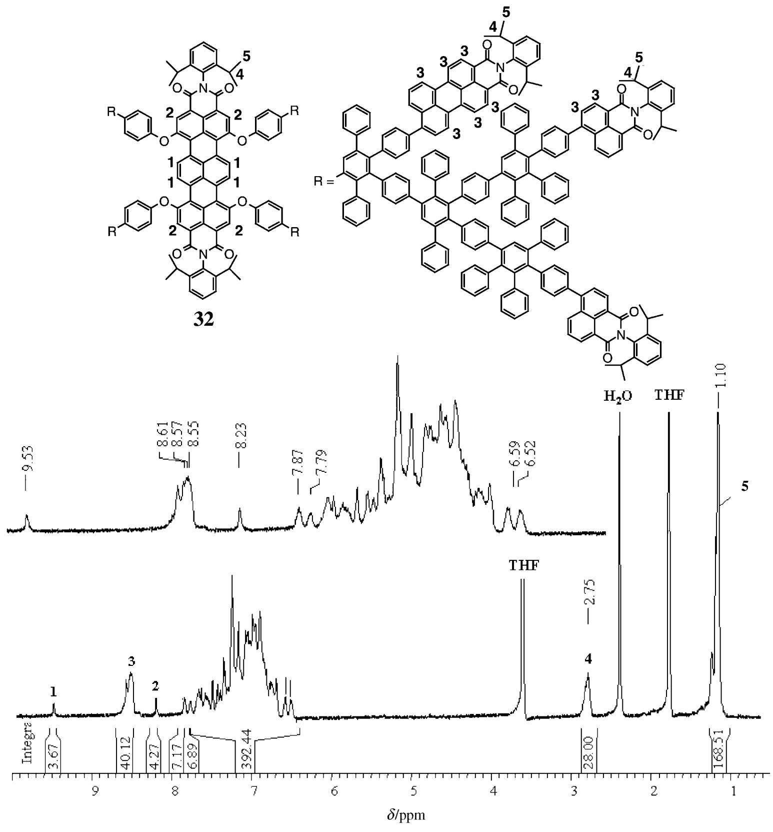


Figure 6. 500 MHz ^{1}H NMR spectrum of triad **32** in [D$_8$]THF at 298 K.

nism[49,50] requires a sufficient spectral overlap of the constituent chromophores. Therefore, the PMI chromophores in the dendritic scaffold play an essential role in transferring excitation energy from the NMI donors towards the TDI acceptor. In this way, it is a key feature that the well-separated peripheral chromophores allow the transfer of excitation energy to the center without sustaining losses due to the formation of excimers.

Conclusion and Outlook

We have presented a new synthetic approach to dendritic multichromophores containing up to three different rylene chromophores at distinct positions within the dendrimer. A key step was the development of new building blocks which open up the unique possibility to incorporate functionalities in the center, scaffold, and periphery of the dendrimer. In this way, the herein-reported building-block chemistry allows the synthesis of a large variety of different multichromophores in which the number of chromophores and the interchromophore distances can easily be changed. To realize this concept, two different dyads **29** and **30** containing a TDI core and a PMI periphery were prepared. With regard to synthesis the dendritic triad **32** consisting of NMI chromophores at the periphery, PMI chromophores within the dendritic scaffold, and a TDI chromophore at the center is the first example of a dendrimer bearing three different types of chromophores. As a special feature, the chromophores with different absorption and emission wavelengths are localized precisely and form an energy gradient from the periphery towards the center. The occurrence of energy transfer was shown for the dyads and

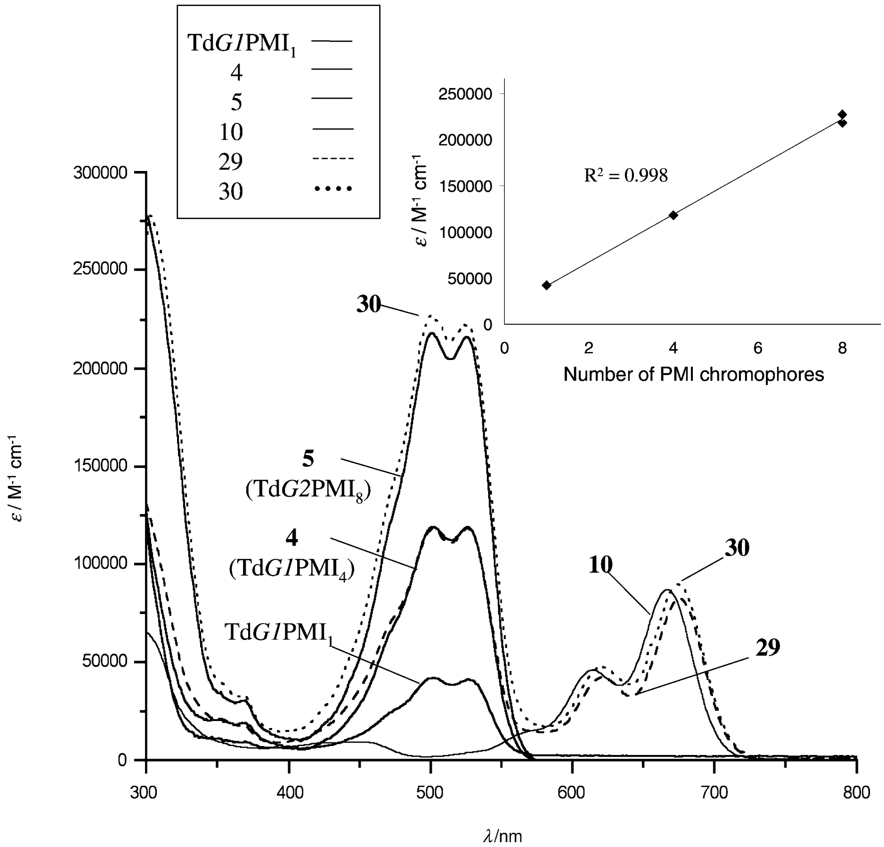
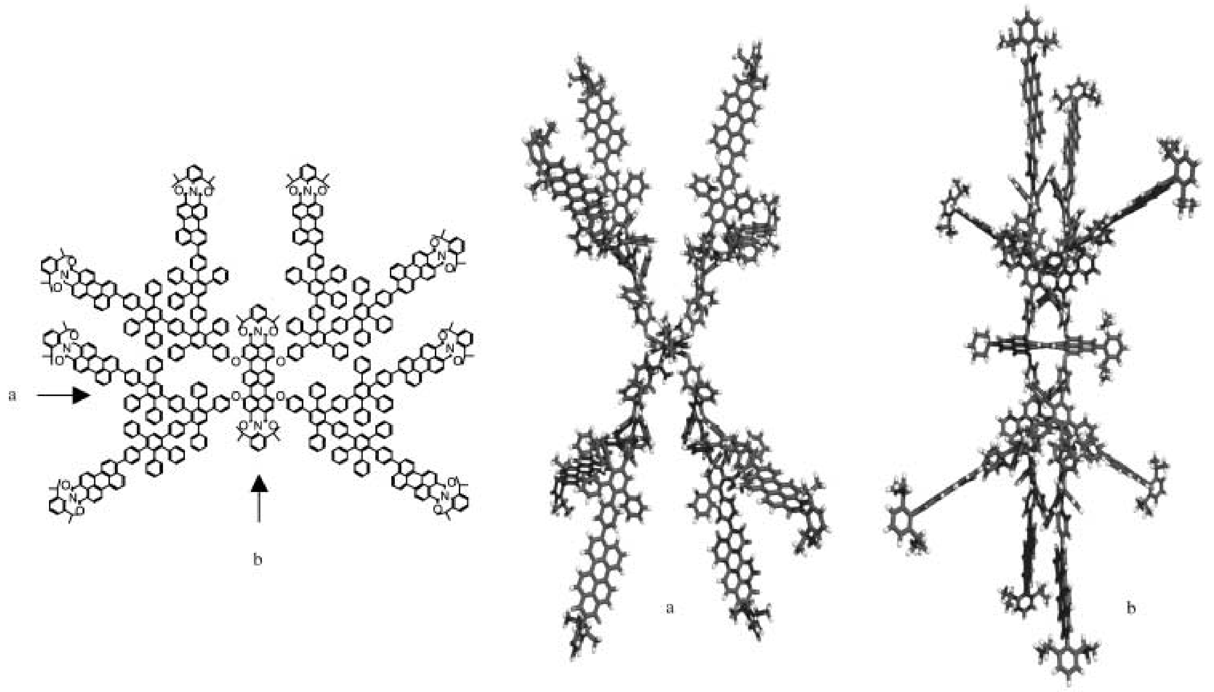


Figure 7. Absorption spectra of a series of polyphenylene dendrimers based on a tetrahedral core bearing one (Td*G1*PMI$_1$), four (**4**, Td*G1*PMI$_4$), and eight (**5**, Td*G2*PMI$_8$) PMI chromophores at the periphery, as well as of the TDI core **10** and the dyads **29** (dashed line) and **30** (dotted line) in toluene. Inset: Number of PMI chromophores of the dendrimer versus the extinction coefficient at the first absorption maximum of the PMI unit and correlation function with correlation factor.

for the triad. In case of the dendritic triad, vectorial energy transfer proceeds stepwise from the chromophores at the periphery over the functionalized scaffold towards the center. Time-resolved fluorescence spectroscopy measurements, which are currently underway, will provide deeper insight into the energy-transfer processes taking place in such a complex but still highly ordered macromolecule as the herein-presented triad.

The chief merits of these new dendrimers are high spatial resolution of different types of chromophores by a stiff backbone which, due to its structure, isolates the chromophores and does not participate in energy transfer. Due to the high photochemical stability of the chromophore units, the dendritic dyads and triad reported herein can be used for single-molecule spectroscopy, which could give new insight into interactions of chromophores in close proximity and defined environment. Thus, these novel dendrimers



Length = 7.8 nm, Width = 5.8 nm

Figure 8. Left: 2D structure of **30**. Middle: 3D structure of **30** with view over a) the imide structure and b) the bay-region of the central TDI-chromophore.[51]

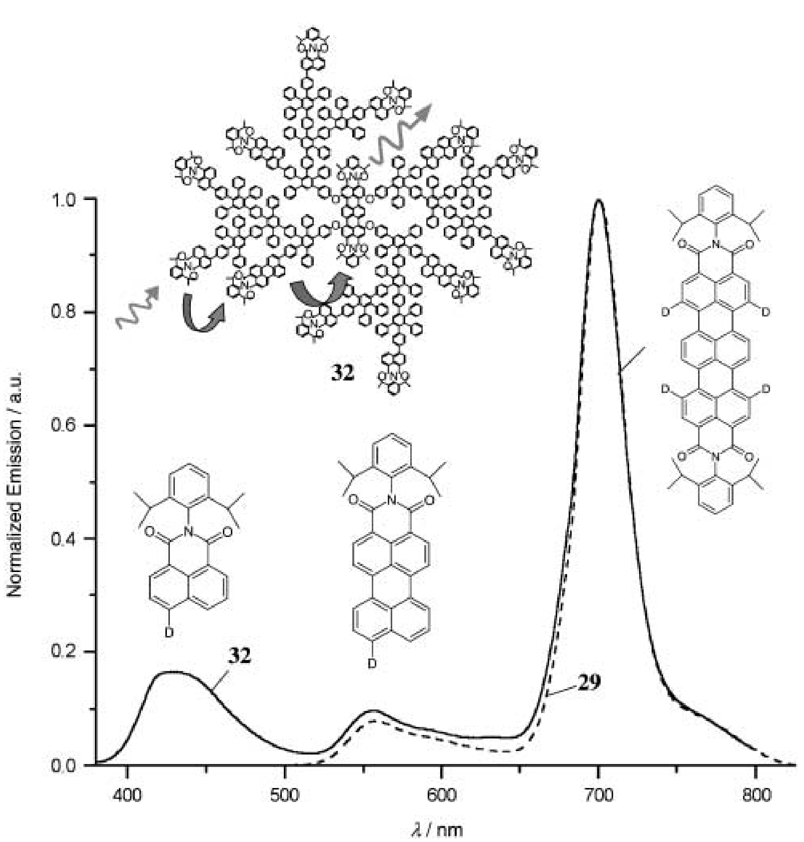


Figure 9. Emission spectra of dyad **29** ($\lambda_{exc}=488$ nm, dashed line) and triad **32** ($\lambda_{exc}=370$ nm, straight line) in toluene, and chemical structure of the chromophore units at their emission area (D marks the positions at which the polyphenylene dendrons are attached to the chromophore).

are attractive candidates for a better understanding of photophysical processes such as those observed in natural multichromophore arrays. Since the dendritic triad absorbs light energy over the whole visible spectrum, this compound is currently being investigated with a view to its suitability for the development of novel emissive layers for the design of photonic devices.

Experimental Section

General: The solvents used were of commercial grade; THF was dried over potassium; toluene was distilled from sodium. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 (500 and 125 MHz, respectively) or Bruker AMX 300 (300 and 75 MHz, respectively). Mass spectra were recorded on a Bruker MALDI-TOF spectrometer. UV/Vis data were obtained on a Perkin-Elmer Lambda 9, and fluorescence spectra were measured on a SPEX Fluorolog 2 Type 212 spectrometer. $[Pd(PPh_3)_4]$ and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) catalysts were purchased from ABCR.

***N,N′*-Bis(2,6-diisopropylphenyl)-1,6,9,13-tetrabromoterrylen-3,4:11,12-tetracarbooxdiimide (7)**: *N,N′*-Bis(2,6-diisopropylphenyl)terrylen-3,4:11,12-tertacarboxdiimide (**6**, 834 mg, 1 mmol) was dissolved in chloroform (50 mL). Then bromine (5 mmol) was added and the reaction mixture was heated to reflux for 12 h with exclusion of light. Thereafter, the mixture was flushed with nitrogen to remove remaining bromine, and the solvent was evaporated under vacuum. Column chromatography on silica gel with dichloromethane as eluent afforded **7** (900 mg, 75 %) as a blue solid, m.p. >300 °C; MS (FD, 8 kV): *m*/*z* (%): 1145.3 $[M]^+$; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.52$ (s, 2H), 8.92 (s, 2H), 7.44 (t, $^3J(H,H)=7.78$ Hz, 2H), 7.29 (d, $^3J(H,H)=7.94$ Hz, 4H), 2.70 (m, 4H), 1.16 ppm (d, $^3J(H,H)=6.71$ Hz, 24H); ^{13}C NMR (67 MHz, CD_2Cl_2): $\delta=161.4$, 144.93, 137.7, 137.4, 133.5, 129.6, 129.4, 128.4, 128.3, 127.1, 126.12, 123.3, 120.9, 119.7, 28.8, 23.5 ppm; IR (KBr pellet): $\tilde{\nu}=$ 2963, 2927, 2867, 1711 (C=O), 1672 (C=O), 1583, 1465, 1389, 1347, 1308, 1236, 1172, 1198, 846, 810 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon)=656$ (93325), 605 (46773), 559 nm (15848 $M^{-1}cm^{-1}$); Elemental analysis (%) calcd for $C_{58}H_{42}N_2O_4Br_4$: C, 60.55; H, 3.68; N, 2.43; Found: C, 60.52; H, 3.69; N, 2.44.

8: Compound **7** (224 mg, 0.195 mmol), 4-iodophenol (644 mg, 2.925 mmol), and K_2CO_3 (202 mg, 1.46 mmol) were heated in *N*-methylpyrrolidone (34 mL) at 90 °C under argon for 17 h. After cooling to room temperature the reaction mixture was poured into HCl (2 N, 100 mL). The crude solid was separated under vacuum, dissolved in dichloromethane, and dried over $MgSO_4$. Column chromatography on silica gel with dichloromethane as eluent gave **8** (182 mg, yield: 55 %) as a blue solid, m.p. >300 °C; MS (FD, 8 kV): *m*/*z* (%): 1707 $[M]^+$, 853 $[M]^{2+}$, (calcd for $C_{82}H_{58}I_4N_2O_8$: 1707.00); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 363 K): $\delta=9.29$ (s, 4H), 8.18 (s, 4H), 7.66 (d, $^3J(H,H)=8.85$ Hz, 8H), 7.37 (t, $^3J(H,H)=7.65$ Hz, 2H), 7.21 (d, $^3J(H,H)=7.65$ Hz, 4H), 6.91 (d, $^3J(H,H)=8.85$ Hz, 8H), 2.58 (sept., $^3J(H,H)=6.7$ Hz, 4H), 1.15 (s, 84H), 1.05 (d, $^3J(H,H)=6.75$ Hz, 24H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 363 K): $\delta=161.4$, 154.7, 153.1, 144.9, 138.8, 138.6, 137.7, 137.4, 133.5, 130.4, 129.9, 129.6, 128.5, 128.3, 127.9, 127.1, 126.1, 125.4, 123.3, 122.5, 121.7, 120.4, 119.7, 28.3, 23.1 ppm; IR (KBr pellet): $\tilde{\nu}=3052$, 3023, 2962, 2869, 1702, 1664, 1590, 1498, 1357, 1243, 1176, 1072, 840, 811, 754, 700 cm^{-1}; Elemental analysis (%) calcd for $C_{82}H_{58}I_4N_2O_8$: C, 57.70; H, 3.42; N, 1.64; Found: C, 57.61; H, 3.36; N, 1.62.

9: Compound **8** (181 mg, 0.106 mmol), triisopropylsilylacetylene (0.12 mL, 0.530 mmol), copper(I) iodide (8.1 mg, 0.0424 mmol), triphenylphosphane (11 mg, 0.0424 mmol), and $[PdCl_2(PPh_3)_2]$ (15 mg, 0.0212 mmol) were dissolved in dry THF (7 mL) and dry triethylamine (2.3 mL) at RT under argon with exclusion of light. After 24 h, the reaction mixture was poured into a solution consisting of distilled water (50 mL) and hydrochloric acid (25 mL, 2 N) and stirred for a few minutes. Then, the mixture was extracted several times with dichloromethane and then with a saturated solution of ammonium chloride. The organic phases were washed with distilled water, dried over $MgSO_4$, and purified by column chromatography with dichloromethane/petroleum ether as eluent (1/1, $R_f=0.94$). Mixed fractions were separated by further column chromatography with petroleum ether/dichloromethane (1.5/1, $R_f=0.32$) to afford **9** (115 mg, 60 %) as a blue solid, m.p. >300 °C; MS (FD, 8 kV) *m*/*z* (%): 1925 $[M]^+$, 962 $[M]^{2+}$ (calcd for $C_{126}H_{142}N_2O_8Si_4$: 1925); ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=9.31$ (s, 4H), 8.22 (s, 4H), 7.44 (d, $^3J(H,H)=8.55$ Hz, 8H), 7.40 (t, $^3J(H,H)=7.95$ Hz, 2H), 7.23 (d, $^3J(H,H)=7.95$ Hz, 4H), 7.03 (d, $^3J(H,H)=9.2$ Hz, 8H), 2.61 (sept., $^3J(H,H)=6.7$ Hz, 4H), 1.15 (s, 84H), 1.04 (d, $^3J(H,H)=$ 6.7 Hz, 24H); ^{13}C NMR (75 MHz, $[D_2]CD_2Cl_2$): $\delta=163.00$ (q, C=O), 156.34 (q), 153.61 (q), 146.11(q), 134.25 (t), 131.25 (q), 131.02 (q), 129.59 (t), 129.43 (q), 129.06 (t), 128.87 (q), 126.97 (q), 124.95 (t), 124.15 (t), 123.91 (q), 122.62 (q), 118.7 (t), 118.23 (q), 107.79 (q, C ethynyl), 90.96 (CH ethynyl), 29.17 (t, $CHCH_3$), 23.78 (t, $CHCH_3$), 17.57 (CH TiPS), 12.44 (CH_3-TiPS); Elemental analysis (%) calcd for $C_{126}H_{142}N_2O_8Si_4$: C, 78.62; H, 7.44; N, 1.46; Found: C, 78.73; H, 7.39; N, 1.44.

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10: Compound **9** (211 mg, 0.191 mmol) was dissolved in freshly distilled THF (12 mL) and flushed with argon for 10 min. Then, a solution of $Bu_4NF{\cdot}3H_2O$ (60 mg, 0.191 mmol) in dry THF (2 mL) was added. The reaction mixture immediately turned dark, and the progress of the reaction was monitored by TLC with petroleum ether/dichloromethane (1/1, $R_f = 0.71$). After 4 min the reaction was finished, and distilled water (20 mL) was added. Then the crude mixture was extracted with dichloromethane and washed with water. The organic phases were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Column chromatography with dichloromethane/petroleum ether (1/1) gave **9** (226 mg, 91 %) as a dark blue solid, m.p. >300 °C; MS (FD, 8 kV): $m/z = 1299$ $[M]^+$ (calcd for $C_{90}H_{62}N_2O_8 = 1299$ g/mol); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 9.30$ (s, 4H), 8.23 (s, 4H), 7.44 (d, $^3J(H,H) = 8.55$ Hz, 8H), 7.40 (t, $^3J(H,H) = 7.95$ Hz, 2H), 7.24 (d, $^3J(H,H) = 7.95$ Hz, 4H), 7.03 (d, $^3J(H,H) = 9.2$ Hz, 8H), 3.04 (s, 4H), 2.62 (sept., $^3J(H,H) = 6.7$ Hz, 4H), 1.04 (d, $^3J(H,H) = 6.7$ Hz, 24H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 163.00$ (q, C=O), 156.34 (q), 153.61 (q), 146.11(q), 134.25 (t), 131.25 (q), 131.02 (q), 129.59 (t), 129.43 (q), 129.06 (t), 128.87 (q), 126.97 (q), 124.95 (t), 124.15 (t), 123.91 (q), 122.62 (q), 118.7 (t), 118.23 (q), 82.70 (q, C ethynyl), 77.28 (CH ethynyl), 29.17 (t, $CHCH_3$), 23.78 (t, $CHCH_3$); UV/Vis ($CHCl_3$): λ_{max} (ε) = 665 nm (88865 $M^{-1}cm^{-1}$); IR (KBr pellet): $\tilde{\nu} = 2921$ (s), 2850 (s), 1702, 1660, 1589, 1504, 1463, 1328, 1278, 1207 cm^{-1}; Elemental analysis (%) calcd for $C_{90}H_{62}N_2O_8$: C, 83.19; H, 4.81; N, 2.16; Found: C, 83.01; H, 4.78; N, 2.13.

12: Compound **17** (1 g, 1.44 mmol) and **15** (0.450 g, 1.81 mmol) were dissolved in toluene (82.5 mL). Ethanol (6.05 mL) and a solution of K_2CO_3 (9.75 g) in water (32 mL) were added, and the mixture was flushed with argon. $[Pd(PPh_3)_4]$ catalyst (84 mg, 0.073 mmol) was added, and the reaction mixture stirred at 80 °C for 12 h. The resulting solution was washed three times with distilled water and dichloromethane. The organic phases were separated and dried over $MgSO_4$. The crude product was purified by chromatography with dichloromethane ($R_f = 0.77$). Mixed fractions were purified by column chromatography with dichloromethane/petroleum ether (1.5/1, $R_f = 0.2$) to give **17** (3.35 g, 59 %) as a red solid; m.p. > 300 °C; MS (FD, 8 kV): m/z (%): 1044 (100) $[M]^+$ (calcd for $C_{74}H_{65}NO_3Si$: 1044.43); ^1H NMR (250 MHz, $[D_8]THF$, 289 K): $\delta = 8.59$–8.52 (m, 6H), 7.93 (d, $^3J(H,H) = 8.37$ Hz, 1H), 7.63 (m, 2H), 7.45–7.04 (m, 21H), 2.80 (sept., 5H), 1.14 ppm (br, 30H); ^{13}C NMR (75 MHz, $[D_8]THF$, 289 K): $\delta = 200.13$ (q, C=O), 164.60 (q, C=O), 154.99 (q), 154.54 (q), 147.15 (q), 143.56 (q), 141.44 (q), 138.63 (q), 138.38 (q), 135.00 (q), 134.99 (q), 133.62 (q), 133.03 (q), 132.74 (t), 132.26 (q), 132.10 (q), 131.67 (q), 131.38 (t), 131.05 (q), 130.88 (t), 130.13, 129.9, 129.82, 129.65, 129.48, 129.12 (t), 129.06 (t), 128.65 (t), 128.24 (q), 128.11 (q), 127.10 (q), 126.93 (q), 125.33 (q), 124.92 (t), 124.77 (q), 124.60 (t), 122.64 (q), 122.58(q), 122.88 (t), 121.72 (t), 108.44 (q), 92.56 (q), 30.92 (t, $CH(CH_3)_2$), 24.49 (t, $CH(CH_3)_2$), 19.36 (t, $SiCH(CH_3)_2$), 12.56 ppm (t, $SiCH(CH_3)_2$); IR (KBr pellet): $\tilde{\nu} = 3056$, 2961, 2928, 2867, 1701, 1661, 1592, 1574, 1443, 1358, 1293, 1245, 1197, 1178, 911, 834, 811, 752, 725, 706, 693 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 250 (56400), 482 (43000), 505 nm (42000 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{74}H_{65}NO_3Si$: C 85.10, H 6.27, N 1.34; found: C 84.83, H 6.45, N 1.33.

13: Compounds **27** (1 g, 0.767 mmol) and **28** (1.26 g, 2.61 mmol) were dissolved in toluene (31 mL). Ethanol (6 mL) and a solution of K_2CO_3 (5.1 g) in H_2O (15 mL) were added, and the mixture was flushed with argon. $[Pd(PPh_3)_4]$ catalyst (100 mg, 0.0865 mmol) was added, and the reaction mixture stirred at 80 °C for 12 h. The resulting solution was washed three times with distilled water and dichloromethane. Then, the organic phases were separated and dried over $MgSO_4$. The crude product was purified by chromatography with dichloromethane ($R_f = 0.50$). Mixed fractions were purified thereafter by column chromatography with dichloromethane/petroleum ether (1.5/1, $R_f = 0.12$) to give **13** (612 mg, 43 %) as a brownish yellow solid; m.p. >300 °C; MS (FD, 8 kV): m/z: 1856 $[M]^+$ (calcd for $C_{137}H_{102}N_2O_5 = 1856.35$); ^1H NMR (300 MHz, CD_2Cl_2, 298 K): $\delta = 8.63$–8.57 (m, 4H), 7.93–7.91 (m, 1H), 7.86–7.83 (m, 1H), 7.74–7.59 (m, 6H), 7.50–7.46 (m, 2H), 7.35–6.89 (m, 60H), 6.72–6.69 (m, 4H), 2.73 (sept., $J = 6.7$ Hz, 4H), 1.11 ppm (d, $J(H,H) = 6.7$ Hz, 24H); ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): $\delta = 200.39$ (q, C=O), 164.56, 154.47, 147.47, 143.71, 142.51, 142.45, 142.27, 142.01, 141.66, 141.43, 141.22, 141.09, 136.45, 136.21, 133.33, 132.91, 132.28, 132.17, 131.63, 131.30, 130.86, 130.55, 130.35, 129.96, 129.75, 129.51, 129.19, 128.93, 128.77, 128.10, 127.92, 127.62, 127.13, 126.94, 126.85, 126.35, 125.93, 124.46, 123.59, 123.47, 123.71, 121.99, 29.56, 24.04 ppm; elemental analysis (%) calcd for $C_{137}H_{102}N_2O_5$: C 88.64, H 5.54, N 1.51; found: C 88.19, H 5.38, N 1.43.

14: Compound **27** (1.89 g, 1.4 mmol) and **15** (3 g) were dissolved in toluene (59 mL). Ethanol (11 mL) and a solution K_2CO_3 (9.65 g) in water (28 mL) were added, and the mixture was flushed with argon. $[Pd(PPh_3)_4]$ catalyst (167 mg, 0.14 mmol) was added, and the reaction mixture stirred at 80 °C for 24 h. The resulting solution was washed three times with water and dichloromethane. The organic phases were separated and dried over $MgSO_4$. The crude product was purified by chromatography with dichloromethane to afford **14** (1.24 g, 42 %) as a red solid; m.p. >300 °C; MS (FD, 8 kV): m/z (%): 2104 (87) $[M]^+$, 1052 (13) $[M]^{2+}$ (calcd for $C_{157}H_{110}N_2O_5$: 2104.64); ^1H NMR (250 MHz, $[D_8]THF$): $\delta = 8.56$–8.54 (m, 12H), 7.62–6.71 (m, 72H), 2.78 (sept., 4H, $CHCH_3$), 1.12 ppm (d, $^3J(H,H) = 6.48$ Hz, 24H, $CHCH_3$); ^{13}C NMR (75 MHz, $[D_8]THF$): $\delta = 200.18$ (q, C=O), 164.60, 154.95, 147.13, 143.07, 142.96, 142.39, 142.32, 141.95, 141.75, 141.43, 141.21, 141.06, 138.68, 138.52, 138.25, 133.9, 132.88, 132.62, 132.38, 131.69, 131.28, 131.26, 131.11, 130.74, 130.58, 130.28, 129.96, 129.75, 129.51, 129.19, 128.93, 128.77, 128.10, 127.92, 127.62, 127.13, 126.91, 126.63, 126.41, 125.18, 124.82, 124.58, 122.54, 122.41, 121.72, 121.50, 30.27, 24.57 ppm; IR (KBr pellet): $\tilde{\nu} = 3063$, 2963, 2868, 1698, 1659, 1593, 1570, 1505, 1467, 1449, 1403, 1360, 1329, 1294,1247, 1201, 1170, 1164, 1135, 1034, 946, 906, 875, 854, 844, 813, 753, 713, 703, 689, 658, 645 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 482 (43000), 505 nm (42000 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{157}H_{110}N_2O_5$: C 89.60, H 5.27, N 1.33; found: C 89.14, H 5.23, N 1.31.

***N*-(2,6-Diisopropylphenyl)-9-(4,4,5,5-teramethyl-1,3,2-dioxaborolan-2-yl)-perylene-3,4-dicarboximide (15)**: A mixture of *N*-(2,6-diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide (1.1 g, 0.2 mmol), bis(pinacolato)diboron (558 mg, 2.5 mmol), and potassium acetate (588 mg, 5.3 mol) was dissolved in dioxane (20 mL) under an argon atmosphere. $[PdCl_2(dppf)]{\cdot}CH_2Cl_2$ catalyst (44 mg, 0.1 mmol) was added, and the resulting mixture stirred for 16 h at 70 °C. Then the product mixture was washed with distilled water and dichloromethane. The dichloromethane layer was separated, dried over $MgSO_4$, and the crude product purified by column chromatography with dichloromethane to afford **15** (0.9 g, 75 %) as a red solid, m.p. >200 °C; MS (FD, 8 kV): m/z (%): 607.4 (100) $[M]^+$; ^1H NMR (250 MHz, CD_2Cl_2, 25 °C): $\delta = 8.86$ (d, $J = 8.25$ Hz, 1H), 8.62 (dd, 2H), 8.43 (m, 4H), 8.16 (d, $J^3(H,H) = 7.57$ Hz, 1H), 7.63 (t, 7.59 Hz, 1H), 7.50 (t, 7.74 Hz, 1H), 7.35 (d, $^3J(H,H) = 7.58$ Hz, 2H), 2.79 (h, 2H), 1.46 (s, 12H), 1.15 ppm (d, 12H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 25 °C): $\delta = 165.85$, 165.80, 147.94, 139.57, 138.93, 137.83, 133.59, 133.46, 133.39, 133.17, 132.13, 131.07, 130.55, 129.31, 128.73, 128.50, 125.80, 125.46, 124.60, 123.02, 122.56, 122.47, 122.04, 86.09, 30.69, 26.60, 25.56, 25.53 ppm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 241 (28159), 265 (30569), 485 (36712), 515 nm (36897 $M^{-1}cm^{-1}$); IR (KBr pellet): $\tilde{\nu} = 2970$, 2862, 1708, 1667, 1594, 1512, 1470, 1429 1367, 1336, 1243, 1144, 1113, 963, 865, 818, 762 cm^{-1}; elemental analysis (%) calcd for $C_{40}H_{38}NO_4B$: C 79.08, H 6.30, N 2.31; found: C 78.53, H 6.91, N 2.25.

3-(4-Bromophenyl)-2,5-diphenyl-[4-(triisopropylsilylethynyl)phenyl]cyclopenta-2,4-dien-1-one (17): 4,4′-Bis(triisopropylsilylethynyl)benzil (**23**, 4.92 g, 23.4 mmol) and 1,3-diphenylacetone (**24**, 10 g, 21.3 mmol) were heated in *tert*-butyl alcohol (30 mL) at 80 °C. Tetrabutylammonium hydroxide (10.11 mL) in methanol (0.8 M) was added, and the reaction mixture was stirred for 15 min at 90 °C. The reaction mixture was washed three times with water and dichloromethane, and the organic phases were separated and dried over $MgSO_4$. The crude product was purified by column chromatography with dichloromethane/petroleum ether (1/1) to give **17** as a brown powder (2.1 g, 78 %); m.p. 100–115 °C (decomp); MS (FD, 8 kV): m/z (%): 643 (100) $[M]^+$ (calcd for $C_{40}H_{39}BrOSi$: 643.75); ^1H NMR (300 MHz, $[D_8]THF$, 298 K): $\delta = 7.40$ (d, $^3J(H,H) = 8.37$ Hz, 2H), 7.31 (d, $^3J(H,H) = 8.76$ Hz, 2H), 7.23–7.19 (m, 10H), 6.95 (d, $^3J(H,H) = 8.4$ Hz, 2H), 6.89 (d, $^3J(H,H) = 8.4$ Hz, 2H), 1.15 ppm (m, 21H, H_{alkyl}); ^{13}C NMR (75 MHz, $[D_8]THF$, 298 K): $\delta = 199.59$, 153.94, 153.79, 134.33, 133.26, 132.51, 132.29, 132.13, 131.66, 131.64, 131.03, 130.99, 130.40, 128.79, 128.34, 126.78, 124.47, 123.61, 108.01, 92.28, 19.05, 12.24 ppm; elemental analysis (%) calcd for $C_{40}H_{39}BrOSi$: C 74.63, H 6.11; found: C 74.65, H 6.21.

4-(Bromophenylethynyl)trimethylsilane (19): 4-Bromoiodobenzene (**18**, 50 g, 0.1767 mol), trimethylsilylacetylene (34.88 mL, 0.246 mol), copper(I) iodide (4.5 g, 0.0237 mol), triphenylphosphane (3.6 g, 0.0137 mol), and

$[PdCl_2(PPh_3)_2]$ catalyst (5 g, 0.007 mol) were dissolved in dry toluene (270 mL) and dry triethylamine (450 mL) under argon at room temperature with exclusion of light. After 24 h, the reaction mixture was poured into a solution of distilled water (50 mL) and hydrochloric acid (25 mL, 2 N) and stirred for a few minutes. The mixture was extracted several times with dichloromethane and then with a saturated solution of ammonium chloride. The organic phases were washed with distilled water, dried over $MgSO_4$, and purified by column chromatography with petroleum ether to afford **19** (40 g, 89 %) as a colorless oil; MS (FD, 8 kV): *m*/*z* (%): 253 (100) $[M]^+$ (calcd for $C_{11}H_{13}BrSi$: 253.22); ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=7.44$ (d, J(H,H), 8.45 Hz, 2H), 7.33 (d, $J(H,H)=8.49$, 2H), 0.05 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=133.55$, 131.65, 123.17, 104.04, 95.59, 78.37 (CBr), 0.08 ppm; IR (film): $\tilde{\nu}=3267$, 2976, 1902, 1584, 1484, 1069, 821 cm^{-1}.

1-(Triisopropylsilanylethynyl)-4-trimethylsilanylethynylbenzene (20): Compound **19** (45 g, 0.1772 mol), triisopropylsilylacetylene (32 g, 0.1772 mol), copper(I) iodide (4.5 g, 0.0237 mol), triphenylphosphane (3.5 g, 0.0134 mol), and $[PdCl_2(PPh_3)_2]$ (5 g, 0.007 mol) were dissolved in toluene (270 mL) and triethylamine (450 mL) according to the procedure for the synthesis of **19**. After column chromatography with petroleum ether **20** (60.1 g, 95 %) was isolated as a colorless oil. MS (FD, 8 kV): *m*/*z* (%): 354 (100) $[M]^+$ (calcd for $C_{22}H_{340}Si_2$: 354.69); ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=7.39$ (s, 4H), 1.12 (m, 21H), 0.25 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=131.86$, 131.76, 123.59, 122.99, 106.61, 104.67, 96.16, 92.81, 18.71, 11.33, 0.04 ppm; IR (film): $\tilde{\nu}=2159$ cm^{-1} (m, $C\equiv C$).

(4-Ethynylphenylethynyl)triisopropylsilylsilane (21): Compound **20** (60 g, 0.169 mol) was dissolved in THF (500 mL). Then ethanol (500 mL) and sodium hydroxide (6.77 g) dissolved in water (170 mL, 1 M) were added, and the reaction mixture was stirred for 2 h at 80 °C under argon. Then the mixture was extracted several times with dichloromethane, and the organic phases were washed with distilled water and dried over $MgSO_4$. After filtration and evaporation of the solvent, **21** (40 g, 84 %) was obtained as a colorless solid; m.p. 43–45 °C; MS (FD, 8 kV): *m*/*z*: 282 $[M]^+$ (calcd for $C_{19}H_{26}Si$: 282.51); ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=7.40$ (s, 4H), 3.13 (s, 1H), 1.19–1.07 ppm (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=131.76$, 131.67, 123.46, 121.99, 106.28, 93.39, 83.17, 78.93, 18.7, 11.34 ppm; IR (KBr pellet): $\tilde{\nu}$3295, 2960, 2899, 2159, 1495, 1403, 1251, 1222, 1103, 1018, 839, 760, 732, 700, 628 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{26}Si$: C 80.78, H 9.28; found: C 80.71, H 9.24.

[4-(4-Bromophenylethynyl)phenylethynyl]triisopropylsilane (22): Compound **21** (40 g, 0.1418 mol), 4-bromiodobenzene (**18**, 40 g, 0.1418 mol), copper(I) iodide (2.68 g, 0.0141 mol), triphenylphosphane (3.695 g, 0.0141 mol), and $[PdCl_2(PPh_3)_2]$ (5.14 g, 0.007 mol) were dissolved in toluene (600 mL) and triethylamine (800 mL) according to the procedure for the synthesis of **19**. After column chromatography with petroleum ether, **22** (50.5 g, 81 %) was isolated as a colorless solid; MS (FD, 8 kV): *m*/*z* (%): 437 (100) $[M]^+$ (calcd for $C_{25}H_{29}BrSi$: 437.5); ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=7.68$ (d, $^3J(H,H)=8.3$ Hz, 2H), 7.45 (s, 4H), 7.23 (d, $^3J(H,H)=8.3$ Hz, 2H), 1.04 ppm (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=137.16$, 133.98, 131.98, 131.49, 123.21, 122.95, 122.58, 104.60, 98.31, 96.58 (CBr), 90.49, 90.40, 19.8, 12.4 ppm; IR (KBr pellet): $\tilde{\nu}=2284$ (w, $C\equiv C$), 2162 cm^{-1} (m, $C\equiv CSi$); elemental analysis (%) calcd for $C_{25}H_{29}BrSi$: C 68.64, H 6.68; found: C 68.57, H 6.66.

26: Diethynylbenzil (**25**, 1.7 g, 6.58 mmol) and 3-(4-bromo-phenyl)-2,4,5-triphenylcyclopentadienone (**16**, 7.3 g, 15 mmol) were dissolved in *o*-xylene (100 mL) and heated for 12 h at 170 °C under inert conditions. After cooling to RT the crude product was dissolved in the minimum amount of dichloromethane and added slowly to methanol (700 mL). The resulting precipitate was collected by filtration under vacuum, redissolved in dichloromethane and reprecipitated by addition to methanol. This procedure was repeated until a bright yellow solid was obtained. To increase the overall yield, the filtrates were collected, the solvent was evaporated, and the crude product was purified by column chromatography with dichloromethane/petroleum ether (1/2, $R_f=0.16$). **26** (7.2 g, 97 %) was isolated as a bright yellow solid, m.p. >300 °C; MS (FD, 8 kV): *m*/*z*: 1129 $[M]^+$ (calcd for $C_{47}H_{48}Br_2O_2$: 1129.01); ^1H NMR (300 MHz, $[D_8]$THF, 298 K): $\delta=7.73$ (d, $^3J(H,H)=8.4$ Hz, 4H); 7.34 (s, 1H); 7.55 (s, 1H); 7.32 (d, $^3J(H,H)=8.4$ Hz, 4H); 7.14–6.70 ppm (m, 38H, H_{arom}); ^{13}C NMR (75 MHz, $[D_8]$THF, 298 K): $\delta=194.51$ (C=O), 149.62 (q), 143.89 (q), 142.62 (q), 142.53 (q), 142.41 (q), 142.15 (q), 141.49 (q), 141.08 (q), 140.87 (q), 140.74 (q), 140.69 (q), 140.61 (q), 140.48 (q), 140.37 (q), 140.23 (q), 134.46 (t), 132.58 (t), 132.44 (q), 132.38 (q), 131.65 (t), 131.27 (t), 131.00 (t), 130.97 (t), 130.27 (t), 128.89 (t), 128.74 (t), 128.46 (t), 128.29 (t), 128.26 (t), 127.96 (t), 127.71 (q), 127.54 (q), 127.41 (q), 127.19 (q), 127.10 (q), 126.83 (q), 120.99 (q), 120.72 ppm (q); elemental analysis (%) calcd for $C_{47}H_{48}Br_2O_2$: C 78.73, H 4.29; found: C 78.13, H 4.26.

27: Compound **26** (3.5 g, 3.1 mmol) and diphenylacetone (**24**, 0.717 g, 3.41 mmol) were dissolved in toluene (100 mL) under inert conditions. The reaction mixture was heated to 90 °C, then tetrabutylammonium hydroxide (2.1 mL, 0.8 M) was added slowly by syringe, and the reaction mixture stirred for 40 min at 90 °C. FD mass spectrometry was used to monitor the reaction. Then, water was carefully added to the hot reaction mixture. After cooling to room temperature, the reaction mixture was washed several times with water and dichloromethane. The organic phases were collected, dried over $MgSO_4$, and the solvent evaporated. Column chromatography with CH_2Cl_2/petroleum ether (1/3, $R_f=0.29$) gave **27** (2.53 g, 63 %) as a brown solid; m.p. >300 °C; MS (FD, 8 kV): *m*/*z* (%): 1303 (68) $[M]^+$; 651 (32) $[M]^{2+}$ (calcd for $C_{89}H_{58}Br_2O$: 1303.26); ^1H NMR (300 MHz, CD_2Cl_2, 298 K): $\delta=7.53$ (s, 2H), 7.26–7.17 (m, 20H, H_{arom}), 7.08 (d, 2H, $^3J(H,H)=8.4$ Hz), 7.04–6.7 (m, 32H, H_{arom}), 6.67 ppm (d, $^3J(H,H)=8.4$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): $\delta=200.34$, 154.44, 142.43, 142.38, 142.04, 141.95, 141.80, 141.38, 141.18, 141.01, 140.81, 140.44, 140.12, 139.95, 139.80, 139.60, 138.70, 133.58, 133.52, 131.87, 131.78, 131.73, 131.38, 131.31, 131.23, 130.51, 130.39, 130.28, 130.11, 129.77, 129.27, 128.35, 128.15, 127.98, 127.71, 127.43, 127.22, 127.16, 126.92, 126.78, 126.43, 126.26, 126.01, 125.71, 120.14, 119.86 ppm; elemental analysis (%) calcd for $C_{89}H_{58}Br_2O$: C 82.02, H 4.49; found: C 82.29, H 4.73.

***N*-(2,6-Diisopropylphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,8-naphthalenedicarboximide (28)**: *N*-(2,6-Diisopropylphenyl)-4-bromo-1,8-naphthalenedicarboximide (1 g, 2.3 mmol), bis(pinacolato)diboron (700 mg, 2.7 mmol), $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (131 mg, 0.16 mmol), and potassium acetate (270 mg, 2.75 mmol) were dissolved in toluene (150 mL) under argon. The reaction mixture was stirred for 48 h at 60 °C. Then the solvent was evaporated under vacuum while keeping the temperature of the reaction mixture below 60 °C. Then the crude product was purified by column chromatography with dichloromethane/pentane (4/1) to afford **28** (533 mg, 48 %) as a light yellow solid; MS (FD, 8 kV): *m*/*z* (%): 483.1 (100) $[M]^+$; ^1H NMR (500 MHz, $CDCl_3$): $\delta=9.18$ (d, $^3J(H,H)=8.16$, 1H), 8.63 (m, 2H), 8.35 (d, $^3J(H,H)=7.22$, 1H), 7.84 (t, $J=7.86$, 1H), 7.48 (t, $J=7.86$, 1H), 7.31 (d, $^3J(H,H)=7.53$, 2H), 2.72 (m, 2H), 1.44 (s, 12H), 1.14 ppm (d, $^3J(H,H)=6.59$, 12H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 90 °C): $\delta=163.96$, 145.67, 135.35, 134.99, 133.97, 131.13, 131.00, 130.83, 129.68, 128.93, 128.15, 126.77, 126.67, 124.33, 123.58, 122.26, 84.29, 28.66, 24.39 ppm; IR (KBr): $\tilde{\nu}=2964$, 2930, 2869, 1711, 1671, 1590, 1469, 1434, 1360, 1239, 1193, 839, 786, 705 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon)=257$ (17446), 356 (10347), 370 nm (8665 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{30}H_{34}BNO_4$: C 74.54, H 7.09, N 2.90; found: C 74.73, H 7.15, N 2.82.

29: Compounds **10** (40 mg, 0.031 mmol) and **11** (150 mg, 0.174 mmol) were heated in *o*-xylene (2 mL) under inert conditions for 12 h at 170 °C. Then, the solvent was evaporated under vacuum, and the crude product purified by column chromatography on silica gel by first eluting with dichloromethane until red fractions were no longer collected. Then acetone was used as an eluent (R_f(**29**)<0.1). Finally, the product was eluted with THF to give **29** (132 mg, 92 %) as a violet solid; m.p. >300 °C; MALDI-TOF MS: *m*/*z*: 4641 $[M]^+$ (calcd for $C_{338}H_{242}N_6O_{16}$: 4643); ^1H NMR (500 MHz, $[D_8]$THF, 298 K): $\delta=9.51$ (s, 4H), 8.55 (m, 24H), 8.24 (s, 4H, H), 7.71 (s, 4H), 7.60–6.91 (m, 122H), 2.80 (m, 12H), 1.14 ppm (m, 72H); ^{13}C NMR (125 MHz, $[D_8]$THF, 298 K): $\delta=164.61$ (q), 163.81 (q), 156.09 (q), 155.61 (q), 147.13 (q), 144.19 (q), 142.83 (q), 142.71 (q), 142.61 (q), 142.52 (q), 142.36 (q), 142.29 (q), 142.22 (q), 141.58 (q), 141.44 (q), 141.13 (q), 140.81 (q), 140.65 (q), 140.40 (q), 140.17 (q), 139.61 (q), 138.74 (q), 138.68 (q), 138.49 (q), 133.93 (q), 133.29 (t), 132.97 (t), 132.80 (t), 132.62 (t), 131.93 (t), 131.23 (t), 131.07 (t), 130.54 (q), 130.25 (t), 129.95 (t), 129.69 (t), 129.66 (t), 129.47 (q), 128.93 (t), 128.47 (t), 128.21 (t), 128.06 (q), 127.69 (t), 127.20 (t), 126.65 (q), 125.21 (t), 124.80 (t), 124.59 (t), 123.85 (q), 122.48 (q), 122.35 (q), 121.65 (t), 121.45 (t), 121.26 (q), 120.99 (q), 120.03 (t), 30.24 (t, $CH(CH_3)_2$), 24.73 ppm (t, $CH(CH_3)_2$); UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon)=509$ (135016), 526 (133404), 675 nm (85635 $M^{-1}cm^{-1}$); IR (KBr pellet): $\tilde{\nu}=700$, 754, 811, 840, 931,

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1074, 1176, 1357, 1498, 1590, 1664, 1702, 2869, 2962, 3025, 3054 cm^{-1}; elemental analysis (%) calcd for $C_{338}H_{242}N_6O_{16}$: C 87.42, H 5.25, N 1.81; found: C 87.33, H 5.14, N 1.79.

30: Compounds **10** (30 mg, 0.023 mmol) and **14** (389 mg, 0.185 mmol) were dissolved in *o*-xylene (3 mL) and diphenyl ether (3 mL) and heated under inert conditions for 48 h at 190 °C. After the mixture had been allowed to cool, the crude product was dissolved in dichloromethane and precipitated in methanol (50 mL). The precipitate was filtered, dried, and purified by column chromatography with dichloromethane and then with acetone, as for **29**. By using THF as eluent, **30** (183 mg, 83 %) was isolated as a violet solid, m.p. >300 °C; MALDI-TOF MS: *m*/*z*: 9703 $[M+Ag]^+$ (calcd for $C_{714}H_{502}N_{10}O_{24}=9594.01$); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 353 K): $\delta=9.39$ (s, 4H), 8.55–8.52 (m, 48H), 8.18 (s, 4H), 7.54–7.57 (m, 306H), 2.69 (m, 20H), 1.11 ppm (d, ^3J(H,H) = 6.1 Hz, 120H); ^{13}C NMR (500 MHz, $[D_2]C_2H_2Cl_4$, 353 K): $\delta=164.03$ (C=O), 146.06 (q), 143.84 (q, br), 142.16 (q), 142.05 (q), 141.70 (q), 141.54 (q), 141.11 (q), 140.93 (q), 140.82 (q), 140.70 (q), 140.42 (q), 140.21 (q), 139.94 (q), 139.69 (q), 138.58 (q), 137.94 (q), 136.99 (q), 136.71 (q), 133.11 (q), 132.07 (t, br), 131.69 (q), 131.36 (t), 130.78 (q), 130.38 (q), 130.24 (t), 130.23 (t), 129.57 (q), 129.35 (t), 128.69 (t), 128.52 (q, br), 128.38 (t), 128.14 (t), 128.07 (t), 127.87 (t), 127.19 (t), 127.10 (t), 126.88 (t), 126.51 (t), 125.85 (t), 124.11 (t), 123.66 (t), 121.38 (q), 121.25 (q), 120.60 (t), 120.34 (t), 29.70 (t, *C*HCH$_3$), 24.22 ppm (t, CH*C*H$_3$); UV/Vis (CHCl$_3$): λ_{max} (ε) = 509 (258150), 526 (251611), 675 nm (85413 M^{-1}cm^{-1}); IR (KBr pellet): $\tilde{\nu}$ = 700, 754, 811, 840, 931, 1074, 1176, 1357, 1498, 1590, 1664, 1702, 2869, 2962, 3025, 3054 cm^{-1}; elemental analysis (%) calcd for $C_{714}H_{502}N_{10}O_{24}$: C 89.28, H 5.27, N 1.46; found: C 88.73, H 5.02, N 1.35.

31a: Compounds **10** (40 mg, 0.031 mmol) and **12** (150 mg, 0.174 mmol) were dissolved in *o*-xylene (2 mL) under inert conditions and heated for 12 h at 170 °C. After the mixture had been allowed to cool, the crude product was dissolved in dichloromethane and precipitated in methanol (50 mL). The precipitate was collected by filtration, dried, and purified by column chromatography with dichloromethane and then with acetone as described above for **29**. By using THF as eluent, **31a** (159 mg, 90 %) was isolated as a violet solid; m.p. >300 °C; MALDI-TOF MS: *m*/*z*: 5365 $[M]^+$ (calcd for $C_{381}H_{318}N_6O_{16}Si_4$: 5365.20); ^{1}H NMR (500 MHz, $[D_8]$THF, 298 K): $\delta=9.51$ (s, 4H), 8.54 (br m, 24H), 8.23 (s, 4H), 7.71 (s, 2H), 7.69 (s, 2H), 7.60–6.91 (m, 118H), 2.80 (m, 12H), 1.16 (m, 72H), 1.05 ppm (d, ^3J = 6.7 Hz, 84H); ^{13}C NMR (125 MHz, $[D_8]$THF, 298 K): $\delta=164.61$ (q), 163.81 (q), 156.09 (q), 155.61 (q), 147.13 (q), 144.19 (q), 142.83 (q), 142.71 (q), 142.61 (q), 142.52 (q), 142.36 (q), 142.29 (q), 142.22 (q), 141.58 (q), 141.44 (q), 141.13 (q), 140.81 (q), 140.65 (q), 140.40 (q), 140.17 (q), 139.61 (q), 138.74 (q), 138.68 (q), 138.49 (q), 133.93 (q), 133.29 (t), 132.97 (t), 132.80 (t), 132.62 (t), 131.93 (t), 131.23 (t), 131.07 (t), 130.54 (q), 130.25 (t), 129.95 (t), 129.69 (t), 129.66 (t), 129.47 (q), 128.93 (t), 128.47 (t), 128.21 (t), 128.06 (q), 127.69 (t), 127.20 (t), 126.65 (q), 125.21 (t), 124.80 (t), 124.59 (t), 123.85 (q), 122.48 (q), 122.35 (q), 121.65 (t), 121.45 (t), 121.26 (q), 120.99 (q), 120.03 (t), 84.81 (q, C ethynyl), 79.15 (CH ethynyl), 78.97 (CH ethynyl), 30.20 (t, CH(CH$_3$)$_2$), 24.68 (t, CH(CH$_3$)$_2$), 24.61 (t, CH(CH$_3$)$_2$), 18.57 (CH TiPS), 13.79 ppm (CH$_3$ TiPS); IR (KBr pellet): $\tilde{\nu}$ = 700, 754, 811, 840, 931, 1074, 1176, 1357, 1498, 1590, 1664, 1702, 2869, 2962, 3025, 3054 cm^{-1}; elemental analysis (%) calcd for $C_{382}H_{322}N_6O_{16}Si_4$: C 85.52, H 6.05, N 1.57; found: C 84.98, H 5.83, N 1.45.

31b: Compound **31a** (180 mg, 0.0335 mmol) was dissolved in freshly distilled THF (8 mL) and flushed with argon for 10 min. Then $Bu_4NF\cdot 3H_2O$ (14 mg, 0.0436 mmol) in THF (2 mL) was added by syringe. The reaction mixture immediately turned dark, and the progress of the reaction was monitored by TLC with petroleum ether/dichloromethane (1/1). After 5 min, the reaction was finished, and distilled water (20 mL) was added. Then the crude product was extracted with dichloromethane and washed with water. The organic phases were dried over MgSO$_4$ and the solvent was evaporated under reduced pressure. Column chromatography with dichloromethane/petroleum ether (1/1) and then with THF gave **31a** (140 mg, 88 %) as a blue solid, m.p. >300 °C; MALDI-TOF MS: *m*/*z*: 4738 $[M]^+$ (calcd for $C_{364}H_{242}N_6O_{16}$: 4739.82); ^{1}H NMR (500 MHz, $[D_8]$THF, 298 K): $\delta=9.50$ (s, 4H), 8.54 (br m, 24H), 8.23 (s, 4H), 7.71 (s, 2H), 7.69 (s, 2H), 7.60–6.91 (m, 118H), 3.48 (s, 2H), 3.44 (s, 2H), 2.80 (m, 12H), 1.16 ppm (m, 72H); ^{13}C NMR: (125 MHz, $[D_8]$THF, 298 K): $\delta=164.61$ (q), 163.81 (q), 156.09 (q), 155.61 (q), 147.13 (q), 144.19 (q), 142.83 (q), 142.71 (q), 142.61 (q), 142.52 (q), 142.36 (q), 142.29 (q), 142.22 (q), 141.58 (q), 141.44 (q), 141.13 (q), 140.81 (q), 140.65 (q), 140.40 (q), 140.17 (q), 139.61 (q), 138.74 (q), 138.68 (q), 138.49 (q), 133.93 (q), 133.29 (t), 132.97 (t), 132.80 (t), 132.62 (t), 131.93 (t), 131.23 (t), 131.07 (t), 130.54 (q), 130.25 (t), 129.95 (t), 129.69 (t), 129.66 (t), 129.47 (q), 128.93 (t), 128.47 (t), 128.21 (t), 128.06 (q), 127.69 (t), 127.20 (t), 126.65 (q), 125.21 (t), 124.80 (t), 124.59 (t), 123.85 (q), 122.48 (q), 122.35 (q), 121.65 (t), 121.45 (t), 121.26 (q), 120.99 (q), 120.03 (t), 84.81 (q, C ethynyl), 79.15 (CH ethynyl), 78.97 (CH ethynyl), 30.20 (t, *C*H(CH$_3$)$_2$), 24.68 (t, CH(*C*H$_3$)$_2$), 24.61 (t, CH(*C*H$_3$)$_2$) ppm; IR (KBr pellet): $\tilde{\nu}$ = 2921 (s), 2850 (s), 1702, 1660, 1589, 1504, 1463, 1328, 1278, 1207 cm^{-1}; elemental analysis (%) calcd for $C_{364}H_{242}N_6O_{16}$: C 87.68, H 5.15, N 1.77; found: C 87.51, H 5.11, N 1.76.

32: Compounds **31b** (30 mg, 0.0063 mmol) and **13** (187 mg, 0.101 mmol) were dissolved in *o*-xylene (3 mL) and diphenyl ether (3 mL) and heated under inert conditions for 3–4 days at 190 °C. After the mixture had been allowed to cool, the crude product was dissolved in dichloromethane and precipitated in methanol. The precipitate was filtered, dried, and purified by column chromatography with dichloromethane and then with acetone, as described above for **29**. By using THF as eluent, **32** (48 mg, 63 %) was isolated as a dark solid, m.p. >300 °C; MALDI-TOF MS: *m*/*z*: 12165 $[M+Ag]^+$ (calcd for $C_{42}H_{40}Si$: 12053); ^{1}H NMR (500 MHz, $[D_8]$THF, 298 K): $\delta=9.53$ (s, 4H), 8.68–8.55 (m, 40H), 8.23 (s, 4H), 7.87 (m, 8H)*, 7.79 (m, 8H)*, 7.68–6.52 (m, 390H), 2.75 (m, 28H), 1.10 ppm (m, 168H); ^{13}C NMR (125 MHz, $[D_8]$THF, 324 K): $\delta=164.93$ (C=O), 164.72 (C=O), 164.64 (C=O), 163.82 (q), 156.24 (q), 156.17 (q), 155.55 (q), 148.19 (q), 148.12 (q), 144.49 (q), 143.28 (q), 143.13 (q), 143.02 (q), 142.93 (q), 142.87 (q), 142.80 (q), 142,78 (q), 142.72 (q), 142.68 (q), 142.58 (q), 142.49 (q), 142.34 (q), 142.29 (q), 142.11 (q), 141.89 (q), 141.79 (q), 141.52 (q), 141.44 (q), 141.38 (q), 141.32 (q), 141.09 (q), 140.86 (q), 140.61 (q), 140.51 (q), 140.41 (q), 140.15 (q), 140.09 (q), 139.74 (q, broad), 138.77 (q), 138.64 (q), 138.38 (q), 137.52 (q), 137.25 (q), 134.10 (q), 133.65 (q), 133.56 (q), 133.10 (t), 132.88 (t), 132.68 (t), 132.36 (t), 132.10 (t), 131.83 (t), 131.70 (t), 131.19 (t), 131.06 (t), 130.85 (q), 130.73 (q), 130.63 (q), 130.40 (t), 130.22 (q), 130.11 (q), 129.95 (t), 129.60, 129.49, 129.19 (t), 128.78 (t), 128.68 (t), 128.55, 128.45, 128.38, 128.20, 128.09 (t, br), 127.81 (t, br), 127.52 (q), 127.39 (q), 127. 30 (q), 126.84, 126.54, 125.17, 124.78, 124 59 (t), 124.48 (t), 123.91, 123.34 (q), 123.31 (q), 122.69 (q, br), 122.63 (q), 122.58 (q), 121.76, 121.59, 121.51 (q), 120.03 (q, br), 30.29 (t, *C*H(CH$_3$)$_2$), 24.66 (t, CH(*C*H$_3$)$_2$), 24.56 (t, CH(*C*H$_3$)$_2$), 24.48 ppm (t, br, CH(*C*H$_3$)$_2$); UV/Vis (CHCl$_3$): λ_{max} (ε) = 371 (182163) 509 (138112), 527 (141218), 677 nm (98578 M^{-1}cm^{-1}); IR (KBr pellet): $\tilde{\nu}$ = 700, 754, 811, 840, 931, 1074, 1176, 1357, 1498, 1590, 1664, 1702, 2869, 2962, 3025, 3054 cm^{-1}; elemental analysis (%) calcd for $C_{890}H_{650}N_{14}O_{32}$: C 88.69, H 5.44, N 1.63; found: C 87.97, H 5.24, N 1.51. * Signals not resolved.

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[51] The minimized structure of multichromophore **30** was obtained by applying the MM+ force field and the Conjugate Gradient algorithm implemented in the HyperChem 6.0 program package. The hypersurface of the TDI core molecule was first calculated separately by using the semiempirical PM3 method, and a global minimum was evaluated. In the next step, the separately minimized dendrimer branches were attached to the core, and the geometry of the complete molecule was calculated with the MM+ force field and the Fletcher Reeves algorithm. Due to the fairly flat hypersurface generally obtained for higher generation dendrimers, the three-dimensional structure of **30** represents one of several possible local minima. However, this structure was found to be sufficient to evaluate the dimensions of the molecules as well as the approximate position of the chromophores with respect to each other.

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