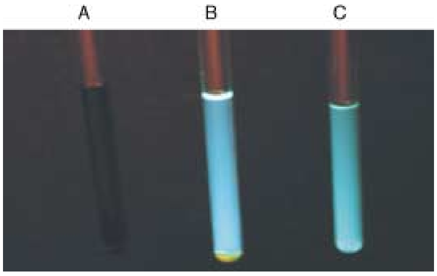

Figure 2. Concentrated solutions (ca. 10^{-2} M) of A) **1**, B) **2** and C) **3** under UV light (366 nm).

Furthermore, exposure of a solution (ca. 10^{-6} M) of **1** to an atmosphere containing 0.05 % (ca. 850 ppm) CO results in a detectable change in emission (not shown), and studies are ongoing to determine the detection range for this sensor complex. Investigations are also underway to determine whether the intensely emissive excimer of **3** can be observed immediately when the reaction with CO occurs at elevated temperature.[14] This would result in a substantial difference in emission intensity from the sensor material before and after CO exposure. Importantly, the drastic difference in behavior of **2** and **3** suggests that luminescence changes may be triggered by subtle changes in the bonding environment at the metal atom. This is significant because it indicates that it may be possible to design sensors based on this approach in which differences in response result not only from selectivity for specific analytes by tuning the reactivity of the metal, but also from steric and electronic considerations which favor or disfavor the formation of pyrene excimers.

Experimental Section

Full experimental and characterization details for POC4Pyr and complexes **1**–**3** are available in the Supporting Information.

Received: November 5, 2001
Revised: March 1, 2002 [Z 18161]

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Shape-Persistent, Fluorescent Polyphenylene Dyads and a Triad for Efficient Vectorial Transduction of Excitation Energy**

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Plants and some bacteria have the unique ability to convert sunlight into chemically bound energy, thus opening up a nearly unlimited energy source.[1] Since supplies of fossil fuels are expected to become exhausted in the near future, there has been an increasing interest in the synthesis of novel organic and polymeric molecules for the efficient harvesting of solar energy as well as for the conversion of solar radiation into electrical energy.[2a–d] The geometry of linear chain macromolecules is not ideal for efficient energy transfer; in particular, it is difficult to achieve an energy gradient for a vectorial transduction of light energy.[3] Not surprisingly, therefore, dendrimers have received great interest. Their globular shape provides a large surface area that can be decorated with chromophores, which thus results in a large absorption cross section and enables efficient capturing of photons.[4] Balzani et al. have synthesized light-harvesting dendrimers that bear an osmium complex in the center and several ruthenium complexes at the periphery.[5] In the phenylacetylene dendrimers reported by Moore and coworkers, a focal perylene chromophore acts as a light-harvesting antenna and there is an energy gradient from the periphery towards the center.[6] For light-harvesting dendrimers based on a flexible scaffold[7a–d] the investigation of energy transfer is often complicated because conformational mobility leads to undesired chromophore interactions such as aggregation, excimer formation, and dye self-quenching.[8, 9] Other drawbacks are often the very limited photostability[9] and low fluorescence quantum yields of the chosen chromophores.

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[**] This research was supported by the TMR European Research Program through the SISITOMAS project, the Volkswagen-Stiftung, and the Bundesministerium für Bildung and Forschung. We also thank S. Spang and C. Beer for support in the synthetic work.

The use of a rigid polyphenylene dendrimer[10a, b] should overcome most of the above-mentioned difficulties[11, 12] since no back-folding of the dendritic branches can occur[13] and self-quenching of the chromophores is not observed.[12] Furthermore, energy-transfer processes, including those at the single-molecule level, were investigated by using polyphenylene dendrimers decorated with very photostable perylene dicarboxmonoimide chromophores; collective effects, quite well known in biological systems, have been recognized.[14a, b] Herein, we present structurally well-defined light-harvesting arrays that consist of up to three different types of chromophores for efficient energy transfer with an energy gradient. The design comprises globular polyphenylene dendrimers that bear a terrylene tetracarboxdiimide chromophore (TDI, Figure 1 b) in the center and perylene dicarboxmonoimide (PMI, Figure 1 b) as well as naphthalene dicarboxmonoimide chromophores (NMI, Figure 1 b) at the periphery (Figure 1 a). We have already demonstrated an efficient energy transfer between perylene and terrylene chromophores in two different systems.[11, 15] The combination of chemically very stable, shape-persistent polyphenylene dendrimers and rylene chromophores (e.g. TDI, PMI, NMI, Figure 1 b), which possess excellent photostability, high extinction coefficients, and show a fluorescence quantum yield close to unity opens up the design of an outstanding multichromophoric array.[16] Figure 1 a shows the envisaged multichromophores: **A** and **B** represent two molecular dyads that have an increasing interchromophoric distance and bear PMI chromophores in the outer sphere as well as a TDI core. **C** represents an NMI-, PMI-, and TDI-containing multichromophore. To clarify the molecular structure, the terms dyad and triad correspond to a multichromophore that bears two and three different types of chromophores, respectively.

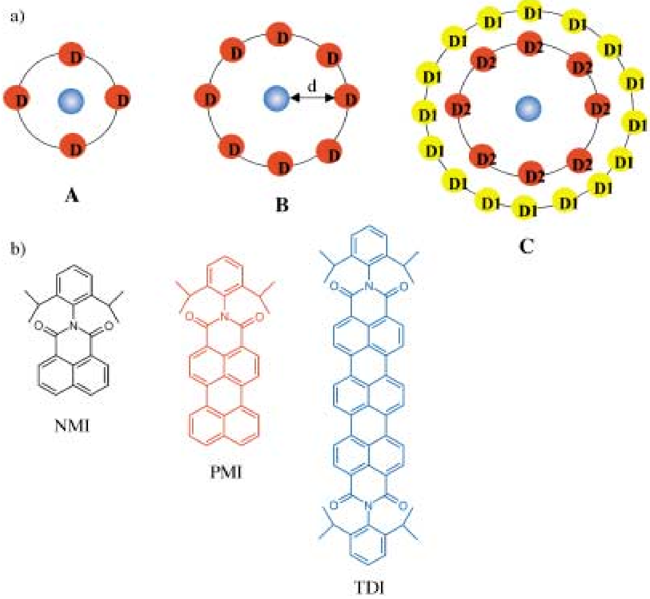
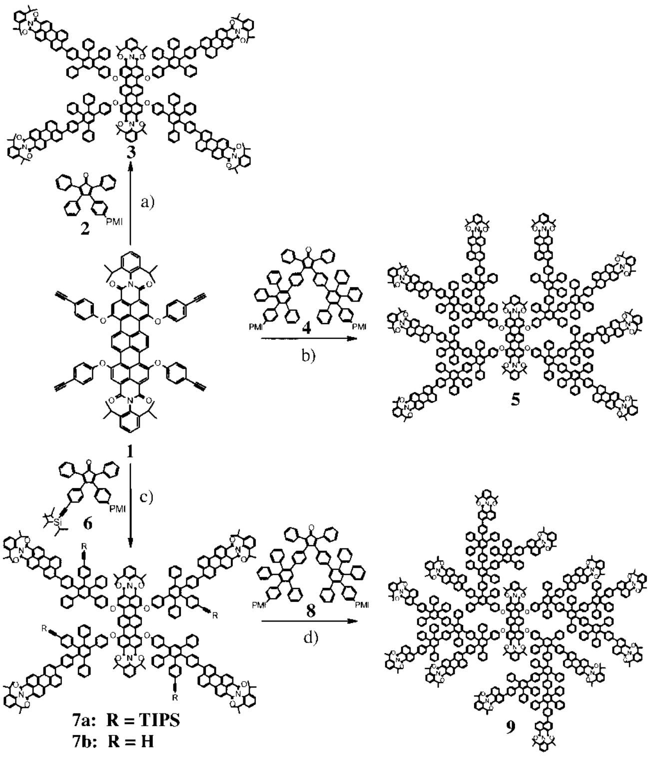


Figure 1. a) Sketch of the synthetic approach. **A** and **B** represent two molecular PMI–TDI dyads, **C** represents an NMI-PMI-TDI triad, and *d* is the distance between one donor and one acceptor chromophore. b) Structures of unsubstituted ryleneimide chromophores: naphthalene dicarboximide (NMI) , perylene dicarboximide (PMI), and terrylene tetracarboxdiimide (TDI).

The synthesis of the novel multichromophores is based on both a convergent[17] and a divergent[18] approach. A tetraethynyl terrylene tetracarboxydiimide chromophore **1**[19] serves as a core molecule that bears four ethynyl groups and therefore allows further dendrimer growth by repetitive Diels–Alder cycloaddition (Scheme 1). The reaction of the TDI core **1** with a cyclopentadienone **2**, which bears a PMI chromophore, proceeded smoothly with the extrusion of carbon monoxide (170 °C, *o*-xylene, 12 h). Column chromatography on silica with dichloromethane eluant afforded first-generation multichromophore **3**, which bears four PMI substituents at the periphery as a purple solid in excellent yields (92 %). The second-generation multichromophore **5** was formed by reacting the TDI core **1** with 10 equivalents of the PMI-substituted dendron **4** (170 °C, *o*-xylene, 3 d); after chromatography, **5** was obtained as a purple solid in 83 % yield. The use of different dendrimer branches **2** and **4** permitted the study of energy transfer as a function of the interchromophoric distance. The synthesis of the dendritic triad **9** required a complex multistep route using cyclopentadienone **6**, which carries a chromophore as well as a protected ethynyl group. This building unit was prepared by means of a six-step reaction sequence, which will be published separately.[19] The TDI core **1** was treated with five equivalents of the PMI-labeled branching agent **6** (170 °C, 12 h), and column



Scheme 1. Synthesis of **3**, **5**, and **9**. Reagents and conditions: a) **2** (5 equiv), *o*-xylene, 170 °C, 12 h, 92 %; b) **4** (10 equiv), *o*-xylene, 170 °C, 3 d, 83 %; c) 1) **6** (5 equiv), *o*-xylene, 170 °C, 12 h, 90 %; 2) tetrabutylammonium chloride · $3H_2O$ (1 equiv), THF, 4 min, 88 %; d) **8** (16 equiv), *o*-xylene/diphenyl ether (1:1), 195 °C, 3 d, 63 %. TIPS = triisopropylsilyl.

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chromatography with dichloromethane gave **7a** in 90% yield. Multichromophore **7a** has nearly the same chemical structure as **3**, the only difference being the four triisopropylsilyl-protected ethynyl groups situated at the periphery of the dendrimer. After the removal of the protecting groups (1 equivalent tetrabutylammonium chloride, THF, 4 min), quenching with water, and filtration through a short pad of silica gel with dichloromethane, pure **7b** was obtained in nearly quantitative yield. This first-generation polyphenylene dendrimer **7b**, which bears two different types of chromophores, was then treated with dendron **8**, which carries two NMI substituents (*o*-xylene/diphenyl ether (1:1), 195 °C, 3 d). In this way, multichromophore **9** was obtained as a dark purple solid in 63% yield.

The structure of all compounds was confirmed by means of NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrometry, with special attention being paid to the complete functionalization of the multichromophores. All MALDI-TOF mass spectra showed only a single peak that corresponded to the molecular mass of the multichromophores **3** (4643 $\mathrm{g\,mol^{-1}}$), **5** (9606 $\mathrm{g\,mol^{-1}}$), and **9** (12053 $\mathrm{g\,mol^{-1}}$). A detailed discussion of the spectra of all the compounds reported herein will be published elsewhere.[19] A key feature of polyphenylene dendrimers as well as of rylene chromophores is their outstanding thermal stability. Thermal gravimetric analysis (TGA) showed decomposition of the multichromophores only at temperatures above 450 °C. Molecular-modeling studies[20] of the dendrimers **3**, **5**, and **9** were used to determine the size, the topology of the functional groups, and the average interchromophoric distances of the multichromophores (Table 1). One can clearly see how the diameter of the multichromophores increases for higher generations, and that the average interchromophoric distances between different types of chromophores are in the range of 2 to 3 nm. The 3D structures of **3**, **5**, and **9** are given in Figures 2 and 5d.

The multichromophores **3**, **5**, and **9** show good solubility in most organic solvents. The color corresponds to the spectral sum of the red PMI and the blue TDI. Dyads **3** and **5** display well-separated absorption envelopes (Figure 2). With increasing dendrimer generation, the extinction coefficients of the multichromophores also increase, and therefore the absolute light intensity harvested by the antenna is dramatically enhanced. Furthermore, no spectral broadening or shifts of the absorption maxima are observed, thus indicating that there is no interaction between the chromophores. An overview of the optical properties of all multichromophores is given in Table 2. Energy transfer only takes place if there is a sufficient spectral overlap of the donor emission and the acceptor absorption. Figure 3 shows the absorption and emission spectra of the separated rylene chromophores. One can clearly see that there is a large spectral overlap of the PMI emission and the TDI absorption. Excitation of a dilute solution (10^{-6} M) of dyads **3** and **5** at 480 nm results in a strong emission, predominantly from the TDI-acceptor chromo-

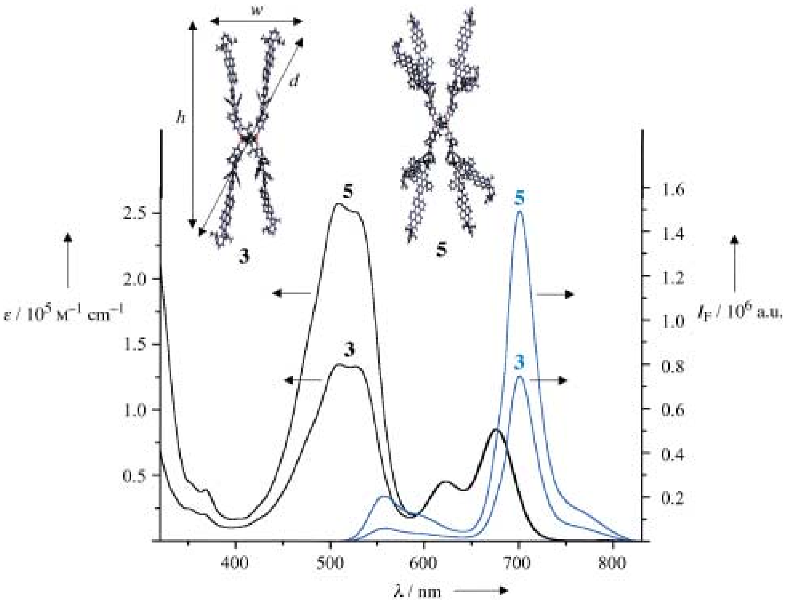

Figure 2. 3D structures of **3** and **5** obtained from molecular-mechanics calculations. UV/Vis absorption (black line, 10^{-5} M) and emission spectra (blue line, $\lambda_{\text{exc.}} = 480$ nm, 10^{-6} M) of **3** and **5** in toluene.

Table 2. Values of $\lambda_{\text{max,abs}}$ (ε), $\lambda_{\text{max,em}}$, and ϕ_f for **1**, **3**, **5**, and **9**.

	λ_{max} (toluene) [nm]	λ_{max} (chloroform) [nm]	λ_{em} (toluene) [nm]	λ_{em} (chloroform) [nm]	ϕ_f[a]
1	667 (87125)	665 (88865)	698	706	0.98
3	501 (118200)	509 (135016)	559	578	0.04
	526 (111350)	526 (133404)	701	709	(PMI)
	675 (85671)	675 (85635)			
5	500 (227270)	509 (258150)	557	577	0.09
	524 (222680)	526 (251611)	702	709	(PMI)
	674 (89990)	675 (85413)			
9	370 (178854)	371 (182163)	431	438	0.17
	501 (134576)	509 (138112)	555	576	(NMI)
	526 (136565)	527 (141218)	700	710	0.20
	676 (98462)	677 (98578)			(PMI)

[a] ϕ_f values of both separate PMI and TDI chromophores of Figure 3 are 0.98 (PMI) and 0.95 (TDI) in toluene.

Table 1. Size and average distances between separate chromophore units of **3**, **5**, and **9** obtained from the 3D structures after energy minimization.

	Height (h) [nm]	Width (w) [nm]	Diameter (d) [nm]	d(NMI →PMI) [nm]	d(PMI →TDI) [nm]	d(NMI →TDI) [nm]
5	7.37	5.85	7.89	–	2.50	–
3	5.87	2.59	6.11	–	1.89	–
9	5.81	6.91	8.1	2.15	1.83	2.85

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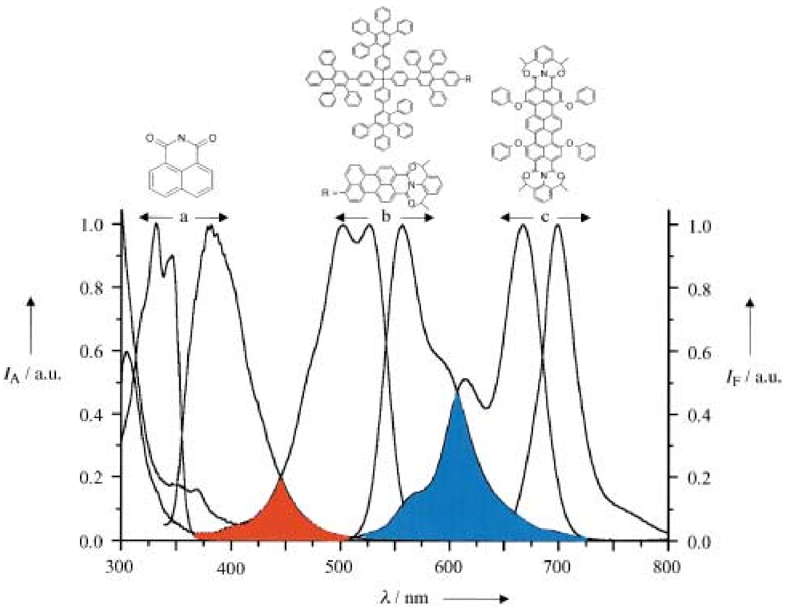

Figure 3. UV/Vis absorption (10^{-5} M) and emission spectra (10^{-6} M) of the separate rylene chromophores in toluene: a) naphthalimide ($\lambda_{exc} = 332$ nm), b) a polyphenylene dendrimer with a single PMI chromophore[11] ($\lambda_{exc} = 480$ nm), and c) a TDI chromophore ($\lambda_{exc.} = 665$ nm).

phore. The almost complete disappearance of the donor emission at 550 nm, which is quenched by about 93 % in comparison to the separate PMI chromophore, along with a strong acceptor emission, indicates a very efficient energy transfer from the PMI donor to the TDI acceptor (Figure 2). This efficient and fast energy transfer can be explained by the large Förster interaction radius ($R_0 = 6$ nm),[21] as well as the high spectral overlap of the PMI emission and the TDI absorption.

The multichromophoric triad **9** absorbs over the whole range of the visible spectrum and also shows well-separated absorption envelopes (Figure 4). This feature opens up the possibility of specifically exciting distinct chromophores within the dendrimer, which is crucial for the investigation of vectorial energy transfer. The NMI emission ($\lambda_{max,em} = 341$ nm) does not coincide with the TDI absorption ($\lambda_{max} = 665$ nm, Figure 3), which is a prerequisite for a well-defined stepwise energy transfer. Excitation of the NMI chromophores of **9** at 370 nm results in weak emissions at 431 nm (NMI) and at 555 nm (PMI), but in a strong acceptor emission at 700 nm (Figure 5 a). This finding indicates the existence of an energy gradient and is consistent with a stepwise energy transfer from the periphery *via* the scaffold towards the center of the dendrimer. Although the Förster radius for the dendritic dyads has been calculated to be quite large, there is no spectral overlap of the NMI emission and of the TDI absorption (Figure 3). Consequently, the energy transfer from the NMI towards the TDI is explained as occurring through a stepwise mechanism across the PMI donors.

A relative fluorescence quantum yield (ϕ_f^{apr}) of the energy-transfer steps can be derived from the observed fluorescence intensities of the chromophores according to Equation (1),[22] in which C

$$\phi_f^{apr}(C) = \left(\frac{Em(C)^{obs}}{Em(C)^{max}}\right)\left(\frac{\varepsilon(C)}{\varepsilon_{370}(C)}\right) \qquad (1)$$

represents the observed chromophores (NMI, PMI, TDI), $Em(c)^{obs}$ is the observed fluorescence intensity of C excited at the absorption maximum, $Em(c)^{max}$ corresponds to the fluorescence intensity of C in the absence of the energy-donor chromophore, $\varepsilon(C)$ is the extinction coefficient of the chromophore under the present experimental conditions, and $\varepsilon(C)_{370}$ is the extinction coefficient of the NMI donor at 370 nm. This method allows the fluorescence quantum yields of the NMI and the PMI chromophores in the triad **9** to be reduced from a value of nearly one to 0.17 and 0.2, respectively.

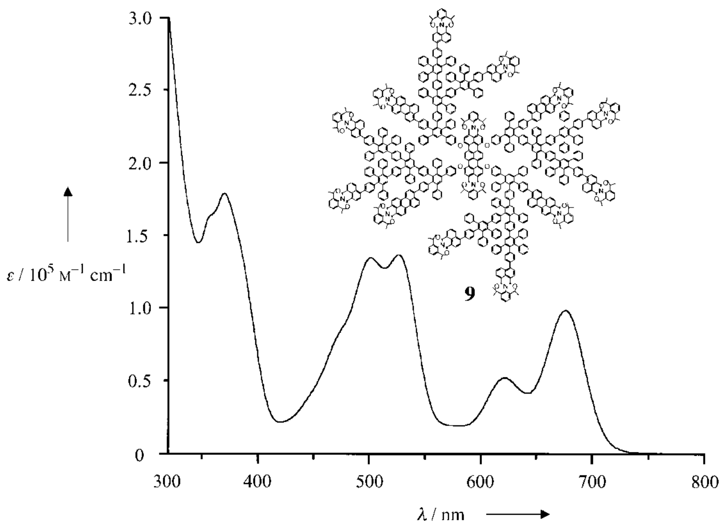

Figure 4. UV/Vis absorption spectrum of **9** in toluene (10^{-5} M).

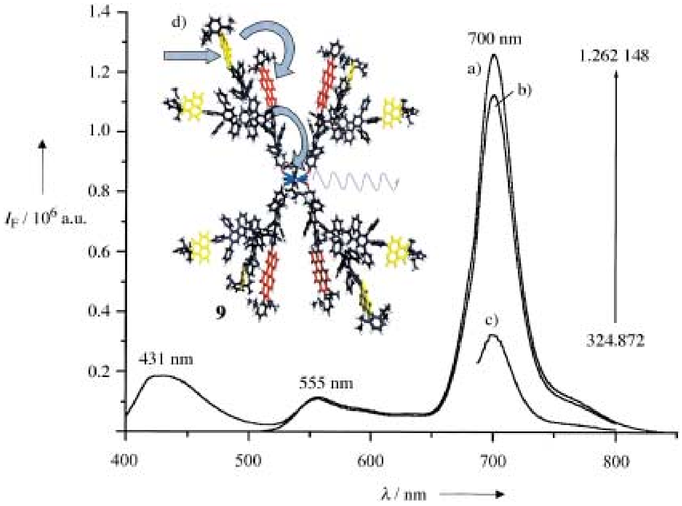

Figure 5. Emission spectra of **9** after excitation of a) the NMI chromophores at the periphery ($\lambda_{exc} = 370$ nm, 10^{-6} M), b) the PMI chromophores in the scaffold ($\lambda_{exc} = 480$ nm, 10^{-6} M), and c) the TDI chromophore in the center ($\lambda_{exc} = 665$ nm, 10^{-6} M). d) 3D structure of **9** obtained from molecular-mechanics calculations and visualization of the vectorial energy transfer from the periphery towards the center.

Figure 5 shows the emission spectra of the dendritic triad **9** when excited at different wavelengths. Upon excitation of the dendrimer periphery at 370 nm, a very strong TDI emission is observed (Figure 5 a). By exciting at the absorption maximum of the PMI chromophores at 500 nm, the fluorescence intensity of the core emission is slightly decreased (Figure 5 b). When exciting the TDI core at 676 nm, a comparatively low emission of the TDI core is detected (Figure 5 c). The intensity of a sensitized emission is stronger than that of a direct-core emission, that is, sensitization of the chromophore by a large light-harvesting antenna is more efficient than direct excitation at the absorption maximum by an external light source. In fact, when the TDI core is excited directly, its emission intensity is reduced by a factor of three. A similar effect has already been described for coumarin-labeled dendrimers[8, 23] as well as for phenylacetylene dendrimers that bear a focal perylene chromophore[6, 24] However, multichromphore **9** represents the first example of a dendritic triad in which the energy transfer as well as the energy gradient are induced by different types of chromophores being located at the periphery, in the scaffold, and in the core of a polyphenylene dendrimer and are thus independent of the dendritic scaffold.

We present a novel synthetic approach towards structurally well-defined polyphenylene multichromophores that bear two or three different types of chromophores at spatially well-defined positions in the core, in the scaffold, and at the periphery of the dendrimer. Different dendritic dyads show an efficient energy transfer from the PMI towards the TDI units. The first example of a dendritic triad **9** covers the whole spectrum of visible light and shows a stepwise energy transfer over a distance of 30 Å from the periphery via the scaffold towards the center of the dendrimer. The high thermal and chemical stability of the novel multichromophores makes them attractive candidates as emissive layers for the design of novel photonic devices as well as for solar-cell applications. Their high photochemical stability further allows single-molecule measurements, which are currently underway. Future work will focus on the combination of these highly emissive macromolecules with artificial reaction centers that convert excitation energy into chemical potential, which is still a challenging task in the design of opto-electronic devices.

Received: November 19, 2001
Revised: February 18, 2002 [Z18242]

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