Review

Fluorescence and Intramolecular Energy Transfer in Polyphenylene Dendrimers

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ABSTRACT: The fluorescence of polyphenylene dendrimers and the intramolecular energy transfer in polyphenylene dendrimers containing a perylenediimide core have been investigated in this paper. Polyphenylene dendrimers composed of tens or hundreds of out-of-plane twisted phenyl units exhibit strong fluorescence, with quantum yields ranging from 0.2 to 0.5 depending on the dendrimer generation and its degree of functionality. The fluorescence of polyphenylene dendrimers can be efficiently quenched by the incorporated perylenediimide core, and consequently, a predominant emission from the core has been observed, indicating a very efficient intramolecular energy transfer.

Introduction

Dendrimers are highly branched and structurally regular macromolecules constructed step by step by either a convergent or divergent strategy.[1−4] Because of the controllable incorporation of various functional groups across the whole structure of dendrimers, they have attracted much attention recently as new systems for the study of intramolecular energy transfer, where the numbers and types of the energy donor at the rim or across the dendrimer branches as well as the distance between the donor and the energy trap at the core can be easily regulated.[5−13] This approach, in which the dendrimer only acts as a scaffold that holds the donor and acceptor chromophores, provides versatility such that additional features can be easily introduced by simply changing the various components of the dendrimer.

Alternatively, the dendrimer backbones themselves can be concurrently used as the energy donor. Several types of chromophoric dendrimer backbones such as poly(phenylacetylene),[14−16] polyphenylene,[17,18] and poly(benzyl ether)[19,20] have been used as light absorbers, and the energy was efficiently funneled to the core acceptor. While the reported intramolecular energy transfer efficiency in such systems was rather high, most of the chromophoric backbones still suffered from a weak fluorescence or a low fluorescence quantum yield. For instance, the quantum yield of the widely used poly(benzyl ether) dendrimer is only less than 1%.[7] Lower generation poly(phenylacetylene) dendrimers have quite high quantum yields; however, they decrease with increasing dendrimer generations.[14c] One exception was phenylacetylene dendritic macromolecules based on unsymmetrical branching, which have high fluorescence quantum yields ranging from 65% to 81%.[16]

In this contribution, we report that polyphenylene dendrimers composed of tens or hundreds of out-of-plane twisted phenyl units can be used as chromophoric backbones. They exhibit strong fluorescence. Moreover, the energy collected by these bulky moieties can be efficiently funneled to the perylenediimide energy sink incorporated in the core of these dendrimers, resulting in an efficient quenching of the polyphenylene fluorescence and a predominant emission from the core.

Experimental Section

Materials. The synthesis of the polyphenylene dendrimers used in this study (structures shown in Figure 1) has already been reported.[21−23] These dendrimers exhibit good solubility in common organic solvents and thus can be characterized by matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS). The perfect agreement between calculated and experimentally determined *m*/*z* ratios for these dendrimers confirms their monodispersity. CH_2Cl_2 (Acros Organics, New Jersey) and THF (Acros Organics, New Jersey) were used as received. All the used solvents are of spectrophotometric grade.

Absorption Spectra. The absorption spectra of the dendrimer solutions were recorded on a Perkin-Elmer Lamdba 40 UV/vis spectrometer. All spectra were measured at room temperature.

Fluorescence Spectra. The steady-state fluorescence spectra of the dendrimer solutions were recorded with a Spex spectrophotometer. The fluorescence quantum yields, obtained in nondegassed solutions, of polyphenylene dendrimers have been determined using quinine sulfate in 0.05 M sulfuric acid as a reference.[24] The fluorescence quantum yields of perylenediimide-core polyphenylene dendrimers have been determined using cresyl violet in methanol as reference.[24] For the deter-

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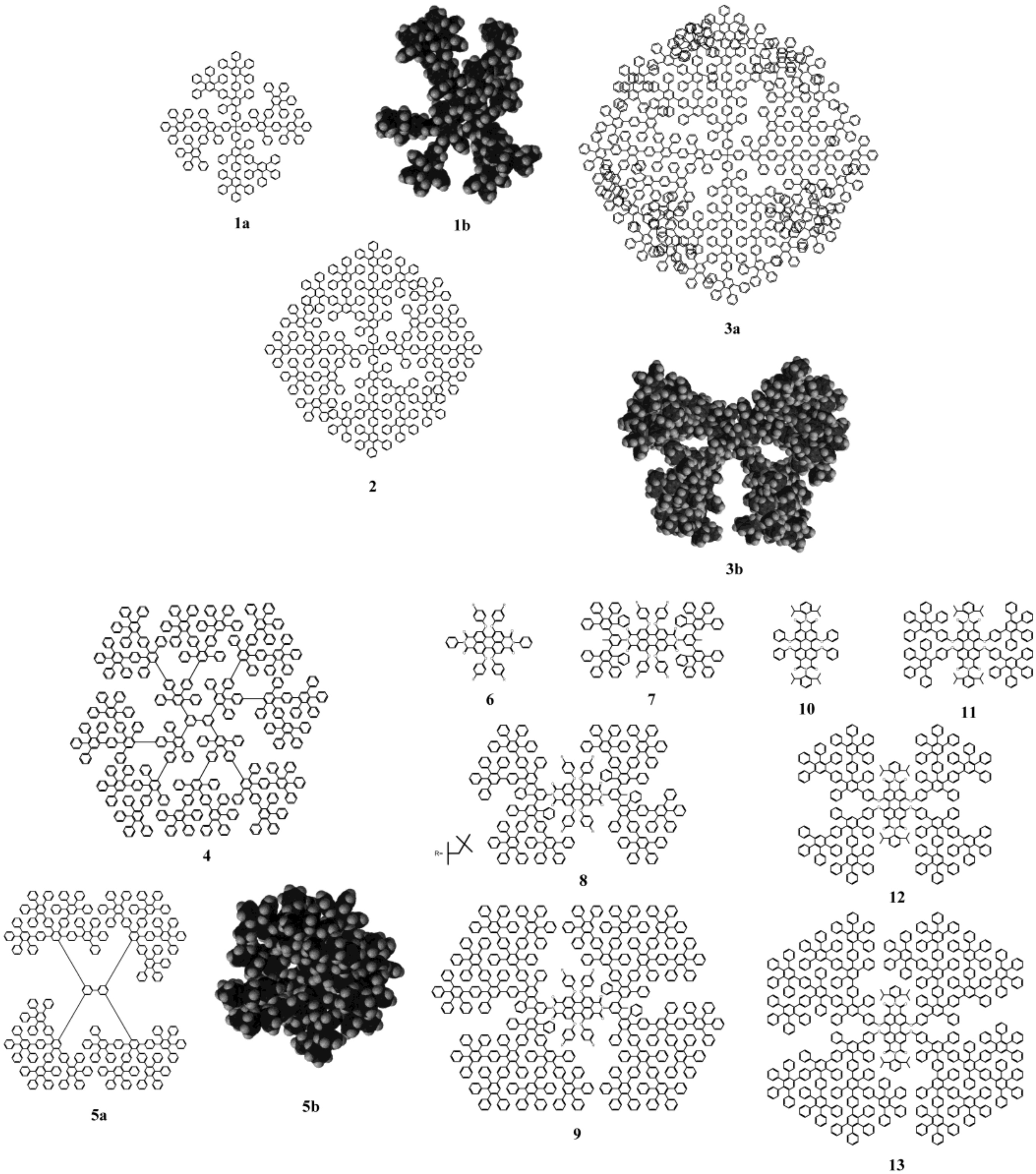

1a
1b
3a
2
3b
4
6
7
10
11
8
12
5a
5b
9
13

Figure 1. Molecular structures of polyphenylene dendrimers used in this study. **1a**, **2**, and **3a** are the second-, third-, and fourth-generation polyphenylene dendrimers with a tetraphenylmethane core. **4** and **5a** are the third- and second-generation polyphenylene dendrimers with a biphenyl core. Dendrimer **5** has a degree of functionality of 4 instead of 2 relative to other polyphenylene dendrimers. **6, 7**, **8**, and **9** are the zero-, first-, second-, and third-generation polyphenylene dendrimers with a perylenediimide core, where the polyphenylene dendrons are attached to the nitrogen atom of perylenediimide core. **10**, **11**, **12**, and **13** are the zero-, first-, second-, and third-generation polyphenylene dendrimers with a perylenediimide core, where the polyphenylene dendrons are attached to the bay position of perylenediimide core by a phenoxy spacer. **1b, 3b,** and **5b** are the space-filling view of dendrimers **1a, 3a,** and **5a** built by a Merck Molecular Force Field (MMFF) method.

mination of the fluorescence quantum yields, the absorbance at the excitation wavelength is around 0.1.

Time-Resolved Fluorescence Measurements. The fluorescence decay times of polyphenylene dendrimers have been determined by the single-photon timing method using a setup described previously.[25,26] In brief, the third harmonic of a Ti: sapphire laser (Tsunami, Spectra Physics) has been used to excite the degassed samples at 282 nm with a repetition rate of 4.09 MHz.[25] The detection system[26] consists of a subtractive double monochromator (9030DS, Sciencetech) and a microchannel plate photomultiplier (R3809U, Hamamatsu). A time-correlated single-photon counting PC module (SPC630, Picoquant GmbH), which has the two constant fraction discriminators (CFD), a time-amplitude converter (TAC), and an analog-to-digital converter (ADC) on board, was used to obtain the fluorescence decay histograms in 4096 channels with time increments of 5 or 10 ps. The fluorescence decays have been recorded at the magic angle, 54.7°, and analyzed globally with time-resolved fluorescence analysis (TRFA) software.[27] The quality of the fits has been judged by the fitting parameters such as χ^2 (<1.2), $Z\chi^2$ (<3), and the Durbin−Watson parameter (1.8 < DW < 2.2) as well as by the visual inspection of the residuals and autocorrelation function.[28]

Molecular Modeling. Geometry optimization of the dendrimer molecules was achieved in a vacuum using a molecular mechanics method (Merck Molecular Force Field)[29] as part of the Spartan program (Wave Function Inc., Irvine, CA).

Results and Discussion

1. Fluorescence of Polyphenylene Dendrimers. 1.1. Absorption Spectra of Polyphenylene Dendrimers. The molecular structures of polyphenylene dendrimers used in this study are shown in Figure 1. **1**, **2**, and **3** are the second-, third-, and fourth-generation polyphenylene dendrimers with a tetraphenylmethane core, respectively. **4** and **5** are the third- and second-generation polyphenylene dendrimers with a biphenyl core, respectively. Dendrimer **5** has a degree of functionality of 4 instead of 2 relative to polyphenylene dendrimers **1**, **2**, **3**, and **4**. These dendrimers consist of tens or hundreds of phenyl units and thus have high absorption in the UV region. The molar extinction coefficients of polyphenylene dendrimers as a function of wavelength are shown in Figure 2A,B, from which it can be seen that the extinction coefficients of polyphenylene dendrimers increase with the dendrimer bulkiness. For dendrimers **1**, **2**, and **3**, the extinction coefficient almost doubles with increasing generation, which reflects the corresponding change in the number of phenyl rings within these dendrimers. (There are 64, 144, and 304 phenyl rings in dendrimer **1**, **2**, and **3**, respectively.) Because of the out-of-plane twist of the phenyl units with respect to one another (see molecular models in Figure 1), no significant conjugation among these phenyl groups is expected. However, electronic interactions or couplings between the phenyl groups are clearly evidenced from the absorption spectra of these dendrimers. (1) The absorption spectra of polyphenylene dendrimers have an appreciable red shift relative to the sum of the absorption of all individual phenyl units. Compared to the absorption spectra of linear oligophenyls,[30] the absorption spectra of polyphenylene dendrimers are red-shifted relative to biphenyl absorption but are blue-shifted relative to that of *p*-quaterphenyl. (2) The shape of these absorption spectra varies with the dendrimer generation and its degree of functionality. Normalized absorption spectra of polyphenylene dendrimers at short wavelength (e.g., 275 nm) are shown in the insets of Figure 2A,B: increasing the dendrimer generation (insets in Figure 2A) and the degree of functionality (inset in Figure 2B) results in a relative high absorption at longer wavelength, suggesting stronger or extended inter-phenyl interactions with increasing phenyl density in the dendrimer arms. Molecular models shown in Figure 1 indicate that polyphenylene dendrimers with a degree of functionality of 2 such as dendrimers **1**, **2**, **3**, and **4**, irrespective of the generation and nature of the cores, possess rather separated branches due to the well-defined three-dimensional dendrimer structures (1**b** and 3**b** in Figure 1). Dendrimers **2** and **4**, which have the same dendritic arms but different cores (biphenyl or tetraphenylmethane), have almost overlapping normalized absorption spectra (inset in Figure 2B), suggesting that the effect of the core on the inter-phenyl electronic interactions is negligible and the interactions within the branches are more important. However, when the degree of functionality of the dendritic arms is increased to 4, for example in dendrimer **5**, the dendrimer branches become spatially more crowded and the dendrimer structure resembles a closed spherical shape (**5b** in Figure 1). Such a dendrimer structure leads to stronger inter-phenyl through-space electronic interactions among dendrimer branches and a consequent red shift in the absorption spectra (inset in Figure 2B).

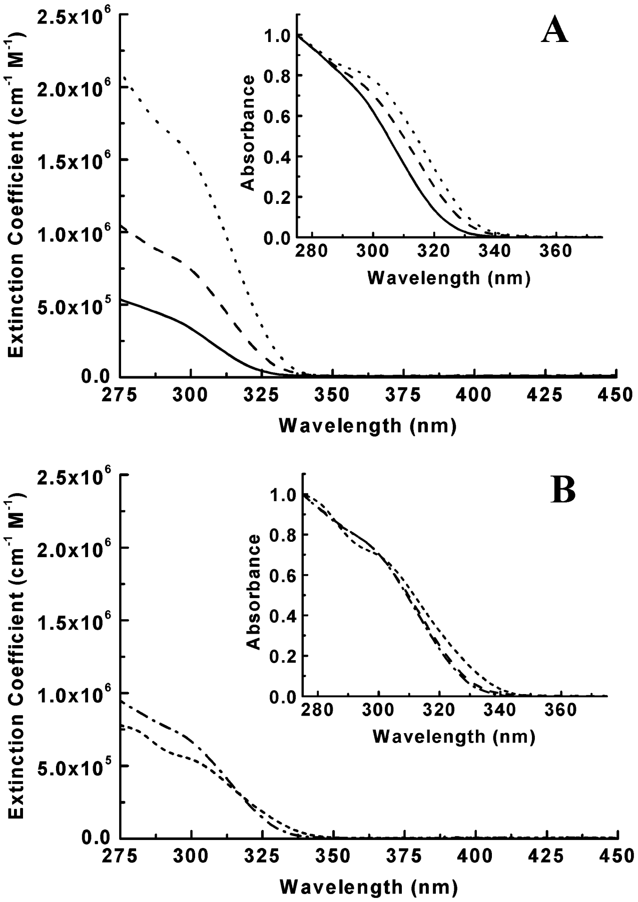

Figure 2. (A) Extinction coefficients of polyphenylene dendrimers **1** (solid), **2** (dash), and **3** (dot) in CH_2Cl_2. Inset shows the absorption spectra of dendrimer **1** (solid), **2** (dash), and **3** (dot) normalized at short wavelength (275 nm). (B) Extinction coefficients of polyphenylene dendrimers **4** (dash dot) and **5** (short dash) in CH_2Cl_2. Inset shows the absorption spectra of dendrimers **2** (dash), **4** (dash dot), and **5** (short dash) normalized at short wavelength (275 nm).

1.2. Fluorescence Spectroscopy of Polyphenylene Dendrimers. Polyphenylene dendrimers emit a strong fluorescence in various solvents such as CH_2Cl_2 and THF with a maximum in emission at ca. 365 nm, as shown in Figure 3A. As an example, the excitation fluorescence spectrum of dendrimer **2** is shown in Figure 3B. The fluorescence parameters for these dendrimers are collected in Table 1. The emission maximum of polyphenylene dendrimers shows a slight bathochromic shift with increasing degree of functionality of the dendritic arms, which could be a result of

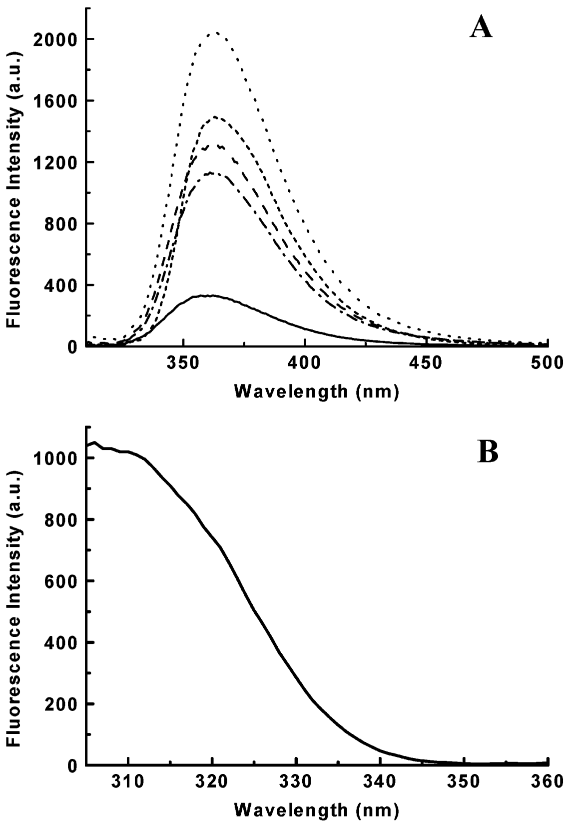

Figure 3. (A) Emission spectra of polyphenylene dendrimers **1** (solid), **2** (dash), **3** (dot), **4** (dash dot), and **5** (short dash) in THF normalized to the same molar concentration. Excitation wavelength is 310 nm. (B) Excitation fluorescence spectrum of dendrimer **2** in THF. The detected emission wavelength is 365 nm.

Table 1. Fluorescence Maxima (λ_{max}) and Quantum Yields (ϕ) of Polyphenylene Dendrimers

		ϕ	
dendrimers	λ_{max}, nm	in CH_2Cl_2	in THF
1	362	0.17	0.18
2	363	0.28	0.30
3	366	0.25	0.27
4	365	0.24	0.26
5	368	0.46	0.45

excimer-like interactions in the densely packed arms (Table 1). Generally speaking, all polyphenylene dendrimers in this study have a rather high quantum yield, as indicated from Table 1. The quantum yield increases at higher generations. It is important to note that the quantum yield of dendrimer **5** improves significantly with respect to other dendrimers, which could be related to a decrease in the nonradiative decay processes as a result of an increased crowding and rigidity, decreasing tortional and rotational motion and vibration. It should also be pointed out that dendrimers **2** and **4** have similar emission spectra shape and emission intensity, suggesting again negligible interbranch interactions in dendrimers with separated branches.

The fluorescence decay times of polyphenylene dendrimers in CH_2Cl_2 have been measured by time-correlated single-photon counting. The samples were degassed and excited at 282 nm, and the fluorescence decay was monitored at several wavelengths. The recovered decays can be analyzed as three exponential. The decay times vary between 0.1 and 2 ns, demonstrating the complexity of the excited-state processes occurring in these dendrimers. The values of the main fluorescence decay times at 400 nm are 0.46 ns for **1**, 0.74 ns for **2**, 0.73 ns for **3**, 0.80 ns for **4**, and 1.15 ns for **5**. It demonstrates that the main decay time of the polyphenylene dendrimers increases from the second-generation dendrimer **1** to higher-generation dendrimers **2** and **3**. Dendrimer **2** and **4** have a similar main decay time. The densely packed dendrimer **5** has a longer main decay time compared to those of other dendrimers with a degree of functionality of 2, in line with the fluorescence quantum yields.

2. Intramolecular Energy Transfer in Polyphenylene Dendrimers Containing a Perylenediimide Core. The intramolecular energy transfer in polyphenylene dendrimers containing a perylenediimide core was investigated on two series of dendrimers. In the first series, the polyphenylene dendrons are substituted on the imide nitrogen of the perylenediimide core (**7**, **8**, and **9** in Figure 1). Compound **6** was used as a perylenediimide model compound for **7**, **8**, and **9**. In the second series, the polyphenylene dendrons are attached to the core in the bay position through four phenoxy substituents (**11**, **12**, and **13** in Figure 1). Compound **10** was used as a core model compound for **11**, **12**, and **13**. The decoration of the perylenediimide dye with a rigid polyphenylene dendrimer shell can suppress the aggregation of the chromophore, which is important since aggregation often leads to fluorescence quenching.[22] In this study, we are able to show that the polyphenylene dendritic arms give rise to an extra excitation band for the perylenediimide core in the UV region via efficient intramolecular energy transfer.

The absorption spectra of perylenediimide decorated with different generations of polyphenylene dendritic arms are shown in Figures 4A and 5A. As can be seen from the spectra, there are two distinct bands: one in the visible region (400−600 nm) and the other one in the UV region (280−350 nm). The absorption in the visible region is due to the perylenediimide chromophore. Between 480 and 600 nm the absorption reflects the S_0-S_1 electronic transition of perylenediimide along the long axis.[31] An additional peak between 400 and 460 nm corresponds to the S_0-S_2 transition of which the transition dipole moment is along the short axis.[31] The absorption below 350 nm, which increases significantly from **6** to **9** (Figure 4A) and from **10** to **13** (Figure 5A), is predominantly attributed to the polyphenylene dendritic arms. The absorption of the perylenediimide and the polyphenylene dendritic arms is well-separated, which provides the possibility to selectively excite the polyphenylene dendrons for the study of intramolecular energy transfer. It is noted from Figure 4A that there is a slight blue shift (from 577 to 571 nm) in the absorption maxima of the dendronized perylenediimide **7**, **8**, and **9** compared to that of the model compound **6**. This might be related to the twisting of phenyl units at both ends of the perylenediimide core due to the addition of the bulky polyphenylene dendritic arms. On the contrary, it can be seen from Figure 5A that there is a gradual red shift (from 567 to 575 nm) in the absorption maxima of perylenediimide core from **10** to dendronized perylenediimide **11**, **12**, and **13**, which might be ascribed to the electron-donating capacity of the bulky phenoxy dendrons.

The emission spectra of **6**−**9** at two excitation wavelengths (310 and 530 nm) are shown in Figure 4B. Again, the perylenediimide decorated with polyphe-

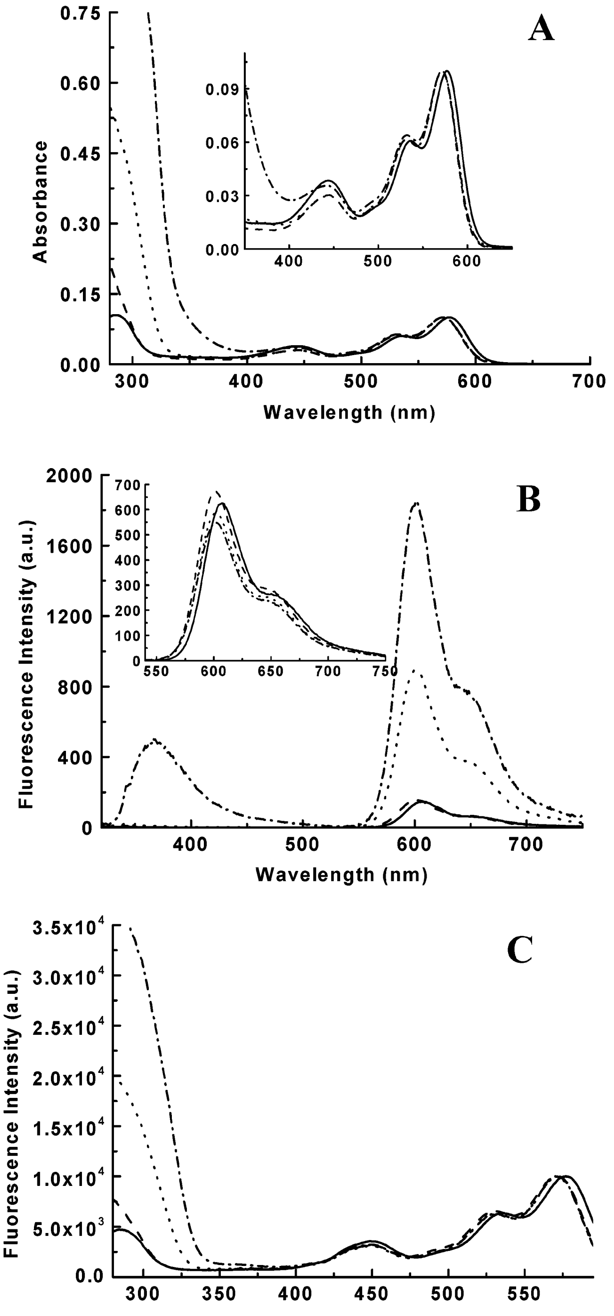

Figure 4. (A) Absorption spectra of **6** (solid), **7** (dash), **8** (dot), and **9** (dash dot) in THF normalized to the same concentration of perylenediimide. The inset shows the enlarged absorption spectra at long wavelength. (B) Emission spectra of **6** (solid), **7** (dash), **8** (dot), and **9** (dash dot) in THF excited at 310 nm. The inset shows the emission spectra of **6** (solid), **7** (dash), **8** (dot), and **9** (dash dot) in THF excited at 530 nm. The spectra are normalized to the same concentration of perylenediimide. (C) Excitation fluorescence spectra of **6** (solid), **7** (dash), **8** (dot), and **9** (dash dot) in THF. The monitoring emission wavelength is 600 nm. The spectra are normalized to the same concentration of perylenediimide.

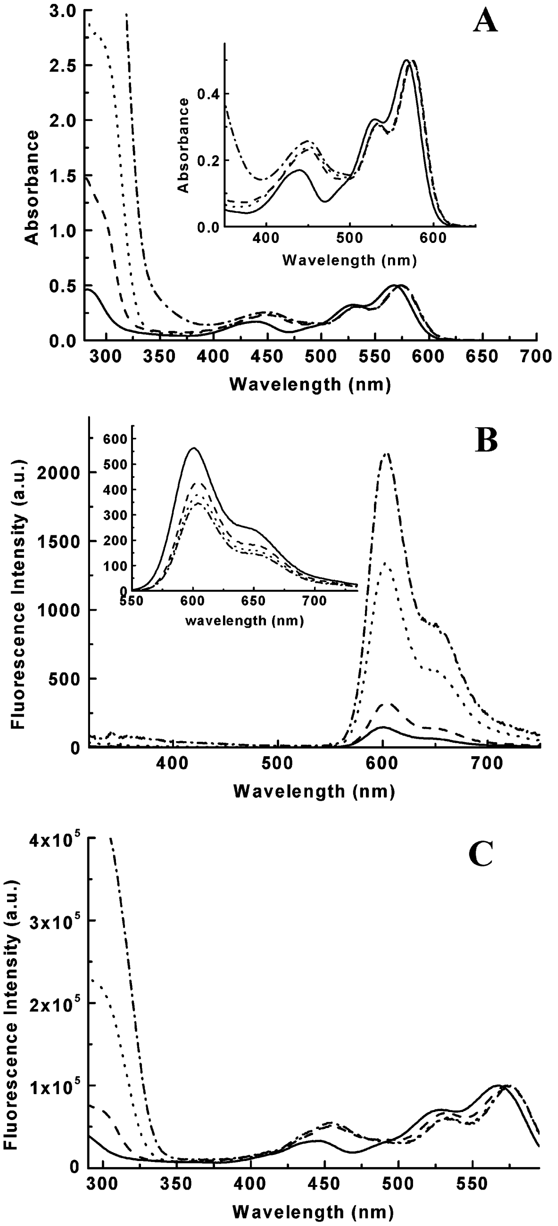

Figure 5. (A) Absorption spectra of **10** (solid), **11** (dash), **12** (dot), and **13** (dash dot) in THF normalized to the same concentration of perylenediimide. The inset shows the enlarged absorption spectra at long wavelength. (B) Emission spectra of **10** (solid), **11** (dash), **12** (dot), and **13** (dash dot) in THF excited at 310 nm. The inset shows the emission spectra of **10** (solid), **11** (dash), **12** (dot), and **13** (dash dot) in THF excited at 530 nm. The spectra are normalized to the same concentration of perylenediimide. (C) Excitation fluorescence spectra of **10** (solid), **11** (dash), **12** (dot), and **13** (dash dot) in THF. The monitoring emission wavelength is 600 nm. The spectra are normalized to the same concentration of perylenediimide.

Table 2. Fluorescence Quantum Yields (ϕ) of Perylenediimide with Attached Polyphenylene Dendritic Arms in THF Excited at 530 nm at Room Temperature

dendrimers	ϕ	dendrimers	ϕ
6	0.95	**10**	0.96
7	0.97	**11**	0.71
8	0.85	**12**	0.63
9	0.81	**13**	0.57

nylene dendrons exhibits a blue shift in its emission spectrum compared to that of **6**. The quantum yields of the perylenediimide core when excited at 530 nm were measured using cresyl violet in methanol as a reference and are listed in Table 2. The fluorescence quantum yield decreases slightly with increasing generation in the first series of dendrimers (**6**−**9**). The emission spectra of **10**−**13** at the same excitation wavelengths are shown in Figure 5B and reveal a red shift of the emission maxima for **11**−**13** compared to that of **10**. Table 2 indicates that the decrease in the fluorescence quantum yields of **11**−**13** is significant compared to that of **10**. The decrease in the quantum yields of the perylenediimide core with increasing dendrimer generation in THF indicates that the attachment of bulky polyphenylene dendrons creates extra nonradiative pathways for the relaxation of the excited states of perylenediimide. The steady-state spectroscopic measurements of the second series of dendrimers (**10**−**13**) in methylcyclohexane exhibit blue-shifted absorption and emission spectra (relative to those in THF) and only slight decrease of perylenediimide quantum yields upon increasing dendrimer generation,[32] indicating that the solvation of dendrimers plays an important role in their photophysical processes. A detailed investigation on the photophysics of these dendrimers is in progress and will be reported in due time.

When **6**−**13** are excited at 310 nm where most of the radiation is absorbed by the polyphenylene dendrons as known from the absorption spectra, predominant emission from the perylenediimide core was observed, with a negligible or weak residual fluorescence of polyphenylene dendrons at about 365 nm (Figures 4B and 5B). Furthermore, the fluorescence intensity increases with increasing generation of the dendritic arms, even though the decoration of perylenediimide core with polyphenylene dendrons results in a decrease in its fluorescence quantum yield when directly exciting the perylenediimide core. The fact that the excitation of the polyphenylene moieties leads to perylenediimide core fluorescence, whose fluorescence intensity also increases with the bulkiness of polyphenylene arms, undoubtedly indicates that intramolecular energy transfer has occurred in these dendrimers. The excitation spectra of **6**−**13** are shown in Figures 4C and 5C. These spectra are similar in shape to the corresponding absorption spectra, which also indicates that the dendrimer branches are also responsible for the population of the emitting excited state of the perylenediimide core.

It can be seen from Figure 4B that the residual fluorescence of polyphenylene dendritic arms becomes stronger at higher generation (dendrimer **9**), indicative of a decreased energy-transfer efficiency. The decreased energy-transfer efficiency at higher-generation dendrimers can be interpreted as a result of the increased distance between the donor and acceptor. For dendrimers **7**, **8**, **11**, **12**, and **13**, an almost complete intramolecular energy transfer is observed given the negligible residual fluorescence of polyphenylene dendritic arms at about 365 nm. For dendrimer **9**, an intramolecular energy-transfer efficiency of 86% was obtained by comparing the fluorescence of the donor chromophore (polyphenylene) with and without energy sink (perylenediimide). Because of the negligible interbranch interactions in polyphenylene dendrimers with separated arms, dendrimer **4** was used as the model donor chromophore for dendrimer **9**. It is reasonable to conclude that the intramolecular transfer in the second series of dendrimers (for example **13**) is more efficient than that in the first series of dendrimers (for example **9**) given that they have the same donor and acceptor chromophores.

The high extinction coefficients of polyphenylene dendrimers at short wavelength and their strong emission intensity, together with the highly efficient intramolecular energy transfer from the polyphenylene dendritic arms to the perylenediimide core, result in a stronger emission from the perylenediimide core by indirect exciting higher-generation polyphenylene dendritic arms, as can be clearly seen from the excitation spectra shown in Figures 4C and 5C. For instance, the emission spectra of dendrimer **13** in THF excited at 310 nm and at the absorption maximum (575 nm) of the perylenediimide core are shown in Figure 6. There is a 10-fold increase in perylenediimide fluorescence intensity in dendrimer **13** when excited at 310 nm compared to that when excited at 575 nm, corresponding to the fact that the extinction coefficient for dendrimer **13** at 310 nm is exactly 10 times higher than that at 575 nm. While in the literature, this effect is coined as light harvesting, in reality it is only due to increased absorption cross section of the dendritic structures.

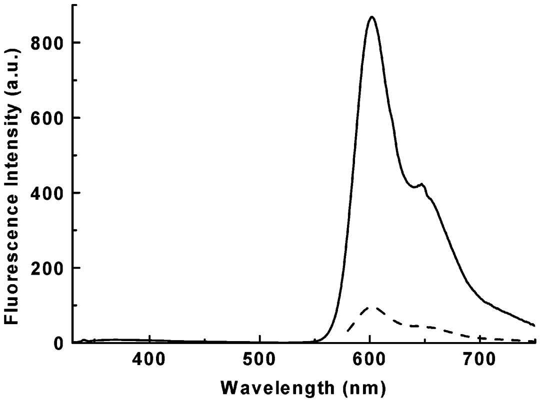

Figure 6. Fluorescence emission spectra of **13** in THF excited at 310 nm (solid) and at the absorption maximum of perylenediimide 575 nm (dash).

Within the framework of the Förster formulations, an effective interaction radius can be calculated from the steady-state spectra and the fluorescence quantum yield of the donor chromophore (ϕ_D) with the eqs 1 and 2[33]

$$R_0^{\,6} = 8.875 \times 10^{-5} \frac{\kappa^2 \phi_D J}{n^4} \qquad (1)$$

where κ^2 in a first approximation is equal to $^2/_3$ for the usually assumed random orientation of the chromophores, ϕ_D is the donor fluorescence quantum yield, n is the refractive index of the solvent, and J is the spectral overlap integral defined by

$$J = \frac{\int F_D(\lambda)\, \epsilon_A(\lambda) \lambda^4 \, d\lambda}{\int F_D(\lambda)\, d\lambda} \qquad (2)$$

where $\epsilon_A(\lambda)$ represents the molar extinction coefficient of the acceptor and $F_D(\lambda)$ represents the donor fluorescence spectrum on a wavelength (λ) scale.

Assuming a quantum yield of 0.25 for polyphenylene dendrimers,[34] the calculated values are about $J = 8.2 \times 10^{13}$ M^{-1} cm^{-1} nm^4 and $R_0 = 2.4$ nm for polyphenylene dendrimers containing a perylenediimide core. It should be noted that the calculation of spectral overlap integral J is based on the absorption of **6**. Therefore, the radius R_0 slightly varies when applied to the polyphenylene dendronized perylenediimide since the attachment of polyphenylene dendritic arms changes the extinction coefficients of perylenediimide (vide infra).

Provided that the emission spectra of the polyphenylene dendritic arms overlap with the absorption spectra of the perylenediimide core due to the S_0−S_2 transition but not the S_0−S_1 transition (Figure 3 and Figures 4A and 5A), the efficient intramolecular energy transfer might occur from excited states of polyphenylene dendrons through higher-level excited states (S_2) of perylenediimide and the subsequent rapid internal conversion to the first singlet excited state. The intramolecular energy transfer via higher level excited states of the acceptor has been used to construct an ultraviolet to near-infrared converter in another dendritic system.[5g]

There are two possible explanations for the fact that more efficient intramolecular energy transfer occurs in the second series of dendronized perylenediimide (**10**−**13**) than that in the first series (**6**−**9**). First, since the polyphenylene dendrons are attached to the perylenediimide core through phenoxy substituents in the second series of dendrimers, they could fold toward the perylenediimide core. This makes the distance between the donor and the acceptor shorter than when the polyphenylene dendrons are attached to the perylenediimide core through rigid carbon−carbon bonds in the first series of dendrimers. Second, attaching polyphenylene dendrons in the bay position of perylenediimide through phenoxy substituents in the second series of dendrimers (**11**−**13**) increases the extinction coefficients of the S_0-S_2 transition around 450 nm (Figure 5A). For example, the extinction coefficients for dendrimer **11**, **12**, and **13** at 445 nm are about 18 000, 18 000, and 21 000 cm^{-1} M^{-1}, respectively, compared to the values of 12 000, 12 000, and 14 000 cm^{-1} M^{-1} for dendrimers **7**, **8**, and **9**, respectively. The increased extinction coefficients of S_0-S_2 transition upon substitution of the bay position of perylenediimide with phenoxy substituents improve the spectral overlap integral and hence result in a more efficient intramolecular energy transfer.

Conclusion

It has been demonstrated in this study that polyphenylene dendrimers, although composed of out-of-plane twisted phenyl units, exhibit strong fluorescence, with quantum yields ranging from 0.2 to 0.5 depending on the dendrimer generation and its degree of functionality. For polyphenylene dendrimers with separated branches, the interbranch electronic interactions are negligible.

The efficient intramolecular energy transfer in polyphenylene dendrimers containing a perylenediimide core has been confirmed by steady-state fluorescence measurements. The intramolecular energy transfer might occur from excited states of polyphenylene dendrons via higher-level excited states (S_2) of the perylenediimide core and the subsequent rapid internal conversion to the first singlet excited state of perylenediimide. The high extinction coefficients of polyphenylene dendritic arms at short wavelength and their strong fluorescence intensity, together with the efficient intramolecular energy transfer, result in a stronger emission from the perylenediimide core by indirectly exciting the higher-generation polyphenylene dendritic arms. The decoration of perylenediimide unit with polyphenylene dendritic arms not only suppresses its aggregation but also gives rise to an extra and efficient excitation band in the UV region.

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