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...f l u o r e s c e n c e o f p o l y p h e n y l e n e d e n d r i m e r s c a n b e e f f i c i e n t l y q u e n c h e d 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. 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. 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) 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%. Lower generation poly(phenylacetylene) dendrimers have quite high quantum yields; however, they decrease with increasing dendrimer generations. One exception was the quantum yield of the widely used...poly-(phenylacetylene) dendritic macromolecules based on unsymmetrical branching which have high fluorescence quantum yields ranging from 65% to 81%.

In this contribution, we report that 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.

Experimental Section
Materials. The synthesis of the polyphenylene dendrimers used in this study (structures shown in Figure 1) has already been reported. These dendrimers exhibit good solubility in common organic solvents and thus can be characterized by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The perfect agreement between calculated and experimentally determined m/z ratios for these dendrimers confirms their monodispersity. CHCl3 (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 Lambda 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. The fluorescence quantum yields of perylenediimide-core polyphenylene dendrimers have been determined using cresyl violet in methanol as reference.
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. In brief, the third harmonic of a Ti:sapphire laser (Tsunami, Spectra Physics) has been used to excite the degassed samples at 262 nm with a repetition rate of 4.09 MHz. The detection system consists of a subtractive double monochromator (9030DS, ScinTech) and a micro-

![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 perylenedimide core, where the polyphenylene dendrons are attached to the nitrogen atom of perylenedimide core. 10, 11, 12 and 13 are the zero-, first-, second-, and third-generation polyphenylene dendrimers with a perylenedimide core, where the polyphenylene dendrons are attached to the bay position of perylenedimide 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.](image)
channel plate photomultiplier (R3800U, Hamamatsu). A time-correlated single-photon counting PC module (SPC630, Picquant 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. The quality of the fits has been judged by the fitting parameters such as \( \chi^2 < 1.2 \), \( Z < 2 \), and the Durbin–Watson parameter \( 1.8 < DW < 2.2 \) as well as by the visual inspection of the residuals and autocorrelation function.

**Molecular Modeling.** Geometry optimization of the dendrimer molecules was achieved in a vacuum using a molecular mechanics method (Merck Molecular Force Field) 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. Figure 1. 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 (1b and 3b 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).

1.2. **Fluorescence Spectroscopy of Polyphenylene Dendrimers.** Polyphenylene dendrimers emit a strong fluorescence in various solvents such as CH\(_2\)Cl\(_2\) 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...
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 phenox 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. 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. 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. 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-
nymene 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 methycyclohexane 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 4A). 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 of perylenediimide 575 nm (dash). There is a 10-fold increase in perylenediimide fluorescence intensity in 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.

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 (φD) with the eqs 1 and 2:

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

where κ² in a first approximation is equal to 2/4 for the usually assumed random orientation of the chromophores, φD is the donor fluorescence quantum yield, n is the refractive index of the solvent, and J is the spectral overlap integral defined by

\[
J = \frac{\int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int F_D(\lambda) d\lambda} (2)
\]

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

Assuming a quantum yield of 0.25 for polyphenylene dendrimers, the calculated values are about J = 8.2 \times 10^{33} M^{-1} cm^{-1} nm^4 and \(R_0 = 2.4 \text{ nm}\) 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 S0–S2 transition but not the S0–S1 transition (Figure 3 and Figures 4A and 5A), the efficient intramolecular energy transfer...
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 in-tramolecular 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.58

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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References and Notes


(27) Homemade program developed in cooperation between The Management of Technology Institute (Belarusian State University) and The Division of Photochemistry and Spectroscopy (Katholieke University Leuven).


(32) The measured quantum yields of 10, 11, and 12 in methylcyclohexane are 0.96, 0.93, and 0.91, respectively.


(34) The quantum yields of polyphenylene dendrimers depend on their generation. This approximation gives rise to an error of less than 5% for $R_0$. 

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