Intramolecular Energy Hopping and Energy Trapping in Polyphenylene Dendrimers with Multiple Peryleneimide Donor Chromophores and a Terryleneimide Acceptor Trap Chromophore

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Abstract: Intramolecular Förster-type excitation energy transfer (FRET) processes in a series of first-generation polyphenylene dendrimers substituted with spatially well-separated peryleneimide chromophores and a terryleneimide energy-trapping chromophore at the rim were investigated by steady-state and time-resolved fluorescence spectroscopy. Energy-hopping processes among the peryleneimide chromophores are revealed by anisotropy decay times of 50–80 ps consistent with a FRET rate constant of $k_{\text{FRET}} = 4.6 \text{ ns}^{-1}$. If a terryleneimide chromophore is present at the rim of the dendrimer together with three peryleneimide chromophores, more than 95% of the energy harvested by the peryleneimide chromophores is transferred and trapped in the terryleneimide. The two decay times ($\tau_1 = 52 \text{ ps}$ and $\tau_2 = 175 \text{ ps}$) found for the peryleneimide emission band are recovered as rise times at the terryleneimide emission band proving that the energy trapping of peryleneimide excitation energy by the terryleneimide acceptor occurs via two different, efficient pathways. Molecular-modeling-based structures tentatively indicate that the rotation of the terryleneimide acceptor group can lead to a much smaller distance to a single donor chromophore, which could explain the occurrence of two energy-trapping rate constants. All energy-transfer processes are quantitatively describable with Förster energy transfer theory, and the influence of the dipole orientation factor in the Förster equation is discussed.

1. Introduction

Dendrimers have drawn lots of attention because of their highly branched structures capable of being used as building blocks for photonic devices.1,2 Several reports on dendrimers have been published in different areas such as guest-host chemistry,3 analytical chemistry,4 optoelectronics,5 catalysis,6 and biology.7 As dendrimers are also used to mimic the photosynthetic-light-harvesting antenna system, different types of dendritic and related chromophore assemblies have been designed and investigated to harvest light energy.8–12 A general pursuing sophisticated goal is to combine the artificial antenna system with an efficient energy trap to control the energy pathways. Only a few examples have recently been reported.8–13 However, the absence of shape persistence usually prevents a fully quantitative description.

Recently, investigations of dendrimers with a polyphenyl core around a central biphenyl unit decorated at the rim with...
peryleneimide chromophores have been reported\textsuperscript{14–17} at the ensemble and single molecule level leading to the understanding of the time and space resolved excited-state behavior of these peryleneimide dendrimers. It has been shown that the conformational distribution plays an important role in the dynamics of the photophysical processes involved.

With the aim of getting a better control over the spatial and orientational distribution of the peripheral chromophores, a series of dendrimers with a stiff core has been prepared\textsuperscript{18} consisting of a central $sp^3$ hybridized carbon to which the chromophores are arranged along the corners of the tetrahedron.

In a first series of systems, the chromophores are linked at the meta position of the outer phenyl group.\textsuperscript{19} In these dendrimers, a variable number (1–4) of peryleneimides are placed at the end of the polyphenyl arms. Direct excitation of the peryleneimide chromophore results in energy hopping among identical chromophores. The extent and rate constant of energy hopping was determined. As meta substitution results in a small configurational and conformational fraction of molecules in which peryleneimide leads to an “excited dimer”, a series of similar compounds, but with substitution in the para position of the outer phenyl group, was synthesized\textsuperscript{19} and is studied here (see Chart 1). Furthermore, to analyze energy transfer to a fluorescent trap, a dendritic structure with three peryleneimides and one teryleneimide is additionally investigated (Chart 1).

ensemble photophysics in toluene of this series of molecules is reported here.

2. Experimental Section

Materials. The synthesis of these rigid dendrimers having a tetrahedral core with a different number of peryleneimide and teryleneimide chromophores on the polyphenylene rim I required a novel approach, which is being published separately.\textsuperscript{18}

The samples were dissolved in toluene (Aldrich) to have an optical density below 0.1 in a 1 cm cell at the absorption maximum (495 nm), which corresponds to a concentration of $\sim 10^{-7}$ M.

Steady-State Measurements. Steady-state absorption and corrected fluorescence spectra were recorded with Lambda 40 (Perkin-Elmer) and SPEX spectrophotometers, respectively. The fluorescence quantum yields have been determined using a polyphenylene dendrimer (G1R1\_m) as a reference,\textsuperscript{19} that is substituted by a single peryleneimide in meta position.

Picosecond Time-Resolved Measurements. The fluorescence decay times have been determined by the single photon timing method using a setup described previously.\textsuperscript{21} In brief, the second harmonic of a Ti:sapphire laser (Tsunami, Spectra Physics) has been used to excite the samples at 488 nm with a repetition rate of 4.09 MHz. The detection system consists of a subtractive double monochromator (9030DS, Scin Barrettech) and a microchannel plate photomultiplier (R3809U, (23) Maus, M.; Rousseau, E.; Cotlet, M.; Schweitzer, G.; Hofkens, J; Van der Auweraer, M.; De Schryver, F. C.; Krueger, A. Rev. Sci. Instrum. 2000, 72, 36.
Figure 1. Steady-state absorption and emission spectra of the compounds G1Rn\_p (circles), the donor acceptor system G1R3\_ter\_p (solid lines), and terylene imide model compound TI-m (triangles).

Hamamatsu). A time-correlated single photon counting PC module (SPC 630, Picoquant GmbH), which has the two constant fraction discriminators (CFD), a time-to-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 three different orientations of the emission polarizer relative to the polarization plane of the excitation light, that is, 54.7° (magic angle), 0° (lpar), and 90° (lperp). The magic angle decays were analyzed globally with a time-resolved fluorescence analysis (TRFA) software. The quality of the fits has been judged by the fitting parameters such as χ² (a < 1.2), 2Z/khi (a < 3) and the Durbin-Watson parameter (1.8 < DW < 2.2) as well as by the visual inspection of the residuals and autocorrelation function.

This simple model predicts a double-exponential anisotropy decay with an amplitude ratio of (i1). If rotational movements are absent (Θrot = 0), a constant term r0 gives the well-known leveling off at long times.

In case of the presence of an energy trap, the function for the anisotropy decay remains the same as far as the fluorescence of the donor chromophores is concerned. However, to obtain an analytical expression for the intensity decay of a molecular system consisting of i donor chromophores and an emitting-energy trap A, the following master equation has to be solved

\[
\frac{dP}{dt} = KP
\]

where \( P \) is the vector of the time-dependent individual excitation probabilities for \( i \) donors and a single acceptor

\[
P(t) = \begin{pmatrix} D_1(t) \\ D_2(t) \\ \vdots \\ D_i(t) \\ A(t) \end{pmatrix}
\]

and \( K \) is the matrix of rate constants


\[24\) Homemade program developed in a cooperation between The Management of Technology Institute (Belarusian State University) and The Division of Photochemistry and Spectroscopy (Katholieke Universiteit Leuven).


Intramolecular Energy Hopping and Trapping

\[ K = \begin{pmatrix}
\sum_{j=1}^{i} k_{ij} - k_{1A} - \tau_i(D_1)^{-1} & k_{21} \\
- \sum_{j=1}^{i} k_{ij} - k_{2A} - \tau_i(D_2)^{-1} & \cdots & k_{i1} & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
\end{pmatrix}\] (7)

where \( k_{ij} \) represents the energy-hopping rate constants from donor \( i \) to donor \( j \), \( k_{ij} \) corresponds to the rate constant for energy trapping of donor \( j \) to the acceptor, \( \tau_i(D) \) and \( \tau_A(A) \) are the fluorescence lifetimes of the \( j \)th donor and the acceptor chromophore, respectively. For the simplest case of identically and equivalently behaving donor chromophores resulting in full energy-hopping cross talk (\( k_{ij} = k_{hop} \)) and a single energy-trapping rate constant (\( k_{ij} = k_{trap} \), the intensity decays of the donor and acceptor fluorescence can be described by

\[ I_i^D(t) = \alpha \sum_{i}^{1} \frac{1}{t} D_i(t) = \alpha \exp\left(\frac{k_{trap} + ik_{hop} + \tau_i(D)^{-1} - \tau_i(A)^{-1}}{t}\right) \] (8)

\[ I_i^A(t) = \gamma A(t) = \frac{2}{k_{trap} + ik_{hop} + \tau_i(D)^{-1} - \tau_i(A)^{-1}} \times \left(\exp\left(\frac{-ik}{k_{trap} + ik_{hop} + \tau_i(D)^{-1} - \tau_i(A)^{-1}}{t}\right) - \exp\left(\frac{-ik}{k_{trap} + ik_{hop} + \tau_i(D)^{-1} - \tau_i(A)^{-1}}{t}\right)\right) \] (9)

More complex solutions are discussed in the text.

4. Results

**Steady-State Spectra.** The steady-state absorption and fluorescence spectra of the dendrimers (G1R1_p, G1R3_p, G1R4_p) (Figure 1) containing only peryleneimide chromophores are identical, whereas for the dendrimer G1R3ter_p (Figure 1) the spectra show the sum of that of peryleneimide and teryleneimide chromophores. The absorption spectra of all the dendritic compounds in toluene show two vibronic maxima at 495 and 520 nm; in addition, the dendrimer G1R3ter_p shows three more vibronic bands at 592, 645, and 700 nm due to the teryleneimide chromophore. The fluorescence spectra show emission maxima at 560 and 595 nm for all above-mentioned dendrimers with an additional emission maximum at 730 nm for the dendrimer G1R3ter_p. The band at 730 nm is found if the molecule is excited at 680 nm in the teryleneimide absorption band and also at 495 nm in the peryleneimide absorption band. The fluorescence quantum yields (\( \phi_f = 0.98 \pm 0.05 \)) of the dendrimers G1R1_p, G1R3_p, G1R4_p have been found to be the same within the experimental error. The intensity of the perylene emission of G1R3ter_p has been found to be reduced by 95% based on fluorescence decay measurements (vide infra).

**Time-Resolved Measurements.** To investigate the excited-state deactivation taking place in these molecules, the time-resolved fluorescence measurements were undertaken. The fluorescence decay times for all the dendrimers were measured in toluene by the single photon counting method, detecting the emission under magic angle condition. The dendrimers were excited at 488 nm, the fluorescence decays were monitored at different emission wavelengths, and the decay traces were globally analyzed. The quality of the fitted decays was judged by the distribution of weighted residuals (Rw) and autocorrelation function (ac). A fluorescence decay trace of G1R3ter_p is given in Figure 2 and the respective decay parameters are collected in Table 1.

The global analysis of nine wavelength-dependent fluorescence decays in the range of 550–780 nm results in very good statistical fit quality parameters (\( R^2 = 1.05, DW = 1.9, Z^2 = 1.8 \)) if two decay times (\( \tau_1 = 52 \text{ ps} \) and \( \tau_2 = 175 \text{ ps} \)) for the perylene emission band and the same time constants \( \tau_1 \) and \( \tau_2 \) as two rise times together with the fluorescence lifetime (\( \tau_3 = 2.5 \text{ ns} \)) of teryleneimide for the teryleneimide emission band are used. Neglecting the rise of one decay (τ₁) component leads to a mean rise (decay) time of 148 ps with poor statistical fit quality parameters (\( R^2 = 2.04, DW = 1.0, Z^2 = 39 \)) proving the necessity of the two decay and rise times \( \tau_1 \) and \( \tau_2 \).

In addition, the time-resolved emission spectra were recorded for different time windows (Figure 3). The time zero corresponds to the onset of the first fluorescence photons.

**Time-Resolved Polarization Measurements.** To get a better insight into the dynamics involved, time-resolved anisotropy measurements were carried out. The anisotropy decay times (\( \Theta_i \)) and the associated anisotropy (\( \beta \)) have been determined for all the compounds using eq 10

\[ r(t) = \sum_{i}^{n} \beta_i \exp\left(-\frac{t}{\Theta_i}\right) \quad \text{and} \quad r_0 = \sum_{i}^{n} \beta_i \] (10)

For the dendrimer with one chromophore (G1R1_p), a monoeponential function is found to be sufficient to fit the anisotropy decay trace which can be related to the relaxation time of \( \Theta_1 = 1.4 \text{ ns} \pm 30 \text{ ps} \) with \( \beta_1 = r_0 = 0.34 \pm 0.04 \) (Table 2). However, the anisotropy decay traces for the dendrimers having more than one chromophore (G1R3_p, G1R4_p, G1R3ter_p) can only be fitted with two exponential decay functions (Figure 4). The magnitude of the long depolarization time component increases as the number of chromophores increases from 1 to 4, while the value of the fast component (\( \Theta_2 \)) changes from 70 ps for G1R3_p to 50 ps in G1R4_p (Table 2).

5. Discussion

**Fluorescence from Localized Species.** The steady-state properties of the dendrimers (G1R1_p, G1R3_p, G1R4_p) in terms of spectral shape, fluorescence maxima, and fluorescence quantum yield are within experimental error. This differs from observations made for the meta-substituted peryleneimide dendrimers\(^{19}\) where these steady-state spectral properties are found to be influenced by the formation of an excimer-like species.

Table 1 shows that the lifetimes of G1R1_p, G1R3_p, G1R4_p are the same, which is expected as the fluorescence is emitted from peryleneimide chromophores. No long decay component of 7.4 ns is observed as obtained for dendritic structures with a similar core, where the peryleneimide chro-
mophores are substituted in the meta position of the pentaphenylbenzene building block\(^{19}\) instead of the para position for the dendrimers studied here. Therefore, the absence of the long decay component is due to the different position of substitution leading to a better spatial separation of the individual chromophores. This is also supported by a comparison of the molecular mechanics structures of the para- (Chart 1) and meta-substituted dendrimers, since the center-to-center distance among the chromophores is 29 Å for the para series, but only 26 Å for the meta series.

Excitation of the dendrimer G1R3ter-p at 495 nm (the peryleneimide absorption maximum) results not only in residual peryleneimide emission but also in emission at 730 nm that corresponds to the teryleneimide emission, which demonstrates unidirectional energy transfer from peryleneimide to the trap teryleneimide chromophore. This energy-trapping process is discussed in detail below. As concerns the localized peryleneimide and teryleneimide fluorescence, both time-resolved and steady-state results indicate the absence of intramolecular excimer-like chromophore interaction also in G1R3ter-p.

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Table 1. Fluorescence Decay Times (\(\tau_i\)) and Associated Relative Amplitudes (\(\alpha_i\)) for the Dendrimers Measured in Toluene at Room Temperature Using \(\lambda_{\text{exc}} = 488\) nm

<table>
<thead>
<tr>
<th>compound</th>
<th>(\tau_1) (ns)</th>
<th>(\tau_2) (ns)</th>
<th>(\tau_3) (ns)</th>
<th>(\alpha_1) (%)</th>
<th>(\alpha_2) (%)</th>
<th>(\alpha_3) (%)</th>
<th>(\alpha_1) (%)</th>
<th>(\alpha_2) (%)</th>
<th>(\alpha_3) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1R1–p</td>
<td>4.0</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1R3–p</td>
<td>4.0</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1R4–p</td>
<td>4.0</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1R3ter–p(^a)</td>
<td>0.052</td>
<td>0.175</td>
<td>2.51</td>
<td>62.1</td>
<td>37.9</td>
<td>0</td>
<td>−30.9</td>
<td>−15.7</td>
<td>53.4</td>
</tr>
</tbody>
</table>

\(^a\) 2% of the decay at 600 nm was due to less than 0.1% peryleneimide dendrimer impurity in the sample that could not be separated by purification. This contribution is not considered.

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Figure 2. Time-resolved fluorescence decays of (a) G1R3–p and (b) G1R3ter–p with fits. The upper level shows the weighted distribution of residuals (\(R_i\)), and the lower one represents the auto-correlation (ac) functions for the decay. The excitation wavelength, \(\lambda_{\text{exc}}\), is 488 nm.

Figure 3. Time-resolved emission spectra of G1R3ter–p in toluene. The time zero is defined as the time of the arrival of the first fluorescence photon in the corresponding fluorescence decay. The spectra correspond to the time ranges 0.04 ± 0.04 ns, 0.145 ± 0.065 ns, 0.30 ± 0.095 ns, 0.55 ± 0.15 ns, 1.35 ± 0.65 ns, 3.40 ± 1.40 ns, 9.7 ± 5 ns. They are corrected for the detector–spectral response and the measured time window. The excitation wavelength, \(\lambda_{\text{exc}}\), is 488 nm.

Table 2. Fitting Parameters of the Fluorescence Anisotropy Decays Measured for the Dendrimers in Toluene with $\lambda_{exc} = 488$ and $\lambda_{em} = 600$ nm and Calculated Average Peryleneimide—Peryleneimide Distances ($d_{RET}$)

<table>
<thead>
<tr>
<th>compound</th>
<th>$r_0$</th>
<th>$\Theta_1$ (ns)</th>
<th>$\Theta_2$ (ns)</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_2/r_0$</th>
<th>$d_{RET}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1R1_p</td>
<td>0.34</td>
<td>1.4</td>
<td></td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1R3_p</td>
<td>0.31</td>
<td>1.6</td>
<td>0.07</td>
<td>0.09</td>
<td>0.22</td>
<td>71</td>
<td>27.3</td>
</tr>
<tr>
<td>G1R4_p</td>
<td>0.34</td>
<td>2.0</td>
<td>0.05</td>
<td>0.07</td>
<td>0.27</td>
<td>79</td>
<td>27.4</td>
</tr>
<tr>
<td>G1R3ter_p</td>
<td>0.33</td>
<td>2.3</td>
<td>0.075</td>
<td>0.09</td>
<td>0.24</td>
<td>72</td>
<td>27.5</td>
</tr>
</tbody>
</table>

* Using $r_0 = 44.3$ Å in eq 16.

Figure 4. Time-resolved anisotropy decays (scattered symbol) and the fits (solid line) for the dendrimers from 1 to 4: 1, open squares, G1R1_p; 2, full diamonds, G1R3_p; 3, open triangles, G1R4_p; 4, full circles, G1R3ter_p. The excitation and emission wavelengths are 488 and 600 nm, respectively.

Size of the Dendrimers. The single anisotropy decay time ($\Theta_1$) of about 1.4 ns (Table 2) for the dendrimer G1R1_p obtained from fluorescence anisotropy measurements can be associated with the rotational relaxation time ($\Theta_{rot}$) of the whole dendrimer. The corresponding long polarization time constant ($\Theta_2$) increases to 2.3 ns in G1R3ter_p. Assuming a spherical volume of the rotor, the diameters ($d_{rot}$) can be calculated with eq 11

$$d_{rot} = \sqrt{\frac{6 \eta f}{\pi}}$$  \hspace{1cm} (11)

on the basis of the Debye–Stokes–Einstein relation given by eq 12

$$\Theta_{rot} = \frac{V_{rot} f C}{k_B T}$$  \hspace{1cm} (12)

where $\Theta_{rot}$ is the rotational relaxation time obtained from $\Theta_1$, according to eq 4 and 10 with $h_{hopp} = 4.6$ ns$^{-1}$ (vide infra), $V$ is the hydrodynamic volume, $\eta$ is the solvent viscosity, $k_B$ is the Boltzmann constant, $T$ is the temperature, $f$ is a form factor set to 1 for spherical objects, and $C$ is a correction factor varying between 0 and 1 depending on sticking or slipping conditions.\(^{25a}\) On the basis of the Gierer–Wirtz model,\(^{25b}\) using the calculated van der Waals volumes of solvent and solutes, a correction factor of 0.45 is obtained leading to a hydrodynamic radius in the order of 25 Å. The resulting increase in rotational correlation times for G1R1_p to G1R3ter_p scales well with the expected increase of the hydrodynamic volume with the introduction of more chromophores in the dendritic structure. Moreover, these values are consistent with the increase of the dimensions deduced from molecular-modeling structures (Chart 1c and 1d)$^{27}$ and, as expected, in comparison to the corresponding meta-substituted dendrimers, the rotor diameters are larger in para-substituted dendrimers.

Intramolecular Excitation Energy Hopping. The process of energy hopping can be investigated by time-resolved anisotropy data. The relatively large value for the limiting anisotropy ($r_0$) of G1R1_p confirms an almost parallel orientation of the absorption and emission dipole moment for a single chromophore.

In contrast to the mono-exponential anisotropy trace of monochromophoric G1R1_p, the corresponding traces of the polychromophoric dendrimers G1R3_p, G1R4_p, and G1R3ter_p reveal a second and fast anisotropy decay component in the order of 50–80 ps. This fast depolarization process can be related to excitation energy hopping among the identical peryleneimide chromophores. From the time scale of these processes, it is apparent that the energy hopping takes place through the Förster mechanism in the same way as has been discussed previously for the corresponding meta series of dendrimers.$^{19}$ Within the framework of the Förster formulation,$^{26,28–30}$ an effective interaction radius ($R_0$) can be calculated from the steady-state spectra and the fluorescence quantum yield of the donor chromophore ($\phi_D$) with the equations (13) and (14)

$$R_0^6 = 8.875 \times 10^{-3} \frac{k^2 \phi_D f}{n^2}$$  \hspace{1cm} (13)

where $k^2$ is used as a first approximation equal to two-thirds for the usually assumed random orientation of the chromophores, $\phi_D$ is the donor fluorescence quantum yield, $n$ is the refractive index of the solvent (1.496 for toluene), and $J$ is the spectral overlap integral defined by

$$J = \frac{\int F_D(\lambda) \epsilon_D(\lambda) \lambda^4 d\lambda}{\int F_D(\lambda) d\lambda}$$  \hspace{1cm} (14)

where $\epsilon_D(\lambda)$ represents the molar extinction coefficient of the acceptor, and $F_D(\lambda)$ represents the donor fluorescence spectrum on a wavelength (\(\lambda\)) scale. The calculated values of $R_0$ is 38 Å and $J = 2.5 \times 10^{-14}$ M$^{-1}$ cm$^{-1}$ nm$^4$, using the spectral data ($\epsilon_{max} = 38.300$ M$^{-1}$ cm$^{-1}$,$^{18}$ $\phi_D = 98\%$) of the trichromophoric G1R3_p compound, are on the typical order of magnitude to be expected for FRET.$^{31}$

Information about the rate constant of hopping ($h_{hopp}$) through FRET can be derived from the fast anisotropy decay time ($\Theta_2$). However, to take into account the possibility of multiple hopping channels in the case of a multichromophoric system containing identical chromophores among which efficient dipole–dipole interaction occurs, the measured decay time $\Theta_2$ can be related to $h_{hopp}$ according to the energy-hopping model$^{19}$ by combining

\(^{27}\) Spartan Program, Wave function, Inc., 17401 Von Karman Ave., Ste. 370, CA 92612.
\(^{31}\) A collection of various references can be found in: Haughland, R. P. Handbook of Fluorescent Probes and Research Chemicals, 6th ed.; Molecular Probes Inc.: Eugene, OR, 1996; p 46.
\[ \Theta_{\text{rot}} = \Theta_{i} \text{, eq 4 and eq 10}, \] giving eq 15

\[ k_{\text{hopp}} = \frac{1}{i \Theta_{2}} - \frac{1}{i \Theta_{1}} \] (15)

where the value of \( i \) represents the number of chromophores sufficiently interacting in both forward and backward directions. On the basis of eq 15, a value of around 4.6 ns\(^{-1}\) is obtained for \( k_{\text{hopp}} \) of G1R3_p, G1R4_p, and G1R3ter_p, respectively. It seems surprising that this value is more than twice as large than that \( (k_{\text{hopp}} = 2 \text{ ns}\(^{-1}\)) \) obtained for the meta-substituted dendrimers, even though the interchromophoric distances is ca. 2 Å larger in the para series. In fact, by employing the excited-state lifetime \( \tau_{D} = 4 \text{ ns} \), using the above derived values of \( R_{0} = 38 \text{ Å} \) and \( k_{\text{FRET}} = k_{\text{hopp}}, \) the calculation of the distance between two chromophores through the Förster eq 16\(^{28}\)

\[ d_{\text{FRET}}^2 = \frac{R_{0}^6}{k_{\text{FRET}}^2 \tau_{D}} \] (16)

yields too small values of interchromophoric distances \( d_{\text{FRET}} \) for the peryleneimide chromophores in the order of 23 Å, despite the expected 28 Å from molecular-modeling structures (Chart 1). The only reason for this discrepancy can be the wrong estimated value of \( R_{0} \) because of the too simplified assumption of the dipole–dipole orientation factor \( \kappa^2 \) value of 2/3, which is strictly valid only for a random orientation of the chromophores. Here, this assumption is not true anymore, because of the attachment of chromophores into the dendrimer backbone. The values of \( \kappa^2 \) have been calculated from the three-dimensional molecular mechanics structures by eq 17

\[ \kappa = \sin(\delta_{D}) \sin(\delta_{A}) \cos(\varphi_{DA}) - 2 \cos(\delta_{D}) \cos(\delta_{A}) \] (17)

where \( \varphi_{DA} \) is the azimuthal angle between the involved transition dipole moment directions of the energy-donor D and energy-acceptor A, and \( \delta_{D} \) and \( \delta_{A} \) are the angles between the corresponding dipole directions of D and A with the intramolecular D–A axis, respectively. Indeed, average values of around 0.8 are obtained for the chromophore orientations in the meta-substituted dendrimers, confirming that the approximation of \( \kappa^2 = 2/3 \) made previously\(^{19} \) was reasonable. However, for the para-substituted dendrimers, the average \( \kappa^2 \) value is clearly larger, being around 2.1. The ratio of the calculated \( \kappa^2 \) values for the para vs the meta series is about 2.6. This value is in nice agreement with the respective ratio of the experimentally determined hopping rate constants, being about \( k_{\text{hopp}}(\text{para})/k_{\text{hopp}}(\text{meta}) = 2.3 \) or, if the slightly different interchromophoric distances \( (d \approx 26 \text{ Å} \) for meta and \( d \approx 28 \text{ Å} \) for para) are taken into account, being about \( k_{\text{hopp}}^2(\text{para})/k_{\text{hopp}}^2(\text{meta}) = 3.5 \).

Consequently, the faster energy-hopping kinetics in the para series can directly be traced back to a better orientation of the peryleneimide chromophores toward each other, yielding a much larger Förster interaction radius \( R_{0} = 44 \text{ Å} \) than in the meta series. Employing this value of \( R_{0} \) in eq 16 indeed leads to values of \( d_{\text{FRET}} = 27–28 \text{ Å} \) (Table 2), which agree with the average interchromophoric distances from molecular mechanics modeling.

**Intramolecular Excitation Energy Trapping.** The perylene chromophore in G1R3ter_p can be expected to act as an energy sink for the energy harvested by the peryleneimide chromophores excited in their absorption maximum at 495 nm. This expectation is derived from the large overlap integral \( J = 4.2 \times 10^{19} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^{-1} \) and the correspondingly large interaction radius \( R_{0} = 60 \text{ Å} \), calculated by eqs 13 and 14 using the spectral data of G1R3_p and a tereyleneimide model chromophore \( (\epsilon_{\text{max}} = 80,000 \text{ M}^{-1} \text{ cm}^{-1}, \phi_{f} = 98\%) \) and assuming \( \kappa^2 = 2/3 \) as a first approximation for an average of all possible chromophore orientations. Furthermore, by employing a distance \( d_{\text{FRET}} \) of about 28 Å between the donor and acceptor chromophores, that was also obtained for the peryleneimide interchromophoric distances (Table 2) and that can be expected from the three-dimensional molecular modeling structure of G1R3ter_p (Chart 1d), \( k_{\text{FRET}} \) in eq 16 predicts an efficient rate constant of energy trapping \( (k_{\text{hopp}}) \) from the perylene to the tereylene imide of about 20 ns\(^{-1}\) in G1R3ter_p.

Experimentally, the steady-state fluorescence spectrum of G1R3ter_p (Figure 1b) directly proves the trapping of the excitation energy in the peryleneimides by the tereylene chromophore, because the intense fluorescence band of the tereylene emission at 730 nm is observed by excitation at 495 nm, even though tereyleneimide itself does not absorb at this wavelength, while, on the other hand, the fluorescence band of the peryleneimide at 560 nm in G1R3ter_p is strongly quenched as compared in G1R3_p or G1R4_p. Quantitative information can be extracted from the drop of the fluorescence quantum yield of the peryleneimide emission in G1R3ter_p \( (\Phi_{f} = 4\%) \) compared with respect to that in G1R3_p \( (\Phi_{f} = 98\%) \).

Using eq 18\(^{29,30}\)

\[ \eta_{\text{trap}} = 1 - \frac{\Phi_{f}^D(AD)}{\Phi_{f}^D(D)} = 1 - \frac{\tau_{f}^D(AD)}{\tau_{f}^D(D)} \] (18)

the energy-trapping efficiency \( \eta_{\text{trap}} \) is calculated to be 95%, which, in accordance with the above considerations, yields a quenched mean donor lifetime \( \tau_{f}^D(AD) \) of around 160 ps. The time evolution of the energy-trapping process can visually be followed by the time-resolved emission (TRES) spectra in Figure 3. One can see that in the first 500 ps, the intensity decrease of the peryleneimide band at 560 nm is associated with a concomitant intensity increase or rise of the tereyleneimide band at 740 nm, proving the precursor–successor relationship for the donor and acceptor population, respectively. The kinetics for both band maxima are well described by a mean decay and rise time of about 200 ps, which is in good agreement with the value expected from the steady-state considerations using eq 17.

Moreover, the first time-resolved fluorescence spectrum in Figure 3 obtained within the first 80 ps of the arrival of fluorescence photons demonstrates another interesting feature. Already at this early time, tereyleneimide emission is observed. This indicates that another but more rapid energy-transfer process from the perylene to the tereylene occurs that is faster than the fwhm (ca. 70 ps) of the detection for this measurement.

The single photon timing global fluorescence decay analysis, which is more precise in determining decay and rise times, indeed reveals that a single rise time is insufficient to fit the experimental decay curves (Figure 2). Instead of only a single decay and rise time, two decay and rise times are recovered, namely, 172 and 52 ps. This means that two channels of energy trapping occur related to two different interaction types or strengths between peryleneimides (donor) and the tereyleneimide (acceptor) chromophore.

Very important quantitative information is given by the relative amplitudes of these two time constants in the donor and acceptor emission. The global analysis of decays at several emission wavelengths confirms that the 172 ps component is...
connected with 2/3 of the decay as well as −2/3 of the rise components, while the 52 ps component is associated with the residual 1/3 of the decay as well as −1/3 of the rise components (Table 1). This indicates that on average two peryleneimide chromophores experience a slower energy transfer and a faster energy transfer process.

To simulate the experimental decay behavior, we applied the general kinetic model presented in Scheme 1 and tested different rate constants, $k_{ij}$ for the donor−donor hopping processes and $k_{iA}$ for the donor−acceptor energy trapping processes, among the three donor species and one acceptor species and solved the associated differential equations according to eqs 5−7. Finally, only two basic kinetic models cannot be rejected but can account for the observed time constants and their amplitude ratios as well as for the observed anisotropy decay behavior. Both models involve two fully equivalent peryleneimide chromophores $D_1$ and $D_2$ among which energy hopping occurs bidirectionally with $k_{ij} \{i, j = 1, 2\} = k_{hopp} = 4.6$ ns$^{-1}$, and which energy is trapped by the terylene acceptor $A$ with a rate constant $k_{iA} = k_{2A} = k_{trap} = 5.5$ ns$^{-1}$. The fluorescence lifetime of the donors and acceptor is in both models $\tau_D(D) = 4$ ns and $\tau_A(A) = 2.5$ ns, respectively. The nonradiative behavior of the third donor $D_3$ determines which of the two alternative models is correct. The first model capable of explaining the observed amplitude ratios and decay times considers the single donor chromophore $D_3$ as either being not involved in the energy hopping ($k_{ij} \{i, j = 3, 3\} = 0$ ns$^{-1}$), or it only collects the energy from other donors (unidirectional energy transfer); its energy is faster trapped by the terylene acceptor chromophore with a rate constant of about $k_{iA} = k_{trap} = 20$ ns$^{-1}$. The second alternative model considers the condition that the third donor chromophore is also fully involved in the donor−donor energy-hopping process, that is, all $k_{ij} \{i, j = 1, 2, 3\} = k_{hopp} = 4.6$ ns$^{-1}$, but that its energy is trapped substantially faster than in the first model, that is, $k_{iA} = k_{trap} > 20$ ns$^{-1}$.

Regardless which of the two models is correct, one of the donors experiences at least four times faster energy trapping by the acceptor. The residual question is which physical reasons can explain this phenomenon of dual energy-trapping efficiencies. An intramolecular exciplex formation between donor and acceptor can also be excluded for various reasons, that is, because the donor and acceptor emission spectra are not changed with respect to the model compounds ($G1R1_p$ and teryleneimide), an additional decay time for exciplex-type emission is absent, and the molecular modeling results indicate that a close contact between two chromophores is unlikely in the present para series of multichromophoric dendrimer compounds.

The only explanation for the occurrence of a very fast and a slower energy trapping is that on average one of the three donor chromophores takes a much better through-space orientation or smaller interchromophoric distance toward the terylene acceptor than the other two. To evaluate this possibility, different conformations were modeled, and the chromophore−chromophore center−center distance ($d$) and orientation ($\kappa^2$) were inspected. For example, the rate constants $k_{FRET}$ calculated by eq 13 and 16 using the obtained values of $\kappa^2$ and $d$ for the donor−donor energy hopping in $G1R3_p$ and $G1R3ter_p$ are all very similar and in the range of 2.8−3.6 ns$^{-1}$. These values, as well as the similarity of all calculated rate constants, are consistent with the experimental value of $k_{hopp} = 4.6$ ns$^{-1}$ and the experimental observation of a single (anisotropy) decay time related to energy hopping and the anisotropy ratios $\beta_2/r_0$ pointing to full hopping among all donor chromophores.

On the other hand, a much larger variation of $k_{FRET}$ values calculated on the basis of molecular modeling of $G1R3ter_p$ for donor−acceptor chromophore pairs is found between $0.3$ ns$^{-1}$ and mostly $100$ ns$^{-1}$. But in certain cases, where the distances between donor and acceptor come small ($16$ Å), values up to $1000$ ns$^{-1}$ are found. The crucial spatial coordinate seems to be the rotation angle of the bulky and oblate-shaped teryleneimide acceptor. Depending on this angle, this acceptor chromophore can come very close to one single donor chromophore, from which the energy trapping might be very fast. Therefore, the experimentally observed rise time values could be a complex combination of rotation, energy hopping, trapping, and fluorescence rate constants.

Conclusions

The dynamics of intramolecular energy hopping and energy trapping in a series of shape-persistent polyphenylene dendrimers substituted in para position at the rim with peryleneimide chromophores and a teryleneimide energy-trapping chromophore are quantitatively studied. Because of the well-defined molecular core structure and high shape persistence, which is responsible for the spatially well-separated energy donor and acceptor chromophores, both energy hopping and trapping can quantitatively be described in terms of Förster-type resonance energy transfer.

The energy hopping takes place among all peryleneimide chromophores with a hopping rate constant experimentally determined to be $k_{hopp} = 4.6$ ns$^{-1}$. This value agrees with theoretically derived rate constants on the basis of molecular modeling structures. By a comparison with previous photophysical studies on a similar series of polyphenylene dendrimers, where the peryleneimide chromophores were attached in meta instead of para position, the importance of the dipole orientation factor $\kappa^2$ could experimentally be demonstrated in excellent agreement with the theoretical Förster equation. While the value of $\kappa^2$ = 0.8 in the meta series yields a hopping rate constant of $k_{hopp} = 2$ ns$^{-1}$, the improved orientation of peryleneimide chromophores in the para series as connected with a larger $\kappa^2$ value of about 2.1 leads to the observed more than two times faster hopping dynamics.

A teryleneimide chromophore attached to the dendrimer rim traps more than 95% of the excitation energy collected by three peryleneimides over a distance of ca. 28 Å. The energy of two of the peryleneimide donor chromophores is trapped with a rate that is similar or only slightly larger than that of the energy hopping, while on average one of the three donor chromophores transfers its energy to the trap chromophore at least four times faster. Molecular modeling based structures tentatively indicate
that the rotation of the terryleneimide acceptor group can lead to a much smaller distance to one single donor chromophore, which could explain the experimentally observed amplitude ratios of the rise times and the trapping decay time.

Consequently, the novel molecular design of this type of multichromophoric dendrimers allows investigating experimentally the theory of Coulombic energy transfer.

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