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Effect of the Chain Length on the Photonic Efficiency of Aromatic−Aliphatic Dendronized Polyethers

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ABSTRACT: Polychromophores comprised of rigid−flexible alternating polyethers have been synthesized. In these polymers, the rigid part of the main chain is a quinquephenyl fluorophore decorated with two second generation Fréchet-type side dendrons, while the flexible part is an aliphatic chain of 11 or 12 methylene groups. The effect of the length of the flexible spacer on the photoluminescence of these dendronized polyethers was examined in solution and in the solid state. It was found that even a subtle change in this length, from 11 to 12 methylene groups, had a strong effect on the fluorescence quantum yield of thin films, a fact which is of the greatest importance for the potential applications of these polymers as OLEDs.

Introduction

Up to now, numerous pathways have been adopted for the construction of lengthy, but at the same time well-defined, conjugated oligo- or polymeric materials to improve and control their final optoelectronic properties.[1] In particular, rigid−flexible polymers containing conjugated segments as their rigid part offer the possibility of creating processable polymeric materials with interesting photonic properties, since even a few conjugated segments are enough to provide the desirable optical characteristics. Thus, various kinds of conjugated segments have been employed, resulting in materials with tunable color emission.[2] One interesting approach for the development of such materials has been the incorporation of lengthy oligophenylene monomers, responsible for the emission itself, and their polymerization thereafter, leading to easily processable and stable film forming polymers, capable of producing a clean and bright color.[3] Nevertheless, the development of efficient and stable blue light emitting polymeric materials is still an important issue of investigation.

Evidently, one of the most important aspects in designing such polymers is their fluorescence quantum yield Φ_f, particularly in the solid. It has been observed that an undesirable phenomenon which reduces the Φ_f of these materials is the formation in the solids of "excimer-like" traps, which quench the fluorescence of the conjugated moieties.[4] Such excimers are formed due to fluorophore intra- or interchain interactions, induced by the solid-state packing. It has been suggested[5] however that, by the proper choice of the size and shape of dendrons in dendronized photonic polymers, one should be able to control main-chain separation in the solid. Note that dendronized polymers constitute a new, fully emerging class of macromolecules capable of combining the unique characteristics of dendrimers with the well-established properties of the conventional polymers.[6,7] In addition, suitably periphery-functionalized side chain dendritic polymers may offer the possibility of creating a light-harvesting antenna effect by transferring excitation to the backbone conjugated fluorophores.[8] As far as the photophysics of these polymers is concerned, it has been shown that dendronization by second generation Fréchet-type dendrons offers the best protection against aggregation in the solid state.[5]

In the present paper we wish to report on the synthesis and photophysical characterization of dendronized rigid−flexible alternating polyethers, carrying *p*-quinquephenyl moieties as their rigid parts and aliphatic chains as the flexible ones. The π-conjugated groups are decorated with two Fréchet-type poly(benzyl ether) dendritic wedges[9] of the second generation on the middle ring of each quinquephenyl. Thus, these polyethers can be considered as structures consisting of three major parts: the conjugated quinquephenyl units, the side dendritic moieties, and the aliphatic main-chain flexible spacers. The conjugated group sets the wavelength of the emission, while the dendron generation affects the polymer aggregation in the solid and consequently the extent of the fluorescence quenching and also the solubility of the final polymer.[10] The effect of the flexible spacer, however, on the emissive properties of these polymers has not been examined. Therefore, it was the aim of the present study to investigate this effect. To this end, we synthesized and examined, by means of steady-state and time-resolved fluorescence methods, the two homologues **DP11** and **DP12** (see Scheme 1), in which the flexible spacers (aliphatic chains) differ in length by less than 10%.

Experimental Section

Materials. Dibromide (**1**),[11] 4-(tetrahydropyran-2-yloxy)-1,1′-biphenyl-4′-ylboronic acid (**2**),[12] and catalyst $PdCl_2(dppf)$[13] were prepared according to literature procedures. All chemicals and reagents were supplied from either Aldrich or Merck and were used without further purification, unless noted otherwise. In particular, dibromododecane was recrystallized from methanol, and tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone prior to use. All reactions were carried out under an argon atmosphere.
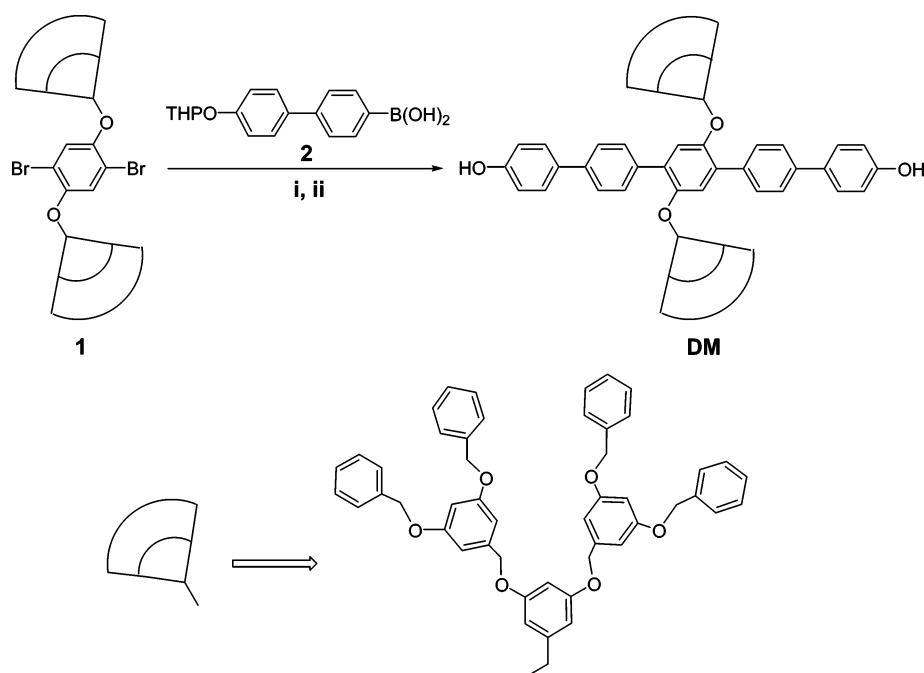
Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 and 100 MHz spectrometer,

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Scheme 1

respectively, with deuterated CHCl$_3$ or DMSO and TMS as internal standard. Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer with two Ultra Styragel linear columns (10^4, 500 Å), UV detector (254 nm), polystyrene standards, and CHCl$_3$ as eluent. Differential scanning calorimetry (DSC) tests were performed using a TA DSC Q100 instrument. The heating rate was 10 °C min^{-1}, and the temperature region extended from −50 to 250 °C.

Fluorescence equipment and methodology have been described elsewhere.[14] Steady-state fluorescence anisotropy, r_{ss}, was measured directly on the Perkin-Elmer LS 50B luminescence spectrometer Time-resolved anisotropy $r(t)$, defined as $r(t) = D(t)/S(t) = (GI_{par} − I_{per})/(GI_{par} + 2I_{per})$, was measured using the time-correlated single photon counter FL900 of Edinburgh Instruments. I_{par} is the fluorescence intensity when the excitation and emission polarizers are parallel, I_{per} is for mutually perpendicular polarizers, and $G = I_{par}/I_{per}$ is a correction factor dependent on the emission wavelength. Since our pulse width (∼1 ns) is comparable to the decay times of our samples, we were unable to use direct fitting procedures to the $r(t)$ data points. Instead, we have chosen to use the impulse reconvolution analysis method, which is applicable to similar situations.[15] In the relevant eq 1 reconvolution fitting to $D(t)$ was performed, and a typical fit is shown in Figure 1.

$$D(t) = r(t) \, S(t) = [r(\infty) + A \exp(−t/\Theta)]S(t) \qquad (1)$$

In the fitting procedure the program takes into account the impulse response function $Is(t)$, obtained by exponential fitting to the experimentally derived sum function $S(t)$. In eq 1 $r(\infty)$ is the residual anisotropy, i.e., the anisotropy at long time after the excitation pulse, A is a preexponential factor, and Θ is the rotational (and/or energy transfer) correlation time. The anisotropy at time $t = 0$ is $r(0) = r(\infty) + A$.

Thin polymeric films were prepared by the spin-coating method. A 13 mg sample of the polymer was dissolved in 2 mL of 1,1,2,2-tetrachloroethane, and the solution was then spin-coated at 3000 rpm on a quartz plate. For the measurements of the fluorescence quantum yield of thin films, a film made of ∼10^{-3} M 9,10-diphenylanthracene in PMMA having $\Phi_f = 0.83$[16] was used as the standard.

Monomer Synthesis. 2″,5″-Di[3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy]-*p*-quinque phenylene-4,4″″-diol (DM): A carefully degassed mixture of dibromide 1 (1.72 g, 1.00 mmol), boronic acid 2 (1.19 g, 4.00 mmol), PdCl$_2$(dppf) (0.04 g, 0.06
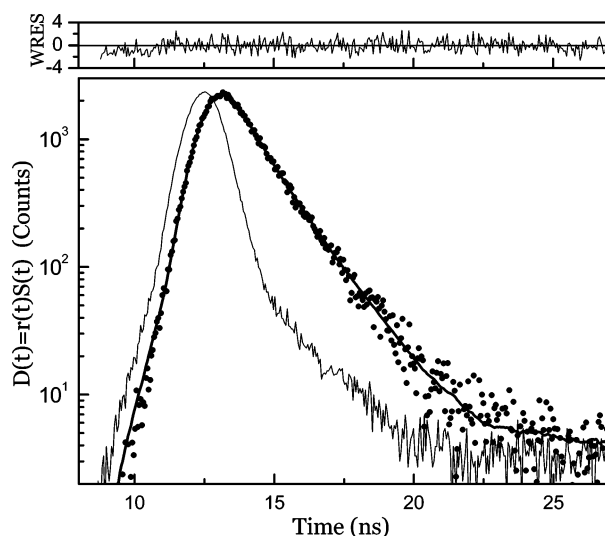

Figure 1. Fluorescence decay profile of $D(t)$ and best-fitting curve obtained from a frozen solution of **DP11** in MeTHF. Excitation was set at 340 nm and emission recorded at 420 nm. WRES are the corresponding weighted residuals, $\chi^2 = 1.09$. Obtained fitting parameters, $r(0) = 0.38$, $r(\infty) = 0.2$, and $\Theta = 465$ ps.

mmol), THF (80 mL), and NaOH (3 N) (4 mL, 12.00 mmol) was vigorously stirred at reflux for 48 h. After cooling to room temperature the organic phase was separated and filtrated, and MeOH was then added in order to precipitate the THP-protected macromonomer as a white powder. This was then dried and redissolved in THF (30 mL), and to that solution camphorosulfonic acid (CSA) (1.86 g, 8.00 mmol) and MeOH (2 mL) were then added. The mixture was stirred at room temperature for 48 h. Filtration and addition of a 10-fold amount of MeOH precipitated the final diphenol, which was recrystallized from toluene. Yield 1.00 g (53%); mp 180.5 °C. ^{1}H NMR (DMSO-d_6): 4.93 (s, 8H), 5.01 (s, 16H), 5.1 (s, 4H), 6.52 (t, 2H), 6.6 (t, 4H), 6.63 (d, 12H), 6.75 (d, 4H), 7.2 (s, 2H), 7.25−7.38 (m, 44H), 7.59 (d, 4H), 7.67 (d, 4H). ^{13}C NMR (DMSO-d_6): 69.99, 70.19, 71.00, 102.02, 106.56, 107.34, 116.56, 116.89, 126.38, 128.44−128.66, 129.24, 130.48, 130.73, 131.27, 136.62, 137.75, 139.84, 140.16, 140.81, 150.27, 158.02, 160.28, 160.42.

Scheme 2

DP12 : *x = 12*
DP11 : *x = 11*
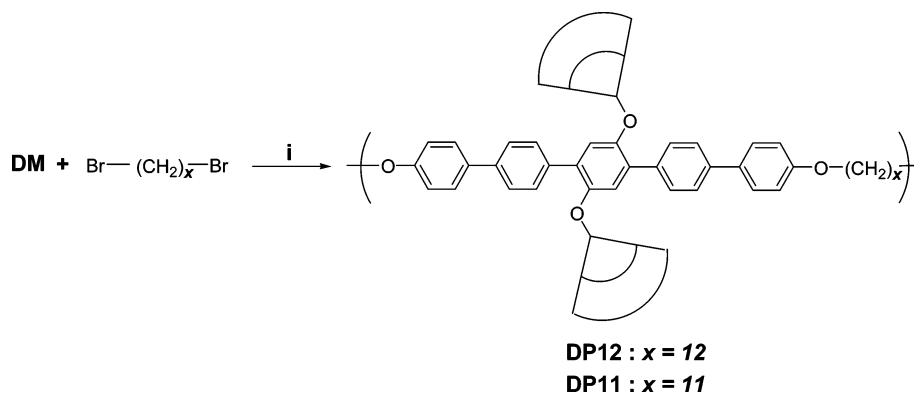
General Polymerization Procedure. To a carefully degassed mixture of diphenol DM (0.15 mg, 0.08 mmol), aliphatic dibromide (0.08 mmol), and *tert*-butylammonium hydrogen sulfate (TBAH) (1.07 mg, 0.32 mmol) were added *o*-DCB (0.40 mL) and NaOH (10 N) (0.40 mL). The mixture was vigorously stirred under a continuous stream of argon at 120 °C for 2 days. CHCl$_3$ was then added, and the polymer was obtained after precipitation in a 10-fold amount of MeOH, filtration, and drying under vacuum.

Polyether DP11. ^{1}H NMR (CDCl$_3$): 1.26−1.43 (two broad, 14H), 1.75 (broad, 4H), 3.85 (broad, 4H), 4.84 (s, 8H), 4.95−4.98 (two s, 20H), 6.48−6.59 (four broad, 18H), 6.82 (d, 4H), 7.1 (s, 2H), 7.23−7.39 (m, 40H), 7.42 (d, 4H), 7.58 (d, 4H), 7.68 (d, 4H). ^{13}C NMR (CDCl$_3$): 26.49, 29.76−29.96, 68.4, 70.38, 70.47, 71.77, 102.12, 106.05, 106.83, 115.16, 117.22, 126.62, 127.92−128.93, 130.43, 131.34, 132.58, 133.2, 136.86, 137.21, 139.63, 140.05, 140.22, 150.64, 159.18, 160.35, 160.53.

Polyether DP12. ^{1}H NMR (CDCl$_3$): 1.25−1.42 (two broad, 16H), 1.75 (broad, 4H), 3.86 (broad, 4H), 4.85 (s, 8H), 4.95−4.99 (two s, 20H), 6.48−6.59 (four broad, 18H), 6.82 (d, 4H), 7.1 (s, 2H), 7.2−7.38 (m, 40H), 7.42 (d, 4H), 7.58 (d, 4H), 7.68 (d, 4H). ^{13}C NMR (CDCl$_3$): 26.51, 29.58−30.03, 68.4, 70.38, 70.47, 71.79, 102.1, 106.6, 106.83, 115.16, 117.25, 126.63, 127.93−128.94, 130.43, 131.33, 132.58, 133.19, 136.86, 137.22, 139.63, 140.04, 140.23, 150.64, 159.17, 160.36, 160.54.

Results and Discussion

Monomer and Polymer Syntheses. We have adopted the well-established "macromonomer" route toward dendronized polymers.[7,17] Accordingly, we initially synthesized a quinquephenyl macromonomer diphenol bearing two Fréchet side dendrons of the second generation[9] in its middle phenylene ring. Thus, palladium-mediated Suzuki coupling[18] was employed between the aromatic dibromide **1** carrying the two side dendritic wedges[11] and the THP-protected hydroxylbiphenylboronic acid **2**.[12] The obtained THP-end protected macromonomer was afterward subjected to a simple and straightforward deprotection reaction using CSA (camphorosulfonic acid) that afforded the desirable dendronized dihydroxyl-functionalized quinquephenyl diol **DM** (Scheme 1).

Polymerization thereafter of macromonomer diphenol **DM** with α,ω-aliphatic dibromides was performed under phase transfer conditions (Scheme 2).[19] Great differences between the molecular weights of the monomers and the fact that no optimization was made as far as the polymerization conditions are concerned may be responsible for the medium molecular weights of the polymers (Table 1). However, it must be kept in mind that the molecular weights of such dendronized systems tend to be underestimated at least by a factor of 2 from GPC measurements vs a polystyrene calibration.[7,11,17]

Table 1. GPC Data for Polyethers DP11 and DP12

polyether	$M_n{}^a$	$M_w{}^a$	$M_w/M_n{}^a$
DP12	16 800	37 700	2.3
DP11	17 900	36 800	2.1

^{a} Determined by GPC with a UV detector, CHCl$_3$ as eluent, and polystyrene standards.

Both polymeric samples showed excellent solubilities in common chlorinated solvents like chloroform. Their ^{1}H and ^{13}C NMR characterization is in full agreement with the proposed structures, with complete assignment of all peaks. A representative ^{1}H NMR spectrum for the polyether having 12 carbon atoms along the main flexible spacer (**DP12**) is given in Figure 2, together with the corresponding spectrum of the initial diphenol **DM** (inset). No end groups throughout the main polymeric chains are detectable; thus, we were not able to evaluate the molecular weights of the polymers using end group analyses.

Thermal characterization of polyethers **DP11** and **DP12** was performed by means of differential scanning calorimetry. Only second heating runs were taken into account, in which both polymers exhibited transitions between ~45 and ~60 °C, as shown in Figure 3, but none of them revealed either melting endotherms during heating or crystallization exotherms on cooling. The above transitions are in the same temperature region as the glass transitions of the respective second generation terphenyl main chain aromatic−aliphatic polyethers,[11] but because of overlapping their nature cannot be clearly distinguished.

Photophysical Characterization. Steady-state and time-resolved fluorescence techniques, both in isotropic solution and in the solid state, have been employed for the investigation of the emitting behavior of **DM**, **DP11**, and **DP12**.

In Solution. In dilute solutions (concentration ca. 1.5 × 10^{-6} M) of the good solvent methyltetrahydrofuran (MeTHF), the monomer **DM** and the two polymers **DP11** and **DP12** have almost identical absorption−fluorescence spectra, as shown in Figure 4.

Thus, the absorption spectra consist of two maxima: the one at 332 nm is typical of substituted quinquephenyl moieties,[20] and the other at 285 nm is a superposition of two absorption bands, one belonging to the quinquephenyl unit and the other to the aromatics of the Fréchet-type side dendron.[5] The fluorescence spectra, on the other hand, show a maximum at 398 nm and a shoulder at 420 nm, both belonging to the quinquephenyl moiety.[20]

Moreover, at room temperature all three molecules— **DM**, **DP11**, and **DP12**—have very similar quantum
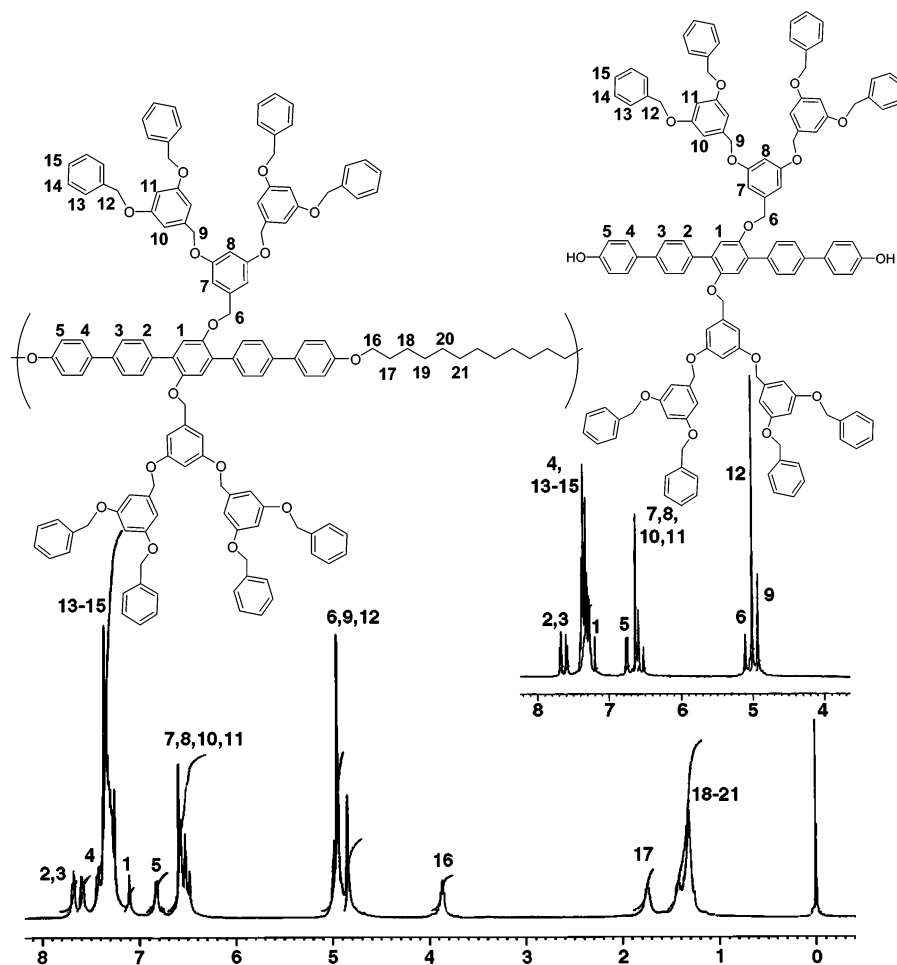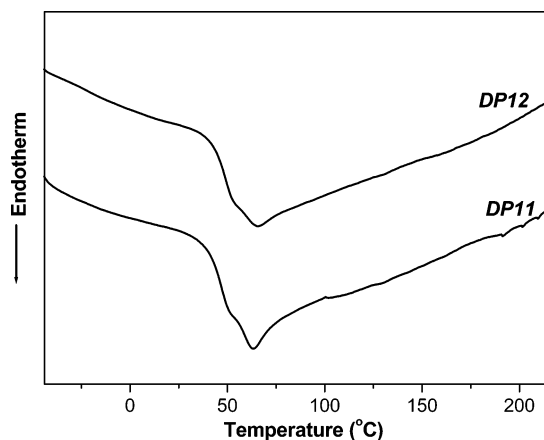
Figure 2. ¹H NMR spectra of **DM** and **DP12**.

Figure 3. Thermal characterization of polyethers **DP11** and **DP12** using differential scanning calorimetry.

Figure 4. Absorption−fluorescence spectra of **DM** (dotted line) and the polymer **DP11** (solid line) in MeTHF, at $T = 298$ K. **DP12** has identical spectra with **DP11**.

yields and lifetimes, viz. $\Phi_f = 0.86$, 0.83, 0.78 and $\tau = 1.02$, 1.03, 1.04 ns, respectively. These findings ensure that intrachain interactions between the π-conjugated systems (the quinquephenyls), toward formation of "excimer-like" energy traps,[4b] do not occur in the present case. This was rather expected in view of the large separation (ca. 20 Å) between the conjugated units along the polymeric backbone and the uncoiled conformation adopted by the polymers at low concentration in a good solvent.

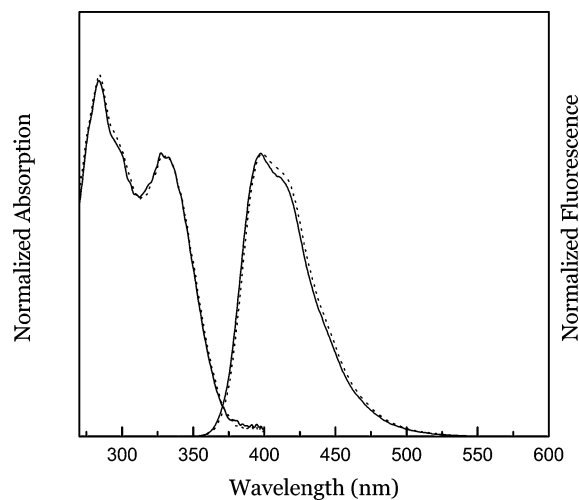Another important spectroscopic parameter is the room temperature steady-state fluorescence anisotropy r_{ss}, which was found equal to 0.133 for **DM**, 0.175 for **DP11**, and 0.17 for **DP12** (excitation at 340 nm). These low values or r_{ss}—compared to the theoretically expected $r_{ss} = 0.4$—reflect the depolarization of the fluorescence caused by molecular and segmental motions in the fluid environment. When these motions were frozen by lowering the temperature down to 100 K, the fluorescence anisotropy was drastically increased. Thus, in **DM** r_{ss} went up to 0.38, instead of $r_{ss} = 0.4$ expected for parallel absorption and emission dipoles, indicating that these two dipoles form an angle equal to ca. 10°. The

important point however is that the r_{ss} value at 100 °C is 0.28 for **DP11** and 0.31 for **DP12**, instead of a value equal to the corresponding value of **DM**, viz. 0.38. These lower values of r_{ss} indicate that despite the rigid environment, an excited quiquephenyl group in the two polymers loses part of its fluorescence polarization, evidently due to electronic excitation energy transfer to other such groups along the polymeric chain.[4b] This energy migration occurs via resonance interactions (Förster mechanism) and is characterized by the so-called Förster distance R_0, i.e., the fluorophore separation at which energy transfer is 50% efficient. The value of R_0 for a given donor−acceptor system can be calculated by means of the well-known[21] equation

$$R_0 = 0.21(\kappa^2 \eta^{-4} Q_d J(\lambda))^{1/6} \qquad (2)$$

where Q_d is the fluorescence quantum yield of the donor (**DM**), η is the refractive index of the solvent (MeTHF), κ is an orientational parameter for which the dynamic average $\kappa^2 = {}^2/_3$ is used, and $J(\lambda)$ is the overlap integral which expresses the degree of spectral overlap between the donor emission and acceptor absorption. Note that R_0 has the same value for **DM**, **DP11**, and **DP12** since its magnitude depends only on the nature of the donor−acceptor pair (quinquephenyl−quinquephenyl) and the solvent. Using the following values, obtained from our spectral measurements or from tables, $Q_d = 0.83$, $\eta = 0.6$ cP, and $J(\lambda) = 3.87 \times 10^{12}$ M^{-1} cm^3 nm,[4] we found R_0 equal to 19 Å, very close to the values reported for other p-quinquephenyl derivatives.[22]

Time-resolved fluorescence anisotropy $r(t)$ measurements provide further information about energy migration. In the decay law of the fluorescence anisotropy, expressed as eq 1, the temporal parameter Θ accounts for the effect on $r(t)$, of all molecular rotations, and also of the migration of the excitation. In rigid media, where all rotations are impeded, Θ refers only to the energy transfer, Θ_{et}, while when energy transfer cannot occur, e.g. in **DM**, and only molecular rotations contribute to the fluorescence depolarization, Θ refers to the rotational correlation time, Θ_{rot}.[15] Note that in the general case the exponential part of eq 1 is a summation over all possible rotations and energy migrations; however the fitting of our experimental data was in all cases obtained by a single exponential, i.e., $r(t) = r(\infty) + A \exp(t/\Theta)$ and $r(0) = r(\infty) + A$.

In the case of a dilute solution of **DM** at room temperature, in which resonance energy transfer cannot occur, i.e., $\Theta_{et} = \infty$, the fitting gave $r(0) = 0.38$ and $\Theta_{rot} = 550$ ps. These values agree very well with the previously found steady-state anisotropy $r_{ss} = 0.133$, since they satisfy the Perrin equation (3) ($r_{ss} = 0.133$, $r(0) = 0.38$, $\tau = 1.03$ ns, and $\Theta_{rot} = 0.55$ ns) to better than 1.5%.

$$\frac{1}{r_{ss}} = \frac{1}{r_0} + \frac{\tau}{r_0 \Theta} \qquad (3)$$

In the case of the polymers **DP11** and **DP12**, the time-resolved fluorescence anisotropy, shown in Figure 5 (excitation 340 nm; emission 420 nm), was measured in frozen solutions in order to eliminate contributions from molecular motions $\Theta_{rot} = \infty$ and therefore to determine the depolarization due only to energy transfer. Thus, for **DP11** in MeTHF at 100 K we found $r(0) = 0.38$, $\Theta_{et} = 465$ ps, and $r(\infty) = 0.2$. It has been shown
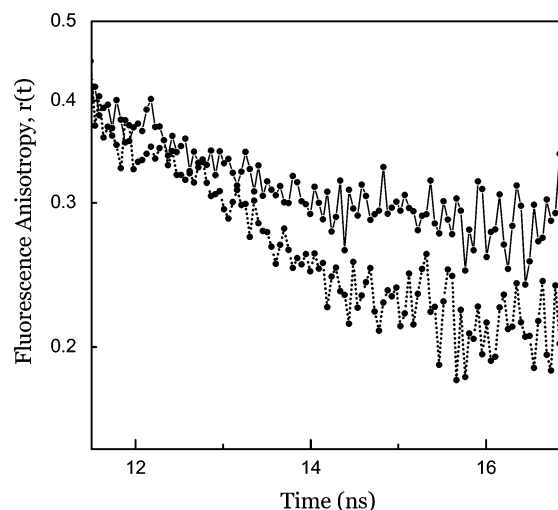

Figure 5. Time-resolved fluorescence anisotropy $r(t)$, of frozen solutions of **DP11** (dotted lines) and of **DP12** (solid lines) in MeTHF. Flled circles correspond to experimental points. For the analysis see text.

that when $\Theta_{rot} = \infty$ and the excitation energy is randomly distributed among the fluorophores, then $r(\infty) = r(0)/i$, where i is the number of the sites (quinquephenuls) among which energy is exchanged.[23] Since for **DP11** $r(0) = 0.38$ and $r(\infty) = 0.2$, $i \cong 2$; therefore, we conclude that electronic energy is exchanged between two neighboring fluorophores along the polymeric backbone. Moreover, the rate of energy transfer is $k_{et} = 1/ix\Theta_{et}$,[23] which in the present case yields $k_{et} = {}^1/_2 \times 0.465 = 1.08 \times 10^9$ s^{-1}. Applying the formula $k_{et} = 1/\tau(R_0/R)^6$ from Förster's theory and using $\tau = 1.2$ ns—the lifetime of **DP11** at 100 K—and the previously calculated Förster distance $R_0 = 19$ Å, we found $R = 18$ Å. This is the average distance between the two quinquephenyls which exchange the energy. It turns out that this number is comparable to the distance between two neighboring quinquephenyls in an extended **DP11** chain (ca. 19−20 Å). In the case of **DP12** the situation is quite different.

Thus, at 100 K, the parameters obtained from analysis of the decay of the fluorescence anisotropy are $r(0) = 0.38$, $r(\infty) = 0.3$, and $\Theta_{et} = 250$ ps. Clearly, in this polymer the relationship $r(\infty) = r(0)/i$ cannot be satisfied for i an integer. This may imply that in **DP12** energy transfer does not lead to an equal distribution, of the initial excitation energy, among the quinquephenyl groups in which the excitation has migrated, due possibly to the nonrandom orientation of the transition moments of these fluorophores.[24] This may also account for the fact that in **DP12** the energy transfer is quite faster than in **DP11** ($\Theta = 250$ ps in **DP12** compared to $\Theta = 465$ ps in **DP11**), although the distance between two neighboring quinquephenyls is on the average larger in **DP12** than in **DP11**.

In Thin Films. In thin film form the absorption-fluorescence spectra of the two polymers are red-shifted with respect to their corresponding spectra in MeTHF, from ca. 399 to 406 nm. Also, a red tail has appeared in the fluorescence spectra, being more pronounced in **DP12**, as shown in Figure 6. These findings indicate "excimer-like" interactions between conjugated units, evidently arising from the fact that in the solid state two quinquephenyl moieties either from the same or from different polymeric chains are brought within interaction range. Despite the evidence for excimer-like
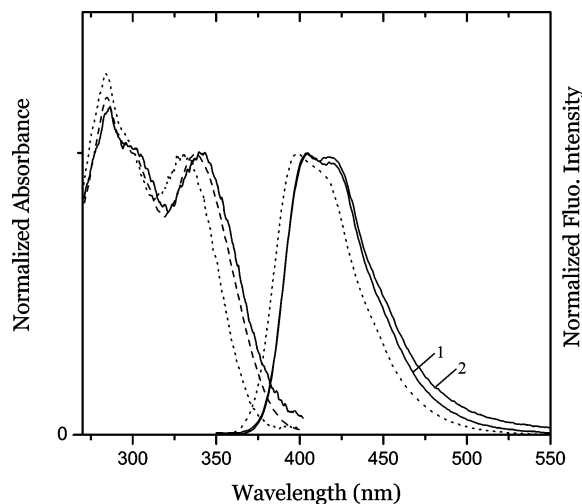
Figure 6. (left) Normalized absorption spectra of **DP11**: dotted line, in MeTHF solution; solid line, as thin film; dashed line, excitation spectrum of **DP11** as thin film (independent of emission wavelength). (right) Fluorescence spectra of **DP11** in MeTHF (dotted line) and of thin films of **DP11** (1) and **DP12** (2).

interactions, the excitation spectra of the two polymers, monitored at 390 and 460 nm, closely match their corresponding absorption spectra (see Figure 6). This means that the interactions responsible for the formation of the species emitting at the red end of the fluorescence spectrum do not lead to the formation of ground-state species; instead, these interactions become effective only in the excited state. However, when the decay was monitored at the long wavelength, we did not observe any rise time indicative of excimer formation; therefore, we conclude that the formation of the excimer-like species must occur faster than the time resolution of our instrument (ca. 800 ps).

Additional proof for the existence of excimer-like interactions comes from the fluorescence lifetimes of the two homologues, **DP11** and **DP12**. Thus, while in the good solvent both polymers demonstrate well-defined monoexponential decays corresponding to $\tau = 1.04$ ns, in the films three different exponentials are required to fit the data, corresponding to three different lifetimes, viz. 0.38, 1.1, and 4.0 ns (see Figure 7). Moreover, the percentages of the species corresponding to these lifetimes were wavelength dependent, with the long one having its maximum contribution when the decay was monitored at the red end of the fluorescence spectrum (see Table 2). We have assigned the long lifetime (4 ns) to the decay of the excimer-like species and the intermediate (1.1 ns), which matches the lifetime of **DM**, to the decay of the noninteracting quinquephenyl units, while the short lifetime (0.38) we have attributed to the fast "decay" of excited fluorophores toward formation of the excimer-like species. This fast formation of the excimer-like species explains the previously mentioned fact, that we did not observe any rise time when the fluorescence decay was monitor at the wavelength of the red emission tail.

A consequence of these excimer-like interactions in the solid state is a decrease of Φ_f, which in the case of **DP11** was reduced from $\Phi_f = 0.83$ in MeTHF to $\Phi_f = 0.58$ in the film (ca. 30% reduction), while in the case of **DP12** the reduction was nearly twice as much, viz. 57% (from $\Phi_f = 0.78$ in MeTHF to $\Phi_f = 0.33$ in the film). Note that the smaller decrease of Φ_f, from solution to
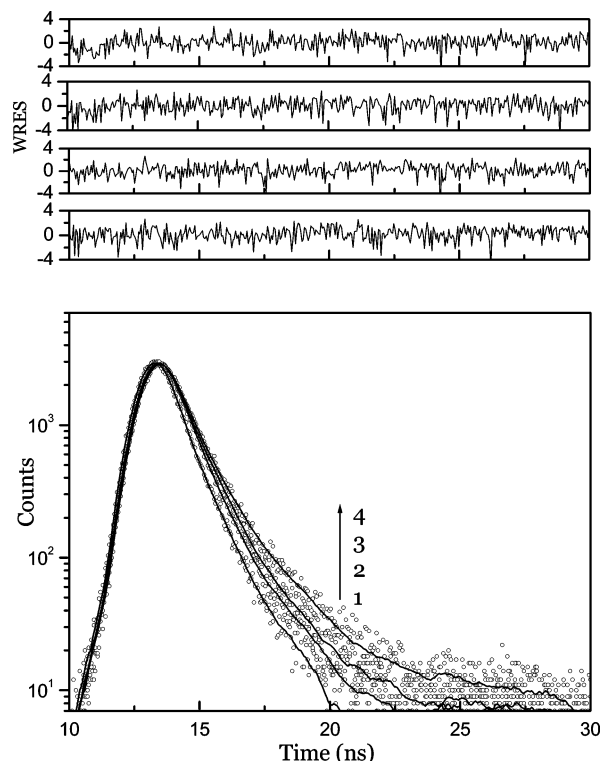

Figure 7. Fluorescence decay profiles and best-fitting curves obtained from a thin film of **DP12** at various wavelengths; 1–4: 390, 410, 430, and 450 nm, respectively. The excitation was set at 332 nm. The corresponding weighted residuals (WRES) are shown on top in the same order. Obtained fitting parameters and goodness of the fits for the two polymers are listed in Table 2.

Table 2. Recovered Decay Times τ (ns), Percentages (% τ), and Statistical Parameters of the Emitting Species of Polymers DP12 and DP11 Thin Films at Various Wavelengths (nm)

emission wavelength	τ_1	τ_2	τ_3	% τ_1	% τ_2	% τ_3	χ_ν^2
			Polyether **DP12**				
390	0.38	1.02		66	34		1.08
410	0.43	1.01	4.0	58	40	2	1.01
430	0.38	0.98	4.0	44	52	4	1.09
450	0.4	1.02	4.0	40	53	7	1.16
			Polyether **DP11**				
390	0.38	1.10		33	64		1.07
410	0.40	1.08	4.0	28	70	2	1.06
430	0.39	1.10	4.0	19	78	3	1.09
450	0.35	1.11	4.0	16	80	4	1.08

solid in **DP11**, compared to the same change in **DP12**, agrees with the weaker excimer-like emission observed in thin films of the former compared to the latter, as shown in Figure 6. The important point here is the decrease of the solid-state fluorescence quantum yield by ca. 50% caused by a small increase in the length of the flexible spacer, viz. from 11 to 12 methylene groups. This fact reveals the importance of the detailed polymeric structure on the final photophysical properties of these materials. It is also worth mentioning here that the fluorescence quantum yield, $\Phi_f = 0.58$, of **DP11** thin films is quite high compared to those of other similar materials[25] and that the dendritic moieties do not seem to disturb its good optical properties. These, plus the fact that DP11 is a fully amorphous material, constitute definite advantages for its applications in OLEDs.

Another observation which needs explanation here is the fact that in the rigid environment of the film the

two polymers were found to have equal room temperature steady-state fluorescence anisotropy, viz. $r_{ss} = 0.1$. Comparing this value to the previously mentioned values in the good solvent at 100 K (**DP11** $r_{ss} = 0.28$ and **DP12** $r_{ss} = 0.31$), where molecular motions are also frozen, we find that in the thin film r_{ss} is quite lower than in the frozen solvent. This increased depolarization in the film compared to the good solvent reflects the fact that in the former case chains fold on themselves and also approach each other, whereas in the latter, each polymeric chain is uncoiled and isolated from the others. Therefore, in the film, energy can migrate not only to neighboring quinquephenyl units along the same polymeric chain—as it does in the good solvent—but also to nonneighboring units of the same folded chain as well as to quinquephenyl units of neighboring chains.

Conclusions

Dendronized rigid–flexible alternating polyethers have been synthesized, bearing onto every single repeating unit two Fréchet-type dendrons of the second generation. The rigid part is the *p*-quinquephenyl moiety, while the flexible consists of an aliphatic chain of 11 (**DP11**) or 12 (**DP12**) methylene units. The resulting polymeric materials emit in the blue spectral region (ca. 400–450 nm) with high fluorescence quantum yield in solution (ca. 0.8), which in the case of **DP11** retains a relatively high value in the solid state as well ($\Phi_f \cong 0.6$).

However, the main conclusion is that even a very small change, from 11 to 12 methylene groups, in the length of the aliphatic spacer causes dramatic changes in the emissive properties of these polymers in the solid state. Thus, it was found that while **DP12**, in going from the solution to the film, undergoes a 57% reduction of its fluorescence quantum yield (from $\Phi_f = 0.78$ to $\Phi_f = 0.33$), in the slightly different homologue **DP11** the corresponding reduction is only 30% (from $\Phi_f = 0.83$ to $\Phi_f = 0.58$). Obviously, this finding is very important from the point of view of the utilization of this type of polymers in organic light-emitting devices.

In addition, changes in fluorescent lifetimes and anisotropy point out to the same conclusion, viz. that the final photophysical characteristics of these dendronized polyethers strongly depend on the precise polymeric structure.

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