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Excited-State Dynamics of Polyfluorene Derivatives in Solution

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The excited-state dynamics of two polyfluorene copolymers, one fully conjugated containing phenylene vinylene units alternated with 9,9′-dihexylfluorenyl groups and the other segmented by $-(CH_2)_8-$ spacer, were studied in dilute solution of different solvents using a picosecond single-photon timing technique. The excited-state dynamics of the segmented copolymer follows the Förster resonant energy-transfer model which describes intrachain energy-transfer kinetics among random oriented chromophores. Energy transfer is confirmed by analysis of fluorescence anisotropy relaxation with the measurement of a short decay component of about 60 ps. The fluorescence decay surface of the fully conjugated copolymer is biexponential with decay times of about 470 and 900 ps, ascribed to deactivation of chain moieties containing trans and cis isomers already in a photostationary condition. Thus, energy transfer is very fast due to the conjugated nature and rigid-rod-like structure of this copolymer chain.

Introduction

The use of conjugated polymers as semiconductor materials in optoelectronic devices has motivated a large number of studies on these materials. The understanding of optical and electronic processes is an important issue in optimization of several applications of conjugated polymers.[1–5] Another point is the photophysics of conjugated polymers in the excitation stages after photon absorption. There are aspects still remaining in debate, like the nature and extension of the primary excitation (excitons or polarons), its propagation along and among the chains (coherent and incoherent transport), and the interaction between the electronic (excited and ground) states. The exciton migration along the chain by incoherent transport or hopping can be described approximately by the Förster resonant energy-transfer model (FRET) within the point dipole approximation.[6,7] Among several types of conjugated polymers, polyfluorene and its derivatives have attracted considerable attention, owing to their special properties like high photoluminescence efficiency and tunability.[8–13]

In this contribution we report the results of excited-state dynamics studies of two polyfluorene derivatives in solution: one is fully conjugated containing 9,9′-dihexylfluorene groups interspersed between phenylene−vinylene units, namely, poly(9,9′-*n*-dihexyl-2,7-fluorenediylvinylene-alt-1,4-phenylenevinylene), PFPPV (**6**, Scheme 1), and the other is a multiblock conjugated−nonconjugated copolymer containing the fluorene−phenylenevinylene blocks separated by $(CH_2)_8$ spacers, namely, poly[9,9′-*n*-dihexyl-2,7-fluorenediylvinylene-alt-4,4′-{1,1′-(octamethylene-1,8-diyloxy)}-3,3′,5,5′-tetramethoxydiphenylenevinylene], PFOPPV (**10**, Scheme 2). For our purposes, working in dilute solution brings the advantage of promoting a scenario where the macromolecules are isolated from each other without the effect of morphology variation related to the usual film formation techniques. Here we explore the change in conjugation length and presence of isomer chromophores cis/trans in the behavior of the fluorescence dynamics.

Experimental Section

The copolymers were synthesized by the well-known Wittig method for the preparation of alkenes[14–16] through the reaction of aldheydes (or ketones) with phosphonium ylides. FTIR spectra were collected in a BOMEM, M-B series spectrometer using KBr pellets. ^1H NMR were taken in a BRUKER AC200 MHz spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Size exclusion chromatography (SEC) was made in Agilent 1100 chromatograph using polystyrene as standard and THF as the eluent. The solvents, chloroform (J. T. Baker, HPLC grade), decalin (mixture of isomers (Fluka, HPLC grade)), toluene (J. T. Baker, HPLC grade), and cyclohexane (Synth, PA) used in the sample preparation were dried with 4 Å molecular sieves prior to use. The sample solutions were made in appropriated concentrations in order to have maximum absorbance of about 0.1 and kept under N_2 atmosphere to avoid oxidation. Fluorescence quantum yields (ϕ) were calculated using quinine sulfate in 0.1 N H_2SO_4 ($\phi = 0.577$) as standard, corrected for the refractive indices of the sample and standard solution in different media.[17]

Absorption spectra were taken in a Cary model 5G spectrometer using a 1 cm quartz cuvette. Steady-state fluorescence measurements were made in a HITACHI model F4500 spectrometer. Time-resolved fluorescence of the copolymers were measured by time-correlated single-photon counting using a homemade picosecond spectrometer equipped with Glan-Laser polarizers (Newport), a Peltier-cooled PMT-MCP (Hamamatsu R3809U-50) as the photon detector, and Tennelec-Oxford counting electronics. The light pulse was provided by frequency doubling the 200 fs laser pulse of a Mira 900 Ti−Sapphire laser pumped by a Verdi 5 W coherent laser, and the pulse frequency was reduced to 800 kHz using a Conoptics pulse picker. The system provides an instrument response function (irf) of about 40 ps at fwhm.[18] The fluorescence decays were taken in magic angle ($\lambda_{exc} = 400$ nm) and analyzed by a reconvolution procedure with instru-

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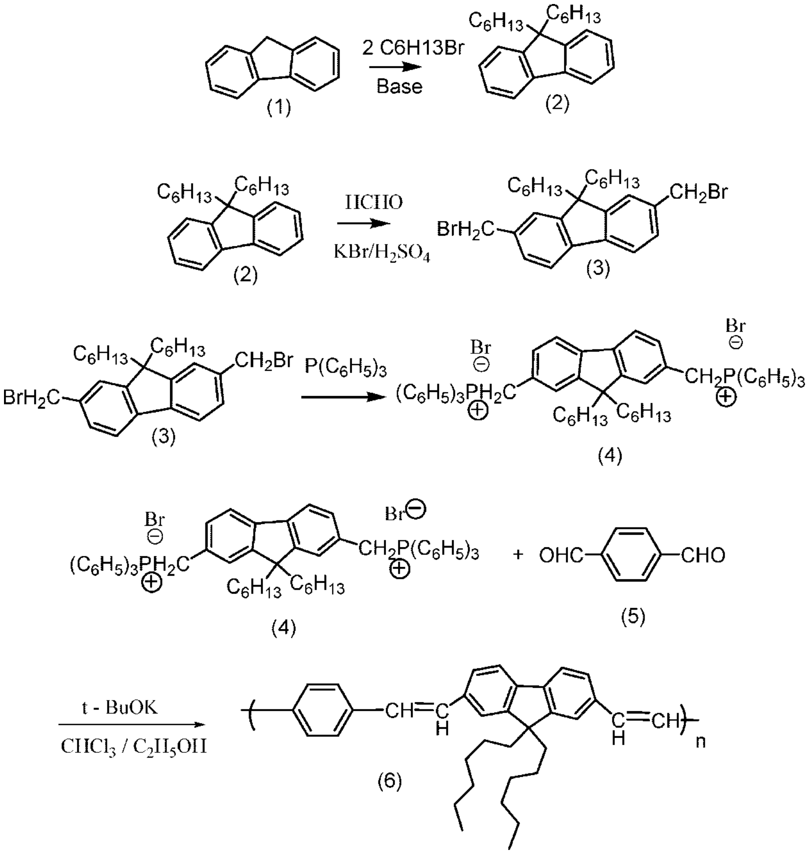
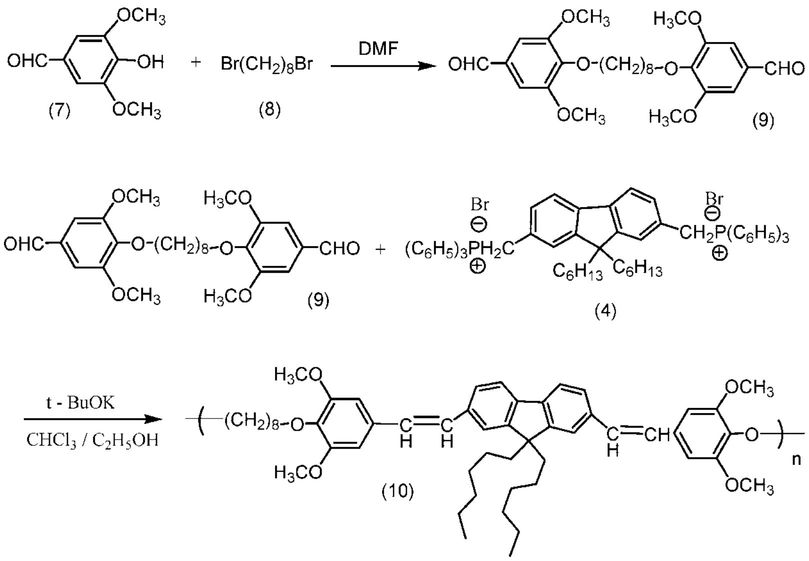
SCHEME 1: Synthetic Route to Poly(9,9′-*n*-dihexyl-2,7-fluorenediylvinylene-alt-1,4-phenylenevinylene) (PFPPV)



SCHEME 2: Synthetic Route to Poly[9,9′-*n*-dihexyl-2,7-fluorenediylvinylene-alt-4,4′-{1,1′-(octamethylene-1,8-diyloxy)}-3,3′,5,5′-tetramethoxydiphenylenevinylene] (PFOPPV)



ment response function (irf). Fluorescence anisotropy decays were constructed from the measured decays with polarizers in parallel and perpendicular directions.

Results and Discussion

Schemes 1 and 2 depict the synthetic routes used in the preparation of the polymers.

Synthesis. FTIR and ^{1}H NMR spectra confirmed the structure of the copolymers, revealing the presence of vinylene isomers of cis (PFOPPV, 6.5 ppm and 826 cm^{-1}; PFPPV, 6.5 ppm and 823 cm^{-1}) and trans (PFOPPV, 7.1 ppm and 957 cm^{-1}; PFPPV, 7.1 ppm and 960 cm^{-1}) in both copolymers. The Wittig reaction is regiospecific but not stereoselective since it depends on several factors like the type of ylide and solvent, for instance. The percent of the cis isomer was estimated from the comparison of the integrated ^{1}H NMR signals of the isomers, and the results have indicated about 23% of cis content in the copolymers. From SEC analysis, weight-average molecular weights (M_w) were 9666 and 56 750 g/mol for PFPPV and PFOPPV with a polydispersity of 2.0 and 2.9, respectively.

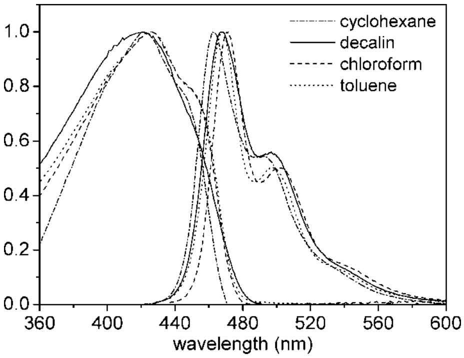


Figure 1. Normalized absorption and emission spectra of PFPPV solutions in different solvents.

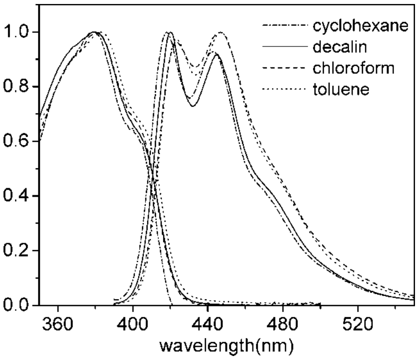


Figure 2. Normalized absorption and emission spectra of PFOPPV in different solvents.

TABLE 1: Molecular and Spectroscopic Properties of the Copolymers[a]

	solvent	M_w (g/mol)	n	λ_{abs} (nm)	λ_{fluo} (nm)	$\Delta\nu$ (cm^{-1})	E_{0-0} (eV)
PFOPPV	chloroform	56 750	71	380	447(424)	3922	3.02
	toluene			382	447(424)	3785	3.00
	decalin			379	420(445)	2561	3.03
	cyclohexane			379	418(443)	2448	3.04
PFPPV	chloroform	9666	21	426	470(500)	2185	2.70
	toluene			426	469(498)	2140	2.69
	decalin			420	466(497)	1787	2.70
	cyclohexane			421	462(494)	2096	2.74

[a] Polymerization degree (n), absorption and emission maxima (λ_{abs}, λ_{fluo}), Stokes shift ($\Delta\nu$), and energy gap ($E_{0\text{-}0}$).

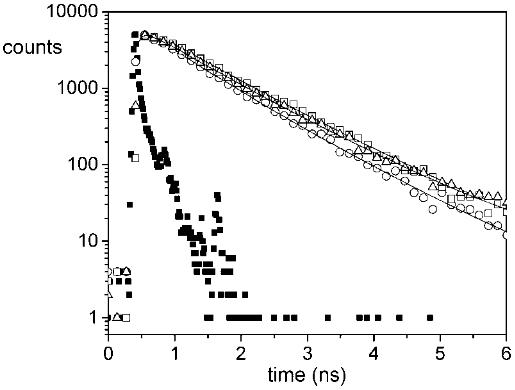


Figure 3. Fluorescence decays of PFOPPV in different solvents (decalin (□); toluene (○); chloroform (△)) and the instrument response function (■). Fitting curves according to eq 1.

Steady-State Absorption and Fluorescence. Absorption and fluorescence spectra of PFPPV and PFOPPV in the different solvents used are shown in Figures 1 and 2, respectively. In PFPPV, random defects and torsions along the chains, mainly due to the cis configuration, seem to lead to a distribution of segments with different conjugation lengths, bringing about a broadening of its absorption band as observed. Its low solubility in decalin decreases further the effective conjugation length, shifting the absorption to the blue region. Nevertheless, the profiles of the fluorescence spectra of PFPPV in the solvents used are quite similar (see Figure 1). Emission spectra have a well-resolved vibronic structure with an energy progression between 1200 and 1500 cm^{-1} assigned to C=C stretching modes, which is characteristic of extended π-conjugated systems.[19]

Absorption of PFOPPV is almost independent of the solvents used; only a slight blue shift in decalin and cyclohexane is observed. The emission in these considered poor solvents like decalin and cyclohexane, however, shows a change in the relative intensities of the 0−0 and 0−1 vibronic bands when compared to the profiles observed in better solvents like toluene and chloroform with emission more in the red (see Figure 2). Considering the difference in solvent viscosity between cyclohexane and decalin but providing similar emission profiles, conformation relaxation governed by solvent friction is not the major factor which defines the spectral properties of PFOPPV in solution.

Since the segmented copolymer has a well-defined conjugation length, its spectral profile should be consistent with those of the corresponding chromophoric (fluorenevinylene−phenylenevinylene) unit. A comparison of the absorption and emission spectra of the two copolymers is reported in Table 1. Although the methoxy groups could lower the HOMO−LUMO transitions in PFOPPV, due to their electron-donating capacity, the extended conjugation of PFPPV is capable to shift further to the red its transitions in about 0.3 eV as compared to the isolated chromophore. This conclusion is based on the values of the calculated E_{0-0} energy level as reported in Table 1.

Fluorescence Decay Times. Fluorescence decays of the PFOPPV in toluene, decalin, and chloroform are quite similar, but the transients in all cases are not exponential (see Figure 3). However, contrasting with PFPPV, the decay surface cannot be described globally using a biexpoential decay function.

The Förster formalism has been widely used to describe the excited-state dynamics of polymeric systems containing tagged chromophores which are able to display energy-transfer processes.[20−23] Considering this fact and assuming that the segmented PFOPPV contains well-separated chromophoric units, an intrachain energy transfer would be possible between chromophores (formally it will be a kind of energy migration). However, in the analysis of the fluorescence decay of PFOPPV, we found a rising term that may indicate formation of a second species after prompt excitation of the samples. Thus, the process may start with energy migration between the trans isomers (major fraction) followed by an energy transfer from the trans to the cis isomer in the same polymer chain. In the dipole−dipole approximation for a random 3D distribution of the donor/acceptor species (the isomers in a flexible copolymer chain), the decay dynamics may be represented by a Förster decay term plus a rising exponential component ($b_2 < 1$) due to formation and emission contribution of the cis isomer, as given below

$$f(t) = b_1 \exp\left(-\frac{t}{\tau_1} - \gamma\left(\frac{t}{\tau_1}\right)^{1/2}\right) + b_2 \exp\left(-\frac{t}{\tau_2}\right) \qquad (1)$$

The γ parameter is related with the critical Förster radius (R_0) and given by

$$\gamma = \frac{4}{3}\left(\frac{3}{2}\langle\kappa^2\rangle\right)^{1/2}\pi^{3/2}R_0^3N_a \qquad (2)$$

N_a is the density of the chromophore isomers, and $\langle\kappa^2\rangle$ is the average dipole−dipole orientation factor. In the dynamic limit of fast reorientation of dipoles in an isotropic fluid, $\langle\kappa^2\rangle = 2/3$, but in a static limit, it has a value of 0.476.[17] Typical decay profiles and fitting are illustrated in Figure 3, and after the rising edge, a small growing step is evident in all decays. The fitting parameters of the fluorescence decay of PFOPPV in the solvents used are reported in Table 2.

The value of τ_1 is practically constant with emission wavelength and nearly the same among the three solvents. The mean values are 1.25, 1.33, and 1.45 ns for decalin, chloroform, and toluene, respectively. However, the component τ_2 has a typical decay time between 50 and 200 ps. The value of b_2 in Table 2 has larger amplitude at 465 nm (a longer wavelength than the center of the emission band), which means that the cis isomer may have slightly lower energy than the trans isomer, and therefore, back energy transfer can be neglected. The γ parameter is practically independent of the emission wavelength and has average values of 0.804, 0.307, and 0.485 in toluene, decalin, and chloroform, respectively.

The R_0 values of PFOPPV in the three solvents used were estimated from the spectral overlap of absorption and emission and also from the fluorescence quantum yield. The results obtained together with the value of γ are reported in Table 3.

The value estimated for R_0 is in agreement with γ in toluene and chloroform, and both indicate that FRET is more favored in the latter solvent (toluene is considered a better solvent for PFOPPV). However, the γ parameter points to a lower FRET efficiency in decalin than in $CHCl_3$, contrasting with the indication given by the values of R_0 in these two solvents. This discrepancy may be related to several factors including differences in chain conformation with solvent. In decalin, the $(CH_2)_8$ segments are well solvated and the aliphatic chains will assume a more extended conformation than in chloroform. This effect will separate the chromophores, resulting in lower chromophore concentration within the Förster radius in decalin than in chloroform, which means a reduction of N_a in eq 2.

TABLE 2: Decay times ($\tau_{1,2}$) and Fitting Parameters of the Fluorescence of PFOPPV[a]

	λ (nm)	τ_1 (ns)	b_1	τ_2 (ps)	b_2	γ	χ^2
toluene	423	1.52	0.386	196	−0.093	0.946	0.973
	435	1.44	0.372	155	−0.085	0.818	1.055
	447	1.36	0.359	146	−0.096	0.701	1.217
	465	1.35	0.472	100	−0.564	0.706	1.070
	483	1.59	0.386	156	−0.108	0.847	1.286
decalin	423	1.24	0.531	166	−0.086	0.374	1.161
	435	1.20	0.292	134	−0.104	0.337	0.975
	447	1.24	0.179	57	−0.624	0.383	1.078
	465	1.22	0.317	62	−0.878	0.321	1.109
	483	1.36	0.378	95	−0.587	0.434	1.163
chloroform	423	1.34	0.303	180	−0.036	0.559	1.191
	435	1.32	0.270	129	−0.036	0.494	1.069
	447	1.22	0.281	46	−0.206	0.386	1.023
	465	1.38	0.353	95	−0.339	0.510	1.132
	483	1.41	0.309	76	−0.156	0.476	1.062

[a] λ is the emission wavelength, and χ^2 is the chi-square value of the decay fitting with eq 1.

TABLE 3: Fluorescence Quantum Yield ϕ and Förster Radius R_0 of the PFOPPV Copolymer[a]

solvent	ϕ	J (M^{-1} cm^{-1}) × 10^{-12}	R_0 (Å)	$\langle\gamma\rangle$
toluene	0.77	7.41	94	0.804
decalin	0.51	5.09	83	0.370
chloroform	0.36	1.82	67	0.485

[a] J is the spectral overlap integral value, and $\langle\gamma\rangle$ is the fitting parameter obtained in the decay analysis with eq 1.

TABLE 4: Decay Parameters of PFPPV in a Global Biexponential Fit[a]

	λ (nm)	τ_1 (ps)	b_1	τ_2 (ps)	χ^2	χ^2_g
toluene	470	451	0.819	873	1.058	1.080
	485		0.833		0.944	
	500		0.848		1.074	
	520		0.816		1.171	
	540		0.814		1.151	
decalin	470	453	0.683	805	1.071	1.060
	485		0.704		0.972	
	500		0.725		1.129	
	520		0.716		1.080	
	540		0.673		1.049	
chloroform	470	517	0.697	1050	0.930	1.042
	485		0.705		1.097	
	500		0.705		1.064	
	520		0.656		1.069	
	540		0.643		1.049	

[a] b_1 is the normalized pre-exponential factor of the biexponential decay ($b_2 = 1 - b_1$). χ^2 and χ^2_g are the local and global chi-square values of the decay surface fitting.

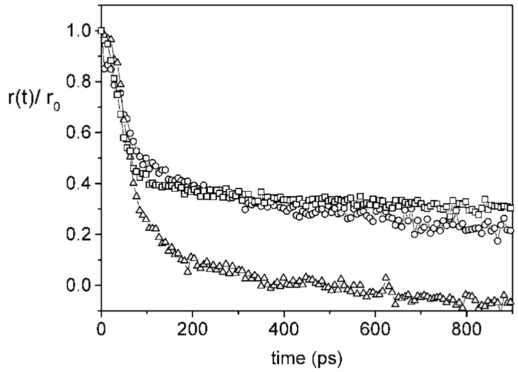


Figure 4. Normalized fluorescence anisotropy of PFOPPV in solution (decalin (□); toluene (○); chloroform (Δ)).

Conformational relaxation leading to nonexponential deactivation of the excited state usually occurs in the short time regime of a few picoseconds and may be a competing process with fast energy migration. However, energy migration described by the Förster mechanism in PFOPPV is observed on a slightly longer time scale where the excited-state copolymer conformation is already in thermal equilibrium, which minimizes the cited effect.

Time-resolved measurements of PFPPV were fitted properly by two exponential decay components in a global analysis with linked decay times, and no rising term was found. The decay parameters are summarized in Table 4. Some authors have reported exciton migration in polymers like poly(*p*-phenylenevinylene)s (PPVs) and polyfluorene as being a very fast process with relaxation and migration occurring in a few picoseconds followed by a long decay usually with one or two components of positive amplitudes.[24,25] In recent publications, the fluorescence of poly(fluorenevinylene)[26,27] and poly(fluorenevinylene-*co*-phenylenevinylene)[28,29] was reported as being single exponential with a lifetime of about 732−777 and 120−130 ps, respectively, for these two systems. Those polymers were synthesized by Heck reaction, and ^1H NMR spectra indicated the presence of only the trans isomer.

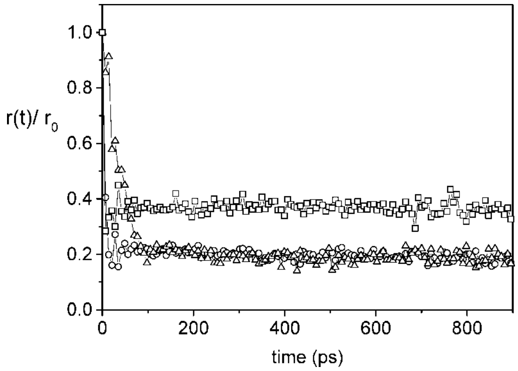


Figure 5. Normalized fluorescence anisotropy of PFPPV in solution (decalin (□); toluene (○); chloroform (Δ)).

In this way, the two decay times with positive amplitudes found in PFPPV can be ascribed to decay of the chain moieties containing the cis and trans isomers already in a photostationary condition. In our case, τ_1 would correspond to the trans isomer, with values of 451 ps in toluene, 453 ps in decalin, and 517 ps in $CHCl_3$, whereas the cis isomer, with decay time τ_2, has values of 873, 805, and 1050 ps in the same series of solvents.

The fluorescence lifetime as a function of the number *n* of fluorene units in a series of oligofluorenes was approached in a recent work.[30] The lifetimes followed the relation τ (ps) = 386 + 808/*n* in methyltetrahydrofuran (MTHF) solution at room temperature. In spite of the differences between the PFPPV and the oligofluorene models, the value previously determined for $n = 21$ resulted in a lifetime of 424 ps. The experimental value of 517 ps obtained in chloroform (among the solvents used, the nearest in polarity to MTHF) is higher than the calculated value, and this difference could be attributed to the presence of cis defects in the chain that break the conjugation length, and therefore, should provide a smaller value of *n* than 21. In some way, the fraction of isomers is related to the normalized amplitudes of the two decays weighted by the respective emission quantum yields. Averaged values of the amplitudes found (see Table 4) indicate, in the assumption of constant emission yield with solvent, that the fraction of cis isomer is about 17, 30, and 32% in toluene, decalin, and $CHCl_3$, respectively. These values are somewhat consistent when compared with the ^{1}H NMR data that indicated a content of the cis isomer about 20%, and the differences are ascribed to solvent dependent emission quantum yields.

One of the common defects in polyfluorenes is the presence of traces of fluorenone, which acts as a low-energy charge-transfer exciton trap in the polymer chain. Its presence results in an emission band at 535 nm with a long decay time on the order of 4−8 ns.[31−33] In our case, however, the presence of 9,9′-dihexyl branches at C9 in the fluorene moieties and the absence of such long-lived species in the red part of the emission spectra are two arguments that strengthen the assumption that the copolymers prepared are fluorenone-free defects.

Fluorescence Anisotropy Decays. Fluorescence depolarization in conjugated polymers may result from fast energy migration and transfer combined with slow polymer segments motion. Figures 4 and 5 illustrate the time-resolved anisotropy profiles of PFOPPV and PFPPV, respectively.

Fluorescence anisotropy of PFOPPV has clearly a biexponential relaxation with a fast component τ_{an} with values of 44 ± 2, 66 ± 6, and 68 ± 3 ps in decalin, toluene, and chloroform, respectively. The slow component has decay times on the order of 2.05, 1.15, and 1.25 ns in the same solvent series. It is noteworthy that the fast depolarization process occurs in the same time range of the rising component τ_2, previously ascribed to the interplay between the trans and cis isomers in an energy-transfer process (see τ_2 values reported in Table 2). Thus, the initial time regime of anisotropy decay reveals that energy transfer (or migration) occurs accompanied by reorientation in transition dipole moment, which is consistent with the presence of chromophores randomly oriented due to the presence of flexible spacers. The fast fluorescence depolarization is followed by a slow decay due to diffusion motion of polymer chain segments at longer times. This process is slower in decalin (2.05 ns) than in toluene (1.15 ns) and chloroform (1.25 ns) because it is affected by the medium viscosity.

If one assumes that the fast depolarization occurs by dipole−dipole interaction of neighboring fluorene chromophores of the PFOPPV chain in a quasi static picture of random dipoles, the ratio between the fluorescence decay time τ_1 and the fast depolarization decay time (τ_{an}) would be approximately $0.714(R_0/d)$,[6] where *d* is the average distance of energy transfer leading to fluorescence depolarization. Using the values of τ_1 and R_0 of Tables 2 and 3 and the previous values of the fast anisotropy decay time (τ_{an}), *d* is estimated as 53, 45, and 39 Å in toluene, decalin, and chloroform, respectively. These values are about 1.3−1.8 times the center to center distance between two fluorene groups of the PFOPPV structure obtained by molecular simula-

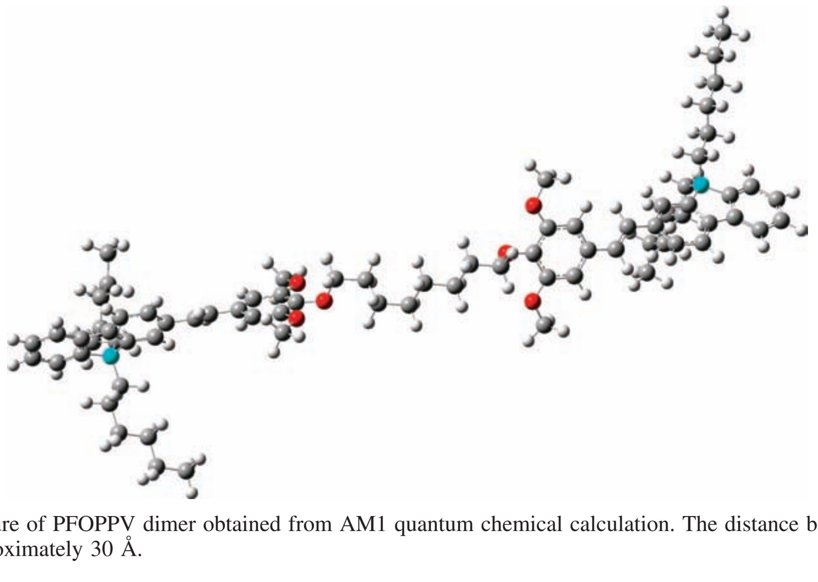


Figure 6. Molecular structure of PFOPPV dimer obtained from AM1 quantum chemical calculation. The distance between central carbon atoms of the two fluorenes is approximately 30 Å.

tion. The molecular structure of PFOPPV dimer was obtained by quantum chemical calculation using the semiempirical AM1 method starting from preoptimized molecular group structures and is illustrated in Figure 6. The distance between the two fluorenes from the central carbon atom is evaluated as 30 Å from this simulation.

This result means that one or two incoherent energy-transfer steps between neighboring chromophores in PFOPPV will be enough to depolarize the initial state in a large amount as observed in the fluorescence anisotropy relaxation measurements.

For PFPPV, depolarization was roughly observed in the time window of less than 20 ps where a steep decay occurs, but it hits thereafter a constant value (see Figure 5). This means that the stationary condition between the trans and cis isomers is achieved very fast, followed by emission without significant reorientation of the transition dipole moment, due to the rigid-rod-like structure of the PFPPV chains. The first steps of fluorescence decay of conjugated polyfluorenes in solution are a result of fast conformational relaxation and exciton migration along the polymer chain, and the whole process occurs in a range of 10−20 ps.[34,35]

Conclusions

The excited-state properties of two polyfluorene derivatives were investigated by time-resolved fluorescence and anisotropy decay measurements. The fluorescence behavior of the segmented copolymer PFOPPV is described by energy transfer between chromophores and isomers separated by the flexible $-O-(CH_2)_8-O-$ spacer with rates on the order of 2×10^{10} s^{-1} compatible with the magnitude of the Förster radius and chromophore neighboring distance in the copolymer molecular structure. The fully conjugated copolymer PFPPV has biexponential decay, which may represent the averaged decay times of the cis and trans isomers already in a photostationary condition due to the fast exciton diffusion in its conjugated chain.

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