Influence of Aggregates and Solvent Aromaticity on the Emission of Conjugated Polymers

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Influence of Aggregates and Solvent Aromaticity on the Emission of Conjugated Polymers

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The influence of aggregates and solvent aromaticity on the photophysics and fluorescence dynamics of two conjugated polymers is studied. The two polymers are derivatives of poly(*p*-phenylene vinylene) (PPV) containing different kinked moieties along the main chain. The polymers contain 2,6-diphenylpyridine and *m*-terphenyl kinked moieties and they are abbreviated as PN and PC, respectively. The insertion of kinked segments along the main chain shifts the emission spectrum from the yellow-orange spectral region, common to PPV derivatives, to the blue-green spectral region. The results show that in dilute solutions the polymers decay monoexponentially, while in concentrated ones the fluorescence decays biexponentially, indicating fluorescence quenching. This is attributed to an energy transfer process from polymer chains to aggregates that occurs within a few tens of picoseconds. By comparing the photophysics and fluorescence dynamics of polymer PN in a nonaromatic and an aromatic solvent, we conclude that the polymer conformation adopted in the aromatic solvent leads to a higher fluorescence quantum yield and a longer fluorescence lifetime. Furthermore, the fluorescence quenching of PN because of aggregates is faster and more efficient in the aromatic than in the nonaromatic solvent. These results can be explained through a more extended chain conformation of PN in the aromatic solvent.

Introduction

Since the first demonstration of a light-emitting diode (LED) based on a conjugated polymer,[1] a great amount of work has been done toward the understanding of the properties of conjugated polymers. The research efforts combine chemical synthesis of new advanced polymers and study of their optical and physical properties as well as device fabrication. These efforts have led to major progress in polymer technology, and nowadays conjugated polymers are successfully used in optoelectronic and microelectronic devices such as LEDs,[2−5] lasers,[6−9] photovoltaic cells,[10,11] photodetectors,[12] and field effect transistors.[13,14]

Among many conjugated polymers, poly(*p*-phenylenevinylene), PPV, and its derivatives are the most widely used in applications. However, most PPVs are suitable for application in LEDs emitting in the yellow-orange region of the spectrum. Emission at shorter wavelengths from PPV derivatives can be achieved by the insertion of nonconjugated segments[15−17] or kinked segments[18,19] in the main chain. A drawback of PPVs is that they are predominantly hole-transporting materials leading to an unbalanced charge carrier transport in LEDs. The substitution of electron-deficient segments in the polymer's main chain provides a way for achieving balanced carrier transport. Pyridine is a well-known electron-deficient structure, and poly-(pyridine)s are better electron transporting materials than unsubstituted PPVs.[20,21]

The use of a conjugated polymer in a device is greatly dependent on its excitation and decay procedures as well as on their dynamics. The excitation of a polymer chain leads to the creation of an exciton that can undergo different decay procedures: (i) radiative or (ii) nonradiative decay to its ground state, (iii) migration along the polymer chain, (iv) transfer to an adjacent chain, (v) dissociation (i.e., separation of the electron and hole), etc. A certain decay procedure can be either useful or detrimental concerning the device to be fabricated. For example, radiative decay of the exciton is desirable in LEDs and lasers but it should be avoided in photovoltaics. Understanding the contribution of each decay procedure to the overall polymer performance, as well as the study of the parameters (i.e., environment, aggregation, polymer chain morphology, etc.) that affect these procedures, is necessary for the future application of polymers in devices.

Aggregation is a factor that significantly affects the polymer's properties and consequently the performance of a device.[22,23] In most cases, where efficient emission of light is required, aggregation is undesirable since it reduces the fluorescence quantum yield of the polymer.[24−35] However, it has been shown that controlled aggregation can increase the efficiency of LEDs because it can increase the carrier mobility due to the overlapping of the π-orbitals of adjacent chains.[36] Additionally, polymer chain conformation greatly affects both quantum yield and mobility.[22,24] An open (more conjugated) conformation can increase the mobility but can also lead to an increased tendency toward aggregation, reducing the fluorescence quantum yield. All the above indicate that careful control of the amount of aggregates as well as an optimized chain conformation can improve the performance of polymeric devices. There have been several reports on the role of chain conformation in photophysics.[22,24,35] However, significant work needs to be done on the effect of chain conformation on the fluorescence dynamics and especially on the dynamics of aggregation quenching to further improve the fundamental knowledge on conjugated polymers.

In this paper, we study the photophysics and decay dynamics of two conjugated polymers in order to examine the role of aggregation and chain conformation on these properties. The polymers are PPV derivatives containing 2,6-diphenylpyridine (PN) and *m*-terphenyl (PC) kinked moieties along the main chain, and they were synthesized in order to achieve emission

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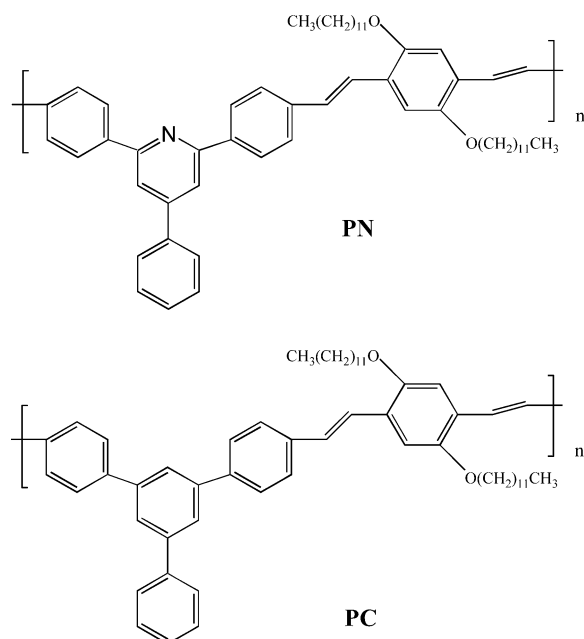
Figure 1. Chemical structures of the two polymers abbreviated as PN and PC.

Figure 2. (a) Absorption and fluorescence spectra of PN in (—) THF and (---) CB. (b) Absorption and fluorescence spectra of PN in dilute (—, 10^{-3} wt %) and concentrated (---, 10^{-1} wt %) THF solutions.
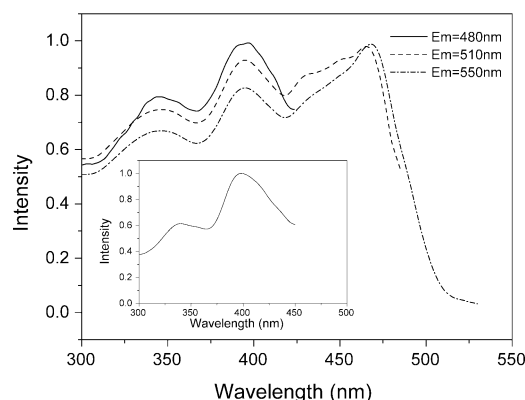
in the blue-green spectral region. The photophysics was investigated by absorption, excitation, and fluorescence spectra, while the decay dynamics was examined by femtosecond time-resolved fluorescence spectroscopy. The polymers were studied in solutions of various concentrations in order to probe the effect of aggregation. Additionally, an aromatic and a nonaromatic solvent were used to determine the role of the different chain conformation adopted in each solvent on the photophysics, dynamics, and aggregation. We provide evidence that, in the aromatic solvent, fluorescence quenching because of aggregates is faster and more efficient than in the nonaromatic solvent.

Experimental Section

Materials. The two polymers under study are shown in Figure 1. They are PPV derivatives containing kinked segments along the main chain. Specifically, the polymers contain 2,6-diphenylpyridine and *m*-terphenyl kinked moieties and they are abbreviated as PN and PC, respectively. They were synthesized by Heck coupling of 2,5-didodecyloxy-1,4-divinylbenzene with 2,6-bis(4-bromophenyl)-4-phenylpyridine (PN) or 4,4″-dibromo-3′-phenyl-*m*-terphenyl (PC), and their molecular weights are 6500 and 7100, respectively. Their detailed synthesis and chemical characterization[37] as well as their electroluminescence[38] and stimulated emission properties[37] have been published recently.

The polymers are studied in solutions with tetrahydrofuran (THF) and chlorobenzene (CB) as the nonaromatic and aromatic solvent, respectively. This was realized in order to examine the effect of solvent aromaticity and consequently the effect of polymer chain conformation on the optical properties. Both dilute (nonaggregated) and concentrated (aggregated) solutions were studied in order to determine the role of aggregates on the fluorescence dynamics.

Steady-State and Time-Resolved Spectroscopy. Steady-state fluorescence and photoluminescence excitation spectra were taken on a Perkin-Elmer LS55B luminescence spectrometer, while the absorption spectra were taken with a Beckman DU-640 spectrometer. The excited-state dynamics were studied by a femtosecond time-resolved fluorescence spectroscopy
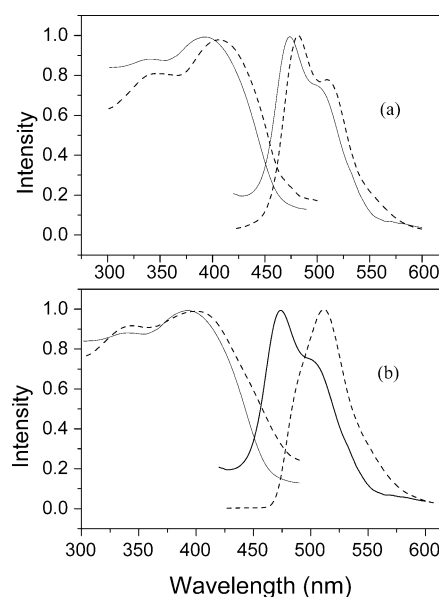
employing the upconversion technique. The experimental setup has been described in detail previously.[39,40] Briefly, a mode-locked Ti:sapphire laser was used as the light source. The laser emits a pulsed beam with 80 fs pulse duration that can be tuned from 750 to 850 nm. The samples were placed in a 1 mm thick quartz cuvette and they were excited by the second harmonic of the laser (~6 mW average power). The fluorescence of the samples was collected and focused onto a BBO crystal together with the delayed fundamental laser beam used as the gate beam. The fluorescence and the gate beam are mixed in the crystal and an upconversion beam is produced. This beam is separated from the fundamental and fluorescence beams by an iris and filters and is directed into a monochromator. Finally, it is detected by a photomultiplier connected with a photon counter. The temporal resolution of our system was determined by the full width at half-maximum of the upconversion signal between the gate and that scattered from the sample excitation pulses and it was found approximately 250 fs. The spectral resolution of our system is 2.5 nm. The dynamics of the molecules was detected at different wavelengths across the emission spectrum under magic-angle conditions (54.7°) to avoid dependence of the dynamics on rotational motions.

Results and Discussion

Steady-State Spectroscopy. Figure 2a shows the absorption and fluorescence spectra of PN in dilute THF and CB solutions. In both solutions PN emits in the blue-green spectral region. Specifically, PN in THF shows two absorption maxima at 340 and 390 nm and two fluorescence maxima at 475 and 497 nm. The spectra in CB are similar, although they exhibit a ~10 nm red shift. This shift can be explained through a different conformation adopted by PN in the two solvents. In the aromatic solvent (CB), which preferentially interacts with the aromatic main chain, the polymer adopts a more open and planar conformation leading to a longer conjugation than in THF.[24] The quantum yield of PN was determined in both solvents and it was found equal to 0.61 and 0.77 in THF and CB, respectively.

In Figure 2b, the absorption and fluorescence spectra of PN in THF are shown for two different concentrations, namely, 10^{-3} and 10^{-1} wt %. In the concentrated solution, a red shift is

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Figure 3. Fluorescence excitation spectra of PN in concentrated THF solution (10^{-1} wt %) obtained for three emission wavelengths. (Inset) Fluorescence excitation spectrum of dilute PN/THF solution.
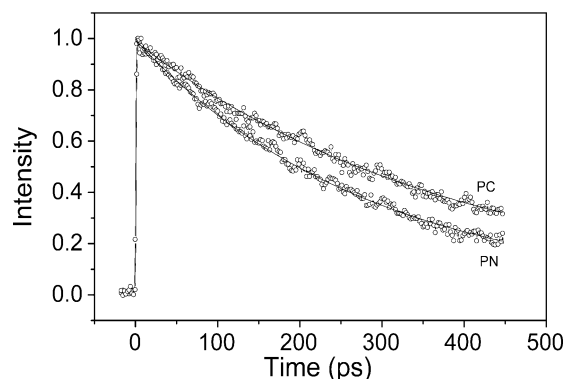
Figure 4. Fluorescence dynamics of PN and PC in dilute THF solution. The excitation wavelength was 400 nm.

observed in the spectra, indicating the existence of aggregates. In the fluorescence spectrum of the concentrated solution, a suppression of the intensity at short wavelengths is also observed. This may be due to self-absorption. Similar spectra were obtained for PN in CB. The photoluminescence excitation spectra of PN in concentrated THF solution (10^{-1} wt %) are shown in Figure 3. The spectra were taken by collecting the fluorescence at three different emission wavelengths ($\lambda_{em} = 480$, 510, and 550 nm). When the emission wavelength is located at the blue edge of the fluorescence spectrum ($\lambda_{em} = 480$ nm), two peaks appear in the excitation spectrum at 340 and 395 nm, being very close to the two absorption maxima. However, when the emission wavelength is shifted to the red ($\lambda_{em} = 510$, 550 nm), a new peak appears at ∼465 nm and its relative intensity becomes highest at the emission wavelength of 550 nm. It is reasonable to attribute this new peak to the excitation of aggregates. It is noted that the excitation spectrum of dilute PN solution does not depend on the emission wavelength and this spectrum is shown in the inset of Figure 3, exhibiting two peaks at 338 and 397 nm. Finally, similar spectroscopic behavior was observed from polymer PC. The quantum yield of PC was found equal to 0.4 and 0.55 in THF and CB, respectively.

Time-Resolved Fluorescence Spectroscopy. Initially, dilute solutions of PN and PC were prepared and studied concerning their decay dynamics. Figure 4 shows the fluorescence decay of PN and PC in THF (10^{-3} wt %) detected at 480 nm with excitation wavelength at 400 nm. The fluorescence of both polymers exhibits a single exponential and almost wavelength-independent decay with time constent equal to 300 and 400 ps for PN and PC, respectively. This result indicates the existence of essentially one specific chromophore segment in the polymer

TABLE 1: Fitting Parameters of the Fluorescence Dynamics of PN[a]

concn, wt %	λ_{det}, nm	solvent	τ_1, ps	τ_2, ps
10^{-3}	480	THF	300 ± 12 (1.0)	
10^{-3}	480	CB	400 ± 18 (1.0)	
10^{-1}	480	THF	50 ± 8 (0.10)	285 ± 13 (0.90)
10^{-1}	480	CB	25 ± 4 (0.18)	390 ± 25 (0.82)
10^{-1}	540	THF	53 ± 8 (−0.33)	450 ± 27 (1.18)
10^{-1}	540	CB	22 ± 4 (−0.3)	520 ± 30 (1.11)

[a] In parentheses, the preexponetial factors α_i are shown.

TABLE 2: Fitting Parameters of the Fluorescence Dynamics of PC[a]

| concn, wt %	λ_{det}, nm	solvent	τ_1, ps	τ_2, ps
10^{-3}	480	THF	400 ± 15 (1.0)	
10^{-1}	480	THF	50 ± 8 (0.12)	390 ± 18 (0.88)
10^{-1}	540	THF	54 ± 8 (−0.26)	640 ± 30 (1.12)

[a] In parentheses, the preexponetial factors α_i are shown.

chains. All the fitting parameters for PN and PC are summarized in Tables 1 and 2, respectively.

A change in the dynamics is observed as the polymer concentration increases. Figure 5a shows the fluorescence dynamics of PN in a concentrated THF solution (10^{-1} wt %) at two wavelengths, that is, 480 and 540 nm, located in the isolated and aggregated chains emission bands, respectively. The fluorescence at 480 nm in the concentrated solution (Figure 5a) decays faster than that of the dilute solution (Figure 4) and it was fitted by a double-exponential function with decay times equal to 50 and 285 ps. The longer fluorescence decay time (i.e., 285 ps) is similar to the normal fluorescence lifetime of PN as observed in dilute solutions. On the other hand, a slow fluorescence rise is observed at 540 nm with a rise time of ∼53 ps followed by a slow decay time of 450 ps. As is clear from the fitting results, the fast decay time at 480 nm closely matches the rise time at 540 nm. This suggests an energy transfer process from high-energy species (isolated chains) to lower energy ones (aggregates).[41,42] Finally, the decay at 480 nm with time constant of 285 ps can be attributed to isolated chains not participating in the energy transfer process, while the 450 ps decay at 540 nm could be the decay of the aggregates' fluorescence. From the decay of the concentrated PN solution at 480 nm, it is understood that a percentage of the polymer chains participates in the energy transfer while another percentage does not. Since energy transfer presupposes that the donor and acceptor molecules are found within a small energy-transfer distance, we believe that the polymer chains can be separated into the following types: those that are found in proximity to an aggregate (conditions for energy transfer are met) and those that are far from an aggregate (conditions for energy transfer are not met).

In order to examine the excitation mechanism of aggregates in more detail, the first few picoseconds of the fluorescence at 540 nm were detected. The results are shown in Figure 5b together with the corresponding results at 480 nm and the temporal response function of the system. As is seen, the fluorescence rise at 480 nm follows the experimental temporal response function while the rise at 540 nm is slower, revealing two excitation mechanisms of aggregates. Initially, a fast excitation mechanism, following the temporal response function of our system, is observed and is attributed to the direct excitation of aggregates. Afterward, there is a slower excitation mechanism that can be attributed to the excitation energy transfer from isolated polymer chains to aggregates. This slow excitation ceases at ∼50−60 ps as shown in Figure 5a.
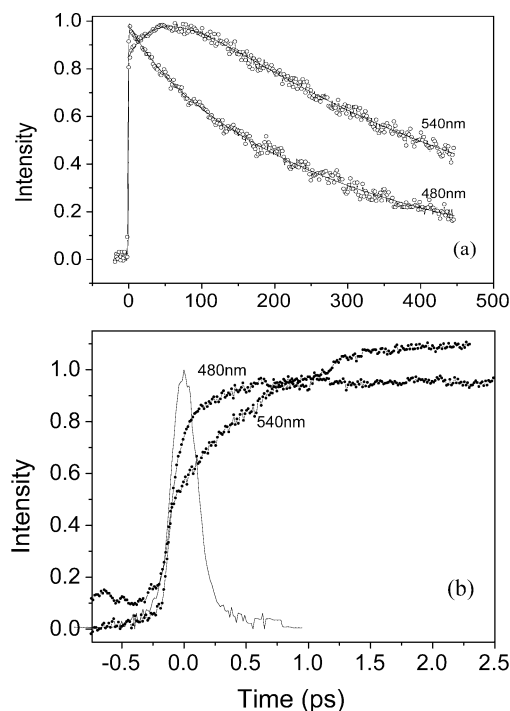
Figure 5. (a) Fluorescence dynamics of PN in concentrated THF solution (10^{-1} wt %) at two wavelengths. The excitation wavelength was 400 nm. (b) Fluorescence at the same two wavelengths within the first 2.5 ps, together with the temporal response function of the system (solid line).
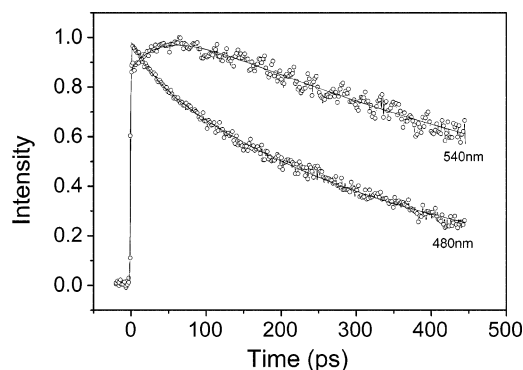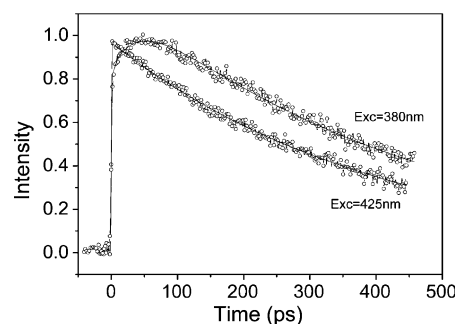

Figure 6. Fluorescence dynamics of PC in concentrated THF solution (10^{-1} wt %) at two wavelengths. The excitation wavelength is 400 nm.

Figure 6 shows the fluorescence dynamics of PC in concentrated THF solution (10^{-1} wt %) at two emission wavelengths, 480 and 540 nm. As in the case of PN, a fast decay is observed at 480 nm as well as a slow rise and a subsequent slow decay at 540 nm. The results at 480 nm were best fitted by a double exponential with decay times of 50 and 390 ps, respectively, while the fitting at 540 nm gave a 54 ps rise time followed by a 640 ps decay. The fast decay at 480 nm together with the slow rise at 540 nm constitute again indications of an energy transfer process to aggregates. The increased lifetime of the aggregates' fluorescence in PC (640 ps) compared to that in PN (450 ps) may indicate that larger aggregates are formed in PC.

A favorable way for a further verification of the energy transfer from isolated polymer chains to aggregates is the selective excitation in the aggregates (red edge) or in the isolated chains (blue edge) excitation band. This can be achieved in our case by tuning the laser system to the desired wavelength. Therefore, for the excitation of aggregates and isolated chains, the excitation wavelength was set to 425 and 380 nm,
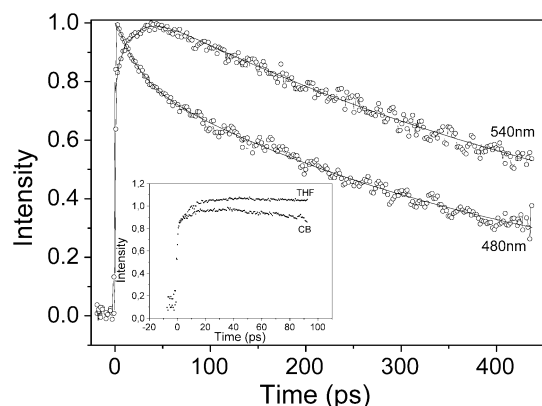

Figure 7. Fluorescence dynamics of PN in concentrated THF solution for two different excitation wavelengths, 380 and 425 nm. The detection wavelength was 512 nm.
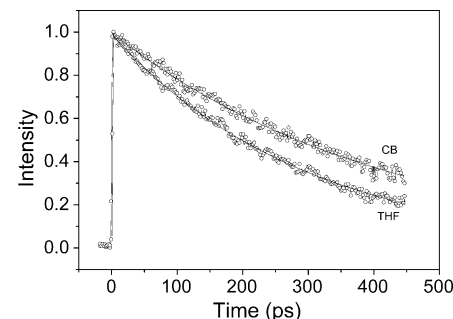
Figure 8. Comparison of the fluorescence decay of PN in dilute THF and CB solutions.

respectively. In each case the fluorescence was detected at the maximum of the fluorescence spectrum of the concentrated solution, namely, at 512 nm (this spectrum is shown in Figure 2b). The results of this selective excitation experiment are shown in Figure 7 for PN in THF (10^{-1} wt %). When the excitation wavelength is located at the aggregates' band (425 nm), the fluorescence intensity does not show a slow rise, indicating that the excitation of aggregates through energy transfer could be excluded. On the contrary, it seems that the aggregates are directly excited by their fundamental ground state. The fluorescence decay of the directly excited aggregates is single-exponential with decay time ~440 ps, that is, similar to the decay time of aggregates obtained by the results in Figure 5a (450 ps). Finally, when the excitation is at 380 nm, the fluorescence decay is similar to that obtained after excitation at 400 nm, exhibiting a clear slow rise attributed to excitation of aggregates through excitation energy transfer.

Apart from the effect of aggregation on the dynamics and consequently on the overall performance of a polymer, the conformation of polymer chains also plays a crucial role on their optical properties. Chain conformation can be controlled by the proper choice of solvent.[22,24] It has been reported in the past that a polymer chain adopts a planar conformation in aromatic solvents, while in nonaromatic ones the chains are more restricted, obtaining a more coiled conformation. This is also verified in the present paper through the steady-state spectra shown in Figure 2a. In order to determine the effect of chain conformation on the fluorescence dynamics and on aggregation, we studied PN in CB (aromatic solvent) and we compared the results with those in THF (nonaromatic solvent). Figure 8 shows the fluorescence decay of PN in dilute CB solution (10^{-3} wt %) at 480 nm together with the corresponding results in a THF solution. It is obvious that in CB the fluorescence decay is slower than in THF with a lifetime of 400 ps (in THF the lifetime is 300 ps). The faster decay in THF indicates the existence of more fluorescence quenching sites (defects) in PN chains dissolved in THF attributed to the more twisted chain

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Figure 9. Fluorescence dynamics of PN in concentrated CB solution (10^{-1} wt %) at two emission wavelengths. (Inset) Fluorescence of PN detected at 540 nm in concentrated THF and CB solutions within the first 100 ps. The two curves have been slightly shifted for clarity.

conformation. This result is in agreement with the different fluorescence quantum yields of PN in THF and CB (0.61 in THF and 0.77 in CB). By use of the experimental measurements of fluorescence lifetime and quantum yields, a radiative time of ~0.5 ns is calculated for PN in both solvents.

Although in dilute solutions the choice of an aromatic solvent (CB) seems to be suitable concerning the quantum yield, the situation is different when the concentration increases. This is concluded by the fluorescence dynamics obtained from a concentrated solution of PN in CB (10^{-1} wt %). These dynamics are shown in Figure 9 for two characteristic wavelengths, 480 and 540 nm. A fast decay at the short wavelength as well as a slow rise at the long wavelength are observed as in the case of THF solution. However, the time constants determining the fluorescence quenching because of aggregates are different in CB and THF. More specifically, in CB, the fast decay time at 480 nm as well as the slow rise time at 540 nm are both ~25 ps, while the corresponding times in THF are ~50 ps (Figure 5). In the inset of Figure 9, the first 100 ps of the fluorescence of PN in CB is shown at 540 nm together with the corresponding results in THF for comparison. It is obvious in this figure that the fluorescence rise in CB is faster than that in THF. The above results indicate that the undesirable energy transfer to aggregates, leading to quenching of the polymer's fluorescence, occurs faster in CB than in THF. According to our opinion, this can be attributed to two reasons based on the different conformation of the polymer chains in CB and THF. The first reason is the easier aggregation of polymer chains in the aromatic solvent, because the open chain conformation adopted in this solvent leads to an increased overlapping of the π-orbitals of adjacent chains. This could lead to larger and/or more aggregates in CB than in THF. The second reason is the easier exciton migration along the open polymer chain in CB than in THF. Consequently, excitons are more likely to be found close to an aggregate site, increasing the possibility for their transfer to the aggregate.

As discussed before in this paper, the existence of aggregates (acceptors) in a polymeric solution results in a faster fluorescence decay of the polymer chains compared to the case where no aggregates exist. This is an indication of a nonradiative energy transfer.[43] On the other hand, if radiative energy transfer was dominant, the decay time of the polymer chains would be slower or unchanged if the donor and acceptor molecules are the same or different, respectively.[43] According to the above, reabsorption could not be taken into account for the interpretation of the dynamics, although the samples used in this work are concentrated. When reabsorption occurs, a photon is initially emitted by a certain molecule and is then reabsorbed by another molecule, leading to its excitation. Therefore, reabsorption is actually a radiative energy transfer process that could not lead to faster dynamics.[44]

By use of the decay times obtained from our results for PN in THF and CB (Table 1), the energy transfer rate constant k_{ET} and quantum yield Φ_{ET} for nonradiative energy transfer can be calculated through the relationships[43]

$$k_{ET} = 1/\tau_1 \text{ and } \Phi_{ET} = 1 - \frac{\langle \tau \rangle}{\tau_0}$$

where τ_1 is the fast decay time of the fluorescence in concentrated solutions, that is, the energy transfer time, and τ and τ_0 are the lifetimes in the presence and absence of aggregates (acceptors), respectively. k_{ET} can be alternatively calculated from the slow rise of the acceptor's fluorescence τ_{rise} through the equation $k_{ET} = 1/\tau_{rise}$.[45] Both calculations lead to the same result. Note that k_{ET} refers only to the rate constant attributed to energy transfer and not to the other decay processes. Since in the presence of aggregates (i.e., in concentrated solutions) the decay is biexponential, an amplitude averaged lifetime $\langle \tau \rangle$ is used for the calculation of Φ_{ET}. Finally, the values obtained for PN are $k_{ET} = 2 \times 10^{-10}$ s^{-1} and $\Phi_{ET} = 0.13$ in THF, and $k_{ET} = 4 \times 10^{-10}$ s^{-1} and $\Phi_{ET} = 0.19$ in CB. This analysis gives a quantitative indication that the efficiency of the energy transfer toward aggregates is higher in CB than in THF. Specifically, the increase of the energy transfer quantum yield in CB is ~40%. The aggregation quenching is therefore more efficient in the aromatic solvent than in the nonaromatic one, which is a consequence of the different conformation of polymer chains in the two solvents.

Conclusions

The photophysics and fluorescence dynamics of two PPV derivatives with kinked structures along the main chain were studied, with a focus on the role of aggregates and solvent aromaticity. This was realized by steady-state and time-resolved fluorescence spectroscopy. It was shown that both polymers emit in the blue-green spectral region, although red-shifted emission is exhibited in concentrated solutions and is attributed to aggregates. In both polymers, aggregation quenching occurs because of energy transfer from polymer chains to aggregates. In the aromatic solvent, this energy transfer is faster and more efficient, indicating that the chain conformation adopted in the two solvents greatly affects the dynamics and the quenching behavior.

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