Photophysics and Solvent-Induced Aggregation of 2,7-Carbazole-Based Conjugated Polymers

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ABSTRACT: We report on the optical, photophysical, and solvatochromic properties of five carbazole-based polymers, namely poly(*N*-octyl-2,7-carbazolediyl) (POC), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl) (PEHC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene) (POCT), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-thiophene) (PEHCT), and poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE). Compared to their corresponding triads, the absorption and fluorescence spectra of polycarbazoles in chloroform are red-shifted due to an increase of the effective conjugation length. Among the polycarbazoles investigated, the optical spectra of POCT are the more red-shifted due to the electron donor properties of the thiophene rings. The variation of the photophysical properties of the polycarbazoles mainly involves radiative processes (k_F). From steady-state and time-resolved fluorescence studies in chloroform/methanol mixtures, all polymers have revealed solvatochromic effects, which have been related to the formation of H- and/or J-aggregates. On one hand, the aggregation process found on homopolymers (POC and PEHC) and copolymers involving thiophene units (POCT and PEHCT) is accompanied by a strong quenching of the photoluminescence efficiency. On the other hand, for POCE, the molecular interactions between the polymeric chains are not strong enough to induce a deactivation of the fluorescence. Finally, it is observed that the nature of alkyl chains on the nitrogen atoms of the carbazole moieties has a significant effect on the emission properties of the polymers.

Introduction

π-Conjugated polymers are an important class of materials because of their electrical and optical properties.[1] These electroactive and photoactive materials are generally based on organic moieties such as thiophene, pyrrole, phenylene, fluorene, etc.[2−5] Recently, novel homopolymers and copolymers derived from *N*-alkyl-2,7-carbazoles have been synthesized and characterized by Leclerc's research group.[6,7] Advantages of these polymers include their capability to emit in the blue region of the visible spectrum, their chemical and photochemical stability in air, and the high purity with which they can be synthesized. Moreover, all these polymers can be processed by spin-coating, yielding thin polymer films with relatively high quantum efficiency, making them promising materials for electroluminescent devices.[8] Recently, light-emitting diodes derived from this new class of conjugated polymers have been reported.[9]

Among other interesting applications of these materials, chromic effects have allowed the development of smart materials and sensors.[10−14] These optical properties have been related to intramolecular conformational changes of the backbone, which induce a modification of the effective conjugation length causing optical shifts in the UV−vis absorption spectra of the conjugated materials.[15−19] However, in the case of π-conjugated materials, facile interaction between polarizable π-electron clouds of large chromophores favors aggregate formation, which affect the optical properties of the materials. Recent studies show that aggregation of π-conjugated molecules leads to formation of weakly emissive interchains species in thin films that significantly reduce the luminescence quantum efficiency of light-emitting diode (LED) devices.[20,21] Understanding the formation and structure of aggregation, which represents an early stage in forming the solid-state films, will provide valuable guidance to develop materials of improved luminescence efficiency.

Molecular aggregation in solution can be conveniently detected by UV−vis absorption[22,23] and fluorescence.[24] Formation of aggregation is commonly induced by changing the nonsolvent/solvent ratio, as observed from poly(*p*-phenyleneethynylene) derivatives.[23] Clearly, significant nonsolvent in solution makes solute−solvent interaction energetically less favorable, thereby forcing polymer chain segments to approach each other for aggregate formation. Recently, we have studied the intermolecular aggregation of 2,7-carbazole-based conjugated polymers from the recording of their absorption spectra in chloroform/methanol mixtures.[25] All polymers have revealed solvatochromic effects, which have been interpreted in terms of the formation of H- and/or J-aggregates. To further investigate the aggregation behavior of these polymers, we have investigated the solvatochromism of these polymers from steady-state and time-resolved fluorescence measurements. In the first part of this paper, we report on the optical and photophysical properties of various 2,7-carbazole-based conjugated polymers: namely, poly(*N*-octyl-2,7-carbazolediyl) (POC), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl) (PEHC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene) (POCT), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-thiophene) (PEHCT), and poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE) in 100% chloroform solutions. In the second part, the poor solvent-induced aggregation

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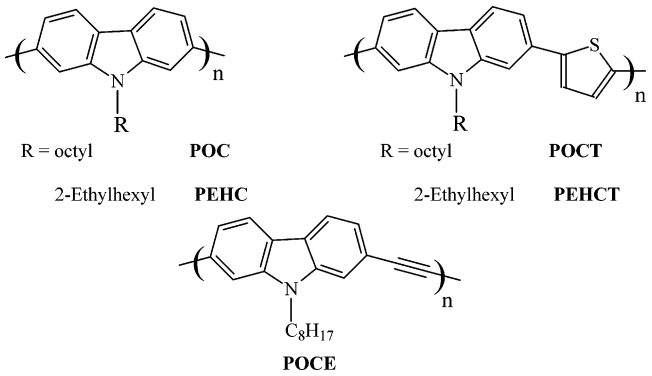

Figure 1. Molecular structure of the carbazole-based polymers.

process is studied from steady-state and time-resolved photoluminescence properties of these polymers in chloroform/methanol mixtures. Solvatochromic effects have been found for all the polymers investigated, which (except for POCE) are accompanied by a large decrease of their fluorescent efficiency. All this information should help in the rational design of tunable light-emitting materials based on polycarbazoles. The molecular structures of the carbazole-based polymers investigated are shown in Figure 1.

Experimental Section

Materials. Chloroform (A & C American Chemicals Ltd., spectrograde) and methanol (Aldrich Chemicals, spectrophotometric grade) were used as received. Prior to use, the solvents were checked for spurious emissions in the region of interest and found to be satisfactory. The synthesis and the characterization the carbazole-based polymers are described elsewhere.[25]

Instrumentation. Absorption spectra were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer at room temperature using 1 cm quartz cells and solute concentrations of $\sim 10^{-6}$ M based on the repeat unit, giving absorbances of ~ 0.1. Fluorescence spectra were obtained on a Spex Fluorolog-2 spectrofluorimeter with a F2T11 special configuration by exciting the polymer samples at the wavelength corresponding to the absorption maximum. Excitation and emission bandpasses used were 2.6 and 1.9 nm, respectively.

Fluorescence quantum yields (or photoluminescence efficiencies, ϕ_F) were calculated by the relative method, based on the comparison of the areas of the fluorescence spectra of a reference and of the sample. The experimental spectra were multiplied by a correction curve that considers the dependence of the spectrofluorimeter detecting system response on the photon energy. The polymer solutions used in these studies were saturated with argon, with solute concentrations of about 10^{-6} M, so that their maximum absorbance values were ~ 0.1 to avoid inner-filter effects. As a reference substance, we used 9,10-diphenylanthracene in cyclohexane ($\phi_F = 0.90$).[26] In ϕ_F calculations, we have taken into account the refractive indexes of the (diluted) solutions, which were considered equal to those of the pure solvents.

Fluorescence lifetimes were measured on a multiplexed time-correlated single photon counting fluorimeter (Edinburgh Instruments, model 299T) at 298 K. Details on the instrument have been published elsewhere.[27] The instrument incorporates an all-metal coaxial hydrogen flashlamp. Reconvolution analysis was performed by fitting over all the fluorescence decay including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, reduced χ^2 values, and Durbin−Watson (DW) parameters.

Results and Discussion

Optical Properties. Figure 2 shows the absorption and fluorescence spectra of the five carbazole-based polymers in dilute chloroform solutions at room temperature. Their spectral data are reported in Table 1.

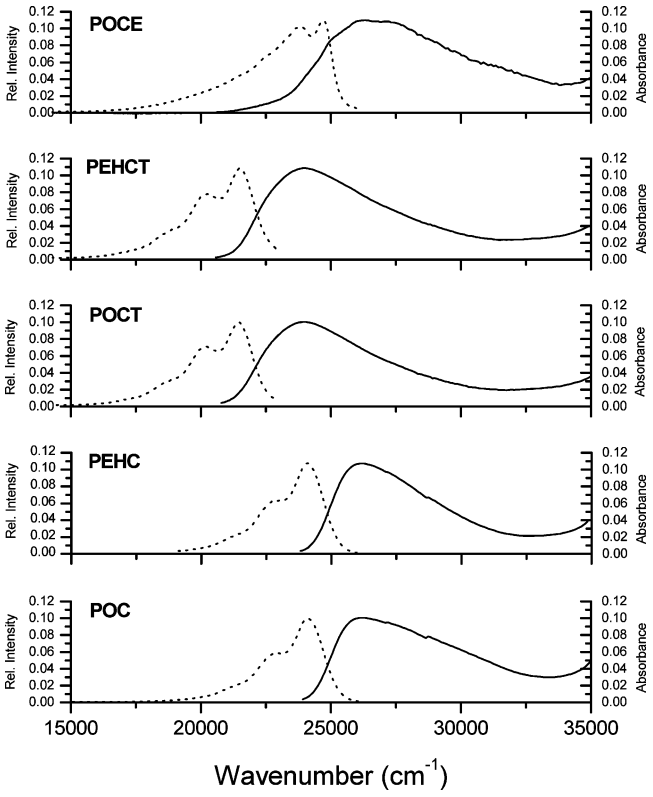

Figure 2. Absorption (—) and fluorescence (· · ·) spectra of the carbazole-based polymers in chloroform. The fluorescence spectra intensities have been normalized relative to the absorption band of each compound. Wavelength at the maximum of the absorption band of each compound was used for the recording of the fluorescence spectra.

Table 1. Spectroscopic Parameters of Polycarbazoles in Chloroform at Room Temperature

molecule	$\lambda_A{}^a$ (nm)	$\nu_A{}^b$ (cm^{-1})	$fwhm_A{}^d$ (cm^{-1})	$\lambda_F{}^e$ (nm)	$\nu_F{}^f$ (cm^{-1})	$fwhm_F{}^g$ (cm^{-1})
POC	380	26 300	6100	415	24 100	2300
PEHC	381	26 300	4700	416	24 000	2400
POCT	419	23 900	5200	467	21 400	2500
PEHCT	419	23 900	5400	467	21 400	2500
POCE	375	26 700	7100	406	24 600	3500

[a] Absorption wavelengths taken at the maximum of the absorption band. [b] Absorption wavenumbers taken at the maximum of the absorption band. [c] Absorption coefficient at the maximum of the absorption band. [d] Full width at half-maximum (fwhm) of the absorption band. [e] Fluorescence wavelengths at the maximum of the 0−1 vibronic peak. [f] Fluorescence wavenumbers at the maximum of the 0−1 vibronic peak. [g] Full width at half-maximum (fwhm) of the fluorescence band.

The first absorption band of POC is centered at 26 300 cm^{-1} and does not show any vibronic peaks. This strongly suggests that this polymer is quite flexible and nonplanar in its ground state. In contrast, the fluorescence spectrum of POC shows two shoulders at 24 100 cm^{-1} and around 22 800 cm^{-1} and is much sharper than its absorption counterpart (see Figure 2 and Table 1). This suggests that the homopolymer is more planar in its first relaxed excited state. Recently, a similar spectroscopic behavior was observed for carbazole-based diads[28,29] and triads.[30] From ab initio calculations, it was found that these molecules are nonplanar in their ground electronic state (S_0), whereas they almost reach planarity in their S_1 relaxed excited state. Moreover, it

was found that the absorption and fluorescence spectra of POC are red-shifted compared to those of the corresponding triad (CCC), showing that the effective conjugation length is longer for the polymer.[30]

Absorption and fluorescence bands of PEHC appear at about the same positions than that of POC (see Figure 2 and Table 1). As expected, the presence of a branched alkyl chain on the nitrogen atoms does not affect the intrachain electronic delocalization along the molecular frame. However, one can see in Table 1 that the absorption bandwidth of PEHC is much smaller than that of POC. We believe that the replacement of octyl chains by 2-ethylhexyl groups on nitrogen atoms could weaken interchain interactions in solution for PEHC. This will be confirmed below from steady-state and time-resolved fluorescence studies in chloroform/methanol mixtures.

The alternating copolymerization of thiophene with *N*-octyl-2,7-carbazole was shown to decrease the energy of the absorption and fluorescence bands of the copolymer (POCT) in comparison with those of the homopolymer (POC). Similar results were observed for the corresponding triad couples (CPC and CTC).[30] The decrease of the $\pi-\pi^*$ transition energy upon substitution of the phenylene ring by a thiophene unit is attributed to charge-transfer interactions (thiophene is an electron-rich system), which contribute to the reduction of the optical gap, and to an increase of the polymer chain planarity and the consequent increase of the effective conjugation length (increased delocalization). Note that the twist angles in CTC are predicted to be smaller than those in CPC.[30] Similar red shifts of the absorption and emission spectra, upon substitution of a phenylene by thiophene unit in alternating copolymers based on 9,9-dioctylfluorene, were also observed.[31] As observed for POC, the optical transitions of POCT are red-shifted compared to those of the corresponding triad (CTC) due to an increase of the effective conjugation length in the copolymer. Similarly, the presence of branched alkyl chains on the nitrogen atoms (PEHCT) does not change the spectral positions of POCT.

Finally, Figure 1 shows that the absorption and fluorescence spectra of POCE are blue-shifted relative to those of POC. This blue shift is attributed to a shorter effective conjugation length for POCE. Moreover, the absorption and fluorescence spectra of POCE are much broader than those of POC, suggesting that POCE is not well-solvated in chloroform (see Figure 2 and Table 1). Thus, the replacement of carbazole units by ethylylene segments seems to significantly increase interchain interactions for POCE in chloroform. This will be confirmed below from fluorescence time-resolved measurements.

Photophysical Properties. Fluorescence quantum yields (ϕ_F) and lifetimes (τ_F) as well as the radiative ($k_F = \phi_F/\tau_F$) and nonradiative ($k_{nr} = k_F(1 - \phi_F)/\phi_F$) decay rate constants of the carbazole-based polymers in dilute chloroform solutions are compiled in Table 2. For all fluorescence decay profiles (except POCE, see below), it was observed that single-exponential fits gave good correlation parameters ($\chi^2 < 1.3$ and DW ≈ 1.7).

The fluorescence quantum yield of POC is 0.80, which is higher than that of its corresponding triad (CCC, $\phi_F = 0.62$).[30] An increase of the k_F value of POC ($k_F = 17 \times 10^8\ s^{-1}$) compared to that of CCC ($k_F = 7.1 \times 10^8\ s^{-1}$) is responsible for this behavior. Similarly, the ϕ_F value of CCC is much higher than its corresponding dyad (CC, $\phi_F = 0.27$).[29] Thus, it seems that the high ϕ_F value obtained for POC can be related to a longer effective conjugation length experienced by this polymer, as observed from the spectral data discussed above. One can see in Table 2 that PEHC possesses a ϕ_F slightly higher than that of POC, which mainly involves a decrease of the k_{nr} value of the former molecule. As discussed above, weaker interchains interactions for PEHC in chloroform might be responsible for this behavior.

Table 2. Photophysical Properties of Polycarbazoles in Chloroform at Room Temperature

molecule	ϕ_F	τ_F (ns)	$10^{-8}k_F$[b] (s^{-1})	$10^{-8}k_{nr}$[c] (s^{-1})
POC	0.80	0.48	17	4.3
PEHC	0.90	0.49	18	2.0
POCT	0.63	0.71	8.9	5.2
PEHCT	0.65	0.71	9.2	5.0
POCE	0.69	$\langle 0.76\rangle$ [a]	9.1	4.1

[a] $\langle\tau_F\rangle = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$. [b] $k_F = \phi_F/\tau_F$. [c] $k_{nr} = k_F(1 - \phi_F)/\phi_F$.

The copolymerization of carbazole with thiophene brings about a reduction of ϕ_F down to 0.63 for POCT in chloroform solution. A similar reduction of ϕ_F was reported for fluorene-based alternating copolymers, when thiophene units were used instead of phenylene comonomers.[31] For oligothiophenes, this variation was attributed to the heavy-atom effect of sulfur in the thiophene unit, which facilates the intersystem crossing to triplet excited states.[30,32] But, in the case of POCT, this deactivation pathway is surely less effective since its k_{nr} value is only slightly higher than that of POC. On the other hand, on going from POC to POCT, an important decrease of the k_F value is found (see Table 2). Along these lines, it was observed that the oscillator strength (f) of the emission transition from the relaxed singlet excited state ($S_1 \rightarrow S_0$) of CTC is significantly smaller than that of CCC.[27] Thus, radiative processes mainly govern the variation in the fluorescence quantum yield. Table 2 also shows that the photophysical parameters of POCT and PEHCT are very similar, showing that the nature of the alkyl chain on the nitrogen atoms does not seem to influence the conformational order of the copolymer chains.

Finally, it can be seen in Table 2 that the fluorescence quantum yield of POCE is smaller than that of POC. But in contrast to the homopolymer, the fluorescence decay profile of POCE cannot be fitted to a single exponential but is best described by a sum of two exponentials (see Table 3). We did not observe any significant excitation and/or emission wavelength dependence on the fluorescence decay parameters. Even if the long lifetime component has a small preexponential factor, it is genuine in view of the significant improvement in χ^2 values going from single-exponential to double-exponential fits. The emitting species associated with the long lifetime component should be weakly coupled to the ground state and probably involves intermolecular interactions as reported for several polymers in the solid state (thin films).[33−35] These intermolecular interactions are not strong enough to provoke the appearance of distinct fluorescence bands, but as discussed above, the fluorescence bandwidth of POCE is significantly larger than that of the other carbazole-based polymers investigated in this work. For POCE, Table 2 reports the mean fluorescence lifetime ($\langle\tau_F\rangle$), such that k_F and k_{nr} values of this polymer can be evaluated. It is observed that both k_F and k_{nr} values

Table 3. Summary of the Fluorescence Decay Parameters for the Single-Exponential (SE) and Double-Exponential (DE) Fits of Polycarbazoles in $CHCl_3$/MeOH Mixtures

		SE		DE				
polymer	MeOH (%)	τ (ns)	χ^2	τ_1[a] (ns)	B_1[b]	τ_2[a] (ns)	B_2[b]	χ^2
POC	0	0.48	1.13	0.48	1.000			1.02
	20	0.50	1.14	0.48	0.996	1.71	0.004	1.09
	40	0.53	1.39	0.50	0.993	1.92	0.007	1.12
	60	0.73	6.17	0.57	0.979	2.98	0.021	1.08
	80	1.56	11.1	0.62	0.89	3.31	0.11	1.21
PEHC	0	0.49	1.00					
	20	0.51	1.21					
	40	0.55	1.12					
	60	0.61	1.09					
	80	0.68	1.34					
POCT	0	0.71	1.20					
	20	0.74	1.22					
	40	0.76	1.19					
	60	0.79	1.08					
	80	0.81	1.17					
PEHCT	0	0.71	1.26					
	20	0.74	1.32					
	40	0.79	1.42					
	60	0.83	1.24					
	80	0.84	1.10					
POCE	0	0.76	2.75	0.65	0.974	2.18	0.026	1.09
	20	0.80	2.79	0.69	0.974	2.28	0.026	1.08
	40	0.82	2.60	0.71	0.972	2.28	0.028	1.04
	60	0.86	2.79	0.75	0.976	2.53	0.024	1.08
	80	0.90	2.96	0.79	0.980	2.90	0.020	1.16

[a] τ_1 and τ_2 denote the fluorescence lifetimes associated with the two exponentials obtained from the reconvolution fits. [b] B_1 and B_2 denote the relative preexponential factors of each exponential (normalized so that they sum to 1).

of POCE are smaller than those found for POC. However, the predominant factor is the variation of k_F, which contributes to decrease the quantum yield of POCE. Moreover, the fact that the copolymer possesses a smaller k_{nr} value than that of the homopolymer indicates that the interchain interactions are not strong enough to induce an effective quenching of the fluorescence.

Steady-State Fluorescence Solvatochromic Properties. As mentioned above, significant intermolecular interactions are observed for several polymers in the solid state (thin films).[33−35] The optical properties induced by the intermolecular interactions have been explained by the exciton model.[36] In this model, a splitting (Davydov splitting) of the absorption band can be induced by the two orientations of the molecular transition dipole moments, giving rise to H-aggregates (parallel orientation of the molecules) and J-aggregates (head-to-tail orientation). Recently, we have reported excitonic effects for some oligothiophenes,[37−39] oligofluorenes,[40] and fluorene-based polyesters.[41]

Molecular aggregation can also be induced by the addition of a nonsolvent to the polymer solutions. Clearly, the presence of significant amount of nonsolvent in solution makes solute−solvent interaction energetically less favorable, thereby forcing polymer chain segments to approach each other for aggregate formation. To investigate the aggregation phenomenon, the steady-state and time-resolved fluorescence properties of the polycarbazoles in chloroform/methanol mixtures have been studied. As reported in our previously published work,[25] the absorption spectra of the polycarbazoles in chloroform significantly change if a nonsolvent such as methanol is added. For instance, it was observed that the absorption bands of POC and PEHC are red-shifted as the content of methanol is increased, which has been explained by the formation of J-aggregates. On the other hand, it was reported that the absorption bands of POCT and PEHCT are blue-shifted when the quality of the solvent decreases. These results have been interpreted in terms of the formation of H-aggregates. Finally, upon the addition of the bad solvent, a clear broadening of the absorption band of POCE has been observed with the appearance of a red-shifted tail, suggesting the formation of both H- and J-aggregates. It is worth pointing out that the presence of branched alkyl chains (2-ethylhexyl) on the nitrogen atoms did not seem to significantly affect the absorption spectra of the polycarbazoles recorded in chloroform/methanol mixtures.

The fluorescence spectra of the polycarbazoles measured in chloroform/methanol mixtures are shown in Figures 3−7. As can be seen in Figure 3A, addition of methanol to a solution of POC in chloroform leads to a dramatic drop in quantum yield ($\phi_{0\%}/\phi_{80\%} = 70$ at $\lambda = 415$ nm). These results are similar to what is observed in spin-cast conjugated polymer films as compared to solution.[33−35] More recently, a similar behavior was reported for the fluorescence of poly(*p*-phenylenevinylene)[42] in good/poor solvent mixtures, which as been ascribed to interchain π-stacked aggregates. Moreover, the appearance of a new red-shifted band around 430 nm is observed as the content of the poor solvent is increased (Figure 3B). As suggested from absorption measurements reported elsewhere,[25] we believe that the appearance of the fluorescence red-shifted band can be interpreted by the molecular exciton model, assuming J-aggregates formed by head-to-tail orientation of the chromophores. Thus, the quenching of the photoluminescence efficiency would arise from J-aggregates formation. Time-resolved fluorescence measurements described below are in agreement with this statement.

As the nonsolvent (methanol) component is added to PEHC in chloroform, it can be seen that the emergence of the new band is almost prevented (see Figure 4B). Consequently, as the methanol concentration increases,

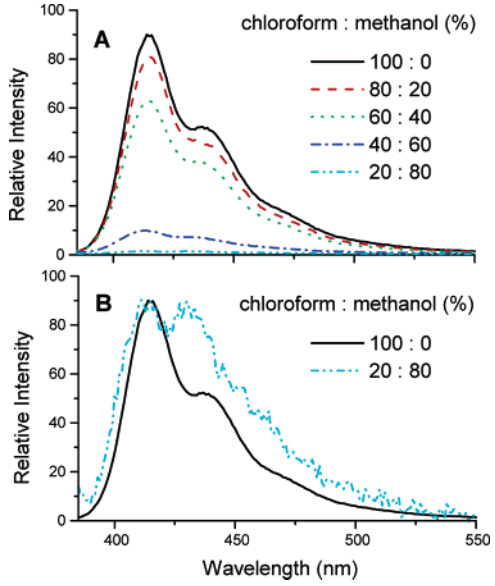

Figure 3. (A) Fluorescence spectra of POC in mixed chloroform/methanol solvents (v/v) with varying solvent composition as noted in the legend. (B) Fluorescence spectrum of POC at the 80% methanol content normalized to its value at 0%.

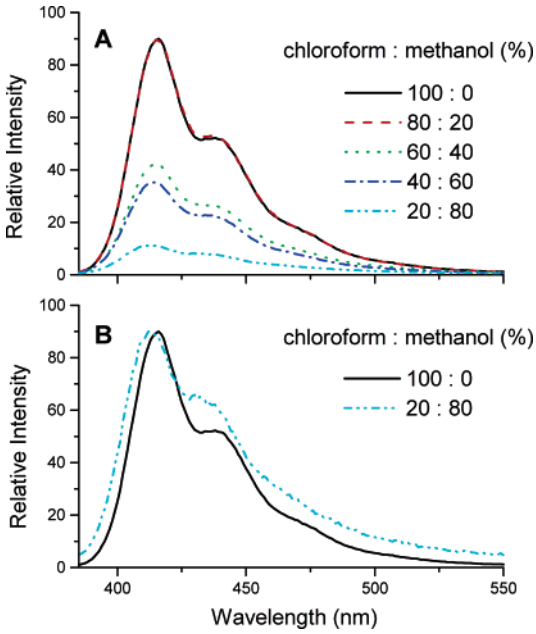

Figure 4. (A) Fluorescence spectra of PEHC in mixed chloroform/methanol solvents (v/v) with varying solvent composition as noted in the legend. (B) Fluorescence spectrum of PEHC at the 80% methanol content normalized to its value at 0%.

a much smaller decrease of the fluorescence efficiency is found for PEHC ($\phi_{0\%}/\phi_{80\%} = 8$ at $\lambda = 415$ nm). Thus, the presence of branched alkyl chains on the nitrogen atoms seems to reduce the formation of aggregates for the homopolymer. These results can be compared to those of Teetsov and Fox.[43] In that study, it was observed that films of polyfluorene derivatives with bulky side chains had higher fluorescence quantum yields compared to those with smaller side chains. Clearly, the side chain has an impact on the extent of interchain interactions. A small side chain can result in stronger interactions, which in turn will result in luminescence quenching due to an increased probability of excitation transfer to quenching and defect sites.

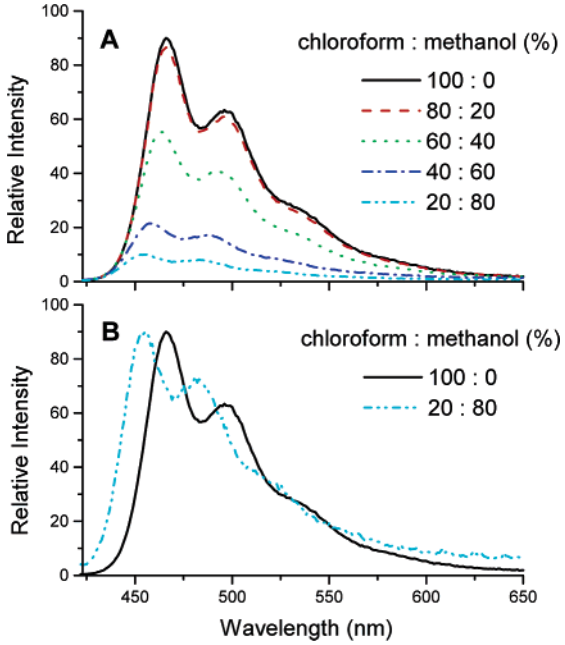

Figure 5. (A) Fluorescence spectra of POCT in mixed chloroform/methanol solvents (v/v) with varying solvent composition as noted in the legend. (B) Fluorescence spectrum of POCT at the 80% methanol content normalized to its value at 0%.

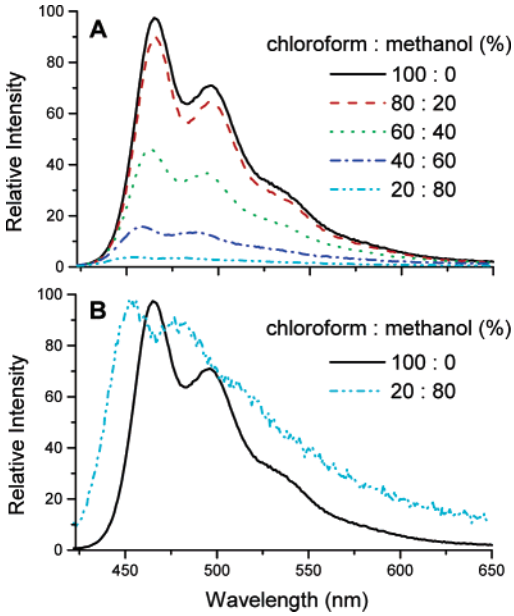

Figure 6. (A) Fluorescence spectra of PEHCT in mixed chloroform/methanol solvents (v/v) with varying solvent composition as noted in the legend. (B) Fluorescence spectrum of PEHCT at the 80% methanol content normalized to its value at 0%.

In sharp contrast to POC, POCT exhibits a very different solvatochromic behavior in various ratios of chloroform/methanol solutions (see Figure 5). Indeed, an important hypsochromic shift of about 13 nm is observed for the fluorescence spectra measured in 80% methanol content relative to its value at 0%, without the appearance of a new band. As suggested from absorption measurements reported in our recent paper,[25] the blue shift in the fluorescence spectra is probably due to the formation of H-aggregates, characterized by a more or less parallel arrangement of the polymer chains. Recently, sharp blue-shifted aggregate

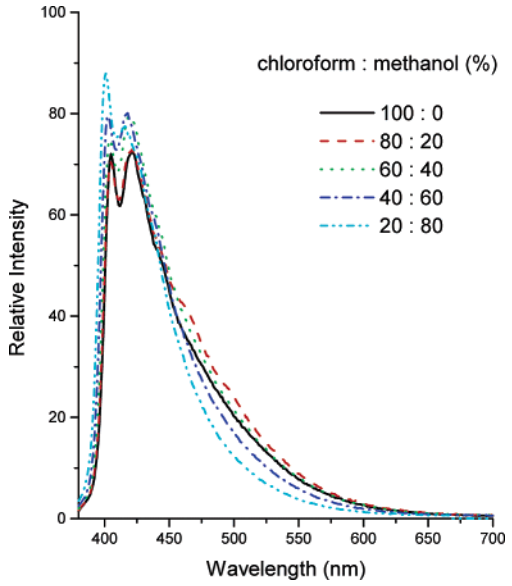

Figure 7. Fluorescence spectra of POCE in mixed chloroform/methanol solvents (v/v) with varying solvent composition as noted in the legend.

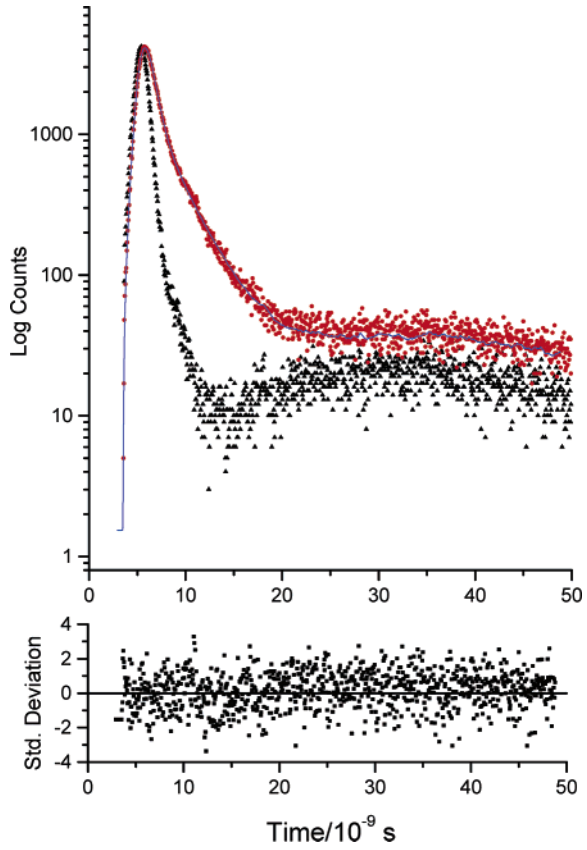

Figure 8. Fluorescence decay profile and the residuals of POC in mixed chloroform/methanol solvents (v/v, MeOH = 80%) for the sum of two exponentials: lamp profile (up triangle), fluorescence decay profile (circle), and fitted curve (solid).

bands have been found for wire-type dendrimers in good/poor solvent mixtures, which has been ascribed to parallel interchain interactions.[44] The formation of H-aggregates in the carbazole-based polymers has been correlated to their respective theoretical rotational barriers between neighboring rings in the polymer chains.[25] Indeed, it has been found that the barrier to rotation between carbazole and thiophene rings is lower than that between two carbazole units. Thus, the planarization of POCT should be more favored than that of POC, giving rise to stronger parallel interchain interactions (H-aggregates). Figure 5 also shows that the formation of H-aggregates is accompanied by a strong deactivation of the fluorescence ($\phi_{0\%}/\phi_{80\%} = 11.7$ at $\lambda = 466$ nm). Recently, a large decrease of the fluorescence efficiency has been observed for a polystyrene−oligo(*p*-phenyleneethynylene)−polystyrene triblock copolymer in 1,1,2,2-tetrachloroethane/methanol mixtures, which has been interpreted in terms of H-aggregates formation.[45]

The replacement of the octyl chains by 2-ethylhexyl fragments (PEHCT) did not affect the blue shift experienced by POCT. Thus, it seems that the 2-ethylhexyl chain is not bulky enough to prevent the conjugated backbone of this copolymer from forming parallel interchain π-stacked aggregates. Moreover, a red fluorescence tail is revealed for PEHCT as the content of methanol is increased (see Figure 6). This suggests that some amount of J-aggregates are formed in PEHCT solutions rich in methanol. This goes along with the experimental fact that the fluorescence of PEHCT is more deactivated ($\phi_{0\%}/\phi_{80\%} = 27$ at $\lambda = 466$ nm) than that of POCT, where no J-aggregates were detected.

Finally, the fluorescence spectra of POCE in $CHCl_3$/MeOH mixtures are shown in Figure 7. It can be seen that the spectra are slightly blue-shifted (~4 nm) on going from 80% methanol content to its 0% value, without the emergence of any new aggregated band in the red region. This behavior suggests that some H-aggregates could be formed as the methanol content is increased. But in contrast to the other carbazole-based polymers, the fluorescence intensity slightly increases upon the addition of the nonsolvent. Thus, one must conclude that the intermolecular interactions are not strong enough to induce an effective quenching of the photoluminescence efficiency of this polymer.

Time-Resolved Fluorescence Solvatochromic Properties. The fluorescence decay profiles of the polycarbazoles have been measured in chloroform/methanol mixtures. The fluorescence decay parameters, as well as the quality of the fits described by χ^2 values, are reported in Table 3.

It is observed that the fluorescence decay profile of POC in 100% chloroform can be expressed as a single-exponential fit with a very good χ^2 value. But, as the methanol content is increased, the quality of the fit becomes very poor (see Table 3). Fluorescence decays measured in chloroform/methanol mixtures needed two components in order to obtain acceptable fits to the data ($\chi^2 < 1.3$). The decays were dominated by a short component (0.48−0.62 ns) followed by a longer component (1.7−3.3 ns) having a much smaller preexponential factor (B_2). Moreover, it can be seen in Table 3 that B_1 diminishes whereas B_2 gradually increases when the concentration of methanol is increased. This goes along with steady-state measurements described above, showing the emergence of a new emissive species in the red region as the methanol concentration increases. We believe that the long lifetime component can be associated with the formation of J-aggregates. A similar behavior has been observed recently from time-resolved luminescence of an alternating copolymer of fluorene and dialkoxyphenylene in solution.[33] It is worth pointing out that both lifetimes increase as the solutions become richer in methanol content (see Table 3). This could be

related to the polarity of the environment, which increases with the amount of methanol present in the solutions.

In sharp contrast to POC, all the fluorescence decays of PEHC can be fitted to single exponentials (see Table 3). Thus, one can conclude that no significant amount of J-aggregates is formed when the poor solvent content is increased, as shown above from steady-state fluorescence measurements. This further confirms that the longer lifetime found for POC in $CHCl_3$/MeOH mixtures could be associated with J-aggregates.

Similarly to PEHC, no long lifetime component is detected from the fluorescence decay profiles of POCT in various ratios of chloroform/methanol. These results are in agreement with the steady-state measurements reported above, showing that POCT does not give rise to significant J-aggregation. But, as mentioned before, the fluorescence of POCT is efficiently quenched, as the solvent quality is decreased due to the formation of H-aggregates. Thus, it seems that the formation of H-aggregates does not lead to any new lifetime component within our instrument limit detection ($\tau_F \geq 200$ ps). A similar trend was observed for the fluorescence decay profiles of PEHCT in methalonic solutions, suggesting that the presence of branched alkyl chains on nitrogen atoms does not much influence the interactions between the polymer chains of these copolymers.

Finally, as discussed above, the fluorescence decay profile of POCE in 100% chloroform is characterized by a sum of two exponentials, which strongly suggests the presence of aggregates for this polymer even in the good solvent. But Table 3 shows that the addition of methanol does not much affect the decay parameters of POCE. These results suggest that the presence of methanol does not significantly modify the molecular arrangement of the polymeric chains for POCE. This goes along with the steady-state measurements reported above, showing that the fluorescence of POCE is not quenched in the presence of methanol. This is in sharp contrast with previous results reported for *N*-alkyl-poly(3,6-carbazolyleethynylene)s where a significant blue shift and quenching of their solution fluorescence are observed upon addition of methanol to their chloroform solution.[46] These results clearly show that subtle changes into the polymer geometry and conformational structures may lead to significant modifications of their optical properties.

Conclusions

On going from the corresponding triad to the polymer, the absorption and fluorescence spectra exhibit red shifts, which are due to an increase of the effective conjugation length. The nature of the alkyl chains on the nitrogen atom does not affect the spectral positions of the polymers. All the polycarbazoles show intense photoluminescence efficiencies. The variation of these values are mainly governed by radiative processes (k_F), which are higher for the homopolymers.

Steady-state and time-resolved fluorescence measurements in chloroform/methanol mixtures show solvatochromic changes, which have been interpreted in terms of H- or J-aggregates. It is found that the poor solvent-induced aggregation process of POC involves J-aggregates formation, whereas POCT is associated with H-aggregates when the quality of the solvent diminishes. The formation of these aggregates is accompanied by an effective deactivation of the fluorescence. Moreover, the nature of the alkyl chains on the nitrogen atom significantly affects the emissive properties of the polycarbazoles. Finally, POCE shows aggregates formation even in 100% chloroform solution, but the intermolecular interactions are not strong enough to induce a quenching of the photoluminescence efficiency.

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