

# Spectral and Photophysical Properties of Fluorene-Based Polyesters in Solution and in the Solid State

Soujanya Tirapattur,<sup>†,‡</sup> Michel Belletête,<sup>†</sup> Nicolas Drolet,<sup>‡,§</sup> Mario Leclerc,<sup>‡</sup> and Gilles Durocher<sup>\*,†</sup>

Laboratoire de photophysique moléculaire, Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-Ville, Montréal, Québec H3C 3J7, Canada; Chaire de recherche du Canada en polymères photoactifs et électroactifs, Centre de recherche en sciences et ingénierie des macromolécules (CERSIM), Département de chimie, Université Laval, Cité Universitaire, Québec G1K 7P4, Canada; and Institute of Microstructural Sciences, National Research Council of Canada, M-50, Montreal Road, Ottawa, Ontario K1A 0R6, Canada

Received June 17, 2002

**ABSTRACT:** The optical and photophysical properties of fluorene-based polyesters in solution and in the solid state (thin films) are reported. The red-shifted emission bands observed in the photoluminescence spectra of the thin films are rationalized in terms of stronger  $\pi$ – $\pi$  intermolecular interactions due to the closeness of the molecules (molecular packing) in the solid state. This is further corroborated by time-resolved fluorescence decay measurements. However, these electronic interactions are not strong enough to induce excimer or aggregate formation. As such, the quenching excimer and/or aggregate deactivation channel found in many polymeric systems are less efficient in the present polyesters. As expected, the presence of ester linkages between adjacent oligomers causes an interruption of the electronic conjugation, thus limiting the fluorescence to the blue region. The fluorescence efficiencies of thin films, estimated from lifetime measurements of the polyesters in solution and in the solid state, are relatively high (10–25%). Hence, these materials are promising candidates in the fabrication of blue-emitting LED devices.

## Introduction

Conjugated oligomers and polymers have been investigated intensively in the past few decades because of their promising electrical and optical properties, making them applicable to electronic and photonic devices such as field-effect transistors and light-emitting diodes (LED).<sup>1–4</sup> Among these materials, polyfluorene derivatives present an interesting approach to blue-light-emitting polymers. These polymers show high luminescence efficiencies in solution, which are largely maintained in the polymer films. The facile functionalization at the C-9 position offers the prospect of controlling both the polymer solubility and the potential interchain interactions in films.<sup>5–18</sup> Major drawbacks of polyfluorenes, however, are that they could show excimer and/or aggregate formation in thin films or upon thermal annealing.<sup>11,19–22</sup> Continuing efforts have been made to suppress excimer formation and improve efficiency in polyfluorenes like copolymerization with anthracene,<sup>11</sup> end-capping with sterically hindered groups,<sup>20,21</sup> and by incorporating pendant or bulky dendron groups in the polymer backbone.<sup>23,24</sup>

The incorporation of fluorene derivatives in polyesters is another alternative route to inhibit the excimer or aggregate formation. Along these lines, we recently synthesized and studied the optical and photophysical properties of fluorene-based polyesters in dilute solution.<sup>25–27</sup> As previously found with similar conjugated/nonconjugated alternating copolymers,<sup>28–31</sup> these fluorene-based polyesters show optical properties very close to those of the isolated molecules. Moreover, the luminescence intensity of polyesters is found to be quite

intense in solution, thus encouraging us to carry out further studies on these promising materials in the solid state for LED applications.

This paper is organized into two sections. The first section deals with the study of the spectral properties of the fluorene-based polyesters in solution (cyclohexane) and the comparison with those in the solid state (thin films). The second section reports the time-resolved fluorescence decay analysis of the polyesters and the corresponding oligomers. From fluorescence decay lifetime measurements in both media, the luminescence efficiency of the polyesters in the solid state is estimated.

## Experimental Section

**Materials.** Cyclohexane was purchased from A & C American Chemicals Ltd. (spectrograde) and used as received. Prior to use, the solvent was checked for spurious emission in the region of interest and found to be satisfactory. The syntheses of the oligomers shown in Scheme 1 and polyesters shown in Scheme 2 are reported elsewhere.<sup>25–27</sup> DSC measurements revealed an amorphous morphology for these polyesters with glass transition around room temperature (between 15 and 50 °C).

**Instrumentation.** Absorption spectra were recorded on a Varian Cary 1 Bio UV/vis spectrometer, at room temperature, using 1 cm quartz cells and solute concentrations  $(1–3) \times 10^{-5}$  M. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrometer with a F2T11 special configuration. Each solution was excited near the absorption wavelength maximum using a 1 cm path length quartz cell. Solution concentrations used were  $(1–3) \times 10^{-6}$  M, giving absorbances always less than 0.1 to avoid any inner-filter effects.

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.<sup>32</sup> The instrument incorporates an all-metal coaxial hydrogen flashlamp. Reconvolution analysis was performed by fitting over all the fluorescence decay

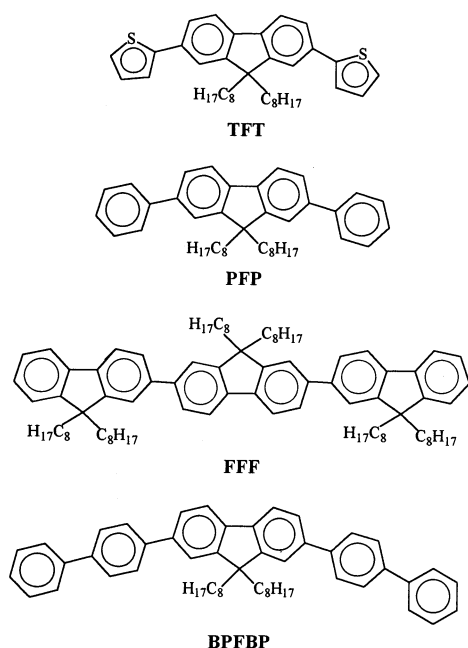
<sup>†</sup> Université de Montréal.

<sup>‡</sup> Université Laval.

<sup>§</sup> National Research Council of Canada.

\* To whom correspondence should be addressed.

Scheme 1



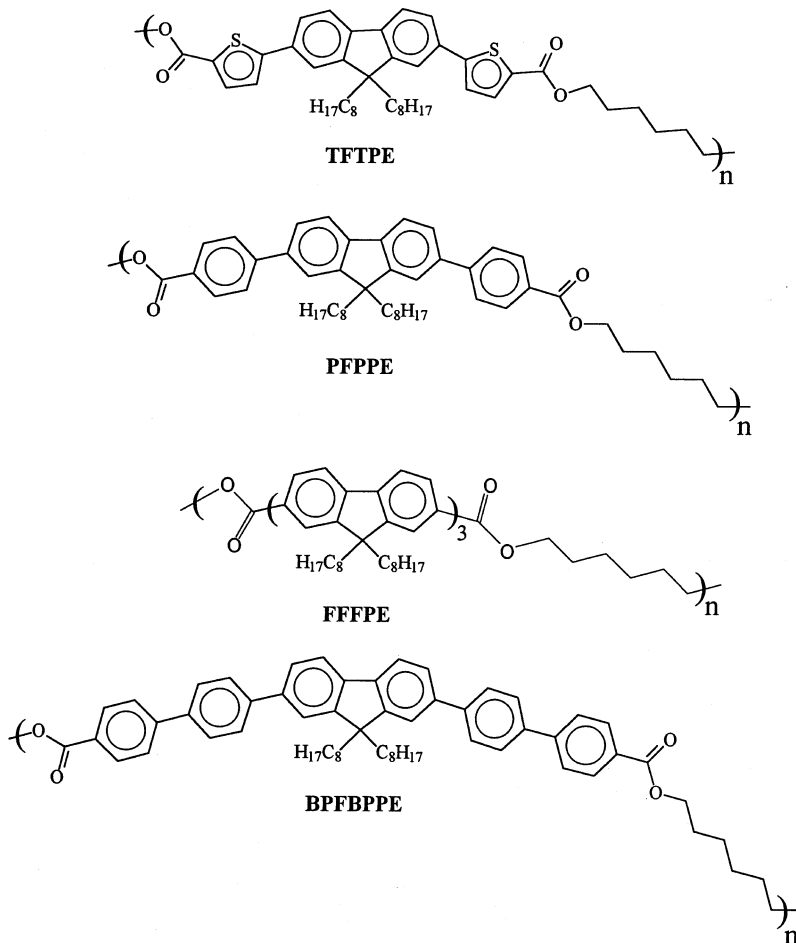
including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighed residuals, reduced  $\chi^2$  values, and Durbin–Watson (DW) parameters.

Thin films have been prepared by the spin-coating method using few drops of the oligomer or polymer dissolved in chloroform. The solutions have been spin-coated at 1500 rpm for 50 s. The solid sample holder has been used for steady state and time-resolved fluorescence spectroscopy of thin films.

## Results and Discussion

**Optical Properties.** The absorption and fluorescence spectra of PFPPE, TFTPE, FFFPE, and BPFBPPE, shown in Scheme 2, have been recorded in cyclohexane and in the solid state (thin films), at room temperature, and are shown in Figures 1–4, respectively. Their spectral data are reported in Table 1. For all the polyesters, the emission spectra, both in solution and in the solid phase, are found to be insensitive to the excitation energy. To minimize the solvent effects, the spectra of the polymers have been recorded in an apolar solvent (cyclohexane). It is found that the absorption and fluorescence spectra in cyclohexane are slightly blue-shifted compared to those reported previously in chloroform.<sup>26,27</sup> For all the polyesters, the first absorption band does not show any resolvable vibronic fine structure, suggesting that the molecules are relatively flexible in their electronic ground state. On the other hand, one can see in Table 1 that the first absorption band of phenylene–fluorene-based polyesters (PFPPE and BPFBPPE) is blue-shifted compared to that of thiophene–fluorene-based polyester (TFTPE). This can be explained by the fact that a five-membered aromatic ring (thiophene) creates less steric hindrance than a six-membered aromatic ring (phenylene).<sup>33</sup> Thus, more planar conformers are obtained for thiophene-based polyesters, giving a better electronic conjugation. Moreover, from our previous theoretical calculations performed on the corresponding oligomers (PFP, BPFBP, and TFT), it was found that the replacement of a phenyl group by a thiophene group slightly destabilizes the

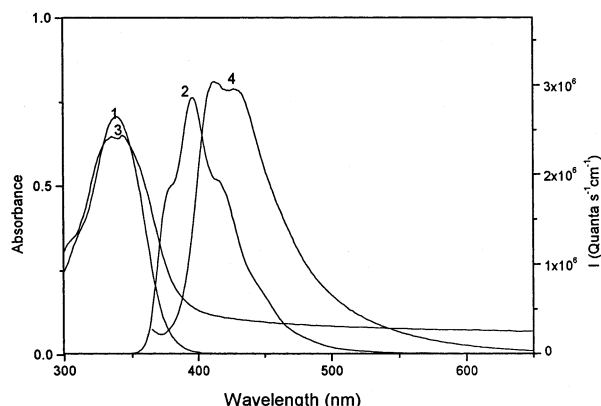
Scheme 2



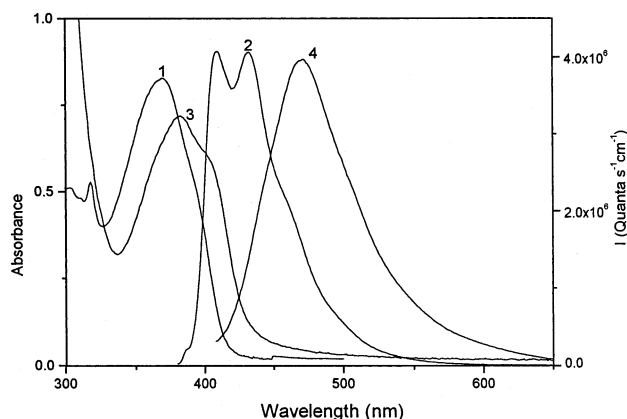
**Table 1. Absorption and Fluorescence Data of Polyesters in Cyclohexane and in Solid State at Room Temperature (298 K)**

molecules	cyclohexane			thin film		
	$\lambda_A^a$ (nm)	$\lambda_F^b$ (nm)	$\text{fwhm}_F^d$ ( $\text{cm}^{-1}$ )	$\lambda_A^a$ (nm)	$\lambda_F^b$ (nm)	$\text{fwhm}_F^d$ ( $\text{cm}^{-1}$ )
PFPPE	340	380	3600	343	413	3600
TFTPE	370	409	3500	383 <sup>c</sup>	471	3300
FFFPE	360	399	2600	364	413	3000
BPFBPPE	343	395	3300	344	416	4500

<sup>a</sup> Absorption wavelengths taken at the maximum of the absorption band. <sup>b</sup> Fluorescence wavelengths at the maximum of the first vibronic peak (0–0) band. <sup>c</sup> Fluorescence wavelength at the maximum of the emission band. <sup>d</sup> Full width at half-maximum (fwhm) of the fluorescence band.



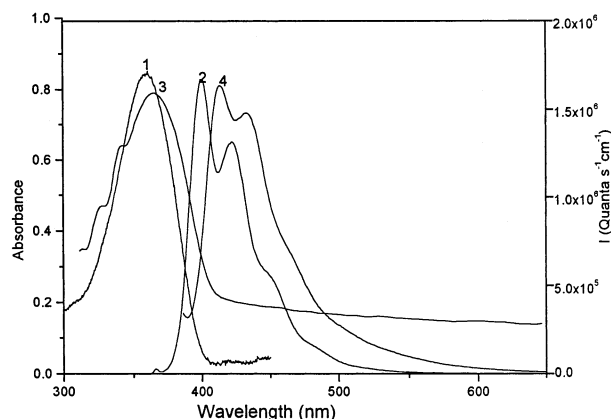
**Figure 1.** Absorption (1) and fluorescence spectra (2) of PFPPE in cyclohexane and absorption (3) and fluorescence spectra (4) in solid state at room temperature. The excitation wavelength was near the maximum of the absorption spectra. All intensities are arbitrarily chosen in order to fit optimally the graph.



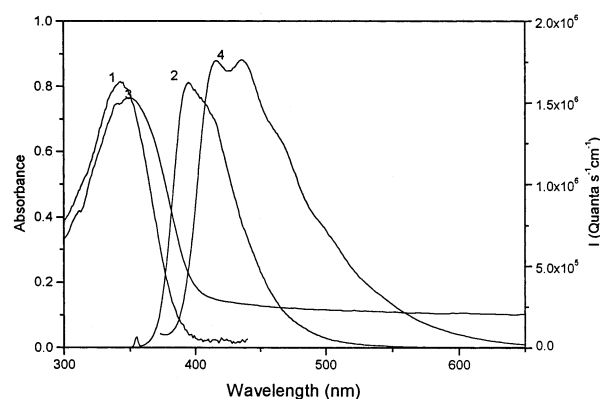
**Figure 2.** Absorption (1) and fluorescence spectra (2) of TFTPE in cyclohexane and absorption (3) and fluorescence spectra (4) in solid state at room temperature. The excitation wavelength was near the maximum of the absorption spectra. All intensities are arbitrarily chosen in order to fit optimally the graph.

HOMO orbital but significantly stabilizes the LUMO orbital, giving rise to a decrease in the HOMO–LUMO energy gap of TFT compared to that of PFP.<sup>33</sup> Consequently, a red-shifted absorption band is obtained for thiophene–fluorene-based polyesters. However, in the case of FFFPE, the locking of each biphenyl moiety by a C-9 carbon atom forces the polymer to become more planar, resulting in a much red-shifted absorption band for FFFPE compared to that of BPFBPPE.

In contrast to the absorption spectra, the fluorescence spectra of all the polyesters show a better vibronic resolution and are sharper. This strongly suggests that the molecules are more rigid in the first excited singlet state, resulting in a narrower distribution of conformers.



**Figure 3.** Absorption (1) and fluorescence spectra (2) of FFFPE in cyclohexane and absorption (3) and fluorescence spectra (4) in solid state at room temperature. The excitation wavelength was near the maximum of the absorption spectra. All intensities are arbitrarily chosen in order to fit optimally the graph.



**Figure 4.** Absorption (1) and fluorescence spectra (2) of BPFBPPE in cyclohexane and absorption (3) and fluorescence spectra (4) in solid state at room temperature. The excitation wavelength was near the maximum of the absorption spectra. All intensities are arbitrarily chosen in order to fit optimally the graph.

Moreover, the lack of mirror-image relationship as well as the large Stokes shifts observed between absorption and fluorescence spectra recorded in cyclohexane shows that the conformational changes that accompany the relaxation of the excited state are quite pronounced. This is further supported by recent CIS/6-31 G\* ab initio calculations performed on fluorene–thiophene and fluorene–phenylene dyads. According to these calculations, these molecules which are twisted in the ground state to about 45°<sup>33</sup> will attain more planar geometries (0–15°) in their first singlet excited state with shorter bond lengths between adjacent rings and higher rotational barriers against planarity.<sup>34</sup>

Except for TFTPE, the absorption band maxima of the polyesters in the solid state do not change much from those recorded in solution. The significant red shift (13 nm) observed for the absorption band of TFTPE in the solid state is well correlated with the theoretical ground-state potential energy surfaces of thiophene–fluorene (FT) and phenylene–fluorene (FP) dyads.<sup>35</sup> Indeed, both molecules are twisted in their ground state, but the rotational energy barrier against planarity is much less for FT (1.2 kcal/mol) than for FP (3.8 kcal/mol). Therefore, a low barrier of rotation for FT would make the molecule more flexible, at room temperature, and should favor a more planar conformation in the solid state, due to packing effects. On the other hand, a higher rotational energy barrier for FP would hinder the rotation between fluorene and phenyl moieties such that the molecules should remain twisted in the thin films. The same behavior should be observed in the corresponding polyesters.

In general, the fluorescence spectra of the polyesters in the solid state remain structured but are significantly red-shifted compared to those recorded in solution. This gives rise to important Stokes shifts between absorption and fluorescence spectra of the polyesters in thin films (50–80 nm, see Table 1). Going from solution to solid state, a similar behavior (large red shifts accompanied by a decrease in fluorescence quantum yields) has been observed recently for the fluorescence spectra of alternating copolymers between 9,9-bis(2'-ethylhexyl)fluorene and thiophene-based moieties.<sup>36</sup> The authors have explained their results in terms of a planarization of the polymer backbone due to the packing effects present in the solid state. We do not believe that the significant red shifts observed in the fluorescence spectra of the thin films investigated in this paper can be explained by similar conformational changes due to packing effects. Indeed, CIS/6-31 G\* *ab initio* calculations performed on the isolated dyads (FP and FT) clearly show that these molecules, which are twisted in their ground state, become nearly planar in their first excited singlet state.<sup>34</sup> Thus, a close packing of the molecules, in the solid state, should not significantly modify the structure of the polyesters in their first singlet excited state, ruling out any important shifts in the fluorescence wavelengths due to conformational changes triggered by packing effects. Moreover, recent work on poly(phenyleneethylenes) by Garcia-Garibay et al. shows that the planarization gives rise to relatively modest shifts (20–30 nm) while retaining high quantum yields.<sup>37</sup> For many polyfluorenes, a close packing of the molecules in the thin films leads to very strong intermolecular interactions giving rise to broad excimer and/or aggregate bands in the range 500–750 nm in the fluorescence spectrum of these polymers.<sup>6,11,19–22</sup> No indication of such distinct bands at longer wavelengths has been observed in the fluorescence spectra of the polyesters investigated. Moreover, one can see in Table 1 that the fluorescence bands of the polyesters in solution and in the solid state possess similar bandwidths, suggesting that the intermolecular interactions are relatively weak in the solid state. This behavior is due to the presence of the alkyl chains in the 9-position of the fluorene rings, which prevent a close packing of the molecules.<sup>38</sup> However, species found as a result of distinct intermolecular  $\pi$ – $\pi^*$  interactions and having weak emissions not spectrally resolved from the main fluorescence band could be present for the polyesters in the solid state. If

this is the case, a markedly different molecular dynamics should be observed for the polyesters in the solution and in the solid state. As reported recently on fluorene-based copolymers by Zhu et al.,<sup>24</sup> though small red shifts in fluorescence spectra indicated the absence of aggregates, the reported bandwidths of fluorescence spectra are broader than those in the solution. Therefore, in the absence of quantum yield values in the solid state for their systems, there is speculation for existence of quenching (radiative or nonradiative) channels in these systems. Though several time-resolved fluorescence studies have been reported for many polyenes,<sup>39–43</sup> we did not find similar studies on fluorene-based polymers, except for a very recent publication on fluorene-based copolymer.<sup>43</sup> We have therefore measured the fluorescence decay profiles of all the polyesters in cyclohexane and as thin films.

**Fluorescence Decay Analysis.** The fluorescence decay parameters of the polyesters in cyclohexane and as thin films are reported in Table 2. To account for the possible effects of the incorporation of oligomers in the polymeric chain on the excited dynamics, we also measured the fluorescence decay profiles of the corresponding oligomers in both media, and the corresponding decay parameters are also included in Table 2. The fluorescence decay profiles and the corresponding residuals of the fits for a sum of two and three exponentials for TFTPE in the solid state (thin film) are shown in Figure 5 as an example. For all fluorescence decay profiles measured in solution (oligomers and polyesters), single-exponential fits give acceptable statistics ( $\chi^2 < 1.2$  and DW  $\approx 1.7$ ) with relatively short fluorescence lifetimes ( $\tau_F \approx 1$  ns). On the other hand, in the solid state, the fluorescence decay profiles of oligomers and the corresponding polyesters are best described by a sum of three exponentials. We did not observe any significant excitation and/or emission wavelength dependence on the fluorescence decay parameters. For all the cases, two dominant lifetime components are very short, but a third component possessing a much longer lifetime ( $\tau_F > 7$  ns) is also detected. Even if the long lifetime component has a very small preexponential factor, it is genuine in view of the significant improvement in  $\chi^2$  values going from biexponential to triexponential fits (see Figure 5). The emitting species associated with the long lifetime component should be weakly coupled to the ground state and probably involve a  $\pi$ – $\pi$  stacking of the molecules in the thin films. Similar results have been reported for several polymers (thin films).<sup>39–43</sup> Particularly, very long lifetime components have been detected from fluorescence decay curves of polythiophenes in their solid state, which are interpreted in terms of interchain aggregates.<sup>42d</sup> We believe that the existence of multicomponents in the fluorescence decay profiles of fluorene derivatives (oligomers and polymers) in the solid state is caused by several distinct intermolecular  $\pi$ – $\pi^*$  interactions. However, these interactions are not strong enough to provoke the appearance of distinct fluorescence bands or even increasing the bandwidths of the emission bands recorded in solution.

On the other hand, a similar multicomponent relaxation dynamics is observed for the oligomers and polyesters in the solid state. This shows that the  $\pi$ – $\pi$  stacking of the molecules in the thin films is not greatly affected by the incorporation of the oligomers in the polyesters. In other words, as observed from spectro-



**Table 2. Summary of the Fluorescence Decay Parameters and the Fluorescence Quantum Yields of Polyesters and the Corresponding Oligomers in the Solution and Thin Films at Room Temperature**

name	$\lambda_{\text{exc}}^a$ (nm)	$\lambda_{\text{em}}^b$ (nm)	fit	$\tau_1^c$ (ns)	$B_1^d$	$\tau_2^c$ (ns)	$B_2^d$	$\tau_3^c$ (ns)	$B_3^d$	$\chi^2$	$\phi_F$ (soln)	$\phi_F$ (solid)
TFT												
solvent	350	390	F1	0.96						1.02	0.75	0.14
thin film	350	420	F2	0.23	0.987	1.92	0.013			2.08		
			F3	0.16	0.975	0.84	0.025	48	$4 \times 10^{-5}$	1.11		
TFTPE												
solvent	380	420	F1	0.80						0.99	0.46	0.23
thin film	380	475	F2	0.25	0.963	0.95	0.037			1.31		
			F3	0.35	0.950	1.25	0.049	13.5	$8.2 \times 10^{-4}$	1.10		
PFP												
solvent	330	360	F1	0.88						1.10	0.64	0.42
thin film	330	415	F2	0.43	0.658	0.92	0.342			1.55		
			F3	0.30	0.508	0.84	0.491	90	$1.8 \times 10^{-4}$	1.03		
PFPPE												
solvent	330	390	F1	0.86						1.12	0.62	0.24
thin film	350	420	F2	0.14	0.997	1.58	0.003			1.50		
			F3	0.23	0.936	1.34	0.059	7	$5.1 \times 10^{-3}$	1.19		
BPFBP												
solvent	350	380	F1	0.72						0.99	0.65	0.27
thin film	350	440	F2	0.27	0.874	0.60	0.127			1.09		
			F3	0.23	0.777	0.51	0.223	14.4	$7.3 \times 10^{-5}$	1.01		
BPFBPPE												
solvent	350	400	F1	0.74						1.20	0.57	0.15
thin film	350	420	F2	0.19	0.999	29	0.001			1.40		
			F3	0.17	0.891	0.36	0.108	19	$2.9 \times 10^{-4}$	1.16		
FFF												
solvent	350	400	F1	0.74						1.10	0.88	0.28
thin film	350	420	F2	0.25	0.23	0.14	$4.9 \times 10^{-3}$			1.86		
			F3	0.21	0.958	0.83	0.0418	24	$1.1 \times 10^{-4}$	1.26		
FFFPE												
solvent	350	410	F1	0.70						1.13	0.76	0.10
thin film	350	420	F2	0.18	0.999	39	0.001			3.2		
			F3	0.07	0.997	0.73	0.003	57	$1.95 \times 10^{-5}$	1.42		

<sup>a</sup> Excitation wavelengths used. <sup>b</sup> Monitored emission wavelengths. <sup>c</sup>  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  denote the fluorescence lifetimes associated with the two or three exponentials obtained from the reconvolution fits. <sup>d</sup>  $B_1$ ,  $B_2$ , and  $B_3$  denote the relative preexponential factors of each exponential (normalized so that they sum to 1).

scopic measurements, each oligomer is well isolated in the polymer chain. It is worth pointing out here that the fluorescence decay profiles of the oligomers measured at 77 K in isopentane do not show a multicomponent behavior.<sup>38</sup> This clearly indicates that intermolecular interactions are much stronger in thin films than at low temperatures.

Quantum yields of fluorescence of organic conjugated systems are relatively straightforward to measure for dilute solutions, but not in thin solid films. Indeed, many corrections have to be made to allow for the level of absorption, the self-absorption of the emission, and the total internal reflection of the emission due to high refractive indices in the thin films. However, assuming that radiative decay constants ( $k_F$ ) are similar in solution and in the solid state, luminescence efficiencies in the solid state can be estimated from time-resolved fluorescence measurements obtained in both media.<sup>39b</sup> We consider this assumption approximately valid since the electronic structure of the fluorene derivatives seems to be similar in solution and in the solid state, as shown by the similarity of their absorption spectra. The main difference between the molecules in solution and the solid film is that there is significant intermolecular interactions between neighboring molecules in the film, and although this is important for transport properties, it has only a small effect on the electronic structure; hence, we expect it to have only a small effect on the radiative decay rate constant. In this situation, changes in the decay rate arise from the effectiveness of the competing nonradiative decay channels.

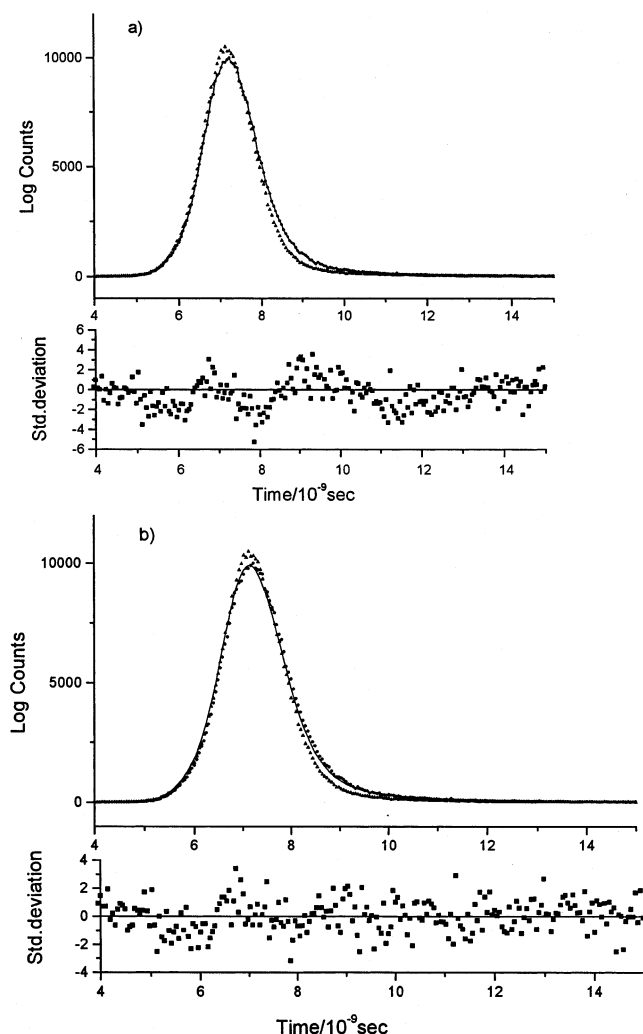
Thus, we can estimate the quantum yield of all the thin films of polyesters and their corresponding oligomers from the fluorescence quantum yields in solution and lifetime measurements in solution and in the solid state. The quantum efficiency for fluorescence ( $\phi_F$ ) can be related to the measured lifetime of the fluorescence ( $\tau_F$ ) by

$$\phi_F = k_F \tau_F$$

Assuming that, going from the solution to the solid state,  $k_F$  remains constant, the fluorescence quantum efficiency of the thin films can be obtained by the relation

$$\phi_{F(\text{film})} = \phi_{F(\text{soln})} (B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3)_{(\text{film})} / \tau_{F(\text{soln})}$$

Though this method is less accurate than the technique involving the use of an integrated sphere to detect the total fluorescence intensity,<sup>44</sup> we believe that the fluorescence quantum yields obtained are good enough to be compared with those measured in solution. It is worth mentioning here that some authors also use a standard (9,10-diphenylanthracene) dispersed in PMMA film for the determination of quantum yields in the solid state.<sup>45,46</sup> But to our opinion, this procedure is inappropriate due to big discrepancies that should occur for the reflection, transmission, and refractive indices of the standard and the thin film. Fluorescence quantum yields of the polyesters measured in solution and calculated for the thin films are reported in Table 2. One



**Figure 5.** Fluorescence decay profiles and the residuals of TFTPE in solid state (thin film) at room temperature for the sum of two exponentials (a) and for the sum of three exponentials (b). Lamp profile (up triangle), fluorescence decay profile (circle), and fitted curve (solid).

can see that intermolecular interactions cause a significant fluorescence quenching for the polyesters in the solid state. However, the luminescence efficiency of the thin films remains high enough to be used in LED applications. Indeed, other systems having similar fluorescence efficiencies (20–30%) have been used for LED devices.<sup>47,48</sup>

We can now have a better picture of the spectroscopy and photophysics of the fluorene-based polyesters in the solid state. Going from the solution to the solid state, the observed red shifts in the fluorescence spectra are not caused by conformational changes due to packing effects. Indeed, for the isolated molecules, CIS/6-31 G\* ab initio calculations predict that these systems are very close to the planarity in the first singlet excited state. Therefore, significant  $\pi$ – $\pi$  intermolecular interactions should be responsible for the optical properties in the solid state. These interactions are indeed detected from fluorescence time-resolved measurements, which clearly show a multicomponent lifetime distribution for the thin films. This causes an overall quenching of the luminescence intensity, but the fluorescence efficiency remains relatively high. However, these interactions are not strong enough to induce an increase in the fluorescence bandwidths or to provoke the appearance of distinct

emission bands (excimer or/and aggregate formation). The presence of the alkyl chains in the 9-position of the fluorene rings is responsible for this behavior, avoiding a close packing of the molecules.

It is worth pointing out that the absorption and fluorescence spectra of fluorene-based polyesters are much blue-shifted compared to those of the corresponding alternating copolymers.<sup>22</sup> Indeed, the presence of ester linkages between oligomer moieties causes an interruption of the electronic conjugation limiting the luminescence to the blue region. Similar observations have been found from copolymers containing conjugated and aliphatic nonconjugated blocks.<sup>28–31</sup> Moreover, it is well-known that polyfluorenes have a great tendency to form excimers in the solid state, causing the appearance of red-edge emission bands and an overall quenching of the luminescence. This is a major drawback for making efficient blue LED devices based on polyfluorenes. On the other hand, the thin films of fluorene-based polyesters do not show any low-energy fluorescence bands while their luminescence efficiencies are relatively high. These optical properties make them excellent candidates to be used in the fabrication of blue LED devices. Preliminary measurements on polymeric light-emitting diodes show promising results,<sup>49</sup> and more efficient electrooptical devices will be designed and tested in the near future.

### Concluding Remarks

On going from the solution to the solid state, the absorption spectra of fluorene-based polyesters are not much affected whereas their fluorescence spectra exhibit important red shifts. This behavior is not caused by important conformational changes but involves significant  $\pi$ – $\pi^*$  intermolecular interactions, which are stronger in the excited state. Time-resolved fluorescence measurements of the polyesters, which show single-exponential fluorescence decay profiles in solution but a sum of exponentials in the solid state, further substantiate this. However, these intermolecular interactions are not strong enough to induce the appearance of red-edge emission bands. The luminescence efficiencies of the thin films of the polymers, estimated from lifetime measurements in the solution and in the solid state, are smaller than those measured in solution but remain relatively high. This is due to the presence of alkyl chains in the 9-position of the fluorene rings, which prevents strong packing effects in the solid state. Hence, we consider these materials as good candidates for the fabrication of blue LED devices.

**Acknowledgment.** This work was supported by strategic and research grants from NSERC. The authors thank S. Beaupré and J. F. Morin for the syntheses of the polyesters and related oligomers.

### References and Notes

- (1) *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundstrom, I., Rånby, B., Eds.; Oxford University Press: Oxford, 1993; pp 65–169.
- (2) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradely, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.
- (3) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature (London)* **1998**, *10*, 365.
- (4) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature (London)* **1997**, *388*, 845.

- (5) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.
- (6) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
- (7) Yang, Y.; Pei, Q. *J. Appl. Phys.* **1997**, *81*, 3294.
- (8) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
- (9) Yoshida, K.; Fujii, A.; Ohmori, Y.; Yoshino, K. *Appl. Phys. Lett.* **1996**, *69*, 734.
- (10) Grell, M.; Long, X.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798.
- (11) Kreyenschmidt, M.; Klärner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099.
- (12) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867.
- (13) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Göbel, R. O.; Müllen, K.; Bassler, H. *Chem. Phys. Lett.* **1995**, *240*, 373.
- (14) Grüner, J.; Wittmann, H. F.; Hamer, P. J.; Friend, R. H.; Huber, J.; Scherf, U.; Müllen, K.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1994**, *67*, 181.
- (15) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.
- (16) Bliznyuk, M.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.
- (17) Klärner, G.; Lee, J. I.; Lee, V. Y.; Chan, E.; Chen, J. P.; Nelson, A.; Markiewicz, D.; Siemen, S. R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.
- (18) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature (London)* **1992**, *356*, 47.
- (19) Lee, J. I.; Hwang, D.-H.; Park, H.; Do, M. L.; Chu, H. Y.; Zyung, T.; Miller, R. D. *Synth. Met.* **2000**, *111–112*, 195.
- (20) Klärner, G.; Davey, M. H.; Chen, W. D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1988**, *10*, 993.
- (21) Lee, J.-I.; Klärner, G.; Chen, J. P.; Scott, J. C.; Miller, R. D. *SPIE. Int. Soc. Opt. Eng.* **1999**, *3623*, 2.
- (22) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2000**, *12*, 1931.
- (23) Geng, Y.; Katsis, D.; Culligan, S. W.; Ou, J. J.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 463.
- (24) Zhan, X.; Liu, Y.; Xia, W.; Wang, S.; Zhu, D. *Macromolecules* **2002**, *35*, 2529.
- (25) Belletête, M.; Morin, J. F.; Beaupré, S.; Leclerc, M.; Durocher, G. *Synth. Met.* **2002**, *126*, 43.
- (26) Belletête, M.; Ranger, M.; Beaupré, S.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **2000**, *316*, 101.
- (27) Belletête, M.; Morin, J. F.; M.; Beaupré, S.; Ranger, M.; Leclerc, M.; Durocher, G. *Macromolecules* **2001**, *34*, 2288.
- (28) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.
- (29) Hu, B.; Karasz, F. E. *Synth. Met.* **1998**, *92*, 157.
- (30) Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114.
- (31) Zheng, M.; Sarker, A. M.; Gürel, E. E.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **2000**, *33*, 7426.
- (32) Zelent, B.; Ganguly, T.; Farmer, L.; Gravel, D.; Durocher, G. *J. Photochem. Photobiol.* **1991**, *56*, 165.
- (33) Belletête, M. M.; Beaupré, S.; Bouchard, J.; Blondin, P.; Leclerc, M.; Durocher, G. *J. Phys. Chem. B* **2000**, *104*, 9118.
- (34) Soujanya, T.; Belletête, M.; Leclerc, M.; Durocher, G. Manuscript in preparation.
- (35) Blondin, P.; Bouchard, J.; Beaupré, S.; Belletête, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2000**, *33*, 5874.
- (36) Charas, A.; Morgado, J.; Martinno, J. M. G.; Alcácer, L.; Cacialli, F. *Synth. Met.* **2002**, *127*, 251.
- (37) Levitus, M.; Schmieder, K.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259.
- (38) Soujanya, T.; Belletête, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem. B* **2002**, *106*, 8959.
- (39) (a) Schennig, A. P. H.; Tsipis, A. C.; Meskers, S. C. J.; Beljonne, D.; Meijer, E. W.; Brédas, J. L. *Chem. Mater.* **2002**, *14*, 1362. (b) Samuel, I. D. W.; Crystall, B.; Rumbles, G.; Burn, P. L.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1993**, *213*, 472.
- (40) Theander, M.; Anderson, M. R.; Inganäs, O. *Synth. Met.* **1999**, *101*, 331.
- (41) Bongiovanni, G.; Botta, C.; Di Silvestro, G.; Mura, A.; Tubino, R. *Phys. Lett.* **1995**, *208*, 165.
- (42) (a) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (b) Oelkrug, D.; Egelhaaf, H.-J.; Gierschner, J.; Tompert, A. *Synth. Met.* **1996**, *76*, 249. (c) Sun, R. G.; Wang, Y. Z.; Wang, D. K.; Zheng, Q. B.; Kylo, E. M.; Gustafson, T. L.; Wang, F.; Epstein, A. J. *Synth. Met.* **2000**, *111–112*, 595. (d) Ruseckas, A.; Namas, E. B.; Theander, M.; Svensson, M.; Yartsev, A.; Zigmantas, D.; Andersson, M. R.; Inganäs, O.; Sundström, V. *J. Photochem. Photobiol. A: Chem.* **2001**, *144*, 3. (e) Jenekhe, S. A.; Lu, L.; Alam, M. *Macromolecules* **2001**, *34*, 7315.
- (43) Pålsson, L.-O.; Wang, C.; Russell, D. L.; Monkman, A. P.; Bryce, M. R.; Rumbles, G.; Samuel, D. W. *Chem. Phys.* **2002**, *279*, 229.
- (44) De Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.
- (45) Ahn, T.; Song, S.-Y.; Shim, H. K. *Macromolecules* **2000**, *33*, 6764.
- (46) Liu, B.; Yu, W.-L.; Lai, Y. H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984.
- (47) Pei, J.; Yu, W.-L.; Huang, W.; Heeger, A. J. *Macromolecules* **2000**, *33*, 2462.
- (48) (a) Barbarella, G.; Fararetto, L.; Sotgiu, G.; Antolini, L.; Gigli, G.; Cingolani, R.; Bongini, A. *Chem. Mater.* **2001**, *13*, 4112. (b) Yu, W. L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837. (c) Pei, J.; Yu, W. L.; Huang, W.; Heeger, A. J. *Chem. Commun.* **2000**, 1631. (d) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.
- (49) Beaupré, S.; Leclerc, M.; Lévesque, I.; D'Iorio, M. *Mater. Res. Soc. Symp. Proc.* **2001**, *665*, C5.34.1.

MA0209444