Steady state and time-resolved photoluminescence properties of alternating polyfluorene copolymers

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Abstract

We present the photoluminescence properties of two alternating copolymers combining 9,9-di(2’-ethylhexyl)fluorene with a phenylene or a thiophene comonomer, in cyclohexane solution. Their picosecond time-resolved fluorescence decay is fitted to three exponential components. We associate the faster component to a relaxation of the exciton electronic energy and the two slower components to exciton decay at two distinct sites, which we tentatively identify as the central parts of the polymer chains and the chain ends, in view of the relatively short chain lengths.

Keywords: Photoluminescence; Time-resolved spectroscopy

1. Introduction

We have recently reported on the preparation and properties of a series of novel alternating copolymers, combining 9,9-di(2’-ethylhexyl)fluorene with various comonomers, such as thiophene and thiophene derivatives, phenylene and vinylene groups [1,2]. These were prepared by the Suzuki coupling reaction, combining the fluorene boron ester with the dibrominated comonomer. In this communication, we report on the steady state and picosecond time-resolved photoluminescence, PL, studies on PFP and PFT (Figure 1) in solution (cyclohexane).

![Structure of the copolymers](image)

**Fig. 1. Structure of the copolymers.**

2. Results and Discussion

Figure 2 shows the absorption and PL spectra of the two copolymers and of the fluorene homopolymer, PF, which was obtained with shorter chain length (degree of polymerization n=6, compared with 27 and 31 for PFP and PFT, respectively). Solution (cyclohexane) PL efficiencies, η PL,(relative error of about 10%) are 100% and 51% for PFP and PFT, respectively. For PF in chloroform, we obtained 64%. Fluorescence decay curves at several emission wavelengths, following excitation at 340 nm, were obtained by the time-correlated single photon timing technique. The PL decay (20000 counts at channel of maximum intensity) was fitted to a sum of three exponentials, I PL(t)=\(a_1e^{-t/\tau_1}\), by making a global analysis to the decays at the wavelengths indicated in Figure 2, with \(\chi^2<1.2\) (Table 1). The faster component, \(\tau_3\), has positive amplitude, \(a_3\), for the shorter wavelength reading, and is negative for the redder part of the emission spectrum. This component is associated to a spectral diffusion of the emission spectra, due to a reduction of the exciton electronic energy. Figure 3 shows the time-resolved PL spectrum of PFT, obtained from the fluorescence decay data at various wavelengths. The exact mechanism behind this spectral diffusion is not yet established. We note that a similar process has been identified in polymer films and attributed to a migration of excitons to lower energy sites [3] or local phenomena, such as intramolecular vibrational relaxation [4].

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which, according to NMR studies, we conclude to be bromine atoms, left after the synthesis.

The amplitudes of $\tau_1$ and $\tau_2$, $a_1$ and $a_2$, respectively, normalized to unity, vary from polymer to polymer. $a_1$ is about 0.36 for PF, 0.89 for PFP and 0.46 for PFT, when emission is detected at shorter wavelength. In going to longer wavelengths, we observe that $a_1$ is slightly reduced, which we take as an indication that the emissive site characterized by $\tau_1$ has slightly higher energy. The fact that we obtain the two lifetimes, means that there is a slower transfer process, compared to the decay rates, between the two sites, emphasized by the unidimensionality of the system.

On the basis of the expected heavy atom effect of the bromine end atoms, there shall be an increase of the intersystem crossing rate, if exciton decay occurs at chain ends. Furthermore, in view of the high PL efficiency value of PFP, the radiative decay rate, $k_r$, at the two decay sites should also be different. That is, according to equation 1, if we assume that $k_{11} = k_{22}$, we do not obtain reasonable values for $k_{m2}$, even if we take the lower limit of 0.9 for the PL efficiency of PFP, based on 10% error of $\eta_{PL}$.

$$\eta_{PL} = a_1 k_{11} \tau_1 + a_2 k_{22} \tau_2$$

(1)

Therefore, we cannot simply assign the shorter decay time to the chain ends emissive sites. On the contrary, based on the similarity with the decay time of 370 ps observed for poly(9,9-dioctylfluorene), PFO, with $n = 500$, in toluene solution[5], it appears as if the shorter lifetime, $\tau_1$, is in fact associated to the decay at the central parts of the polymer chains, away from chain ends, while the longer component, $\tau_2$, is associated to the decay of excitons at the chain ends. In this case, the higher lifetime of the excitons decaying at the chain ends, should be associated to a reduced $k_r$, to overcompensate for the anticipated higher $k_{m2}$, in case the bromine end atoms do significantly increase the intersystem crossing rate. According to equation 1, the reduction of $k_r$ at chain ends would also lead to a smaller contribution of the excitons decaying at the chain ends to the overall $\eta_{PL}$, which would be consistent with the high $\eta_{PL}$ of PFP. The sizeable contribution of the chain ends to the excited state dynamics of the polymers under study, is due to their relatively short chain lengths.

References