The effect of aggregates on the decay dynamics of a conjugated polymer studied by femtosecond time resolved spectroscopy

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Abstract. We study the excited state dynamics of a blue emitting conjugated polymer in isolated and aggregated chain environments in order to examine its potential applications in Light Emitting Diodes (LEDs) and solid state lasers. The study was realized using a femtosecond time resolved fluorescence spectroscopy which employs the upconversion technique. Polymeric samples where the chains are isolated show an identical excited state lifetime at all emission wavelengths meaning that well defined chromophores exist in the polymer chains. On the other hand, samples where both isolated and aggregated polymer chains exist, exhibit an increase of the excited state lifetime with the emission wavelength, which is attributed to aggregates. However, the emission properties of isolated chains are not affected by the presence of aggregates in the samples since no energy transfer among these two species occurs. This is due to the localization of the excitons in the conjugated segments of isolated chains and renders the polymer an important candidate for use in LEDs and lasers.

1. Introduction
Photonic-conjugated polymers combine the semiconducting properties of inorganic semiconductors with the mechanical properties of polymers constituting a very important class of materials with application in LEDs [1,2] and Lasers [3,4]. The understanding of the aggregates influence on the optical properties of a polymer and the knowledge of the chain packing within the nanoscale play an important role on the efficiency and longevity of a polymeric device [5-6]. Blue emission from a polymeric material is obtained by synthesizing partially conjugated polymers which contain alternating conjugated and non-conjugated segments. They exhibit easy control of the conjugation length and high quantum yield [7-9]. In this work, we study the excited state dynamics of a blue emitting partially conjugated photonic polymer as well as the role of the aggregates on this dynamics. The study was realized using a femtosecond time resolved fluorescence spectroscopy.

2. Experimental
The chemical structure of the polymer, P1, is shown in figure 1a. P1 contains conjugated segments related to the poly (phenylene vinylene) structure, interrupted by non-conjugated methylene moieties [9]. It emits blue light with a quantum efficiency equal to 0.9 and it has been thoroughly studied concerning its laser and spectroscopic properties [10,11].

The experimental set-up of the femtosecond spectroscopy has been described in details previously [12] and it is shown in figure 1b. Briefly, a mode-locked Ti:Sapphire laser, emitting pulses at 800 nm with 82 MHz repetition rate and 80 fs duration is used as the light source. The laser beam is frequency doubled.
and the second harmonic excites the polymeric sample, contained in a 1 mm thick quartz cuvette. The remaining fundamental laser beam after passing through an optical delay line is focused together with the fluorescence of the sample on a nonlinear BBO crystal where an upconversion UV beam is generated [13].

![Figure 1. a) The chemical structure of P1, b) The experimental set-up](image)

The upconversion beam is then detected by a photomultiplier connected with a photon counter. The fluorescence dynamics of P1 were measured in dilute solutions in tetrahydrofuran (THF) where the molecules are isolated as well as in concentrated THF solutions and in mixtures of THF and methanol (MeOH), which is a poor solvent for P1. In the latter cases the P1 chains form aggregates.

3. Results and discussion

The photoluminescence excitation and fluorescence spectra of P1 in dilute and concentrated THF solutions as well as in a mixture of MeOH-THF are shown in figure 2a. The concentrated P1 solution and the solution of P1 in MeOH-THF exhibit red-shifted spectra in comparison to the dilute solution indicating the formation of aggregates [6].

![Figure 2. a) The PL excitation and fluorescence spectra of P1 in dilute THF, concentrated THF and MeOH/THF solutions b) The fluorescence dynamics of P1 in dilute THF solutions at two wavelengths](image)

The fluorescence dynamics of P1 in dilute THF solutions (0.01 % wt) are shown in figure 2b at two wavelengths. The dynamics exhibit a single-exponential decay with no wavelength dependence. The decay time was found ~280 ps at all emission wavelengths, indicating the existence of a single emission
species namely the P1 chains contain specific and well-defined chromophores. This is attributed to the insertion of methylene groups in the main chains causing exciton localization within the conjugated segments.

The fluorescence dynamics of P1 in concentrated THF solutions are shown in figures 3a and 3b at representative wavelengths. In both cases the decay has single exponential behavior and is wavelength dependent showing an increased decay time at the long wavelength edge (red edge) of the spectrum. Especially, for concentration 0.5 % wt (figure 3a), the decay times at 450 and 500 nm are 285 and 350 ps respectively while for concentration 1 % wt (figure 3b), the decay times at 450, 470 and 500 nm are 275, 380 and 450 ps respectively. These results show that the decay at 450 nm (blue edge) is similar to that in dilute P1 solutions.

**Figure 3.** The fluorescence dynamics of P1 in (a) and (b) concentrated THF solutions and c) MeOH-THF mixture

The dynamics of P1 in MeOH-THF at three wavelengths are shown in figure 3c exhibiting a wavelength dependent decay. The decay time increases with the emission wavelength and is equal to 590 ps at 520 nm. However, at the blue edge of the spectrum (450 nm) the decay time is 280 ps as in dilute THF solutions.

The wavelength dependent dynamics in figures 3a,b,c indicate the existence of different emission species in the solutions. Particularly, the slower decay at the red edge of the spectrum is attributed to the aggregated chains formed because of the high concentration or the addition of the poor solvent. On the other hand, the almost unaffected decay time at the blue edge of the spectrum proves that the fluorescence in this spectral region is due to the isolated chains. The fact that the decay mechanism of isolated chains is not affected by the presence of aggregates means that no energy transfer from the isolated chains (higher band gap species) to the aggregated ones (lower band gap species) is observed. This is attributed to the insertion of non-conjugated segments in the main chain which hinder exciton diffusion to aggregates. This is why an aggregated solution of P1 in MeOH-THF exhibits amplified spontaneous emission originating from the isolated chains as we have shown in previous papers [10,11].

In figure 4a the fluorescence spectra of P1 in MeOH-THF are shown at different times after excitation. At short times, the blue spectral region (~450 nm), which is attributed to isolated chains, is dominant. However, the blue region decays faster than the red one causing a red shift and a broadening of the fluorescence spectra at long times. The peak wavelength and the linewidth of the spectra are shown in the inset of figure 4a as a function of time.

In figure 4b the spectra at 10 and 400 ps are shown in normalized units. The spectrum at 10 ps mainly originates from the isolated chains while the spectrum at 400 ps originates from both the isolated and aggregated chains. Therefore, by subtracting the two spectra we obtain the fluorescence spectrum of the aggregated chains, also shown in figure 4b, exhibiting a peak at 470 nm. The above analysis shows that
the total fluorescence of P1 in MeOH-THF is a superposition of the fluorescence of isolated and aggregated chains.

4. Conclusions
In conclusion, the study of the excited state dynamics of a partially conjugated blue emitting polymer has shown that it contains well defined chromophores in its main chains where the excitons are localized. This localization hinders energy transfer from isolated chains to aggregates. The above conclusion renders the polymer as an important candidate for use in LEDs and lasers in the blue spectral region.

Figure 4. a) The fluorescence spectra of P1 in MeOH-THF at different times. The inset shows the spectral peak and linewidth versus time. b) The spectrum of P1 in MeOH-THF at 10 and 400 ps in normalized units as well as the aggregates spectrum

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6. References
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