

Excited state dynamics of a partially conjugated polymer studied by femtosecond fluorescence upconversion spectroscopy

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Abstract

The decay dynamics of a partially conjugated polymer has been studied by femtosecond fluorescence upconversion spectroscopy. Dilute polymer solutions exhibit wavelength independent decay, indicating the existence of a well-defined chromophore in the polymer chains. Concentrated polymer solutions or solutions with poor and good solvent exhibit an increased decay time as the emission wavelength increases, attributed to aggregates. Energy transfer from isolated to aggregated chains is hindered and this is due to exciton localization. The transient fluorescence spectra of the polymer in poor–good solvent exhibit a red shift as well as a broadening, both attributed to the aggregates emission.

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1. Introduction

Photonic polymers combining the opto-electronic properties of inorganic semiconductors and the mechanical properties of polymers constitute important candidates for application in Light Emitting Diodes (LEDs) [1] and solid-state lasers [2,3]. Especially, blue emitting polymers are required for multicolor large area displays. An attractive approach for obtaining blue emission is the synthesis of partially conjugated polymers which contain alternating conjugated segments linked by non-conjugated aliphatic linkages [4,5]. These polymers exhibit easy control of the conjugation length and high quantum yield [6]. An issue that needs to be clarified before using a polymer in LEDs and lasers, is the role of aggregates on its optical properties especially on the excited state dynamics [7–12].

In a previous Letter, we studied the lasing properties of a partially conjugated polymer with phenylene vinylene related conjugated segments (shown in Fig. 1a) ex-

hibiting maximum gain at 450 nm [13]. We have also studied the role of aggregates on the amplified emission and we have determined the size distribution of aggregates [13,14]. Finally, a comparative study of this polymer with its model oligomer concerning their spectroscopic and lasing properties has been reported [15].

In the present Letter, we study the excited state dynamics of this blue emitting partially conjugated polymer in isolated and aggregated chain environments using femtosecond fluorescence upconversion spectroscopy. The dynamics of its model oligomer is also studied. The results show that the polymer exhibits a slower decay than the oligomer. Additionally, exciton localization (confinement) within the well defined chromophore segments of the isolated polymer chain occurs, hindering the energy transfer to aggregates.

2. Experimental

The chemical structures of the polymer P1 and oligomer O1 are shown in Fig. 1a. P1 contains phenylene

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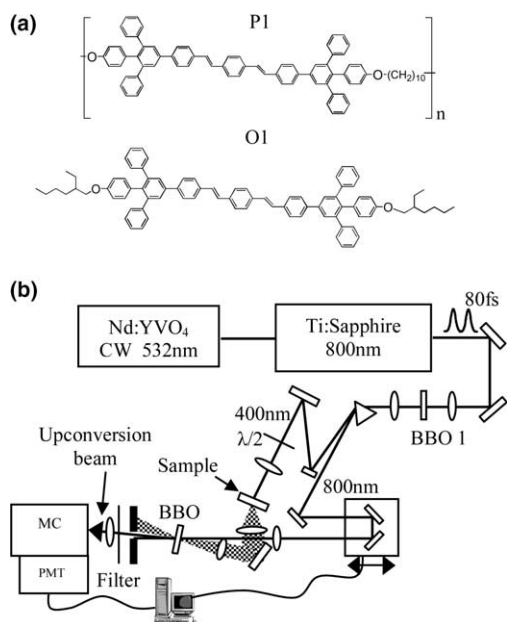


Fig. 1. (a) The chemical structures of O1 and P1. (b) The experimental set-up of the femtosecond upconversion spectroscopy.

vinylene related conjugated segments interrupted by methylene moieties. Its quantum yield is 0.9 while its molecular weight is 3600 [5]. O1 is a model compound for P1 exhibiting identical fluorescence spectrum with P1 with a quantum yield equal to 0.95 [15].

The samples under study were dilute solutions of P1 and O1 in tetrahydrofuran (THF) with isolated molecules. P1 was also studied in concentrated THF solutions and in mixtures of THF and methanol (MeOH), which is a poor solvent for P1. In both cases the P1 chains form aggregates.

The absorption spectra were taken with a Beckman DU-640 spectrometer while the photoluminescence excitation and the steady-state fluorescence spectra were taken using a Perkin Elmer LS55B luminescence spectrometer.

The experimental set-up of the femtosecond time resolved fluorescence upconversion spectroscopy [16–18] is shown in Fig. 1b. A mode-locked Ti:Sapphire laser (Tsunami, Spectra Physics) pumped by a frequency doubled Nd:YVO₄ continuous wave laser (Millennia V_s, Spectra Physics) was used as the light source. The laser emits pulses at 800 nm with 80 fs duration and 82 MHz repetition rate. The laser beam is focused onto a BBO crystal (1 mm thickness, Fujian Castech) generating a second harmonic beam at 400 nm (6 mW average power) which excites the polymeric sample. The remaining fundamental laser beam (gate beam), after passing through an optical delay line, (driven by a Newport ESP300 DC motor) is focused together with the fluorescence of the sample onto a second BBO crystal (1.5 mm thickness, Fujian Castech) generating an upconversion beam (type I phase matching). This upconversion beam

is separated from the fundamental and fluorescence beams by an iris and filters (UG-11 glass filters), and is directed into a 0.25 m monochromator (ORIEL 77200). Finally, it is detected by a photomultiplier (Becker-Hickel PMH-100-3) connected with a photon counter (Becker-Hickel PMS-400). For determining the temporal resolution of our system, upconversion signals (cross correlation signals) from the gate and the samples fluorescence were obtained. For achieving phase matching the polarization of the excitation pulse was rotated so that the gate and excitation pulses are vertically polarized. The full width at half maximum of these upconversion signals, corresponding to the temporal resolution of the system, is ~ 280 fs. The spectral resolution of our system is 2.5 nm. The dynamics of the molecules was detected for different wavelengths across the emission spectrum under magic angle conditions.

3. Results and discussion

The absorption, photoluminescence excitation and fluorescence spectra of P1 in dilute and in concentrated THF solutions as well as in a mixture of MeOH–THF are shown in Fig. 2a,b. Dilute P1 solutions exhibit a smooth absorption peak at ~ 380 nm, an excitation peak at 386 nm and two fluorescence peaks at 430 and 450 nm. The concentrated P1 solution as well as the solution of P1 in MeOH–THF exhibit red-shifted absorption, excitation and fluorescence spectra in

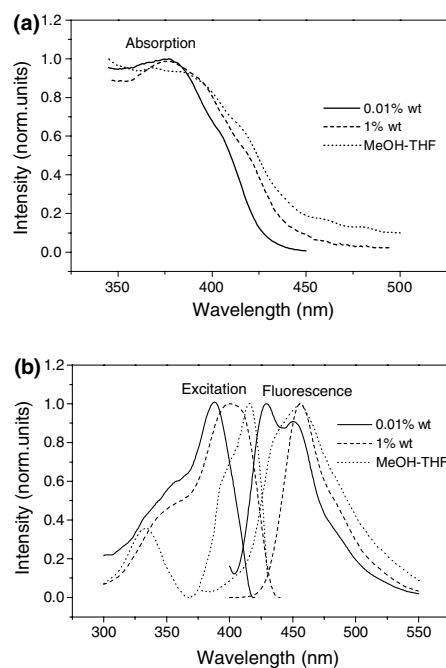


Fig. 2. The absorption (a) and photoluminescence excitation and fluorescence spectra (b) of P1 in dilute and concentrated THF solutions as well as in MeOH–THF.

contrast to the dilute solution indicating the formation of aggregates [11].

The fluorescence dynamics of P1 in dilute THF solutions with concentration 0.01 wt% is shown in Fig. 3a at two representative wavelengths exhibiting an ultrafast risetime (≤ 280 fs). Initially the results were fitted to a two and three exponential function. However in all cases the fitting function after the iterative process resulted to be a single exponential one with no wavelength dependence. The results were fitted with the equation

$$I = I_0 \exp(-t/\tau_0), \quad (1)$$

where τ_0 is the decay time which was found approximately 280 ± 10 ps at all emission wavelengths. The fact that τ_0 is independent on the emission wavelength indicates that a single chromophore is responsible for the

emission across the whole fluorescence spectrum. This means that all P1 chains contain the same well-defined chromophore [6,7]. This is attributed to the insertion of methylene groups (saturated groups) in the main P1 chains causing interruption of the conjugation and consequently of the chromophore parts [4–6].

The dynamics of O1 in THF solution with concentration equal to 9×10^{-4} M was also studied at different wavelengths and the results at 450 nm are shown in Fig. 3a. O1 exhibits a 170 ± 6 ps decay time that is smaller than that of P1. Using the equations

$$\Phi = \tau_0/\tau_{SP} \quad (2)$$

and

$$\sigma = A \times (1/\tau_{SP}), \quad (3)$$

where Φ is the quantum yield, τ_{SP} the radiative lifetime, σ the emission cross-section and A a proportionality constant (which depends on the index of refraction, the normalized spectral distribution of emission and the wavelength) and bearing in mind that the quantum yields of O1 and P1 are almost equal, we estimate that $\sigma_{O1} \cong 1.65\sigma_{P1}$ at 450 nm. In this estimation we also assumed that the proportionality constant A is the same for P1 and O1. The relationship between σ_{O1} and σ_{P1} is in agreement with our previous results which have shown that O1 is more efficient than P1 concerning stimulated emission [15].

The fluorescence dynamics of P1 in concentrated THF solutions is shown in Fig. 3b,c at representative wavelengths. The concentrations used were 0.5 wt% (Fig. 3b) and 1 wt% (Fig. 3c). In both cases an increased decay time at the long wavelength spectral edge (red edge) is observed. Especially, in Fig. 3b, the decay times at 450 and 500 nm are 285 ± 8 and 350 ± 8 ps, respectively while in Fig. 3c, the decay times at 450, 470 and 500 nm are 275 ± 8 , 380 ± 10 and 450 ± 10 ps, respectively. These results also show that the decay at 450 nm (blue edge) is similar to that in dilute P1 solutions.

In Fig. 4a the dynamics of P1 in a MeOH–THF mixture are shown at three representative wavelengths. The MeOH:THF ratio is 0.4 while the P1 concentration is 0.4 wt%. The aggregates formation in this MeOH–THF mixture is caused by the addition of MeOH and does not depend on the P1 concentration as reported recently [13]. The decay time increases with the emission wavelength and is equal to 590 ± 15 ps at 520 nm. However, at the blue spectral edge (450 nm) the decay time is not affected by the poor solvent and remains 280 ± 8 ps as in dilute THF solutions.

The wavelength dependent dynamics in Figs. 3b,c and 4a indicate the existence of different emission species in the solutions. Particularly, the slower decay at the red spectral edge is attributed to the aggregated chains formed because of the high concentration or the addition of MeOH. On the other hand, the almost unaffected

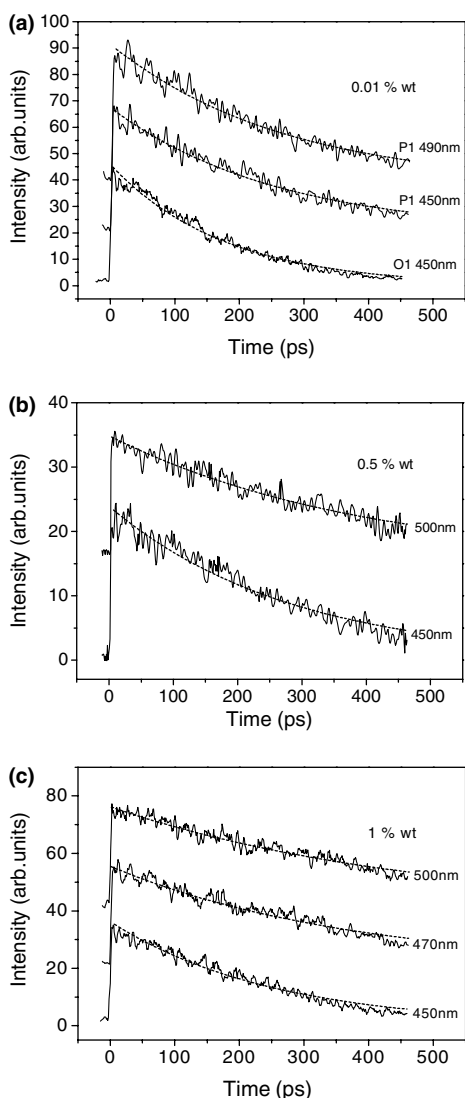


Fig. 3. The dynamics of P1 and O1 in dilute solutions (a) and the dynamics of P1 in concentrated solutions with concentrations 0.5 wt% (b) and 1 wt% (c) at representative wavelengths. The solid lines are the experimental data while the dashed lines are the theoretical fits.

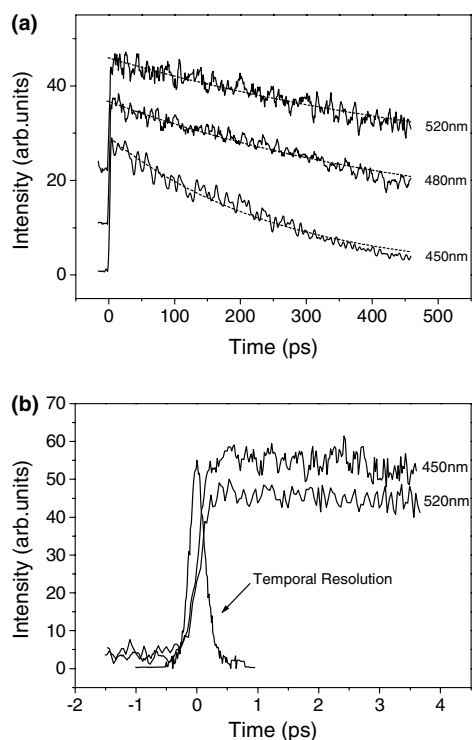


Fig. 4. The dynamics (a) and the fluorescence risetime (b) of P1 in MeOH-THF at representative wavelengths.

decay time at the blue spectral edge, despite the high concentration or the MeOH addition, proves that the fluorescence in this spectral region is due to the isolated chains. It is therefore concluded that the emission in concentrated solutions or in mixtures of poor–good solvents originates from both isolated and aggregated chains. The former emit at the blue edge of the spectrum while the latter emit at the red one. However, the isolated chains decay faster than the aggregated ones and therefore the emission of the latter mainly dominates in the steady-state fluorescence spectra (Fig. 2b).

In addition, the fact that the decay of isolated chains is not affected by the existence of aggregates means that no energy transfer from the isolated (higher band gap species) to the aggregated chains (lower band gap species) occurs. This conclusion is additionally supported by the comparison of the fluorescence risetime of the isolated and aggregated chains namely the risetime at the blue and the red spectral edge of the MeOH-THF solution. The results are shown in Fig. 4b together with the temporal resolution of our system. At both cases the risetime falls within the temporal resolution meaning that the aggregates are directly excited by their ground state (like the isolated chains) and not by an energy transfer process. If energy transfer from isolated to aggregated chains was involved, the isolated chains would exhibit a reduced decay time in the aggregated solutions compared to the dilute ones and additionally the aggregates would have a longer fluorescence risetime [10–12,19].

We suggest that the absence of energy transfer is attributed to the insertion of saturated (non-conjugated) segments in the main polymer chains. This localizes the excitons within the chromophores of isolated chains hindering exciton diffusion to aggregates. This could be the reason 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 [13,14]. In the opposite case, where exciton diffusion to aggregates occurs, the population of the excited isolated chains (responsible for the amplified spontaneous emission) would rapidly reduce, because of transfer to aggregates and the emission could not be amplified.

Finally, the time resolved fluorescence spectra of P1 in MeOH-THF are shown in Fig. 5a, fitted with a Lorentzian function. At 10 ps there is a high intensity peak at the blue spectral region (at 446 nm) attributed to the emission from isolated chains. Within the first 150 ps, the blue spectral region (~ 450 nm) remains dominant while the red one exhibits low intensity. However, as it was discussed previously, the blue edge decays faster than the red one causing a red shift of the fluorescence spectra and a change in their linewidth. The peak wavelength and the linewidth are shown in the inset of Fig. 5a as a function of time. The peak is red-shifted from 446

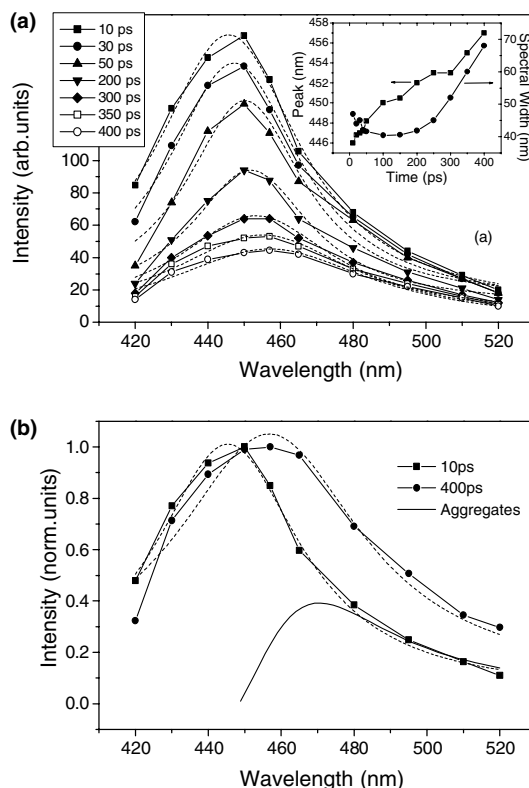


Fig. 5. (a) The fluorescence spectra of P1 in MeOH-THF at different times. The inset shows the peak wavelength and the linewidth versus time. (b) The normalized fluorescence spectra of P1 in MeOH-THF at 10 and 400 ps and the fluorescence spectrum of aggregates.

to 457 nm. This is attributed to the emission of aggregates which becomes significant at long times. Additionally, the linewidth initially decreases, because the blue edge of the spectrum decays faster than the red one, but it increases at long times.

The red shift and the broadening of the spectra as the time increases are more obvious in Fig. 5b, where the spectra at 10 and 400 ps are shown in normalized units. As mentioned earlier the spectrum at 10 ps mainly originates from the isolated chains. The spectrum at 400 ps is identical to the steady-state spectrum of the MeOH–THF mixture shown in Fig. 2b. In this spectrum there is a significant contribution from the long lived aggregates emission in the red region which was not shown in the 10 ps spectrum. Additionally, the blue emission (~450 nm) is still observed in the 400 ps spectrum indicating that at long times the emission originates from both the isolated and aggregated chains. However, the contribution of aggregates at the 400 ps spectrum is more important than that of isolated chains as it is obvious from the red shift of the spectrum. Subtracting the spectrum at 400 ps containing the contribution of both isolated and aggregated chains from the 10 ps spectrum containing mainly the contribution of isolated ones, we obtain the fluorescence spectrum of the aggregated chains. This is also shown in Fig. 5b, exhibiting a peak at 470 nm. The above analysis, based on time resolved spectroscopy, constitutes a useful tool in separating the contribution of isolated and aggregated chains to the total emission.

4. Conclusions

We have studied the excited state dynamics of a partially conjugated blue emitting polymer and its model oligomer. The polymer contains well-defined chromophore segments and decays slower than the oligomer. Exciton localization within the chromophores of isolated chains occurs hindering the exciton migration to aggregates. The aggregated chains emit at a longer wavelength than the isolated ones with longer decay time. The transient fluorescence spectra of P1 in a mixture of poor–good solvent exhibit a gradual red shift and a broadening because of the aggregates emission.

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