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# Excitation energy transfer in a cationic water-soluble conjugated co-polymer studied by time resolved anisotropy and fluorescence dynamics

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## Abstract

The excitation energy transfer in a new water-soluble poly(fluorenevinylene-*co*-phenylenevinylene) is investigated by time resolved anisotropy and fluorescence dynamics. This is realized in concentrated aqueous and EtOH solutions using femtosecond time resolved upconversion spectroscopy. At short emission wavelengths, the anisotropy dynamics indicate a single depolarization mechanism attributed to the reorientation of isolated chains. At long emission wavelengths, two depolarization mechanisms are observed. The fast one, occurring within 10–20 ps, is ascribed to interchain energy transfer, while the slow one is attributed to reorientation of isolated and aggregated chains. Isotropic fluorescence dynamics also reveal a fast decay mechanism supporting the energy transfer conclusion.

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## 1. Introduction

Conjugated polymers are widely used in optoelectronics and microelectronics because of their exceptional electronic, optical and mechanical properties [1–3]. Especially, water-soluble conjugated polymers (WSCPs) can be used in biosensors for the detection of various biomolecules [4–6]. An ideal optical biosensor should change its emission colour in the presence of a target molecule and completely recover to its initial emission colour when the target molecule is drawn away. WSCPs are used in biosensors due to their light harvesting properties and their ability for efficient excitation energy transfer (EET) to nearby molecules having opposite charge [4–6]. In this case the electrostatic forces between the opposite charged molecules bring them in proximity facilitating the energy transfer process. Therefore, the synthesis and study of novel, versatile and inexpensive WSCPs for applications in biosensors is of great scientific and economic importance.

Cationic WSCPs are interesting compounds as they can be used for the detection of the negatively charged DNA [5,7,8]. Although WSCP based biosensors have been reported previously [4,5], there are yet a number of issues that need to be clarified towards the optimization of such sensors. These issues are focused on the role of the chemical structure, molecular conformation and aggregation on the optical properties and especially on the energy transfer processes of these polymers.

In this Letter, a recently synthesized cationic water soluble poly(fluorenevinylene-*co*-phenylenevinylene) (PFV-*co*-PV) is presented and its excitation energy transfer dynamics in concentrated aqueous and EtOH solutions is investigated. Measurements of time resolved anisotropy and fluorescence dynamics have been performed at short and long emission wavelengths using a femtosecond time resolved upconversion spectroscopy.

## 2. Experimental

The cationic polymer PFV-*co*-PV (inset of Fig. 1) was synthesized by the quaternization of its neutral parent

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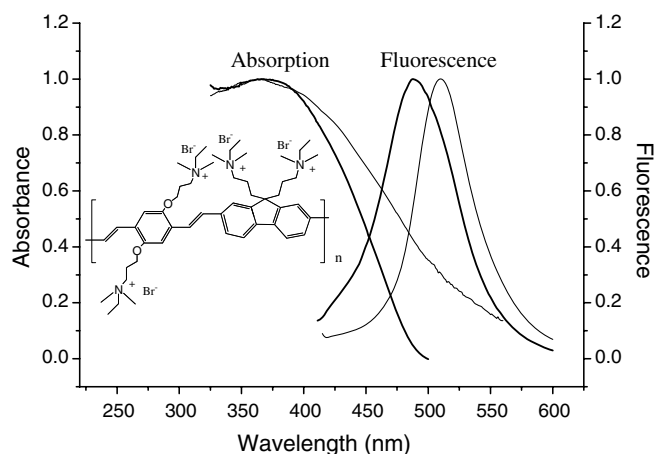


Fig. 1. Absorption and fluorescence spectra of PFV-co-PV in water in dilute ( $10^{-5}\%$ wt, thick line) and concentrated ( $10^{-1}\%$ wt, thin line) solutions. The inset shows the chemical structure of the polymer.

polymer i.e. by reacting the neutral polymer with bromoethane in THF solution at room temperature for several days. The detailed synthesis will be published elsewhere [9]. The cationic polymer is soluble in environmentally friendly solvents, such as alcohols and water. Both the neutral and the cationic polymer were characterized by  $^1\text{H-NMR}$  and FT-IR spectroscopy showing high chemical purity. The molecular weight  $M_w$  of the neutral polymer was determined by Gel Permeation Chromatography using polystyrene as a standard and was found equal to 73200 with polydispersity of 1.57. Direct measurement of the cationic polymer's molecular weight was difficult because of the polymer aggregation on the column fillers induced by the ionic nature of the side chains [10,11]. However, since the quaternization reaction took place under mild conditions, the molecular weight and polydispersity of the cationic polymer are expected to be comparable with those of its neutral parent polymer. The quantum yield of the cationic polymer was found to be 0.14 using quinine sulphate as a standard while its molar absorption coefficient at 400 nm was found to be approximately  $3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (per repeat unit).

Steady-state and time resolved spectroscopic measurements were performed in aqueous and EtOH solutions. Absorption spectra were taken with a Beckman DU-640 spectrometer while steady-state photoluminescence measurements were performed using a Perkin Elmer LS55B luminescence spectrometer. Time resolved anisotropy and fluorescence dynamics measurements were performed using a femtosecond time resolved upconversion technique. The experimental set-up has been described previously [12,13]. Briefly, a mode-locked Ti:Sapphire laser emitting pulses at 800 nm with 80 fs duration is used as the light source. The laser beam is focused onto a BBO crystal and is frequency doubled. The second harmonic beam after passing through a  $\lambda/2$  plate is used for the excitation of the polymeric samples while the remaining fundamental laser beam is used as the gate beam. The fluorescences of the samples

and the gate beam are focused onto a second BBO crystal generating an upconversion beam. Finally, this upconversion beam is dispersed through a monochromator and is detected by a photomultiplier connected with a photon counter. The temporal and spectral resolution of the system are 250 fs and 2.5 nm, respectively. Polarized fluorescence decay dynamics were recorded by rotating the  $\lambda/2$  plate in order to detect the fluorescence intensities polarized parallel  $I_{\parallel}(t)$  and perpendicular  $I_{\perp}(t)$  with respect to the excitation polarization. The anisotropy was calculated using the relationship [12]

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (1)$$

Finally, isotropic measurements were also performed under magic angle conditions.

### 3. Results and discussion

The absorption and fluorescence spectra of PFV-co-PV in dilute ( $10^{-5}\%$ wt) and concentrated ( $10^{-1}\%$ wt) aqueous solutions are shown in Fig. 1. The spectra of the concentrated solutions are clearly red-shifted compared to those of the dilute solutions. Specifically, the absorption of concentrated and dilute solutions experience a peak at the same wavelength (380 nm). However, the spectrum of the concentrated solution is extended to longer wavelengths in comparison to that of the dilute solution. Additionally, the peak of the fluorescence spectrum shifts from 488 nm, in dilute, to 510 nm in concentrated solutions. The observed spectroscopic differences between concentrated and dilute solutions, are reasonably attributed to inter-chain aggregates existing in concentrated solutions [14–16]. It is also observed in Fig. 1 that the fluorescence spectrum of the concentrated solution is narrower than that of the dilute solution. This is caused by a lowering of the fluorescence intensity at short wavelengths because of self absorption as well as EET from high energy band gap species to low energy ones as will be discussed in details below. The spectra obtained in EtOH are almost similar to those in water except from the fluorescence spectrum of the concentrated EtOH solution. This spectrum is less red-shifted than that of the aqueous solution experiencing a peak at 500 nm (data not shown). The smaller red-shift observed in the concentrated EtOH solutions compared to that in water may indicate the formation of less or smaller aggregates in EtOH.

The anisotropy dynamics is a powerful method for examining fluorescence depolarization which could originate from molecular rotation, energy transfer, Brownian motion etc. [17–19]. In Fig. 2 the polarized fluorescence dynamics and the corresponding anisotropy data for a concentrated aqueous solution of PFO-co-PV ( $10^{-1}\%$  wt), are shown at 500 and 540 nm. The shorter wavelength lies in the spectral region where only isolated chains emit (Fig. 2a) while the longer one lies in the spectral region where both isolated and aggregated chains emit (Fig. 2b).

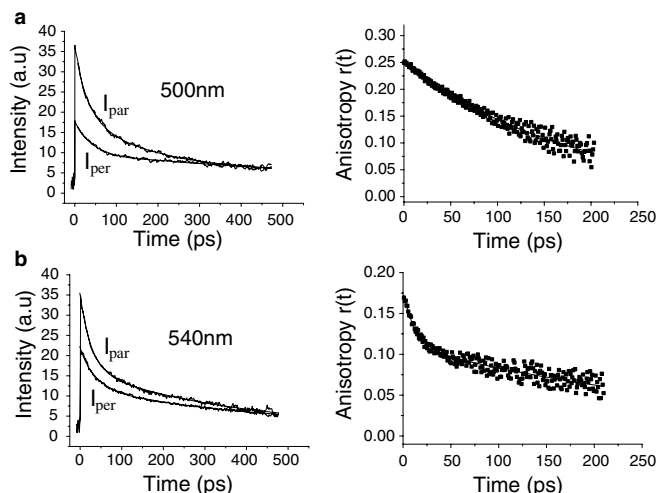


Fig. 2. Polarized fluorescence dynamics of PFV-*co*-PV in water ( $10^{-10}$ wt) at (a) 500 nm and (b) 540 nm together with the corresponding anisotropy results. The excitation wavelength was 400 nm (absorption coefficient  $\sim 6 \text{ mm}^{-1}$ ).

The anisotropy decay at 500 nm was successfully fitted using the following exponential decay function:

$$r(t) = r_0 \cdot \exp(-t/\tau) \quad (2)$$

where  $r_0$  is the initial anisotropy and  $\tau$  is the anisotropy correlation time. The parameters  $r_0$  and  $\tau$  were found to be 0.25 and 175 ps, respectively. On the other hand, the anisotropy decay at 540 nm (Fig. 2b) was fitted with a bi-exponential function i.e.,

$$r(t) = r_0[b \exp(-t/\tau_1) + (1 - b) \exp(-t/\tau_2)] \quad (3)$$

where time constants 12 and 340 ps were resolved, respectively, while  $r_0$  was found to be 0.17. All the parameters obtained from the fitting procedures are summarized in Table 1. Anisotropy dynamics of a dilute PFV-*co*-PV (concentration lower than  $10^{-40}$ wt) showed a single exponential decay with no wavelength behavior and correlation time equal to  $190 \pm 25$  ps.

The polarized fluorescence and anisotropy dynamics obtained from a concentrated EtOH solution of PFV-*co*-PV ( $10^{-10}$ wt) are shown in Fig. 3 for two wavelengths i.e 470 and 500 nm. Again the long wavelength corresponds to the emission spectral region of both isolated and aggregated chains while the short one lies in the isolated chains spectral region. As in the case of the aqueous solution, the anisotropy at the short wavelength was fitted with a single-exponential decay function with  $r_0 = 0.27$  and  $\tau = 190$  ps, respectively. Additionally, the anisotropy at the long wavelength was fitted with a bi-exponential decay function with

Table 1  
Fitting parameters of the anisotropy decay results for a PFV-*co*-PV aqueous solution ( $10^{-10}$ wt)

$\lambda$ (nm)	$r_0$	$\tau_1$ (ps)	$\tau_2$ (ps)	$\alpha$
500	0.25	$175 \pm 25$	–	$29^\circ$
540	0.17	$12 \pm 4$	$340 \pm 40$	$38^\circ$

$\alpha$  is the angle between the absorption and emission dipole.

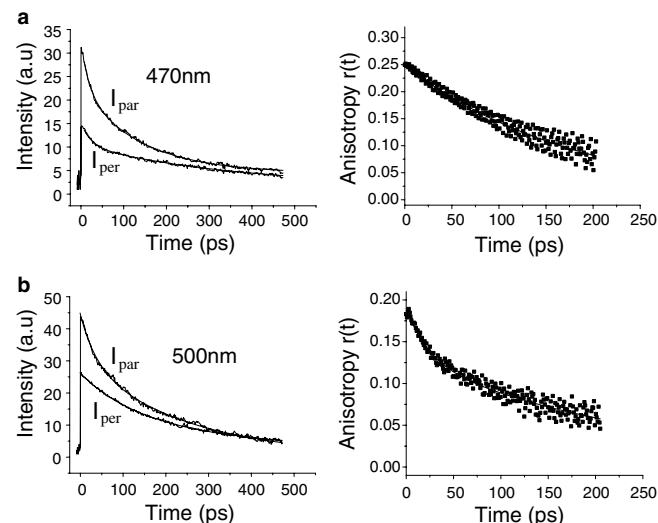


Fig. 3. Polarized fluorescence dynamics of PFV-*co*-PV in EtOH ( $10^{-10}$ wt) at: (a) 470 nm and (b) 500 nm. The corresponding anisotropy results are also shown. The excitation wavelength was 400 nm.

Table 2

Fitting parameters of the anisotropy decay results for a PFV-*co*-PV EtOH solution ( $10^{-10}$ wt)

$\lambda$ (nm)	$r_0$	$\tau_1$ (ps)	$\tau_2$ (ps)	$\alpha$
470	0.27	$190 \pm 20$	–	$28^\circ$
500	0.19	$20 \pm 5$	$250 \pm 35$	$37^\circ$

$\alpha$  is the angle between the absorption and emission dipole.

$\tau_1 = 20$  ps,  $\tau_2 = 250$  ps and  $r_0 = 0.19$ . The results are summarized in Table 2.

It is obvious from our results in Figs. 2 and 3 that the initial anisotropy  $r_0$  is lower than the theoretical value 0.4 which is obtained for parallel absorption and emission dipoles. Using the equation

$$r_0 = \frac{1}{5}(3 \cos^2 \alpha - 1) \quad (4)$$

the angle  $\alpha$  between the absorption and emission dipoles can be deduced. For isolated chains (short wavelengths) in water and EtOH,  $\alpha$  was calculated to be equal to  $28^\circ$ – $29^\circ$  while for aggregates the angle  $\alpha$  is larger being  $37^\circ$ – $38^\circ$ . The calculated values of  $\alpha$  are also given in Tables 1 and 2.

The observation of two anisotropy decay components at long wavelengths in both aqueous and EtOH solutions indicates that two physical mechanisms contribute to fluorescence depolarization occurring at different time scales [20]. The fast decay mechanism could not be due to reorientational motion of the polymer since this process would need much longer time to complete.

In order to gain insight on the origin of the anisotropy dynamics, isotropic fluorescence dynamics were also studied. This was done for PFV-*co*-PV in water and EtOH at 540 nm and 500 nm, respectively, where both isolated and aggregated chains emit. The results are shown in Fig. 4a and b together with the anisotropy ones for comparison. The fluorescence decays are best

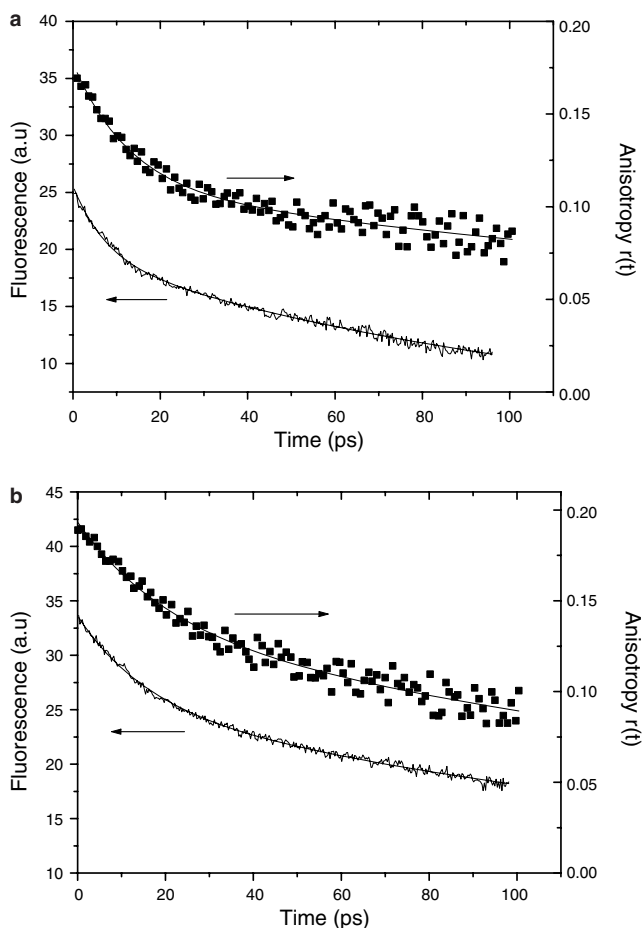


Fig. 4. Isotropic fluorescence dynamics and anisotropy decay of PFV-co-PV in: (a) water at 540 nm and in (b) EtOH at 500 nm. The excitation wavelength was 400 nm and the concentration was  $10^{-10}$  wt.

fitted with double exponentials with fast decay times of  $13 \pm 2$  ps and  $18 \pm 3$  ps in water and EtOH, respectively. These times are very similar to the fast decay times of the anisotropy at the same wavelengths. This indicates that the same physical mechanism is responsible for the fast decay of both anisotropy and fluorescence. This mechanism can be reasonably attributed to interchain excitation energy transfer [21–23]. This transfer is facilitated in concentrated solutions of PFV-co-PV, since the probability for isolated chains and interchain species (aggregates) to be found within a Förster transfer radius is enhanced.

Apart from the fast anisotropy decay mechanism attributed to EET, a slow decay mechanism ( $>250$  ps) of anisotropy is also observed at long wavelengths (540 and 500 nm for aqueous and EtOH solutions, respectively). This can be attributed to the reorientation of the polymer chains. At these wavelengths, reorientational motions of both isolated and interchain species, having different volumes, are probed and an average reorientation time is obtained. On the other hand, at short wavelengths (500 and 470 nm for aqueous and EtOH solutions, respectively), the anisotropy decay lacks a fast depolarization process indicating that no energy transfer is detected. The anisotropy decay at short

wavelengths is attributed only to the reorientational motion of isolated chains emitting at these wavelengths.

As discussed previously, EET is observed in the anisotropy dynamics at long wavelengths and not at short ones. This can be understood bearing in mind that at short wavelengths the detected light originates only from isolated chains while at long ones the light originates from both isolated and aggregated chains. Initially, the isolated chains which have their absorption dipoles parallel to the polarization of the excitation beam are preferentially excited. Gradually, these chains reorient while, simultaneously, a part of them transfers its energy to the aggregates. This causes a fast decay of the anisotropy at long wavelengths (where both isolated and aggregated chains contribute to the anisotropy) because the transferred energy is distributed among the almost randomly oriented aggregates. Subsequently, the aggregates emit almost randomly polarized light reducing the total polarization. At short wavelengths (where only isolated chains contribute to the anisotropy) the observed depolarization is attributed to the reorientation of isolated chains and thus the anisotropy decays slowly.

From the results summarized in Tables 1 and 2 it is concluded that the EET in EtOH is slower than in water. This, according to Förster energy transfer theory, indicates that the mean distance between isolated and aggregated chains is longer in EtOH than in water. This means that either less or smaller aggregates are formed in EtOH in agreement with the conclusion obtained from steady-state fluorescence spectra.

#### 4. Conclusions

Motivated by the need for designing and studying new WSCPs for potential use in biosensors, a new cationic water soluble poly(fluorenevinylene-co-phenylenevinylene) was studied through steady-state and femtosecond time resolved spectroscopy. Steady-state spectra have shown that the polymer emits at the blue-green spectral region and that aggregates are formed in concentrated solutions. Time resolved anisotropy and fluorescence dynamics indicated a rapid interchain excitation energy transfer occurring within less than 20 ps. Anisotropic fluorescence parameters such as reorientation times and the angle  $\alpha$  between emission and absorption dipoles were given.

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