Nature and dynamics of photoexcited states in an electroluminescent poly(phenylene vinylene-co-fluorenylene vinylene)-based π-conjugated polymer

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ABSTRACT

This paper describes the optical properties of an electroluminescent poly(phenylene vinylene-co-fluorenylene vinylene) (BPPPV-PF)-based π-conjugated polymer using absorption, photoluminescence (PL), time-resolved photoluminescence (TRPL), continuous wave (CW) and transient-photoinduced absorption (PA) spectroscopic techniques. The TRPL decay spectra of BPPPV-PF in chloroform and film exhibit single exponential decay with PL lifetimes of 0.8 ns and 0.2 ns, respectively. The CW-PA spectrum exhibits a single well-defined band centred at 1.5 eV, which is assigned to the T–T* transition of the triplet excitons. The monomolecular lifetime (τ) of the triplet excitons was estimated from the intensity dependence of CW-PA and found to be $\sim$1.2 ms at 80 K. The temperature dependence of the CW-PA signal at 1.5 eV was studied for a temperature range from 80 K to 298 K. It was observed that the PA signal at 1.5 eV was persistent to relatively high temperatures, which may be due to the bulky side chain of the polymer and morphology of the film. The relaxation process of this triplet excitation was studied by measuring the transient decay of the PA signal for various temperatures. The transient-PA signal shows monomolecular recombination process at all recorded temperatures and the temperature dependence of monomolecular lifetime (τ) was studied. It was found that the monomolecular lifetime (τ) is dependent on temperature but independent of the laser excitation intensity. The obtained results are analyzed based on the molecular structure of the PPV-PF copolymer.

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1. Introduction

Light emitting π-conjugated polymers have attracted significant research interest for display applications due to their ease of processing and flexibility in synthesis. Poly(*p*-phenylene vinylene) (PPV) and its derivatives have excellent electroluminescence properties and have been widely used for polymer light emitting diode (PLED) applications [1–3]. For the development of practical PLEDs with a high quantum efficiency, low operating voltage, and long lifetime, it is required to design processable conjugated polymers with high chemical purity, photoluminescence (PL) efficiency, good thermal and oxidation stability, and balance of charge carrier mobility. Some of these can be satisfied by introducing long side chains to the polymer backbone or by controlling the

highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels through chemical modification. For example, the introduction of electron donating or electron withdrawing side groups to the polymer backbone or interruption of the conjugation length through copolymerization techniques can modify solubility and permit tuning of the emission color as well as control the charge carrier mobility [4–7]. It is also important to control the nature and dynamics of photoexcited states in these polymers in order to improve the efficiency of the devices. For example, the formation of triplet excited states and their recombination properties can significantly change the performance of the electroluminescent devices [8,9]. Generally, the triplet excited states have much longer lifetime than the singlet excited states, hence it can quench many singlet excited states before relaxing to the ground state. The photoexcited triplet states are formed via intersystem crossing from the excited singlet states. The branching between the formation of long-lived neutral and charged excited states depends on the chemical structure of the

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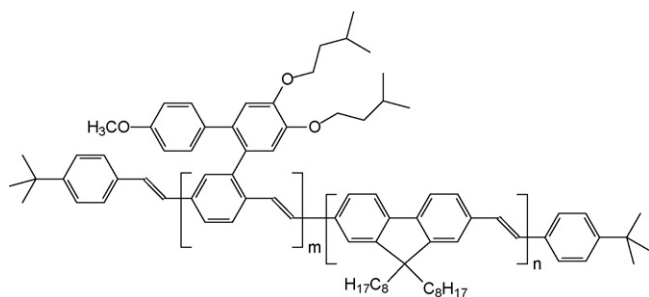*E-mail address:* c-vijila@imre.a-star.edu.sg (C. Vijila).

Fig. 1. Chemical structure of the polymer BPPPV-PF.

polymer as well as the film morphology [10,11]. It has been shown that the intersystem crossing rate in conjugated polymers can be controlled through modification of the chemical structure [12,13]. As a result, there are varieties of PPV derivatives and polyfluorene (PF) derivatives have been synthesized and their photoexcited state properties have been investigated [14–18]. It has been reported that the photoinduced absorption (PA) spectrum for highly oriented, structurally ordered MEH-PPV film shows a single peak due to T–T* transition without any spectral features due to charged excited states (polarons) [19]. The absence of polaronic bands in the PA spectrum was attributed to the suppression of interchain interaction and the reduced structural disorders in the polymer film. Recently, it has been shown that the biphenylyl substituted PPVs have negligibly small structural disorders compared to other PPV derivatives and thus, they are promising materials for PLED's with higher efficiency and longer operational lifetime [20–22]. Hence, these polymers are under investigation for further development. However, there is no known report on the optical properties of biphenylyl substituted PPV derivatives. Therefore, we have developed a biphenylyl substituted PPV-PF-based π-conjugated polymer: poly{[2-(4′,5′-bis(3″-methylbutoxy)-2′-p-methoxy-phenyl)phenyl-1,4-phenylene vinylene]-co-(9,9-dioctyl-2,7-fluorenylene vinylene)} (BPPPV-PF) and studied its photoexcited state properties. The synthesis detail of BPPPV-PF is described elsewhere [22,23]. The chemical structure of the polymer is shown in Fig. 1. The main focus of this work is to understand the effect of molecular structure and their structural purity on the nature and dynamics of the photoexcited states in this BPPPV-PF polymer. We have used various optical spectroscopies such as absorption, PL, time-resolved photoluminescence (TRPL), continuous wave (CW) and transient-PA techniques. The TRPL technique has been used to study the dynamics of singlet excited states. Transient and CW-PA techniques were used to study the long-lived photoexcited species and their recombination dynamics.

2. Experimental

The BPPPV-PF film was prepared by solution casting from chloroform solution (concentration: 4 mg/ml) on sapphire substrate. The absorption and PL spectra were recorded using a Shimadzu UV 3101PC UV–vis spectrophotometer and a PerkinElmer LS 50B luminescence spectrometer, respectively. For the TRPL measurements, the samples were excited using the frequency-doubled output of a mode-locked Ti:sapphire femtosecond laser from Spectra-Physics, operating at 400 nm with a pulse width of 100 fs at a 82 MHz repetition rate. The time-evolution of luminescence was recorded using a streakscope from Hamamatsu with a time resolution of 15 ps.

The PA spectra (0.3–2.2 eV) were measured using a standard PA technique, which probes the changes, ΔT, in the optical transmission T [24]. The exciting pump beam (multiline UV with $\lambda \sim 360$ nm

of an Ar+ laser) was modulated by a mechanical chopper, and the laser beam was focused on a 2 mm × 8 mm area of the sample using a cylindrical lens. The probe light from a 250-W incandescent tungsten lamp was focused on the same spot as the laser beam using a spherical mirror, and collected into a monochromator (Acton, SpectraPro-300i) with proper filters. The light from the monochromator was detected with Si, Ge and liquid nitrogen cooled InSb detectors depending on the wavelength range, and the signal was amplified with a preamplifier (EG&G Judson, PA-7) before reaching the lock-in amplifier (Stanford, SR830). The time-resolved decay of the transient absorption was measured by replacing the Ar+ laser with a pulsed Nd:YAG laser (355 nm, pulse width ∼7 ns) and using a digital oscilloscope (Tektronix, TDS 680B) instead of the lock-in amplifier.

3. Results and discussion

3.1. Absorption and photoluminescence spectra

The absorption and PL spectrum of the polymer film is shown in Fig. 2. The absorption spectrum shows a broad structureless band with a maximum at 375 nm and the PL spectrum shows a maximum at 510 nm with well-resolved vibronic shoulders at around 542 nm and at 586 nm. It is found that there is a large difference between the spectral shapes of the absorbance and PL bands, which indicates that this polymer (BPPPV-PF) has considerable degree of conformational freedom. The band gap of the polymer is found to be ∼2.5 eV, which is 0.15 eV higher than the values reported for PPV and for the biphenylyl substituted homo PPV derivatives (BPPPV) [22]. The relative PL quantum efficiency of this polymer in chloroform solution was found to be 42% using quinine sulfate (1×10^{-5} M dissolved in 0.1 M H_2SO_4) as a reference [25].

3.2. Time-resolved photoluminescence

The TRPL decay spectra of the polymer in chloroform solution and in film was studied. Fig. 3 shows the TRPL decay of BPPPV-PF in chloroform solution and in film state. The TRPL decays in solution and film exhibit single exponential decay, indicating the presence of a single component and that the formation of excited state complexes or interchain excitons is negligible in this polymer. The PL lifetimes of BPPPV-PF in chloroform solution and film form were found to be around ∼0.8 ns and ∼0.2 ns, respectively. The faster PL decay of BPPPV-PF in film form compared to the PL decay in solution is attributed to the nonradiative recombination due to the conformational changes in the film state.
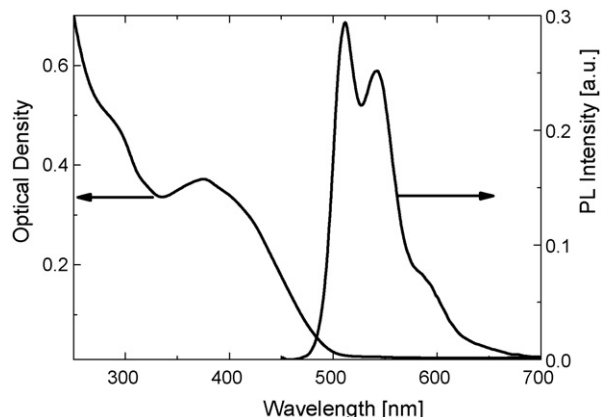

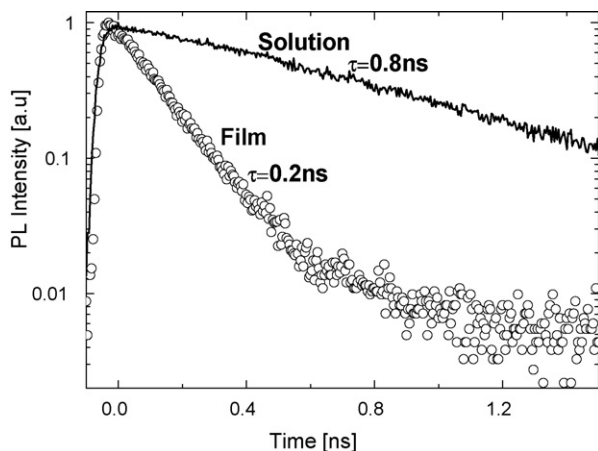**Fig. 2.** Absorption and photoluminescence spectrum of BPPPV-PF film.

Fig. 3. Time-resolved photoluminescence decay of BPPPV-PF in chloroform (solid line) and in film form (open circles).

3.3. Photoinduced absorption

3.3.1. Continuous wave (CW) photoinduced absorption

The CW-PA spectrum of BPPPV-PF is shown in Fig. 4. The spectrum was recorded at temperature $T = 80$ K with exciting wavelength 355 nm, modulation frequency 133 Hz and laser power 200 mW. The PA spectrum shows a high-energy band (HE) peaked at 1.5 eV and a very weak shoulder at around 1.9 eV. There are no features seen in the low energy region. The HE PA peak at 1.5 eV is assigned to the T–T* transition of the triplet excitons. The observed PA spectral features are similar to the spectra reported for the solution state MEH-PPV [26] and the glassy phase of poly(9,9-dioctylfluorene) (PFO) [17] without any features due to charged excitations. The obtained value of T–T* transition energy for BPPPV-PF is also consistent with the reported values for the structurally related polymers. The reported values of T–T* transition energy for PPV and PFO was 1.45 eV and 1.5 eV, respectively [26,17]. The energy position of the T–T* transition in BPPPV-PF also indicates that their effective conjugation length is extended, as the peak energy is higher for the oligomers and lower for long-conjugated polymeric chains [9]. The absence of charged excited states in BPPPV-PF is due to the reduced interchain coupling, which quenches the interchain cha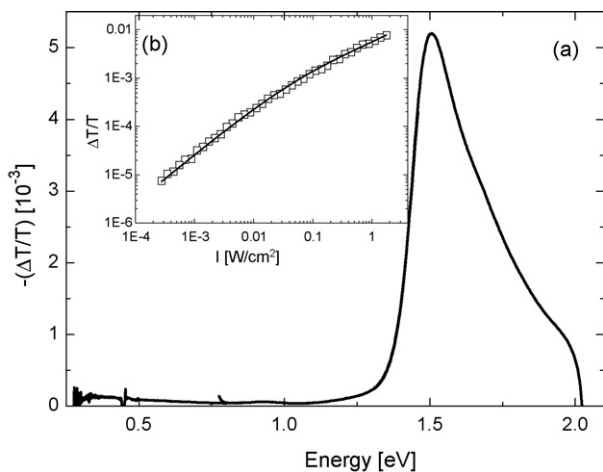rge separation routes necessary for the formation of charged excitons. It has already been reported that PPV's with bulky biphenylyl substitutions can rarely form good packing between the polymer backbones [22]. Hence, the reduced interchain coupling in BPPPV-PF is attributed to the bulky biphenylyl substitutions and or the steric effect associated with the position of side chain substitution in BPPPV-PF.

The pump intensity dependence of the PA band at 1.5 eV was shown in Fig. 4(b). The intensity dependence of PA at 1.5 eV shows linear dependence at low intensities and approaches square root dependence at high intensities. The intensity dependence of the PA band at 1.5 eV can be explained using a rate equation with mixed monomolecular and bimolecular recombination (BR) of the excited states [27], described as $dn/dt = g(x, t) - (n/\tau) - (\beta n^2)$, where n is the density of photoexcited state, τ is the monomolecular lifetime, β is the bimolecular annihilation coefficient, $g(x, t)$ is the sinusoidal generation, $(G/2)\exp(-\alpha_L x)(1 + \cos(\omega t))$, which represents the modulated pump beam using an acousto-optic modulator. We assume that the generation follows Lambert–Beer's law in the sample; α_L is the absorption coefficient of the sample at the laser wavelength. The detailed discussion of mixed monomolecular and bimolecular recombination process is described elsewhere [27]. In order to obtain the monomolecular lifetime and bimolecular recombination coefficient, the intensity dependence of PA at 1.5 eV was fitted with mixed monomolecular and bimolecular recombination rate equation (shown as a solid line in Fig. 4). The monomolecular lifetime $\tau_I = 1.2$ ms and the bimolecular recombination coefficient $\beta_I = 1.99 \times 10^{-15}$ cm^3/s were estimated from the fit using the film thickness $d = 8.17 \times 10^{-4}$ cm. The obtained triplet excited state lifetime for BPPV-PF is in good agreement with the value reported for PFO (1.8 ms) [28]. The bimolecular recombination process observed for BPPPV-PF at high excitation intensities are attributed to the triplet–triplet annihilation. The bimolecular recombination process due to triplet–triplet annihilation was also observed for poly(*para*-phenylene) (PPP) [29] and dendronically substituted PFs [30]. The annihilation parameter obtained for BPPPV-PV ($\beta_I = 1.99 \times 10^{-15}$ cm^3/s) is in good agreement with the value reported for poly(dialkylfluorene), which was 3×10^{-15} cm^3/s [30]. The triplet state diffusion radius in BPPPV-PF was calculated using the annihilation parameter ($\beta_I = 1.99 \times 10^{-15}$ cm^3/s) and the triplet state lifetime ($\tau_I = 1.2$ ms). The triplet state diffusion radius in BPPPV-PF was found to be around 30 nm, which is in the same range with the value reported for PF [30].

The temperature dependence of the PA band at 1.5 eV was also studied for two different laser intensities and is shown in Fig. 5. It is found that the PA signal at 1.5 eV shows weak temperature dependence from 80 K to 140 K and the PA decreases strongly at
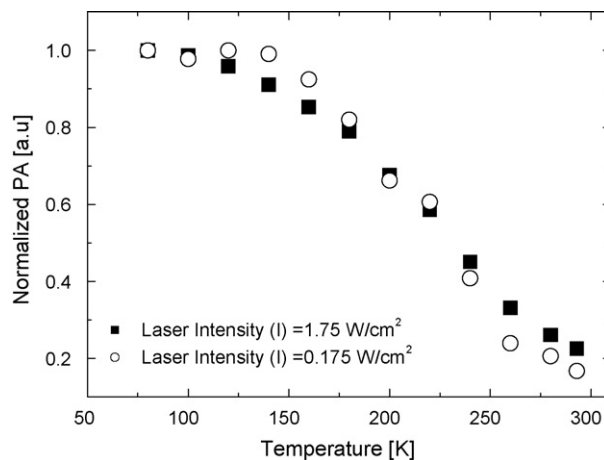

Fig. 4. (a) PA spectrum for BPPPV-PF at 80 K using the modulation frequency 133 Hz, the excitation wavelength 355 nm, and the laser power 200 mW; inset (b): laser intensity dependence of the PA at 1.5 eV. The solid line is a fit with mixed mono and bimolecular recombination rate equation.

Fig. 5. Temperature dependence of the CW-PA at 1.5 eV.

$T > 140$ K. At higher laser intensity, the PA signal started decreasing at lower temperature compared to the PA signal at lower laser intensity. However, the rate of change of PA signal with temperature is not as strong as the temperature dependence of PA observed for lower laser intensity. It is also seen that for $T > 140$ K the PA signal for both laser intensities show almost similar temperature dependence. The temperature dependence of PA in BPPPV-PF is different from the trend reported for PPV derivatives, where the PA signal due to triplet excited states decreases dramatically with increasing temperature [15]. The temperature dependence of the PA signal due to triplet excitons depends on both the triplet generation and decay channels. However, it was assumed that the generation rate of triplet photoexcitations is independent of temperature for PPV; the photoinduced triplet–triplet absorption data is proportional to the temperature-dependent triplet lifetime [31]. It has also been reported that the existence of deep traps in conjugated polymers, which could capture triplets at room temperature [32]. However, the detailed charge transport studies in our BPPPV-PF polymer using time of flight (TOF) photoconductivity studies indicate that the chemical purity and structural regularity of this polymer is very good [23]. The slower decrease of PA signal due to triplet excitons was also observed in the neat, planarized films of ladder-type poly(*para*-phenylene) [29]. Therefore the slower decrease of PA signal with increase of temperature in BPPPV-PF may be due to the combination of bulky side chain substitution in the polymer backbone and the complex morphology of the BPPPV-PF film. The slower decrease of PA signal with temperature was also observed for dendronically substituted PF derivatives [30], in which the triplet migration is inhibited by the side chains.

3.3.2. Transient-photoinduced absorption

The recombination processes and the lifetime of the triplet excited state at 1.5 eV were also studied by measuring the transient decay of the PA signal at various temperatures and by varying the laser intensity. The decay of the transient-PA at 1.5 eV for different temperatures is shown in Fig. 6(a). It is found that the decay of the transient-PA at 1.5 eV follows the single exponential decay function as $PA(t) = n(0)\sigma d \exp(-t/\tau)$. By fitting the transient decay curves using the exponential decay function, the monomolecular lifetimes for the temperature range from 80 K to 298 K were obtained. The monomolecular lifetime at temperature 80 K was found to be 1.4 ms, which is slightly higher than the value obtained from the intensity dependence of CW-PA (1.2 ms). Fig. 6(b) shows the variation of monomolecular decay rate with temperature. The
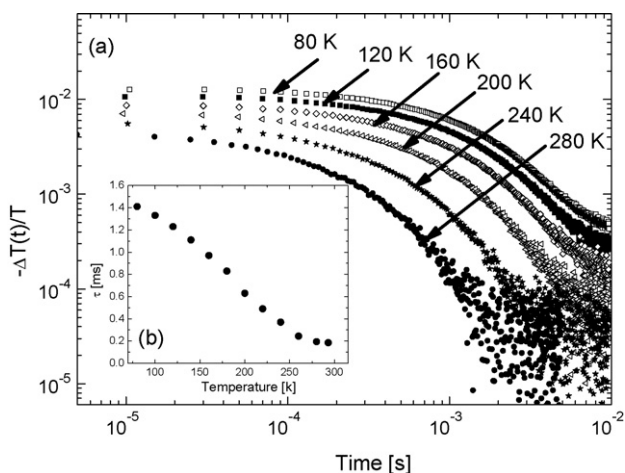

Fig. 6. (a) Decay of the transient-PA at 1.5 eV for various temperatures; inset (b) variation of monomolecular lifetime with temperature.
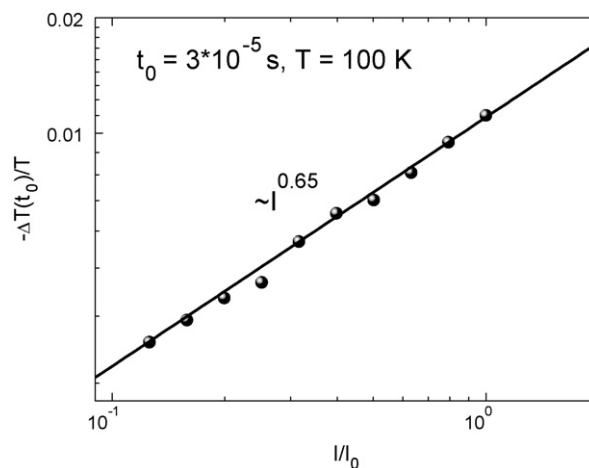

Fig. 7. Variation of transient-PA signal at 1.5 eV with laser excitation intensity.

monomolecular lifetime for triplet decreases with the increase of temperature. The temperature dependence of the monomolecular lifetime can be explained with the temperature-assisted migration of triplet excited states towards the trapping centers and their subsequent deactivation. The temperature dependence of monomolecular lifetimes obtained for BPPPV-PF is also in agreement with the measurements on triplet excitations in PF derivatives [27,28,30].

The dependence of monomolecular lifetime on laser excitation intensity was also studied by measuring the transient-PA for various laser excitation intensities. It was found that the monomolecular lifetime is independent of laser excitation intensity, which is consistent with the assignment of the PA at 1.5 eV to the triplet state excitons. The variation of PA signal with laser intensity (I) shows that the PA signal does not follow the linear laser intensity dependence expected for monomolecular decay process. The experimental data can be fitted with an $I^{0.65}$ law (Fig. 7). This sub-linear dependence could be due to the saturation of excited state population or of the sites available for trapping the photoexcitations [33].

4. Conclusion

We have studied the optical properties of a new biphenylyl substituted PPV-PF copolymer. The PA spectrum of BPPPV-PF shows only the T–T* transition of the triplet excitons at 1.5 eV without any polaronic bands. The temperature dependence of CW-PA at 1.5 eV shows persistent PA at high temperatures, which was different from the temperature dependence of triplet excitons in structurally related PPV and PF derivatives. The monomolecular lifetime of the triplet excitons was found to be around 1.2 ms at 80 K. The monomolecular lifetime decreases with increase of temperature, which was consistent with the monomolecular decay process of triplet excitons in structurally related conjugated polymers. The absence of charged photoexcitations in the PA spectrum and the persistent triplet PA signal at high temperatures in BPPPV-PF indicate that the bulky biphenylyl substitution in the polymer backbone reduces the interchain interaction, which is in good agreement with the high PL property of this polymer.

Acknowledgement

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