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Morphology-dependent optical properties of substituted poly(p-phenylene–ethynylene) (PPE) films

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Abstract

Two different batches of substituted poly(p-phenylene–ethynylene) [PPEs] were synthesized, where the substituents: di-2-butyl(a) and di-2-ethylhexyl(d), were placed on the 2 and 5 positions of the backbone phenyl rings. The photoinduced absorption (PA) spectrum of PPE(a) shows a polaron band at about $850\,cm^{-1}$, whereas PPE(d) does not show polaron bands at all. At $T = 10\,K$ the PA spectrum of PPE(a) in the visible spectral range has two main bands around 1.25 and 1.9 eV, respectively, and a broad shoulder at 2.1 eV. Using the photoinduced absorption detected magnetic resonance (PADMR) spectroscopy, we found that in PPE(a) the 1.9 eV PA band is associated with spin $\frac{1}{2}$, thus it is due to long-lived photogenerated polarons, whereas both the 1.25 eV PA band and 2.1 eV band do not have any spin $\frac{1}{2}$, resonance. In PPE(d) there is a very sharp peak at 1.45 eV, which is due to triplets excitons, and a broad band around 2.0 eV similar to PPE(a), which is due to aggregates.
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1. Introduction

Ever since the first report about electroluminescence devices based on poly(phenylene–vinylene) in 1990 [1], π-conjugated polymers have found their way to the fabrication of light-emitting-diodes, non-linear optical devices and thin-film-transistors [2,3]. Previously poly(p-phenylene–ethynylene) (PPE) was used to fabricate LEDs [4,5], plastic lasers [6] as well as polarizers in logic circuit displays [7].

In this paper we focus on two PPE batches that have different substituents [8]; PPE(a), which stands for di-butyl side-group, and PPE(d) with di-2-ethylhexyl substituted. Fig. 1 insets show the molecular structures of both materials. When drop-casting from chloroform solution on either glass or cesium iodide (CsI) substrates, the rigidity of the backbone enhances the formation of regular layered arrays. The twist between adjacent planes of the phenyl rings in the backbone increases with the size of the side group, resulting in polymer chains with longer conjugation length in PPE(a) films.

In this work we study the optical properties of PPE(a) and PPE(d) thin films. Absorption (ABS) and photoluminescence (PL) spectroscopies were

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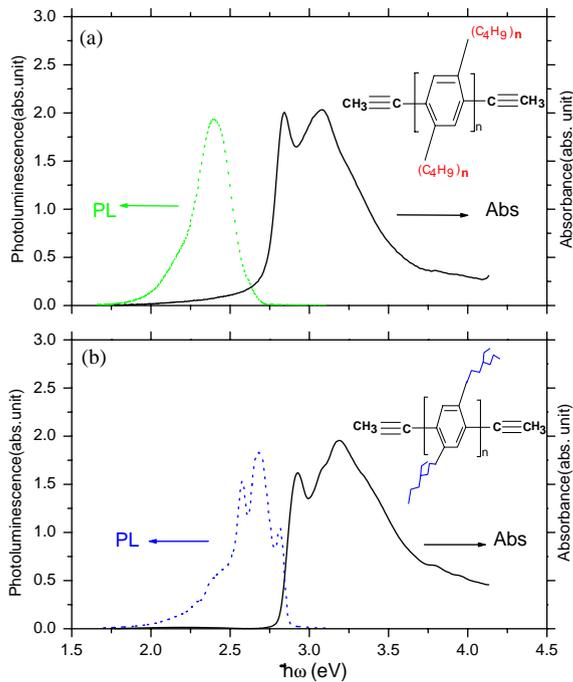E-mail address: jiangxm@physics.utah.edu (X.M. Jiang).

Fig. 1. The absorption and photoluminescence spectra of films of PPE(a) (a) and PPE(d) (b) at room temperature. The insets show the respective polymer repeat unit.

applied to investigate the electronic structure of the PPEs, and photoexcitation dynamics were studied by measuring the photo induced absorption (PA) and photo induced absorption detected magnetic resonance (PADMR) spectra. Various dependences [such as frequency dependence (f-dep), Intensity dependence (I-dep) and temperature dependence (T-dep)] were also measured to further characterize the different photoexcitation dynamics.

2. Experimental

The PPE powders of both (a) and (d) polymers were dissolved in chloroform with the ratio of powder to solvent of 10 mg: 1 ml. Thin films of PPE(a) and PPE(d) were prepared by drop-casting the solution on glass and CsI substrates, and allowing natural evaporation to occur.

The film deposition was done in a nitrogen gas environment using a glove box to avoid possible oxygen contamination. All films were put in vacuum for 24 h before the measurements to ensure complete evaporation of the solvent.

Absorption spectra were measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer, photoluminescence (PL) emission was collected with a Spex Fluorolog 1680 0.22 m double spectrometer, where the samples were excited with a monochromatic 150W Xenon arc lamp, and detected with a photomultiplier tube (PMT) detector. Absorption and PL measurements were performed in an ambient environment at about 300 K.

The photogeneration mechanism and photoexcitation dynamics were studied by PA and PADMR spectroscopies. In these techniques we used a continuous wave Ar^+ laser as a pump light excitation. A combination of various incandescent lamps, diffraction gratings, optical filters and solid state detectors was used to span the probe energy between 0.2 and 3 eV. The change, ΔT of the optical transmission, T was measured versus the probe photon energy, $\leftarrow\omega$ using phase-sensitive methods, where we have $(-\Delta T/T) = n\sigma d$, where n is photoexcitation density, σ is the excitation cross section and d is the thickness of the film. The low energy (infrared range) PA spectrum was measured using a modified Bruker IFS88 Fourier-transform infrared spectrometer equipped with a high sensitivity detector in the range of 400–5000 cm^{-1}, which allowed an Ar^+ laser beam to excite the polymer film. The film was placed into a low-temperature cryostat in the sample chamber of the spectrometer. We measured alternate transmission spectra, T of the film with the laser on and off until resolution of 10^{-5} (when averaging about 20,000 scans) in T was achieved. We then normalize the difference in T, $\Delta T = T_{off} - T_{on}$ by T_{off} to get the PA spectrum. For PADMR the sample was mounted in a high Q microwave cavity at 3GHz equipped with a superconducting magnet and illuminated by the pump and probe beams. We measured the λ-PADMR spectrum, in which the change in transmission, δT due to resonant microwave absorption in a magnetic field is measured at a fixed resonant magnetic field, while the wavelength is scanned. Through PADMR measurements we could obtain the spin states of the photoexcitations

that are associated with specific bands in the PA spectra.

3. Results and discussion

The molecular structure of PPE(a) and PPE(d) are given in Fig. 1 insets. The backbone is quite rigid so that the regular array-like formation is enhanced. Fig. 1 shows the absorption (ABS) and PL spectra of PPE(a) and PPE(d) films. The π–π^* transition (the lowest energy band) shows a small blue shift from PPE(a) (3.06 eV) to PPE(d) (3.14 eV), indicating decreased conjugation length in PPE(d). PPE(a) also has a large Stokes shift of 0.45 eV between the PL 0–0 band and the absorption onset, which is typical for aggregate emission of solid films in many conjugated polymers [9]. In addition, the PL spectrum is rather broad and featureless, which is also characteristic of aggregate emission. On the other hand, PPE(d) has a relatively small Stokes shift of 0.12 eV between the PL 0–0 transition edge and the

absorption and its PL spectrum shows well-resolved vibronic bands, which is consistent with emission from localized states. The PL quantum efficiency of PPE(a) is about 3% and is 8% for PPE(d).

Fig. 2 shows the PA spectra of PPE(a) and PPE(d) at 10 K. The PA spectrum of PPE(a) consists of three bands: P_1 at very low energy (~ 0.1 eV), P_2 at 1.9 eV, which is superimposed on a broad band, and IEX (Interchain Exciton) at 1.2 eV. P_1 and P_2 are correlated with each other by their frequency dependence, intensity dependence and temperature dependence, but not to the IEX band. The spin $\frac{1}{2}$ λ-PADMR of PPE(a), shown in Fig. 3(a), consists of a $\delta n < 0$ band at P_2 energy position and an onset of a negative band that is due to the tail of the P_1 band. These two negative PADMR bands are due to spin $\frac{1}{2}$ polarons. We tentatively assign the positive PADMR band seen at 0.8–1.6 eV (Fig. 3(a)) to a singlet exciton absorption band caused by excess single excitons population, which results from the excess spin
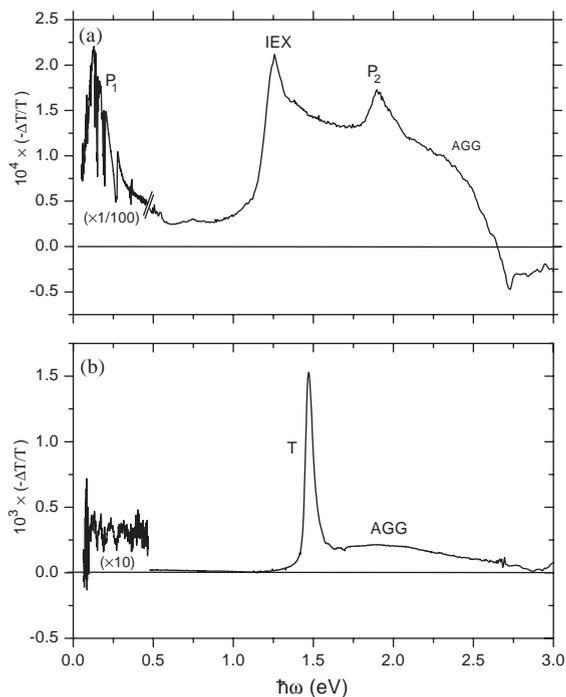

Fig. 2. The PA spectra of PPE(a) (a) and PPE(d) (b) at $T = 10$ K. Various PA bands such as P_1, P_2, IEX, T and AGG are assigned (see text).
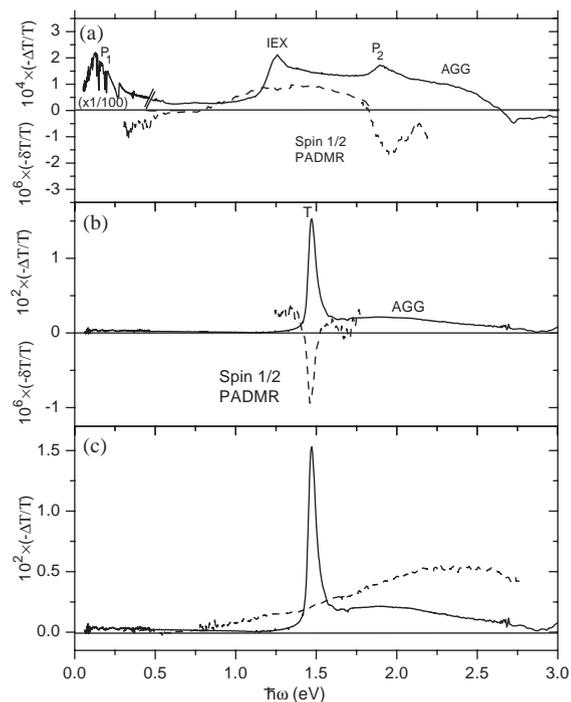

Fig. 3. The PA (solid line) and PADMR (dashed line) spectra of PPE(a) (a) and PPE(d) (b) at $T = 10$ K. (c) The PA spectrum of PPE(d) before (solid line) and after (dashed line) photo-oxidization.

anti-parallel polaron pairs created upon micro-wave absorption [10].

On the contrary, the photoexcitations in PPE(d) are quite different (Fig. 2(b)). The PA spectrum is dominated by a sharp band at 1.45 eV and a broad band around 2.0 eV. In addition, there is no evidence for photoinduced infrared active vibrations (IRAVs), which usually accompany charged excitations in conjugated polymers [11,12]. We assigned the 1.45 eV PA band to excited state absorption of triplet excitons (abbreviated as T), whereas the broad featureless band at about 2.0 eV (abbreviated as AGG) is probably due to aggregates. This could be further verified by measuring PA following photo oxidization, which is shown in Fig. 3(b) (dotted line). The triplet excitation has completely disappeared and the PA spectrum is now dominated by aggregates. The PL was also quenched upon photooxidation; the PL quantum efficiency decreased from 8% to 0.2% after photooxidation. The λ-PADMR spectrum for

PPE(d) is rather simple (Fig. 3(b)); it only consists of a single small band at 1.45 eV, which coincides with the triplet band.

We also measured the pump intensity dependence of the various PA bands in PPE(a) and PPE(d). Fig. 4(a) shows the I-dep in PPE(a). The PA intensity of the polaron band and the aggregate band are linear with pump intensity, showing monomolecular recombination process. The IEX band, on the other hand shows sub linear relation ($\sim I^{0.9}$), indicating a bimolecular recombination mechanism. All three PA bands have a tendency towards saturation at high laser power; this results most probably from traps that enhance recombination as they become saturated. Fig. 5 shows the intensity dependence of the PA bands in PPE(d) at $T = 80$ K. The I-dep of the aggregates band could not be fit using a linear curve. We thus fit it using polynomials, indicating more than one kind of recombination mechanism. The triplet band has also a linear intensity relation, showing a monomolecular recombination process.
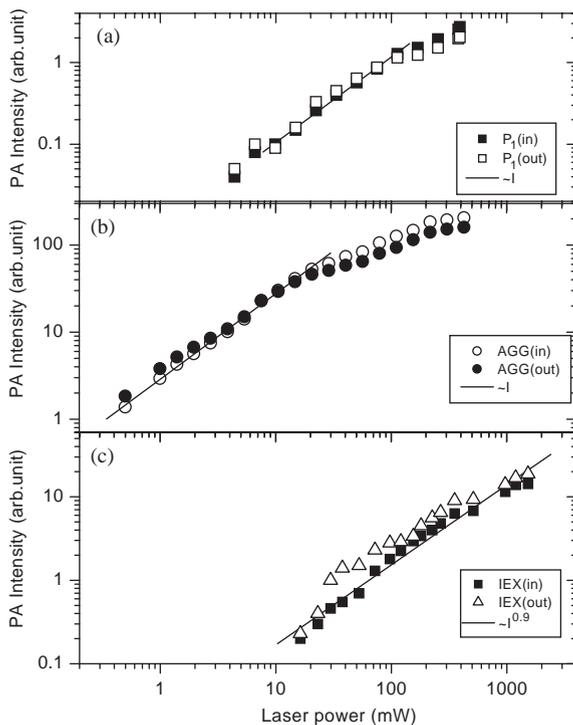

Fig. 4. Intensity dependence of the in-phase and quadrature components for various PA bands in PPE(a). (a) is for polaron (P_1), (b) for aggregates (AGG) and (c) for IEX.
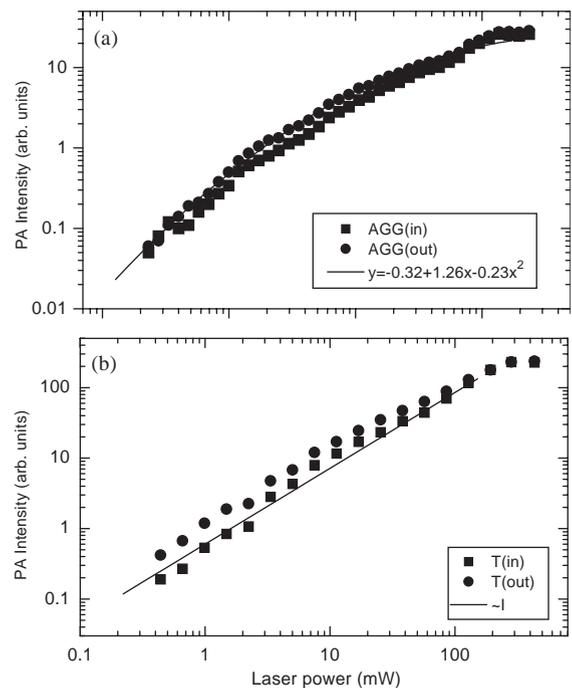

Fig. 5. Intensity dependence of the in-phase and quadrature components of various PA bands in PPE(d). (a) is for aggregates (AGG) and (b) for triplets (T).

4. Conclusions

We have used several optical spectroscopies for studying the influence of film morphology on the optical properties of PPE polymer films. PPE(a) with linear side group [(di-2-butyl) substituent] has essentially a planar backbone structure in the film and self-assembles to form layered, regular arrays; whereas PPE(d) with bulky side group has less order in the film, thus the absorption and photoexcitations are very different in these two polymer films. Polarons are formed in the better-ordered PPE(a), whereas triplet excitations are dominant in PPE(d). We also found that aggregate formation is important for both polymers.

Acknowledgements

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