

Photoluminescence quenching in poly(*p*-phenylene vinylene) derivatives

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Abstract

We investigated the photoluminescence (PL) quenching of the copolymer, poly(2,5-dimethyl-phenylenevinylene-*co*-2-methoxy-5-hexyloxy-phenylenevinylene (DMPPV-*co*-MHOPPV), focusing on the difference between pure films and copolymer-poly(ethylene oxide) (PEO) blends with and without applied bias in the LEDs. PL quenching of DMPPV-*co*-MHOPPV is decreased by dispersion in an inert host, PEO. Results show that the introduction of alkyl groups in the main backbone or copolymer, which can affect the interaction of polymer chain, and the PL quenching, can be decreased due to the decreasing of dissociation of bound excitons and limiting excitons to migrate quenching sites. In the LEDs, by studying the different PL quenching with the negative and positive bias, we infer that the internal field in the LEDs decreases the probability of dissociation of bound excitons. Our experimental results suggest that by means of tuning the chemical structure of polymers and the internal field of LEDs, the dissociation of excitons will be controlled and the luminescence quantum yield can be improved. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Photoluminescence quenching; Poly(*p*-phenylene vinylene); Luminescence quantum yield

The optical and electronic properties of conjugated polymers have been the focus of interest in the past few years, since the observation of electroluminescence from poly(*p*-phenylene vinylene) (PPV) [1]. Conjugated polymers may offer many advantages over the traditional materials used in the present generation of LEDs. For example, properties of conjugated polymers can be tuned by chemical modification. The addition of a side chain onto the conjugated polymer PPV enables solubility of conjugated polymers. In fact, polymer light-emitting devices (LEDs) show attractive characteristics, including efficient light generation and tuning colors. This indicates that conjugated polymers taken as materials for electroluminescence devices have enormous potential applications. As long as conjugated polymers were fabricated electroluminescence devices, many problems existed, such as efficiency and stability. At present, the simplest organic LEDs consist of a thin, light-emitting polymer film sandwiched between two metal electrodes. Even in these structures there is a need for a better understanding of the mechanisms of operation and methods to control the optical and electrical properties of the polymer film to optimize charge injection, charge transport, charge recombination and light-emission processes. Studying the photoluminescence quenching of

polymers helps us to understand the light-emission processes of polymers.

In the light-emitting diodes, one of the major aspects determining the quantum yield for electroluminescence (or photoluminescence) is the competition between radiative and nonradiative decays of the electron–hole pairs that are created within the polymer. In conjugated polymers, electron–hole pairs form polaron excitons; this means that the pairs are bound both by a local geometry relaxation and through the Coulomb effects (exciton). The pairs can migrate along the chains and are therefore susceptible to trapping at quenching sites where nonradiative processes can occur. As a result, it is highly desirable to try and control the migration of the electron–hole pairs (excitons) into chain segments where radiative decay could perfectly occur [2]. However, an important reason for luminescence quenching of conjugated polymers is that singlet excitons are dissociated into the polarons (or dipolarons). This is because the binding energy of excitons is finite (in the range of several hundred meV). Frankevich et al. have attained binding energies of polymers of about 0.17, 0.3 and 0.23 eV for PPV, poly(1,4-phenylene-1,2-dimethoxy-phenylene vinylene) (DMOP-PPV) and poly(2-pyrenylene-1,4-phenylene vinylene) (PPPV), respectively [3]. In fact, the different interaction of polymer chains can affect the dissociation of excitons [4]. In the light-emitting diodes, it is also an important reason that the high electric field

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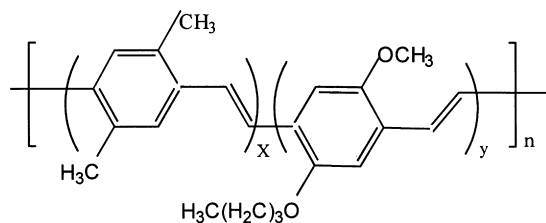


Fig. 1. The chemical structure of copolymer, DMPPV-co-MHOPPV.

results in luminescence quenching. The bound excitons will be dissociated polarons (or bipolarons) when the energy of electric field is greater than the binding energy of excitons [5]. Cw-luminescence experiments on dye-doped polymers and inorganic semiconductors have shown that applications of an electric field reduces the PL yield [6,7].

In this paper, we studied the PL quenching of copolymers with and without the electric field, to detect the mechanism of luminescence quenching in pure film and inert-host blends and find some methods to improve the luminescent efficiencies.

1. Experiments

The chemical structure of the copolymer, poly(2,5-dimethyl-phenylene vinylene-co-2-methyl-5-hexyloxy-phenylene vinylene) (DMPPV-co-MHOPPV), is shown in Fig. 1 Poly(ethylene oxide), PEO was purchased from ACROS and the average molecular weight was 100,000. PEO was used as the inertial material for copolymer blends and did not produce fluorescence. Both DMPPV-co-MHOPPV and PEO were dissolved into chloroform, respectively. Films of pure film and dilute blends with 0.3 μm thickness were spin cast onto quartz from chloroform solutions. In order to investigate PL quenching with the applied electric field, samples consisting of about 100–200 nm thickness were also spin coated polymer layer sandwiched

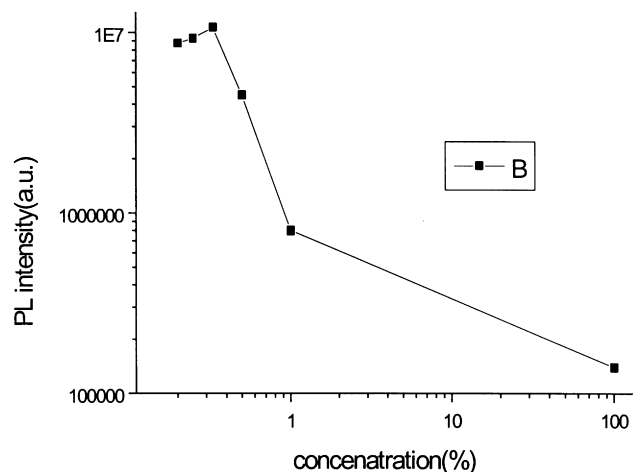


Fig. 3. The concentration dependence on brightness intensity in dilute blends.

between a transparent indium-tin-oxide (ITO) coated glass substrate and an aluminum (Al) electrode. The photoluminescence spectra were measured with a Spex Fluorolog 3 spectrometer. The absorption spectrum was taken using an UV-3101 absorption spectrometer.

2. Results and discussion

Fig. 2 shows the absorption spectrum of pure film and PL spectra in the pure film and blend. DMPPV-co-MHOPPV has a broad featureless absorption with a maximum at 445 nm. By extrapolating the absorption spectrum, the optical band gap was estimated to be 2.18 eV (about 570 nm). The PL spectra were measured with the excitation at 466 nm. The PL spectra of thin films are largely blue-shifted, featureless and broader in diluted blends. The peak position of the PL spectrum is independent of excitation wavelength in high concentrations (greater than 0.3%).

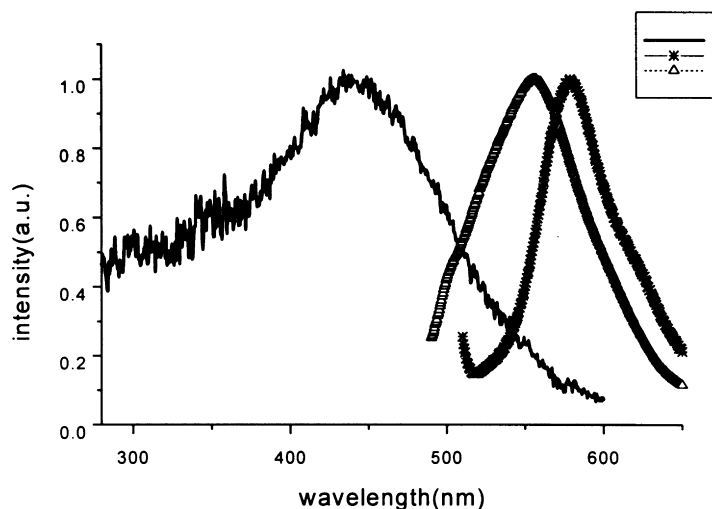


Fig. 2. The absorption spectrum of pure film (solid line) and PL spectra of pure film (open star) and blend (0.1%) (open up triangle).

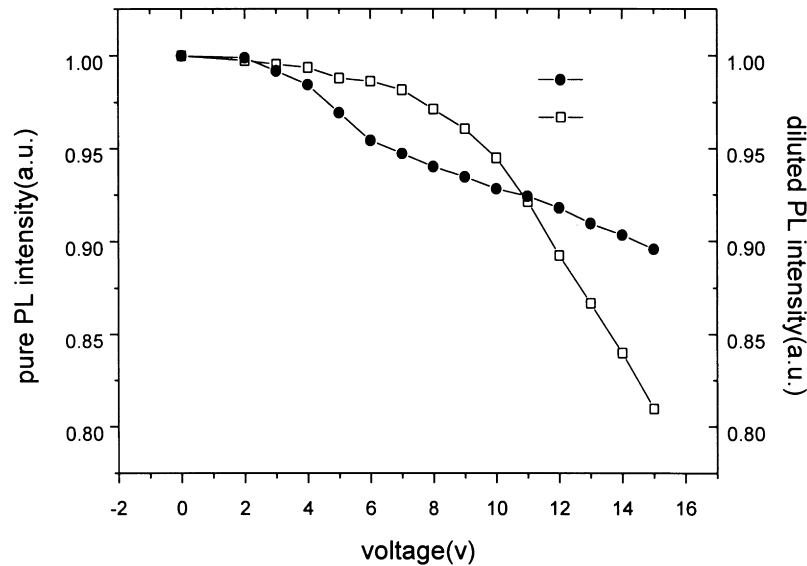


Fig. 4. The amount of PL quenching of pure film (open square) and blend (0.1%) (full circle) in dependence on the applied positive bias.

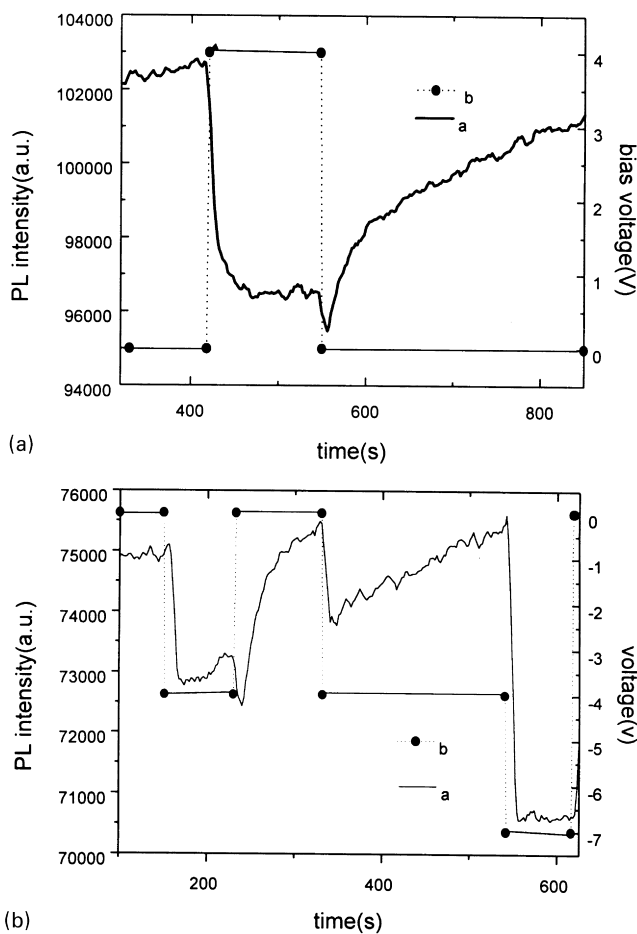


Fig. 5. PL quenching of pure film dependence on the applied bias voltage (4 V). The solid lines (a) show PL quenching dependence on time with and without the bias (4 V). The solid lines between full circles represent the applied bias in LEDs.

When the blends are further diluted, the peak of emission depends on the excitation energy (not shown). This suggests that excitons formed by photon absorption on high band gap segments of chains can easily migrate or hop to lower energy segments before emitting photons in concentrated blends. The interaction of the interchain is very weak and the exciton can only migrate along the same chain in further dilute blends. This is a copolymer of poly(2,5-dimethylphenylene vinylene) (DMPPV) and (2-methyl-5-hexyloxyphenylene vinylene) (MHOPPV). Since the latter compound possesses a lower band gap (by about 0.2–0.3 eV) than DMPPV, it was expected that the electrons and the holes would get confined within MHOPPV segments of the copolymer chains, where they would more readily recombine [2]. Thus, the excitons are localized and the emission comes from the intrachain singlet excitons in dilute blends.

Fig. 3 shows the concentration dependence on brightness intensity in dilute blends. The relative intensity of PL brightness promptly increases from pure film to the diluted blends (about 0.3%), and then tends to maximize the quantum yield of copolymers in further dilute concentrations. This result indicates that the packing of copolymer chains will be influenced and the interchain coupling might be very weak when the copolymer is dispersed into the inert material of PEO. Therefore, we can conclude that the incorporation of the flexible alkyl groups into the rigid rod-like backbone will reduce the stiffness of the polymer backbone and influence the packing of adjacent molecules. In the literature it is reported that the one-dimensional self-localized polaron (or dipolarons) will not be stable if the strength of the interchain coupling exceeds the magnitude of the polaron binding energy [4]. In our experiments, we do not have sufficient evidence to explain that the dissociation of excitons results in photoluminescence quenching. However, according to the literature, the emission comes

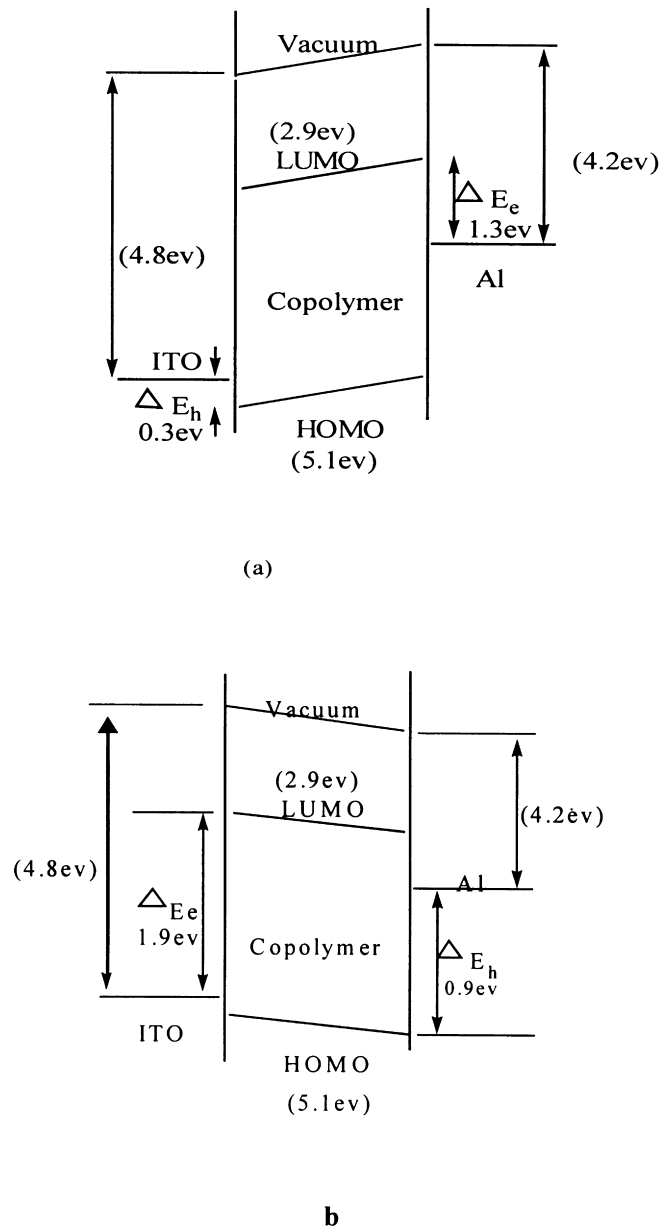


Fig. 6. The illustration of the HOMO and LUMO of DMPPV-co-MHOPPV with the bias. ΔE_h and ΔE_e represent the barrier for hole and electron injected, respectively. (a) Barrier for hole and electron injection with the positive bias. (b) Barrier for hole and electron injection with the negative bias.

from the radiative decay of singlet excitons [2,8]. Therefore, PL quenching, in great part, is attributed to the dissociation of excitons. Hence, it is very important to know how to reduce the dissociation of excitons in LEDs.

Fig. 4 shows the amount of photoluminescence quenching in dependence on the applied positive bias. In the experiments, we find that the quenching of pure films is stronger than that of blends (about 0.5%), which suggests that introduction of alkyl groups in the main back can decrease the dissociation of excitons. On the other hand, the luminescence quenching with the high electric field indicates that many bound excitons are dissociated. Similar results as shown in Fig. 4 are obtained for PPV sandwiched between ITO and the Al electrode [9]. The luminescence quenching

will lead to sublinear dependence on applied bias of the light emission of polymer based LED. Hence, the condition for LED operation should be chosen such as to minimize the driving field. To further research the mechanism of PL quenching, we also studied luminescence quenching in the applied positive and negative bias (Fig. 5). After the applied positive bias of 4 V, the photoluminescence is rapidly quenched and then gradually trends to balance. But the luminescence first decreases instantly and then enhances gradually at the applied negative bias of 4 V. In the meantime, we also found that the photoluminescence intensity minimizes, which had a few seconds time after the applied bias. This does not correspond with the fact that the luminescence quenching continues on the time scale of several

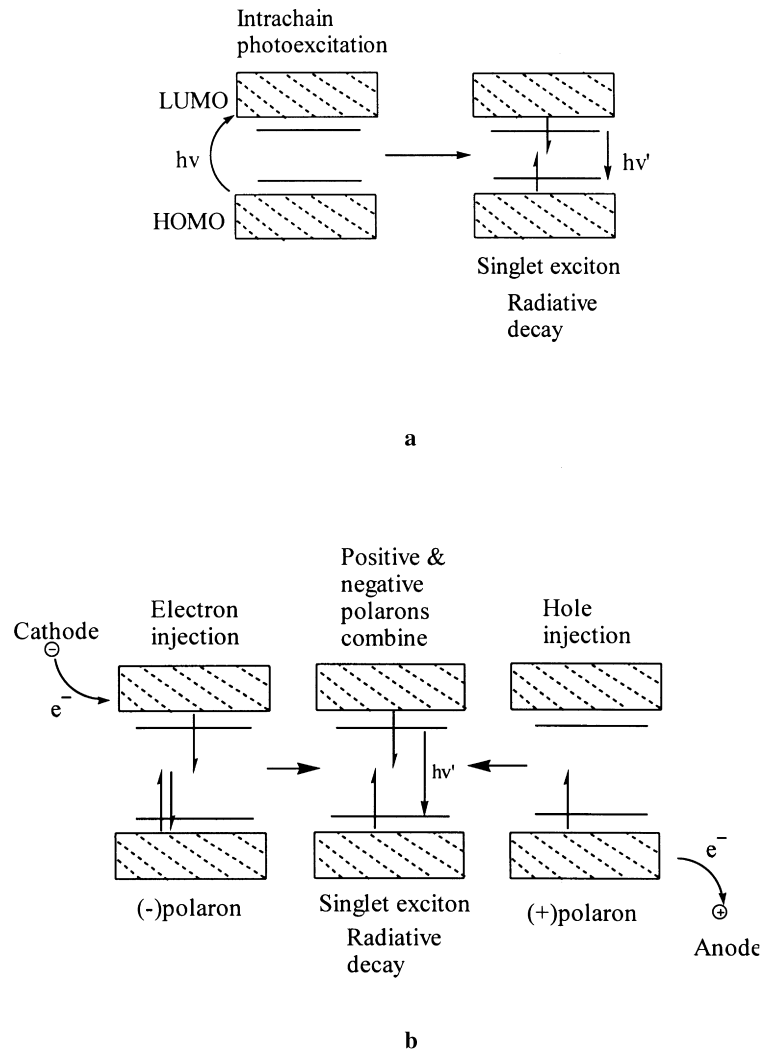


Fig. 7. (a) Scheme for photoluminescence. (b) Scheme for electroluminescence.

hundred ps [5]. However, one fact in Fig. 5 reveals that the luminescence intensity taken in the balance is a long process when the bias is applied or ruled out. The reason will be explained later. In the LEDs, charge carriers are injected into the copolymer layer and the singlet exciton-free carried interaction can result in luminescence quenching. However, the current quickly tends to become constant after applying the bias voltage. Hence, the free-carriers injected is not the main reason that results in the unbalance of a long time in PL intensity. The reason is that the intensive electric field of negative bias is more stronger than that of positive bias due to the different barriers for electrons and holes injections (Fig. 6). When LED is applied, positive bias, barriers of holes and electrons injection from ITO and AL electrodes are about 0.2 and 1.2 eV, respectively; barrier of holes and electrons injected from Al and ITO electrodes are 1.9 and 0.9 eV. Hence, the injection of carriers with negative bias is more difficult than that of positive bias. The bound excitons are dissociated into charge carriers that cannot easily inject into two electrodes and gradually accumulate copolymer

and electrode interfaces. Thus, the internal field is gradually found and enhanced, wherein a lot of time has to be spent because of lack of charge carriers. According to the above result, we may further deduce that if proper free charge carriers existed in the surface between copolymers and electrodes, the PL or EL quenching may be reduced due to the suppression of exciton dissociation. However, in our experiments, the declining of luminescence quenching sacrifices many carriers injected to decrease the dissociated excitons. Therefore, this is not beneficial for improving the brightness of LEDs if the carriers too lack in EL devices. However, deMello et al. and Pei et al. have reported that the movement of the ions in the light-emitting electrochemical cells (LECs) is responsible for the Ohmic electrode-polymer contacts [10,11]. This implies that the lack of carriers may be overcome by the addition of ions in devices. To the best of our knowledge, there are no reports in the literature as to whether the dissociation of excitons is decreased or not. When the high electric field (such as 7 V) was applied, the external field greatly exceeds the intensive

field and hence the quenching does not apparently decrease.

To further understand the luminescence quenching of polymer LEDs, we should compare the processes of PL and EL (Fig. 7). Photo-excitation of an electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) generates a single exciton which can decay radiatively with emission of light at a longer wavelength than the absorbed. In the EL experiment, injection of electrons into the LUMO and holes into the HOMO generates negative and positive polarons, respectively, which migrate under the influence of the applied electric field and combine on a segment of the polymer chain to form the same singlet exciton as is produced in the PL experiment. Depending on the mechanism of electric field-induced singlet exciton of dissociation, the singlet excitons are probably dissociated into polarons under enough high electric field and luminescent quenching takes place. Thus, the driving field of the devices operation should become low as soon as possible.

3. Conclusion

On the basis of the luminescence quenching experiments and mechanism, we may improve the efficiencies and minimize luminescence quenching by the following methods. By the addition of properly alkyl chain into the main backbone or copolymer; this may improve the chemical and electronic structure and the interaction of the polymer chain, which can limit excitons to migrate to quenching sites and decrease the dissociation of excitons. In the LEDs, if considerable negative and positive carriers exist, which can be found the internal field in the applied bias balanced in part of the

external field, this will decrease the probability of dissociation of bound excitons. If the injection of negative and positive carriers can be solved by some methods (such as the mobility of ions), the efficiencies in LEDs will be greatly improved.

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