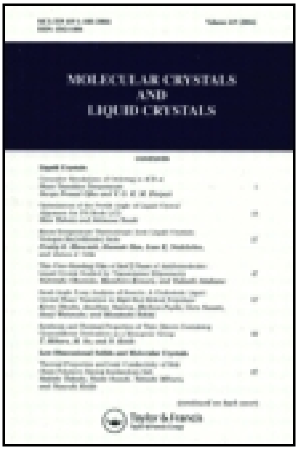

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Photoinduced Electron Transfer in PPV-Viologen Composites

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Photoinduced Electron Transfer in PPV-Viologen Composites

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PPV was sensitized by ethyl viologen which is well known as a good electron acceptor, to achieve efficient ionization of the excitons created by photoexcitation of PPV. PPV/ethyl-viologen composites were successfully prepared from PPV-precursor and ethyl-viologen because both compounds could be soluble in polar solvents such as methanol, water etc. We observed dramatic decrease of photoluminescence efficiency in the PPV/ethyl-viologen composite film as compared with PPV film. This is attributed to photoinduced electron transfer in PPV/ethyl-viologen composites and the efficient ionization of the excitons was occurred in this composite film. Time-resolved photoluminescence of composite films was also studied to obtain the information of this photoinduced electron transfer dynamics.

Keywords: PPV, photovoltaic, electron transfer, viologen

INTRODUCTION

Conjugated polymers have attracted much research interest in science and technology in the past few decades as semiconductors and electroactive materials for diverse applications[1]. Recently, the discovery of polymer light-emitting diodes (LEDs) and the development of processible semiconducting polymers with improved quality have stimulated that photonic devices made with such polymers as the active materials have received renewed attention[2]. There has been interest in the photovoltaic and photoconductive properties of poly(1,4-phenylenevinylene) (PPV) and its derivatives over many years[3,4], but devices made with semiconductors of this type tend not to show useful efficiencies. There are several reasons for this, of which the difficulty in achieving efficient ionization of the excitons initially created by photon absorption is probably the most important, though poor electron or hole mobilities are also problematic. The energy conversion efficiencies of photovoltaic cells made with pure conjugated polymers were typically 10^{-3} to 10^{-2} %, too low to be used in applications. Heeger *et al*[4], reported the improved energy conversion efficiencies of photovoltaic cells made with composites of conducting polymers as donors and buckminsterfullerene (C_{60}) and its derivatives as acceptors. The ultrafast photoinduced electron transfer between donor and acceptor provides an effective way to overcome early time-carrier recombination in organic systems and thus to enhance their optoelectronic response.

In the present works, PPV and its derivatives (PPVs) were sensitized by ethyl viologen which is well known as a good electron acceptor, to achieve efficient ionization of the excitons created by photoexcitation of PPVs. Their structures are shown in Fig. 1. Viologen derivatives have been subjected to numerous photochemical studies as an electron acceptor and the good solubility of them in water and methanol enables to form a composite film with polyelectrolyte PPV precursor polymer. As expected, ultrafast photoinduced electron transfer was observed in above composite films and the increases of the quantum efficiency for the free carrier generation and the photocurrent of photovoltaic cell are expected.

EXPERIMENTAL

Ethyl viologen dibromide was purchased from Aldrich Chemical Co. PPV was prepared via the sulphonium salt precursor route as reported by previous papers. Ethyl viologen dibromide was dissolved in the PPV precursor solution in methanol and water (vol. ratio = 1:1) with different concentrations. Three different composite solutions were prepared. Precursor composite films were prepared by spin-coating of above composite solutions onto the useful substrates, fused silica and glass for spectroscopic studies. The optical density and the thickness of the polymer coating were controlled by the spinning rate.

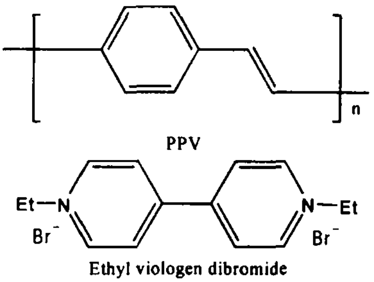

FIGURE 1 Molecular structures of PPV & ethyl viologen dibromide.

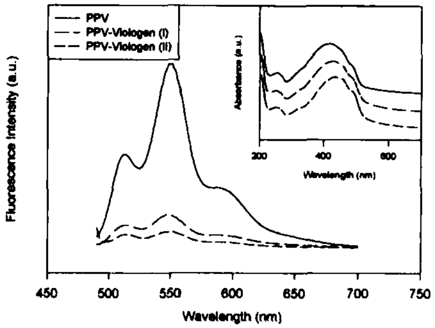

FIGURE 2 Fluorescence spectra of PPV & viologen doped PPVs (I-17 wt %, II-46 wt % doping). The inset shows absorption spectra.

Conversion to PPV was achieved by heating under vacuum at 200 °C for 6 h. Steady-state PL spectra of the films were taken by pumping with the cw 488 nm from a argon ion laser. Fluorescence decay was recorded by the time-correlated single-photon counting method. The light source was second harmonic (405 nm) of a Ti:Sapphire laser.

RESULTS & DISCUSSION

Ethyl viologen dibromide was dissolved in PPV precursor in methanol/water cosolvents with two different weights. The viscosity of precursor polymer solution decreased as the viologen contents increased and this phenomenon could be explained by the salt effect in polymer electrolyte. The viologen contents of composite polymers were determined by gravimetric method and were 17 and 46 wt %, respectively. As the decomposition temperature of viologen is 278 °C, we could expect that viologen might be stable during the thermal elimination of PPV precursor which was performed at 200 °C. Transparent films were obtained and phase separation or crystallization of viologen was not observed.

Absorption spectra of PPV and viologen doped PPVs are shown in the inset of Fig. 2. There was no significant change in absorption spectra of viologen doped PPVs except slight red-shift of π-π^* transition absorption peak. It may not result from the ground state interaction between PPV and viologen such as ground state charge transfer. It can be explained by morphological change of PPV induced by doping of viologen.

Fig. 2 shows steady-state photoluminescence (PL) spectra of PPV and viologen doped PPVs at room temperature. PPV shows typical PL spectrum of emission maxima around 513, 550, and 591 nm. In viologen doped PPVs, we could observe dramatic PL decreases without emission feature change. The relative PL efficiencies of viologen doped PPVs are about 20 % for 17 wt % doping and 10 % for 46 wt % doping as compared with PL of PPV. This is attributed to photoinduced electron transfer between PPV and viologen and the efficient ionization of the excitons was occurred in these composite films. It is well known that viologen derivatives can accept electron and conjugated polymers can donate electron[5], and then singlet exciton from photoexcitation of PPV can be ionized easily into charged species. These phenomena may be similar to the fact observed in photoexcitation of MEH-PPV and C_{60} composite films previously reported[4].

Time-resolved PL of viologen doped PPVs (not shown here) showed faster decay than that of PPV, which is also attributed to photoinduced electron transfer. From the above results, it is expected that high performance photonic devices such as photodiode and photovoltaic cell can be developed using the viologen doped PPVs and these studies are under investigation.

Acknowledgments

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