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Pyridine-Based Conjugated Polymers: Photophysical Properties and Light-Emitting Diodes

by

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13. ABSTRACT (Maximum 200 words)

We study the photophysical properties of the pyridine-based polymers poly (*p*-pyridyl vinylene) (PPyV) and poly (*p*-pyridine) (PPy). The primary photoexcitations in the pyridine-based polymers are singlet excitons. We observe direct intersystem crossing (ISC) on picosecond timescales with the volume density of triplet excitons varying with the sample morphology (film or powder). These effects are demonstrated clearly by examining the millisecond photoinduced absorption characteristics of powder and film forms of PPyV. The pyridine-based polymers have been shown to be promising candidates for polymer light-emitting devices , both the "conventional " diode device and symmetrically configured ac light-emitting (SCALE) device. Here we examine the role of "insulating" layers and their interfaces with the emitting layer and electrodes in the SCALE device operation, with emphasis on the central role of the polymer-polymer interfaces.

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PYRIDINE-BASED CONJUGATED POLYMERS: PHOTOPHYSICAL PROPERTIES AND LIGHT-EMITTING DEVICES

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Abstract:
We study the photophysical properties of the pyridine-based polymers: poly(*p*-pyridyl vinylene) (PPyV) and poly(*p*-pyridine) (PPy). The primary photoexcitations in the pyridine-based polymers are singlet excitons. We observe direct intersystem crossing (ISC) on picosecond time scales with the volume density of triplet excitons varying with the sample morphology (film or powder). These effects are demonstrated clearly by examining the millisecond photoinduced absorption characteristics of powder and film forms of PPyV. The pyridine-based polymers have been shown to be promising candidates for polymer light-emitting devices, both "conventional" diode device and symmetrically configured ac light-emitting (SCALE) device. Here we examine the role of "insulating" layers and their interfaces with the emitting layer and electrodes in the SCALE device operation, with emphasis on the central role of the polymer-polymer interfaces.

INTRODUCTION

Of considerable interest of late in the conjugated polymer field is the electroluminescent capabilities of conjugated polymers such as poly(*p*-phenylene) (PPP) and poly(*p*-phenylene vinylene) (PPV) (Refs. 1,2). The nature of the primary excitations in PPV has been under considerable discussion (Refs. 3-7). Some authors propose that charged carriers, such as polarons or bipolarons, are produced directly upon photoexcitation, due to a strong electron-phonon coupling with a weak Coulombic interaction (Ref. 3). Others suggest that excitons are the primary excitation because of a strong Coulomb interaction (Refs. 4-7).

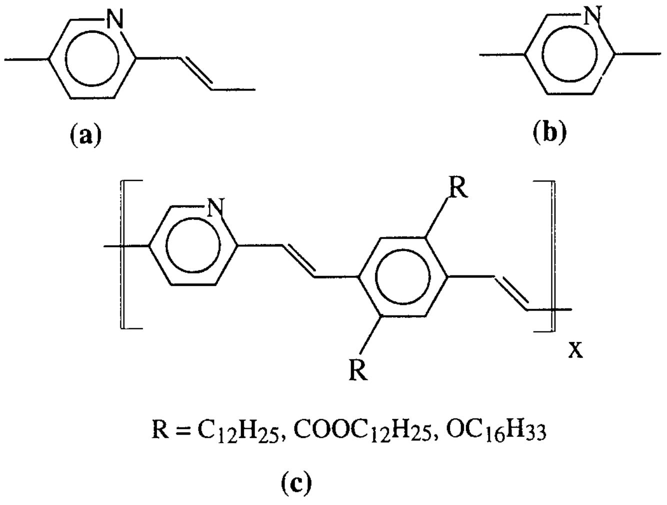

Fig. 1 Schematic structure of (a) poly(*p*-pyridyl vinylene) (PPyV), (b) poly(*p*-pyridine), and (c) copolymers of PPyV and PPV derivatives.

The pyridine based analog of PPV, poly(p-pyridyl vinylene) (PPyV), offers the possibility of examining the underlying photophysics of the PPV system. The schematic structures of PPyV, poly(*p*-pyridine) (PPy) and copolymers of PPyV and PPV derivatives are shown in Figure 1. The charge conjugation symmetry associated with PPV is broken by the addition of the nitrogen heteroatom in PPyV. Unlike PPV, the nitrogen heteroatom allows the polymer to be studied in powder, film and solution forms. The nonbonding (n,π^*) states enhance intersystem crossing (ISC) to the triplet manifold via spin orbit interaction (Ref. 8).

The pyridine-based polymers have been shown to be promising candidates for polymer light-emitting devices (Ref. 9). As compared to PPP and PPV, PPy and PPyV show larger electron affinity, which lowers the LUMO level (or conduction band edge). As a result, the pyridine-based polymers exhibit excellent stability against oxidation and show better electron transport properties.

We summarize absorption and photoexcitation studies on powder and film forms of PPyV and the application of these materials to LED (light-emitting diode) and particularly, SCALE (symmetrically configured AC light-emitting) devices.

Immediately following excitation (~ ps), intrachain singlet excitons are created in PPyV in both forms. The time dynamics of the photoluminescence (PL), photoinduced absorption (PA) and stimulated emission (SE) indicate that all three stem from the singlet exciton (Ref. 10). In addition, triplet excitons are produced *directly* from singlet excitons via an enhanced ISC from the singlet exciton manifold (Ref. 10). The differing morphologies of the powder and film forms show differing levels of triplet exciton and polaron production. The time dynamics of the longer lived signal (> 1 ns) in the picosecond photoinduced absorption (ps PA) experiment indicate that more triplets are produced in powders than films. From millisecond photoinduced absorption (ms PA), triplet excitons are the dominant photocreated species in powders of PPyV. In films, the triplet signal is much smaller; polarons are the dominant state on the millisecond time scale.

PHOTOPHYSICS

The ps PA absorption spectra at 0 ps time delay for powder and solution forms of PPyV are shown in Figure 2. The solid line represents data taken on a broadband femtosecond system. The squares and circles are data taken on a picosecond system. The cw PL (---) and absorption (-.) are shown for comparison. The ps PA spectrum consists of three regions: PA peaking around 1.4 eV, stimulated emission (SE) ~ 2.1 - 2.6 eV and photoinduced bleaching (PB) at the absorption edge beginning around 2.6 eV. The 1.4 eV feature may be a result of transitions between singlet exciton states (Ref. 11). The observed SE is a direct result of singlet exciton states, indicating a potential in these systems for laser operation, provided there is a high enough gain. The PB feature is a result of a loss of oscillator strength in the absorption band associated with the photoinduced energy transition. In the case of the solutions, the ps PA at 1.4 eV and SE at 2.2 eV follow the PL decay for times less than 1.3 ns for PA and 300 ps for the SE indicating that the PA and SE originate from singlet excitons. A crossover to a longer lived state is observed in the

SE at 2.2 eV for times greater than 300 ps, indicating the existence of another photoexcited species in addition to the singlet exciton (Ref. 10). The ps PA signal is independent of solution concentration and has linear intensity dependence, strongly suggesting that the long-lived species is a triplet exciton.

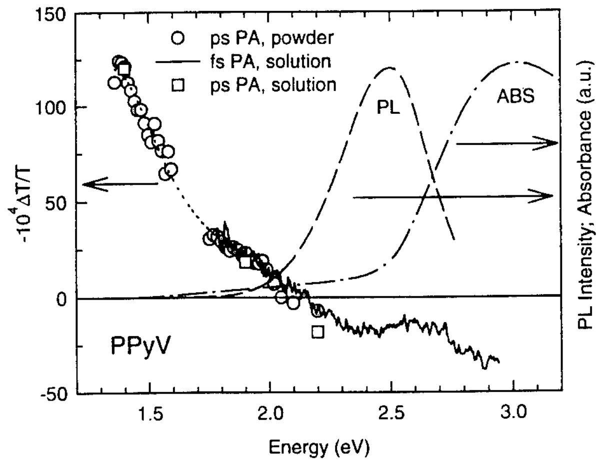

Fig. 2: The ps PA at 0 ps for powder (○) and ~ 10^{-2} M solution in HCOOH (□ and —). The PL (---) and absorption (–.) spectra are shown for comparison (from Ref. 10).

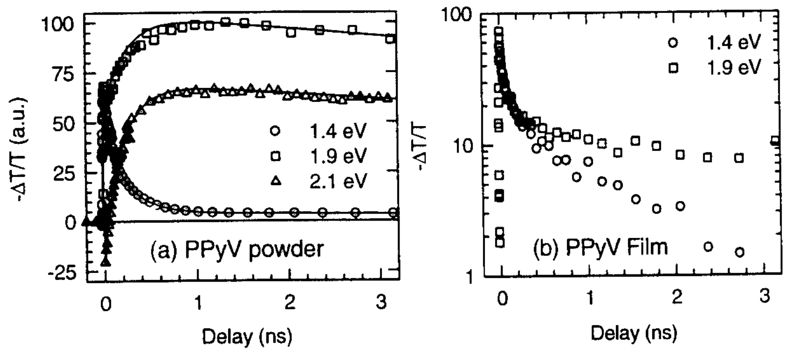

Fig. 3: (a) Decay of PA at 1.4 eV (○), 1.9 eV (□) and 2.1 eV (△) for PPyV powder. (b) Decay of PA at 1.4 eV (○) and 1.9 eV (□) for a PPyV film cast from HCOOH solution (Ref. 11).

Fig. 3(a) shows the decay of PA at various probe energies (E_{pump} = 2.8 eV) for a powder form of PPyV. The 1.4 eV PA follows the decay at the corresponding energy in the solution PA and PL (not shown), indicating the PA arises from singlet excitons (Ref. 10). At higher energies, the decay of the ps PA is is swamped by a longer lived signal for times greater than ~ 100 ps. As will be shown below, the 1.9 eV feature can be attributed to triplet excitons. The rise of the 1.9 eV feature can be correlated with the decline of the 1.4 eV, indicating that triplet excitons are directly produced via intersystem crossing (ISC).

The ps PA measurement for films of PPyV are similar to the powder/solution results with the only difference being the lack of observed SE and the relation of the PA to the PL (Ref. 11). The lack of SE in films may be attributed to aggregate sites, as discussed elsewhere (Ref. 12). Fig. 3(b) shows the PA decay of PPyV film. Once again the 1.9 eV feature deviates from the 1.4 eV feature for times greater than 500 ps, consistent with triplet exciton production. The magnitude of the deviation is, however, about 20 times smaller than in powders indicating that powders have enhanced triplet exciton production, as discussed below.

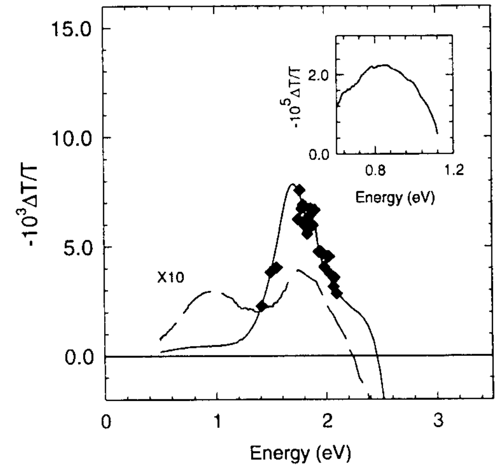

Fig. 4: The millisecond photoinduced absorption spectra of powders (—) and films (– –) of PPyV at 80 K using a pump beam energy of 2.71 eV. The spectral response of the 1.9 eV ps PA at 1 ns time delay (◆) is also plotted. The inset shows the quadrature signal for powder samples.

Figure 4 shows the ms PA of powders and films of PPyV. The samples were excited with the 2.71 eV line from an Ar^+ laser with an incident intensity of 150 mW/cm^2 and chopped with a mechanical chopper at 15 Hz. Also displayed is the spectral response (◆) of the ps PA signal in powder form at a 1 ns time delay. The spectral response closely resembles the ms PA signal (– –), which is attributed to longer lived triplet exciton production. As discussed above, the signal at 1 ns is linear with excitation intensity, observable in dilute solutions and has an extremely slow decay time, further supporting the assignment of triplet exciton production from singlet excitons. Depending upon the sample morphology, a difference in the photoinduced absorption spectrum is seen. Films have photoinduced features at 0.9 eV and 1.9 eV, with the onset of photoinduced bleaching at 2.2 eV (consistent with a longer tail into the IR). In addition, the film signal is an order of magnitude smaller than the powder signal. Powders have a large feature at 1.9 eV and a shoulder at 0.9 eV, with the onset of photoinduced bleaching at 2.5 eV. The quadrature signal (inset Fig. 4) shows that the 0.9 eV shoulder is a PA feature with a lifetime longer than the in-phase component of the signal. In addition, photoinduced infrared active vibrational (IRAV) modes in powders indicate the existence of a charged photocreated species.

LIGHT-EMITTING DEVICES

Since the initial report of electroluminescence of PPV in 1990 (Ref. 1), a variety of PPV derivatives and other conjugated polymers and/or copolymers have been determined to exhibit electroluminescent properties (Refs. 13,14). Most of the conjugated polymer-based light-emitting devices in their simplest sandwich structure have been shown to be tunneling diodes (Ref. 15) which only can operate under forward DC driving field. Recently there have been some reports of the observation of electroluminescence (EL) in reverse bias for certain systems in the simple sandwich structure (Refs. 16-18) and in multiple bilayer structures prepared by dip coating technique (Ref. 19) although some of the devices show unstable electroluminescence (EL) and/or need much higher driving voltage under reverse bias. More recently we have reported the fabrication of symmetrically configured AC light-emitting (SCALE) devices based on PPy and PPyV by introducing two "insulating" layers, such as the emeraldine base (EB) form of polyaniline, sandwiching the emitting layer (Ref. 20). The SCALE devices emit light under both forward and reverse DC bias as well as AC driving voltage. These devices emit light symmetrically in both forward and reverse DC bias with almost symmetric current-voltage characteristics. This unusual behavior is attributed to the effects of charge accumulation at the polymer/polymer interfaces (Ref. 20). We examine the role of EB layers in the SCALE device operation by fabricating several single- and multi- layer devices ITO/PPy/Al, ITO/EB/PPy/Al, ITO/PPy/EB/Al, ITO/EB/PPy/EB/Al, and ITO/EB/PPy/EB/Au, and comparing the device characteristics.

Figure 5 compares the current-voltage characteristics for ITO/PPy/Al, ITO/EB/PPy/Al, ITO/PPy/EB/Al, and ITO/EB/PPy/EB/Al devices. The light intensity follows closely with the corresponding I-V curve except for the ITO/PPy/EB/Al device in reverse bias, in which case no light was observed although there is significant current flow. Notice that the turn on voltage is lower and the current is higher at any given applied voltage when EB layers are added, indicating that EB facilitates, instead of limits, charge injection into the emitting polymer.

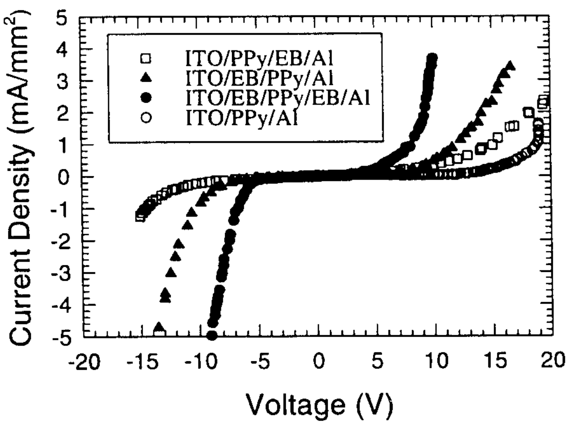

Fig. 5 I-V characteristics of four devices with different structures as shown in the figure. Note that the turn on voltage *decreases* as the total number of layers *increases* (From Ref. 20b).

Optical studies show that positive (P^+) and negative (P^-) polaron levels exist inside the π-π* band gap associated with benzenoid and quinoid levels, respectively(Ref. 21). They may play an important role in charge injection and transport. Specifically, under low bias voltages, electrons and holes can be injected from the electrodes into the quinoid and benzenoid levels of EB and form negative and positive polarons, respectively. Because the polarons levels are within the π-π* band gap of EB, and are also likely within the band gap of PPy, the barriers for charge injection from electrodes to polaron levels of EB are significantly reduced as compared to injection directly to conduction and valence bands of PPy. Within this model, the limiting barriers for charge injection are changed from the electrode/polymer contacts as proposed (Ref. 15) for conventional polymer LEDs to the polymer/polymer (EB/PPy) interfaces of the SCALE devices.

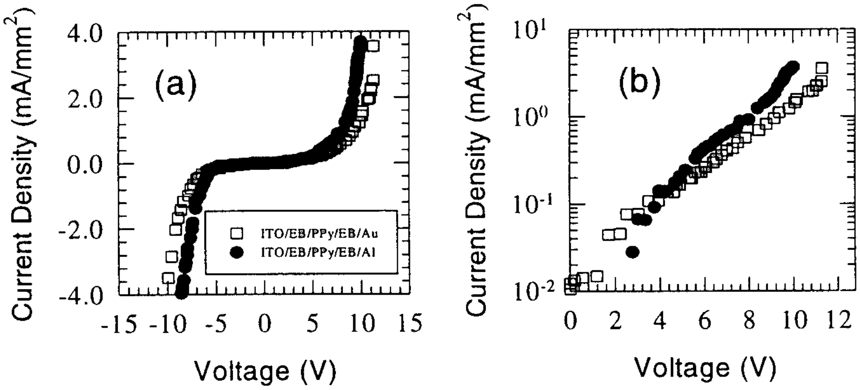

Fig. 6 I-V characteristics of ITO/EB/PPy/EB/Al and ITO/EB/PPy/EB/Au devices plotted in (a) linear scale in forward and reverse bias and (b) semi-log scale in forward bias.

We point out that the significant reduction of barrier height at the electrode/EB interface enables the use of stable high workfunction metals, such as Au, as electrodes, which may reduce the problems of aging of contacts in polymer light-emitting devices. Figure 6 compares the I-V characteristics for EB/PPy/EB SCALE devices utilizing ITO/Al and ITO/Au as electrode pairs. The two devices emit light under both forward and reverse bias, and show similar I-V characteristics with similar turn on voltages despite the fact that Al and Au have much different workfunctions (4.2 eV vs 5.3 eV) (Ref. 13). The nearly linear log(I) ~ V curve for the Au device indicate that the charge injection is exponential at high voltages.

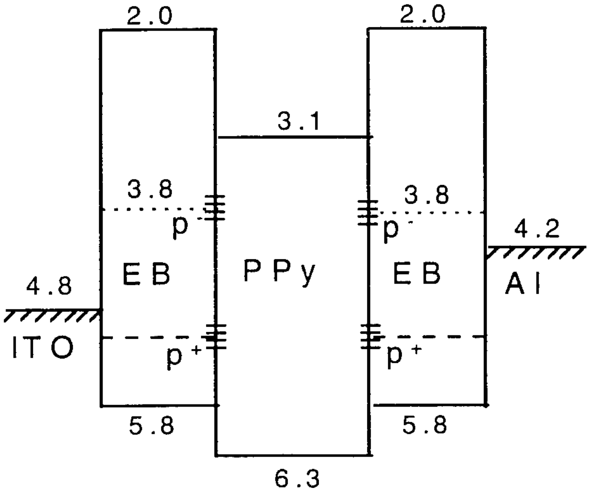

Fig. 7 Energy diagram showing the role of positive (P^+) and negative (P^-) polaron levels of EB and the interface states in the SCALE device operation.

We propose the following mechanism for the SCALE device operation (Ref. 20). Under low bias voltage, electrons and holes are injected from the electrodes to the gap states of EB and form negative and positive polarons, respectively. These polarons transport to the EB/PPy interfaces via a hopping mechanism and populate the EB/PPy interfaces at the polaron levels (see Fig. 7). When the applied electric field is high enough, the stored charges begin to tunnel into the conduction and valence bands of PPy. When they meet, the injected charges may form intrachain excitons and decay radiatively to emit photons or follow other nonradiative decay paths. If the charge injection is not balanced, as is the case for most polymer LEDs, the excess charge carriers may migrate through the PPy layer without decaying. Most of these charges will be trapped in the opposite PPy/EB interface. When the bias voltage is reversed, the shallow trapped charges will be released from the interfaces and contribute to the recombination current. The deep trapped charges which act as quenchers or injection limiters in DC devices will be neutralized. We point out that the use of stable high workfunction metals, such as Au, as electrodes to inject both electrons and holes for the SCALE devices may reduce the problems of aging of contacts of polymer light-emitting devices. Also, continuous reversal of the sign of the driving voltage under AC operation may reduce degradation.

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