Blue electroluminescent diodes utilizing blends of poly(*p*-phenylphenylene vinylene) in poly(9-vinylcarbazole)

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Abstract

We report blue light emission from diodes made from polymer blends composed of poly(*p*-phenylphenylene vinylene) (PPPV) in a hole-transporting polymer, poly(9-vinylcarbazole) (PVK). The soluble PPPV and PVK allow fabrication of light-emitting diodes (LEDs) by spin-casting the electroluminescent polymer blend from solution at room temperature with no subsequent processing or heat treatment required. The initial devices utilized calcium as the electron-injecting (rectifying) contact on the front surface of a PPPV/PVK film spin-cast onto a glass substrate partially coated with a layer of indium/tin oxide (ITO) as the hole-injecting contact. The LEDs turn on at ~30 V and have a peak emission wavelength in the blue at 495 nm (at room temperature). The quantum efficiency is measured as a function of PPPV content in the blend; the maximum efficiency is approximately 0.16% photons/electron at a concentration of only 2% PPPV in PVK.

Introduction

Semiconducting and luminescent π-conjugated polymers offer a number of important advantages over conventional inorganic semiconductors for light emitting diode (LED) applications. The ability to alter the π–π^* energy gap through controlled changes in the molecular structure promises to provide colors which span the visible spectrum; the ability to fabricate the LED structure by casting the active luminescent polymer layer from solution promises a significant manufacturing advantage; the ability to construct polymer LEDs on flexible substrates promises to enable the fabrication of novel light sources and displays in a variety of unusual shapes.

Initial results from such polymer LEDs have already demonstrated that the full spectrum of colors (red, yellow, green and blue) can be realized with impressive efficiency, brightness and uniformity [1–7]. The unique processing advantages and mechanical properties of polymers have been demonstrated [8] through the fabrication of flexible LED structures in which the hole-injecting polymer electrode and the semiconducting luminescent polymer layer are spin-cast from solution onto a transparent polymer substrate. Switching on and off is RC limited (R is the series resistance and C is the capacitance); polymer LEDs have been fabricated

with on and off transients in the 10–50 ns regime [9]. The fast response plus the linearity of the light output with current implies that multiplexing will be possible.

Although there has been rapid progress in research on polymer LEDs, the number of soluble conjugated polymers with relatively high luminescence efficiency is limited; the principal examples being poly(2-methoxy, 5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) [10] and poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene) (BCHA-PPV) [11]. Both MEH-PPV and BCHA-PPV are soluble in the conjugated form in common organic solvents. LEDs fabricated with MEH-PPV emit orange light; LEDs fabricated with BCHA-PPV emit yellow light [12]. Recently, Martelock *et al.* [13] reported the synthesis of poly(*p*-phenylphenylene vinylene) (PPPV) using a Heck reaction from ethylene and 2,5-dibromobiphenyl. Vestweber *et al.* [14] fabricated green LEDs using this material as the active electroluminescent layer.

In the search for new materials for polymer LEDs, we have investigated a novel polymer blend as the emitting layer; the blend is composed of a soluble conjugated polymer in a matrix of hole-transporting polymer. For the conjugated luminescent polymer, we selected poly(*p*-phenylphenylene vinylene) (PPPV), a soluble derivative of poly(*p*-phenylene vinylene). The PPPV was blended with poly(9-vinylcarbazole) (PVK),

PPPV   PVK
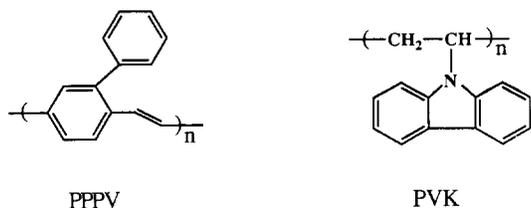
Fig. 1. Structure of poly(p-phenylphenylene vinylene) (PPPV) and poly(9-vinylcarbazole) (PVK).
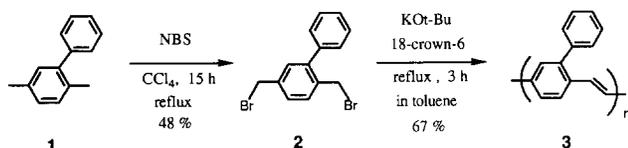
Scheme 1.

a commercially available hole-transporting polymer. The molecular structures of poly(p-phenylphenylene vinylene) (PPPV) and poly(9-vinylcarbazole) (PVK) are shown in Fig. 1. Both PPPV and PVK are soluble in common organic solvents.

We describe the monomer synthesis, polymer synthesis and device fabrication, which is simplified because the blends can be spin-cast from a stable solution at room temperature. We present the results of electrical and optical characterization of the devices. The initial devices utilized calcium as the electron-injecting (rectifying) contact and indium/tin oxide (ITO) as the hole-injecting contact. The LEDs turn on at ~30 V and have a peak emission wavelength in the blue at 495 nm (at room temperature). The quantum efficiency is measured as a function of the PPPV content in the blend; the maximum efficiency is approximately 0.16% photons/electron at a concentration of only 2% PPPV in PVK.

Experimental details

Synthesis of the poly(p-phenylphenylene vinylene)

PPPV used in this study was prepared by a poly-dehydrohalogenation reaction from 2,5-bis(bromomethyl)biphenyl (Scheme 1). We used a modification of a synthesis initially developed by Gilch and Wheelwright [15] and by Hörhold and Opfermann [16] to obtain PPPV. Similar conditions were reported by Wudl et al. to prepare BCHA-PPV [11].

The monomer, 2,5-bis(bromomethyl)biphenyl (2), was prepared from 2,5-dimethylbiphenyl (1) [17] via bromination with N-bromosuccinimide (NBS). PPPV (3) was obtained from 2 by polydehydrohalogenation in the presence of potassium-t-butoxide in toluene under reflux. Catalytic amounts of 18-crown-6-ether were added to the reaction mixture. PPV formation started immediately after addition of the base and could be observed by the strong photoluminescence of the reaction mixture when irradiated with UV light of $\lambda = 365$ nm.

Monomer synthesis — 2,5-bis(bromomethyl)biphenyl

A mixture of 6.70 g (37 mmol) of 2,5-dimethylbiphenyl (1) [17], 14.00 g (78 mmol) of N-bromosuccinimide (NBS) and 10 mg (0.04 mmol) of dibenzoylperoxide in 100 ml of dry carbon tetrachloride was heated to reflux for 15 h under argon atmosphere. A red solution with precipitated succinimide was obtained. The warm reaction mixture was filtered. The solid was extracted twice, each time with 150 ml of hot hexane. The organic phases were combined and the solvents evaporated. A pale yellow oil remained. The oil was cooled at -10 °C overnight to yield a crystalline raw product. The product was recrystallized from hexanes (50 ml) to give white crystals. Yield: 6.0 g (48%) of 2. Purity determined by GC: > 99%; m.p. = 80 °C.

IR (KBr): 3020 (w, CH), 1438 (m, CH), 1215 (s), 780 (s), 700 (s), 651 (s). MS (70 eV): m/z 340 (M^+ of molecule containing one ^{81}Br and one ^{79}Br), 261 ($M^+ - {^{79}Br}$), 259 ($M^+ - {^{81}Br}$), 179 ($M^+ - 2Br$), 165 ($M^+ - 2Br - CH_2$). ^1H NMR (CDCl$_3$) δ: 4.43 (s, CH$_2$), 4.49 (s, CH$_2$), 7.20–7.60 (m, aryl-H). Intensity ratio = 2:2:8.

Polymer synthesis — poly(p-phenylphenylene vinylene)

Under inert conditions (argon), 340 mg (1.0 mmol) of 2 and 20 mg of 18-crown-6-ether were dissolved in 50 ml of dry toluene, and a warm solution of 672 mg (6.0 mmol) of potassium-t-butoxide in 50 ml of toluene was added within 2 min. After 1 min, the mixture turned yellow and cloudy. The mixture was heated to reflux for 3 h and cooled to room temperature. Thin layer chromatography control indicated that no monomer or other low-molecular-weight substances were present after completion of the reaction. The reaction mixture was filtered to separate a precipitated insoluble product (18%). The filtrate was concentrated to a volume of 30 ml on the rotavap and precipitated with 200 ml of methanol. The precipitated yellow solid was filtered off, washed with methanol and dried. Yield of 3: 87 mg (49%). PPPV polymer (3) showed sufficient solubility in chloroform (max. 0.6 mg/ml). For the characterization and for casting thin films for LEDs, 80 mg of the second fraction of 3 were extracted with 50 ml of chloroform at room temperature for 3 weeks. The insoluble remainder was filtered off. The filtrate showed a concentration of 0.6 mg/ml of 3 and was used for the subsequent characterization and LED fabrication.

Anal. Calc. for monomer unit C$_{14}$H$_{10}$: C, 94.34; H, 5.66. Anal. Calc. for polymer with 40 repeat units: C, 92.23; H, 5.52; Br, 2.19. Found: C, 92.07; H, 5.80; Br,

2.18. The elemental analysis revealed that the polymer still contained 2.18% bromine. This indicates an average degree of polymerization of 40 monomeric units under the assumption that all residual bromine atoms are located at the end groups.

UV (film on glass): $\lambda_{max} = 425$ nm. IR (KBr): 3022 (w, CH), 1482 (w), 1384 (vs), 958 (w, trans-C=C), 766 (m), 697 (s). ^{1}H NMR (CDCl$_3$) δ: 6.80–7.60 (m, aryl-H and vinyl-H). GPC (CHCl$_3$): $M_n = 6300$ g/mol, $M_w = 26\,600$ g/mol (calibrated with polystyrene standards).

LED device fabrication

PVK was obtained from Aldrich (catalog no. 18,260-5) and used as received. As a result of the phenyl side groups, PPPV is soluble in the conjugated form. A master solution of PPPV in chloroform (stable at room temperature) was prepared. The appropriate amounts were added to a solution of 30 mg PVK in 1 ml chloroform to give PPPV/PVK ratios varying from 1/1000 to 1/10 (wt./wt.). To obtain PPPV/PVK films with concentration 1/10, 1 ml of the chloroform solution containing 0.6 mg of PPPV and 6 mg of PVK was concentrated to ~1/4 of the original volume just prior to spin-casting. Films of the PPPV/PVK blend can be spin-cast from chloroform solution with excellent reproducibility; the films are light green, homogeneous, dense and uniform.

Recently, electroluminescence devices using a solid state solution of an electron transport small molecule and an emitter molecule dispersed in PVK have been described [18]. In these experiments, PVK was doped with a hole-transporting molecule in an attempt to control the hole mobility. By contrast, we used PVK as received and without subsequent doping.

The LED structure consists of a calcium rectifying contact on the front surface of a PPPV/PVK film which was spin-cast onto a glass substrate partially coated with a layer of indium/tin oxide (ITO) as the hole-injecting contact (see ref. 6 for a schematic diagram). The luminescent thin film layers were prepared by spin-casting the blends from chloroform solution. To determine the optimum concentration of PPPV in PVK, the PPPV/PVK ratio was varied from 1/1000 to 1/10 (wt./wt.). The resulting light green polyblend films have uniform surfaces with thicknesses in the range from 1000 to 3000 Å depending on details (concentration of solution, spin rate, etc.). Electron-injecting calcium contacts were deposited onto the surface of the blend by vacuum evaporation at pressures below 4×10^{-7} Torr, yielding active areas of 0.1 cm^2. All processing steps were carried out in a nitrogen atmosphere. Indium solder was used to connect wires to the electrodes.

For spectroscopic measurements a single-grating monochromator (Spex 340S) with a Photometrics CCD camera (Tektronix TK512 CCD) as a detector without correction for system response was used. Electroluminescence (EL) spectra were recorded while applying direct current. For photoluminescence (PL) spectra, the polymer was excited with ultraviolet light at 365 nm (254 nm was used for obtaining PL spectra of PVK).

Results and discussion

The optical absorption spectra of PPPV, PVK and PPPV/PVK (1/10) thin films are shown in Fig. 2. The onset of the π–π^* transition of poly(p-phenylene vinylene) (PPV) is at about 500 nm at room temperature. The addition of phenyl groups to the benzene ring does not shift the absorption edge of PPV; the onset of π–π^* absorption in PPPV also occurs at around 500 nm and the absorption peak is at 425 nm. The onset of absorption in PVK is at approximately 355 nm at room temperature; PVK exhibits two well-defined spectral features at 343 and 330 nm, respectively. The highest PPPV/PVK ratio we have reached is 1/10, limited by the solubility of PPPV. The PPPV/PVK (1/10) blend has two absorption peaks at 343 and 330 nm, the same as PVK, and a shoulder around 418 nm, attributed to PPPV. The blue shift of the π–π^* transition of PPPV in PVK results in the blue luminescence and electroluminescence which are the focus of this report.

The forward bias current is obtained when the ITO electrode is positively biased and the Ca electrode grounded. Figure 3(a) shows the current versus voltage characteristics measured from a typical Ca/polyblend(1/50)/ITO device. The forward current increases with increasing forward bias voltage and the reverse bias current remains small; the rectification ratio is approximately 10^2–10^3. Figure 3(b) shows the voltage dependence of emission intensity from the same Ca/polyblend(1/50)/ITO device. Light emission first becomes visible at a bias of just under 32 V and a current
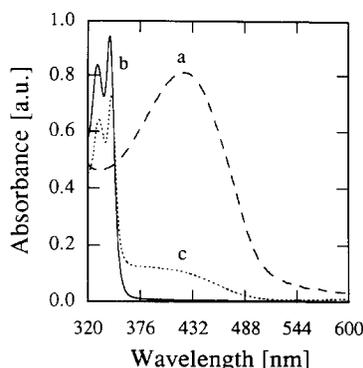
Fig. 2. Absorption spectra (films on glass) of (a) PPPV, (b) PVK and (c) PPPV/PVK blends (1/10).

(a)

(b)
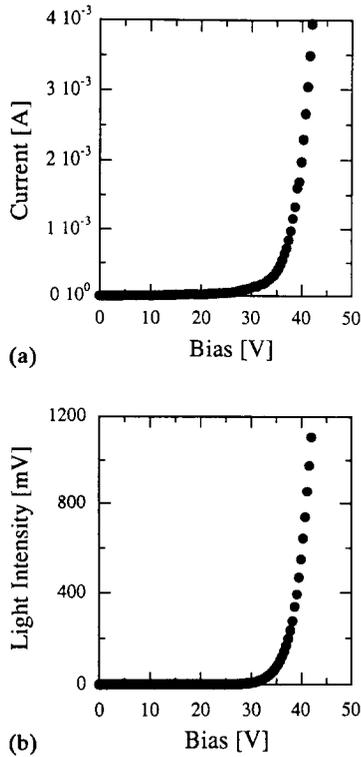
Fig. 3. Dependence of current on applied voltage (a) and emission intensity on applied voltage (b) for PPPV/PVK (1/50) blend LEDs.
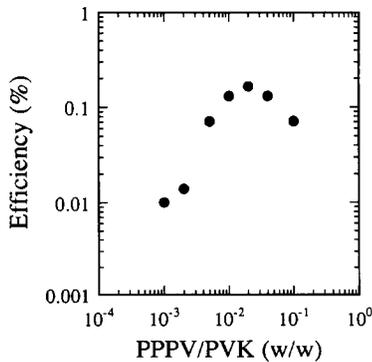
Fig. 4. Dependence of electroluminescence efficiency on the PPPV/PVK ratio.

density of approximately 1.7 mA/cm². Above 35 V, blue light emission is visible in the normal room light of the laboratory.

Figure 4 shows the emission efficiency dependence on PPPV content for devices with different PPPV/PVK ratio (wt./wt.). The efficiency increases with increasing PPPV/PVK ratio while the ratio is below 1/50 and then decreases slightly for ratios above 1/50. The quantum efficiencies are as high as 0.16% photons per electron for the devices in which the PPPV/PVK ratio is 1/50; efficiencies of devices with a PPPV/PVK ratio of 1/1000 are 0.01%, an order of magnitude smaller. The

efficiencies of devices with a PPPV/PVK ratio of 1/50 are twice as great as that of 1/10. To our knowledge, these quantum efficiencies (0.16% photons per electron for the PPPV/PVK LEDs) are the highest reported to date for blue polymer LEDs.

Figure 5 compares the emission intensity dependence on current for devices with various PPPV/PVK ratios. As is typical of the polymer LED devices, the emission intensity exhibits an approximately linear increase with injected current. The highest emission intensities are obtained from the device with PPPV/PVK ratio of 1/50. The emission intensities of devices with PPPV/PVK ratio ranging from 1/10 to 1/200 are much higher than those with 1/500 and 1/1000 ratios.

The emission efficiency is plotted versus current for devices with different PPPV/PVK ratios in Fig. 6. The efficiencies increase sharply with increasing injected current and then tend to saturate. We have found good device-to-device reproducibility. Depending on the PPPV/PVK ratio, the LED emits light blue to light purple light at room temperature.

Figure 7 compares the room temperature electro-luminescence (EL) and photoluminescence (PL) spectra obtained from a PPPV/PVK (1/50) blend film in a device configuration. The electroluminescence and pho-toluminescence spectra of the blend are virtually iden-
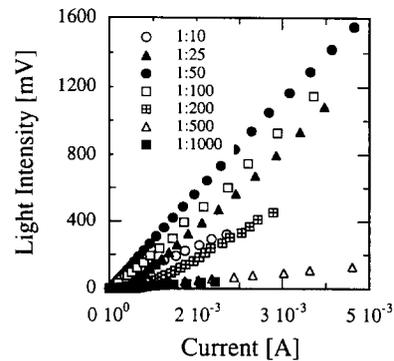
Fig. 5. Emitted light intensity vs. device current (Ca/blend/ITO) for different PPPV/PVK ratios.
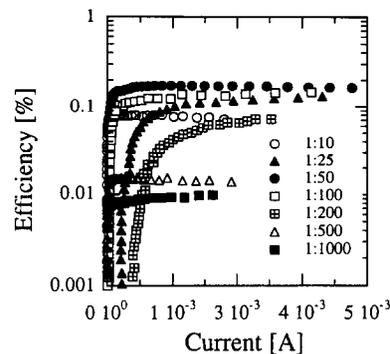
Fig. 6. Electroluminescence efficiencies vs. current for LEDs with different PPPV/PVK ratios.
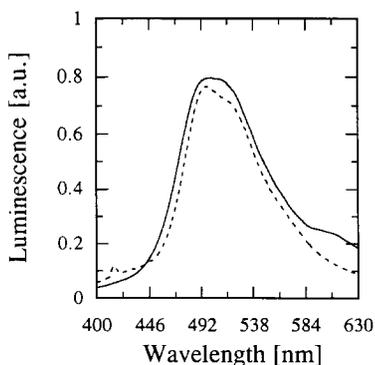
Fig. 7. Electroluminescence (solid line) and photoluminescence (dashed line) from a PPPV/PVK (1/50) blend (room temperature).
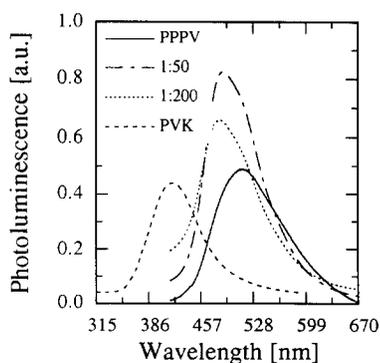
Fig. 8. Photoluminescence of PVK, PPPV/PVK blends and PPPV films at room temperature.

Fig. 9. Electroluminescence spectra of PPPV/PVK blend LEDs (Ca/polymer film/ITO) for different PPPV/PVK ratios.

tical, a feature which is quite generally characteristic of polymer LEDs. Thus, the same excitations (presumably neutral bipolaron excitons) are involved in both cases. In photoluminescence, the neutral bipolaron excitons are formed by lattice relaxation following photo-excitation; in the case of electroluminescence, the same species are formed as the intermediate step in the recombination of an electron polaron and a hole polaron. The emission peak of the PL and EL spectra occurs at around 495 nm, blue shifted by about 55 nm with respect to the 550 nm peak of poly(p-phenylphenylene vinylene) reported in the study by Vestweber et al. [14]. The blue shift in this higher molecular weight material probably results from the chain conformation or aggregation of PPPV in PVK, analogous to the observed blue shift of the π–π* absorption in poly(3-hexylthiophene) on going from the solid state into solution [19].

Photoluminescence spectra of PVK, PPPV/PVK blends and PPPV films are shown in Fig. 8. The emission of PPPV/PVK (1/50) is at 490 nm, in between PVK which is around 418 nm and PPPV which is about 512 nm. As the concentration of PPPV in the blends increases, the photoluminescence emission peak shifts slightly to the red, from 483 nm for 1/200 to 490 nm for 1/50, possibly due to aggregation and interactions of PPPV chains in and with the PVK matrix. The same

red shift of the emission peak as a function of PPPV concentration has been observed in the electroluminescence emission of PPPV/PVK devices (Fig. 9).

In the blend, PVK is believed to serve four functions:

(1) High molecular weight PVK helps to form thin, dense and uniform films. Because the solubility of high molecular weight PPPV in chloroform is limited, a thin film cast from saturated PPPV–chloroform is not thick enough to make LEDs.

(2) The blue shift of the electroluminescence (with respect to that of pure PPPV) results from either the chain conformation of PPPV in PVK or the details of the aggregation of PPPV in PVK.

(3) As a hole-transporting polymer, PVK carries charge to the PPPV in the blend film. The turn-on voltage of LEDs made with blends of PPPV and poly(methyl methacrylate), an inert and inactive polymer, is much higher than for devices made with the PPPV/PVK polyblends.

(4) The dilution effect due to blending helps enhance the probability of radiative recombination.

The latter leads quite naturally to a peak in efficiency as a function of PPPV concentration (consistent with the data shown in Fig. 4); the efficiency will initially increase with density of luminescent sites and then decrease as excitation quenching becomes important at higher concentrations.

Conclusions

We have demonstrated relatively high quantum efficiencies for blue light-emitting diodes made with polymer blends of a soluble derivative of PPV and a hole-transporting polymer. Typical efficiencies of the LEDs with PPPV/PVK (1/50) blend are 0.16% photons per electron.

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