

Exciplex emission in bilayer polymer light-emitting devices

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(Received 5 November 1996; accepted for publication 24 January 1997)

Photoluminescent and electroluminescent studies of bilayer heterojunctions formed from a poly(pyridyl vinylene phenylene vinylene) (PPyVPV) derivative and poly(vinyl carbazole) (PVK) show an emission peak which cannot be ascribed to either the PPyVPV derivative or PVK layer. Through studies of absorption and photoluminescence excitation (PLE) spectra we demonstrate that the additional feature results from an exciplex at the bilayer interface. The photoluminescence efficiency of the exciplex is greater than 20%. The electroluminescence spectrum from the bilayer devices is entirely due to exciplex emission, with internal efficiencies initially achieved exceeding 0.1%. © 1997 American Institute of Physics. [S0003-6951(97)00413-0]

Conjugated polymer based light-emitting devices¹⁻⁸ have become a topic of great interest since the report of electroluminescent (EL) properties in poly(phenylene vinylene) (PPV).¹ A large variety of polymers, copolymers, and their derivatives have been shown to exhibit EL properties, including a relatively new class: polypyridines,^{5,6} and poly(pyridyl vinylene)s.^{6,9} The configurations of these devices may consist of a simple single layer,^{1,2} bilayers,² or blends⁷ used to enhance efficiency and tune the emission wavelength, or multilayers that may allow the device to operate under an ac applied voltage.⁶

In single layer devices the low efficiency frequently is due to the imbalance of electrons and holes. Inserting a hole-transport (electron-blocking) or electron-transport (hole-blocking) layer provides a means to enhance minority carriers and block the majority carriers and confine them to the emitter layer, which increases the probability of recombination.² Poly(N-vinylcarbazole) (PVK) has been used as a hole transport layer⁸ and occasionally in blends with the emitter polymer.^{7,8} PVK is a well-studied photoconductive polymer which often forms exciplexes with organic molecules, e.g., dimethyl terephthalate.¹⁰ An exciplex is a transient donor-acceptor complex between the excited state of the donor and the ground state of the acceptor.¹⁰

Recently, there has been interest in exciplex formation between PVK and conjugated polymers. Osaheni and Jenekhe¹¹⁻¹³ have reported PL due to exciplex formation in bilayers of poly(*p*-phenylene benzobisoxazole) (PBO) and tris(*p*-tolyl)amine, but not EL, although they suggest exciplexes may be important in light-emitting devices.¹¹ Even though many groups have studied bilayer and multilayer devices, EL due to exciplex formation until now has not been reported.² For example, in highly efficient bilayer devices of CN-PPV and PPV² and of PPV and

2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole² exciplex formation is not observed. Recently, PL and EL exciplex emission from blends of PVK and a conjugated/nonconjugated multiblock copolymer was reported,⁷ but emission from separate layers was not studied.

In this letter, we report bilayer devices with PVK as the hole transport layer and a derivative of the copolymer poly(pyridyl vinylene phenylene vinylene) (PPyVPV) as the emitter layer. Absorption, photoluminescence (PL) and electroluminescence (EL) results demonstrate emission due to exciplex formation at the interface between the PVK and copolymer. The PL and EL of bilayer films are dramatically different from that of a single layer film.

The electron withdrawing nature of the side groups make the copolymer PPyVP(COOC₁₂H₂₅)₂V. Figure 1(a), more resistive to oxidation than the unsubstituted copolymer. The copolymer is soluble in common organic solvents such as tetrahydrofuran (THF), xylene, and chloroform. The absorption was measured with a Perkin Elmer Lambda 19 UV/Vis/NIR spectrometer. The PL and EL measurements were made using a PTI QM1 luminescence spectrometer while current-voltage characteristics were recorded using two Keithley 195A digital multimeters with the voltage applied with a Hewlett-Packard 6218A dc power supply. EL quantum efficiency measurements were made with a Si photodiode cali-

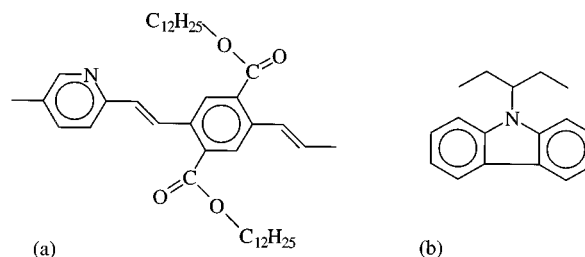


FIG. 1. Molecular repeat unit of (a) PPyVP(COOC₁₂H₂₅)₂V and (b) PVK.

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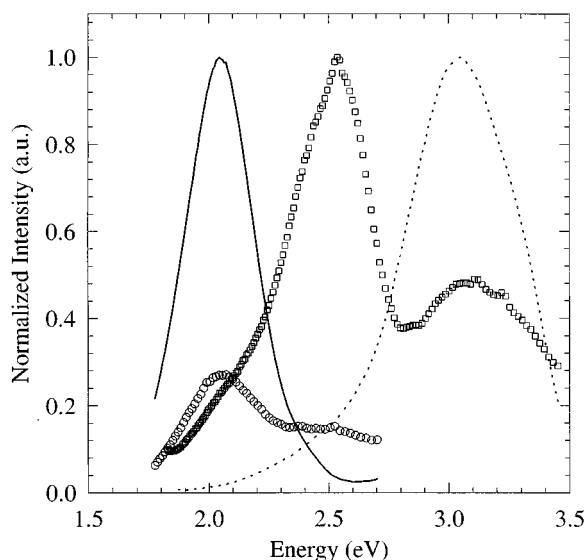


FIG. 2. PL of PPyVP(COOC₁₂H₂₅)₂V at 2.8 eV excitation energy (—), a bilayer of PVK and PPyVP(COOC₁₂H₂₅)₂V at 3.6 eV excitation energy (□) and 2.8 eV excitation energy (○), and PVK at 3.6 eV excitation energy (···), all on quartz substrates.

brated with a quartz-tungsten halogen lamp. All fabrication and measurements were conducted in ambient atmosphere.

PVK [Aldrich Chemical Co., Fig. 1(b)] films were spin-cast at 2000 rpm from a 10 mg/ml THF solution onto quartz substrates. The copolymer layer was subsequently cast onto the PVK film from xylene (1 mg/ml) at 1000 rpm as PVK is insoluble in xylene. The bilayer devices were similarly fabricated in a class 100 clean room from identical solutions as stated above utilizing indium–tin–oxide (ITO) coated glass substrates (20 Ω/□). Aluminum electrodes were thermally evaporated onto the (cooled) copolymer surface at pressures below 10⁻⁶ Torr resulting in active device areas of ~7 mm².

Figure 2 shows the PL of a single layer of the copolymer, a single layer of PVK and a bilayer of PVK and the copolymer. The PL of single PVK layers excited at 3.6 eV has a peak emission energy at 3.05 eV, similar to previous reports of the PL of PVK.^{7,8} The PL for single layer copolymer films excited at 3.1 eV shows an emission peak at 2.05 eV. The bilayer when excited at an energy less than the absorption edge of the PVK, but greater than the absorption edge of the copolymer shows PL peaked at the same energy as for the copolymer along with a low intensity tail to the blue side. When the bilayer was excited at energy equivalent to the excitation energy for the single PVK layer (3.6 eV), the PL emission spectrum contains contributions from both single layers (3.05 and 2.05 eV), as well as from a completely new species, which we identify with an exciplex. To the low energy side of the exciplex PL is a weak shoulder near the PL energy for the single layer of the copolymer. Figure 3 shows the PL intensity as a function of both the *excitation* energy and the *emission* energy. At excitation energies above 3.6 eV the PL due to the exciplex and PVK are apparent, but if the excitation energy is lowered below 3.4 eV these peaks have essentially disappeared. As the excitation energy is further lowered into the peak absorption of the copolymer, PL from the copolymer strongly predominates

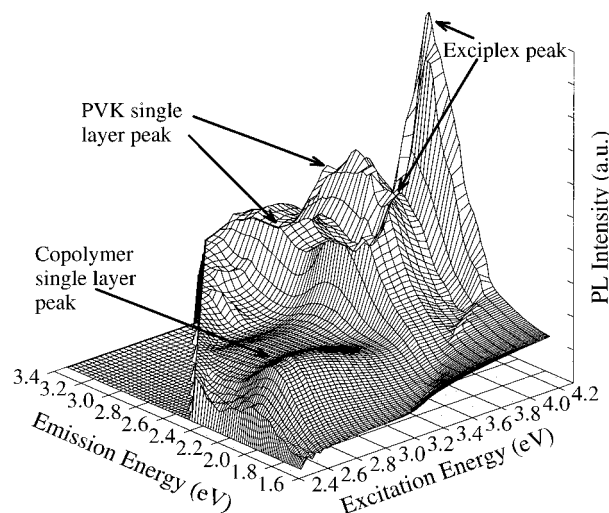


FIG. 3. PL of a bilayer of PVK and PPyVP(COOC₁₂H₂₅)₂V as a function of both emission energy and excitation energy. The 3D plot shows three prominent features: a peak due to the PVK (excitation energy from 3.6 to 4.2 eV, emission energy 2.8 to 3.4 eV), a peak due to the copolymer (excitation energy from 2.4 to 3.0 eV, emission energy 1.8 to 2.2 eV), and the exciplex peak (excitation energy from 3.6 to 4.2 eV, emission energy 2.2 to 2.8 eV).

(excitation energy 2.6–3.0 eV and principal emission energy 1.8–2.2 eV).

The absorption and photoluminescence excitation (PLE) spectra are shown in Figs. 4(a) and 4(b). The onset of the absorption of the single PVK layer is at about 3.5 eV and shows two spectral features at 3.6 and 3.75 eV similar to previous reports.^{7,8} The PLE of PVK follows the absorption showing nearly identical features. The absorption and PLE of the copolymer peak at 2.95 eV, with the onset at about 2.4 eV. The absorption of the bilayer is the sum of the single



FIG. 4. (a) Absorption and (b) PLE of PPyVP(COOC₁₂H₂₅)₂V, PVK, and a bilayer of PVK and PPyVP(COOC₁₂H₂₅)₂V on quartz substrates. The PLEs were recorded at 2.05, 3.05, and 2.55 eV, respectively. Note: The copolymer absorption is 5 times less than shown.

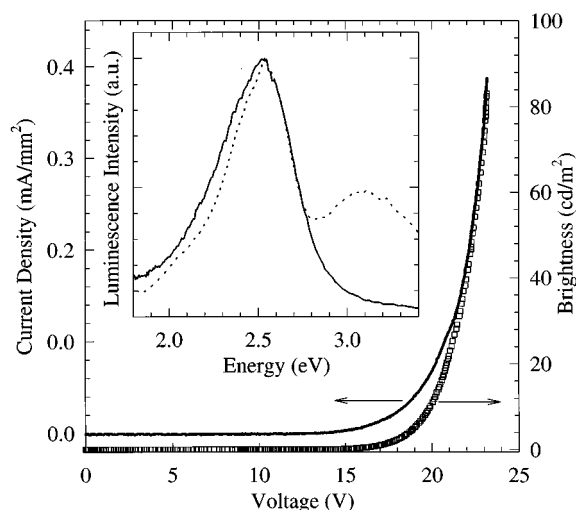


FIG. 5. Current–voltage (—) and brightness–voltage (□) characteristics of a typical bilayer light-emitting device. Inset: PL (···) and EL (—) of a bilayer light-emitting device.

PVK layer absorption and the single copolymer absorption and shows both the copolymer peak at 2.95 eV and the PVK peaks at 3.6 and 3.75 eV. The PLE of the bilayer is also the sum of the PVK PLE and the copolymer PLE and shows both the PVK spectral features and the copolymer peak, although the copolymer peak is shifted to slightly higher energy. *The lack of any new absorption or PLE features in the bilayer films implies that the new species is not directly accessible from the ground state of the copolymer or PVK, consistent with the assignment of an exciplex.*

The PL, PLE, and absorption were measured on the same films making it possible to estimate the relative PL quantum efficiencies of the copolymer emission and the exciplex emission. The copolymer absolute PL efficiency was reported previously to be $\sim 18\%$.⁹ A lower bound on the quantum efficiency of the exciplex was calculated to be $\sim 15\text{--}20\%$, nearly the same as the copolymer efficiency.

We fabricated bilayer devices using ITO as the anode and aluminum as the cathode. The inset of Fig. 5 shows the EL spectrum of a typical device with the PL spectrum from the same device. The devices can easily be seen in a brightly lit room, appear bright green to the eye, and have internal quantum efficiencies of $\sim 0.1\text{--}0.5\%$. Although the PL efficiencies are comparable, the EL efficiency of the bilayer configuration, $\sim 0.1\text{--}0.5\%$, is much greater than for a single layer device which has an EL efficiency of less than 0.0001%. The similarity between the PL and EL of the bilayer device demonstrates that the exciplex is responsible for the EL emission. Figure 5 shows the current–density voltage and brightness–voltage characteristics for a typical bilayer device. The turn-on voltage of the bilayer devices depends on the thickness of the polymer layers and in this case is ~ 18 V, with the brightness following the current. The generality of this concept has been demonstrated using several

other pyridine-based copolymers.¹⁴ Through the use of polyaniline network electrodes¹⁵ we have lowered the threshold voltage to below 10 V while maintaining the same efficiency.¹⁶

The increase in efficiency of the bilayer device compared to the single layer device is primarily due to charge confinement at the PVK/copolymer interface. The electrons are injected from the Al electrode into the conduction band of the copolymer, but are confined when they reach the electron blocking PVK. Also, the holes are injected into the valence band of the PVK and are confined at the interface. The electron and hole blocking at the interface enhances exciplex emission. That the electrons and holes are unable to easily conduct through both layers leads to a small current density (≤ 1 mA/mm²) and hence a greatly increased efficiency. In addition, the buried interface implies that most of the radiative recombination will occur at the interface and away from the EL quenching electrodes.

In summary, heterojunctions of PVK and PPyVP(COOC₁₂H₂₅)₂V show a strong photoluminescence and electroluminescence feature due to exciplex emission at the interface. The absorption and PLE spectra have shown that the exciplex is not directly accessible from the ground state. The exciplex is also the primary species of electroluminescence emission in the bilayer devices. The efficiency of the bilayer devices is greatly enhanced over single layer devices due to charge confinement and exciplex formation and emission at the interface.

This work was supported in part by the Office of Naval Research.

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