

Exciplex emission from bilayers of poly(vinyl carbazole) and pyridine based conjugated copolymers

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We present photoluminescence and electroluminescence studies of bilayers and blends formed from poly(vinyl carbazole) (PVK) and poly(pyridyl vinylene phenylene vinylene) (PPyVPV) copolymer derivatives. Bilayers of PVK and the PPyVPV copolymers have a photoluminescence emission which cannot be assigned to either the photoluminescence of PVK or the PPyVPV layer. The blends of the two polymers show a similar new photoluminescence emission for a large range of concentrations. Absorption and photoluminescence excitation spectra confirm that the additional feature is an excited state species which results from an exciplex at the polymer/polymer interface. Bilayer light-emitting devices utilizing the PPyVPV copolymers show an electroluminescence spectrum consistent with emission from the exciplex. The efficiency of the bilayer devices as compared to single layer devices increases by over three orders of magnitude due to the exciplex formation and the elimination of exciton formation near the luminescence quenching electrodes.

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I. INTRODUCTION

Conjugated polymer based light-emitting devices¹⁻¹⁰ have been a topic of great interest since the report of electroluminescence (EL) in poly(phenylene vinylene) (PPV).¹ A large variety of conjugated polymers, copolymers, and their derivatives^{2,9} exhibit EL properties, including PPVs,^{1,3,10} poly(phenylphenylene vinylene), polyphenylenes, polythiophenes, polyquinolines, polypyridines,^{5,6} poly(pyridyl vinylenes),¹¹⁻¹³ and many derivatives and copolymers of these materials. The configurations of these devices may consist of a simple single layer,^{1,2} or bilayers² and blends⁷ used to enhance efficiency and tune the emission wavelength, or multilayers that may allow the device to operate under an alternating current (AC) applied voltage.^{6,14} One method for improving efficiency is insertion of a hole-transport (electron-blocking) layer between the anode and emitting polymer and/or an electron-transport (hole-blocking) layer between the cathode and emitting polymer. A well known and commonly used hole-transport (electron-blocking) layer is poly(*N*-vinyl carbazole) (PVK), which has a large band gap (3.5 eV) and is itself luminescent.^{7,8,15} PVK is an extensively studied photoconductive polymer which often forms exciplexes with organic molecules, e.g., dimethyl terephthalate.¹⁶ Recently, there has been interest in exciplex formation between PVK and conjugated polymers. Osaheni and Jenekhe¹⁷⁻¹⁹ reported photoluminescence (PL) due to exciplex formation in bilayers of poly(*p*-phenylene benzo-bisoxazole) (PBO) and tris(*p*-tolyl)amine, but not EL, although they suggest exciplexes may be important in light-emitting devices.¹⁷ Recently, PL and EL exciplex emission

from blends of PVK and a conjugated/nonconjugated multi-block copolymer was reported,⁷ but emission from separate layers was not studied.

II. EXPERIMENT

The synthesis of the PPyVPV copolymers is described elsewhere.²⁰ Figure 1 shows the schematic molecular structure of poly(vinyl-carbazole) (PVK) which forms a hole-transport layer and the poly(pyridyl vinylene phenylene vinylene) (PPyVPV) copolymers used in these studies. We report results for a two-ring repeat copolymer [Fig. 1(b)] with side groups $R_1 = \text{COOC}_{12}\text{H}_{25}$, $\text{C}_{12}\text{H}_{25}$ and a macrocycle ("wrap") $\text{OC}_{10}\text{H}_{20}\text{O}$ which connects the two sides of the phenyl ring. Figure 1(c) shows another copolymer with a $\text{OC}_{10}\text{H}_{20}\text{O}$ wrap on every other phenyl ring and side groups of $R_2 = \text{C}_{12}\text{H}_{25}$ or $\text{OC}_{16}\text{H}_{33}$ on the remaining phenyl rings. All of the copolymers are soluble in common organic solvents such as tetrahydrofuran (THF), xylene, and chloroform. The PVK was purchased from Aldrich Chemical Co. The PL and EL measurements were made using a PTI QM1 luminescence spectrometer. The absorption measurements were made using a Perkin Elmer Lambda 19 UV/Vis/NIR spectrometer. The current voltage characteristics were measured using two Keithley 195A multimeters. The voltage was applied using a HP 6218A dc power supply. Quantum efficiency (Q.E.) measurements were made using a calibrated United Detector Technologies Silicon Photodiode (UV-100).

The samples for PL and absorption measurements were spin cast on quartz. The PVK was spin cast (~3000 rpm) from a 10 mg/ml solution in THF. When bilayers were

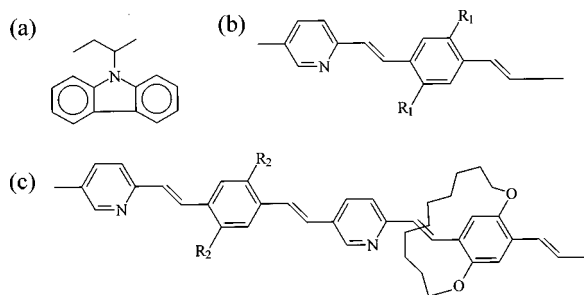


FIG. 1. Molecular repeat unit of (a) PVK, (b) PPyVP (R_1)V, and (c) wrapped PPyVP (R_1)V. The side groups can be $R_1 = \text{COOC}_{12}\text{H}_{25}$, $R_1 = \text{C}_{12}\text{H}_{25}$, or $R_1 = \text{wrap:OC}_{10}\text{H}_{20}\text{O}$ and $R_2 = \text{OC}_{16}\text{H}_{33}$ or $R_2 = \text{C}_{12}\text{H}_{25}$.

made, the copolymers were spin cast (~ 1000 rpm) from xylene (~ 10 mg/ml) so the underlying PVK layer was not dissolved. If single layers of the copolymers were used, either xylene or THF was the solvent. In the case of blends of PVK and the copolymers, a mutually compatible solvent, typically THF, was used. The blend ratios ranged from 0.05% (copolymer in PVK by weight) to 50%, as well as pure PVK and copolymer films. For devices, the polymers were spin cast on indium tin-oxide (ITO) substrates (Donnelly Applied Films), which had previously been patterned and cleaned. The PVK layer in the bilayer configurations was dried for ~ 30 s in a laminar flow hood before the copolymer layer was spin cast. All fabrication steps for the devices were conducted in ambient atmosphere in a Class 100 cleanroom. Aluminum electrodes were thermally evaporated onto the copolymer surface at low pressures ($< 10^{-6}$ Torr). To prevent damage due to heating, the substrates were mounted on a cold water cooled stage during Al deposition. In addition, evaporation rates were ~ 0.5 – 1.4 $\text{\AA}/\text{s}$ for the first 100 \AA of deposition and then increased to ~ 3 – 5 $\text{\AA}/\text{s}$ until the desired thickness was reached (usually 1000 to 2000 \AA). The active area of the devices was 5–7 mm^2 .

III. RESULTS

Figure 2(a) shows the absorption of PVK (dashed), PPyVPV($\text{COOC}_{12}\text{H}_{25}$) (dotted), a bilayer of PVK/PPyVPV($\text{COOC}_{12}\text{H}_{25}$) (solid), and a blend of 10% (wt:wt) PPyVPV($\text{COOC}_{12}\text{H}_{25}$) in PVK (dot-dash). The absorption of the single PVK layer has an onset at 3.5 eV and shows maxima at 3.6 and 3.75 eV, similar to previous reports.^{7,8} It is clear that the absorption of the bilayer system is nearly a sum of the two individual absorptions with no new features, as expected for no significant interaction between the two polymers. Similarly, the blend shows no new ground state transitions, although the concentration of PPyVPV($\text{COOC}_{12}\text{H}_{25}$) in the PVK is small, therefore diminishing the strength of copolymer absorption relative to the PVK absorption. Figure 2(b) shows the same general behavior for the four-ring repeat wrapped copolymer, wrapped PPyVPV($R_2 = \text{OC}_{16}\text{H}_{33}$). In this case, the copolymer film is somewhat thicker and has a higher optical density, leading to the larger absorption. All features in the bilayer or blend absorption spectra are assignable to one of the two constituent polymers.

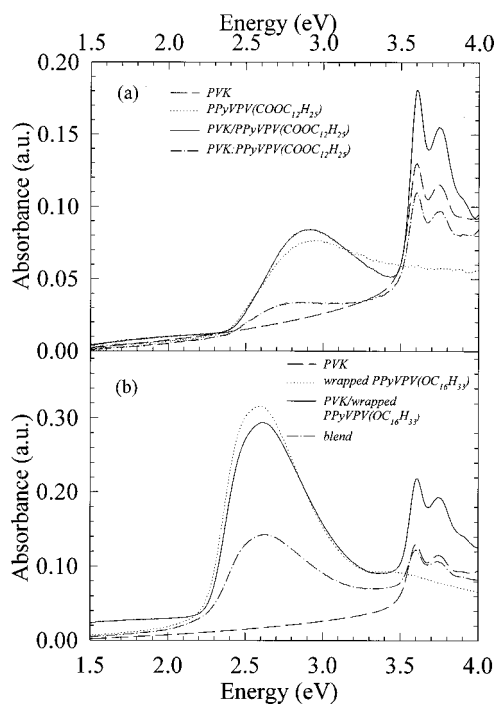


FIG. 2. (a) Absorption of films of PVK (---), PPyVPV($\text{COOC}_{12}\text{H}_{25}$) (···), a bilayer of PVK and PPyVPV($\text{COOC}_{12}\text{H}_{25}$) (—), and a blend (10%) of PPyVPV($\text{COOC}_{12}\text{H}_{25}$) and PVK (— · — ·). (b) Absorption of PVK (---), wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) (···), a bilayer of PVK and wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) (—), and a blend (10%) of wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) and PVK (— · — ·).

The absorption spectra are very similar to the corresponding photoluminescence excitation (PLE) spectra, Figs. 3(a) and 3(b). The PLE also probes the presence of any new ground state transitions, as the PL is monitored at the peak wavelength of the PL while the excitation wavelength is changed. For both bilayer systems the PLE is the sum of the individual PLEs. The blends (10% copolymer in PVK) also show no new absorption features as compared to the individual layers. *The lack of any new absorption or PLE features in the bilayer films or blends implies that the new emissive species giving rise to a new emission in the bilayer or blends is not directly accessible from the ground state of the copolymer or PVK.*

Figures 4(a) and 4(b) show the PL of a single layer of (a) PPyVPV($\text{C}_{12}\text{H}_{25}$) and (b) PPyVPV($\text{COOC}_{12}\text{H}_{25}$), a single layer of PVK, and a bilayer of PVK with each of the two-ring repeat copolymers. The PL of single PVK layers was excited at 3.6 eV and has a peak emission energy at 3.05 eV, as previously reported.^{7,8} The PL for both single layer copolymer films excited at 3.1 eV shows emission peaks near 2.05 eV, which is considerably redshifted due to aggregation^{13,21} from the solution PL (not shown), which is peaked at 2.6 eV. When the bilayers were excited at an energy equivalent to the excitation energy for the single PVK layer (3.6 eV), the PL emission spectrum contained contributions from both individual layers (3.05 and 2.05 eV), as well as from a completely new species emitting at 2.5 eV, which we identify with an exciplex. For the PPyVPV($\text{COOC}_{12}\text{H}_{25}$) copolymer there is a weak shoulder on the low energy side of the exciplex near the PL emission

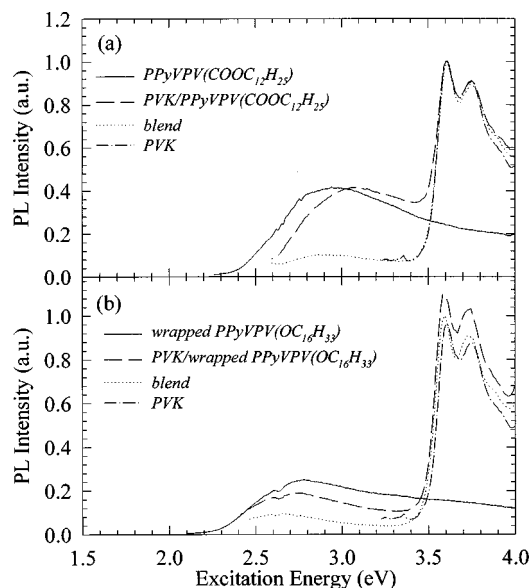


FIG. 3. (a) PLE of films of PVK (---), PPyVPV(COOC₁₂H₂₅) (—), a bilayer of PVK and PPyVPV(COOC₁₂H₂₅) (---), and a blend (10%) of PPyVPV(COOC₁₂H₂₅) and PVK (· · ·). (b) PLE of films of PVK (---), wrapped PPyVPV(OC₁₆H₃₃) (—), a bilayer of PVK and wrapped PPyVPV(OC₁₆H₃₃) (---), and a blend (10%) of wrapped PPyVPV(OC₁₆H₃₃) and PVK (· · ·).

energy for the single layer of the copolymer. In both cases, when the bilayer is excited at an energy less than the absorption edge of the PVK, but greater than the absorption edge of the copolymer, the PL (not shown) is peaked at the same energy as the single layer PL, although there is a low intensity tail to the blue side. The variation in the PL intensity was measured as a function of both the *excitation* energy and the *emission* energy, as is shown in Fig. 5 for PPyVPV(COOC₁₂H₂₅). 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 essentially disappear. As the excitation energy is further lowered

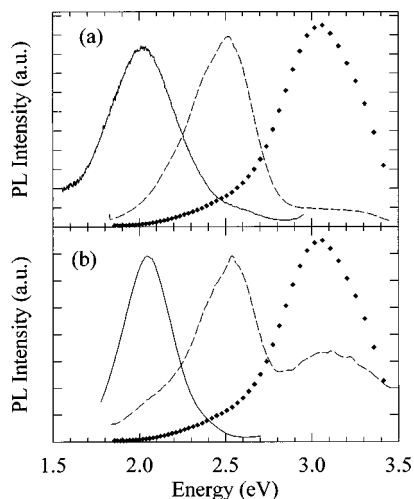


FIG. 4. (a) PL of a PPyVPV(C₁₂H₂₅) film (—) and PVK film (◆), and a bilayer PVK/PPyVPV(C₁₂H₂₅) (---). (b) PL of a PPyVPV(COOC₁₂H₂₅) film (—) and PVK film (◆) and a bilayer PVK/PPyVPV(COOC₁₂H₂₅) (---).

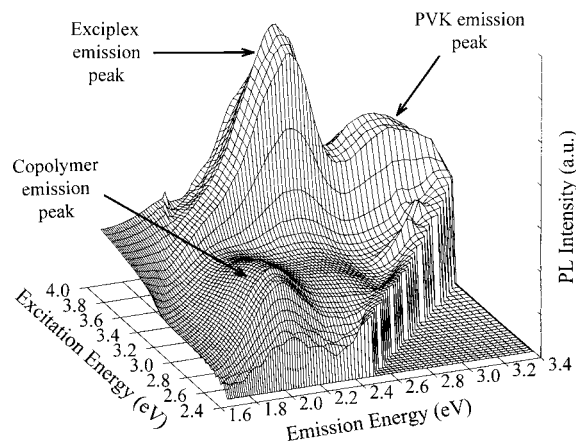


FIG. 5. PL of a bilayer PVK/PPyVPV(COOC₁₂H₂₅), as a function of both excitation energy and emission energy.

into the peak absorption of the copolymer, PL from the copolymer strongly dominates (excitation energy 2.6 to 3.0 eV and principal emission energy 1.8 to 2.2 eV).

The exciplex phenomena are not restricted to the unwrapped copolymers. Figure 6 shows the PL for single layer films (solid), bilayer films (dashed), and PVK (◆), for the three copolymers, wrapped PPyVPV(OC₁₆H₃₃) (a), wrapped PPyVPV(C₁₂H₂₅) (b), and wrapped PPyVPV (c). In each case the excitation energy used to excite the PL in the bilayers is at the first peak of the PVK absorption, with the resulting exciplex emission peak near 2.4 eV. The PLE spectra of the bilayers of wrapped copolymers and PVK are similar to those of the unwrapped copolymers in the same configura-

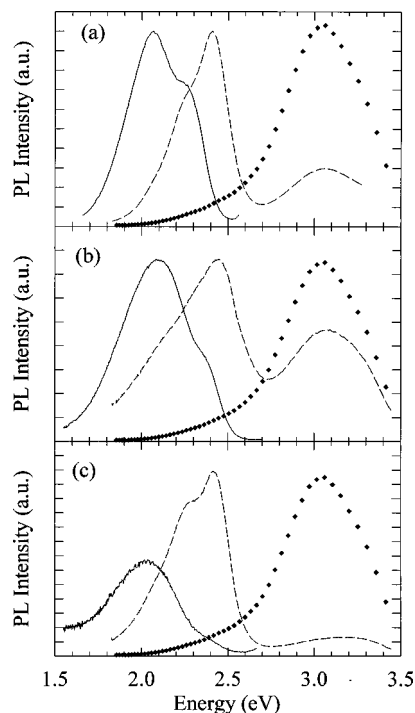


FIG. 6. (a) PL of a wrapped PPyVPV(OC₁₆H₃₃) film (—) and PVK film (◆) and a bilayer PVK/PPyVPV(OC₁₆H₃₃) (---). (b) PL of a PPyVPV(C₁₂H₂₅) film (—) and PVK film (◆) and a bilayer PVK/PPyVPV(C₁₂H₂₅) (---). (c) PL of a wrapped PPyVPV film (—) and PVK film (◆) and a bilayer PVK/PPyVPV (---).

TABLE I. The PL quantum efficiencies (Q.E.) of solutions and films.

Polymer	PL Q.E. solution	PL Q.E. film	PL Q.E. film w/PVK
PPyVPV(C ₁₂ H ₂₅)	0.87	0.14	>0.18
PPyVPV(COOC ₁₂ H ₂₅)	0.70	0.17	>0.10
wrapped PPyVPV(OC ₁₆ H ₃₃)	0.93	0.05	>0.07
wrapped PPyVPV(C ₁₂ H ₂₅)	0.86	0.13	>0.09
wrapped PPyVPV	0.83	0.10	>0.19

tion, with the exciplex emission drastically reduced when the excitation energy falls below 3.5 eV. A notable feature for the wrapped PPyVPV(OC₁₆H₃₃) copolymer is the high energy shoulder in the single layer PL which is closer to the solution PL of this copolymer (not shown) and is attributed to unaggregated sites in the film. The same shoulder (now on the low energy side) also appears in the bilayer film, supporting that the PL has contributions from exciplex sites and from unaggregated regions of the wrapped copolymer. Note that this shoulder appears when the bilayer film is excited and monitored from either side, indicating self absorption is not the cause. The wrap around every other ring tends to disturb the aggregation that occurs in the unwrapped copolymers of this family. The PL of both wrapped PPyVPV(C₁₂H₂₅) and wrapped PPyVPV shows shoulders in their single and bilayer configurations, respectively, that are attributed to unaggregated regions.

The PL efficiency of the bilayer films was measured for the five copolymers and compared to that of the single layer films (Table I). For bilayers excited with wavelengths less than 330 nm, the principle emission is that from the radiative decay of the exciplex at the interface. The reduced emission from exciton creation in the bulk of the PVK and copolymer films implies that a substantial fraction of these excitons migrate through the thin (~40 nm) films to the interface, where they either form exciplexes or undergo nonradiative decay. This exciton diffusion length is similar to that reported for PPV.²² Hence, we use the total absorption of the bilayer film to calculate the PL efficiency (as not all of the excitons migrate to the interface this tends to underestimate the efficiency). All of the copolymers show very high efficiencies in solution, but due to aggregation,^{13,21} the film efficiencies are substantially lower in single layer films.

We have blended wrapped PPyVPV(OC₁₆H₃₃) with PVK at concentrations varying from 0.05% to 50% copolymer in PVK (by weight). Figure 7(a) shows the PL intensity of the blends normalized by the absorption of the PVK at the excitation wavelength (330 nm). The PL of pure PVK (◆) is identical to that shown in Figs. 4 and 6. A PL peak assignable to the exciplex begins to emerge at concentrations as low as 0.05% copolymer, with a clear peak at 2.4 eV observed at concentrations greater than 0.1% (■). An additional shoulder is seen at 2.2 eV for concentrations 0.1% and higher. As the concentration increases to 10% the total PL intensity increases as well, but the peak and shoulder positions do not shift, indicating the effect is not due to dilution of the emissive chromophores by the host polymer PVK. At the highest concentration reported here (50%), both the ex-

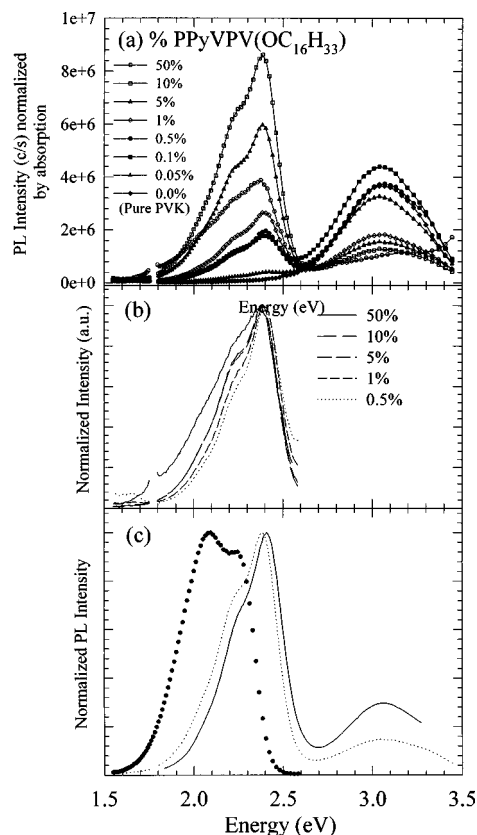


FIG. 7. (a) Normalized PL intensity of films of wrapped PPyVPV(OC₁₆H₃₃) in PVK [% PPyVPV(OC₁₆H₃₃) by total weight]. The PL intensity was normalized by dividing by the absorption at 3.6 eV (excitation energy). (b) PL intensity of the same films as in (a) with intensity normalized to 2.4 eV. The 2.2 eV shoulder in the PL increases with increasing weight % copolymer. (c) PL of a 10% blend of wrapped PPyVPV(OC₁₆H₃₃) in PVK (—), a bilayer PVK/wrapped PPyVPV(OC₁₆H₃₃) (···), and a pure film of wrapped PPyVPV(OC₁₆H₃₃) (●).

ciplex and PVK exciton PL are significantly reduced, but the PL that remains has retained the same features as that of other blend concentrations, with most of the luminescence originating from the exciplex emission. Hence at high concentrations the excitons tend to migrate to the interfaces where they can radiatively decay via exciplexes. When the exciplex PL peak of the blends is normalized (to their maximum value at 2.4 eV), the low energy shoulder of the PL (2.2 eV) increases in intensity as the copolymer concentration increases [see Fig. 7(b)], indicating there is increased emission from the copolymer unaggregated sites (as compared to exciplex emission) in the films. Figure 7(c) shows the PL of the 10% blend with the bilayer of wrapped PPyVPV(OC₁₆H₃₃) and PVK and a single layer of wrapped PPyVPV(OC₁₆H₃₃). The bilayer and blend are very similar, implying that the principle emission is from the same exciplex species.

We fabricated bilayer devices using ITO as the anode and aluminum as the cathode. Figure 8 shows the EL spectrum of typical ITO/PVK/PPyVPV(COOC₁₂H₂₅)/Al and ITO/PVK/wrapped PPyVPV(OC₁₆H₃₃)/Al devices with the PL spectrum from the same devices and individual polymer layers. The devices can easily be seen in a brightly lit room and appear bright green to the eye. The similarity between

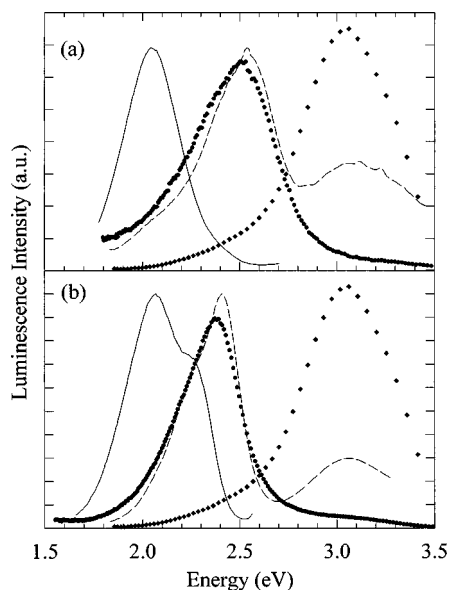


FIG. 8. Electroluminescence (●) of bilayer devices (ITO/PVK/copolymer/Al) for (a) PPyVPV(COOC₁₂H₂₅) and (b) wrapped PPyVPV(OC₁₆H₃₃). The PL (from Figs. 4 and 6) of the single and bilayer films with PVK are shown for comparison.

the PL and EL of the bilayer devices demonstrates that the exciplex is responsible for the EL emission. Figure 9 presents the current density voltage and brightness voltage characteristics for a typical single layer [ITO/wrapped PPyVPV(OC₁₆H₃₃)/Al] and bilayer [ITO/PVK/wrapped PPyVPV(OC₁₆H₃₃)/Al] device. The device structures are shown in the insets. The turn-on voltage of the bilayer devices is significantly increased over the single layer device due to the additional thickness and the insulating nature of PVK. The turn-on voltage for the bilayer in this case is

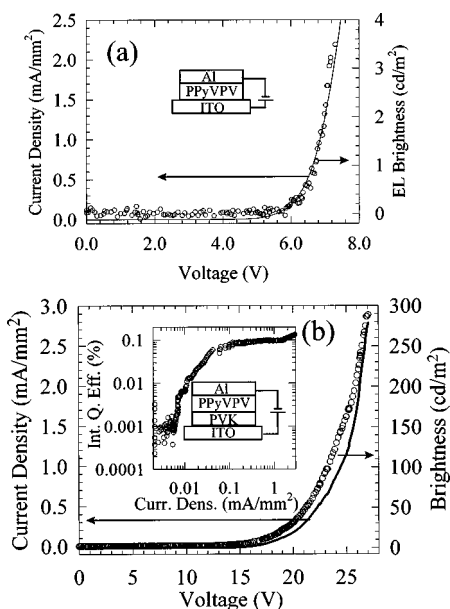


FIG. 9. Current voltage and luminance voltage characteristics for (a) single layer and (b) bilayer devices. The insets show the device structures. The symbol PPyVPV*V represents the copolymer PPyVPV(OC₁₆H₃₃) in the insets. Also shown in (b) is the internal quantum efficiency of the bilayer device.

~18–20 volts, with the brightness following the current. The maximum brightness for the bilayer device shown is 300 cd/m², a more than 50 times increase over the single layer device. In addition to the increased brightness, the current density for the bilayer device is five to ten times lower, indicating an increase in efficiency of three orders of magnitude from less than 0.0001% for the single layer to ~0.1%–0.5% for the bilayer. The increase in turn-on voltage can be remedied through the use of polyaniline network electrodes,^{12,23} which lowers the threshold voltage to below 5 volts while maintaining the same efficiency and brightness.¹²

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 copolymer interface. The electron and hole blocking at the interface enhance exciplex formation. 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.

Quenching at the electrodes has been reported for phenylene vinylene oligomers by Park *et al.*²² and in MEH-CN-PPV by Becker *et al.*²⁴ Becker *et al.* also noted that the removal of the recombination zone away from the metal electrode to a polymer/polymer interface is crucial to increasing the EL efficiency in their PPV/MEH-CN-PPV bilayer devices.²⁴ In order to probe the effect of the electrodes on the luminescence properties of our single and bilayer films, a number of samples were fabricated on ITO. Electrodes were evaporated on single layers of PVK and wrapped PPyVPV(OC₁₆H₃₃). On each film the PL was measured in the vicinity of and far from the electrode, with the exciting light entering the sample from the ITO side and recording the EL from the ITO side. The insets of Fig. 10 show the device configurations. The relative PL intensities of PVK at these two locations for 330 nm excitation wavelength [Fig. 10(a)] show that the PL increases modestly when the excitation light is incident on the electrode. In the absence of quenching, an increase in PL intensity is expected for two reasons: reflection of the excitation light by the Al and reflection of the photoluminescence by the Al. The small increase for PVK indicates significant quenching near the Al electrode. Figure 10(b) shows the same experiment for a single layer of wrapped PPyVPV(OC₁₆H₃₃) using a 450-nm wavelength excitation. The nearly twofold decrease in PL intensity indicates extensive quenching by the Al electrode for this polymer.

For bilayers in which the luminescence occurs primarily at the interface, the PL and EL intensity should be unaffected by the presence of the electrode, i.e., no quenching should occur. Figure 11(b) shows the PL intensity for a PVK/wrapped PPyVPV(OC₁₆H₃₃) bilayer with a 330-nm excitation [experimental configuration shown in Fig. 11(a)]. When the excitation wavelength is incident on the evaporated Al

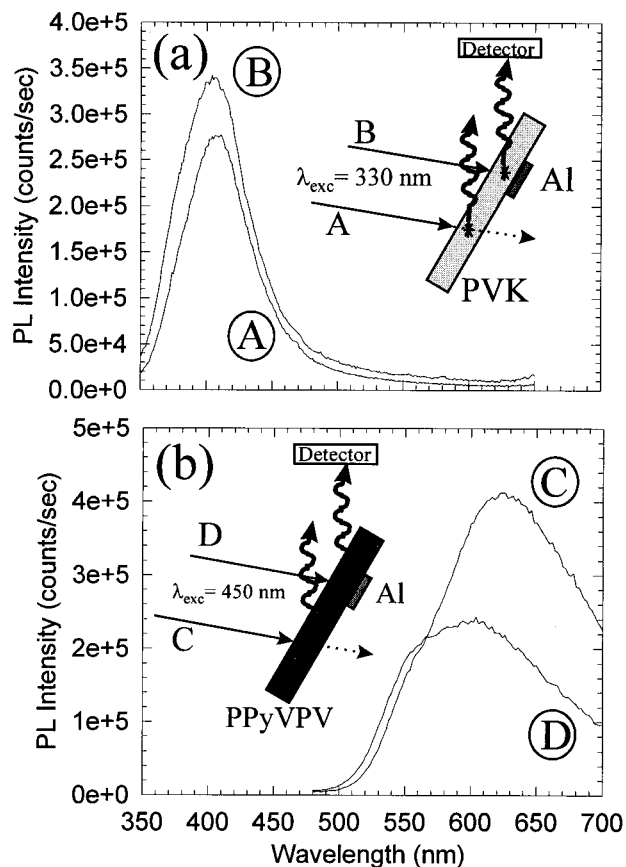


FIG. 10. PL of films of PVK (A,B) and PPyVPV (C,D) for the configurations shown schematically in the insets. (a) 330 nm excitation and (b) 450 nm excitation.

electrode, the PL intensity increases dramatically. The increase is attributed to the reflection of the luminescence and the excitation light. The large increase indicates that very little, if any, quenching occurs at the Al electrode, implying that the emission is primarily occurring at the polymer/polymer interface. Figure 11(c) shows the PL intensity of the bilayer when the lower energy excitation is used (450 nm). In this case, the PL intensity is also increased, but the emission is shifted away from the single layer emission to the exciplex (interface) emission, when the exciting light is incident on the reflecting electrode. Although the low energy excitation is used, the emission at the interface is observed because the wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) PL is quenched at the electrode and the interface emission is enhanced. Energy is transferred from excitons in the wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) to exciplex at the interface. The diffusion coefficient for excitons in the wrapped PPyVPV($\text{OC}_{16}\text{H}_{33}$) can be estimated from the diffusion distance ($\sim 10^{-6}$ cm) and the lifetime of the exciton in the copolymer (~ 1 ns),¹³ giving a diffusion coefficient of $\sim 10^{-3}$ cm²/s. Thus, exciplex emission in the bilayer devices substantially reduces the effects of quenching by electrodes that occurs in single layer devices.

IV. CONCLUSIONS

In summary, bilayers of PVK and poly(pyridyl vinylene phenylene vinylene) copolymers show a new strong photo-

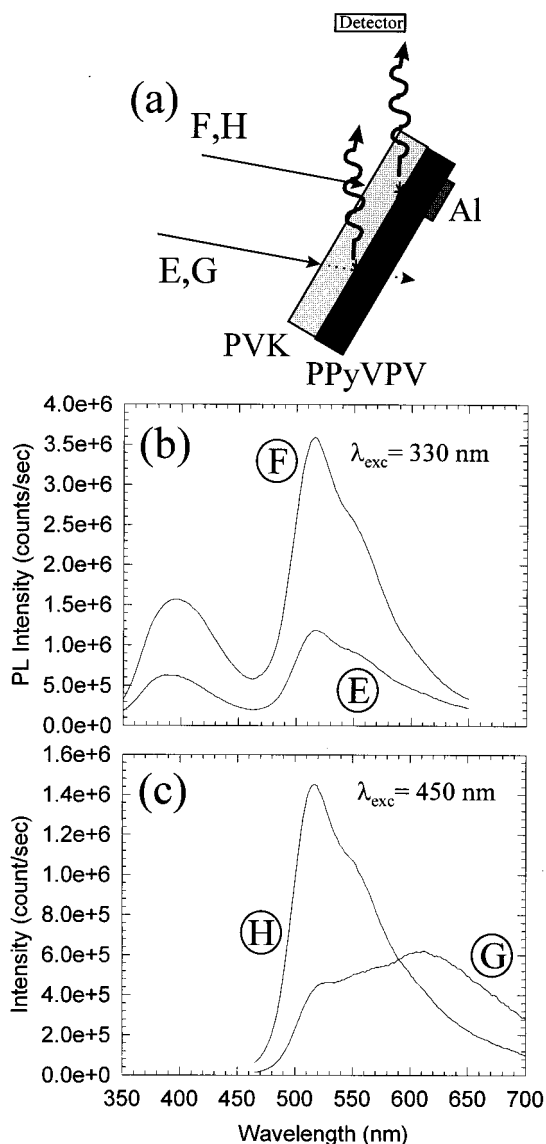


FIG. 11. PL of bilayer films of PVK/PPyVPV with the configuration shown schematically in (a). The excitation energies were (b) 330 nm (E,F) and (c) 450 nm (G,H).

luminescence and electroluminescence feature assigned to exciplex emission at their interface. The absorption and PLE spectra show that the emitting species is not directly accessible from the ground state. Blends exhibit photoluminescence which confirms the presence of exciplex emission. The exciplex is also the primary species of electroluminescence emission in the bilayer devices. The electroluminescence emission sites are removed to the polymer/polymer interface away from the quenching metal/polymer interface, greatly increasing device efficiency.

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