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Interface Control of Light-Emitting Devices Based on Pyridine-Containing Conjugated Polymers

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Introduction

In the past decade, there has been great interest in organic molecular and polymeric electroluminescent devices, particularly conjugated-polymer-based light-emitting devices (LEDs).[1−6] Electroluminescence (EL) is the emission of light generated from the radiative recombination of electrons and holes electrically injected into a luminescent semiconductor. EL combined with other unique properties of polymers, such as solution processibility, band gap tunability, and mechanical flexibility, make conjugated polymers excellent candidates for low-cost large-area display applications.

Typical single-layer polymer LEDs are constructed by sandwiching a thin layer of luminescent conjugated polymer between two electrodes, an anode and a cathode, at least one being transparent or semitransparent. When a high electric field is applied between the two electrodes, electrons are injected from the cathode and holes are injected from the anode into the polymer layer. The injected charges recombine and decay radiatively to emit light. The double charge injection mechanism of such polymer LEDs requires the matching of the cathode (anode) work function to the corresponding LUMO (HOMO) level of the polymer in order to achieve efficient charge injection. Indium−tin oxide (ITO) is widely used as anode material for polymer LEDs because it is conductive and transparent and has a relatively high work function that is close to the HOMO level of most conjugated polymers. On the other hand, because most conjugated polymers have relatively low electron affinity, they require metals with low work functions as cathode material to achieve efficient electron injection. However, low work function metals are generally oxygen reactive; thus, devices with a low work function cathode usually are unstable. Devices may degrade even during storage. To eliminate the use of low work function metals, one can either use polymers with high electron affinities or modify the charge injection characteristics at the polymer/electrode interfaces. Along the first line of reasoning, a number of high electron affinity polymers have been synthesized and successfully utilized in polymer LEDs, among which cyano-[8] and pyridine-containing conjugated polymers[9] are very promising. Along the second approach, some novel device configurations such as symmetrically configured AC light-emitting (SCALE) devices[10] and light-emitting electrochemical cells (LECs)[11] have been reported. These devices modify the charge injection and/or transport characteristics such that their operations are insensitive to the electrode materials used. As a consequence, more stable metals such as Al or Au can be used as electrodes.

LECs have device structures similar to those of polymer LEDs. The difference is that the active layer of a LEC consists of a blend of conjugated luminescent polymers and solid electrolyte together with mobile ions. Upon application of an electric field, the material on the anode side is p-doped and the material on the cathode side is n-doped. Thus, an in situ light-emitting p−n junction is formed. Due to the in situ doping of the active layer, the charge injection from the electrodes into the polymer is nearly ohmic. The operation of such devices is thus not sensitive to the electrodes used. As a consequence, LECs can be operated in both forward and reverse bias. However, due to the involvement of the motion of ionic species in the device operation, the device response time of the LECs is slow. It is noted that the interpretation of the operating mechanism of LECs was recently challenged.[12]

The SCALE devices consist of a light-emitting layer sandwiched between two redox polymer layers. The whole structure is then sandwiched between two electrodes. The introduction of the redox polymer layers between the

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emitting layer and the electrodes modifies the charge injection characteristics such that the devices can also be operated in both forward and reverse bias. Furthermore, as the operation of SCALE devices does not involve the motion of ionic species, the response time of SCALE devices is relatively fast, allowing the devices to be operated in AC modes up to ~100 kHz. In contrast, conventional polymer LEDs can only be operated in forward bias. No light is emitted under reverse bias.

One of the advantages of polymer LEDs is the easy tuning of emission colors through tailoring the chemical structure of conjugated polymers. To date, a variety of conjugated polymers and/or copolymers have been found whose emission colors cover all the visible spectra. However, for most devices the color of the emitted light is fixed once the device is fabricated. Recently there has been great interest in developing color-variable light-emitting devices, i.e., individual devices that can generate two or more colors of light. The colors can be controlled by a number of device parameters such as driving voltage, current, local temperatures, etc. The most common approach to a color-variable device is voltage-controlled multicolor single-layer LEDs. In this approach, a blend of organic materials, either polymers or molecules or both, often is used as the emitting layer. For example, in the devices using a blend of polythiophene derivatives, different components in the blend emit different colors of light simultaneously, with the intensity of each component varying with the applied voltage.[13] Similar voltage-dependent EL was observed in the devices using conducting polymer containing fluorescent dye as the emitting layer.[14] While using a blend is a good approach to white LEDs, it is often difficult to achieve blue emission due to absorption by the low-gap red- or green-emitting components in the blends. Also since blue light is located on the high-energy side of the visible spectrum, blue emission is often accompanied by low-energy emissions such as red, reducing the purity of the blue color.

Multilayer approaches are promising for color-variable devices that can generate relatively pure blue color. So far, the multilayer color-variable light-emitting devices mainly have focused on polarity-controlled two-color light-emitting devices.[15−19] There are very few reports on multilayer devices that can generate more than two colors. In color-variable multilayer devices, interfaces usually play an important role in the device operation.

In the following, we present interface control of a series of novel light-emitting devices based on pyridine-containing polymers, poly(*N*-vinylcarbazole) (PVK), and derivatives of polyacetylene. Pyridine-containing conjugated polymers have been shown to be promising candidates for light-emitting devices.[9] The pyridine-containing polymers are highly luminescent, especially the copolymers with phenylenevinylene. One of the most important features of the pyridine-based polymers is the higher electron affinity as compared to phenylene-based analogues. As a consequence, the polymer is more resistant to oxidation and shows better electron transport properties. The high electron affinity of pyridine-based polymers enables the use of relatively stable metals such as Al or Au or doped polyaniline as electrodes. Taking advantage of the better electron transport properties of the pyridine-containing polymers, bilayer devices utilizing PVK as a hole-transporting/electron-blocking polymer were fabricated, which improves the device efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. An unwanted effect of using PVK is that it increases the device operating voltage significantly. The incorporation of a conducting polyaniline (PAN−CSA) network electrode into PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness. By using the emeraldine base (EB) form of polyaniline as the redox polymer, SCALE devices were fabricated which work under both forward and reverse dc bias as well as in the ac mode. When the EB layer on the cathode side of the SCALE device is replaced with sulfonated polyaniline (SPAN) and the emitting layer is appropriately modified to balance electron and hole transport, color-variable bipolar/ac light-emitting devices were fabricated. These devices can generate different colors of light depending on the polarity of the driving voltages. Under forward bias, red light is generated from the emitting polymer/SPAN interface. Under reverse bias, light is generated from the bulk of the emitting layer whose color is dependent on the materials used. In certain cases, under reverse bias, emission colors are dependent on the magnitude of the applied voltages. Figure 1 shows the chemical structures of the materials that were used in these devices.

Device Fabrication and Test

A typical fabrication process for the polymer LEDs starts from patterning ITO-coated glass substrates. After patterning, each substrate was cleaned rigorously to remove contamination on the surface. For single-layer devices, the emitting layer was spin-cast at 1000−2000 rpm from a solution in a suitable solvent. For bilayer devices, the first layer was similarly spin-coated onto the ITO substrate. After drying, the second layer was coated on top of the first layer from a solution of a different solvent. A third layer can be similarly coated for three-layer devices. The solvents for the second and third layers are chosen such that they do not dissolve the adjacent layer underneath. All the spin-coating procedures were carried out inside a class 100 cleanroom in air. The top metal electrode was deposited by vacuum evaporation at a pressure below 10^{-6} Torr. To prevent damage to the polymers, the substrate was mounted on a cold-water-cooled surface during the evaporation.

Absorption spectra were measured on spin-cast films using a Perkin-Elmer Lambda 19 UV/vis/near-IR spectrometer. Photoluminescence (PL) and EL were measured using a PTI fluorometer (model QM-1). The current−voltage ($I-V$) characteristics were measured simultaneously with EL output while dc voltages were continuously applied by a HP model 6218A dc power supply. The current−voltage data were monitored by two Keithley

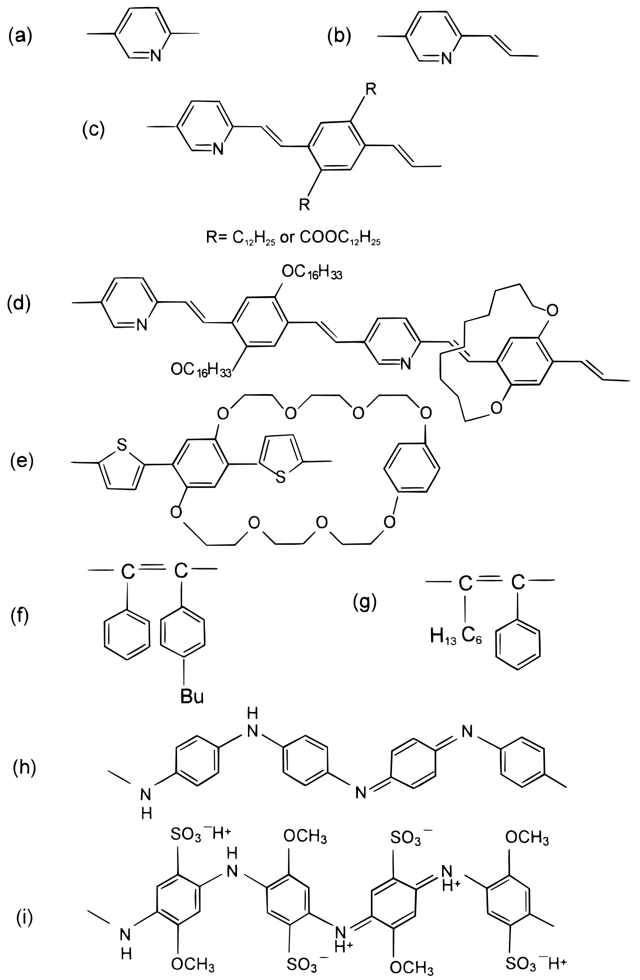

FIGURE 1. Repeat units of the pyridine-containing polymers and other materials used in the study: (a) poly(*p*-pyridine) (PPy); (b) poly(*p*-pyridylvinylene) (PPyV); (c) copolymer of PPV and PPyV (PPyVP-$(R)_2$V); (d) macrocycle-bridged copolymer of pyridylvinylene and phenylenevinylene (@PPyVPV); (e) macrocycle-bridged copolymer of dithienylene and phenylene (@PTP); (f) poly(diphenylbutylacetylene) (PDPA-^{n}Bu); (g) poly(hexylphenylacetylene) (PhPA); (h) emeraldine base (EB) form of polyaniline; (i) sulfonated polyaniline (SPAN).

model 195A multimeters while the EL output was monitored by a calibrated photodiode (UDT UV100). The data were recorded by a computer. Quantum efficiency and brightness were calculated from the *I*−*V*−EL data. We note that all the device-testing procedures were performed in air on as-made devices without any encapsulation.

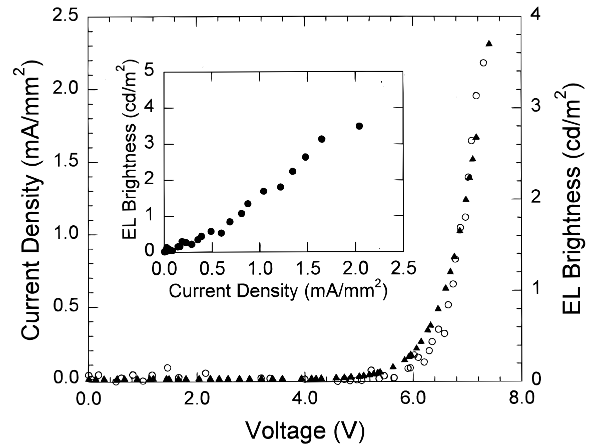

FIGURE 2. Current−voltage and brightness−voltage characteristics of a single-layer ITO/@PPyVPV/Al. Inset: brightness−current characteristics of the same device.

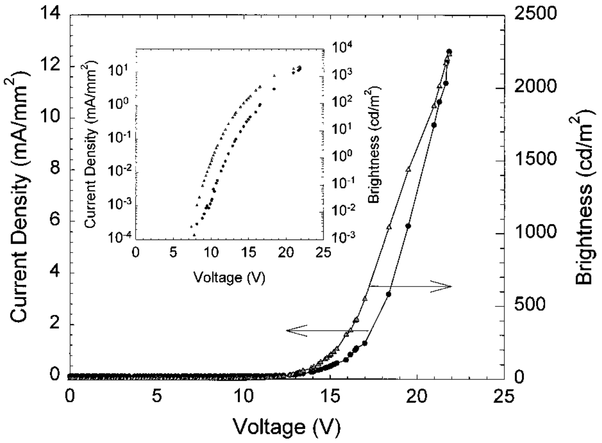

FIGURE 3. Current−voltage and brightness−voltage characteristics of a bilayer layer device, ITO/PVK/@PPyVPV/Al. Inset: same data plotted on a semilog scale.

Diode Devices

Figure 2 shows the current−voltage and brightness−voltage characteristics of a single-layer device using a copolymer of poly(pyridylvinylene) and poly(phenylenevinylene) derivatives with macrocycles bridging some or all of the phenyl groups, @PPyVPV, as the emitting layer (here @ is used to denote the macrocycle bridges; see Figure 1), and ITO and Al as the electrodes. The purpose of introducing the macrocycle bridges to the phenyl groups is to further separate the polymer chains and reduce the aggregate formation. The single-layer devices have a typical operating voltage of 5−10 V. The EL intensity closely follows the current, showing a linear relationship. The quantum efficiency of the single-layer devices is relatively low, typically 10^{-5} photons/electron (~0.001%). The performance of bilayer devices using PVK as the hole-transporting/electron-blocking layer improves dramatically as compared to that of single-layer devices. The maximum external quantum efficiency and maximum brightness of the bilayer devices increase 2−3 orders of magnitude, reaching ~0.8% and over 2000 cd/m^2, respectively, under continuous dc bias. Figure 3 shows the current−voltage and brightness−voltage characteristics of a bilayer device, ITO/PVK/@PPyVPV/Al. PVK is a well-known hole-transporting/electron-blocking polymer.[20] It enhances the transport of holes injected from the anode and blocks the transport of electrons injected from the cathode such that the electrons accumulate at the PVK/copolymer interface. This charge confinement greatly increases the probability of radiative recombination. In addition, the PVK layer moves the recombination zone away from the vicinity of both electrodes so that the radiative recombination is protected against the nonradiative quenching at the electrode/polymer interfaces.

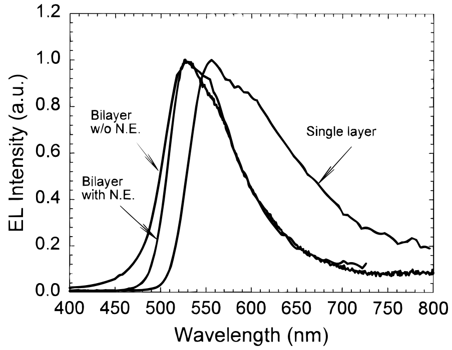

FIGURE 4. Normalized electroluminescence spectra for a single-layer ITO/@PPyVPV/Al device and bilayer ITO/PVK/@PPyVPV/Al devices with and without a PAN−CSA network electrode (N.E.).

An unwanted side effect of using the PVK layer is that it increases the device operating voltage substantially. The incorporation of a high-surface-area PAN−CSA network electrode in PVK effectively reduces the device turn on voltage to below 5 V.[21] The conducting polyaniline network electrode was formed by spin-casting a blend of camphorsulfonic acid-doped polyaniline (PAN−CSA) and low molecular weight host polymer poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in an appropriate ratio (~1:4) in *m*-cresol. The host polymer PMMA was subsequently washed away by xylenes solvent. PVK was then spin-coated on top of the PAN−CSA network electrode. The rough network electrode creates a nonuniform high electric field that enhances the charge injection.[22] Since the incorporation of the network electrode does not modify the PVK/copolymer interface, the high quantum efficiency and brightness of the bilayer device are maintained. The bilayer devices with and without a network electrode show similar EL spectra, which are blue-shifted as compared to that of the single-layer device, Figure 4.

The light generation in the bilayer device is attributed to radiative decay of exciplexes formed at the PVK/@PPyVPV interface. An exciplex is an excited dimer complex defined initially as a transient donor−acceptor complex formed between the excited state of the donor and the ground state of the acceptor.[20] In the unexcited state, the donor does not form a complex with the acceptor. Thus, exciplexes are expected to exhibit new fluorescent spectra but no new absorption features. Figure 5 compares the PL of pure @PPyVPV, pure PVK, and a bilayer of PVK/@PPyVPV, as well as the EL spectra of the bilayer device. The PL of PVK film excited at 345 nm has an emission peak at ~405 nm. The PL of pure @PPyVPV film excited at 468 nm peaks at ~610 nm with a shoulder at ~550 nm. When the PVK/copolymer bilayer film is excited at 345 nm, a new peak appears at ~520 nm with another peak at ~550 nm. The new peak is assigned to exciplex emission at the PVK/@PPyVPV interface. This assignment is supported by the optical absorption and photoluminescence excitation (PLE) measurements. Both the absorption and PLE of the bilayer PVK/copolymer film are the sum of those of individual PVK and copolymer films with no additional new features. Similar results are found for other copolymers without the macrocycle bridges.[23] The EL of the bilayer device follows closely the PL of the bilayer film, confirming that the EL originates almost entirely from the exciplex formed at the PVK/copolymer interface.

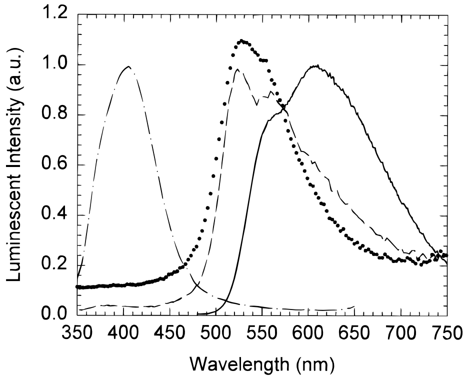

FIGURE 5. Normalized PL spectra of @PPyVPV film (solid line) excited at 2.65 eV, pure PVK film (dash−dotted line) excited at 3.6 eV, and bilayer of PVK/@PPyVPV (dashed line) excited at 3.6 eV, and the EL of the bilayer device (filled circle). The EL spectra are offset for clarity.

The single-layer devices and the bilayer devices (with and without a network electrode) discussed above are unipolar devices operating under a single polarity. Below we discuss two novel device configurations that can be operated in both forward and reverse dc bias as well as in the ac mode: the SCALE devices[10] and color-variable bipolar/ac light-emitting devices.[17]

SCALE Devices

The SCALE devices consist of a light-emitting layer sandwiched between two "insulating" redox polymer layers. The whole structure is then sandwiched between two electrodes. The SCALE device configuration is quite general. It can be applied to a variety of emitting and redox polymers, as well as electrodes.[10,24] For the SCALE device presented here, PPy was used as the emissive layer, EB was utilized as the redox material, and ITO and Al were used as electrodes. The Figure 6 inset shows schematically the structure of such SCALE devices. They emit light under both forward and reverse dc bias as well as under ac driving voltages. Under low-frequency ac (sinusoidal) driving voltage, light pulses with twice the driving frequency were observed. Figure 6 shows the variation of the EL intensity of an ITO/EB/PPy/EB/Al device driven by a 60 Hz sinusoidal voltage. Almost symmetric current−voltage and brightness−voltage characteristics are achieved. This unusual behavior is attributed to the effects of charge accumulation at the polymer/polymer interfaces.[10] Under low bias voltages, electrons and holes injected into the polaron levels of EB from the electrodes transport to the EB/PPy interfaces via a hopping mechanism and populate the EB/PPy interface. When the applied electric field is high enough, the stored charges tunnel into the HOMO and LUMO levels of PPy. The injected charges may form intrachain excitons and decay radiatively to emit photons or follow other nonradiative decay paths. If the charge

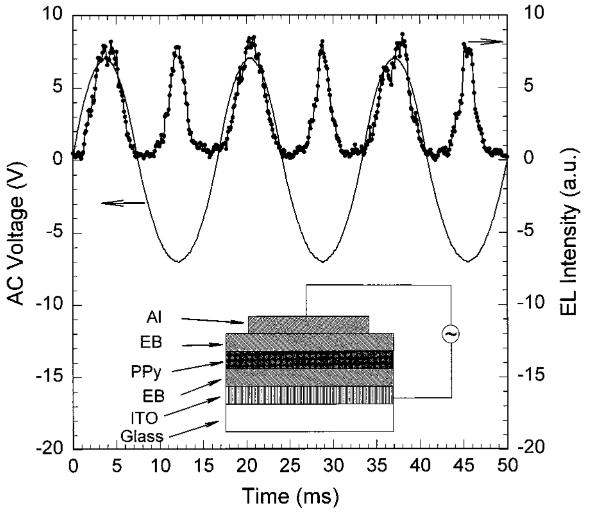

FIGURE 6. EL intensity as a function of time for a SCALE device driven by a 60 Hz sinusoidal voltage. Inset: schematic device structure of the SCALE device.

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 may 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 work function 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 LEDs. Also, experimental evidence supports the finding that continuous reversal of the sign of the driving voltage under ac operation reduces degradation of the devices.[25]

Polarity-Controlled Two-Color SCALE Devices

The SCALE devices generate the same color of light under both forward and reverse bias. When the EB layer on the cathode side is replaced by sulfonated polyaniline (SPAN) and the emitting layer is properly modified to balance electron and hole transport, color-variable bipolar/ac light-emitting devices can be fabricated. Because SPAN is capable of modifying the emission properties of certain pyridine-containing polymers at the interface such that the interface emits different colors of light than the bulk does, the device is able to generate a different color of light under forward and reverse bias. In this approach, the colors of light are controlled by selecting the desired emission locations that in turn are controlled by the polarity of driving voltage and the charge injection and transport properties of the polymer layers. Since motion of ionic species is not required for device operation, unlike the case for the two-color light-emitting electrochemical cells, a relatively fast time response is achieved, allowing the colors to be switched rapidly.

For the devices presented here, the macrocycle-bridged copolymer @PPyVPV and a macrocycle-bridged copolymer of polythiophene and polyphenylene derivative, @PTP, were used as the emitting materials, SPAN and EB were used as the redox materials, and ITO and Al were used as electrodes. The Figure 7 inset shows the schematic diagram of the device structure of the color-variable bipolar/ac light-emitting devices.

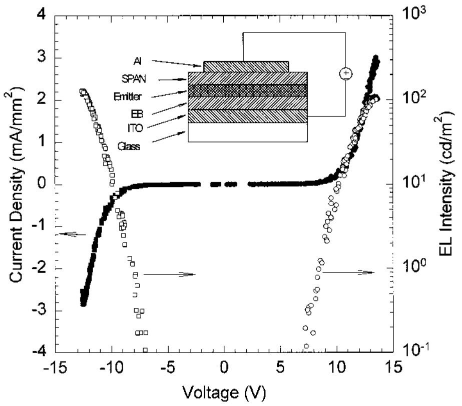

FIGURE 7. Current–voltage and brightness–voltage characteristics of a polarity-controlled two-color device, ITO/EB/@PPyVPV:@PTP/SPAN/Al, under forward and reverse bias conditions. Inset: schematic structure of the polarity-controlled two-color device.

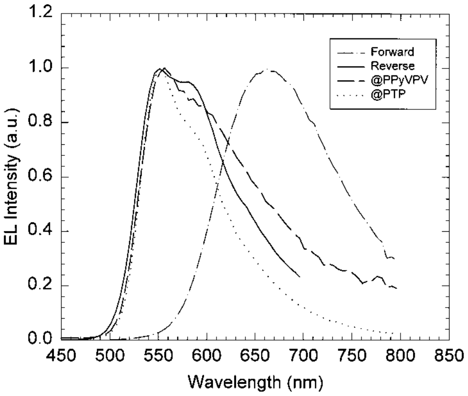

FIGURE 8. EL spectra of the ITO/EB/@PPyVPV:@PTP/SPAN/Al device under forward and reverse bias conditions. For comparison, the EL spectra for single-layer @PPyVPV and @PTP devices also are shown.

Figure 7 shows the typical current–voltage and brightness–voltage characteristics of the polarity-controlled two-color devices. The devices have typical turn on voltages of ~4–8 V depending upon film thickness and work well under both polarities of driving voltage with different colors of light being emitted. The light appeared red and green to the eye under forward and reverse bias, respectively, and was clearly visible under normal indoor lighting. The device efficiency of greater than 0.1% photons/electron has been achieved. Figure 8 shows the EL spectra of the color-variable device under forward and reverse bias. For comparison, the EL spectra for single-layer @PPyVPV and @PTP devices also are shown. The colors of the devices can be switched rapidly, up to ~20 kHz, depending upon device impedance and geometry.

The EL spectrum under forward bias is substantially different from that of the single-layer devices of either @PPyVPV or @PTP, suggesting that the light is generated from the interface between the emitter blend and either EB or SPAN under forward bias. To further clarify this, we fabricated the following devices: ITO/@PPyVPV/Al, ITO/SPAN/@PPyVPV/Al, ITO/@PPyVPV/SPAN/Al, ITO/SPAN/@PPyVPV/SPAN/Al, and similar devices replacing SPAN with EB. All these devices were fabricated and tested under similar conditions in forward bias. Among all these devices, only ITO/@PPyVPV/SPAN/Al and ITO/SPAN/@PPyVPV/SPAN/Al show dramatically red-shifted EL. This clearly demonstrates that the red light is generated from the @PPyVPV/SPAN interface on the cathode side under forward bias. Similar studies using @PTP as the emitting layer show that the emission properties of @PTP are not affected significantly by the presence of the SPAN layer.

The EL spectra of the color-variable device under reverse bias are similar to those of the single-layer @PPyVPV and @PTP devices, implying that the light is generated either in the bulk of the emitting polymer or at the EB interface. The EB layer functions as a charge injection enhancement layer, playing a similar role as it does in SCALE devices reported earlier.[10] Under reverse bias, the SPAN layer on the cathode side plays a similar role. The presence of the EB layer is not critical. In some cases, the device works well without the EB layer.

It is noted that when the blend in the color-variable devices is replaced by pure @PPyVPV polymers, the devices emit red light in forward bias and red-orange light in reverse bias. This indicates that under reverse bias the light is still generated near @PPyVPV/SPAN interfaces. This can be understood in terms of different electron and hole transport properties of the @PPyVPV and @PTP polymers. It is known that most conjugated polymers, including poly(phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), and polythiophene, have better hole than electron transport properties.[3] The addition of a high-electronegativity unit, pyridine, to the backbone is expected to improve the electron transport properties. Therefore, under reverse bias the light is still generated near the SPAN interface for the ITO/EB/@PPyVPV/SPAN/Al device. By adding @PTP, which is expected to have better hole transport properties, to @PPyVPV, the overall hole transport properties of the blend are improved, and hence the light is generated away from the SPAN interface for the ITO/EB/Blend/SPAN/Al device under reverse bias, emitting green light. Figure 9 shows the EL spectra of the ITO/EB/@PPyVPV:@PTP/SPAN/Al devices with different @PPyVPV:@PTP ratios. When the concentration of @PTP increases, the EL spectrum under reverse bias shifts from red to green. Under forward bias, however, the concentration of the @PTP has no significant effects on the EL spectra.

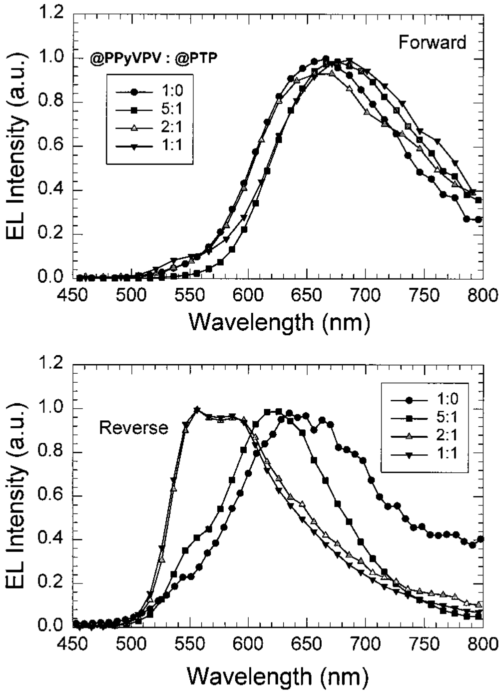

FIGURE 9. Comparison of the EL spectra of ITO/EB/@PPyVPV:@PTP/SPAN/Al devices with different @PPyVPV:@PTP ratios under (a) forward bias and (b) reverse bias. When the concentration of @PTP increases, the EL spectrum under reverse bias shifts from red to green.

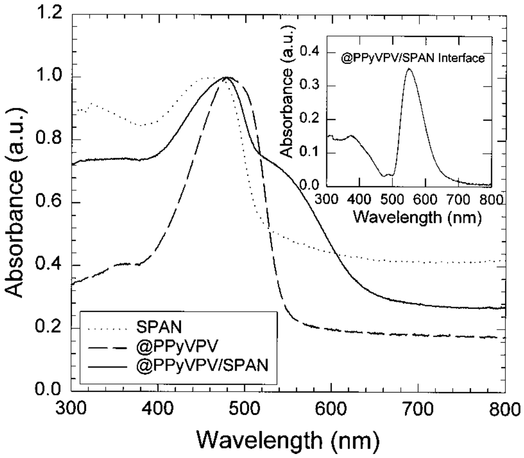

FIGURE 10. Absorbance spectra of a @PPyVPV film spin-cast from xylenes solution, a SPAN film spin-cast from aqueous solution, and a bilayer of @PPyVPV/SPAN. Inset: absorbance spectra as a result of subtraction of the absorbance of each individual layer from that of the bilayer.

The mechanism for the SPAN layer changing the emission properties of the @PPyVPV polymer is attributed to the formation of new emissive species due to protonation of the pyridyl units by SPAN.[17,26] These species were identified by both absorption and PL experiments. Figure 10 shows the absorbance spectra of a @PPyVPV layer, a SPAN layer, and a bilayer of @PPyVPV/SPAN. SPAN is a self-doped, water-soluble conducting polymer with a room-temperature conductivity of 10^{-2} S/cm.[27] It has a wide optical window from green to near-IR. @PPyVPV has an absorption band that peaks around 480 nm. An extra shoulder around 500 nm is present in the absorption spectra of the bilayer of @PPyVPV/SPAN. The extra feature, assigned to the absorption at the interface, is clearly shown in the inset of Figure 10 as a result of subtraction of the absorbance of each individual layer from that of the bilayer. We attribute the interface absorption to new species due to protonation of @PPyVPV by SPAN. One special feature of SPAN is that it is acidic in aqueous solution (it is often termed polyanilinesulfonic

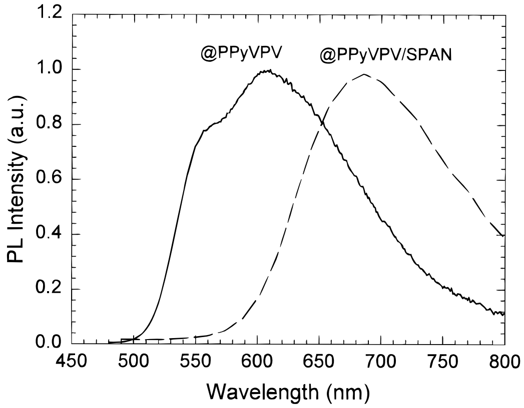

FIGURE 11. PL spectra of @PPyVPV (solid line) and PPyVPV/SPAN (dashed line) films.

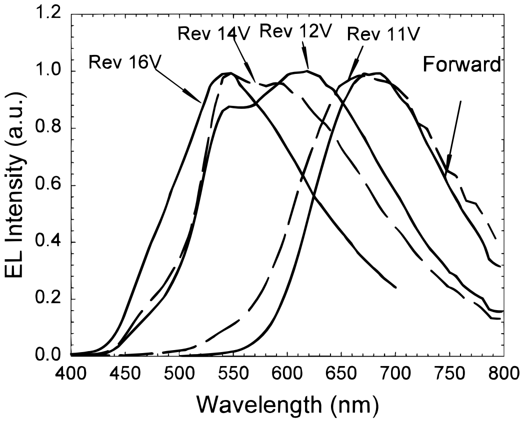

FIGURE 12. EL spectra of an ITO/@PPyVPV:PDPA-^{n}Bu/SPAN/Al device under forward and reverse bias conditions. Under forward bias, the EL spectrum is voltage-independent. Under reverse bias, the EL spectrum shifts from red to green as the voltage increases.

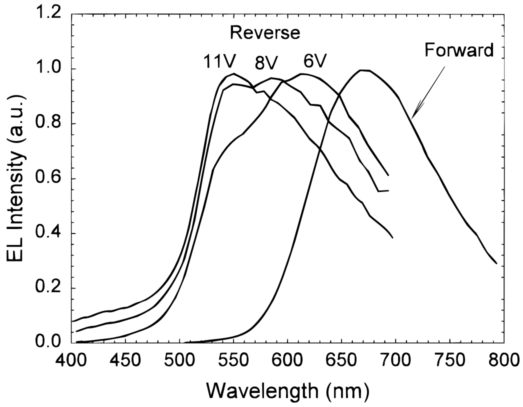

FIGURE 13. EL spectra of an ITO/@PPyVPV:PhPA/SPAN/Al device under forward and reverse bias conditions. Under forward bias, the EL spectrum is voltage-independent. Under reverse bias, the EL spectrum shifts from red to green as the voltage increases.

acid). On the other hand, the pyridyl unit is known to be susceptible to protonation or quarternization by acid.[28] To further clarify this, we performed the same absorption experiment on the films with the same configurations as above but replacing the SPAN with toluenesulfonic acid (TSA). An almost identical absorbance feature to the @PPyVPV/SPAN was found in the @PPyVPV/TSA bilayer, confirming that the new species at the @PPyVPV/SPAN interface originates from the protonated pyridyl units. The new species are emissive and emit red-shifted light as compared to nonprotonated polymer. Figure 11 compares the PL spectra of the @PPyVPV with and without protonation by the SPAN layer. A luminescence red-shift also was found in bipyridine-containing PPV derivatives upon acid protonation.[29]

Polarity- *and* Voltage-Controlled Multicolor Bipolar Devices

When the @PTP is replaced by derivatives of polyacetylene, PDPA-^{n}Bu or PhPA, voltage-dependent emission colors are observed under reverse bias. Figure 12 shows the EL spectra for a ITO/@PPyVPV:PDPA-^{n}Bu/SPAN/Al device under forward and reverse applied voltages. Under forward bias, the device emits almost saturated red light, similar to the polarity-controlled two-color devices.[5,6] Under reverse bias, however, as the voltage increases, the colors vary from red to orange to yellow and then change to green as the voltage further increases. We note that the brightness also increases with the applied voltage.

Figure 13 shows the EL spectra for a ITO/@PPyVPV:PhPA/SPAN/Al device under forward and reverse applied voltages. Again under forward bias, the device emits red light independent of voltage. Under reverse bias, the emission colors change from orange to green as the voltage increases. However, the EL spectrum does not change further to blue at higher voltages beyond 11 V. This result is somewhat surprising. It is expected that the color should shift further to the blue region as the voltage further increases because the PhPA is a blue-emitting polymer.[30] One possible explanation is that the emitted blue light from PhPA at high voltage is absorbed by PPyVPV and re-emits as photoluminescence. When one examines the EL spectrum of PhPA[30] and the absorption spectrum of @PPyVPV (see Figure 10), this scenario is highly probable. PhPA shows a broad EL spectrum peak at 450 nm. On the other hand, the absorption spectrum of PPyVPV peaks at 470 nm with a substantial absorption at 450 nm. Indeed, the PL emission of @PPyVPV at ∼600 nm[21] appears in the EL spectra of the ITO/@PPyVPV:PhPA/SPAN/Al device at higher reverse bias.

In the polarity-controlled two-color devices,[5,6] under reverse bias, we have shown that the exact emission location is determined by the concentration of the hole-transporting @PTP in @PPyVPV. When the @PTP concentration increases, the emission location is further away from the PPyVPV interface into the bulk of the emitting materials, resulting in a gradual color shift from orange-red to green. However, the individual device with fixed @PTP concentration only shows one color under reverse bias. By replacing the @PTP with PDPA-^{n}Bu or PhPA, the emission location under reverse bias now can be controlled by the magnitude of the applied voltage instead of @PTP concentration, implying that the voltage is now playing a role similar to that of the concentration of @PTP. This can be rationalized by assuming a smaller but stronger field-dependent hole mobility of PDPA-^{n}Bu and PhPA than @PTP.

Summary and Conclusion

In summary, we have presented a number of light-emitting devices based on pyridine-containing conjugated polymers and copolymers in various device configurations. Interfaces play a very important role in controlling the device charge transport and emission characteristics.

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