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Direct and Alternating Current Light-Emitting Devices Based on Pyridine-Containing Conjugated Polymers

by

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We present novel direct and alternating current light-emitting devices based on several pyridine-containing conjugated polymers and copolymers in various device configurations. The high electron affinity of pyridine-based polymers improves stability and electron transport properties of the polymers and enables the use of relatively stable metals such as Al or even ITO as electron injecting contacts. Bilayer devices utilizing poly (9-vinyl carbazole) (PVK) as a hole transporting/electron blocking polymer show dramatically improved efficiency and brightness as compared to single layer devices. The incorporation of a conducting polyaniline network electrode into PVK reduces the device turn on voltage significantly while maintaining the high efficiency of the bilayer device. The bilayer device structure can be arranged to enable the device to work under both forward and reverse bias, as well as in AC modes. Interfaces play an important role in the operation of these devices. Furthermore, when the EB is replaced by sulfonated polyaniline (SPAN) on the cathode side and the emitting layer is properly modified to balance electron and hole transport, the device generates different colors of light, red under forward bias and green under reverse bias.

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Direct and alternating current light-emitting devices based on pyridine-containing conjugated polymers

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Abstract

We present novel direct and alternating current light-emitting devices based on several pyridine-containing conjugated polymers and copolymers in various device configurations. The high electron affinity of pyridine-based polymers improves stability and electron transport properties of the polymers and enables the use of relatively stable metals such as Al or even ITO as electron injecting contacts. Bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as a hole transporting/electron blocking polymer show dramatically improved efficiency and brightness as compared to single layer devices. This is attributed to charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of a conducting polyaniline network electrode into PVK reduces the device turn on voltage significantly while maintaining the high efficiency of the bilayer device. The bilayer device structure can be arranged in both

of polyaniline (PAN) on both side of the emitting layer enables the device to work under both forward and reverse bias, as well as in AC modes. Interfaces play an important role in the operation of these devices. Furthermore, when the EB is replaced by sulfonated polyaniline (SPAN) on the cathode side and the emitting layer is properly modified to balance electron and hole transport, the device generates different colors of light, red under forward bias and green under reverse bias.

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) [1-4]. Electroluminescence (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.

Most "conventional" polymer light-emitting devices have been shown to be tunneling diodes and can be operated only under forward DC bias [5]. Among the most important limitations associated with many of the "conventional" polymer light-emitting diodes (LEDs) are poor stability and shelf lifetime. Devices degrade even during storage. The double charge injection mechanism of the "conventional" 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. The relatively low electron affinity of most conjugated polymers requires metals with very low work functions to achieve efficient electron injection. However, since low work function metals are generally oxygen reactive, devices with a low work function cathode usually are unstable. Thus, light-emitting devices with high work function electrodes and high electron affinity polymers are highly desirable. A number of high electron affinity polymers have been synthesized and successfully utilized in polymer light-emitting devices, among which cyano- [6] and pyridine-containing conjugated polymers [7] are very promising.

Recently there have been reports of new device configurations such as symmetrically configured AC light-emitting (SCALE) devices [8] and light-emitting electrochemical cells (LECs) [9]. These devices modify the charge injection and/or transport characteristics such that the device can be operated under both forward and reverse bias and their operation is insensitive to the electrode materials used. As a consequence, more stable metals such as Au can be used as electrodes, potentially reducing unwanted chemical reactions. While the response of the LECc is slow due to the involvement of motion of ionic species in the device operation, the SCALE devices can be operated under AC modes up to ~100 kHz.

To date, a variety of conjugated polymers and/or copolymers have been found to exhibit electroluminescent properties such that all the colors necessary for display applications are obtainable. However, for most devices the color of the emitted light is fixed once the device is fabricated. Recently there has been substantial 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 either magnitude [10] or polarity [11-13] of the driving voltage.

We present a series of novel light-emitting devices based on pyridine-containing conjugated polymers and copolymers. Pyridine-containing conjugated polymers have been shown to be promising candidates for light-emitting devices [7]. The pyridine containing polymers are highly luminescent, especially the copolymers. For example, the internal photoluminescent quantum efficiencies of the copolymers consisting of alternating units of pyridyl vinylene and phenylene vinylene have been measured to be 75-90% in solution and 18-30% in film. As compared to phenylene-based analogues, one of the most important features of the pyridine based polymers is the higher electron affinity. As a consequence, the polymer is more resistant to oxidation and shows better electron transport properties. In contrast, most other conjugated polymers are susceptible to oxidation and exhibit better hole transport properties. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al, Au, or ITO and doped polyaniline as electrodes. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricated bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer, which improves the device efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode into PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness. The high electron affinity of the pyridine-based polymers enables the use of ITO as an electron injecting contact (in addition to its use as a hole injecting contact as in typical polymer light-emitting diodes) to fabricate inverted light-emitting devices [14]. A metal with a high work function, such as Au, is used as a hole injecting contact. By inserting a layer of emeraldine base (EB) form of polyaniline on both side of the emitting polymer, we fabricated symmetrically configured AC light-emitting (SCALE) devices [8] which work under both forward and reverse DC bias as well as in AC modes. When we replace the EB layer on the cathode side of the SCALE device with sulfonated polyaniline (SPAN) and modify the emitting layer to appropriately balance electron and hole transport, color variable bipolar/AC light-emitting devices are fabricated that can generate different colors of light depending on the polarity of the driving voltage, red under forward bias and green under reverse bias. Figure 1 shows the repeat units of the pyridine-containing polymers and other polymers that were used in these devices.

Experiments

For single layer devices, the emitting layer was spin-cast at 1000-2000 rpm from solutions in formic acid (for polypyridine (PPy) and poly(pyridyl vinylene) (PPyV)) or xylenes (for copolymers of pyridyl vinylene (PyV) and phenylene vinylene (PV)) (with a concentration of ~10 mg/ml) onto pre-cleaned patterned ITO substrates with a sheet resistance of ~15 ohm/square. For bilayer devices, the PVK layer was spin coated onto the ITO substrate from solution in tetrahydrofuran (THF) (~10 mg/ml) at ~3000 rpm. The emitting layer was then spin coated on top of the PVK layer from appropriate solutions (typically xylenes). As the solvent for the emitting layer does not dissolve PVK, no significant intermixing of the two polymers is expected. The conducting polyaniline network electrode was formed by spin-casting from a blend (1:4 ratio) of camphor sulfonic acid doped polyaniline (PAN-CSA) and a low molecular weight host polymer poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in *m*-cresol. The host polymer PMMA was subsequently washed away by xylenes. As xylenes is an excellent solvent for PMMA but a poor solvent for PAN-CSA, the extraction of the PMMA left a porous network of PAN-CSA. The PVK and emitting layers were subsequently coated as in the bilayer device. The PVK layer is expected to partially fill the PAN-CSA network, resulting in a structure schematically illustrated in Fig. 2. Similar effects has been reported for the formation of PAN-CSA network within a PPV derivative [15]. For the inverted bilayer device, the emitting layer (PPy) was first spin coated from formic acid onto ITO followed by the PVK coated from THF. The SCALE devices were fabricated by spin-casting a solution of EB in N-methyl pyrrolidinone (NMP) (~5 mg/ml) onto an ITO substrate. After drying in dynamic vacuum, a layer of the emitting polymer was spin-coated on the EB surface. Another EB layer was similarly coated on top of the emitting layer. The spinning speed for all layers is ~ 2000 rpm. The color variable/AC light-emitting devices were similarly fabricated as the SCALE devices except that the top EB layer was replaced by SPAN cast from aqueous solution and the emitting layer was comprised of a blend of polymers. 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/NIR spectrometer. Photoluminescence (PL) and EL were measured using a PTI fluorometer (model QM-1). The current-voltage characteristics were measured simultaneously with EL using two

Keithley model 195A multimeters while dc voltage was applied by a HP model 6218A DC power supply. Quantum efficiency and brightness were measured using a calibrated photodiode (UDT UV100). We note that all the device testing procedures were performed in air on as-made devices without any encapsulation.

Results and Discussion

Figure 3 shows the current-voltage and brightness-voltage characteristics of a single layer device using the wrapped copolymer @PPyVPV as the emitting player. The single layer devices have a typical operating voltage of 5-10 V. The EL intensity follows closely with the current and shows linear relationship. The quantum efficiency of the single layer devices is relatively low, typically ~0.001% photon/electron. The performance of a bilayer devices using PVK as the hole transporting/electron blocking layer improves dramatically as compared to single layer devices. The internal quantum efficiency and brightness of the bilayer devices increase two to three orders of magnitude, reaching ~0.5% and over 300 cd/m^2, respectively. Figure 4 compares the electroluminescence-voltage and electroluminescence-current characteristics for a single layer device and a bilayer device using the wrapped copolymer as the emitting layer. As a well known hole transporting/electron blocking polymer, PVK 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 removes the recombination zone from the vicinity of the electrode so that the radiative recombination is protected against the non-radiative quenching at the electrode/polymer interfaces.

An unwanted side effect of using the PVK layer is that it increases the device operating voltage substantially. One effective way to reduce the device turn on voltage is to use a high surface area network electrode [14]. The rough electrode will create a non-uniform high electric field that enhances the charge injection. This technique has been successfully applied to PPV based single layer devices [15]. Figure 5 compares the electroluminescence-voltage and electroluminescence-current characteristics the bilayer devices with and without the network electrode. For a device emitting at ~50 cd/m^2, the operating voltage is reduced from over 20 V to less than 10 V by introducing the network electrode. Since the incorporation of the PAN-CSA network electrode does not modify the PVK/copolymer interface, the high quantum efficiency and brightness of the bilayer device are maintained. Thus, the incorporation of the network electrode to the bilayer device dramatically improves the power efficiency (light output power/electrical input power) from ~0.07% to ~0.22%. The bilayer devices with and without PAN-CSA network electrode show similar EL spectra, which are blue shifted as compared to that of the single layer device, see Fig. 5 inset. The slightly reduced intensity at high energy tail for the device with network electrode is probably due to absorption by the PAN-CSA.

The light generation in the bilayer device is attributed to decay of exciplexes formed at the PVK/copolymer interface. Figure 6 compares the PL of pure wrapped copolymer, pure PVK, and bilayer of PVK/copolymer, as well as the EL spectra of the bilayer device. The PL of PVK film excited at 3.6 eV has an emission peak at 3.06 eV. The PL of pure wrapped copolymer film excited at 2.65 eV peaks at 2.03 eV with a shoulder at 2.25 eV. When the PVK/copolymer bilayer film is excited at 3.6 eV, a new peak appears at 2.38 eV with another peak at 2.23 eV. The new peak is assigned to exciplex emission at the PVK/copolymer 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 unwrapped copolymers [16]. The EL of the bilayer device follows closely with the PL of the bilayer film in accord with the EL emission originating primarily from the exciplex formed at the PVK/copolymer interface.

The high electron affinity of the pyridine-based polymers enables novel device configurations such as inverted light-emitting devices that are capable of eliminating the use of low work function metals. Poly(*p*-pyridine) has an electron affinity of ~3.5 eV, which allows metals with relatively high work functions as electron injecting contacts. In the inverted light-emitting devices, ITO was used as an electron injecting contact, in contrast to most polymer LEDs which use ITO as the hole injecting contacts. Au, a metal with even higher work function (~5.3 eV), was used as a hole injecting electrode. The inverted (-) ITO/PPy/Au (+) devices show improved device performance including quantum efficiency, brightness, operating stability and storage lifetimes as compared to the usual (+) ITO/PPy/Al (-) device. By inserting a PVK layer in between the PPy and Au, the device performance improves further. Figure 7 shows the current-voltage characteristics of a typical (-) ITO/PPy/PVK/Au (+) device. The device has a typical turn on voltage of ~10 V, and light follows closely with current after turn on. The device structure is shown schematically in the Fig.7 inset.

The single layer devices, the bilayer devices (with and without PAN-CSA network electrode) and the inverted devices discussed above are unipolar devices operating under a single bias condition. Below we discuss two novel device configurations that can be operated in both forward and reverse DC bias as well as in AC modes: the SCALE devices and color variable bipolar/AC light-emitting 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. For the SCALE device presented here, PPy was used as the emissive layer; the emeraldine base (EB) form of polyaniline was utilized as the redox material; ITO and Al were used as electrodes. Figure 8 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 voltage. Under low frequency AC (sinusoidal) driving voltage, light pulses with twice the driving frequency were observed. Figure 8 shows the variation of the EL intensity of a ITO/EB/PPy/EB/Al device driven by a 60 Hz sinusoidal voltage. Under DC bias, these devices emit light in both forward and reverse bias with almost symmetric current-voltage and brightness-voltage characteristics. This unusual behavior is attributed to the effects of charge accumulation at the polymer/polymer interfaces [8]. We examine the role of EB layers in the SCALE device operation by fabricating several single- and multi- layer devices ITO/PPy/Al, ITO/EB/PPy/Al, ITO/PPy/EB/Al, ITO/EB/PPy/EB/Al, and ITO/EB/PPy/EB/Au, and comparing the device characteristics.

Figure 9 compares the current-voltage characteristics for ITO/PPy/Al, ITO/EB/PPy/Al, ITO/PPy/EB/Al, and ITO/EB/PPy/EB/Al devices. The light intensity follows closely with the corresponding current-voltage curve except for the ITO/PPy/EB/Al device in reverse bias, in which case no light was observed although there is significant current flow. Notice that the turn-on voltage is lower and the current is higher at any given applied voltage when EB layers are added, indicating that EB facilitates, instead of limits, charge injection into the emitting polymer.

Photoinduced optical studies show that positive (P^+) and negative (P^-) polaron levels exist inside the π-π^* band gap of EB associated with benzenoid and quinoid levels, respectively [17]. They are believed to play an important role in charge injection and transport. We propose the following mechanism for the SCALE device operation. Under low bias voltages, electrons and holes can be injected from the electrodes into the quinoid and benzenoid levels of EB and form negative and positive polarons, respectively. These polarons transport to the EB/PPy interfaces via a hopping mechanism and populate the EB/PPy interfaces at the polaron levels, as shown in Fig. 10. Because the polarons levels are within the π-π^* band gap of EB, and are also likely within the band gap of PPy, the barriers for charge injection from electrodes to polaron levels of EB are significantly reduced as compared to injection directly to conduction and valence bands of PPy. Within this model, the limiting barriers for charge injection are changed from the electrode/polymer contacts as proposed for conventional polymer LEDs to the polymer/polymer (EB/PPy) interfaces of the SCALE devices. When the applied electric field is high enough, the stored charges begin to tunnel into the conduction and valence bands of PPy. When they meet, the injected charges may form intrachain excitons and decay radiatively to emit photons or follow other nonradiative decay paths. If the charge injection is not balanced, as is the case for most polymer LEDs, the excess charge carriers may migrate through the PPy layer without decaying. Most of these charges will be trapped in the opposite PPy/EB interface. When the bias voltage is reversed, the shallow trapped charges will be released from the interfaces and contribute to the recombination current. The deep trapped charges which act as quenchers or injection limiters in DC devices will be neutralized. We point out that the use of stable high 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 light-emitting devices. Also, continuous reversal of the sign of the driving voltage under AC operation may reduce degradation.

The SCALE devices generate the same color of light under both forward and reverse bias. Recently there has been great interest in developing color variable polymer light-emitting devices, *i.e.*, individual devices that can generate two or more colors of light. A number of approaches have been reported. One approach was based on blends of polythiophene derivatives in which different components emit different colors of light simultaneously with the intensity of each component varying with the applied voltage [10]. Though such devices can emit multiple colors of light, they have very limited control of the brightness at a desired color. Another approach is color variable light-emitting electrochemical cells (LECs) [11] which emit two independent colors of light. The two color LECs offer an improved control of the color and brightness: the color is controlled by the polarity and the brightness is controlled by the magnitude of the driving voltage. However, due to the involvement of ionic species in the device operation, the response of the devices is intrinsically slow and not suitable for applications that requires rapid switching of colors. More recently, multilayer light emitting devices which generate two independent colors were achieved at liquid nitrogen temperature by inserting a blocking layer in between two different emitting polymer layers [12]. The two colors also can be controlled by the polarity of the driving voltage. Such an approach improves the device response time. However it raises the device operating voltage due to the introduction of the charge blocking layer and retains the stability concerns of "conventional" polymer LEDs. We have reported a new approach to the color variable polymer light-emitting devices based on SCALE device structure: color variable bipolar/AC light-emitting devices [13]. In this approach we replace the EB layer on the cathode side of the SCALE device structure with sulfonated polyaniline (SPAN). Because the 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 which 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 a relatively fast time response is achieved, allowing the colors to be switched rapidly.

For the devices presented here, the wrapped copolymer @PPyVPV, and a wrapped copolymer of polythiophene and polyphenylene derivative, @PTP, were used as the emitting materials; SPAN and EB were used as the redox materials; ITO and Al were used as electrodes. Figure 11 shows the schematic diagram of the device structure of the color variable bipolar/AC light-emitting devices.

Figure 12 shows the typical current-voltage and brightness-voltage characteristics of the color variable devices. The devices have typical turn on voltages of ~4-8 V depending upon film thickness and work equally well under both polarities of driving voltage, as reported earlier for similar SCALE devices, 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. Internal device efficiencies of 0.1% photons/electron has been achieved for the initial devices. Figure 13 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 are also shown. The CIE chromaticity x,y coordinates of the two spectra are calculated to be (0.654,0.345) and (0.471,0.519), respectively, showing both colors to be relatively pure (see Fig. 12 inset). 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 redshifted 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 spectrum 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 [8]. Under reverse bias, the SPAN layer on the cathode side plays a similar role.

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(phenylene vinylene) (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 is 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. In fact, a gradual EL spectra shift toward green has been observed for the devices with increasing concentration of @PTP in the blend, as shown in Fig. 14.

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. These species was identified by both absorption and PL experiments. Figure 15 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 [18]. It has a wide optical window from green to near IR. @PPyVPV has an absorption band peaked 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 Fig. 15 as a result of subtraction of the absorbance of each individual layers 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 polyaniline sulfonic acid). On the other hand, the pyridyl unit is known to be susceptible to protonation or quarternization by acid [19]. To further clarify this, we performed the same absorption experiment on the films with the same configurations as above but replacing the SPAN with toluene sulfonic 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 redshifted light as compared to non-protonated polymer.

Our approach to the color variable light-emitting devices presented here has a number of important advantages: (1) The two redox polymers modify the charge injection properties of the polymer/metal interfaces allowing the use of high work function metals as electrodes. This potentially reduces the aging problems associated with "conventional" polymer LEDs which must use reactive low work function metals to achieve efficient electron injection. (2) The introduction of the two redox polymers allows the devices to operate in both forward and reverse bias. Since no ionic species are involved directly in the device operation, the colors can be switched very rapidly, in sharp contrast to intrinsically slow response LECs. (3) The emission zone is confined in between the two emitting polymer/redox polymer interfaces and away from the electrodes, thereby avoiding EL quenching effects near the metal electrodes. (4) The emitting polymers are protected by the redox polymers against direct exposure to air, potentially improving the device stability. (5) AC or periodically reversed operation may retard failure due to migration of metals from the electrodes into the polymer. Such operation also may dissipate built-up of space charges.

Summary and Conclusion

In summary, we have presented a number of DC and AC light-emitting devices based on pyridine-containing conjugated polymers and copolymers. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al as efficient electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we have fabricated bilayer devices utilizing PVK as hole transporting/electron blocking polymer. The bilayer device structure improves the device quantum efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of the conducting polyaniline network electrode within PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness of the bilayer device. The high electron affinity of the pyridine-based polymers also enables the fabrication of novel devices such as inverted light emitting devices, SCALE devices, and color variable bipolar/AC light emitting devices, which are capable of eliminating the use of low work function metals as electrodes, potentially further improving the device operating stability and shelf lifetime.

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References

[1] C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).

[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990).

[3] D. D. C. Bradley, *Synth. Met.* **54**, 401 (1993); J. Kido, *Trends in Polymer Science* **2**, 350 (1994).

[4] See, for example, *Proc. Int. Confs. Sci. Tech. Synth. Met.*, Seoul, Korea, July 21-29, 1994 (*Synth. Met.* **69-71**,1995); Snowbird, Utah, July 28 - Aug. 2, 1996 (*Synth. Met.* **84-86**, 1997); J. W. Blatchford and A. J. Epstein, *Am. J. Phys.* **64**, 120 (1996), and references therein.

[5] I. D. Parker, *J. Appl. Phys.* **75**, 1656 (1994).

[6] N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature* **365**, 628 (1993).

[7] A. J. Epstein, J. W. Blatchford, Y. Z. Wang, S. W. Jessen, D. D. Gebler, L. B. Lin, T. L. Gustafson, H. L. Wang, Y. W. Park, T. M. Swager, and A. G. MacDiarmid, *Synth. Met.* **78**, 253 (1996).

[8] Y.Z. Wang, D.D. Gebler, L.B. Lin, J.W. Blatchford, S.W. Jessen, H.L. Wang, and A.J. Epstein, *Appl. Phys. Lett.* **68**, 894 (1996).

[9] Q. Pei, G. Yu, C. Zhang, and A. J. Heeger, *Science* **269**, 1086 (1995).

[10] M. Berggren, O. Inganas, G. Gustafsson, J. Rusmusson, M.R. Ansersson, T. Hjertberg, and O. Wennerstrom, *Nature* **372**, 444 (1994).

[11] Y. Yang and Q. Pei, *Appl. Phys. Lett.* **68**, 2708 (1996).

[12] M. Hamaguchi and K. Yoshino, *Appl. Phys. Lett.* **69**, 143 (1996).

[13] Y. Z. Wang, D. D. Gebler, D. K. Fu, T. M. Swager, and A. J. Epstein, *Appl. Phys. Lett.* **70**, 3215 (1997).

[14] Y. Z. Wang, D. D. Gebler, D. K. Fu, T. M. Swager, and A. J. Epstein, *Synth. Met*. **85**, 1179 (1997).

[15] Y. Yang, E. Westerweele, C. Zhang, P. Smith, and A. J. Heeger, *J. Appl. Phys.* **77**, 694 (1995).

[16] D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, T. L. Gustafson, D. -K. Fu, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, *Appl. Phys. Lett.* **70**,1644 (1997).

[17] R. P. McCall, J. M. Ginder, J. M. Leng, H. J. Ye, S. K. Manohar, J. G. Masters, G. E. Asturias, and A. G. MacDiarmid, *Phys. Rev. B* **41**, 5202 (1990).

[18] W. Lee, G. Du, S. M. Long, A. J. Epstein, S. Shimizu, T. Saitoh, and M. Uzawa, *Synth. Met.* **84**, 807 (1997).

[19] D. K. Fu, B. Xu, and T. M. Swager, *Tetrahedron*, in press.

Figure captions

Fig. 1 Repeat units of the pyridine-containing polymers and other polymers used in the study.

(a) poly(p-pyridine) (PPy); (b) poly(p-pyridyl vinylene) (PPPyV); (c) copolymer of PPV and PPyV (PPyVP(R)$_2$V); (d) wrapped copolymer of pyridyl vinylene and penylene vinylene (@PPyVPV); (e) wrapped copolymer of dithienylene and phenylene (@PTP); (f) emeraldine base (EB) form of polyaniline; (g) sulfonated polyaniline (SPAN).

Fig. 2 Schematic structure of a bilayer device with conducting polyaniline network electrode.

Fig. 3 Current-voltage and brightness-voltage characteristics of a single layer device using @PPyVPV as the emitting layer. Inset: Brightness-current characteristics of the same device.

Fig. 4 Comparison of (a) brightness-voltage and (b) brightness-current characteristics for a single layer device (square) and a bilayer device (circle).

[illegible] device (circle) and a bilayer device with PAN-CSA network electrode.

Fig. 6 Normalized PL spectra of pure wrapped copolymer film (solid line) excited at 2.65 eV, pure PVK film (dash-dotted line) excited at 3.6 eV, bilayer of PVK/copolymer (dashed line) excited at 3.6 eV, and the EL of the bilayer device (filled circle). The EL spectra are offset for clarity.

Fig. 7 Current-voltage characteristics of an inverted light-emitting device with PPy as the emitting layer and PVK as the hole transporting layer. Inset: schematic device structure of the device.

Fig. 8 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.

Fig. 9 Current-voltage characteristics of four devices with different structures as shown in the legend. Note that the turn on voltage *decreases* as the total number of layers *increases.*

Fig. 10 Energy diagram showing the role of positive (P^+) and negative (P^-) polaron levels of EB and the interface states in the SCALE device operation.

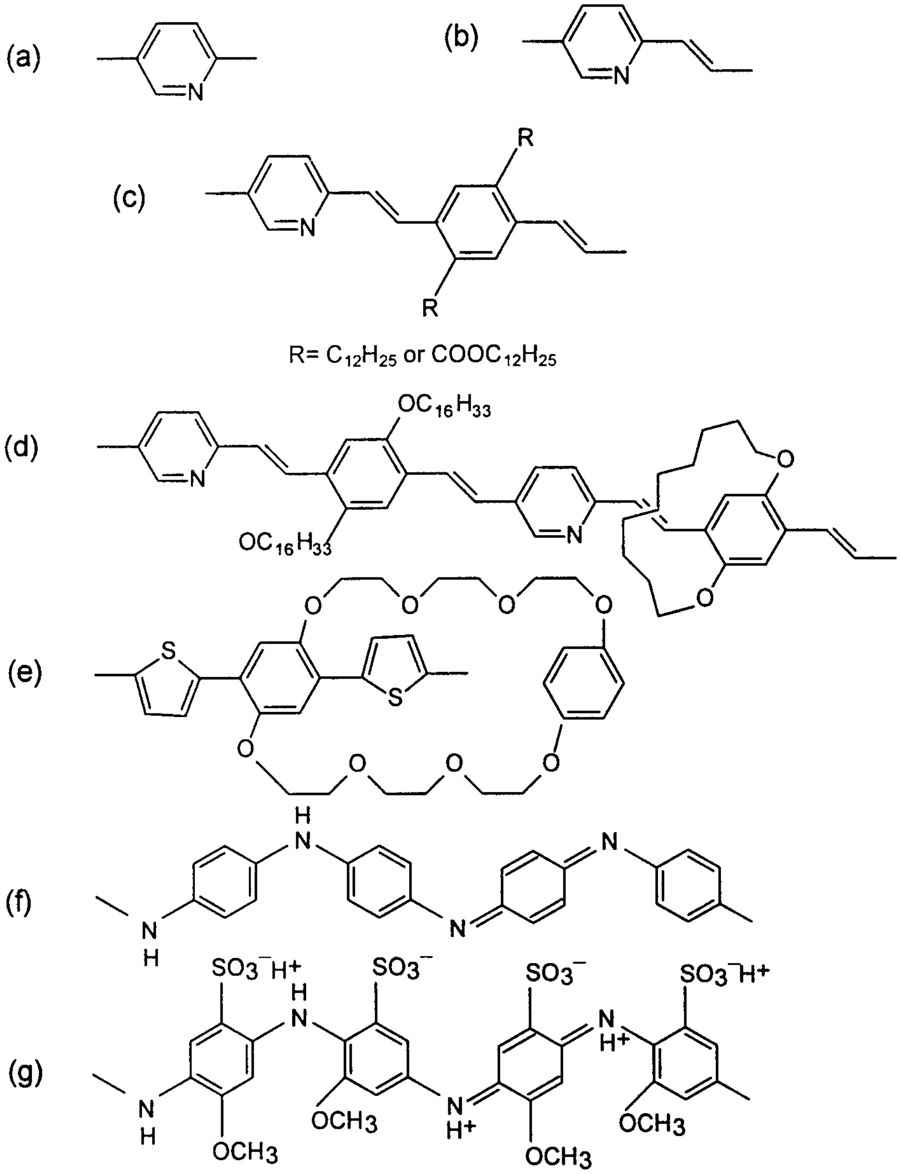
Fig. 11 Schematic structure of the color variable light-emitting devices

Fig. 12 Current-voltage and brightness-voltage characteristics of a color variable light-emitting device under forward and reverse bias conditions. Inset shows the colors of the device under forward and reverse bias in the CIE chromaticity diagram.

Fig. 13 EL spectra of the color variable device under forward and reverse bias conditions. For comparison, the EL spectra for single layer PPyVPV and PTP devices also are shown.

Fig. 14 Comparison of the EL spectra of ITO/EB/@PPyVPV:@PTP/SPAN/Al with different @PPyVPV:@PTP ratios. When the concentration of @PTP increases, the EL spectrum under reverse bias shifts from red to green.

Fig. 15 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 layers from that of the bilayer.



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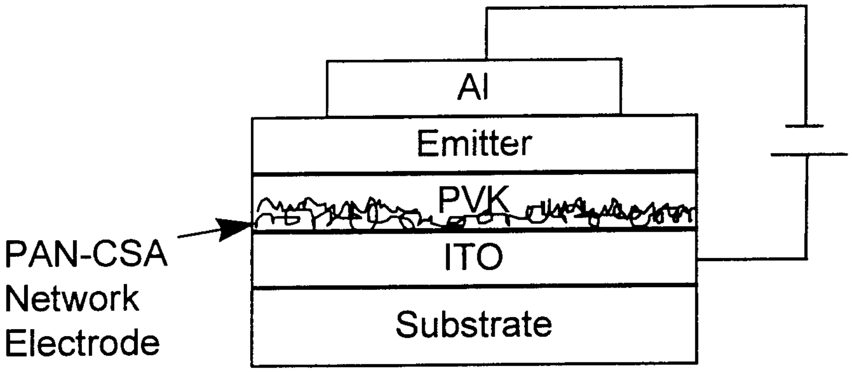

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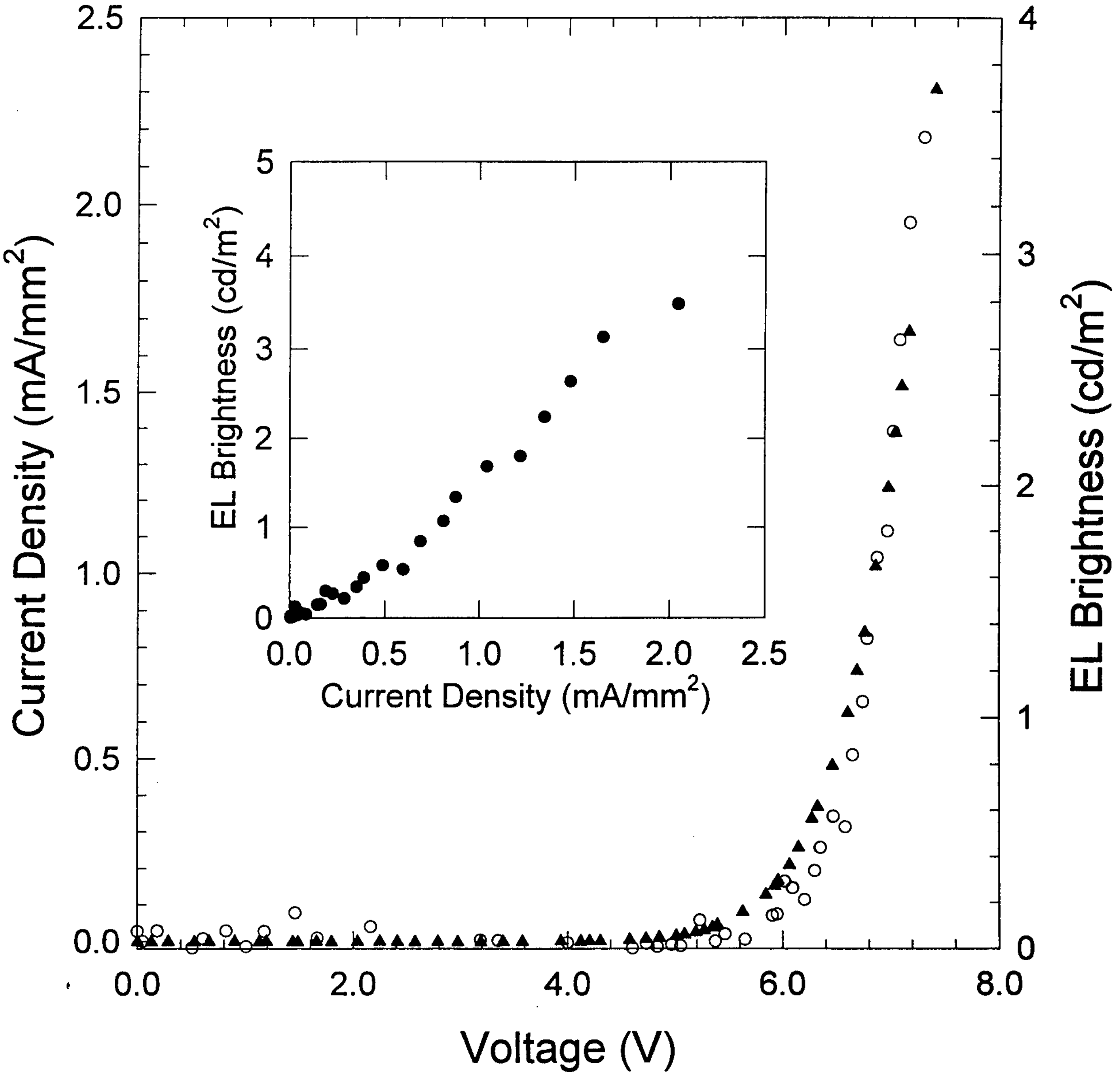

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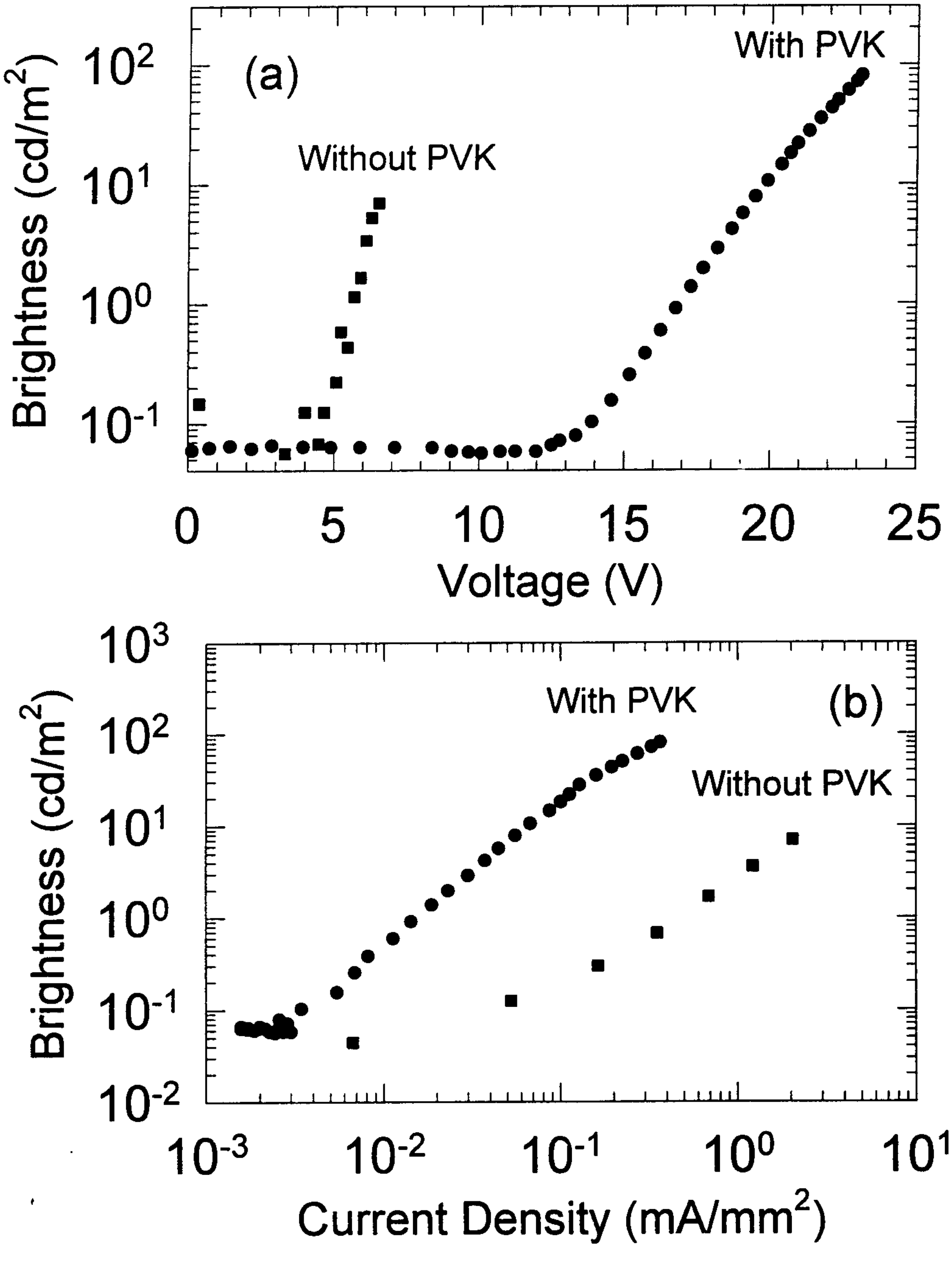

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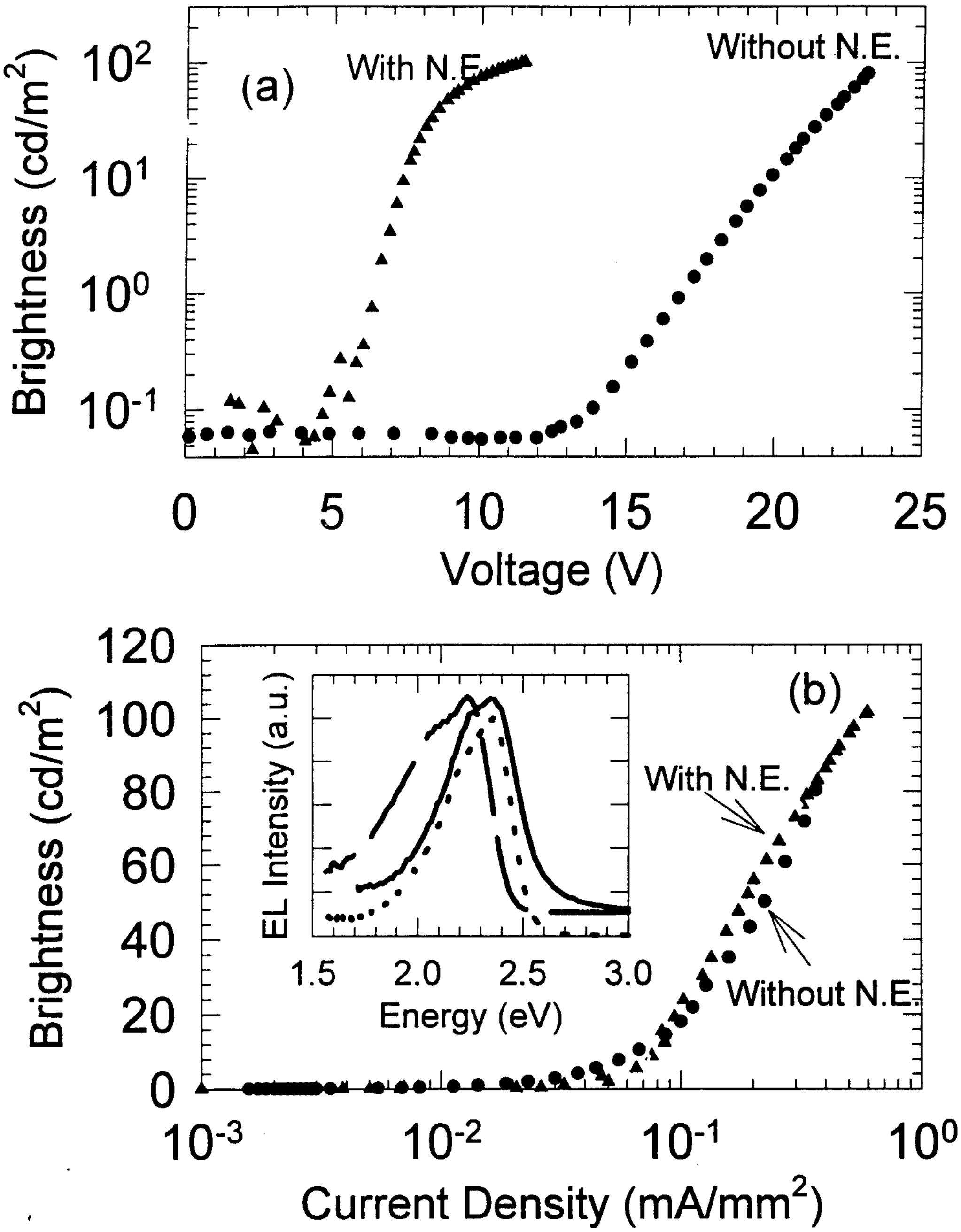

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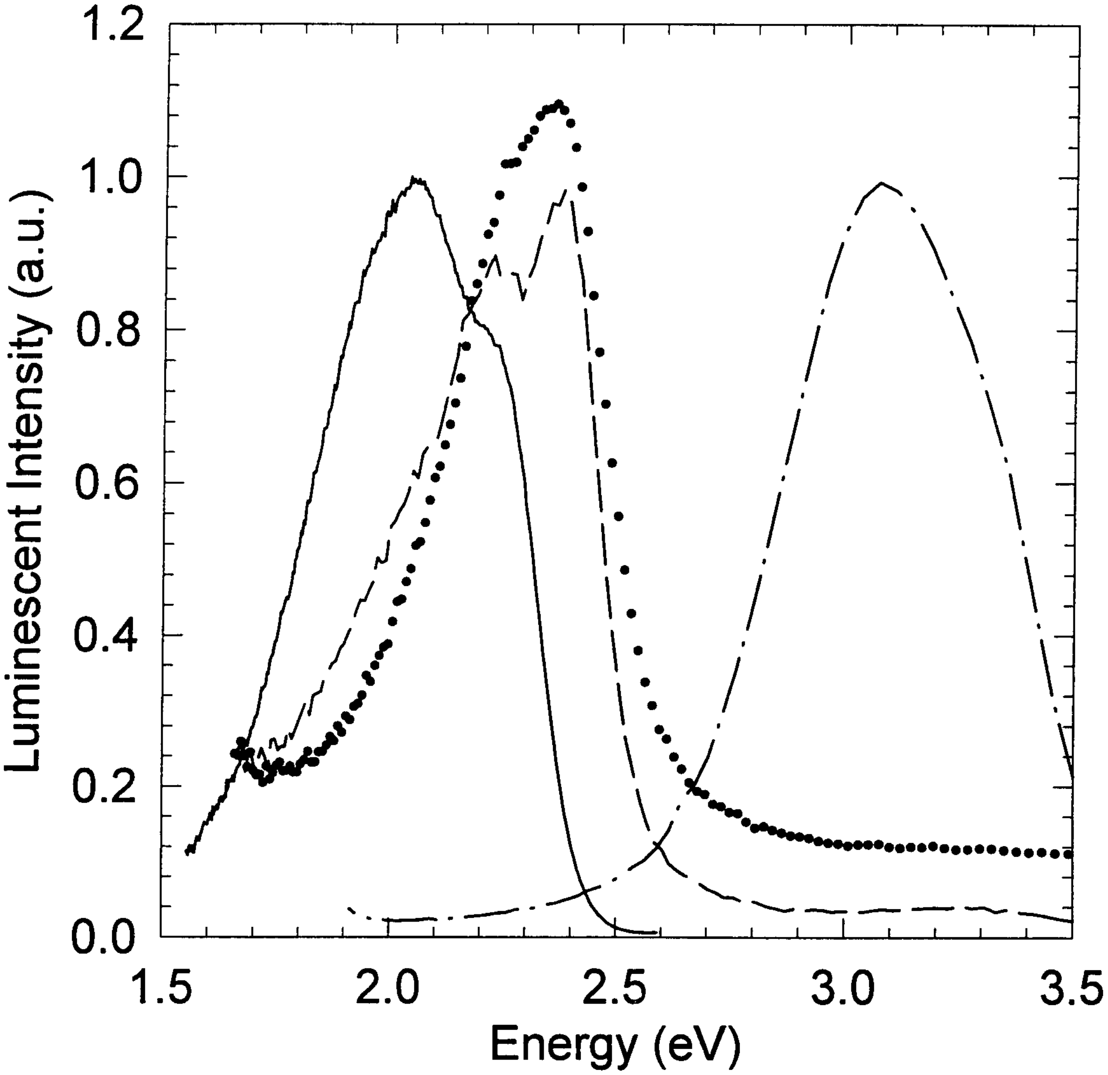

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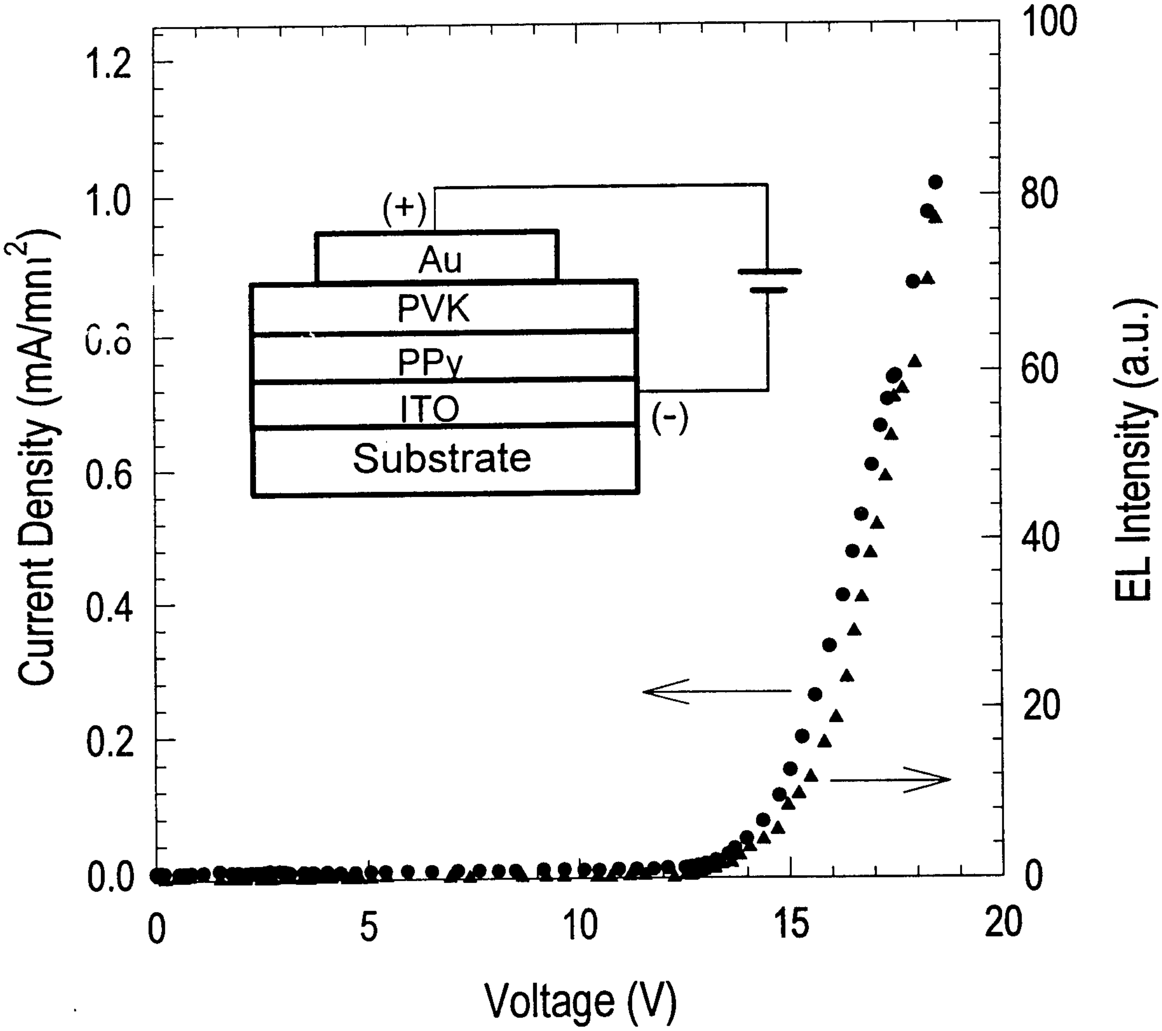

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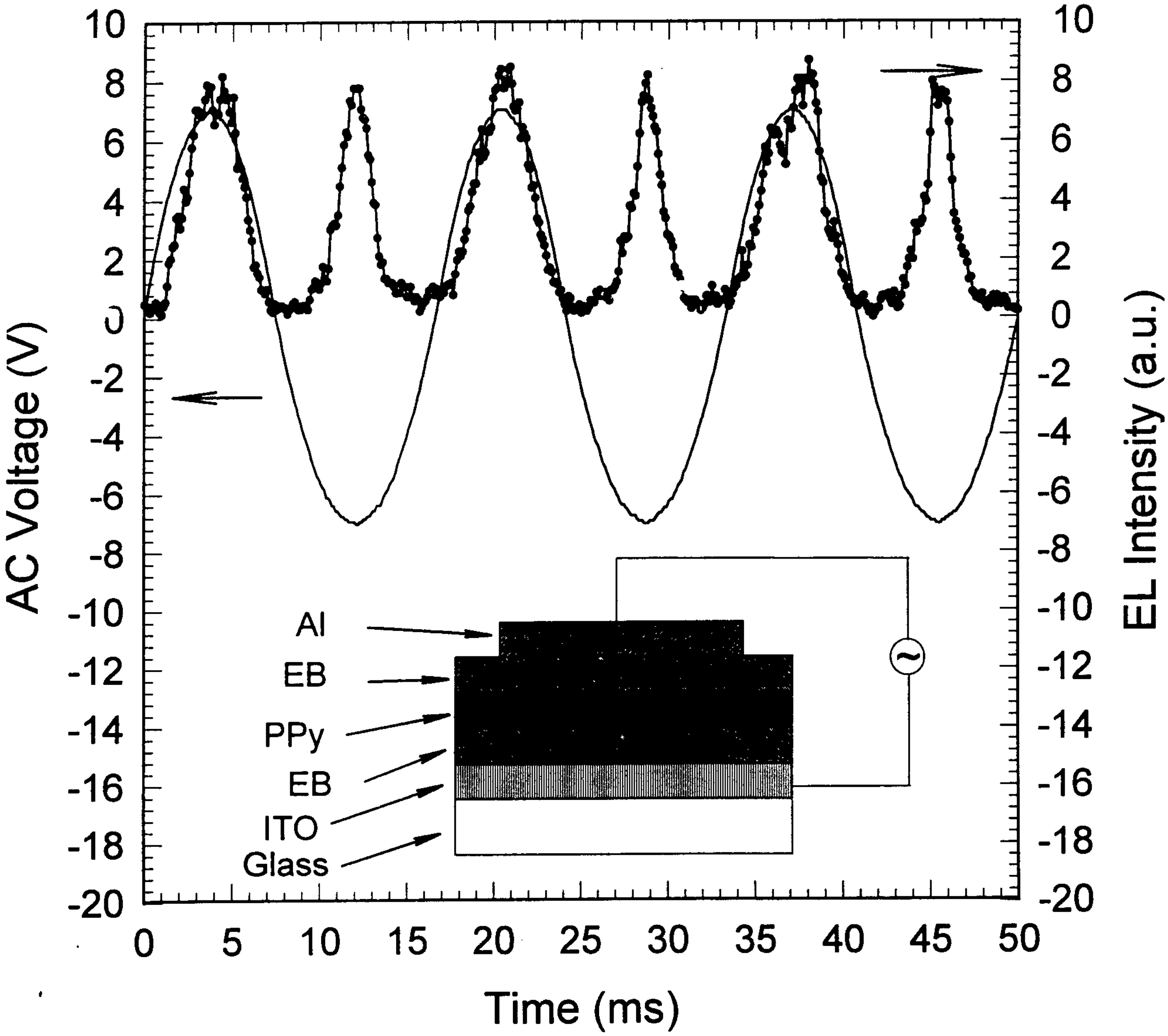

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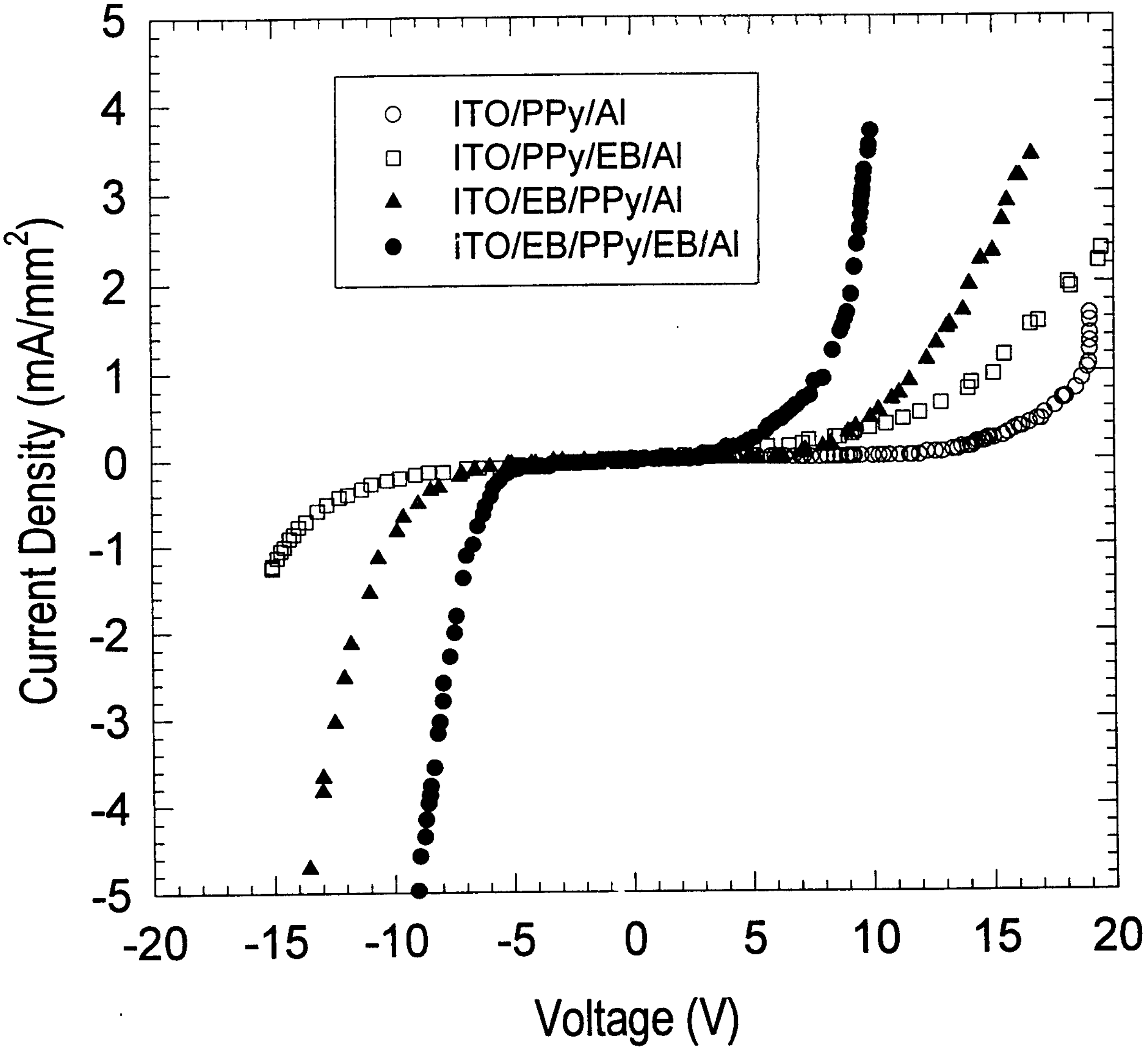

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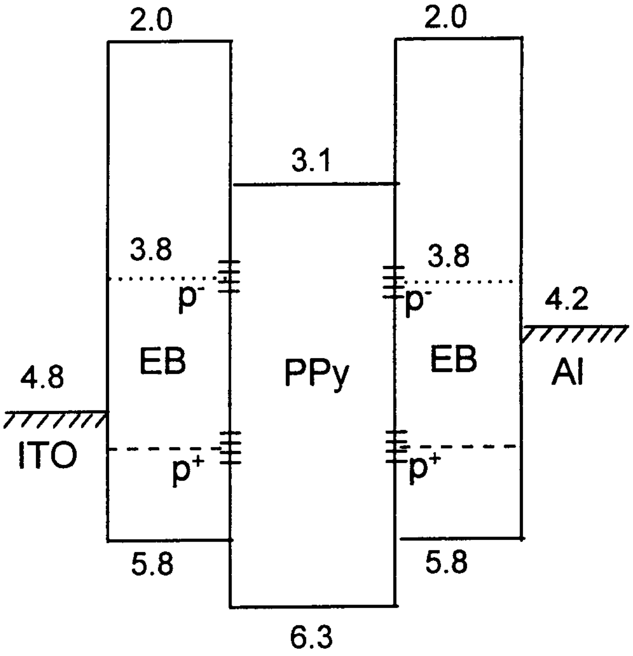

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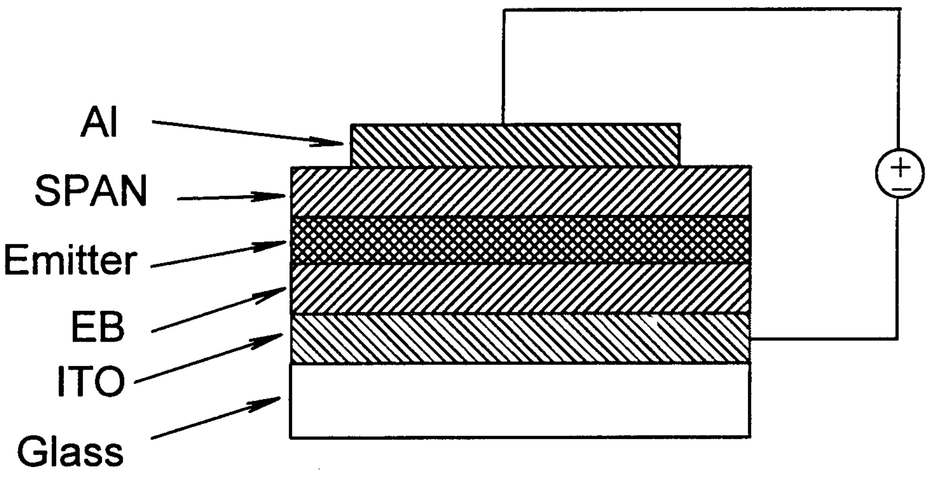

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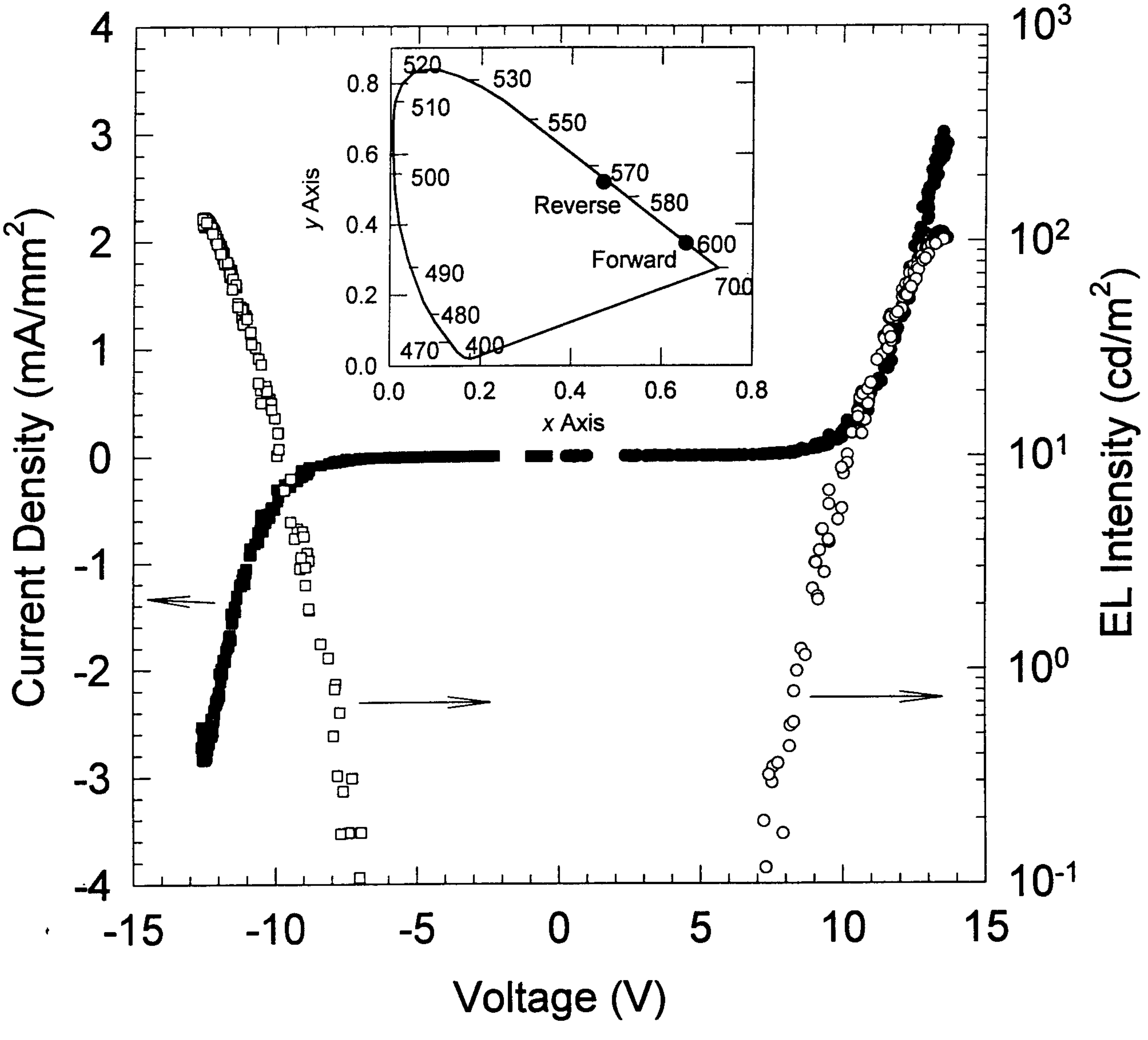

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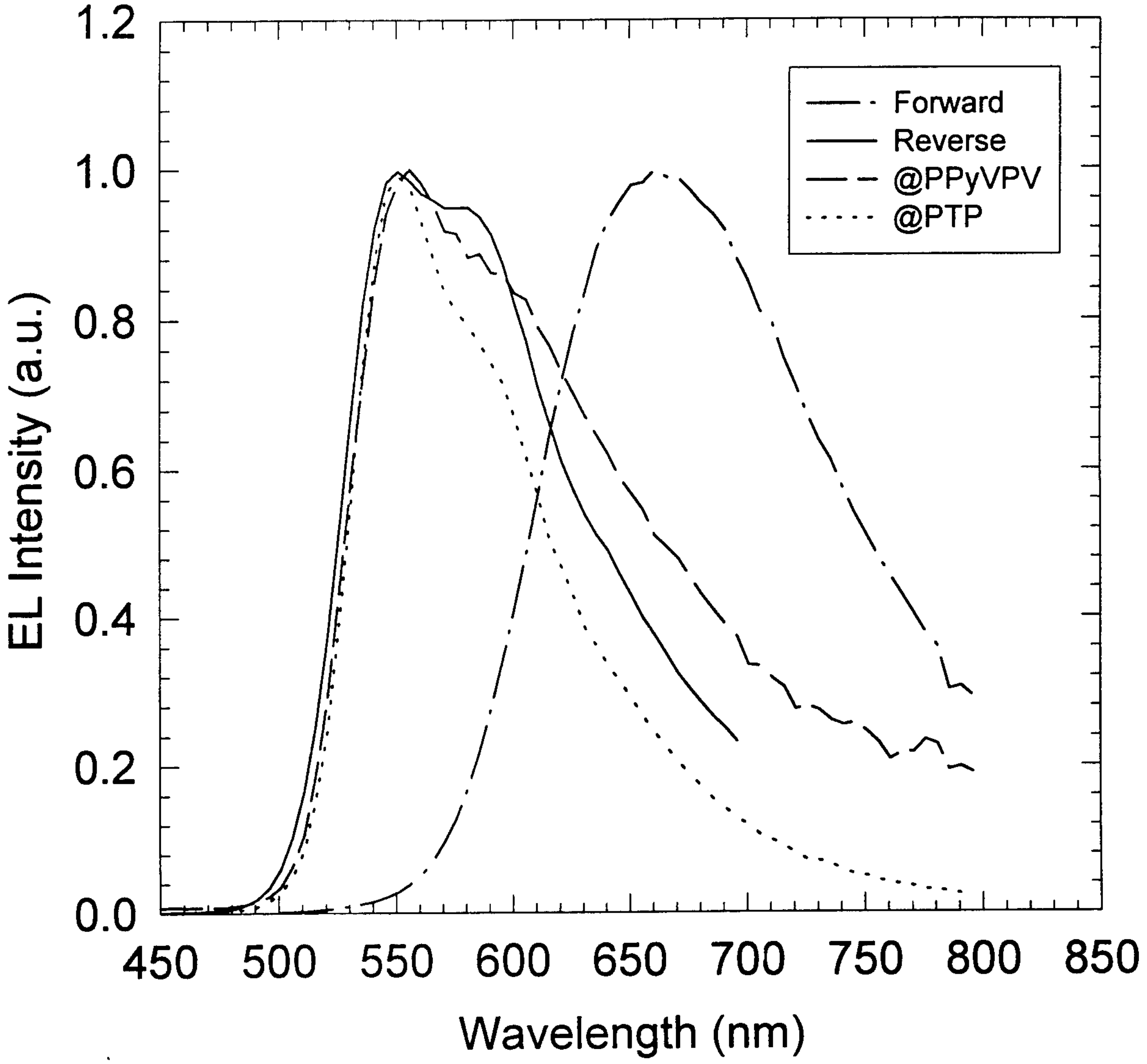

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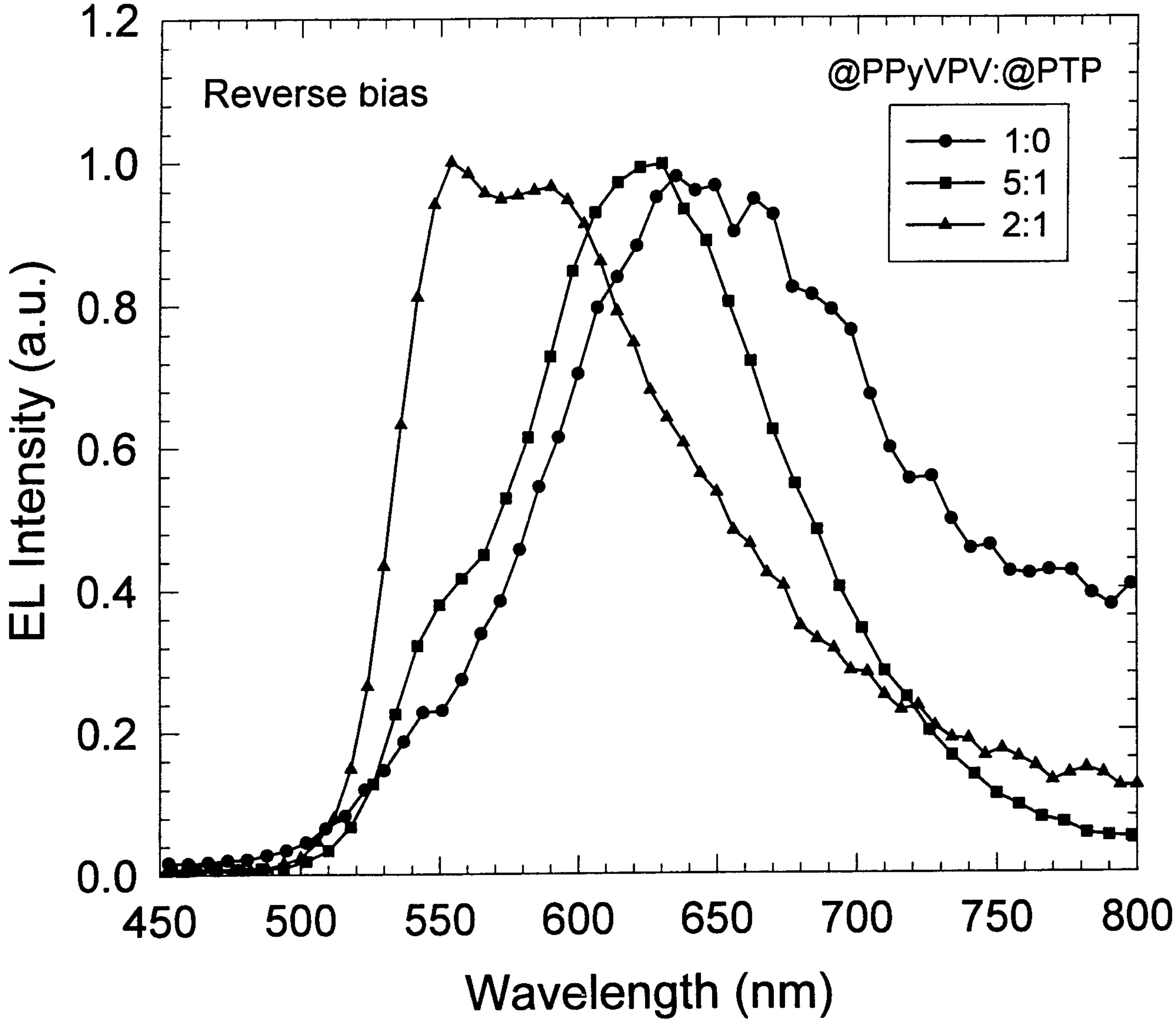

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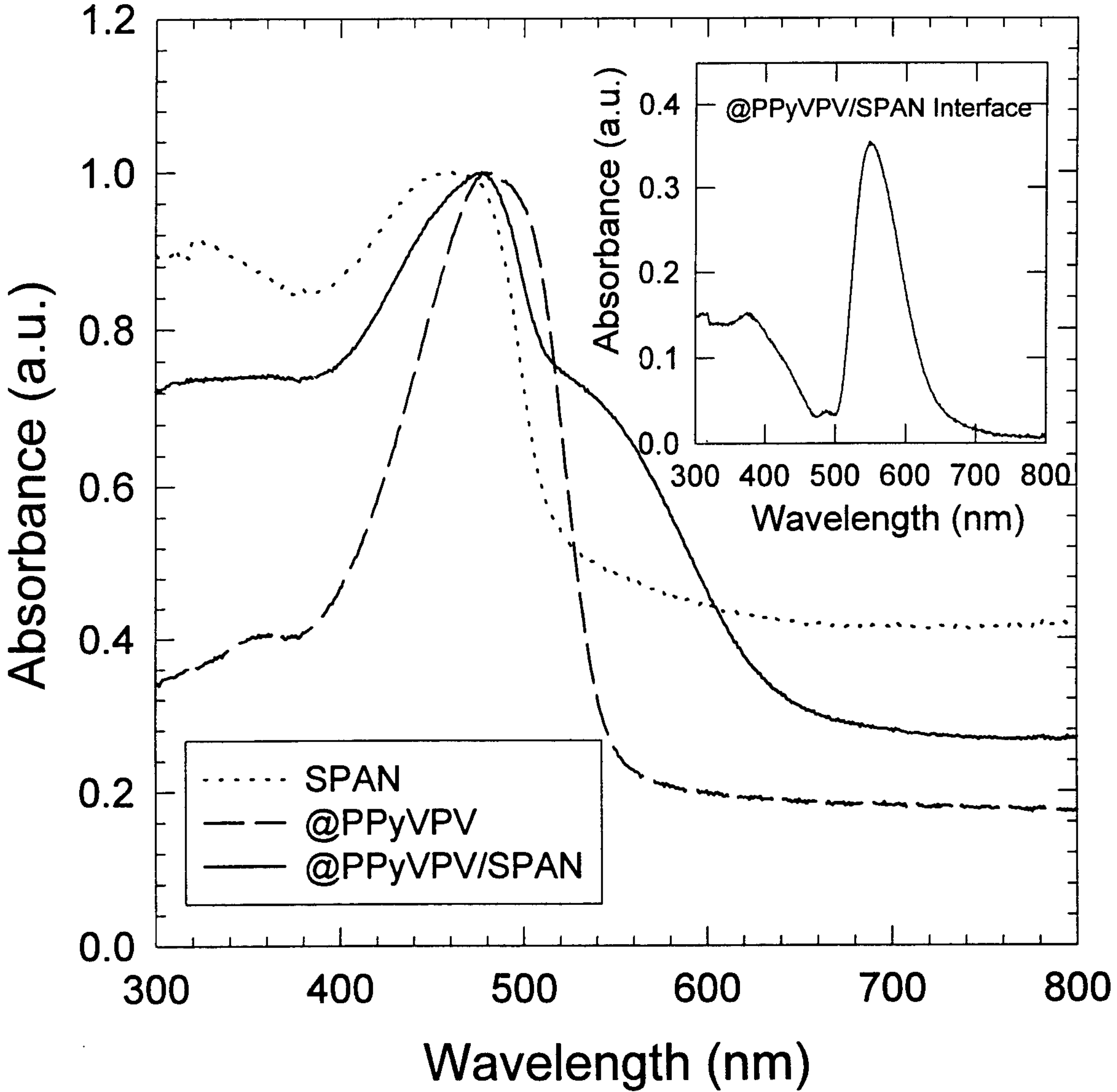

Fig. 15 Wang et al.