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Pyridine Based Polymer Light-Emitting Devices

by

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Prepared for Publication in

Plastics for Portable and Wireless Electronics Conference Proceedings
Phoenix, AZ, November 6-8, 1996

The Ohio State University
Department of Physics
Columbus, OH

19971015 032

September 20, 1997

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 9/20/97	3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE
Pyridine Based Polymer Light-Emitting Devices

5. FUNDING NUMBERS
N00014-95-1-0302,   N00014-92-J-1369

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
P295

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA   22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Pyridine-based conjugated polymers and copolymers have been shown to be excellent candidates for polymer light-emitting devices in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al as an electron injecting contact. Taking advantage of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as a hole transporting/electron blocking layer This 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 quantum efficiency, thus improving the device power efficiency. Novel device configurations such as symmetrically configured AC light-emitting (SCALE) devices enable the device to work under both forward and reverse bias as well as in AC modes, potentially improving the device stability.

14. SUBJECT TERMS
Light-Emitting Polymer Devices, Network Electrodes, SCALE, bilayer, exciplex

15. NUMBER OF PAGES
20

16. PRICE CODE

17. SECURITY CLASS. OF RPT Unclassified	18. SECURITY CLASS OF THIS PG. Unclassified	19. SECURITY CLASS OF ABSTRCT. Unclassified	20. LIMITATION OF ABSTRACT Unlimited

Pyridine based polymer light-emitting devices

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Abstract

Pyridine-based conjugated polymers and copolymers have been shown to be excellent candidates for polymer light-emitting devices in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al as an electron injecting contact. Taking advantage of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as a hole transporting/electron blocking layer. This 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 quantum efficiency, thus improving the device power efficiency. Novel device configurations such as symmetrically configured AC light-emitting (SCALE) devices enable the device to work under both forward and reverse bias as well as in AC modes, potentially improving the device stability.

1. Introduction

Since the report in 1990 of electroluminescence (EL) in poly(p-phenylene vinylene) (PPV) [1], conjugated polymer EL has been considered an important property with many potential applications. Electroluminescence 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. In addition to PPV, a variety of PPV derivatives and other conjugated polymers and copolymers have been found to exhibit electroluminescent properties [2,3]. Light-emitting devices incorporating these materials have demonstrated all the necessary colors needed for display applications. As compared to their conventional semiconductor counterparts, light-emitting devices based on conjugated polymers offer distinct advantages in that fabrication is easy, all colors of visible light can be easily produced, and the devices are thin and can be made large and flexible.

Over the past few years, the performance of polymer based light-emitting devices has been improved dramatically. A number of techniques have been developed to improve the quantum efficiency. One technique is to use a low workfunction metal, such as Ca, as an electron injecting electrode (cathode) [4]. The double charge injection mechanism of polymer light-emitting diodes (LEDs) requires the match of cathode (anode) workfunction to the corresponding LUMO (HOMO) level of the polymer in order to achieve efficient charge injection. The relatively small electron affinity of most conjugated polymers requires metals with very low workfunctions to achieve efficient electron injection. However, since low workfunction metals are generally oxygen reactive, devices with low workfunction cathode usually are unstable. Thus, polymers with high electron affinities are highly desirable.

Pyridine-based conjugated polymers have been shown to be promising candidates for light-emitting devices [5,6]. 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 show better electron transport properties. Figure 1 shows the structures of the pyridine-containing polymers and copolymers, namely poly(p-pyridine) (PPy), poly(p-pyridyl vinylene) (PPyV), and copolymers of PPyV and PPV (PPyVP(R)$_2$V) with various functional sidegroups R = $C_{12}H_{25}$, $OC_{16}H_{33}$, $COOC_{12}H_{25}$. With respect to the π electronic levels, $C_{12}H_{25}$ is slightly electron donating; $OC_{16}H_{33}$ electron donating; and $COOC_{12}H_{25}$ electron withdrawing. The pyridine-based polymers are highly luminescent, especially the copolymers. The internal photoluminescent quantum efficiency of the copolymers have been measured [7] to be 75-90% in solution and 18-30% in film, with the exception of the $OC_{16}H_{33}$ copolymer. The electron donating nature of $OC_{16}H_{33}$ makes the copolymer more susceptible for oxidation. As a result, the PL quantum efficiency of the $OC_{16}H_{33}$ copolymer is only 2% in film although it is high (~80%) in solution. To reduce the oxidation effects, the strapped copolymer (@PPyVPV) was introduced, as shown in Fig. 1 (d). Also the strapped copolymer shows the effects of less aggregation as compared to the "usual" copolymers.
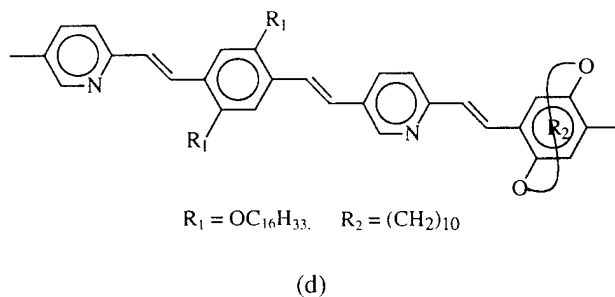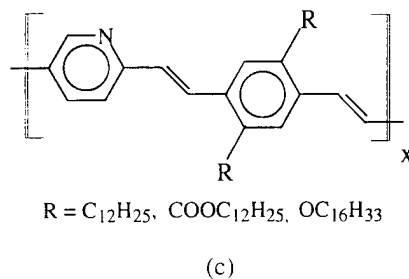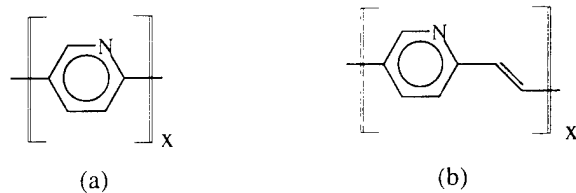
Fig. 1. Structures of pyridine based conjugated polymers and copolymers: (a) poly(p-pyridine) (PPy), (b) poly(p-pyridyl vinylene) (PPyV), (c) copolymers of PPyV and PPV derivatives (PPyVP(R)$_2$V) with various functional sidegroups R = $C_{12}H_{25}$, $OC_{16}H_{33}$, $COOC_{12}H_{25}$, and (d) strapped copolymer (@PPyVPV).

Another common technique to improve device performance is to incorporate charge transporting layers in a multilayer device structure. The charge transporting layer enhances the transport of one type of charge while blocking the other, thus achieving balanced charge injection and transport. In addition, the charge transport layer spatially confines the emission zone away from electrode, avoiding nonradiative quenching effects near electrodes. To date the highest efficiency polymer light-emitting devices reported are multilayer devices [8].

Here we report the fabrication of pyridine-based polymer light-emitting devices in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al as electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate 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 quantum efficiency, thus improving the device power efficiency. By inserting an "insulating" layer on both side of the

emitting polymer, we fabricated symmetrically configured AC light-emitting (SCALE) devices [6] which work under both forward and reverse DC bias as well as in AC modes. The SCALE devices are capable of eliminating the use of low workfunction metals as electrodes, potentially improving the device operating stability and shelf lifetime.

2. Experiments

The synthesis of the pyridine-containing polymers has been reported earlier [9-11]. For single layer devices, the emitting layer was spin-cast 1000-2000 rpm from solutions in formic acid (for PPy and PPyV) or xylenes (for copolymers) (with a concentration of ~10 mg/ml) onto pre-cleaned patterned ITO substrates with a sheet resistance of ~15 Ω/square. For bilayer devices, 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. The conducting polyaniline network electrode was formed by spin-casting a blend of camphor sulfonic acid doped polyaniline (PAN-CSA) and low molecular weight host polymer such as poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in an appropriate ratio in m-cresol. The host polymer PMMA was subsequently washed away by xylenes. The PVK and emitting layers were similarly coated as in the bilayer device. All solutions were filtered using Gelman Acrodisc CR PTFE 1μm filters. 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 evaporation. Figure 2 shows schematically the structure of a bilayer device with PAN-CSA network electrode.
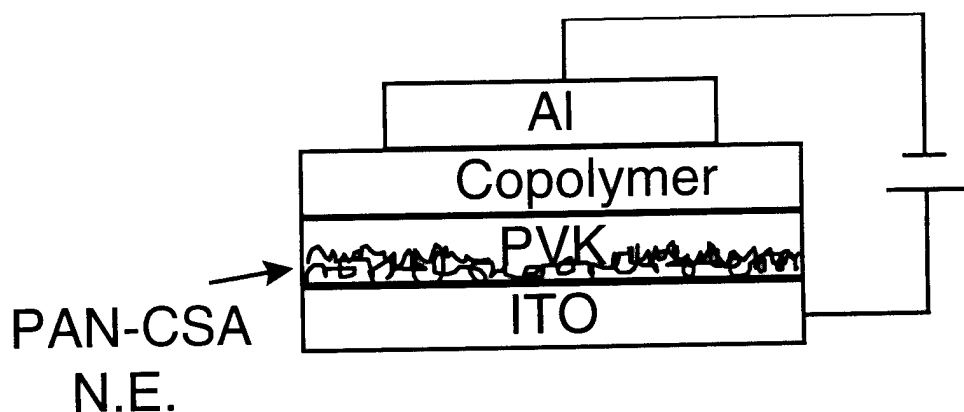

Fig. 2. Schematic structure of a bilayer device with conducting polyaniline network electrode.

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 (I-V) 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).

3. Results and discussion

Figure 3 shows the optical absorption and PL of the strapped copolymer film and EL of a single layer device. For comparison, the PL of the strapped copolymer solution in xylenes is also shown. The film PL peaks at 2.05 eV with a shoulder at 2.25 eV. As compared to the film absorbance, the peak of the film PL is redshifted 0.55 eV, which is attributed to the aggregates formed in the film [12]. The shoulder is suggested to come from the unaggregated site, and is supported by the PL measurements of blends in PMMA. When the concentration of the strapped copolymer decreases, the strength of the shoulder grows and blue shifted towards the solution PL, eventually becomes the dominant feature, indicating that the PL is dominated by unaggregated sites in the blend. It is noted that although the strapped and the corresponding unstrapped copolymer show similar features in solution PL, no shoulder is found in the film PL for the unstrapped copolymer, indicating that the strapped side chains partially break the aggregates formation in the film.
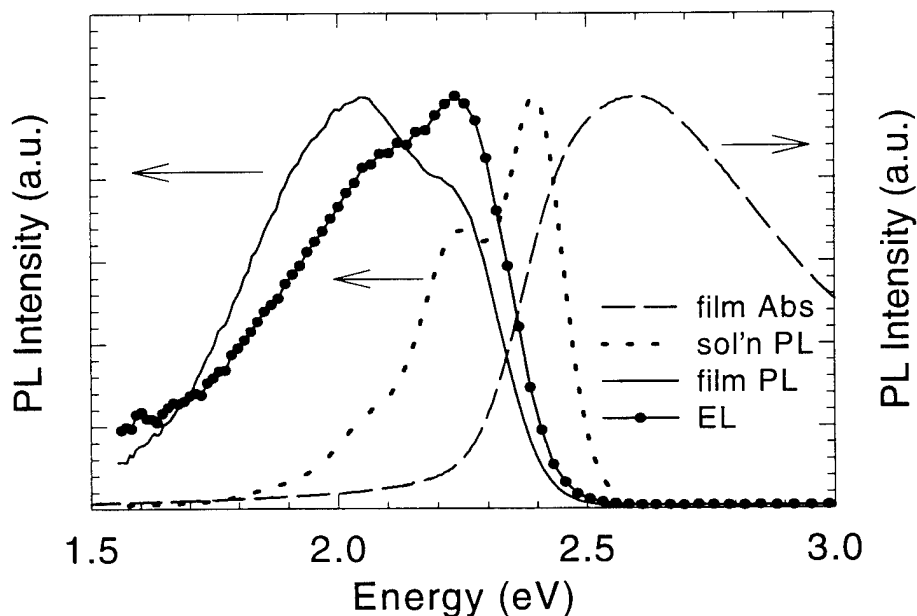

Fig. 3. Normalized optical absorption (dashed line) and PL of the strapped copolymer film (solid line), EL of a single layer device (solid line with dots), and PL of solution in xylenes (dotted line).

Figure 4 compares the light-voltage (L-V) and EL-current (EL-I) characteristics for a single layer device, a bilayer device, and a bilayer device with PAN-CSA network electrode using the strapped copolymer as emitting layer. As compared to that of the single layer device, the quantum efficiency of the bilayer device increase more than two orders of magnitude, reaching ~0.3%. The brightness of the bilayer device follows closely with the current density (not shown), reaching ~50 cd/m^2 at ~0.2 mA/mm^2 (~22 V) and ~300 cd/m^2 at ~2 mA/mm^2 (~27 V). PVK is a well known hole

transporting/electron blocking polymer. Besides enhancing the transport of holes injected from the anode, PVK blocks the transport of electrons injected from the cathode such that the electrons accumulate at the PVK/copolymer interface. This charge confinement greatly enhance the probability of radiative recombination. In addition, the PVK layer separates the recombination zone from the metal electrode so that the radiative recombination is protected against the non-radiative quenching at the metal/polymer interfaces.
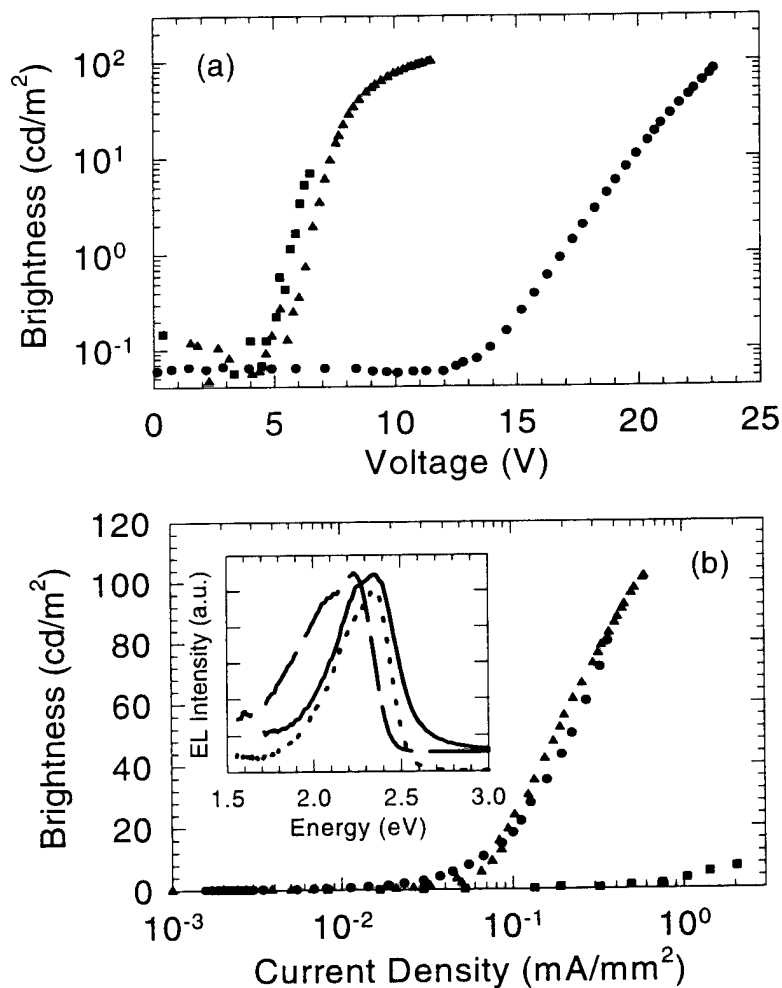

Fig. 4. Comparison of (a) light-voltage and (b) light-current characteristics for a single layer device (square), a bilayer device (circle), and a bilayer device with PAN-CSA network (triangle). Inset: EL spectra for the single layer device (dashed line), the bilayer device (solid line), and the bilayer device with network electrode (dotted line).

One 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 high surface network electrode [13]. The concept behind the network electrode is that a rough electrode will create a non-

uniform high electric field that enhances the charge injection. This technique has been successfully applied to PPV based devices [13]. By applying this technique to the PVK layer, the device operating voltage decreased significantly. The brightness of the bilayer device with network electrode reaches ~50 cd/mm^2 at only ~9 V, instead of ~22 V for bilayer devices without 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 (see Fig. 4 (b)). Thus, the incorporation of the network electrode to the bilayer device improves the power efficiency dramatically. 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. 4 (b) inset. The slightly reduced intensity at high energy tail for the device with network electrode is probably due to absorption of PAN-CSA.
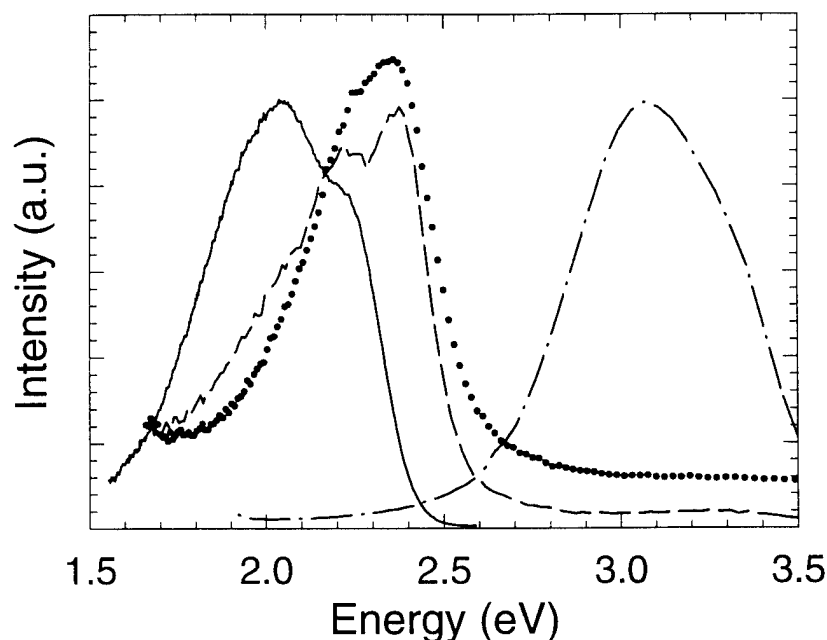

Fig. 5. Normalized PL spectra of pure strapped copolymer (solid line) excited at 2.65 eV, pure PVK (dash-dotted line) excited at 3.6 eV, bilayer of PVK/copolymer (dashed line) excited at 3.6 eV, and the EL of the bilayer device (filled circle). The EL spectra were offset for clarity

The species that is responsible for the light generation in the bilayer device is attributed partially to exciplexes formed at the PVK/copolymer interface and is identified by the PL measurements [14]. Figure 5 compares the PL of pure strapped 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 shows an emission peak at 3.06 eV, agreeing well with the value reported in the literature [15,16]. The PL of pure strapped copolymer film excited at 2.65 eV peaks at 2.03 eV with a shoulder at 2.25 eV. When exciting the PVK/copolymer bilayer film at 3.6 eV, a new peak appears at 2.38 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. As expected, exciplexes do not form when both species are in unexcited states. Similar results are found for other unstrapped copolymers [14]. The EL of the bilayer device follows closely with the PL of the bilayer film suggesting that a significant amount of the EL emission come from the exciplex formed at the PVK/copolymer interface.

The bilayer devices discussed above only can operate under forward (ITO positive) DC driving field. No light was observed under reverse DC bias. Recently we have reported the fabrication of symmetrically configured AC light-emitting (SCALE) devices [6] by introducing two "insulating" layers, such as the emeraldine base (EB) form of polyaniline, sandwiching the emitting layer. The device structure is shown schematically in Fig. 6 inset. The SCALE devices emit light under both forward and reverse DC bias as well as AC driving voltage. Under AC (sinusoidal) driving, light pulses with double the driving frequency are generated. The time dependent EL intensity of a SCALE device using PPy as the emitting material and EB as insulating layers driven by a sinusoidal voltage of 60 Hz is shown in Fig. 6. A light pulse is emitted whenever the applied voltage exceeds the positive or negative threshold voltage.
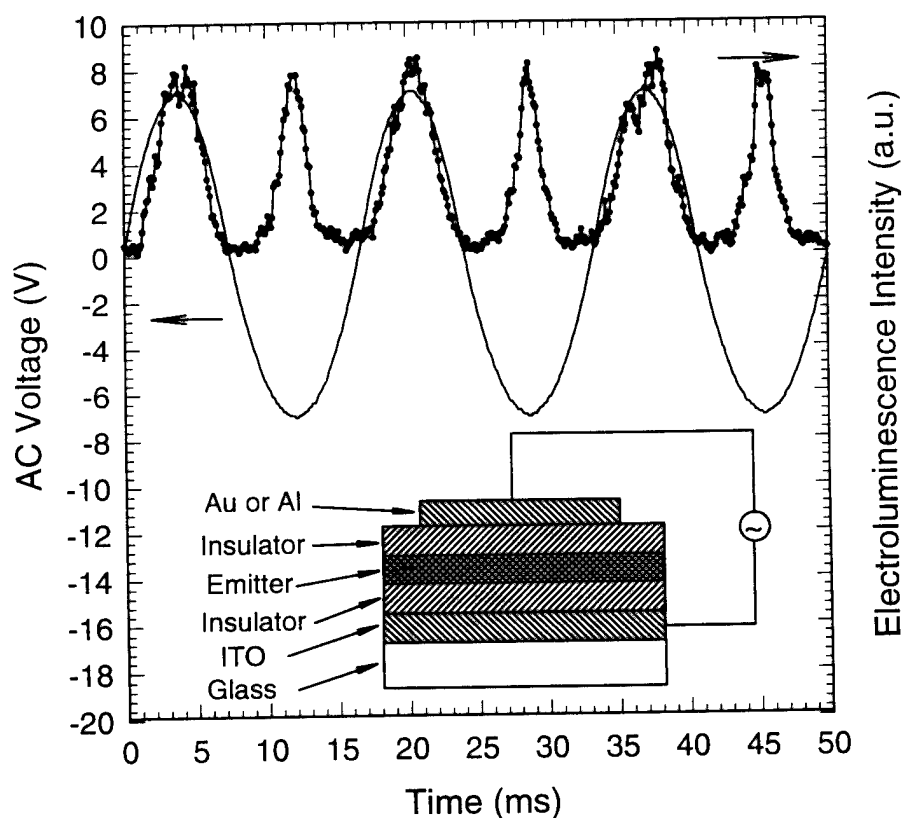

Fig. 6 Electroluminescence intensity as a function of time for a SCALE device ITO/EB/PPy/EB/Al driven by a 60 Hz sinusoidal voltage. Inset: Schematic diagram of the structure of a SCALE device.

The symmetric operation of the SCALE is attributed to the effects of charge accumulation at the polymer/polymer interfaces. As a consequence, the SCALE device performance is not sensitive to the electrodes used. This allows the elimination of the low workfunction metals as electrodes, potentially reducing the aging problems associated with most "conventional" polymer LEDs which must use reactive low work function metals to achieve efficient electron injection. In addition, the AC operation may partially reverse the electrochemical reactions that occur at the interfaces, potentially increasing the device operating lifetime.

4. Conclusion

In summary, pyridine containing conjugated polymers and copolymers are excellent candidates for polymer light-emitting devices. 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 the exciplex emission at the PVK/emitting polymer interface. The incorporation of the conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high quantum efficiency and brightness of the bilayer device. The SCALE devices are capable of eliminating the use of low workfunction metals as electrodes and may partially reverse the electrochemical reactions occurring at the interfaces when operating in AC modes, potentially improving the device shelf lifetime and operating stability.

5. Acknowledgment

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