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Recently there have been reports on color variable light emitting devices. Here we present a new approach to such devices based on conjugated polymers. The device consists of a blend of pyridine-phenylene and thiophene-phenylene based copolymers sandwiched between two redox polymers: emeraldine base form of polyaniline and sulfonated polyaniline (SPAN). ITO and Al are used as electrodes. The devices work under either polarity of driving voltage with different colors of light being emitted from different locations, red from emitting polymer/SPAN interface under forward bias and green from bulk of the emitting polymers under reverse bias. Electroluminescence of the devices peak at 550 nm with a shoulder at 585 nm under reverse bias while they show a single peak at 665 nm under forward bias. The relative fast time response allows the rapid switch of colors and AC operation.

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New approach to color variable light-emitting devices based on conjugated polymers

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ABSTRACT

Recently there have been reports on color variable light emitting devices. Here we present a new approach to such devices based on conjugated polymers. The device consists of a blend of pyridine-phenylene and thiophene-phenylene based copolymers sandwiched between two redox polymers: emeraldine base form of polyaniline and sulfonated polyaniline (SPAN). ITO and Al are used as electrodes. The devices work under either polarity of driving voltage with different colors of light being emitted from different locations, red from emitting polymer/SPAN interface under forward bias and green from bulk of the emitting polymers under reverse bias. Electroluminescence of the devices peak at 550 nm with a shoulder at 585 nm under reverse bias while they show a single peak at 665 nm under forward bias. The relative fast time response allows the rapid switch of colors and AC operation.

Keywords: color variable, LEDs, electroluminescence, conjugated polymers, interface, bipolar, alternating current

1. 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.

Among the most important limitations associated with many of the "conventional" polymer light-emitting diodes are poor stability and shelf lifetime. Devices degrade even during storage. The low work function metal electrodes required for efficient electron injection[5] and/or the poor oxygen stability of most conjugated polymers lead to unwanted chemical reactivity. Recently there have been reports of new device configurations such as symmetrically configured AC light-emitting (SCALE) devices[6] and light-emitting electrochemical cells (LECs).[7] These devices modify the charge injection and/or transport characteristics such that the device operation is insensitive to the electrode materials used. As a consequence, more stable metals such as Au can be used as electrodes, potentially improving the device operating stability and storage lifetimes.

To date, a variety of conjugated polymers and/or copolymers have been found to exhibit electroluminescent properties such that all the necessary colors needed for display applications are obtainable.[3,4] 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. In such devices based on blends 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.[8] Though such devices can emit multiple colors of light, they have very limited control of the brightness at a desired color. Color variable light-emitting electrochemical cells (LECs)[9] which emit two independent colors of light, also have been developed. 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.[10] 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.

Here we report a new approach to color variable light-emitting devices which generates two independent colors of light at room temperatures. The devices consist of a layer of active electroluminescent polymers sandwiched between two different redox polymer layers. The redox polymer layers modify the charge injection and transport properties such that the device can be operated under both forward and reverse bias. Also at least one of the redox polymers is capable of modifying the emission properties of the emitting polymers at the interface such that the interface emits different colors of light than the bulk does. 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 emitting polymers. Since motion of ionic species is not required for device operation a relatively fast time response is expected, allowing the colors to be switched rapidly.

2. EXPERIMENTAL

For the devices presented here, a copolymer of poly(pyridyl vinylene) and poly(phenylene vinylene) derivative, PPyVPV, and a copolymer of polythiophene and polyphenylene derivative, PTP, were used as the emitting materials; sulfonated polyaniline (SPAN) and the emeraldine base (EB) form of polyaniline were used as the redox materials; ITO and Al were used as electrodes. Figures 1 and 2 show the chemical structures of the polymers used and schematic diagram of the device structure, respectively. The polymer layers were formed using spin coating techniques. The EB layer was first spin cast at ~3000 rpm from N-methylpyrrolidinone (NMP) solution (concentration of ~5 mg/ml) onto pre-cleaned patterned ITO coated glass substrates. The emitting layer was then spin coated over the EB layer from a blend of PPyVPV and PTP (3:2 weight ratio) in xylenes or trichloroethylene (total concentration ~10 mg/ml). The SPAN layer was subsequently coated over the emitting layer from an aqueous solution. All the spin coating procedures were carried out inside a class 100 cleanroom. 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. 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 the dc voltage was applied by a HP model 6218A DC power supply. Quantum efficiency and brightness were measured using a calibrated photodiode (UDT UV100).

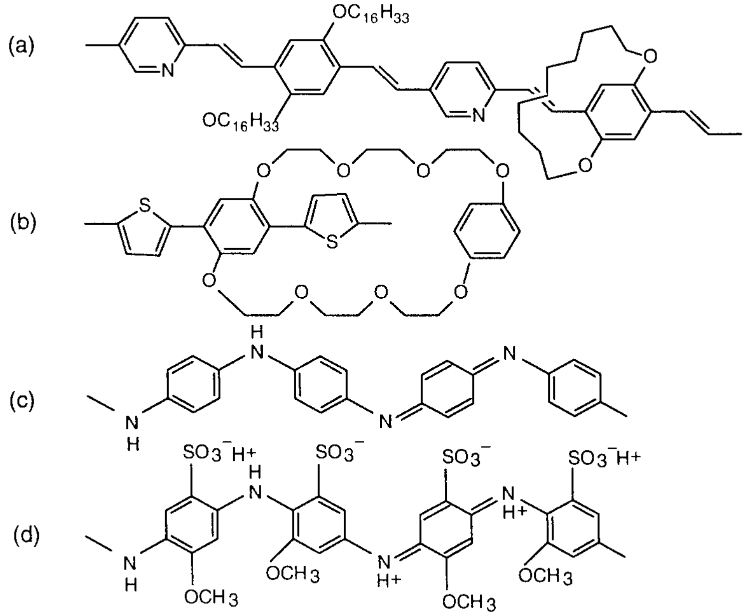

Fig. 1 Repeat units of polymers used: (a) PPyVPV;(b) PTP; (c) EB; and (d) SPAN

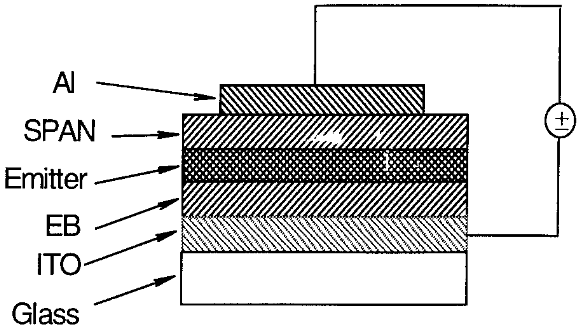

Fig. 2 Schematic structure of the color variable light-emitting devices

3. RESULTS AND DISCUSSION

Figure 3 shows the typical current-voltage (I-V) and luminance-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,[6] 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 up to 0.1% photons/electron has been achieved for the initial devices. Fig. 4 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. 3 Inset). The colors of the devices have been switched rapidly, up to ~20 kHz, depending upon device impedance and geometry.

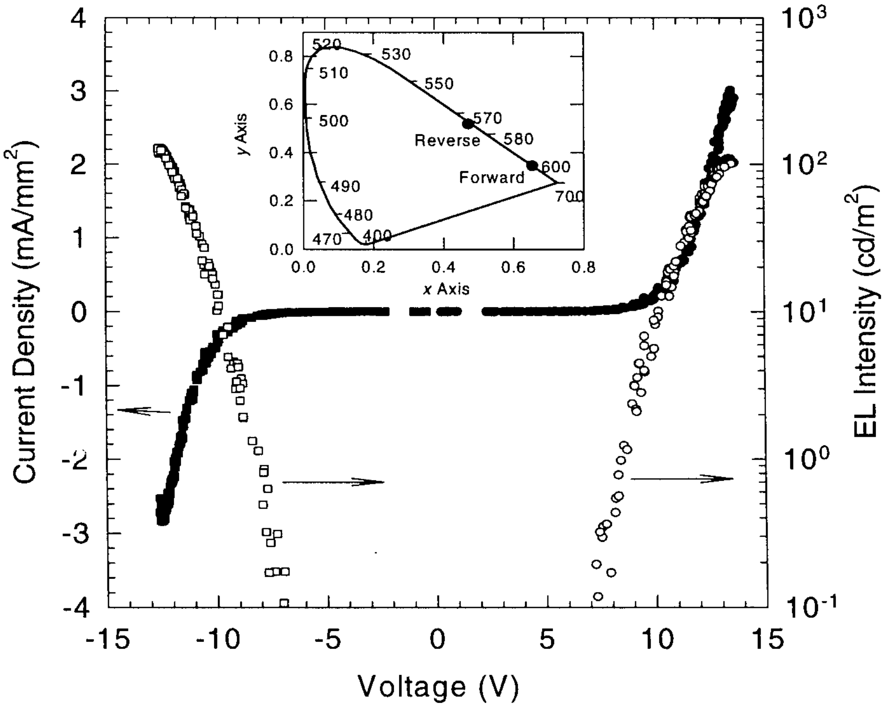

Fig. 3 Current-voltage and light-voltage characteristics of a color variable light-emitting device under forward and reverse bias conditions. Inset shows the colors of the device under forward and reverse bias in the CIE chromaticity diagram.

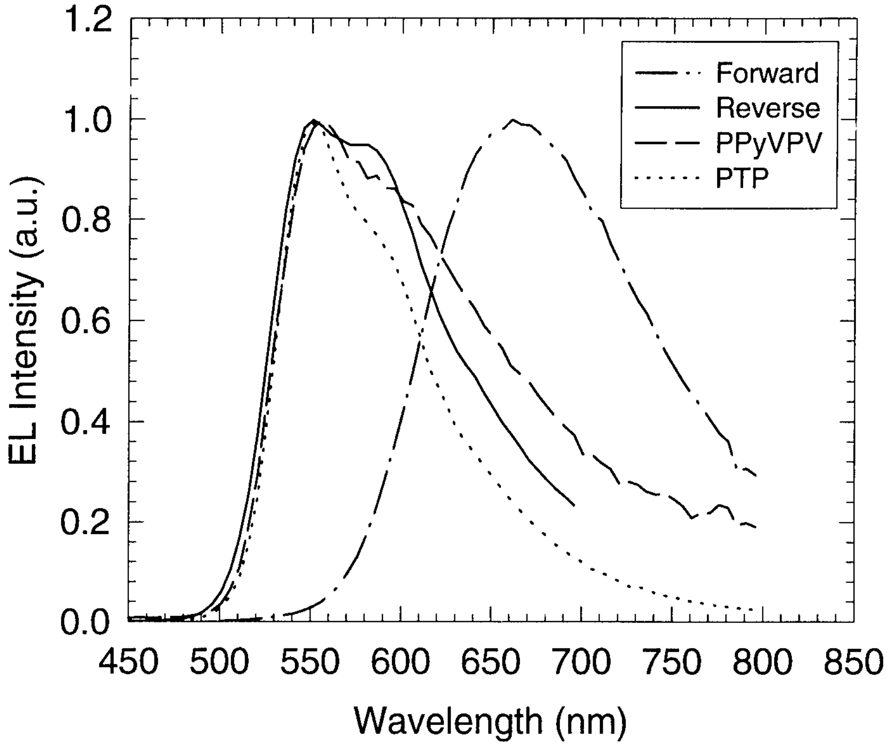

Fig. 4 EL spectra of the color variable device under forward and reverse bias conditions. For comparison, the EL spectra for single layer PPyVPV and PTP devices also are shown.

The EL spectra 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 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. We are not be able to identify the emission zone exactly because the EB layer does not modify the emission properties of the emitting polymer. The EB layer functions as a charge injection enhancement layer, playing a similar role as it does in symmetrically configured AC light-emitting (SCALE) devices reported earlier.[6] 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.[11] 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. 5.

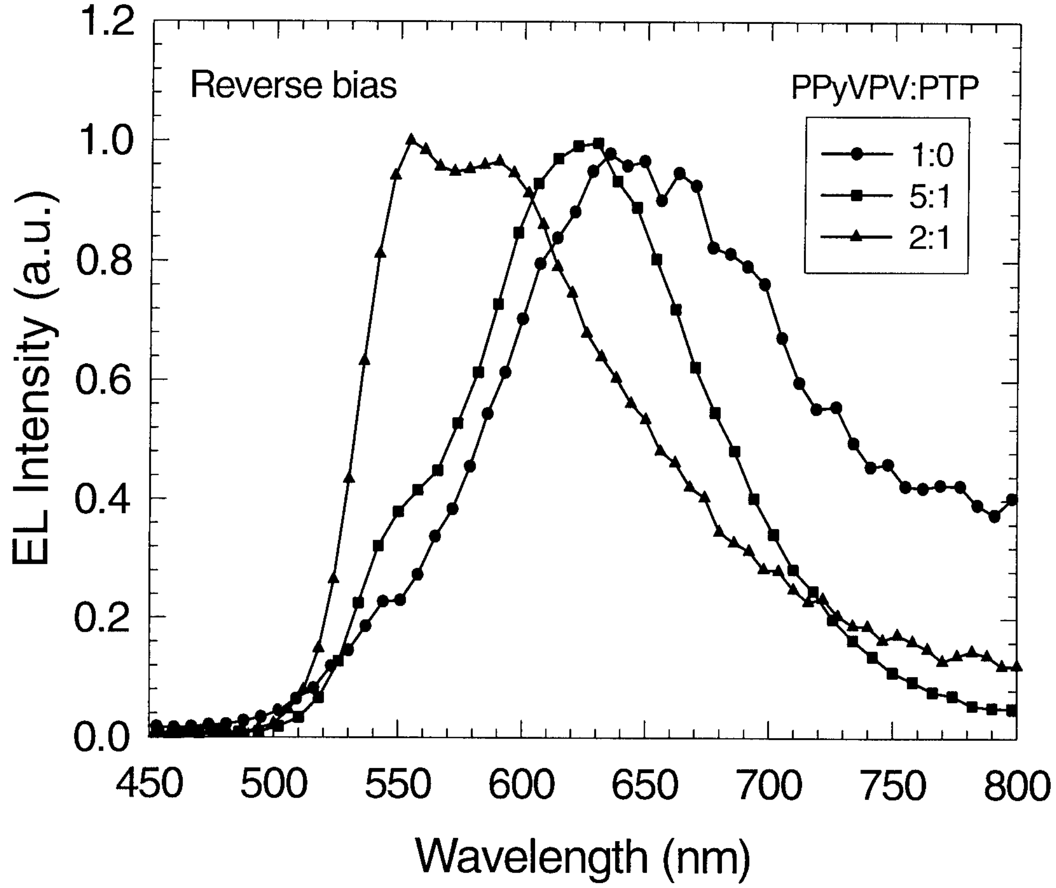

Fig. 5 Comparison of the EL spectra of ITO/EB/PPyVPV:PTP/SPAN/Al with different PPyVPV:PTP ratios. When the concentration of PTP increases, the EL spectra shift from red to green.

The mechanism for the SPAN layer changing the emission properties of the PPyVPV polymer is under further investigation. Initial studies suggest the formation of new emissive species due to protonation of the pyridyl units by SPAN.[12] This species was identified by both absorption and PL experiments. Fig. 6 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. 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 to the absorption at interface is clearly shown in the inset of Fig. 6 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 as a result of protonation of PPyVPV by SPAN. One special feature to SPAN is that it is acidic in aqueous solution and it is often called polyaniline sulfonic acid. On the other hand, the pyridyl unit is known to be susceptible to protonation or quarternization by acid.[13] 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 is originated from the protonated pyridyl units. The new species are emissive and emit redshifted light as compared to non protonated polymer.

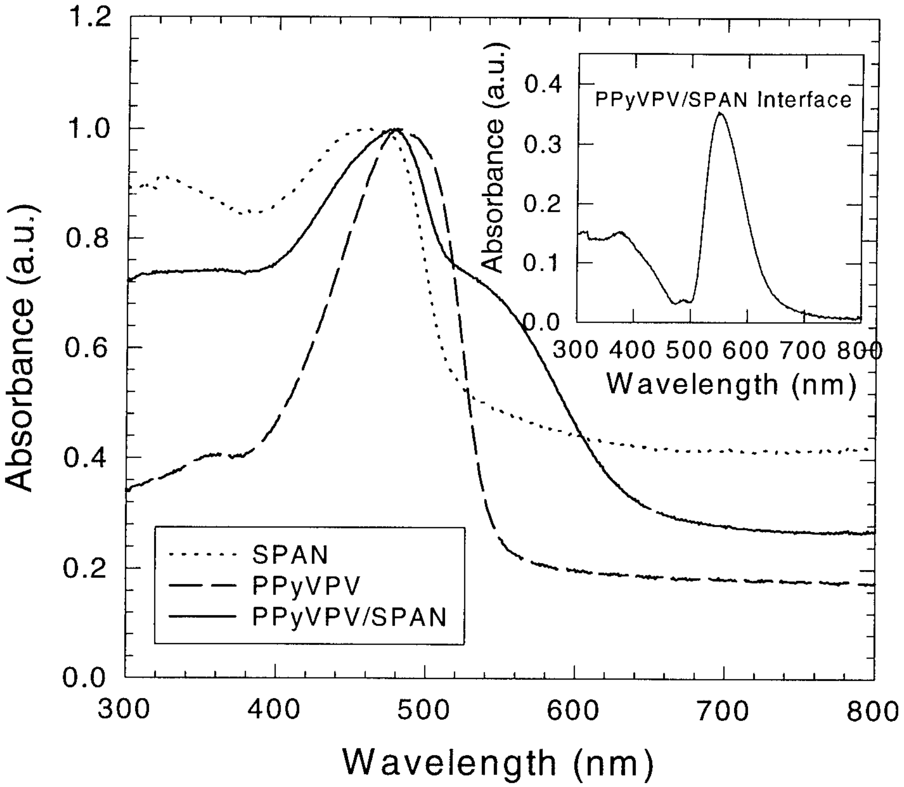

Fig. 6 Absorbance spectra of a PPyVPV film spin cast from xylenes solution, a SPAN film spin cast from aqueous solution, and a bilayer of PPyVPV/SPAN. Inset: Absorbance spectra as a result of subtraction of the absorbance of each individual layers from that of the bilayer.

4. SUMMARY/CONCLUSION

In summary, we have presented a new approach to color variable light-emitting devices which generates two independent colors of light at room temperatures. Instead of inserting a blocking polymer in between two different emitting polymers, we used two stable redox polymers sandwiching the emitting layer. Because at least one of the redox polymers is capable of changing the emission properties of the emitting polymer, the color of light generated at the redox polymer/emitting polymer interface is different from that generated in the bulk of emitting polymer. The emission zone, and hence the color of emitted light can be controlled by the polarities of the driving voltage and the charge transport properties of the emitting polymers. The latter can be controlled by blending two emitting polymers with different charge transport properties in an appropriate ratio.

The new 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 improve 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 build up of space charges.

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