Color variable bipolar/ac light-emitting devices based on conjugated polymers

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There is increased interest in developing color variable light emitting devices. We report here the fabrication of color variable bipolar/ac light-emitting devices based on conjugated polymers. The devices consist of blends of pyridine-phenylene and thiophene-phenylene based copolymers sandwiched between the emeraldine base form and the sulfonated form of polyaniline. ITO and Al are used as electrodes. The devices operate under either polarity of driving voltage with different colors of light being emitted, red under forward bias, and green under reverse bias. The relative fast time response allows the rapid switching of colors and ac operation. © *1997 American Institute of Physics.* [S0003-6951(97)q2624-7]

In the past decade, there has been great interest in organic electroluminescent devices, particularly conjugated polymer based light-emitting devices (LEDs).[1–4] To date, a variety of conjugated polymers and/or copolymers have been found to exhibit electroluminescent (EL) 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 color variable 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.[5] Though such devices can emit multiple colors of light, they have very limited control of the brightness at a desired color. Color variable LECs,[6] 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.[7] 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 so 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.

For 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)[8] 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 the schematic device structure, respectively. The EB layer was first spin coated at ~3000 rpm from N-methyl pyrrolidinone (NMP) solution (concentration of ~5 mg/ml) onto precleaned patterned ITO substrates (with a sheet resistance of 15 $\Omega/\square$). 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 spin 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. Photoluminescence (PL) and EL were measured using a PTI fluoro-
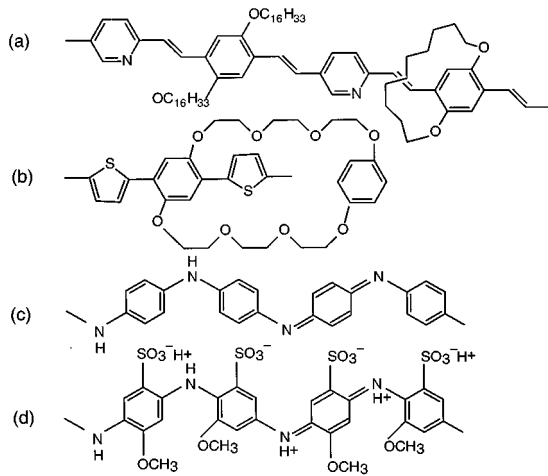
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FIG. 1. Repeat units of polymers used in this study. (a) PPyVPV* [poly-(pyridyl vinylene phenylene vinylene) derivative]; (b) PTP* [poly(thienylene phenylene) derivative]; (c) EB (emeraldine base); and (d) SPAN (sulfonated polyaniline).

FIG. 3. PL and EL spectra of PPyVPV* and PTP* films cast from xylenes solutions.

meter (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 an HP Model 6218A dc power supply. Quantum efficiency and brightness were measured using a calibrated photodiode (UDT UV100).

Figure 3 shows the PL spectra of PPyVPV* and PTP* films cast from xylenes solution. The PL of PPyVPV* peaks at 610 nm with a shoulder at 560 nm. In contrast, the PL of PTP* peaks at 545 nm with a shoulder at 580 nm. Although the two polymers show different PL properties, the EL spectra of their single layer devices with ITO and Al as electrodes are very similar, each of which peaks at ~550 nm with a shoulder at ~580–600 nm. The different properties of PL and EL of PPyVPV* (Ref. 9) and similar materials[10] has been attributed to aggregate formation in these polymer films. The similarity between the PL and EL spectra for the PTP* film suggests that no or very few aggregates were formed in the PTP* film, consistent with the higher density of phenyl bridging groups.

Figure 4 shows the typical I–V and luminance–voltage characteristics of the devices configured as in Fig. 2. 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 symmetrically configured ac light-emitting (SCALE) devices,[11] with different colors of light being emitted. The light ap-
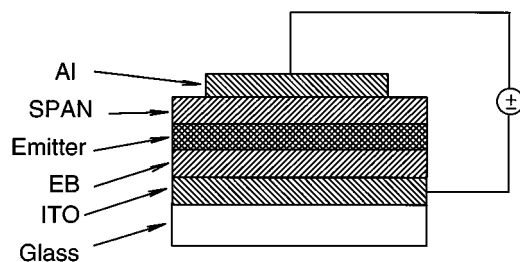

FIG. 2. Schematic diagram of the color variable light-emitting device.
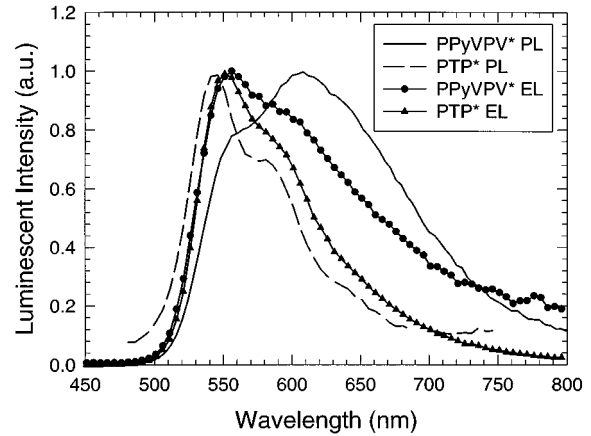
peared red and green to the eye under forward and reverse bias, respectively, and was clearly visible under normal indoor lighting. Internal device efficiencies of up to 0.1% photons/electron has been achieved for the initial devices. The EL spectra under forward and reverse bias are shown in the inset of Fig. 4. 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. The colors of the devices have been switched rapidly, up to ~20 kHz, depending upon device impedance and geometry.

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. While no significant shift of EL spectra from ITO/PPyVPV*/Al were found for ITO/SPAN/PPyVPV*/Al and all EB devices, ITO/PPyVPV*/SPAN/Al and ITO/SPAN/PPyVPV*/SPAN/Al show dramatically redshifted EL spectra. This clearly demonstrates that the red light is generated from the PPyVPV*/SPAN interface on the cathode side under forward bias. The mechanism for the SPAN layer changing the emission properties of the PPyVPV* polymer is under further study. Initial studies suggest the formation of complex species due to the quarternization of the pyridyl units by SPAN.[12] 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 able to exactly identify the emission zone because the EB layer does not modify the emission properties of the emitting polymer. The EB layer serves as a charge injection enhancement layer, playing a similar role as it does
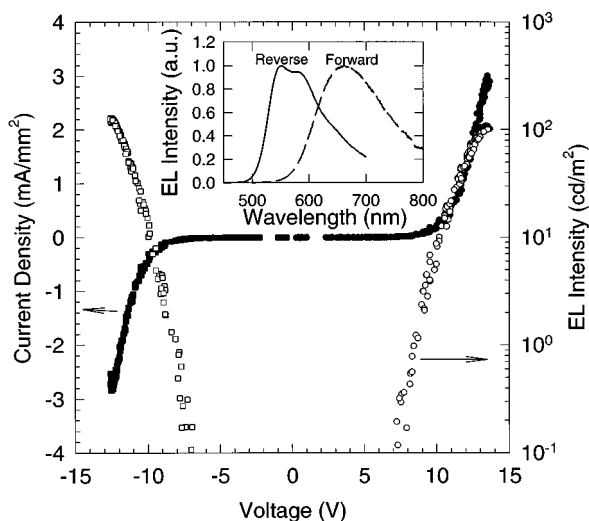
FIG. 4. Current–voltage and light–voltage characteristics of color variable light-emitting devices under forward and reverse bias conditions. The device emits red light under forward bias and green light under reverse bias. Inset shows the electroluminescent spectra of such a device under forward and reverse bias conditions.

in SCALE devices reported earlier.[11] 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 the 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.[13] 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 the 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.[12]

In summary, we have reported a new approach to color variable light-emitting devices which generate two independent colors of light at room temperatures, using two stable redox polymers sandwiching the emitting layer. Since 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 is controlled by the polarities of the driving voltage and the charge transport properties of the emitting polymers. The latter is 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 reported 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 reactive low work function metals.

(2) The introduction of the two redox polymers allows the devices to operate in both forward and reverse bias. Since no ionic species are directly involved in the device operation, the colors can be switched very rapidly, in sharp contrast to intrinsically slow response LECs.

(3) The emitting polymers are protected by the redox polymers against direct exposure to air, potentially improve the device stability.

(4) ac or periodically reversed operation may retard failure due to migration of metals from the electrodes into the polymer. Such operation may also dissipate the buildup of space charges.

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