

# Polarity- and voltage-controlled color-variable light-emitting devices based on conjugated polymers

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There is increased interest in developing multilayer color-variable light-emitting devices. So far, the multilayer color-variable light-emitting devices mainly have focused on polarity-controlled two-color light-emitting devices. We report here the fabrication and study of voltage- and polarity-controlled multilayer multicolor light-emitting devices based on pyridine-containing conjugated polymers and derivatives of polyacetylene. The devices emit red light under forward bias and multiple colors of light (from orange-red to green) under reverse bias. The colors under reverse bias are controlled by the magnitude of the applied voltages. © 1999 American Institute of Physics. [S0003-6951(99)04518-0]

Recently, color-variable organic light-emitting devices (LEDs) have attracted much attention.<sup>1-8</sup> These devices can generate two or more colors of light and the colors can be controlled by device parameters such as driving voltage, current, local temperatures, etc. The most common approach to color-variable devices is voltage-controlled multicolor LEDs. In this approach, a blend of organic materials, either polymers or molecules or both, often is used as the emitting layer. For example, in the devices using a blend of polythiophene derivatives, different components in the blend emit different colors of light simultaneously with the intensity of each component varying with the applied voltage.<sup>1</sup> Similar voltage-dependent electroluminescence (EL) was observed in the devices using conducting polymer-containing fluorescent dye as the emitting layer.<sup>2</sup>

The voltage-controlled multicolor device is typically in a single-layer configuration. When the emitting materials are in separate layers, light emission typically takes place only in one layer. As a result, the devices only show one emission color independent of the magnitude of the applied voltages. In certain multilayer structures that can be operated under both forward and reverse bias, a different color of light can be generated under reverse bias than under forward bias, thus allowing the fabrication of polarity-controlled two-color devices. So far, a considerable amount of research effort has been focused on such polarity-controlled two-color light-emitting devices.<sup>3-8</sup>

In this letter, we report the fabrication and study of voltage- and polarity-controlled multicolor light-emitting devices. The two-layer devices consist of a layer of a blend of two electroluminescent polymers and a separate redox polymer layer. The redox polymer is capable of modifying the

emission properties of at least one of the emitting polymers at the interface such that the interface emits different colors of light than the bulk does. Under forward bias (hole injection into the blend and electron injection into the redox polymer), the light is emitted from this interface. Under reverse bias, the emission location can be controlled by voltage from this interface, to an intermediate region, to deep in the bulk, allowing the voltage-controlled emission colors.

For the devices presented here, a copolymer poly(pyridyl vinylene) and poly(phenylene vinylene) derivative, PPyVPV, and a derivative of polyacetylene, poly(diphenyl butyl acetylene) (PDPA-nBu) or poly(hexyl phenyl acetylene) (PhPA), were used as the emitting materials in the blend. Sulfonated polyaniline (SPAN) was used as the redox materials. ITO and Al were used as electrodes. PPyVPV,<sup>9</sup> PDPA-nBu,<sup>10</sup> and PhPA (Ref. 11) have all been successfully used as active materials in polymer light-emitting devices. Both PPyVPV and PDPA-nBu show green EL while PhPA is a blue emitter. Figure 1 shows the chemical structures of PPyVPV, PDPA-nBu, and PhPA and a schematic diagram of the device structure. The blend layer of PPyVPV and PDPA-nBu or PhPA (1:1 weight ratio) was first spin cast at ~2500 rpm from trichloroethylene or xylenes solution (total concentration of ~10 mg/ml) onto precleaned patterned ITO-coated glass substrates. 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 clean room. The top metal electrode was deposited by vacuum evaporation at a pressure below 10<sup>-6</sup> 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 ultraviolet/visible/near-infrared (UV/VIS/NIR) spectrometer. Photoluminescence (PL) and electrolu-

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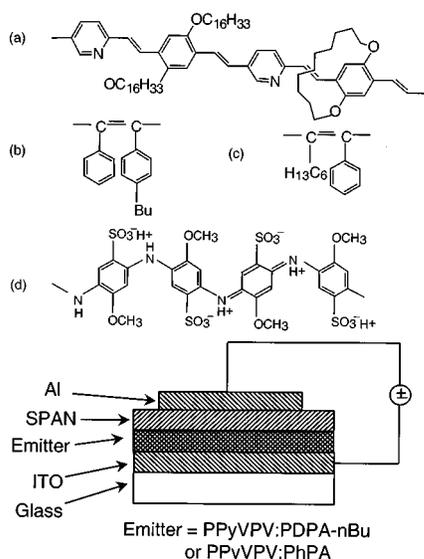


FIG. 1. Repeat units of the materials used in this study and the schematic diagram of the device structure. (a) poly(pyridyl vinylene phenylene vinylene) (PPyVPV); (b) poly(diphenyl butyl acetylene) (PDPA-nBu); (c) poly(hexyl phenyl acetylene) (PhPA); and (d) sulfonated polyaniline (SPAN).

minescence were measured using a PTI fluorometer (model QM-1). Quantum efficiency and brightness were measured by a calibrated photodiode (UDT UV100). We note that all the device-testing procedures were performed in air on as-made devices without any encapsulation.

Figure 2 shows the EL spectra for an ITO/PPyVPV:PDPA-nBu/SPAN/Al device under forward and reverse applied voltages. Under forward bias, the device emits red light independent of voltage, similar to the previous reported polarity-controlled two-color devices.<sup>5,6</sup> Under reverse bias, however, the emission colors are voltage dependent. The emitted colors change from orange-red to green as the voltage increases. The brightness also increases with the applied voltage. Figure 3 shows the trace of the color coordinates in the CIE chromaticity diagram. The device emits almost saturated red light under forward bias. Under reverse bias, as the voltage increases, the colors vary from red to orange to yellow along the edge of the CIE chromaticity

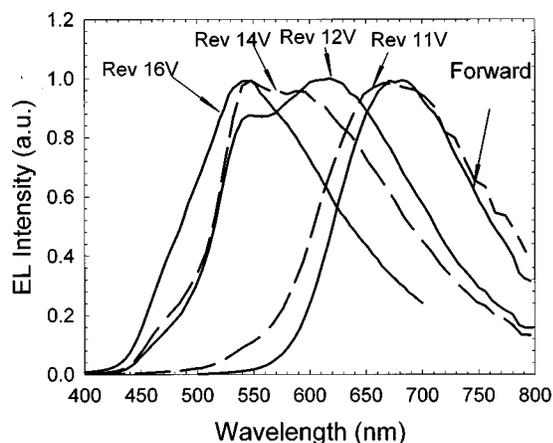


FIG. 2. EL spectra of an ITO/PPyVPV:PDPA-nBu/SPAN/Al device under forward and reverse bias conditions.

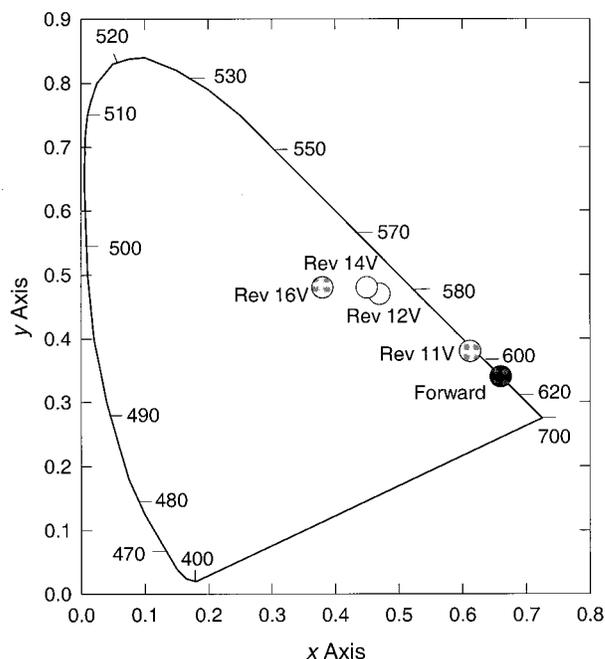


FIG. 3. The CIE color coordinates of the EL spectra of an ITO/PPyVPV:PDPA-nBu/SPAN/Al device under different applied voltages.

diagram, and then change to green as the voltage further increases.

Figure 4 shows the EL spectra for an ITO/PPyVPV:PhPA/SPAN/Al device under forward and reverse applied voltages. Again under forward bias, the device emits red light independent of voltage. Under reverse bias, the emission colors change from orange to green as the voltage increases. However, the EL spectrum does not change further to blue at higher voltages beyond 11 V. This result is somewhat surprising. It is expected that the color should shift further to the blue region as the voltage further increases because the PhPA is a blue-emitting polymer.<sup>11</sup> One possible explanation is that the emitted blue light from PhPA at high voltage is absorbed by PPyVPV and reemits as photoluminescence. The EL spectrum of PhPA and the absorption spectrum of PPyVPV support this scenario. PhPA shows a broad EL spectrum peak at 450 nm.<sup>11</sup> On the other hand, the absorption spectrum of PPyVPV peaks at 470 nm with a

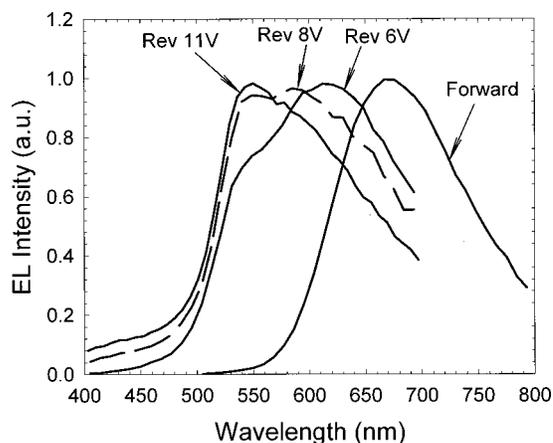


FIG. 4. EL spectra of the ITO/PPyVPV:PhPA/SPAN/Al device under forward and reverse bias conditions.

substantial absorption at 450 nm. Indeed, the PL emission of PPyVPV at  $\sim 600$  nm (Ref. 9) appears in the EL spectra of the ITO/PPyVPV:PhPA/SPAN/Al device at higher reverse bias.

In our previously reported polarity-controlled two-color devices,<sup>5,6</sup> PPyVPV and poly(thienylene phenylene) (PTP), were used as the emitting polymers in the blend. The operating mechanism of such devices is as follows: under forward bias, red light is emitted from the new species at the interface between PPyVPV and SPAN as a result of protonation of the pyridyl units of the PPyVPV by SPAN. Under reverse bias, green light is emitted from the bulk of the emitting layer. We have shown that under reverse bias, the exact emission location is determined by the concentration of the hole transporting PTP in PPyVPV.<sup>6</sup> When the PTP concentration increases, the emission location is further away from the PPyVPV/SPAN interface into the bulk of the emitting materials, resulting in the gradual color shift from orange-red to green. However, the individual device with fixed PTP concentration only shows one color under reverse bias. In the present devices, by replacing the PTP with PDPA-nBu or PhPA, the emission location under reverse bias now can be controlled by the magnitude of the applied voltage instead of PTP concentration, implying that the voltage is now playing a similar role as the concentration of PTP. This can be rationalized by assuming a smaller but stronger field-dependent hole mobility of PDPA-nBu and PhPA than PTP.

In summary, we have presented polarity- and voltage-controlled multicolor light-emitting devices based on pyridine-containing conjugated polymers and derivatives of

polyacetylenes. Under forward bias, the devices emit red light from the interface between the emitting polymer and the redox polymer. Under reverse bias, the devices emit multiple colors of light from orange-red to yellow to green originated from the interface, to intermediate region, to deep in the bulk. The colors can be controlled by the polarity and magnitude of applied voltages.

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