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INTERFACE CONTROL OF POLYMER BASED LIGHT EMITTING DEVICES

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ABSTRACT

Bilayer and multilayer polymer structures provide opportunities for new photophysics and new types of light emitting devices. Photoluminescent and electroluminescent studies of bilayer heterojunctions formed from a poly(pyridyl vinylene phenylene vinylene) (PPyVPV) derivative and poly(vinyl carbazole) (PVK) show an emission peak which cannot be ascribed to either the PPyVPV derivative or PVK layer. Through studies of absorption and photoluminescence excitation (PLE) spectra we demonstrated that the additional feature results from an exciplex at the bilayer interface. The photoluminescence efficiency of the exciplex is greater than 20%. We also discuss 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.

Conjugated polymer based light-emitting devices[1,2,3,4,5,6,7,8] have become a topic of great interest since the report of electroluminescent (EL) properties in poly(phenylene vinylene) (PPV).[1] A large variety of polymers, copolymers, and their derivatives have been shown to exhibit EL properties, including a relatively new class: polypyridines,[5,6] and poly(pyridyl vinylene)s.[6,9] The configurations of these devices may consist of a simple single layer,[1,2] bilayers,[2] or blends[7] used to enhance efficiency and tune the emission wavelength, or multilayers that may allow the device to operate under an ac applied voltage.[6]

In single layer devices the low efficiency frequently is due to the imbalance of electrons and holes. Inserting a hole-transport (electron-blocking) or electron transport (hole-blocking) layer provides a means to enhance minority carriers and block the majority carriers and confine them to the emitter layer, which increases the probability of recombination.[2] Poly(N-vinylcarbazole) (PVK) has been used as a hole transport layer[8] and occasionally in blends with the emitter polymer.[7,8] PVK is a well-studied photoconductive polymer which often forms exciplexes with organic molecules, e.g., dimethyl terephthalate.[10] An exciplex is a transient donor-acceptor complex between the excited state of the donor and the ground state of the acceptor.[10]

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.[11] Though such devices can emit multiple colors of light, they have very limited control of the brightness at a desired color. Color variable LECs,[12] 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 require 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.[13] 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 discuss here bilayer devices with PVK as the hole transport layer and a derivative of the copolymer poly(pyridyl vinylene phenylene vinylene) (PPyVPV) as the emitter layer. Absorption, photoluminescence (PL) and electroluminescence (EL) results demonstrate emission due to exciplex formation at the interface between the PVK and copolymer. The PL and EL of bilayer films are dramatically different from that of a single layer film.

We also discuss 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.

Figure 1 presents the chemical structures of PPyVP$(COOC_{12}H_{25})_2$V and PVK. Figure 2 shows the PL of a single layer of the copolymer, a single layer of PVK and a bilayer of PVK and the copolymer. The PL of single PVK layers excited at 3.6 eV has a peak emission energy at 3.05 eV, similar to previous reports of the PL of PVK.[7,8] The PL for single layer copolymer films excited at 3.1 eV shows an emission peak at 2.05 eV. The bilayer when excited at an energy less than the absorption edge of the PVK, but greater than the absorption edge of the copolymer shows PL peaked at the same energy as for the copolymer along with a low intensity tail to the blue side. When the bilayer was excited at energy equivalent to the excitation energy for the single PVK layer (3.6 eV), the PL emission spectrum contains contributions from both single layers (3.05 and 2.05 eV), as well as from a completely new species, which we identify with an exciplex. To the low energy side of the exciplex PL is a weak shoulder near the PL energy for the single layer of the copolymer. Figure 3 shows the PL intensity as a function of both the *excitation* energy and the *emission* energy. At excitation energies above 3.6 eV the PL due to the exciplex and PVK are apparent, but if the excitation energy is lowered below 3.4 eV these peaks have essentially disappeared. As the excitation energy is further lowered into the peak absorption of the copolymer, PL from the copolymer strongly predominates (excitation energy 2.6-3.0 eV and principal emission energy 1.8-2.2 eV).

We fabricated bilayer devices using ITO as the anode and aluminum as the cathode. The inset of Fig. 4 shows the EL spectrum of a typical device with the PL spectrum from the same device. The devices can easily be seen in a brightly lit room, appear bright green to the eye, and have internal quantum efficiencies of ~0.1%-0.5%. Although the PL efficiencies are comparable, the EL efficiency of the bilayer configuration, ~0.1%-0.5%, is much greater than for a single layer device which has an EL efficiency of less than 0.0001%. The similarity between the PL and EL of the bilayer device demonstrates that the exciplex is responsible for the EL emission. Figure 4 shows the current-density voltage and brightness-voltage characteristics for a typical bilayer device. The turn-on voltage of the bilayer devices depends on the thickness of the polymer layers and in this case is ~18 V, with the brightness following the current. The generality of this concept has been demonstrated using several other pyridine-based copolymers.[14] Through the use of polyaniline network electrodes[15] we have lowered the threshold voltage to below 10 V while maintaining the same efficiency.[16]

Thus heterojunctions of PVK and $PPyVP(COOC_{12}H_{25})_2V$ show a strong photoluminescence and electroluminescence feature due to exciplex emission at the interface. The absorption and PLE spectra have shown that the exciplex is not directly accessible from the ground state. The exciplex is also the primary species of electroluminescence emission in the bilayer devices. The efficiency of the bilayer devices is greatly enhanced over single layer devices due to charge confinement and exciplex formation and emission at the interface.

For two-color 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)[17] and the emeraldine base (EB) form of polyaniline were used as the redox materials; ITO and Al were used as electrodes. Figures 5 and 6 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 ~5mg/ml) onto precleaned patterned ITO substrates (with a sheet resistance of 15 Ω/square). The emitting layer was then spin coated over the EB layer from a blend of PPyVPV* and PTP* (3:2 weight ration) in xylenes or trichloroethylene (total concentration ~10 mg/ml). The SPAN layer was subsequently spin coated over the emitting layer from an aqueous solution. This device differs from the prior SCALE device[18] in having different polyaniline forms on the two sides of the light emitting polymer. Figure 7 shows the typical I-V and luminance-voltage characteristics of the devices configured as in Figure 6. 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, 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. The EL spectra under forward and reverse bias are shown in the inset of Fig. 7. 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 ~20kHz, 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. The red light is generated from the PPyVPV*/SPAN interface on the cathode side under forward bias. Studies suggest the formation of complex species due to the quarternization of the pyridyl units by SPAN.

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 improving 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.

In sum, bilayer and multilayer structures show unusual photophysics phenomena and provide means of fabricating unusual devices with new functions.

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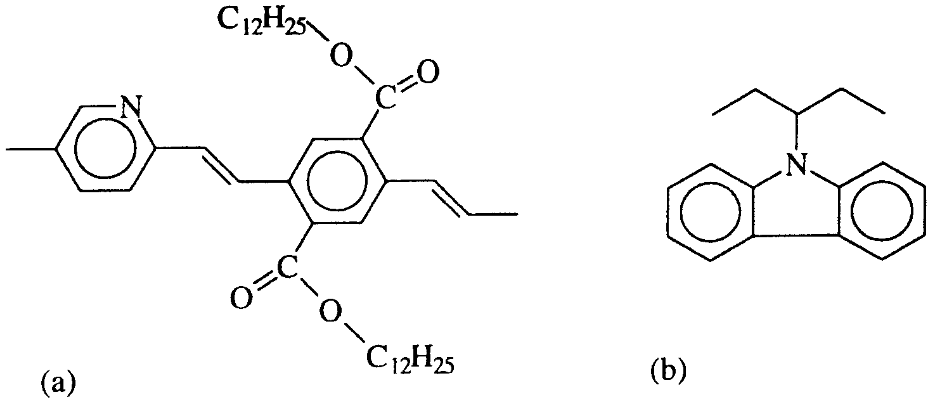

Figure 1. Molecular repeat unit of (a) PPyVP($COOC_{12}H_{25}$)$_2$V and (b) PVK.

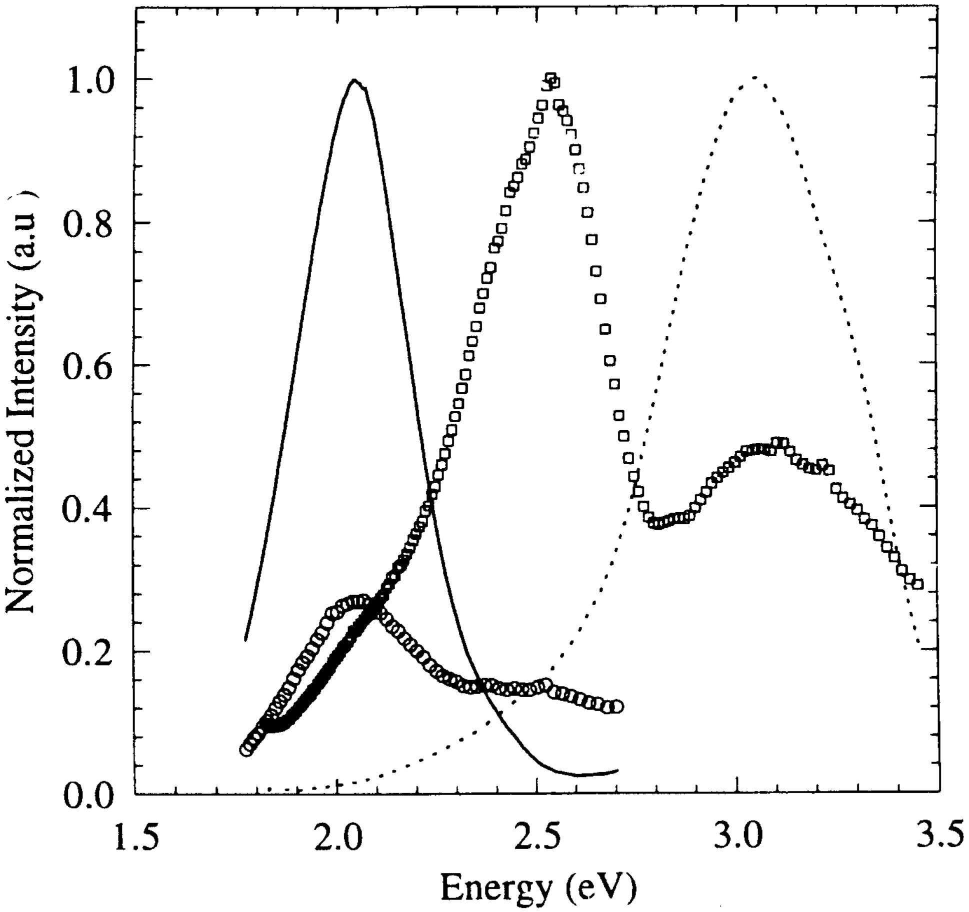

Figure 2. PL of PPyVP($COOC_{12}H_{25}$)$_2$V at 2.8 eV excitation energy (—), a bilayer of PVK and PPyVP($COOC_{12}H_{25}$)$_2$V at 3.6 eV excitation energy (square) and 2.8 eV excitation energy (O), and PVK at 3.6 eV excitation energy (···), all on quartz substrates.

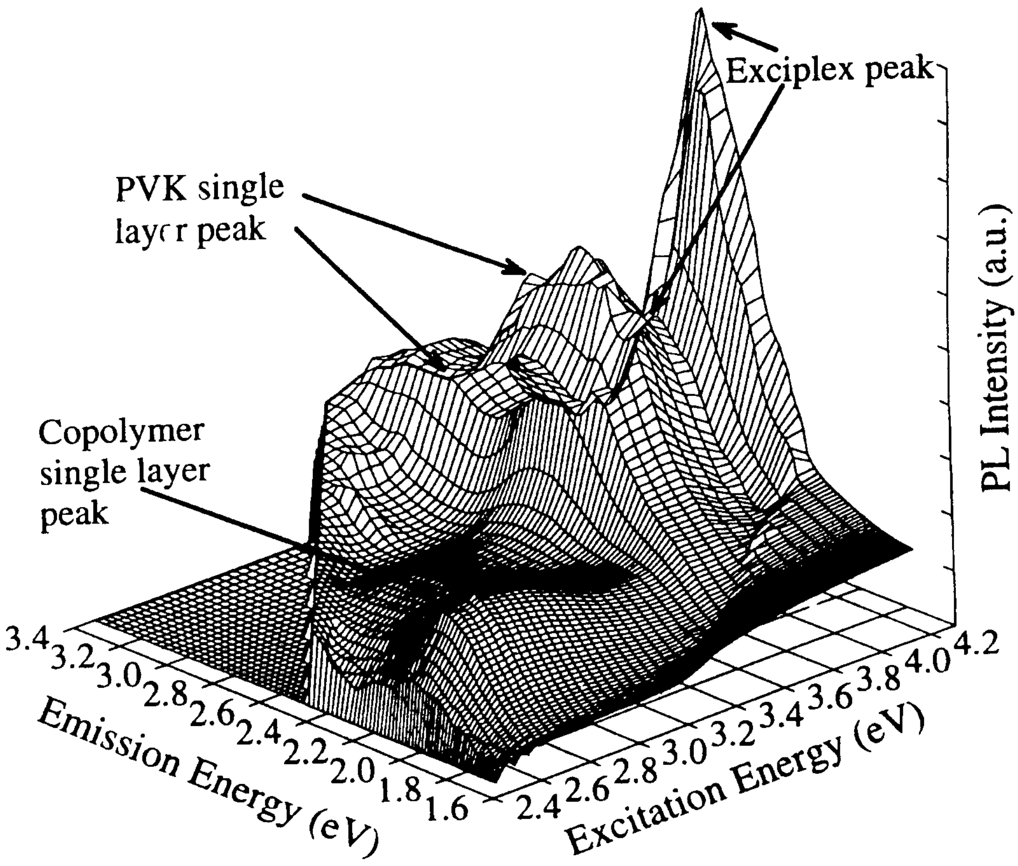

Figure 3. PL of a bilayer of PVK and PPyVP(COOC$_{12}$H$_{25}$)$_2$V as a function of both emission energy and excitation energy. The 3D plot shows three prominent features: a peak due to the PVK (excitation energy from 3.6 to 4.2 eV, emission energy from 2.8 to 3.4 eV), a peak due to the copolymer (excitation energy from 2.4 to 3.0 eV, emission energy 1.8 to 2.2 eV), and the exciplex peak (excitation energy from 3.6 to 4.2 eV, emission energy 2.2 to 2.8 eV).

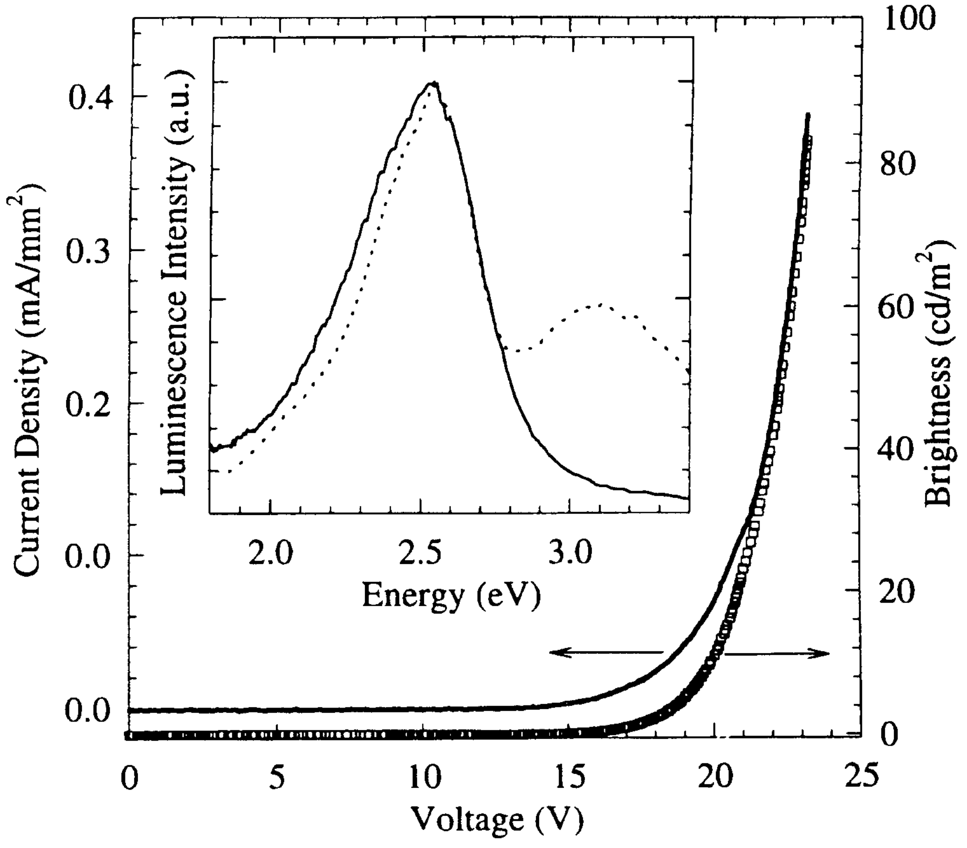

Figure 4. Current-voltage (—) and brightness-voltage (square) characteristics of a typical bilayer light-emitting device. Inset: PL(···) and EL(—) of a bilayer light-emitting device.

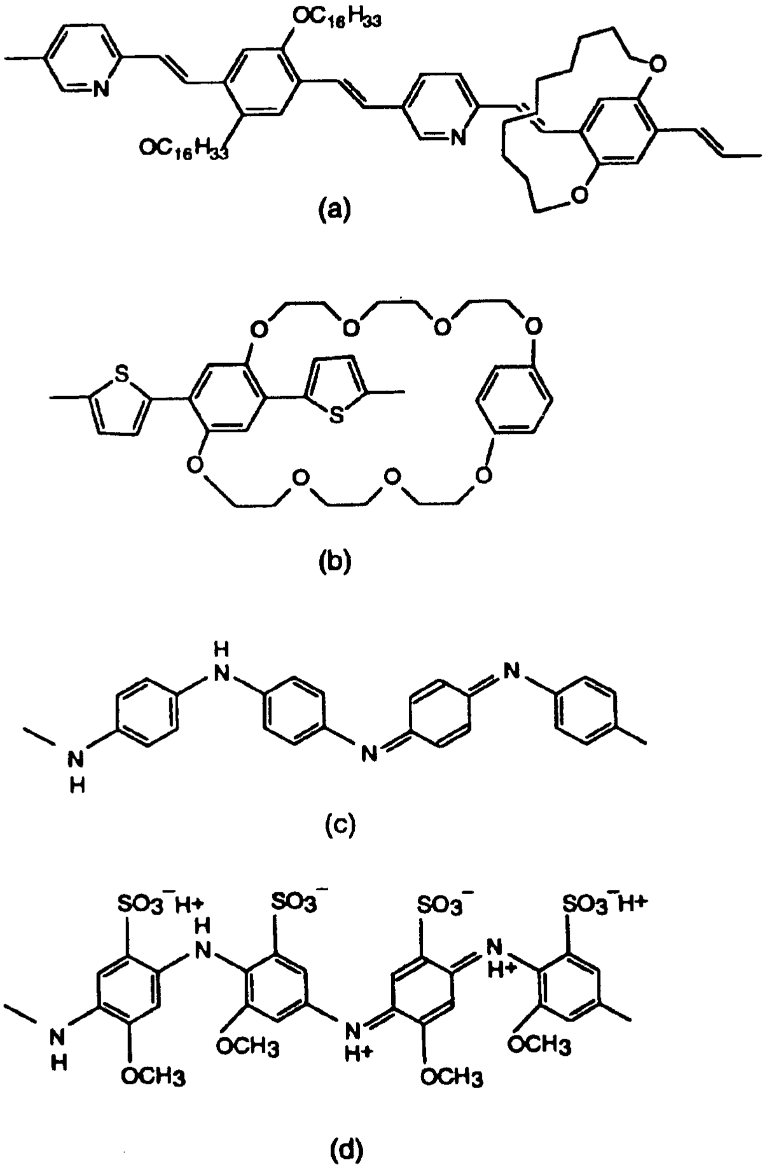

Figure 5. Repeat units of polymers used in this study. (a) PPyVPV* [poly(pyridyl viylene phenylene vinylene) derivative]; (b) PTP* [poly(thienylene phenylene) derivative]; (c) EB (emeraldine base); and (d) SPAN (sulfonated polynaniline).

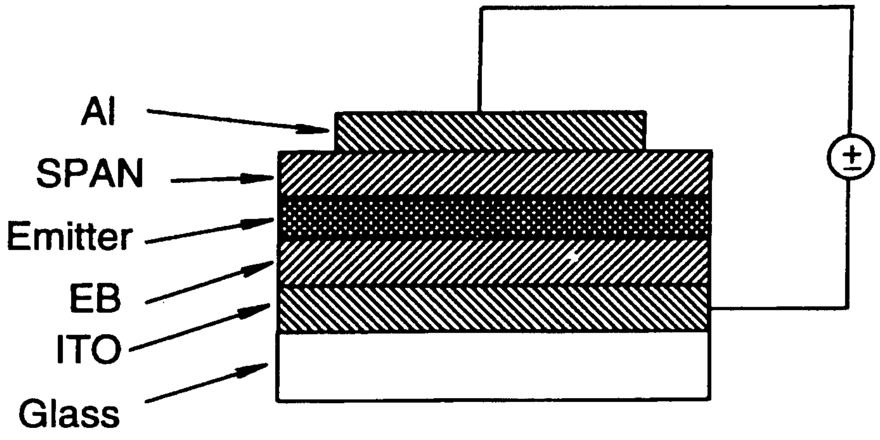

Figure 6. Schematic diagram of the color variable light-emitting device.

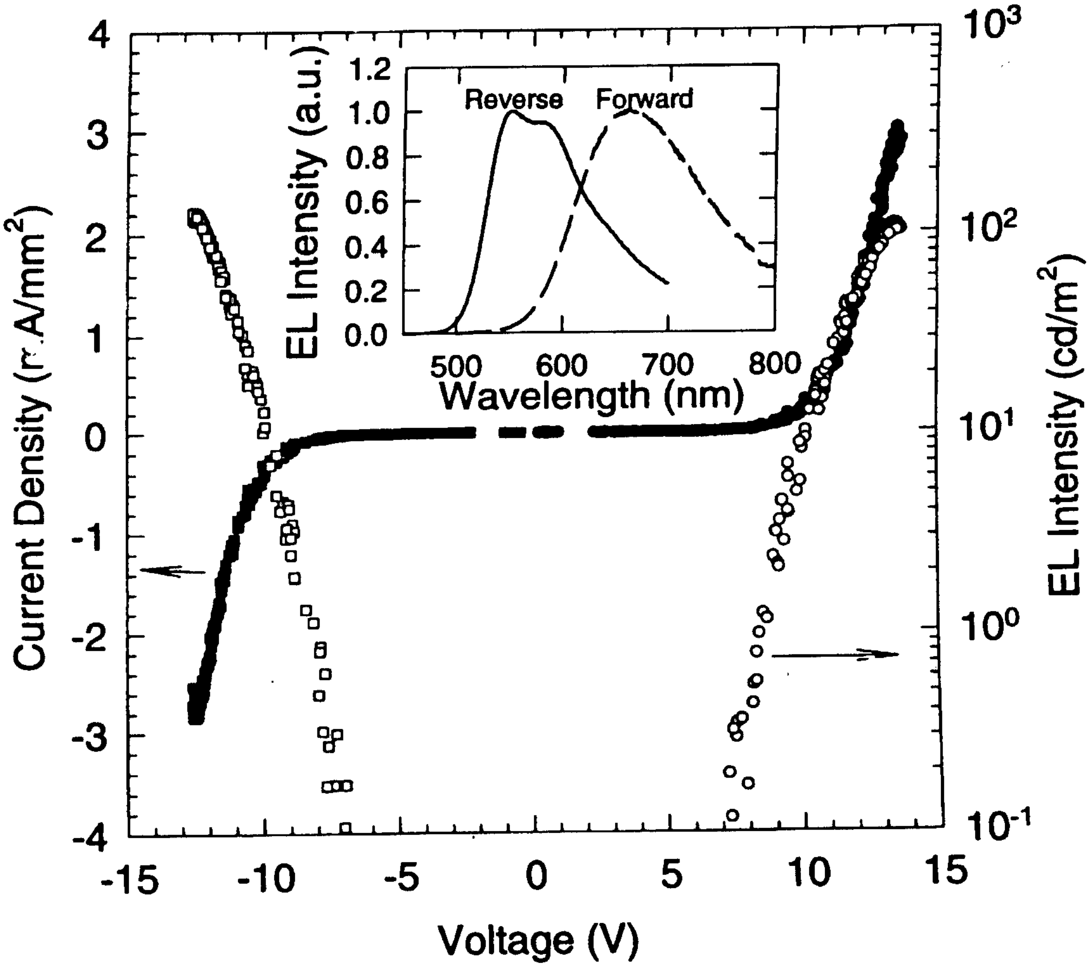

Figure 7. Current-voltage and light-voltage characteristics of color variable light-emitting devices under forward and reverse bias conditions. The device emits red light under forward bias and green light under reverse bias. Inset shows the electroluminescent spectra of such a device under forward and reverse bias conditions.