Formation of Intragap States and Achieving Balance in Carrier Mobilities for a PPV Derivative Bearing the Carbazole Pendants

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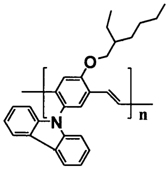
Summary: We have found by NEXAFS spectroscopic studies that a PPV derivative (CzEh-PPV) bearing the carbazole pendants form new intragap states when contacted with calcium metal. Moreover, the polymer exhibited much more balanced mobilities of holes and electrons than PPV and MEH-PPV. Such characteristics are believed to bring about low turn-on electric field and improved efficiency for the LED device fabricated with the polymer.

Introduction

Since the pioneering work by the Cambridge group on the electroluminescence (EL) properties of ligh-emitting diodes (LEDs) based on poly(p-phenylenevinylene) (PPV),[1] there have been many reports on the EL characteristics of a wide variety of PPV derivatives.[2-8]Recently, we reported[9] that the following polymer, CzEh-PPV, exhibited a very high device efficiency, low turn-on electric field, and a very high maximum brightness when the LED device had the configuration of ITO/ POEDOT/ polymer/ Ca.



CzEh-PPV

The polymer bears the 2-ethylhexyloxy and carbazole pendant groups, both of which are electron-donating groups. This polymer could be easily prepared by the Gilch polymerization method[10] and are soluble in common organic solvents such as tetrahydrofuran, 1,1,2,2-

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tetrachloroethane, and chloroform. The LED device constructed with this polymer emits green light. The HOMO and LUMO levels of the polymer determined by the UPS method[11] are 5.5 and 3.2 eV, respectively.[9]

In this communication, we would like to report the evolution of the near-edge X-ray absorption fine structure (NEXAFS) spectrum during the deposition of calcium metal on the thin film of CzEh-PPV and carrier mobilities of the polymer measured by the time-of-flight method.

Characteristics of the LED Device Fabricated with CzEh-PPV

Table 1 summarizes the LED device characteristics of CzEh-PPV. The maximum emitted light intensity is observed at 528 nm. For the sake of comparison characteristics of LED devices constructed with PPV and MEh-PPV also are included in the table.

Table 1. LED device characteristics of CzEh-PPV

Device Structure	Φ_{Ext} (%)	Electric Field for 0.1 mA/m^2 (MV/cm)	Maximum Brightness (cd/m^2)
ITO/ PPV/ Al	2.0×10^{-4}	1.1	5
ITO/ CzEh-PPV/ Al	0.010	0.63	20
ITO/ CuPc/ CzEh-PPV/ Li:Al	0.040	0.4	350
ITO/ CzEh-PPV/ Alq_3/ Li:Al	0.38	1.0	1650
ITO/ PEDOT/ MEh-PPV/ Ca/ Al	1.1	0.4	20540
ITO/ PEDOT/ CzEh-PPV/ Ca/ Al	4.4	0.5	30390

A close examination of the experimental data given in Table 1 teaches us several important points: (1) The metal cathodes of lower work function exhibit better device performance. (2) The device of CzEh-PPV reveals a lower turn-on electric field than that of PPV. (3) Utilization of a conducting layer between the anode and the light emitting layer lowers the threshold electric field of the device. (4) The device constructed with CzEh-PPV performs much better than PPV and MEH-PPV. The observations described in (1) and (3) are rather well known facts.[12] Those described in (2) and (4), however, require proper explanations. We believed that NEXAFS spectroscopy and XPS measurement of carrier mobility will be provide us with answers to the scientific questions.

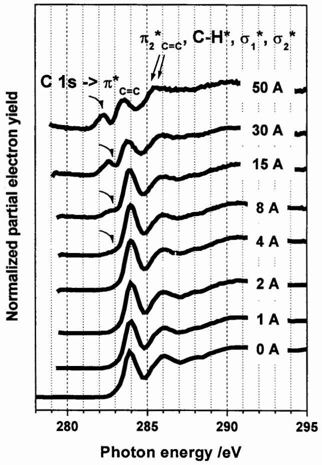

Figure 1. Evolution of NEXAFS C 1s peak spectra during Ca deposition on the film surface of CzEh-PPV.

NEXAFS Spectroscopy and XPS

We studied how NEXAFS spectrum[13, 14] changes on deposition of calcium metal on a thin film of CzEh-PPV and the spectral changes are shown in Figure 1. The figure shows that CzEh-PPV in the virgin state exhibits the lowest energy peak for $C_{1s} \rightarrow \pi^*$ electronic transition at 283.9 eV. The NEXAFS spectrum, however, shows appearance of a new peak within the leading edge of π^* resonance when the thickness of the calcium layer reaches 8Å. The new peak grows in intensity as more calcium is deposited. It also is noted that the original peak position is shifted to slightly lower energy side, 283.5 eV. And the energy difference between the new peak and the original one is 1.3 eV. Although the NEXAFS spectra for MEh-PPV are not given, formation of new intra gap states was observed, just as described for CzEh-PPV.

As one can see from Table 1, the turn-on electric field of LED devices is in the order of MEh-PPV ≈ CaEh-PPV < PPV. This order appears to correlate well with the polymers' ability to form new valence states within the band gap when contacted to the calcium metal. The formation of the intragap states is expected to enhance the electron injection into the emitting polymer layer from the calcium electrode by providing additional, lower energy states for electron transfer from near the Fermi level of the cathode metal.

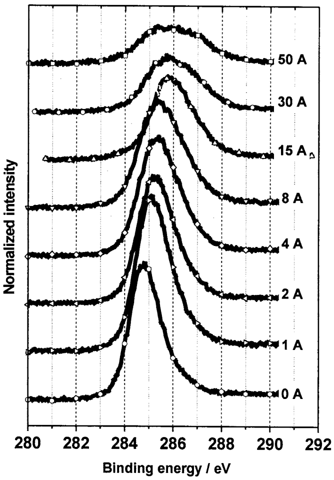

Figure 2. Evolution of XPS C 1s spectra during Ca depositon on CzEh-PPV.

We further studied the interface formation between calcium and CzEh-PPV by the XPS method. We collected the XPS spectra (Figure 2.) of C_{1s} electrons with increasing calcium coverage. We clearly note from Figure 2 that the C_{1s} peak steadily shift to the higher energy side as the thickness of deposited calcium layer increased. This is interpreted as originated from energy level bending induced by the calcium layer. The energy level bending amounts to about 0.7 eV when the thickness of calcium layer reach 30 Å. It, however, should be noted that the bending occurs even when Ca atoms are scarcely deposited, indicating that this bending does not require for the Ca coverage to be metallic. It is conjectured that the individual Ca atoms are involved in electron transfer that results in polaron formation. These polarons formed in the backbone π-electron system will eventually form new states as discussed about in the NEXAFS studies. In other words, the new gap states created near the surface of the polymer layer due to the electron transfer from Ca to the polymer causes the energy level shift resulting in band bending. There are some theoretical studies supporting this supposition.[13, 15]

Balance in Mobilities of Carriers

One of the major reasons for the poor device performance of PPV LEDs is ascribed to the much higher mobility of positive holes than that of electrons.[16] Such an imbalance will result in annihilation of most of the injected holes on the surface of the cathode before they are captured by electrons to form excitons.[17, 18] In order to reduce the undesirable waste of holes, one may apply an electron-transporting / hole-blocking layer between the cathode and the PPV layer. Instead, we have attached the carbazole pendants in CzEh-PPV and wanted to study their influence on the mobilities of carriers and balance in their mobilities. The pendants are directly attached to the phenylene rings of the PPV backbone.

Table 2. Comparison of carrier mobilities*

Polymer	Time of Flight		
	μ_h	μ_e	μ_h/μ_e
PPV	7.0×10^{-4}	3.0×10^{-6}	230
MEh-PPV	1.2×10^{-6}	$\sim 10^{-8}$	$>10^2$
CzEh-PPV	4.0×10^{-5}	7.5×10^{-6}	5.3

*in $cm^2/V \cdot S$

Table 2 summarizes the carrier mobilities of the three polymers measured by the time-of-flight method. [19-21] It is observed that, indeed, the hole mobility in PPV is higher than two hundred times the electron mobility. Surprisingly enough, a similar imbalance is observed for MEh-PPV. We, however, understand that LED devices prepared from MEh-PPV perform much better than those from PPV. This is attributed to mainly three factors: easier electron injection as predicted by the MEh-PPV's LUMO level, formation of intragap states on contact with Ca, and increased interchain distance owing to the presence of two alkoxy pendants one of which is fairly bulky. Increased interchain distance will hinder the formation of interchain polaron pairs[22, 23] that are expected to reduce the radiative relaxation. In contrast, CzEh-PPV shows impressively balanced mobilities of the two opposite carriers, although mobilities of both carriers are much diminished when compared with those of PPV and MEh-PPV. As one can see from Table 2, the ratio of hole mobility to electron mobility is 5.3 for CzEh-PPV.

Let's first pay our attention to the mobilities of the two carriers in CzEh-PPV. We note that, compared to PPV, the hole mobility is reduced to a greater extent than the electron mobility. In fact, the electron mobility remains about the same. This is rather surprising in the light of the fact that the polymer bears the hole-transporting carbazole pendants. It is our present conjecture that the positive holes traveling through the backbone π-electron system are stabilized by the carbazole pendant, which, in turn, is expected to diminish the hole mobility. This conjecture is supported by optically detected magnetic resonance studies of the polymer.[24]

Other Pertinent Experimental Results

Construction of the LED devices requires spin coating of polymers either on the surface of ITO-coated glass or on the surface of electrically conducting PEDOT clad on the ITO electrode. We became interested in the surface composition of the polymers after being coated on the ITO anode. We determined the surface composition by XPS and found that the concentration of the carbazole structures, due to their polar nature, are much less on the surface than in bulk. Since air is hydrophobic, it is expected that film surface is richer in hydrophobic moieties than in polar structures. In other words, the carbazole groups tend to orient themselves in such a way that they are more in contact to the ITO surface. Such an orientation of pendant groups will facilitate hole injection in CzEh-PPV. This may be one of the reasons for the significantly lower turn-on electric field for CzEh-PPV than for PPV. In short, surface composition, not the bulk composition, must be playing a very important role in interface formation and carriers' transfer between the electrode and the polymer.

We also observed that surface composition depends strongly on the polarity of solvent used in spin-coating. In addition, surface smoothness or morphology, strongly dependent on the nature of solvent is critical in achieving high device performance, which emphasizes the importance of better contact between the emitting polymer layer and electrodes.

Experimental

Device fabrication and characterization: The patterned ITO-coated glass slides were cleaned by sequential ultrasonication in acetone, 2-propanol and distilled water for 13 minutes, respectively, and finally cleaned by ultraviolet - ozone for 13 minutes. The conducting polymer solution of poly(3,4-ethylenedioxy-2,5-thiopene) doped with polystyrene sulphonate (PEDOT : PSS) (Bayer) was spin coated with 3300 rpm for 1min and dried at 150 °C for 30 minutes. The electrical conductivity of this film measured by the four line probe method was 10 Scm^{-1}. The solution (1wt %) of polymer in purified 1,1,2,2-tetrachloroethane was spin coated at 1000 rpm for 1 min. And the film was subjected to thermal treatment at 150 °C for 1h under vacuum. The Ca cathode 2000 Å thick was vacuum deposited from the tungsten boat at deposition rates of 2Å/s under the pressure of 3.0×10^{-7} torr. An Al capping layer was then evaporated to protect the Ca cathode at a deposition ratio of 4 Å/s under the same pressure. The active area of the EL devices was 4 mm^2. Photoluminescence (PL) and

Electroluminescence (EL) spectra were recorded on a PC1 photon counting spectrofluorometer (ISS Inc., USA). Current-voltage (I-V) characteristics and the intensities of EL emission were simultaneously measured with a Keithley 238 SMU electrometer and a BM7 luminance meter (Topcon Technologies, Inc., USA). Device fabrication and all the measurements were performed in a dry argon filled glove box without exposing to air.

Time-of-flight measurement: Sandwich-type structures of ITO/ polymer (3 um)/ Al (30 nm) were fabricated for the measurement. For carrier generation, an Nd-YAG laser of emitting wavelength of 355 nm and pulse with (FWHM) of 7 nm was used as a light source, and the polymer films were directly exposed to irradiation of the laser. The laser delay time was 150 ns, and an electric field of 20 kV/cm was applied for duration between 5 and 10 ms.

XPS: X-ray photoelectron spectroscopy (UPS) data were acquired at room temperature with a VG ESCALab 220i spectrometer (UK) with a Mg Kα line (1253.6 eV). The base pressure of the analysis chamber was lower than 1 x 10^{-11} Torr and the combined instrumental resolution was about 1.0 eV. Electron energy analyzer has a hemispherical type.

UPS: Ultraviolet photoelectron spectroscopy (UPS) data were acquired at room temperature with VG ESCALab 220i spectrometer (UK) with a VG UV lamp. UPS analysis was performed using He I (21.2 eV) photons. In the case of UPS, the combined instrumental resolution was about 0.1 eV.

Near-Edge X-Ray Absorption Fine Structure (NEXAFS): NEXAFS experiment was done on the 2B1 spherical grating monochromator beamline at the Pohang Synchrotron Lab. The base pressure of the experimental chamber was 1 x 10^{-10} Torr. For the detection of the output signal as a form of electron or photoelectron, photocurrent was measured, i.e., ‘total electron yield’ method was used.

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