Influence of carrier-injection efficiency on modulation rate of organic light source

Takeshi Fukuda

Optics and Electronics Laboratory, Fujikura Ltd.
Mutsuzaki 1440, Sakura, Chiba 285-8550, Japan

Tomoko Okada, Bin Wei, Musubu Ichikawa and Yoshio Taniguchi

Department of Functional Polymer Science, Shinshu University,
Tokida 3-15-1, Ueda, Nagano 386-8567, Japan

We have investigated a relationship between energy levels of an emissive layer and modulation rate of OLEDs based on distyrylbenzene derivative, 1,4-bis[2-[4-[N,N-di(p-tolyl)amino]phenyl]vinyl]benzene (DSB). By utilizing DSB as an emitting material, high modulation rate can be realized due to its short fluorescence lifetime of 0.2 ns. Furthermore, we also found that an energy gap between an emissive layer and an adjacent organic layer is important parameter to improve modulation rate. DSB doped 4,4-bis(2,2-ditolylvinyl)biphenyl is the best combination of all the organic materials used in this study, and the fastest cutoff frequency of 10 MHz has been achieved for the OLED in spite of the large emitting area of 1 mm². © 2007 Optical Society of America

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In recent years, several breakthroughs have led to significant enhancements of performances in organic light-emitting diodes (OLEDs), such as improvement of charge-carrier balance, low-work function electrode materials, high carrier mobility of electron/hole transport materials, high efficiency fluorescence and phosphorescence emitting materials. Therefore, the internal quantum efficiency of the emitting material has been optimized gradually close to a theoretical limit.

Some research groups have reported a novel application of OLEDs as light sources for optical communications. Several factors to affect modulation rate of OLEDs has been investigated, such as a fluorescence lifetime (FL) of light emitting-materials, carrier mobility of electron/hole transport materials, and particularly capacitance determined by a device area and thicknesses of organic layers. Modulation rate has been estimated as a cutoff frequency of electroluminescence (EL) intensity and the cutoff frequency up to 25 MHz has been achieved for the OLED with a small area of 300 µm circle.

On the other hand, advantages of organic light sources compared to semiconductor devices are large-emitting area, flexibility and low-fabrication cost. Especially, the large-emitting area is necessary to realize easy alignment between organic light sources and organic photo-diodes, which is difficult to achieve by utilizing inorganic devices. However, the large emitting area causes a decrease in modulation rate owing to its large capacitance.

The purpose of this study is an investigation of a relationship between carrier-injection efficiency into a light-emitting layer (EML) and modulation rate to realize the high speed OLED with a large emitting area. We have demonstrated current
density-voltage and transient optical characteristics of three OLEDs with different organic light-emitting materials. We used 1,4-bis[2-[4-[N,N-di(p-tolyl)amino]phenyl]vinyl]benzene (DSB) doped in 4,4-bis(2,2-ditolylnyl)biphenyl (DPVBi), 4,4’-(bis(9-ethyl-3-carbazovinylene)-1,1’-biphenyl (BCzVBi), and 4, 4’-bis(9-dicarbazolyl)-2’, 2’-biphenyl (CBP) as EMLs. By utilizing DSB as a dopant, fast response OLED is considered to be achieved owing to its short FL of 0.2 ns.

OLEDs were fabricated on glass substrates covered with a patterned indium tin oxide (ITO) anode. Prepared glass substrates were cleaned in deionized water, detergent and isopropyl alcohol sequentially under ultrasonic waves, and treated with oxygen plasma. Then, organic layers and a metal cathode were evaporated successively by using a conventional thermal evaporation at a base pressure below $5.0 \times 10^{-6}$ Torr.

Each organic layer consisted of 4,4’-bis[N-(1-napthyl)-N-phenyl-amino]-biphenyl (α-NPD) as a hole transport layer (HTL), DSB doped BCzVBi, DPVBi, and CBP as EMLs, bathocuproine (BCP) as a hole-blocking layer, Alq$_3$ as an electron transport layer (ETL), LiF as an electron injection layer (EIL), and MgAg (9:1 mass ratio) as a metal cathode. Device structures are $\alpha$-NPD (40nm)/0.5 wt.% DSB doped film (20 nm)/BCP (10 nm)/Alq$_3$ (20 nm)/LiF (0.4 nm)/MgAg (150 nm)/Ag (20nm). Here, we used DSB doped BCzVBi, DPVBi, and CBP as EMLs for devices A, B, and C, respectively. Figure 1 shows molecular structures of organic materials used as EMLs. Evaporation rates were maintained at 1.0 Å/s for the HTL and the ETL, 5.0 Å/s for the EML and the metal cathode, 0.1 Å/s for the EIL, as determined by a quartz crystal monitor. Active areas of all the devices were 1 mm$^2$.

To evaluate modulation rate, sine wave and bias voltages were applied to an
OLED using a programmable FM/AM standard signal generator (SG-7200, KENWOOD) and a DC power supply (IPS-3610D, ISO-TECH), respectively. EL intensity was observed using an avalanche photo diode (S5343, Hamamatsu Photonics). Then, frequency dependence of EL intensity was measured by changing modulation frequency of the sine wave voltage. We estimated a cutoff frequency, which was calculated from a frequency when the relative EL intensity reaches -3 dB (50%) compared to the EL intensity at 1 kHz.

The highest occupied molecular orbital (HOMO) levels of each organic layer were measured with a photoelectron emission spectrometer (AC-3, Riken Keiki). Then, the lowest unoccupied molecular orbital (LUMO) level was estimated from the HOMO level and a band-gap, which was determined by a visible absorption spectrum of the organic thin film. In addition, FLs of single-layered organic films were measured by a femtosecond pulse laser. The center wavelength of the femtosecond pulse laser was 390 nm. All the organic films radiated photoluminescences (PLs) when the femtosecond pulse laser was irradiated. The radiated PL was then captured with a streak camera and mono-exponential fitting was employed to derive the FL. We also measured current density-voltage characteristics and EL spectra with a electrometer (HP4140B, Hewlett Packard) and a luminance colorimeter (BM-7, Topcon).

Figure 2 shows relative EL intensity as a function of modulation frequency for three OLEDs with different emitting materials. Amplitude of sine wave voltage was 7 V and a bias voltage was 5 V. As shown in Fig. 2, relative EL intensity of device B at high modulation frequency is higher than those of devices A and C. This result indicates that the device B has faster modulation rate compared to devices A and
C. The maximum cutoff frequency of the device B has been achieved about 10 MHz, while those of devices A and C are about 7 MHz.

The difference of modulation rate can be explained by a barrier height between two organic layers, which is estimated from differences of energy levels between the EML and adjacent organic layers. Figure 3 shows energy diagrams of fabricated OLEDs, which consists of DSB doped (a) BCzVBi, (b) DPVBi, and (c) CBP as EMLs. The barrier height at HTL/EML interface is 0.6 eV, 0.4 eV, and 0.5 eV for devices A, B, and C. So, the device B is considered to achieve high efficiency of the hole injection into the EML. As a result, the device B has higher modulation rate than other devices.

On the other hand, the barrier height at ETL/EML interface of the device C is 0.5 eV, while there is no barrier for devices B and C. Accordingly, electron injection efficiency of the device C is lower than those of devices A and B. As a result, modulation rate of the device C is slow compared to other devices as shown in Fig. 2.

FLs of 0.5 wt.% DSB doped BCzVBi, DPVBi, and CBP films are 0.3, 0.9, and 1.2 ns, respectively. Such short FLs were assumed to give little effect on modulation rate of devices. Therefore, we can surely conclude that the measured frequency dependence of EL intensity was mainly contributed to the influence of the carrier injection efficiency determined by the energy barrier between the EML and adjacent organic materials.

Furthermore, current density-voltage characteristics of all the devices are shown in Fig. 4 (a). The current density is 536 mA/cm² for the device B, while current efficiencies of devices A and C are 74 and 6 mA/cm² at 6 V, respectively. This
result indicates that lower energy gap at HTL/EML and ETL/EML interfaces will cause a higher injection efficiency of hole/electron, and we have demonstrated that modulation rate of the device B is faster than other devices because of high carrier injection efficiency into the EML. An important finding here is that modulation rate of an OLED is affected by carrier injection efficiency into the EML, which has been estimated from current density-voltage characteristics.

EL spectra of all the devices are also found to be different as shown in Fig. 4 (b). The peak EL emission wavelength of devices B and C is 480 nm, and there is a shoulder at the wavelength of 510 nm for device B, and 440 nm for device C. Furthermore, PL spectrum of DSB film are also shown in upper of Fig. 4 (b). The shoulder of device B is contributed by EL emission from DSB molecules, which is consistent with the peak wavelength of PL of DSB. And the shoulder of device C is emission from CBP molecules.

In addition, the device A has a broad EL emission of longer wavelength at 490 nm. The most likely reason is that one port of injected holes leaked from the EML through the HBL to Alq₃ layer due to a low HOMO level difference (0.3 eV) of BCzVBi and BCP. As a result, EL spectra of the device A combined one port of emission from Alq₃ molecules.

In conclusion, we have demonstrated fast response OLEDs with distyrylbenzene derivative for applications of organic light sources for optical communications. The modulation and electro-optical characteristics have been evaluated. By utilizing DSB doped DPVBi with a low HOMO level as an EML, we found that modulation rate can improve compared to other organic materials used in this study. This improvement
is attributed to lower energy barrier at interfaces of the EML and adjacent organic layers.

Capacitance of emitting area limits modulation rate with an emitting area of 1 mm$^2$, so a cutoff frequency of an organic light source is only about 10 MHz. Nonetheless, the organic light source will allow us to expand a novel optical communication field due to a large emitting area.
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