Blue-Violet Organic Electroluminescent Devices Based on Exciton-Confined Structure


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Abstract Three types of blue-violet light-emitting devices based on an exciton-confined structure have been prepared, in which different materials were used as emitting layers and hole-transporting layers. They had structures of ITO/CuPc/NPB/CBP/TPBi/Alq3/LiF/Al (Dsc), ITO/CuPc/J03/CBP/TPBi/Alq3/LiF/Al (Dsc) and ITO/CuPc/J03/FNPD/TPBi/Alq3/LiF/Al (Dsc). Here copper phthalocyanine (CuPc) acted as hole-injecting layer (HIL), N,N-bis-(1-naphthyl)-N,N-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and J03 as hole-transporting layers (HTLs), 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) and FNPD as emitting layers (EMLs), N-arylbenzimidazoles (TPBi) as hole-blocking layer (HBL), and tris(8-quinolinolato)aluminum complex (Alq3) as electron-transporting layer (ETL). TPBi applied here is a good confinement to both charges and excitons, which make the devices emit blue-violet light originating from the emitter, CBP and FNPD. Their characteristics have also been investigated. The result shows that the device Dsc based on NPB/CBP has the best performance among the three devices. The excellence of Dsc is attributed to the better hole-transporting ability of NPB as compared with J03, and the better emitting ability of CBP as compared with FNPD, although the best matching of energy levels is found in the hole-transporting layer and emitting layer of the device Dsc.

Key words exciton-confined structure, blue-violet emitting, hole-transporting ability, emitting ability.

1 Introduction

It is of great interest to develop organic EL devices that emit visible light of short wavelengths, i.e., blue-violet to violet lights, since such devices can be used to generate light of all colors either by direct excitation of fluorescent dyes or complexes or by radiationless energy transfer to emissive dopants. They can also serve as a potential light source for high-density information storage devices. However, it is difficult to obtain such devices because of the wide energy gap of blue-violet fluorescent materials. If a conventional multi-layer structure (usually ITO/HTL/EML/ETL/metal cathode) is used, undesired color element originating from ETL will occur because recombination of excitons generally occurs in ETL for its relatively small energy gap. If excitons are confined to blue-violet emitting layer, blue-violet emission can be obtained. Exciton-confined structure in which a hole blocker needs to be introduced is a good way to accomplish confinement of excitons.

Most of the previously reported blue-violet devices use polymers as the emitters, and their performance is relatively poor. They present either low external quantum yields or high turn-on voltages. The organic EL devices using polysilanes fabricated by Hoshino's group emit light peaking at 405 nm, but the turn-on voltage is as high as 8 V and the external quantum yield is only 0.2%. The devices using poly (N-vinylcarbazole) reported by Kido and N,N'-diethyl-3,3'-bipcarbazole presented by Romero as emitters emit light with peaks at 410 nm and 415 nm, but the luminance is low, i.e., 700 cd/m² at 14 V and 20 cd/m² at 250 A/m², respectively. Huang prepared a device based on a substituted poly (p-phenylene) that emits light peaking at 424 nm with the turn-on voltage of...
Up to now, there have still been few reports of organic EL devices that efficiently emit blue-violet to violet lights. Okumoto et al. developed devices emitting blue-violet lights with good performance, in which small molecules, TPD and p-BPD, act as emitters, F-TBB as hole-blocking layer (HBL), m-MTDATA as hole transporter, and Alq as electron transporter. In this paper, we report three multi-layer blue-violet-emitting organic EL devices by using small molecules, CBP and FNPD, as emitters based on an exciton-confining structure with a HBL, TPBi. Satisfactory performance can be found in one of the three devices, and mechanisms have also been investigated.

2 Experiments

Structures of the three devices fabricated in this paper are as follows: ITO/CuPc/NPB/CBP/TPBi/Alq/LiF/Al(Dc), ITO/CuPc/J0/J03/CBP/TPBi/Alq/LiF/Al(Dc), and ITO/CuPc/J03/FNPD/TPBi/Alq/LiF/Al(Dc). Here copper phthalocyanine (CuPc) acts as HIL, N,N-bis(1-naphthyl)-N,N-diphenyl-1,1'-biphenyl (NPB) and J03 serve as HTLs, 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) and FNPD are blue-violet EMLs, N, arylibenzimidazoles (TPBi) is HBL, and tris(8-quinolinolato)aluminium complex (Alq) is ETL. J03 and FNPD are two new materials synthesized at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, and CBP is fabricated in the authors' laboratory. Fig. 1 shows the structure of the fabricated organic EL devices and the molecular structures of the organic materials used.

The ITO-coated glass substrates were prepared through sonication in organic solution and oxygen plasma cleaning. All the films were evaporated under a chamber pressure of 1.33 x 10^-4 Pa, and the thickness of each layer was monitored by a quartz-crystal monitor. Electrochemical experiment was used to determine HOMOs of materials by using a CHI600A electrochemical analyzer. Photoluminescent (PL) spectra were taken with a Hitachi 850 fluorescence spectrophotometer. The EL spectra and the Commission Internationale de l'Eclairage (CIE) coordinates were measured by a Pro-650 SpectroScan. The current versus voltage and luminance versus voltage characteristics were measured using a Keithley 2400 source meter.

3 Results and Discussion

Figure 2 shows the PL spectra of J03, FNPD, and CBP. From the excitation spectra, the absorption band edges can be obtained and thus the energy gap. Table 1 lists the wavelength/energy of absorption band edges, HOMO and LUMO values of the three materials. LUMO levels are obtained by combining the HOMO values achieved through electrochemical experiments with energy gaps deduced from the excitation spectra. With the above information, an energy level diagram is easily obtained as in Fig. 3. It is obvious that J03 is a good candidate for hole transporter and electron blocker from the standpoint of energy level because of its high positions of HOMO and LUMO. CBP and FNPD have relatively low LUMO positions that are favorable for electrons injected from the cathode to transport herein. However, difficulty exists for holes to be injected if they are directly connected with the anode. Therefore it is necessary to insert a hole-transporting layer between HIL and EML in order to increase the number of holes. Suitable combination of hole transport material and emission material reduces the energy barrier for the injection of charge carriers from the anodes, leading to better balance in the number of injected holes and electrons. Small difference of HOMOs between the two emitters and Alq requires introduction of HBL to the devices to avoid undesired