Efficient Electron Injection Characteristics of Tetra-2-pyridinylpyrazine (TPP) in Organic Light Emitting Diodes

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(Received December 24, 2002; CL-021084)

We showed that tetra-2-pyridinylpyrazine (TPP) and TPP: cesium (1:1 molar ratio) composite layers had excellent electron injection and transport characteristics in organic light emitting diodes. High luminescence efficiency with low driving voltage was observed in various cathode configurations, suggesting that the TPP layer can efficiently accept electrons from metal and metal oxide cathode layers, and transport and inject electrons into an adjacent organic layer.

Further development of electron transport materials is important for various applications of organic light emitting diodes (OLEDs). Particularly, efficient electron injection from a transparent indium-tin-oxide (ITO) cathode into an electron transport layer[1] could result in transparent OLEDs, which will lead to many unique OLED applications, such as an OLED on Si substrate, flexible OLED displays,[2] and organic lasers.[3] However, very few materials, mainly bathocuproine (BCP),[4] bathophenanthroline (BPhen)[5] and phthalocyanine derivatives, have been utilized as electron injection materials. In this study, we demonstrated that a layer of a pyrazine derivative, tetra-2-pyridinylpyrazine (TPP, Aldrich), had excellent characteristics as an electron injection material.

We prepared various configurations of an ITO/4,4′-N,N′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl(α-NPD)/Tris(8-hydroxyquinoline)aluminum(Alq_3)/electron injection layer using TPP/MgAg, Al, and ITO electrodes. In some devices, the TPP layer was doped with cesium (Cs) by co-deposition. The thickness of each layer is shown in Figures 2, 3, and 4. TPP was obtained commercially and purified by train sublimation before device fabrication. The HOMO (highest occupied molecular orbital) level and absorption and photoluminescence spectra were measured with an AC-1 (Riken Keiki Co.) and conventional spectrometers, respectively.

Figure 1 shows absorption (ABS) and photoluminescence (PL) spectra of a TPP-deposited film. Because of the short absorption edge ($\lambda_{ABS} = 365$ nm) and the PL peak ($\lambda_{ABS} = 380$ nm), we can expect that singlet excitons of Alq_3 can be effectively confined inside the emitter layer. In addition, the deep HOMO level of the TPP film, estimated to be larger than 6.8 eV, is favorable for electron transport and injection.

Figure 2 shows OLED characteristics with a MgAg cathode having different TPP thicknesses, (a) 10, (b) 30 and (c) 50 nm. In particular, low onset voltage (2.7 V) of carrier injection was observed in device (a). A high current density of 100 mA/cm^2 was easily realized at less than 10 V and the external quantum efficiency (η_{ext}) reached 1.0%, which is similar to that of the conventional control device.[6] On the contrary, significant increases of driving voltage with low η_{ext} were observed in devices (b) and (c). These results demonstrate that a thin TPP layer well transports and injects electrons, whereas thicker TPP

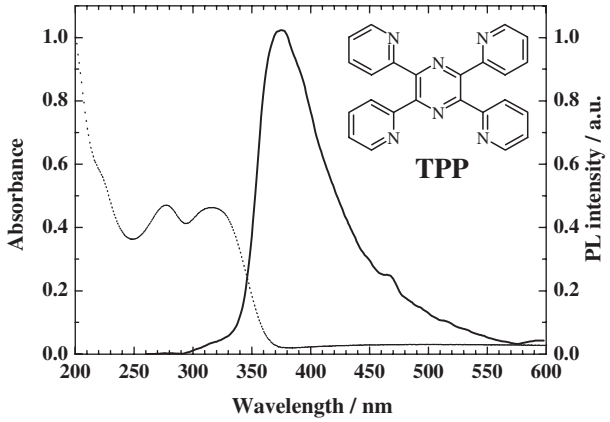

Figure 1. Absorption (- - -) and photoluminescent (—) spectra of a TPP deposited film (50 nm) and a chemical structure of TPP.

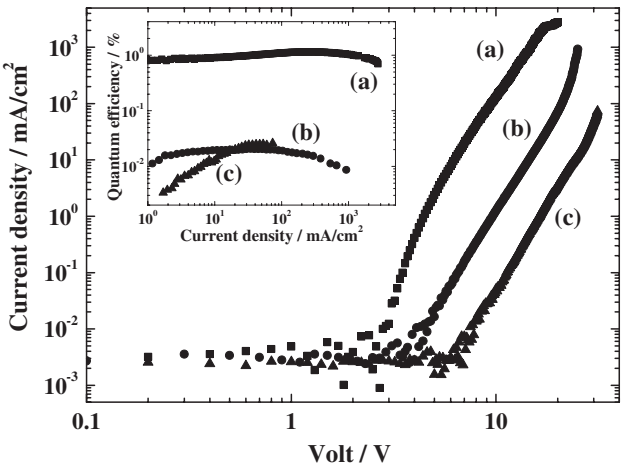

Figure 2. Current density (J)–voltage (V) and quantum efficiency (η_{ext})–J characteristics; (a) ITO/α-NPD(50 nm)/Alq_3(50 nm)/TPP(10 nm)/MgAg(100 nm)/Ag(10 nm), (b) ITO/α-NPD (50 nm) / Alq_3 (30 nm) / TPP (30 nm) / MgAg (100 nm) / Ag (10 nm) and (c) ITO / α-NPD (50 nm) / Alq_3 (50 nm) / TPP (50 nm)/MgAg(100 nm)/Ag(10 nm).

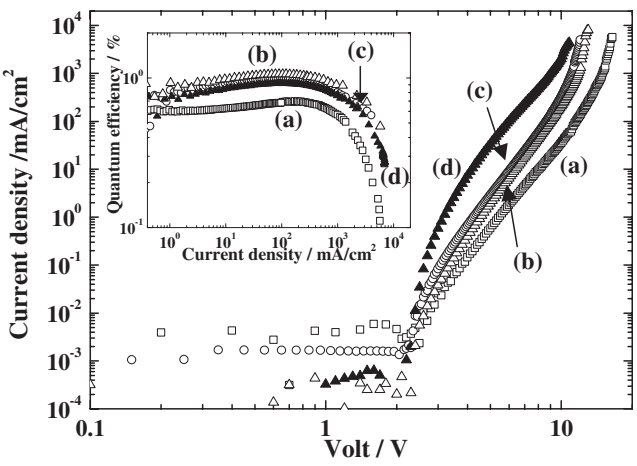

Figure 3. Current density (J)–voltage (V) and quantum efficiency (η_{ext})–J characteristics; (a) ITO/α-NPD(50 nm)/Alq_3(50 nm)/Al(100 nm), (b) ITO/α-NPD(50 nm)/Alq_3(50 nm)/LiF(0.5 nm)/Al(100 nm), (c) ITO/α-NPD(50 nm)/Alq_3(30 nm)/Alq_3:Cs(1:1, 20 nm)/Al(100 nm) and (d) ITO/α-NPD(50 nm)/Alq_3(30 nm)/TPP:Cs(1:1, 20 nm)/Al(100 nm).

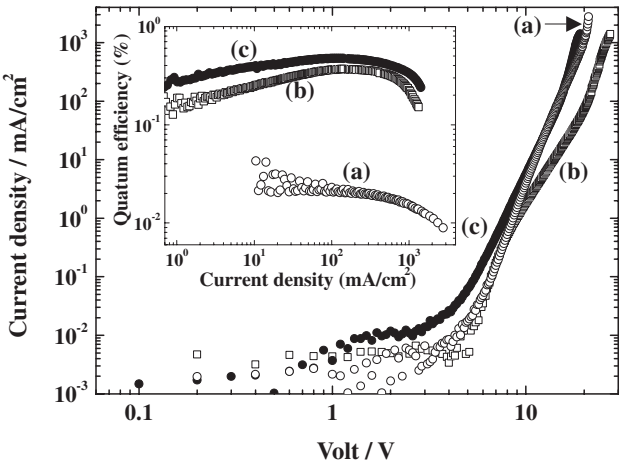

Figure 4. Current density (J)–voltage (V) and quantum efficiency (η_{ext})–J characteristics; (a) ITO/α-NPD(50 nm)/Alq_3(50 nm)/ITO(100 nm), (b) ITO/α-NPD(50 nm)/Alq_3(50 nm)/TPP(10 nm)/ITO(100 nm) and (c) ITO/α-NPD(50 nm)/Alq_3(30 nm)/TPP:Cs(1:1, 20 nm)/ITO(100 nm).

layers lead to higher driving voltages, which may be due to the morphological change of the TPP layer.

Next, we prepared a Cs-doped TPP film as the electron injection layer. Figure 3 compares OLED characteristics of four devices, ITO/α-NPD/Alq_3/[(a) Al, (b) LiF/Al, (c) Alq_3:Cs (1:1)/Al and (d) TPP:Cs (1:1)/Al]. A significant decrease of the driving voltage was observed in the TPP:Cs device (d). High current density of 100 mA/cm^2 was obtained only at 6.0 V and η_{ext} reached ca. 1%. To understand the effect of Cs doping, we measured the absorption spectra and HOMO level of the TPP:Cs film. Although there was no difference in the absorption spectra between TPP and TPP:Cs films, the HOMO level of the TPP:Cs film emerged at 5.3 eV, suggesting that the Cs doping produces a novel energy level that may participate in the electron conduction.

Finally, we employed a transparent ITO electrode as a cathode; ITO/α-NPD/Alq_3/[(a) ITO, (b) TPP/ITO and (c) TPP:Cs (1:1)/ITO]. The three devices demonstrated onset of carrier injection at around 4.0 V. In device (c), high current density J = 1 A/cm^2 was easily obtained at 18 V. In addition, η_{ext} reached 0.5%, which is comparable to that of BCP-based OLED.[4] Thus, we conclude that the TPP layers have the capability to resist plasma damage during ITO formation, probably as a result of the chelate properties of the TPP chemical structure. We expect that further development of metal coordinate materials similar to TPP, BPhen and BCP will provide novel electron injection materials, which in turn will lead to transparent OLEDs and new applications.

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