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Letter

Phosphorescent organic light emitting diodes with a cross-linkable hole transporting material

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ABSTRACT

A cross-linkable hole transporting material PLEXCORE® HTL was incorporated in phosphorescent organic light emitting diodes. This hole transporting material is based on an arylamine derivate. The device performance in terms of efficiency and lifetime was compared to the same devices with a thermally evaporated 4,4′-bis[N-(1-naphthyl)-N-phenylamino] biphenyl (NPB)-based hole transporting layer. The resulting devices with the cross-linkable HTL gave higher efficiency, smaller roll-off and longer lifetime compared with devices with the NPB-based devices. This new hole transporting material paves the road toward solution processed multilayer light emitting devices.

After two decades of research, a lot of scientific progress has been made in organic light emitting diodes (OLEDs) [1,2]. With the recent development made in efficiency and lifetime, OLEDs have been commercialized for display [3,4] and solid state lighting [5] applications. To further advance the technology, solution processing of OLEDs with promises of low cost and large area manufacturing is still a grand challenge [6]. However in solution processed OLEDs, typically devices have lower efficiencies and shorter lifetimes compared with evaporated ones [7,8]. In order to understand the factors limiting the device performance, a systematic study of the functionalities of each solution processed layer is deemed necessary. In OLEDs, the hole transporting layer (HTL) plays an important role in determining the device efficiency and lifetime. More importantly in solution processed OLEDs, HTL is the first layer deposited and it should have the chemical and mechanical robustness to withstand further processing of subsequent layers in the device stack. Therefore, it is important to establish a performance baseline for the solution processed HTL and compare that with the evaporated HTL. Arylamine based HTLs are widely used in multilayer devices because of its chemical and thermal stability as well as its ability to transport holes [9,10]. In addition to hole mobility, their proper Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) energy levels should enable good hole injection and effective electron-blocking. In this letter, we report on the fabrication of OLEDs with a solution processed cross-linkable HTL and compare their performance with similar devices using an evaporated HTL. Specifically, we used the PLEXCORE® HTL [11] as the solution processed HTL and 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (*NPB*) as the evaporated HTL in this study. Our results show that both devices show comparable device efficiency and lifetime indicating that the PLEXCORE® HTL is promising for solution processed OLEDs.

The PLEXCORE® HTL from Plextronics Inc. [12] is a new vinyl based multi-component cross-linkable hole transporting material, which is designed for fully solution processed OLEDs by using a functionalized core structure of N^2, N^7-di(naphthalen-1-yl)-N^2,N^7-diphenyl-9H-fluorene-2,7-diam ine. As shown in Fig. 1(a), the PLEXCORE® HTL is a hole

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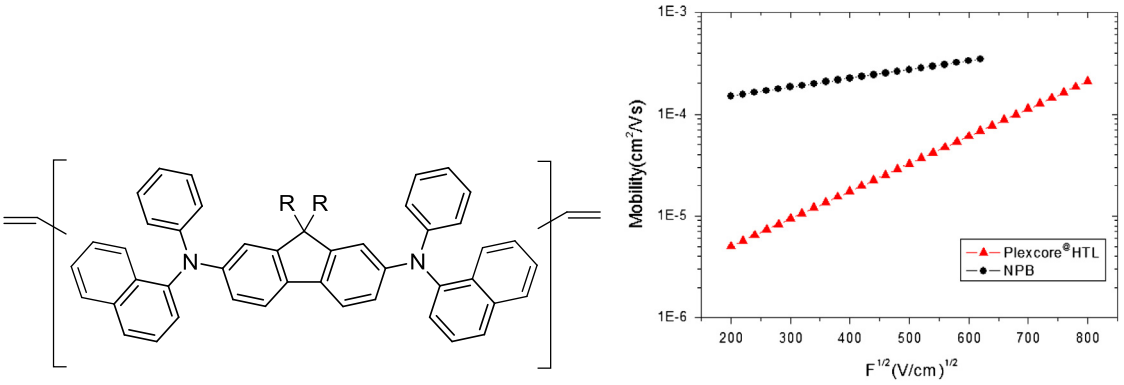

Fig. 1. (a) Molecule structure of PLEXCORE® HTL and (b) the field dependent hole mobility of PLEXCORE® HTL and NPB.

transporting material that can be cross-linked upon heating. The HTL ink is formulated in toluene and its HOMO energy is 5.4 eV which is similar to NPB. It should be noted that there is no material loss when the PLEXCORE® HTL is exposed to solvents such as toluene or o-xylene during deposition of the emitting layer (EML), indicating its chemical robustness for solution processing. It is known that the cross-linkable functional groups might affect the conjugated π bond of arylamines, changing the hole transporting properties [13]. The simplest way to evaluate the transporting ability of this new cross-linkable hole transporting material is to directly compare and evaluate its performance with another commonly used thermally evaporated arylamine. By incorporating this cross-linkable HTL into a phosphorescent OELD, we carried out experiments to study its transporting properties, device performance and lifetime, and compared the results with devices with thermally evaporated NPB as the HTL.

The hole mobility of an HTL can be extracted from fitting of Space Charge Limited Current (SCLC). The current density J_{SCLC} of hole only devices follows the Mott–Gurney Law [14]:

$$J_{SCLC} = \frac{9}{8}\varepsilon\varepsilon_0\mu_0 \exp\left(0.89\beta\sqrt{\frac{V}{d}}\right)\frac{V^2}{d^3}, \quad (1)$$

where the ε_0 is the vacuum permittivity and ε is the relative permittivity. μ_0 is the mobility at zero electrical field, V is the applied voltage and d is the thickness of measured materials. β is the Poole–Frenkel factor. By fitting the current–voltage characteristics with Eq. (1), the values of μ_0 and β were extracted. The Poole–Frenkel field-dependent mobility [15] can be determined as follows:

$$\mu = \mu_0 \exp\left(\beta\sqrt{\frac{V}{d}}\right). \quad (2)$$

Hole only devices were used to extract the mobility. To fabricate the hole only device a 30-nm-thick AQ1200 (available from Sigma Aldrich Inc.) hole injection layer was first spin-coated on the UV Ozone treated ITO glass substrate. Then a 150-nm-thick PLEXCORE® HTL was spin-coated and subsequently annealed at 170 °C in a nitrogen glove box for 40 min. Finally, a 4-nm-thick Molybdenum Oxide (MoOx) and a 100-nm-thick Aluminum cathode layer were thermally evaporated. For comparison, the NPB hole only device has the same structure but with a 150-nm-thick NPB (Lumtech, Corp) layer evaporated. AQ1200 is a water based hole injecting polymer, which has a work function of 5.4 eV [16]. With AQ1200, ohmic contact was formed at the interface of HTL. MoOx/Al was used as a counter electrode to prevent injection of electrons. From the SCLC measurements, the zero field mobility of NPB was determined to be 1.011×10^{-4} cm^2/Vs, which is consistent with values from literature [17,18]. The zero field mobility of PLEXCORE® HTL was 1.459×10^{-6} cm^2/Vs which was two orders of magnitude lower than that of NPB. The lower mobility of PLEXCORE® HTL came from the non-conjugated side chain which affected the conjugated π bond of bone molecule and the reduced packing of molecule in the solution processing. Fig. 1(b) shows the calculated field dependent mobility of PLEXCORE® HTL and NPB. There is a stronger field dependence of mobility observed in PLEXCORE® HTL compared with NPB. With the electrical field increases, the difference between PLEXCORE® HTL and NPB decreases.

The surface morphologies of the HTLs were investigated by atomic force microscopy (AFM) (Veeco Co.). Solution processed PLEXCORE® HTL and vacuum deposited NPB were deposited on top of AQ1200, which had an average surface roughness (root mean square) of <1 nm. Fig. 2 shows the typical AFM images of PLEXCORE® HTL and NPB films. Because the annealing temperature (170 °C) was lower than the glass transition temperature (200 °C) of PLEXCORE® HTL, no crystallization was observed. But clear materials aggregation due to the annealing was detected. On the other hand, the evaporated NPB film was amorphous and showed a smooth surface. The average RMS roughness of vacuum deposited and solution processed films were 2.3 and 2.8 nm, respectively, which indicated the solution processed PLEXCORE® HTL film had a quality as good as evaporated NPB.

To study the effect of HTLs on OLEDs, phosphorescent OLEDs were fabricated with PLEXCORE® HTL and NPB. Fig. 3(a) shows the device structure and the corresponding energy diagram. Except for HIL AQ1200 and PLEXCORE® HTL which were deposited by solution processing, all other layers were thermally evaporated. Taking the advantage of

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