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Multilayer white polymer light-emitting diodes with deoxyribonucleic acid-cetyltrimetylammonium complex as a hole-transporting/electron-blocking layer

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Using a thin film of deoxyribonucleic acid-cetyltrimetylammonium (DNA-CTMA) complex as a hole-transporting/electron-blocking layer, we have developed a sequential solution-processing approach for constructing multilayer (up to five layers) white polymer light-emitting diodes, incorporating the poly(9,9-dioctylfluorene-2,7-diyl)/poly[2-methoxy-5(2′-ethyl-hexyloxy)-1, 4-phenylene vinylene] emissive layer. These devices were demonstrated to show a low turn-on voltage (~5 V), high efficiency (10.0 cd/A), and high brightness (10500 cd/m^2) with an improved white-color stability. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2948864]

White polymer light-emitting diodes[1–13] (WPLEDs) have been previously prepared from polymer blends,[1–4,8–13] such as a blend of poly(9,9-dioctylfluorene-2,7-diyl) (PFO) and poly[2-methoxy-5(2′-ethyl-hexyloxy)-1 4-phenylene vinylene] (MEH-PPV), in which the wide-band-gap PFO acts as a host while the narrow-band-gap MEH-PPV as a dopant. Multilayer configurations, including hole-transporting/electron-blocking layer (HTL/EBL), emissive layer (EML), and electron-transporting/hole-blocking layer (ETL/HBL),[13] are highly desirable to achieve efficient and balanced carrier injection in such WPLEDs involving the wide-band-gap PFO.[14] However, it is difficult to incorporate all the above-mentioned three layers or more into one device by solution processing only due to the solubility mismatch. In recent years, water/alcohol-soluble (solution-processable) inorganic materials[11,12] and conjugated polymers[15–18] have been developed as ETL/HBL to enhance electron injection/transport in multilayer light-emitting devices. For instance, an alcohol-soluble inorganic cesium carbonate (Cs_2CO_3) has been used as the electron injection/hole-blocking layer[11] (EIL/HBL) in a WPLED, achieving the reported highest power efficiency of 16 lm/W.[14–17]

The governing principle for a material to be used as HTL/EBL include: (1) the highest occupied molecular orbital (HOMO) of HTL/EBL must be at an energy level close to, or even within the HOMO of EML and (2) the lowest unoccupied molecular orbital (LUMO) of HTL/EBL must be higher than the LUMO of EML. Although a few of attempts have been made to modify the anode/PFO interface, no organic/polymeric HTL/EBL material was found to be ideal. Sun *et al.*[19] have demonstrated that poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine (poly-TPD) was a promising candidate as HTL in multilayer WPLEDs because its HOMO level (−5.2 eV) is very close to the work function of the indium tin oxide (ITO)/poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) anode. Poly-TPD is also a resister to nonpolar organic solvents (e.g., toluene, xylene) usually used for casting the overlaid

PFO layer. Unfortunately, poly-TPD has no EBL function as its LUMO level (−2.3 eV) is lower than that of PFO (−2.2 eV). Gong *et al.*[13] pioneered in using an alcohol-soluble polymer, PVK-SO_3Li, as HTL/EBL in multilayer PLEDs without interfacial mixing. However, the LUMO (−2.25 eV) and HOMO (−5.75 eV) of PVK-SO_3Li were not ideal for its use in the PFO-based devices.

Further to recent reported work on the use of *vacuum-deposited* deoxyribonucleic acid-cetyltrimetylammonium (DNA-CTMA) complexes for electron blocking in organic light-emitting devices (OLEDs),[20–22] we found that DNA-CTMA *solution cast* under appropriate conditions are promising to be used as HTL/EBL in WPLEDs. The DNA-CTMA complex is exclusively soluble in alcohol, and can be spin cast into optically transparent films to exhibit a HOMO of −5.6 eV and a LUMO of −0.9 eV. Using sequential solution spin coating, we designed, fabricated, and characterized in this study bio-WPLEDs with multilayer (up to five layers) structures, incorporating the DNA-CTMA HTL/EBL.

Four-layer and five-layer WPLEDs with and without the DNA-CTMA HTL/EBL were fabricated. DNA-CTMA was prepared according to the reported procedure.[21] For the fabrication of WPLEDs, we dissolved DNA-CTMA, poly-TPD, PFO doped with 0.2 % (w/w) MEH-PPV, and Cs_2CO_3 in
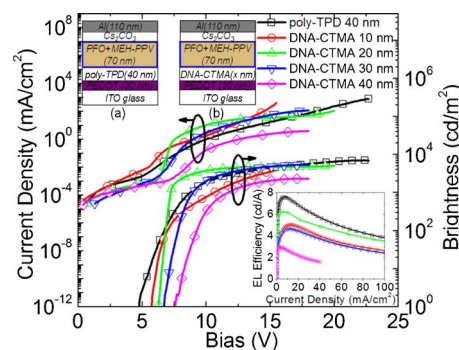

FIG. 1. (Color online) *J-L-V* characteristics of device (a) and device (b) with a 10-, 20-, 30-, 40-nm-thick DNA-CTMA layer. Insets show schematic device configurations for the four-layer WPLEDs (a) and bio-WPLEDs (b), and luminous efficiencies of the devices as a function of the driving current density.

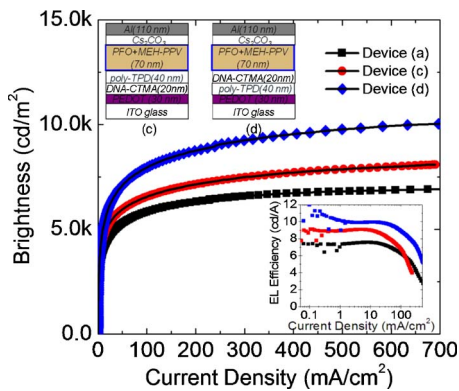a)Author to whom correspondence should be addressed. Electronic mail: ldai@udayton.edu.

FIG. 2. (Color online) *J-L* characteristics of devices (a), (c), and (d). Insets show schematic device configurations for the five-layer bio-WPLEDs, and the luminous efficiency as a function of the current density for devices (a), (c), and (d), respectively.

butanol, chlorobenzene, toluene, and 2-ethoxyethanol, respectively, and their selective solubility enabled us to deposit each of the constituent layers without dissolving the underlying layer by sequential spin coating. Configurations of the four-layer devices are: ITO/PEDOT(30 nm)/poly-TPD(40 nm)/PFO:MEH-PPV(70 nm)/Cs_2CO_3(1–2 nm)/Al [device (a)], and ITO/PEDOT(30 nm)/DNA-CTMA(x nm)/PFO:MEH-PPV(70 nm)/Cs_2CO_3(1–2 nm)/Al, where x =10,20,30,40 nm, respectively [device (b)]. The five-layer devices include: ITO/PEDOT(30 nm)/DNA-CTMA(20 nm)/poly-TPD(40 nm)/PFO:MEH- PPV(70 nm)/Cs_2CO_3(1–2 nm)/Al [device (c)], and ITO/PEDOT(30 nm)/poly- TPD(40 nm)/ DNA-CTMA(20 nm)/ PFO:MEH -PPV (70 nm)/Cs_2CO_3(1–2 nm)/Al [device (d)].

Figure 1 shows the current density-luminance-voltage (*J-L-V*) characteristics for the four-layer WPLED [device (a)] and bio-WPLED [device (b)] with various DNA-CTMA layer thicknesses. The inset shows luminous efficiencies of these devices as a function of the driving current. Device (a) turned on at 4.7 V and exhibited a maximum brightness of 6906 cd/m^2 and a maximum luminous efficiency of 7.6 cd/A at ~10 mA/cm^2. The measured brightness and efficiency for device (a) are much higher those of the corresponding trilayer WPLED with poly-TPD HTL but

without Cs_2CO_3 EIL/HBL,[19] as a chemical reaction occurred between the spin-coated Cs_2CO_3 and thermally evaporated Al to form an Al–O–Cs complex that could significantly reduce the work function of the cathode.[11,12]

The performance of device (b) depends strongly on the DNA-CTMA layer thickness. Among them, the bio-WPLED with 20-nm-thick DNA-CTMA showed the best overall performance. It turned on at ~6.2 V, exhibiting a maximum brightness of 4912 cd/m^2 and a maximum luminous efficiency of 6.3 cd/A. The current density of the bio-WPLED with a 40-nm-thick DNA-CTMA layer was one to two orders of magnitude lower than that of the corresponding device with 20-nm-thick DNA-CTMA. The turn-on voltage increased from 6.2 to 7.6 V, presumably due to an increase in the serial resistance with increasing DNA-CTMA layer thickness. As a result, the maximum brightness and efficiency of device (b) (x=40 nm) reduced to 2291 cd/m^2 and 3.0 cd/A at 10 mA/cm^2, respectively. On the other hand, the bio-WPLED of 10-nm-thick DNA-CTMA exhibited a reduced turn-on voltage (5.7 V), lower maximum brightness (3897 cd/m^2), and luminous efficiency (4.7 cd/A) with respect to device (b) (x=20 nm), attributable to an increased leakage current from the relatively thin DNA-CTMA layer.

Figure 2 shows the *J-L* characteristics for the five-layer bio-WPLEDs with both poly-TPD and DNA-CTMA layers of different sequences [i.e., device (c): DNA-CTMA/poly-TPD, device (d): poly-TPD/DNA-CTMA] as the HTL/EBL. For comparison, the *J-L* characteristics of device (a) was also included in Fig. 2. Both devices (c) and (d) exhibited much improved light outputs than device (a) over a whole range of the driving current. The maximum brightness for devices (c) and (d) reached 8100 and 10500 cd/m^2, respectively. Consequently, devices (c) and (d) also showed higher electromininescenic (EL) efficiencies than that of device (a) (see, inset of Fig. 2).

The enhanced performance of the bio-WPLEDs can be rationalized by the combined effects of hole transporting and electron blocking from DNA-CTMA. The schematic energy level diagrams for materials involved in all of the four devices are given in Fig. 3. As mentioned above, poly-TPD acts only as HTL in device (a). In contrast, DNA-CTMA can act as both HTL and EBL in device (b) since its HOMO is
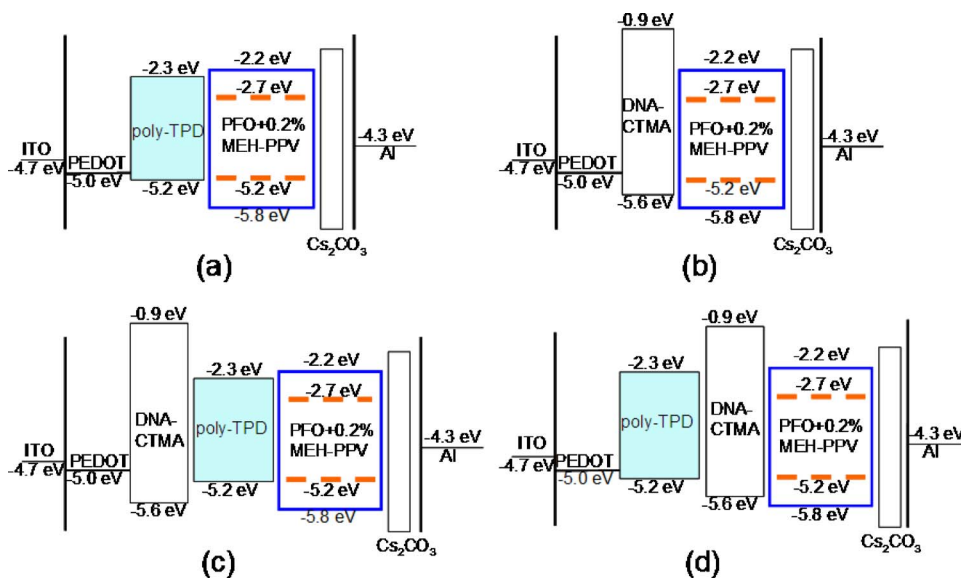

FIG. 3. (Color online) Schematic diagrams of energy levels for all materials involved in the WPLED and bio-WPLEDs.
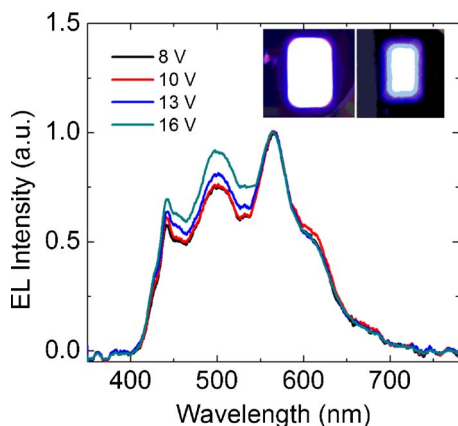
FIG. 4. (Color online) The normalized EL spectra of device (d) operated at different biased voltages. The insets show the photos of device (d) (left) and a device with the configuration of ITO/PEDOT(30 nm)/PFO: MEH-PPV(70 nm)/Cs$_2$CO$_3$(1–2 nm)/Al (right) after continuous operation at ~4000 cd/m^2 for ~14 h in air.

0.2 eV higher than that of PFO and its LUMO is 1.3 eV higher than that of PFO.[21,23] Comparing device (b) with device (a), however, there is a higher energy barrier to overcome for hole injection from anode to DNA-CTMA (0.6 eV) than to poly-TPD (0.2 eV), leading to an increased turn-on voltage for device (b). The lower brightness and EL efficiency for device (b) than those of device (a) (Fig. 1) indicates that the superior hole-transporting mobility of poly-TPD in device (a) over performed the dual hole-transporting and electron-blocking functions of DNA-CTMA.

Comparing with the four-layer devices [i.e., devices (a) and (b)], the five-layer bio-WPLEDs [i.e., Devices (c) and (d)] showed much better performance resulted from both the hole-transporting and electron-blocking capabilities of DNA-CTMA, coupled with the excellent hole-transporting capability of poly-TPD. As can be seen in Fig. 3, device (d) allows an easy hole injection from ITO/PEDOT anode to poly-TPD, followed by an efficient transport through DNA-CTMA into the HOMO of PFO. Meanwhile, electrons at the LUMO level of PFO injected from the cathode were completely blocked by the adjacent DNA-CTMA layer. Consequently, the holes and electrons can undergo radiative recombination most efficiently in the EML in device (d), leading to its superb device performance. In device (c), holes need to overcome the relatively high energy barrier between ITO/PEDOT anode and DNA-CTMA while electrons can still partially transport from the LUMO of PFO to the LUMO of poly-TPD before being blocked by the DNA-CTMA layer. Therefore, device (c) exhibited poorer performance with respect to device (d), as shown in Fig. 2.

Figure 4 shows the voltage dependence of EL spectra for device (d) to demonstrate the color stability of the bio-WPLED. Device (d) exhibited stable and pure white emission that is composed of the blue emission from PFO and the orange emission from MEH-PPV, since all charge carriers were confined within the EML by the use of DNA-CTMA HTL/EBL and Cs$_2$CO$_3$ EIL/HBL. Although the EL spectra shown in Fig. 4 were obtained from 8 to 16 V over more than two orders of magnitude variation of the current density, the emission intensity of PFO only slightly increased compared to that from MEH-PPV. The slight spectrum change with increased voltages is typical for WPLEDs based on polymer blends.[6,19] The emission from the high-energy states

(PFO) starts to be populated after that from the low-energy states (MEH-PPV) becomes saturated. As shown in the inset of Fig. 4, device (d) exhibited an improved white-color stability under continuous operation (left inset of Fig. 4). In contrast, the corresponding device without the poly-TPD and DNA-CTMA HTL with a device structure of ITO/ PEDOT(30 nm)/PFO:MEH-PPV(70 nm)/Cs$_2$CO$_3$(1–2 nm)/ Al showed a decreased orange emission from MEH-PPV during the continuous operation (right inset of Fig. 4),[11] presumably due to a thermal phase separation of dopant from host caused by the inefficient hole injection.

In summary, we have developed a sequential solution-processing approach for constructing multilayer (up to five layers) WPLEDs consisting of a PEDOT hole-injecting layer, poly-TPD HTL, DNA-CTMA HTL/EBL, PFO/MEH-PPV EML, and Cs$_2$CO$_3$ EIL/HBL. The unique hole-transporting/ electron-blocking properties and selective solubility make the DNA-CTMA biopolymer an attractive HTL/EBL material for the development of multilayer polymer devices, as exemplified by the efficient multilayer bio-WPLEDs developed in this study. These bio-WPLEDs were characterized by a low turn-on voltage (~5 V), high efficiency (10.0 Cd/A), high brightness (10500 cd/m^2), and improved white-color stability.

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