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Solution-processed conjugated polymer organic *p-i-n* light-emitting diodes with high built-in potential by solution- and solid-state doping

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Polymer *p-i-n* homojunction light-emitting diodes (LEDs) comprising *p*-doped poly(dioctylfluorene-*alt*-benzothiadiazole) (F8BT) hole-injection, intrinsic F8BT emitter, and *n*-doped F8BT electron-injection layers have been demonstrated. A thin F8BT film was photocrosslinked and bulk *p*-doped by nitronium oxidation, then overcoated with an F8BT layer which was then surface *n*-doped by contact printing with naphthalenide on an elastomeric stamp. These LEDs exhibit high built-in potential (V_{bi}=2.2 V), efficient bipolar injection, and greatly improved external electroluminescence efficiency compared to control devices without the *p-i-n* structure. A modulated photocurrent technique was used to measure this V_{bi}, which systematically improves with diode structure. © *2009 American Institute of Physics*. [doi:10.1063/1.3257979]

Significant advances have taken place recently in evaporated molecular organic semiconductor (OSC) devices primarily through the development of *p-i-n* doped heterostructures to provide Ohmic transport.[1–4] For these molecular OSCs, this is readily achieved by coevaporation of the dopant with the transport layer.[4–7] For solution-processed polymer OSCs, however, this is a considerable challenge because of redissolution, and the difficulty of fixing a *p-i-n* profile. Thus while bulk chemical doping is known for both polarities[8–12] and has been implemented in device structures, e.g., in *p*-doped polymer distributed Bragg reflectors for microcavity light-emitting diodes (LEDs),[13] the general fabrication of polymer *p-i-n* structures remains elusive.

In this letter, we describe a method to fabricate polymer *p-i-n* diodes comprising: (i) photocrosslinking of the first layer using recently developed bis(fluorophenyl azide)s (FPAs)[14,15] followed by bulk *p*-doping by diffusion of solution-state dopant, (ii) deposition of an intrinsic polymer layer, and then (iii) solid-state surface *n*-doping to limit the doping depth in this layer. We show that this *p-i-n* structure gives the expected improvement in diode built-in potential (V_{bi}) and provides efficient hole (h^+) and electron (e^-) injection into the intrinsic polymer layer. Further improvement by incorporating heterostructures and carrier confinement layers is possible. We used poly(9,9-dioctylfluorene-2,7-diyl–benzo-2,1,3-thiadiazole-4,7-diyl) (F8BT, chemical structure in inset of Fig. 1) as model for these experiments, since it has deep highest occupied molecular orbital (HOMO, ionization potential I_p 5.9 eV) and relatively shallow lowest unoccupied molecular orbital (electron affinity 2.2 eV estimated) that makes carrier injection particulary of holes difficult, as is often the case also for deep-blue light-emitting polymers.

To characterize its *p*- and *n*-states, approximately. 120-nm-thick F8BT films were deposited onto clean glass sub-strates from a toluene solution with 2 wt % (based on polymer weight) of an FPA additive,[15] which were then crosslinked by deep ultraviolet light in a glovebox (pO$_2$, pH$_2$O<1 ppm), and developed with anhydrous tetrahydrofuran (THF) on a spinner to remove uncrosslinked low-molecular-weight materials. For *p*-doping, the film was contacted with a freshly prepared 80 mM nitronium hexafluoroantimonate ($NO_{2+}SbF_{6-}$) solution in anhydrous for 30 s, and spin rinsed with dilute $NO_{2+}SbF_{6-}$ (10 mM) also in the glovebox. This *p*-F8BT is charge balanced by the large SbF_{6-} anion. The optical transmission spectrum (Fig. 1) collected inside the glovebox confirms *p*-doping: the π-π* band at 2.7 eV bleaches while a sub-gap polaron transition emerges at 1.8 eV. For *n*-doping, the F8BT film was con-
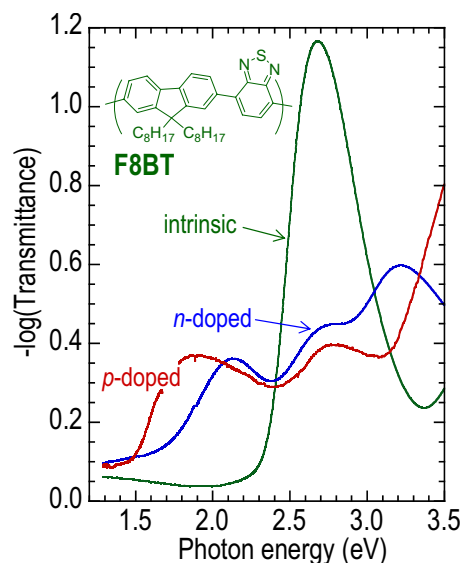

FIG. 1. (Color online) Optical transmission spectra of the intrinsic and doped F8BT films on glass substrates. Chemical structure of F8BT is shown in the inset.

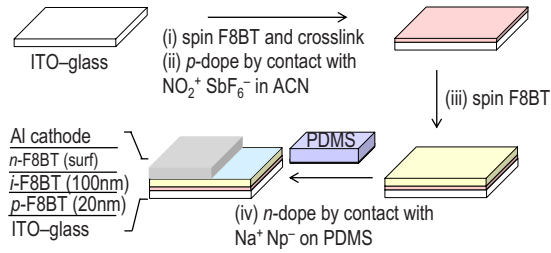a)Electronic mail: phyhop@nus.edu.sg.

FIG. 2. (Color online) Schematic of the fabrication of the *p-i-n* homojunction diode. All steps are conducted in the glovebox.

tacted with another freshly-prepared 100 mM sodium naphthalenide (Na$^+$Np$^-$) solution in anhydrous THF or dimethoxy glycol (DMG) for 30 s, and spin rinsed with anhydrous THF. This was prepared by reacting Np in anhydrous THF with fleshly cut Na. The *n*-F8BT is charge balanced by Na$^+$ which can be exchanged for larger organic cations. The optical transmission spectrum (Fig. 1) confirms *n*-doping: the $\pi - \pi^*$ band bleaches while a (different) subgap polaron transition emerges at 2.1 eV. The asymmetry between the h^+ and e^- polaron bands can be attributed to localization of e^- on the benzothiadiazole ring but h^+ on the fluorene-phenylene backbone.[16]

These processes were reversible which shows that chemical doping rather than degradation had occurred. The *p*-F8BT slowly loses its h^+ polaron band and regains $\pi - \pi^*$ intensity when heated to 120 °C in the glovebox, while the *n*-F8BT dedopes after 1 h with (partial) recovery of the $\pi - \pi^*$ intensity. Since the doped states are far more stable inside the devices, this is likely due to reaction with adventitious impurities in the glovebox, e.g., residual moisture.

Yellow-green-emitting *p-i-n* polymer OLEDs were fabricated as shown in Fig. 2. A 20-nm-thick film of F8BT was deposited on SC1-cleaned indium tin oxide (ITO) glass substrates (toluene, 2 wt % FPA), photocrosslinked, developed with anhydrous THF, bulk *p*-doped with 80 mM NO$_{2+}$SbF$_6$- in ACN, and then spin rinsed with anhydrous ACN. This produces a doping level of the order of 0.1 hole per repeat unit. A 100-nm-thick film of F8BT was then spin cast over this *p*-F8BT, and surface *n*-doped by a 10 s contact with a poly(dimethylsiloxane)-poly(methylhydrogensiloxane) stamp coated with a thin film of Na$^+$Np$^-$ by spin casting from a 100 mM solution. Because even brief contact with dopant solutions that are nonsolvents of the polymer (e.g., ACN and DMG) led to deep diffusion doping of tens of nanometers into the film, this solid-state doping procedure is necessary to limit the dopant profile. The thickness of the surface *n*-doped layer is expected to be of the order of a few nm. A rigorous time link of 10 min was imposed between surface *n*-doping and loading into the evaporator for cathode deposition to avoid degradation. A 120-nm-thick Al film was thermally evaporated through shadow mask to define 4.2 mm^2 contacts that also protected the diodes. Current-density–luminance–voltage (*jLV*) characteristics were measured using a Keithley 4200 semiconductor parameter analyzer with a calibrated large-area Si photodiode. Devices without one or both of the doped layers were also fabricated.

Fig. 3 shows the *jLV* characteristics of (i) ITO/*i*-F8BT/Al, (ii) ITO/*p*-F8BT/*i*-F8BT/Al, and (iii) ITO/*p*-F8BT/*i*-F8BT/*n*-F8BT/Al diodes plotted against the forward bias voltage above flat band, i.e., $V - V_{bi}$. Device (i) shows a low *j* of 1 mA/cm^2 at $V - V_{bi} = 4.0$ V and a very
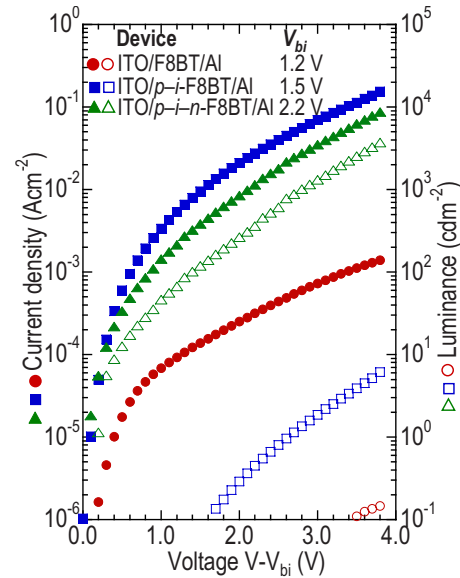

FIG. 3. (Color online) *jVL* characteristics of the devices measured at room temperature.

low *L* of 10^{-1} cd m^{-2} due to poor carrier injections from ITO and Al into *i*-F8BT. Inserting the *p*-F8BT layer, device (ii), increases *j* and *L* by two orders of magnitude, which shows *p*-F8BT provides efficient h^+ injection. The formation of a δ-hole-doped interface has recently been shown to be important for Ohmic contact to the intrinsic OSC layer.[18] However, the electroluminescence quantum efficiency η is still poor ($<0.01\%$ photon-per-electron flow in external circuit) due to poor e^- injection from Al. When an *n*-F8BT layer is also inserted, device (iii), *L* increases by two orders of magnitude without a corresponding increase in *j*, and so η reaches 1.4% ph/el (i.e., 4 cd A^{-1}). Thus the ultrathin *n*-F8BT layer provides efficient e^- injection into the *i*-F8BT layer to give greatly balanced e^- and h^+ currents. The η is nevertheless still limited by carrier leakage,[17,19] and exciton quenching as may be expected from the proximity to the doped layers and the metal cathode, so further buffer interlayers[15] will be needed to screen these. For comparison, devices with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDT:PSSH) anode and Ca cathode shows very poor $\eta < 0.05\%$, because PEDT:PSSH (work function $\phi = 5.1$ eV) does not appear to be able to inject holes efficiently into the HOMO of F8BT.

Thus *p*- and *n*-doped injection layers provide efficient carrier injection of holes and electrons respectively into polymer OSC diodes, as in molecular OSCs, although the injection mechanisms may be very different. The F8BT *p-i-n* diodes here can be repeatedly measured over days and cycled between 30 and 353 K, so the doped profiles have some stability. However an undesirable dopant migration appears to occur at elevated temperatures which degrades injection and quenches luminescence. This may be suppressed, e.g., through the use of even larger charge-compensating ions.

To demonstrate the presence of the *p*- and *n*-doped interfaces in the diodes, we measured their V_{bi} using a modulated photocurrent technique (Fig. 4.) which gives the separation of the Fermi levels E_F of the contacts to the intrinsic layer under flat band condition. Direct measurement of this parameter is necessary to demonstrate the expected widening of the E_F gap of the *p*- and *n*-doped contacts, and to estimate
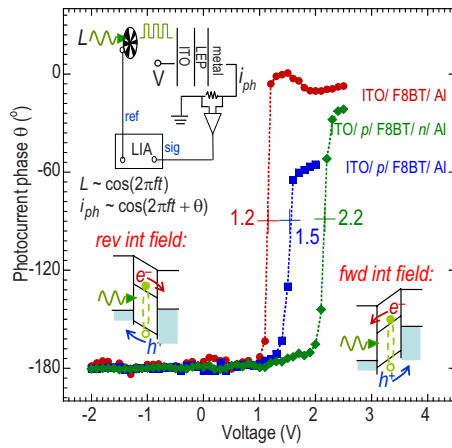
FIG. 4. (Color online) Built-in potential measurement of the devices by a modulated photocurrent technique at room temperature.

the effective ϕ of δ-doped interfaces[18] which can differ significantly from that of isolated bulk chemically doped layers[20,21] due to differing Madelung stabilization.[22] A chopped white light beam ($f = 130$ Hz) was incident on the diode and the modulated photocurrent demodulated at 1ω. For a probe light intensity that varies as $\cos(2\pi ft)$, the induced photocurrent, which varies as $\cos(2\pi ft + \theta)$ where the phase shift $\theta = -180°$ for $V - V_{bi} < 0$, makes a step transition across $\theta = -90°$ at $V - V_{bi} = 0$. This modulation method eliminates the light-independent diode current and leakage background from the measurements to give the true open-circuit voltage, which is also the V_{bi} in these systems with low carrier diffusivity.

For device (i), we obtained $V_{bi} = 1.2$ V, which for an ITO ϕ of 4.5 eV suggests an effective Al ϕ in contact with F8BT of 3.3 eV. When the p-F8BT layer is inserted, device (ii), V_{bi} increases by 0.3 eV. In repeat measurements using electromodulated absorption spectroscopy, we obtained V_{bi} values of 1.8 eV. These results suggest the E_F of the p-doped contact lies at 4.8–5.1 eV with respect to the vacuum level (E_{vac}) of the undoped F8BT. Hence the E_F at the p-doped contact is located 0.8–1.1 eV above HOMO edge of the intrinsic polymer, assuming no change at the cathode contact. It is thus highly remarkable that good hole injection is still obtained. When the n-F8BT layer is also inserted, device (iii), V_{bi} increases to 2.2 eV which places E_F of the n-contact at 2.6 eV below E_{vac}. This systematic evolution in V_{bi} to reach the $\pi - \pi^*$ emission gap of the polymer (2.3 eV) is a clear signature that the p-i-n homostructure has indeed been formed. Further experiments with variable p-doped F8BT suggest that the E_f level is only weakly dependent on the doping level in the range of 1% to few tens of % of hole per repeat unit. These doping levels were estimated from the intensities of their polaron absorption feature assuming the

"fully"-doped form given in Fig. 1 has a doping level of 0.3–0.5 hole per repeat unit.

In summary, we have demonstrated polymer p-i-n homojunction diodes with high built-in potential and excellent electron and hole injection. These will ultimately enable efficient low-voltage polymer light sources. Because the carrier injection efficiencies are no longer dependent on the use of high- and low-work function electrodes, it is now possible to employ a wider range of stable and transparent electrodes and to make transparent polymer OLEDs.

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