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Enhanced hole injection in a polymer light emitting diode using a small molecule monolayer bound to the anode

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Abstract

A monolayer of quarterthiophene-2-phosphonate (4TP) was chemically bound to the surface of indium tin oxide (ITO) and was then p-doped with the strong acceptor, tetrafluorotetracyanoquinodimethane (F_4-TCNQ). This interface modification strongly reduced the barrier for hole injection compared to unmodified ITO. This doped monolayer surface treatment was also superior to the commonly used anode coating poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PPS) at driving voltages above 5.2 V.
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1. Introduction

The electroluminescence of conjugated polymers has received enormous attention in the field of modern display technologies [1]. A simple polymer light emitting diode (PLED) can be constructed as a sandwich that contains a transparent substrate (glass or plastic) coated with indium tin oxide (ITO) to serve as the anode, a layer of light emitting polymer (LEP) such as poly-(*p*-phenylene vinylene) (PPV), and finally a layer of a low work function (ϕ) metal (Ca, Mg or Al) as the cathode [2]. The LEP can be unstable to oxidation [3], and O_2 from the ITO can diffuse into the LEP and cause degradation of the device. Furthermore, In (from ITO) leaching into the active organic material may be an additional reason for early device failure [4]. Finally, the hole injection barrier at the interface, which results from the energy level mismatch between ϕ_{ITO} (4.4 eV [5]) and the LEP highest occupied molecular orbital (HOMO; 5.1 eV for MEH-PPV [6]), translates into inefficient hole injection from the anode [7].

One method to mitigate problems of O_2 or In migration and interface energy mismatch is to insert a layer

of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PPS) between the ITO and the LEP; [8] surface coating with PEDOT: PSS has been shown to increase ϕ, which decreases this energy level mismatch [9,10]. PEDOT:PSS is commonly applied to ITO as an aqueous dispersion, which is spin-coated onto the ITO and baked to remove water [11]. In this way, water is driven out of the polymer layer which then becomes insoluble in organic solvents, an aspect that is critical for further processing with the LEP layer [12]. Unfortunately, PEDOT:PSS as applied in this way onto ITO may not form a stable interface [4,13]. It has been shown that PSS, which is itself hygroscopic, can absorb water from the ambient to create an (aqueous) acidic environment at the interface which can etch the ITO and cause In species to diffuse into the PEDOT:PSS layer [4].

We have recently shown that charge transfer complex monolayers covalently bonded to the ITO surface can be highly effective to enhance hole injection into the hole transport material *N*,*N*′-bis-(1-naphthyl)-*N*,*N*′-diphenyl1-1,1-biphenyl1-4, 4′-diamine (α-NPD) in light emitting diode devices [14]. In that work, a dense monolayer of α-quarterthiophene-2-phosphonate (4TP) [15] was prepared on ITO from a self-assembled monolayer of α-quarterthiophene-2-phosphonic acid (4TPA) and then p-type doped

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with the strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4-TCNQ). This treatment presumably generates surface bound 4TP radical cationic species, and ϕ of the modified ITO increased by 0.35 ± 0.05 eV compared with the untreated material [14]. It was therefore of interest to determine if 4TP-F_4-TCNQ might serve as a suitable substitute for PEDOT:PSS. Because the 4TP units are chemically bonded to the ITO via strong phosphonate bonds, and because of electrostatic attraction with the reduced F_4-TCNQ, spin coating of electroluminescent polymers through solution phase methods seemed possible. We now report that preparing a monolayer of 4TP on ITO followed by p-type doping with F_4-TCNQ does give an anodic material that is highly effective for hole injection in simple PLED devices; in fact, this simple system appears to be functionally superior at high current density than is PEDOT:PSS itself.

2. Experimental

General. Glass slides coated with indium tin oxide (Colorado Concept Coatings, 15 $\Omega/\square$, 1500 Å) were used after appropriate cutting and cleaning. 4TPA was prepared as described [15] F_4-TCNQ (Aldrich) and aluminum (Alfa Aesar) were used as received. Tetrahydrofuran (THF; EM Science) was distilled from Na and was stored under argon. An aqueous dispersion of PEDOT:PSS (Aldrich) was filtered through a 0.45 μm PES syringe filter (Whatman) immediately before use. Poly(2-methoxy-5-[2′-ethylhexyloxy]-p-phenylene vinylene) (MEH-PPV; Aldrich, mol. wt. = 150,000–250,000) was dissolved in chloroform and the solution was filtered though a 0.45 μm PTFE syringe filter (Acrodics) before use. The thickness of spin-coated polymers was measured using a KLA-Tencor P15 Surface Profiler. Reflectance-absorbance infrared spectra were taken using a MIDAC FT-IR for 4TP- and 4TP-F_4-TCNQ-coated ITO; a blank ITO slide served as the background. X-ray photoelectron spectroscopy (XPS) data were collected using a Phoibos 150 hemispherical energy analyzer (SPECS) and a monochromatized Al (1486.6 eV) source. A pass energy of 10 eV was used for high resolution measurements. For quantitative estimations of surface compositions standard atomic photo-ionization cross-section values from the SPECS database were used.

Pretreatment of the ITO. ITO-coated glass slides were cut into 20 mm × 20 mm coupons. A 10 mm × 20 mm strip of ITO was defined by covering the appropriate area with electrical tape and etching the surrounding ITO in 37% HCl. The slides were then brushed with a soft toothbrush soaked with 2% aq. NP-10 Tergitol solution, then sonicated in the same solution following by rinsing away the foam. The slides then were rinsed again thoroughly with deionized water, rinsed with sonication for 5 min in acetone, submerged for 5 min in boiling acetone (3 cycles), submerged for 5 min in boiling isopropyl alcohol (3 cycles), and submerged for 5 min in boiling methylene chloride (3 cycles). They were then blown dry with N_2 and heated under N_2 at 100 °C for 1 h, then stored in a holding chamber under vacuum (10^{-2} Torr).

4TP/ITO. An ITO anode prepared as described above was clamped with an alligator clip and was dipped perpendicularly into a freshly prepared solution of 4TPA in THF (0.1 mM). The THF was allowed to evaporate slowly to give a multilayer of the 4TPA on the ITO surface. The coated ITO was then heated for 48 h under N_2 at 150 °C to give the monolayer of the corresponding phosphonate, 4TP/ITO (Fig. 1a). 4TP/ITO was then sonicated in a mixture of ethanol and 0.5 M aq. K_2CO_3 (2:1), rinsed with distilled water, then blown dry with N_2.

4TP-F_4-TCNQ/ITO. A sample of 4TP/ITO was soaked in a solution of F_4-TCNQ in methylene chloride (1 mM) for several hours, then thoroughly rinsed with methylene chloride and blown dry with N_2 to give 4TP-F_4-TCNQ/ITO.

PEDOT:PSS/ITO. An ITO sample cleaned as described above was spin-coated with a filtered aqueous solution of PEDOT:PSS at 2200 rpm. The resulting film was then cured in air at 150 °C for 20 min and was used immediately.

PLED device fabrication. Four different types of PLED devices were prepared with PEDOT:PSS/ITO, 4TP/ITO, 4TP-F_4-TCNQ /ITO, and ITO used without any modification other than cleaning, as the control. For all devices, a 100 nm thick film of MEH-PPV was spin-coated onto the ITO from a chloroform solution and was annealed at 150 °C under vacuum (10^{-6} Torr) for 2 h. A 60 nm Al cathode was then thermo-evaporated on top of the MEH-PPV. A shadow mask defined the Al cathode area, and the overlap areas between both electrodes were measured to be 0.25 and 0.50 cm^2, respectively. Device testing was done in air using a Keithley 2400 Sourcemeter controlled by Labview software.
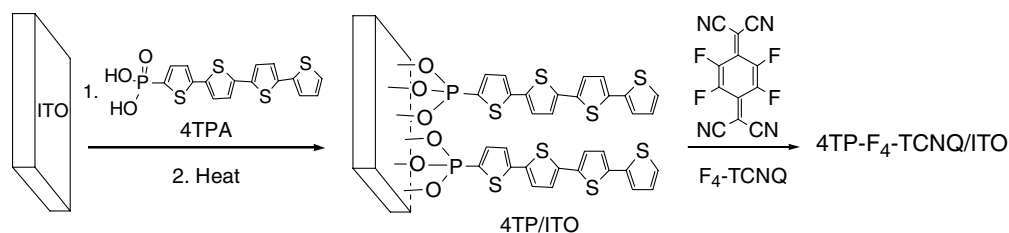

Fig. 1. Preparation of 4TP-F_4-TCNQ on ITO.

3. Results and discussion

4TP/ITO was prepared as previously described (Fig. 1) [14] The IR spectrum of 4TP/ITO showed the characteristic $\nu_{P=O} = 1014\ cm^{-1}$ peak for the bound phosphonate unit and $\nu_{C-H} = 792\ cm^{-1}$ of the thienyl groups. Kelvin probe measurements[16] showed a 0.28 ± 0.05 eV decrease in ϕ for 4TP/ITO vs. untreated ITO and a 0.35 ± 0.05 eV increase in ϕ for 4TP-F4-TCNQ/ITO compared to untreated ITO.

A calibration plot for spin-coated polymer thickness was constructed to relate measurements made by surface profiling and UV–Vis absorption at 505 nm (the absorption maximum of MEH-PPV) and was found to be linear. Simple polymer devices were then fabricated to test the effects of 4TP/ITO and 4TP-F4-TCNQ/ITO surface treatments on hole injection and were compared to ITO and PEDOT:PSS/ITO. MEH-PPV and Al were used as the electroluminescent polymer and the cathode, respectively. The effects of these different surface treatments on device current densities (j) were measured as function of applied voltage (Fig. 2). Work function changes ($\Delta\Phi$) between untreated ITO and 4TP/ITO, 4TP-F4-TCNQ/ITO, and PEDOT:PSS[10] were plotted against these current densities at 2 V, 4 V, 6 V, and 8 V applied voltage (Fig. 3). The nearly linear relationship between $\log(j)$ and $\Delta\Phi$ found above 4 V for ITO, 4TP/ITO, and 4TP-F4-TCNQ/ITO is consistent with the thermionic emission model for charge injection,[17] i.e., the current is injection-limited; thus, the barrier to hole injection can be adjusted by systematic modification of the ITO surface. We do not think that diffusion of F4-TCNQ into the MEH-PPV occurs; MEH-PPV and F4-TCNQ form what is apparently a charge-transfer complex in solution (which is dark green-red) and which does not luminesce. Since our devices are (qualitatively) bright, similar charge-transfer complex formation in them can be ruled out. The fact that $\log(j)$ values for the device
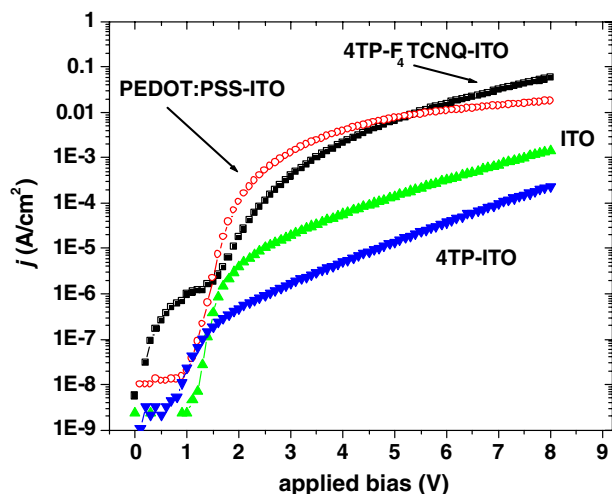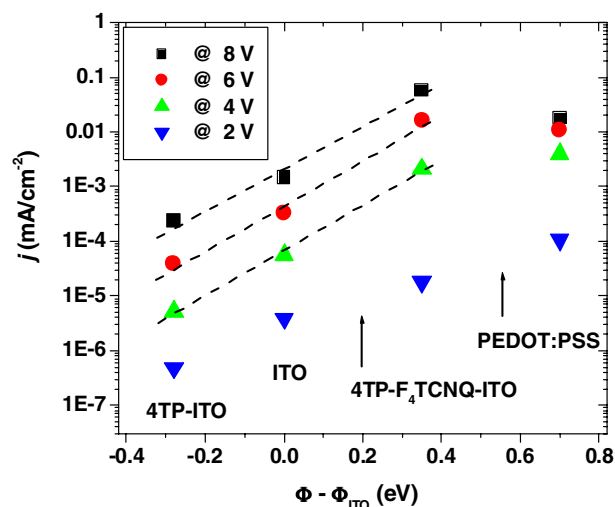

Fig. 3. The relationship between $\Delta\Phi$ and current densities of devices measured at 2 V, 4 V, 6 V, and 8 V applied voltage (as indicated). [Dashed lines are a guide to the eye, indicating a linear relationship between $\Delta\Phi$ and $\log(j)$]. The work function of PEDOT:PSS (5.1 eV) is taken from Ref. 10.

using PEDOT:PSS do not coincide with the proposed linear relationships found for the 4TP-derived anodes (dashed lines in Fig. 3) may be an indication of the intrinsically different nature of a conducting polymer – as opposed to a monolayer surface-modified ITO. Furthermore, since PEDOT:PSS can act as electron blocking layer in PLEDs this affects the electric field distribution within the PLED. [18] Significantly, by comparing current densities above an applied voltage of 5.2 V, it was found that the 4TP-F4-TCNQ-coated ITO surface performs even better, current-wise, than PEDOT:PSS, and devices with 4TP-F4-TCNQ appeared brighter above this voltage than those using 4TP alone or PEDOT:PSS.

4. Conclusion

A possible substitute for PEDOT:PSS to promote hole injection in polymer light emitting diode devices has been prepared and tested. In this case, a dense monolayer of small organic molecules, α-quarterthiophene-2-phosphonate, was bound to the surface of ITO and was then p-doped with an electron acceptor. ITO work function changes due to monolayer preparation and subsequent doping were correlated with current densities in fabricated MEH-PPV-based polymer LED devices, and the barrier to hole injection in these device was related to the anode Φ-LEP HOMO energy mismatch. Current densities and apparent brightness of devices prepared using 4TP-F4-TCNQ/ITO were found to be greater than those for PEDOT:PSS-based ones above a critical driving voltage. Since all α-quarterthiophene phosphonic acid units are converted to phosphonates on monolayer bonding to the ITO, it is possible that 4TP-F4-TCNQ monolayers can passivate the relatively reactive ITO surface.

Fig. 2. *J–V* curves for four devices, with the indicated anode modification.

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