Green Polyfluorene – Conducting Polymer Interfaces: Energy Level Alignment and Device Performance

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Abstract

Photoemission studies on interfaces between an electroluminescent green polyfluorene (GPF) and two conducting polymers comprising ethylenedioxythiophene and sulfonate moieties are reported. Despite the chemical similarity of both conducting polymers, the hole injection barriers to GPF were found to differ by 0.35 eV and the interface dipoles by up to -0.4 eV. Polymer light emitting devices fabricated with the two conducting polymers exhibit nearly identical current-voltage characteristics, but the luminance-voltage characteristic is enhanced by a factor of 20 by the presence of near-surface poly(styrenesulfonate). We attribute the enhancement to the electron blocking behavior of the sulfonate moieties at the GPF interface and the concomitant modification of the device built-in-voltage.

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1. Introduction

Waterborne dispersions of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDT/PSS; BAYTRON[®] P) have become the established material for buffer layers in polymeric light emitting diodes (PLEDs). The coating is applied by spin-coating, ink-jet printing or other printing techniques, and dried at temperatures between 80 to 200 °C. The PEDT/PSS layer improves the hole-injection properties and planarises rough ITO-surfaces¹. In PLEDs the emitting layers are deposited from solution onto the cured PEDT/PSS layer and this interface determines many relevant device properties, such as hole-injection efficiency, exciton quenching, and electron blocking. To improve PLED performance a better understanding of the structural and electronic properties of this region is essential.

The hole injection barrier (Δ_h) is a key parameter determining device performance and it can be determined experimentally using ultraviolet photoelectron spectroscopy (UPS) as the energy difference between the substrate Fermi-energy (E_F) and the low binding energy onset of photoemission from the emitting polymer (i.e., its valence band edge). In the past, Δ_h was often estimated from the values of the substrate electrode work function (ϕ_e) and polymer ionization energy (IE) determined separately, and by assuming a common vacuum level across the interface (i.e. the Schottky-Mott limit)^{2,3}:

$$\Delta_h = IE - \phi_e \quad (1)$$

However, the invalidity of this simple concept for organic/metal interfaces was soon demonstrated^{2,3}, in particular for small molecular materials, where interfaces are formed by vacuum sublimation of the organic material onto the metal electrode surface. It was found that vacuum level discontinuities (often termed *interface dipoles*) at such interfaces are more generally the rule rather than the exception, and a number of possible reasons were discussed, e.g., Pauli-repulsion^{2,4,5}, charge transfer^{2,3,6}, or covalent bond formation^{7,8}. More recently, a systematic study showed that significant vacuum level shifts (Δ_{vac}) of up to 1 eV can exist at interfaces between pentacene and conducting polymers, such as PEDT/PSS^{9,10}. Therefore,

reliable values for Δ_h cannot be derived from (1), and instead the following relation should be used:

$$\Delta_h = IE - \phi_e - \Delta_{vac} \quad (2)$$

Interestingly, there are virtually no reports of significant interface dipoles for interfaces between light-emitting polymers and electrode materials, and one might assume that the Schottky-Mott limit holds for these interfaces ¹¹.

We find significant interface dipoles at such interfaces from our photoemission data and have substantiated the results by device studies. We compare thin films of a commercial dispersion of PEDT/PSS with *in-situ* polymerized ethylenedioxythiophene (IS-PEDT). The chemical structures are shown in Fig. 1. The aqueous solutions are spin-coated onto ITO to be further processed to hole-only devices and to PLEDs in combination with a green emitting polyfluorene (GPF) ¹², or characterized directly after deposition by ultraviolet photoelectron spectroscopy (UPS) or atomic force microscopy (AFM).

2. Experimental

Thin films of the commercial PEDT/PSS-dispersion Baytron[®] P CH 8000 (PEDT:PSS ratio 1:20) ¹³ were prepared by spin coating on freshly cleaned ITO–glass substrates and dried at 150°C for 10 min. For the in situ polymerized PEDT (IS-PEDT) an adhesion layer of Baytron[®] CH8000 was used. IS-PEDT is made by mixing the ethylenedioxythiophene (EDT) monomer (Baytron[®] M) with Fe(III)tosylat (Baytron[®] CB40) and imidazole ¹⁴ in a weight ratio of 1 : 20 : 0.5. After spin coating this solution onto the adhesion layer, the samples were heated at 50°C in air for 5 min. After the polymerization the iron salts were removed by washing with distilled water. The conductivity of such films is in the range of 500 S/cm. For the photoemission studies, green polyfluorene¹² (GPF) layers with various thicknesses (determined afterwards *ex situ* by AFM) were spin coated on the buffer layer. These samples

and also the bare conducting polymer samples were introduced into the ultrahigh vacuum (UHV) system *via* a load lock within 5 min. of preparation.

Ultraviolet photoelectron spectroscopy (UPS) experiments were performed on the FLIPPER II beamline at Hasylab (Hamburg, Germany) ¹⁵. The base pressure in the analysis chamber was 2×10^{-10} mbar. Photoelectron spectra were recorded with a double-pass cylindrical mirror analyzer at a resolution of 150 meV. The incident photon energy was 22 eV. The sample work function was determined as the energy difference between the incident photon energy and the total width of the energy distribution curve. The Fermi-energy position was determined on freshly Ar-ion sputtered Au thin films. The secondary electron cutoff was recorded with the sample biased at -3V relative to the analyzer. The overall error in the energies derived from the UPS experiments is less than ± 0.1 eV. Elimination of sample charging during UPS measurements was achieved by simultaneous sample irradiation with light from a frequency-doubled Nd:YVO₄ laser (532 nm, 50 mW max. output power).

PLEDs were fabricated by coating an 80nm thick layer of the green polyfluorene on top of the buffer layer previously deposited on the ITO-coated glass substrates. After baking the layer stack in a N₂ glove box for 5 min on a hot plate (130°C), metal layers of 5 nm Ba and 200 nm Ag forming the cathode were successively deposited through a shadow mask without exposing the substrate to air. For the hole-only devices, Au contacts were deposited. To avoid cross talk arising from the highly conducting PEDT layer, the isolated circular 2.5mm diameter cathodes were contacted individually using Au wires. The current/voltage (I/V) and luminance/voltage (L/V) characterization was performed with a Keithley 2400 source meter and a Si-photodiode attached to a Keithley 6514 electrometer to record the electroluminescence intensity. A Minolta LS-100 photometer was used to calibrate light output.

3. Results and Discussion

Valence band spectra of CH8000 and IS-PEDT are compared in Fig. 2. The most notable difference between the two buffer layers can be seen close to E_F (in the figure inset). While no significant photoemission intensity can be observed for binding energies (BE) less than 1 eV for CH8000, a clear signature of emission intensity extends up to E_F for IS-PEDT. Assuming that the photoemission cross-sections are similar for the two conducting polymer materials, this observation indicates a significantly higher density of occupied electronic states close to E_F in IS-PEDT. This is fully consistent with the much higher conductivity measured for IS-PEDT (up to 500 S/cm) compared to CH8000 (10^{-5} S/cm)¹³. The work function of these two buffer layers also differs significantly: 5.1 eV for CH8000 compared to 4.3 eV for IS-PEDT. The difference is probably due to different surface dipole distributions at the surface of the two polymers (induced by charge transfer between EDT and sulfonate moieties)^{9,10}. Photoemission measurements were performed on GPF layers with various thicknesses deposited on IS-PEDT substrates. Since the layer thickness was larger than 15 nm in all cases (measured *ex situ* by AFM), significant sample charging was observed, identified by spectral shifts to higher BE by several tenths of an eV and an overall broadening of spectral features. A representative example of sample charging is shown in the lowest curve in Fig. 3. However, the charging effect could be completely eliminated by simultaneous irradiation of the sample with laser light. The charge compensation mechanism can be attributed to internal photoemission at the IS-PEDT–GPF interface^{16,17}. The laser power was increased until no further shifts to lower BE were observed. The occurrence of irreversible damage to the samples due to charging on the timescale of several minutes could be ruled out by comparison with measurements on pristine areas of the sample. The spectra obtained for fully charging-compensated GPF–IS-PEDT samples for thicknesses up to 35 nm are virtually identical, as can be seen from the upper three spectra in Fig. 3. These results show that sample preparation under ambient conditions yields highly reproducible electronic properties of these

polymer bilayers. By analogy to similar polyfluorene-based polymers we can relate the emission feature in the BE region 1.0 – 2.5 eV to the delocalized π -band, and the peak centered at 3.3 eV to localized π -states^{18,19}. The hole injection barrier Δ_h was 1.0₅ eV for these samples. In contrast, Δ_h for GPF (30 nm) deposited onto CH8000 was found to be significantly smaller: 0.7 eV [Fig. 4 (a), (b)] although the same charging compensation procedure was used. Within the Schottky-Mott model, a smaller Δ_h would be expected for CH8000 due its larger work function. However, the measured reduction of the hole injection barrier (0.3₅ eV) does not simply correspond to the work function difference between CH8000 and IS-PEDT (0.8 eV). This implies the formation of an interface dipole at one of these interfaces (*c.f.* Eq. 2), which was in fact experimentally observed. The secondary electron cutoff kinetic energy for pristine IS-PEDT and GPF–IS-PEDT changes by only +0.0₅ eV [Figs. 4 (c), (d)], and thus in this case only a small interface dipole is formed . In contrast, for GPF on CH8000 Δ_{vac} changes by -0.4 eV [Fig. 4 (e)] compared to the pristine conducting polymer surface [Fig. 4 (f)]. This leads to a work function for GPF-coated samples of 4.3₅ eV for IS-PEDT and 4.7 eV for CH8000. For green polyfluorene the ionization energy was determined to be 5.4 eV.

As outlined in section 2, hole-only and bipolar devices were fabricated to systematically investigate the influence of the two different hole injection barriers Δ_h on device performance and the accompanying differences in interface composition and morphology. When comparing the device data, note that all of the parameters except the buffer layer were kept constant. The current/voltage (I/V) and luminance/voltage (L/V) curves of the respective hole-only devices are shown in Fig. 5 (a). Current densities for devices with CH8000–GPF interfaces were nearly three orders of magnitude larger than those with IS-PEDT–GPF interfaces, fully consistent with the different hole injection barriers Δ_h measured

by UPS for these two cases. No significant light emission was observed for both types of hole-only devices.

Corresponding I/V and L/V curves of the PLEDs are shown in Fig. 5 (b). Most notably, for IS-PEDT the luminance is lower by a factor of 20 compared to CH8000, although the current densities are virtually identical. The onset voltage, i.e., the voltage at which the current starts to rise rapidly, is the same (2.1 V) for both device-types. The leakage current of the PLED with CH8000 is somewhat reduced, probably because the CH8000 layer planarizes the rough IS-PEDT surface and reduces the number of micro shorts. The higher luminance of PLEDs with CH8000–GFP interfaces compared to those with IS-PEDT–GPF together with the same current densities translates directly into different device efficiencies: namely 3.5 cd/A for CH8000 and only 0.1 cd/A for IS-PEDT.

In the following we will discuss two effects that could lead to the observed I/V and L/V results for the PLEDs, which at first sight appear to be counterintuitive. First, we consider that the built-in-voltages (BIV) of the two devices are different²⁰. This can be deduced directly from the UPS results, which reveal that the work function is lower for IS-PEDT than that of CH8000, both before and after deposition of GPF. At the same time, the work function at the cathode side is the same for both types of devices as it is pinned by the interaction of GPF with Ba. The BIV difference (Δ_{BIV}) is equal to the work function difference taking into account Δ_{vac} and in this case $\Delta_{\text{BIV}} = 0.35$ eV. This fact, combined with the observation of an almost identical voltage for the onset current, leads us to believe that the device current is electron dominated at low voltages. Additional support is provided by the fact that Δ_{h} is comparably large for both buffer layers (1.05 eV and 0.7 eV), while the electron injection barrier is less than 0.5 eV^{19,21}. Although Ca was used with a polyfluorene in the work of Liao et al.¹⁹, a similar charge-transfer reaction can be assumed to occur between Ba and

polyfluorene. Furthermore, the onset of electroluminescence (EL) occurs at higher voltage for devices with IS-PEDT [2.35 V compared to 2.05 V; see inset in Fig. 5 (b)], reflecting the higher barrier for hole injection compared to CH8000.

Photoelectron spectroscopy monitors energy levels and interface barriers in the absence of free charge carriers. However, hole-injection can be significantly enhanced by electrons trapped at the polymer/anode interface as pointed out by Poplavskyy et al. for the system PEDT:PSS–poly(9,9-dioctylfluorene)²² and by Seeley et al. for PEDT:PSS–poly(9,9-dioctylfluorene-alt-benzothiazole)²³. The early onset of EL at 2.05 V indicates that charged traps at the interface contribute to the reduction of the energy barrier for hole-injection.

Exciton formation close to the anode interface and concomitant electron blocking are strongly influenced by the presence of PSS^{21,24}. The formation of a PSS rich phase on the surface of PEDT/PSS-layers was proposed on the basis of x-ray photoelectron spectroscopy²⁵ and neutron scattering²⁶ experiments. The segregation of significant amounts of PSS at the GPF interface is only expected for CH8000 which has a PEDT:PSS ratio of 1:20¹³. No free sulfonate species are expected for IS-PEDT on general grounds of its synthesis. On account of the random nature of PEDT/PSS mixtures it is reasonable to believe that PEDT free segments of the polymer-mixture will segregate to the surface, forming a PSS-rich phase. On the other hand the PSS-rich surface layer must be very thin, comparable to the charge carrier hopping distance, or locally inhomogeneous, as the hole injection current is not altered by the addition of PSS²⁴. Surface inhomogeneities have been reported for PEDT/PSS²⁷. In PSS-rich regions electrons reaching the interface from the cathode side will be prevented from recombining at the anode. Since PSS is a wide band gap polymer it should block electrons efficiently. Electrons will accumulate at the PEDT/PSS interface leading to an increase in hole injection *via* barrier lowering and the formation of excitons due to better balance of both polarities of injected charge carriers. The PSS-rich layer formed on CH8000 should additionally hinder

exciton quenching at the interface due to a lack of energetically accessible states. In contrast, IS-PEDT consists mainly of low band gap PEDT which will deactivate excitons efficiently.

Recent studies have revealed virtually identical hole injection barriers Δ_h for pentacene deposited on IS-PEDT and CH8000^{9,10}. A charge-exchange reaction, in which pentacene is (partially) reduced by PSS, was invoked to explain the pinning of the pentacene energy levels relative to the Fermi levels of the different conducting polymers^{9,10}. We propose that the difference in Δ_h reported here may be related to the higher ionization energy of GPF (5.4 eV) compared to that of pentacene (5 eV)⁵ and consequently, the reduction of GPF by PSS is weaker than that of pentacene. This, in turn, may diminish the pinning behavior of the energy levels at the interface between GPF and conducting polymers based on EDT and sulfonate moieties.

4. Conclusions

We have investigated the energy level alignment at interfaces between an electroluminescent green polyfluorene and two different conducting polymers as buffer layers, namely IS-PEDT and CH8000. Despite the similar chemical composition of the two conducting polymers, the photoemission measurements revealed significantly different work functions and hole injection barriers to GPF (1.05 eV and 0.7 eV respectively). In addition, a large interface dipole of -0.4 eV between CH8000 and GPF was found. The influence of the different interface energetics on PLED performance was investigated. While the I/V curves for the two buffer layers were very similar, the L/V characteristics of devices with CH8000 were far superior (more than 20 times higher luminance and a 35 times higher efficiency at the same voltage). This was explained by the lower built-in-voltage for devices with IS-PEDT

and a combined electron/exciton-blocking capability of the surplus PSS moieties on the CH8000 surface.

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Figure Captions

Figure 1.

Chemical structures of (a) PEDT/PSS, and (b) IS-PEDT.

Figure 2.

Valence band photoemission spectra of conducting polymer buffer layers on ITO: CH8000 (bottom curve); IS-PEDT (top curve). Inset: close-up of the near- E_F region.

Figure 3.

Valence band photoemission spectra for GPF thin films on IS-PEDT. Film thickness (from top): 35 nm, 26 nm, 15 nm. Bottom spectrum: charging not compensated by light irradiation (15 nm).

Figure 4.

Valence band photoemission spectra of GPF on IS-PEDT (a), and on CH8000 (b). Secondary electron cutoff region for (c) pristine IS-PEDT, (d) GPF-IS-PEDT, (e) GPF-CH8000, and (f) pristine CH8000. Schematic interface energy level diagram for (g) IS-PEDT / PGF, and (h) CH8000 / GPF; E_{vac} ... vacuum level. Optical gap of GPF: 2.5 eV.

Figure 5.

I/V and L/V curves for (a) hole-only devices and (b) PLEDs fabricated with GPF and two different buffer layers (CH8000 on IS-PEDT: open symbols; IS-PEDT only: filled symbols); inset: close-up of the onset-region for electroluminescence. (c) Schematic representation of the electron-blocking mechanism by interfacial wide energy-gap PSS.

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FIG. 5. (Color online) I/V and L/V curves for (a) hole-only devices and (b) PLEDs fabricated with GPF and two different buffer layers (CH8000 on IS-PEDT: open symbols; IS-PEDT only: filled symbols); Inset: Closeup of the onset region for electroluminescence. (c) Schematic representation of the electron-blocking mechanism by interfacial wide energy-gap PSS.