Organic Electronics

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Soluble Self-Doped Conducting Polymer Compositions with Tunable Work Function as Hole Injection/Extraction Layers in Organic Optoelectronics**

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Charge injection/extraction layers greatly affect the efficiency and lifetime of organic optoelectronic devices.[1–5] Therefore, reliable and soluble charge injection/extraction buffer layers, which are widely applicable to various organic optoelectronic devices, should be developed. Solution processable conducting polymers doped with poly(4-styrenesulfonate) are especially good candidates for use as hole injection buffer layers (HILs) and hole extraction buffer layers (HELs) in organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVs).[4–8] However, these polymers have practical limitations for large area electronics because the particles are dispersed in water and thus form poor-quality films with defects caused by aggregation of the particles; they also present a high hole injection/extraction barrier to overlying organic layers, and are hygroscopic. Therefore, to improve the device lifetime and hole injection/extraction capability in organic optoelectronics, a soluble, efficient, and stable buffer layer should be developed. We introduce soluble, self-doped conducting polyaniline graft copolymer compositions based on poly(4-styrenesulfonate)-g-polyaniline (PSS-g-PANI) (Figure 1) that have tunable work functions W_F for HILs/HELs in OLEDs and OPVs. We systematically controlled the self-organized surface-enriched layer of the HIL/HELs after incorporating a perfluorinated ionomer (PFI) into the PSS-g-PANI solutions. Then, we investigated the influence of the surface layer on the values of W_F of spin cast films and the correlation of W_F values with hole injection/extraction capabilities and device lifetimes in OLEDs and OPVs.

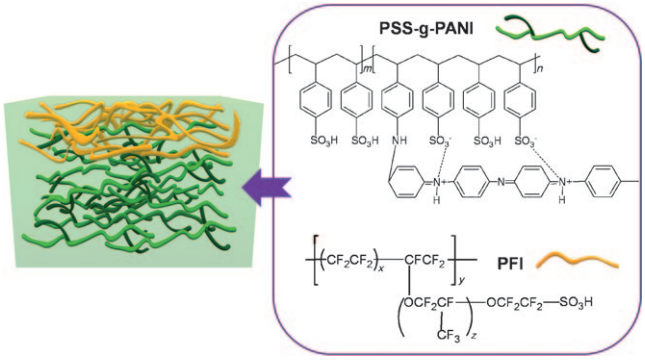

Figure 1. Self-organized film of PSS-g-PANI compositions after spin-coating, and chemical structures of PSS-g-PANI and PFI.

Water-soluble PSS-g-PANI with a 8:1 weight ratio (Figure 1) was synthesized (see the Supporting Information) by oxidative polymerization of aniline with an oxidant and an aqueous solution of random copolymer composed of stryenesulfonate and *p*-aminostyrene derivatives.[9] Doping of the polymeric acid dopant PSS is structurally stable because this graft type conducting polymer bonds covalently to the PSS.[9]

We used ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) at the 4B1 beam line of Pohang Acceleration Laboratory (PAL) to characterize the surfaces of spin-cast films of the soluble conducting polymer and of the blends with the PFI. The value of W_F was affected by the compositions of the solutions (Table 1). In PSS-g-PANI, $W_F = 5.28$ eV, which is higher than that of the

Table 1: Work function of the water soluble conducting polymer compositions used for the HILs/HELs.

Sample code[a]	PFI ratio to PSS-g-PANI	Work function [eV]
PSS-g-PANI	–	5.28
gPNPF321	0.13	5.84
gPNPF161	0.26	5.91
gPNPF81	0.52	6.01
gPNPF41	1.04	6.09

[a] PSS-g-PANI/PFI is abbreviated to gPNPF.

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conventional dispersed conducting polymer, poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT:PSS) ($W_F = 5.1$ eV). We obtained very high W_F values by single spin-coating of blends with the PFI ($W_F = 5.84$, 5.91, 6.01, and 6.09 eV for gPNPF321, gPNPF161, gPNPF81, and gPNPF41), even though the compositions contain very little PFI.

To investigate the molecular distribution of components at the surface of the films, we analyzed the surfaces using XPS analysis. Gaussian–Lorentzian fitting was used to deconvolute the C 1s spectrum of PSS-g-PANI into peaks (Figure 2) at

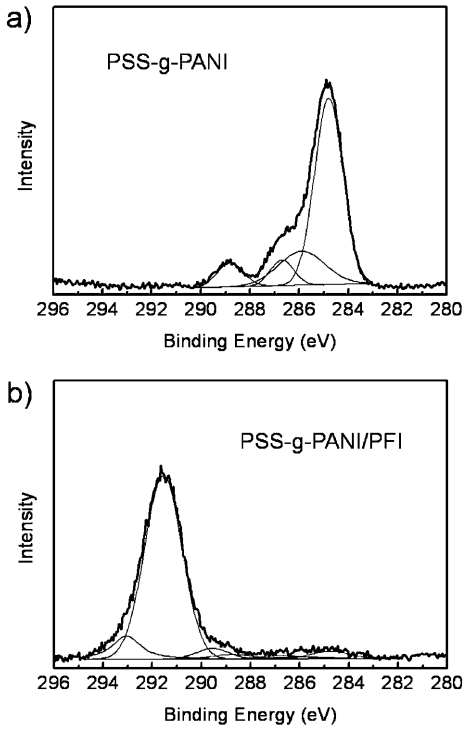

Figure 2. XPS analysis of the self-organized films to investigate the molecular distribution of components. C 1s spectra of a) PSS-g-PANI and b) gPNPF41 layers.

284.8 (C-C/C-H), 285.9 (C=N), 286.7 (C-O), and 288.8 eV (C=O). The C 1s spectrum of the film composed of PSS-g-PANI and PFI has two additional high binding energy peaks, which are attributed to PFI. The area of peaks that are relevant to CF_2 (291.6 eV) and CF_3 (293.9 eV) due to the presence of PFI is much larger than that of lower binding energy peaks. Comparison of UPS and XPS results indicates that the PFI self-organizes on the surface of the films. We confirmed this vertical segregation by performing XPS depth profiling through the film (see Figure S1 in the Supporting Information). The higher PFI concentration at the surface relative to PSS-g-PANI causes the increase in W_F because the perfluorinated chains provide higher ionization potential than the hydrocarbon chains.[5] As a result, the W_F value of HILs/HELs can be controlled by forming self-organized PFI-enriched layers using single spin-coating.

We fabricated (Supporting Information) hole-only devices whose structure was ITO/HIL (40 nm)/NPB (300 nm)/Al with various HILs (ITO = indium tin oxide; NPB = 1,4-bis[(1-

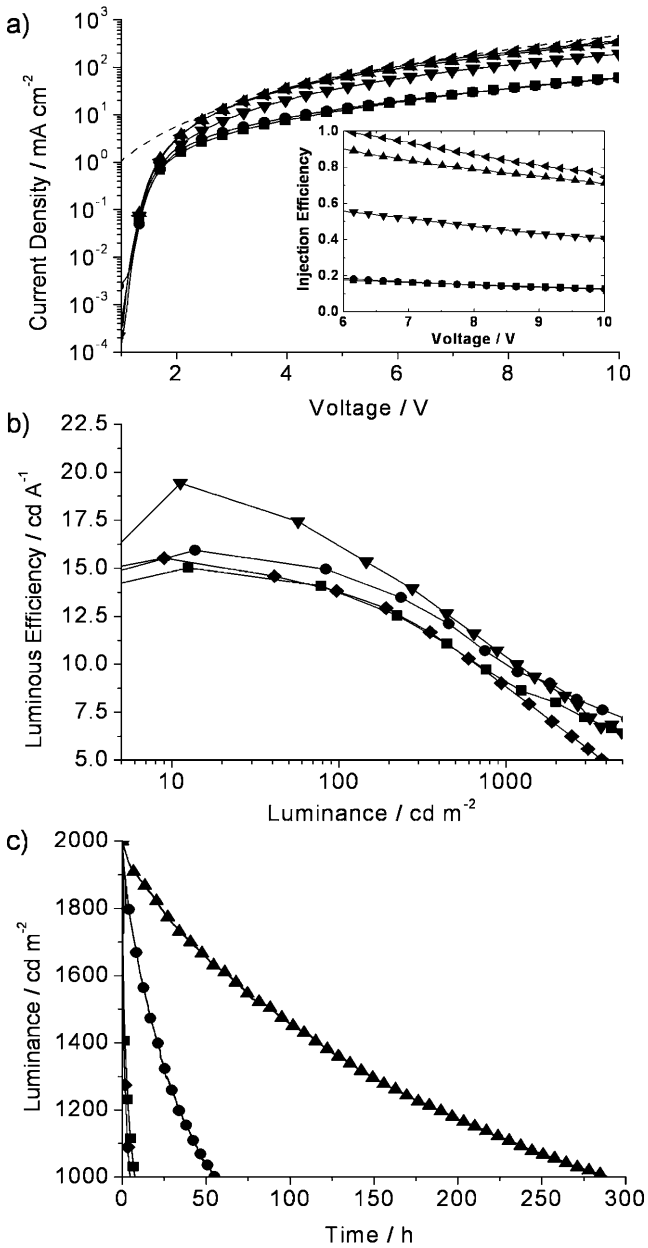

Figure 3. Device characteristics of hole-only devices and OLEDs depending on HILs; PEDOT:PSS (■); PANI:PSS (◆); PSS-g-PANI (●); PSS-g-PANI/PFI : gPNPF161 (◀), gPNPF81 (▲), gPNPF41 (▼); dotted line: calculated current density. a) Hole injection efficiency and current density versus voltage of hole-only devices, b) luminous efficiency versus luminance, c) half-lifetime of small-molecule OLEDs.

naphthylphenyl)amino]biphenyl). Using our HILs with the PFI greatly increased measured current densities J of the hole-only devices (Figure 3a) almost to the ideal J value calculated by combining the space-charge-limited current model and the Poole–Frenkel equation (see the Supporting Information).[10] Hole injection efficiencies η depended on an HIL (inset, Figure 3a; see also the Supporting Information).[11] In gPNPF81 and gPNPF161, $0.7 \leq \eta \leq 1.0$, which is indicative of nearly ohmic contact because the higher W_F facilitated hole injection as a result of the PFI-enriched surface layer. In gPNPF41, $0.4 \leq \eta \leq 0.6$; this lower value can

be attributed to the increased hole injection barrier between the ITO and the gPNPF41 layers by incorporation of a large amount of insulating PFI.

We fabricated (Supporting Information) small-molecule OLEDs using our HILs composed of water-soluble conducting polymer and PFI (device configuration: ITO/HIL/NPB/$Bebq_2$:C545T/$Bebq_2$/Liq/Al; $Bebq_2$ = bis(10-hydroxybenzo [h] quinolinato)-beryllium; Liq = 8-hydroxyquinoline lithium) and measured their luminous efficiencies LE (Figure 3b). The device using PSS-g-PANI as an HIL had an LE value of 15.9 cd A^{-1}, which is slightly higher than those obtained using conventional conducting polymers (PEDOT:PSS, LE = 15.0 cd A^{-1}; PANI:PSS, LE = 15.5 cd A^{-1}). In the device using gPNPF41 as the HIL, LE = 19.4 cd A^{-1}. Because the self-organized PFI layer at the surface of an HIL both blocks electrons from the emitting layer and improves hole injection, this high LE value resulted from the efficient electron–hole recombination in the emitting layer.

Devices fabricated using PSS-g-PANI had remarkably longer device half-lifetimes LT_{50} (ca. 55 h) than devices fabricated using conventional water-dispersed conducting polymers such as PEDOT:PSS (ca. 7.6 h) and PANI:PSS (ca. 4.8 h) (Figure 3c); we attribute this increase to high stability of PSS doping in PSS-g-PANI. The maximum lifetime among devices was 290 h using PSS-g-PANI/PFI (gPNPF81), which is around 38 times longer than the LT_{50} obtained using PEDOT:PSS. The increased LT_{50} value occurs because the PFI surface layer blocks atomic (In/Sn) diffusion from the ITO to the emitting layer[5] and improves hole injection/electron blocking.

We fabricated (Supporting Information) OPVs using PSS-g-PANI with PFI as HELs (device configuration: ITO/HEL/P3HT:PCBM/BaF_2/Al; P3HT = Poly(3-hexylthiophene); PCBM = [6,6]-phenyl C60-butyric acid methyl ester), then measured their current density versus voltage characteristics (Figure 4a) and half-lifetimes (Figure 4b). The power conversion efficiencies of OPVs using PSS-g-PANI (3.3%) and PSS-g-PANI/PFI (3.4%) were slightly higher than those of the standard devices using PANI/PSS (ca. 3.2%) and PEDOT:PSS (ca. 3.2%) (Figure 4a). In OPV devices, the W_F value did not significantly influence the hole extraction because the W_F value of HELs (> 5.2 eV) is pinned to the HOMO level of a photoactive donor (5.2 eV). Because our HELs (PSS-g-PANI/PFI) have a low surface energy (ca. 20 mN m^{-1}) due to PFI-enriched surface layer, P3HT will be more enriched on the HEL surface as a result of the different phase segregation of P3HT:PCBM.[12] However, the device performance was not greatly affected by interfacial segregation of P3HT:PCBM.[12] PFI-enriched surface of HELs in OPVs significantly increased the LT_{50} value. In the OPV using PSS-g-PANI/PFI, $LT_{50} \approx 570$ h; in that using PSS-g-PANI, $LT_{50} \approx 267$ h; both are much greater than in the OPV using PEDOT:PSS ($LT_{50} \approx 186$ h).

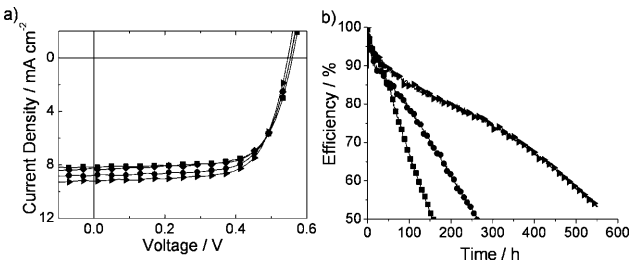

Figure 4. Device characteristics of OPVs with different HILs; PEDOT:PSS (■); PANI:PSS (◆); PSS-g-PANI (●); PSS-g-PANI/PFI (▶, gPNPF321). a) Current density–voltage curve for illumination of 100 mW cm^{-2}, b) device stability measurement under constant illumination (100 mW cm^{-2}) until normalized power conversion efficiencies were reduced by half.

We introduced water-soluble PSS-g-PANI based compositions with tunable W_F values. By single spin-coating of compositions of PSS-g-PANI/PFI, the PFI self-organizes at the surface of the films and increases the W_F value significantly. We achieved a very high LE value (19.4 cd A^{-1}) from OLEDs as a result of enhanced electron–hole recombination. A remarkable increase in device lifetime of OLEDs and OPVs was achieved, which can be attributed to high doping stability of PSS-g-PANI and the diffusion blocking capability of the self-organized PFI surface layer. Water-soluble PSS-g-PANI compositions with a self-organized surface layer appear to be good candidates for reliable HILs/HELs in organic optoelectronic devices.

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