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Hole-injecting conducting-polymer compositions for highly efficient and stable organic light-emitting diodes

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This letter introduces conducting polymer compositions which can be used for hole-injection layer in organic light-emitting diodes. The compositions are composed of poly(3,4-ethylenedioxythiophene) (PEDOT), polystyrene sulfonic acid (PSS) and a perfluorinated ionomer. The films based on these compositions showed much higher workfunction (~ 5.3 – 5.7 eV) than conventional PEDOT/PSS (~ 5.0 – 5.2 eV). When we fabricated blue polymer light-emitting diodes by using these compositions as a hole-injection layer, the luminescent efficiency was improved and the device lifetime was also enhanced relative to the device using the commercially available PEDOT/PSS. These compositions including perfluorinated ionomers can be one of the promising candidates for a hole-injection layer in organic light-emitting devices. © 2005 American Institute of Physics. [DOI: 10.1063/1.2132072]

Since the report of polymer light-emitting diodes (PLEDs) in 1990,¹ the device efficiency and lifetime have been improved gradually. However, the device lifetime still does not meet the requirements for real commercialization. Especially, the lifetime of blue PLEDs is still much shorter than those of green and red color PLED devices. Therefore, although the reliability of the emitting material itself makes a dominant effect on the device lifetime, several approaches for the improvement of the device lifetime in PLEDs have been reported by improving the hole-injection layer (HIL) or by introducing a hole transporting interlayer between the HIL and the emitting layer.^{2,3} Conducting polymer films such as polyaniline, polypyrrole, poly(3,4-ethylene dioxothiophene)(PEDOT)^{4–8} on indium tin oxide (ITO) layer play important roles to improve the device efficiency and the stability because they can enhance the hole injection from the ITO (workfunction: ~ 4.7 – 5.0 eV) and planarize the ITO surface. The commercially available well-known HIL materials are Baytron P series from H. C. Starck, GmbH which are composed of PEDOT and polystyrene sulfonate (PSS) in aqueous solution.⁹ However, PEDOT/PSS has a relatively low workfunction of ~ 5.0 – 5.2 eV⁹ so that the hole injection could be a limiting factor in device performance. For example, the highest occupied molecular orbital (HOMO) level of poly(9,9-dioctylfluorene) (PFO) has been estimated to be ~ 5.9 eV¹⁰ so that the hole injecting energy barrier between PEDOT/PSS and PFO can be as large as 0.7–0.9 eV. Until now, there have not been conducting polymer materials currently available which have also a high enough workfunction to be able to act as an intermediate hole injection layer between the ITO and the emitting layer by providing intermediate energy levels at preferentially 5.4–5.8 eV. Therefore, it is necessary to develop hole injecting materials whose the workfunction is close to or even below the HOMO level of semiconducting polymers which are located next to the HIL. Although a dramatic improvement of the lifetime due to

PEDOT/PSS layer can be achieved, the acidic nature of PEDOT/PSS etches ITO and then indium can migrate into PEDOT/PSS.¹¹ In addition, the degradation of organic LEDs including PEDOT/PSS may be at least partially due to degradation of the PEDOT/PSS film itself during the operation of the devices.¹² In this letter, we introduce hole-injecting conducting polymer compositions including a perfluorinated ionomer, which have high workfunction and improved not only the PLED device efficiency but also the device stability when they were employed as a HIL.

Figure 1 shows the chemical structures of the materials we used to formulate conducting polymer compositions for the HIL in OLEDs. Two different PEDOT/PSS (Baytron P H and Baytron P AI4083) products in aqueous solution were purchased from H. C. Starck. A 5 wt% perfluorinated ionomer (PFI) in mixture of water and alcohol (4.5: 5.5 in volume), was purchased from Aldrich Co. Baytron P H (Sample A) is composed of PEDOT and PSS but the weight ratio is 1:2.5 and the measured conductivity was 1.5×10^{-1} S/cm.

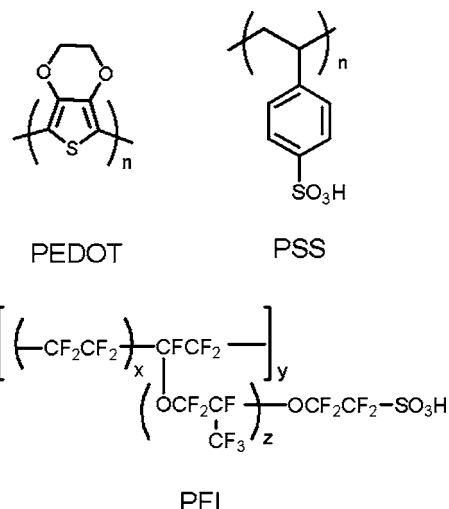


FIG. 1. Chemical structures used in the formulated hole-injecting conducting polymer compositions.

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TABLE I. The five different conducting polymer compositions and their workfunction levels of the films.

Sample	PEDOT/PSS/PFI	PH: 5 wt % PFI	Workfunction (eV)
A	1/2.5/0	1:0	5.05
B	1/2.5/2.92	4:1	5.26
C	1/2.5/5.84	2:1	5.46
D	1/2.5/11.67	1:1	5.70
E	1/6.0/0	AI4083	5.12

Baytron P AI4083 (Sample E) is also composed of PEDOT and PSS at the 1:6 weight ratio and the measured conductivity was 6.06×10^{-4} S/cm. We reformulated the Baytron P H with adding 5 wt% PFI resin. We coded the reformulated samples from B to D with changing the compositions as Table I shows. The workfunction levels were measured by ultraviolet photoelectron spectroscopy. The results are summarized in Table I.

As the content of PFI increases, the workfunction levels also increase. Eventually, we obtained a composition (Sample D) with very high workfunction (5.7 eV). To investigate the effect of PFI on the compositions, we performed density-functional theory calculations to obtain the dipole moments, the ionization potential (IP) and the deprotonation energy (DP)¹³ which are summarized in Table II. All calculations were performed at the B3LYP/6-31G(d,p) level by using GAUSSIAN 98 program.¹⁴ We compared the hetero fluorocarbon sulfonic acids with hydrocarbon [hetero alkyl and alkyl substituted benzene (Ph)] sulfonic acids with changing the chain length. The simulation results showed that the IP levels and the dipole moments of the former are below than those of the latter when the sulfonic acids are deprotonated. In addition, DPs of the hetero fluorocarbon sulfonic acids are lower than those of hydrocarbon sulfonic acids (PSS) so that they can be easily deprotonated. The IP levels and the DPs were not changed as the chain length increases. Therefore, we can infer that the polymers with the hetero fluorocarbon sulfonic acids like PFI can also have lower IP levels with respect to the vacuum level than polystyrene sulfonic acids. To observe the effect of PFI on the workfunction of ITO surface, we formed a self-assembled monolayer on ITO surface by immersing the UV-ozone-treated ITO into the 0.5 wt% PFI solution. Then, it was observed that the water contact angle of the PFI-modified ITO was increased from

55° to 81° which implies the surface became highly hydrophobic and the workfunction was also increased by ~0.5 eV. Therefore, the high workfunction energy levels in the PEDOT/PFI compositions can stem from the properties of the PFI itself which has lower IP levels and higher dipole moments. We also observed by x-ray photoemission spectroscopy that the concentration of the fluorinated carbon chains of PFI have a tendency for a gradual increase toward the top surface of the films.¹⁵ Therefore, our compositions composed of Baytron P H and PFI could have a gradual increase of the workfunction from the bottom to the top surface.¹⁵

We fabricated polymer LEDs by using the conducting polymer compositions, B–D as a HIL and compared with the devices by using the conventional PEDOT/PSS, A and E. The A–E conducting polymer compositions were spincoated to give 50 nm thicknesses on top of ITO/glass. We spin coated a Samsung proprietary blue-emitting polymer (called, DS9) to give 70 nm thickness. The DS9 has the band gap energy of ~2.7 eV and the HOMO level is ~5.3 eV. The Commission Internationale de L'Eclairage 1931 coordinate of the devices was (0.15, 0.30). We deposited 4 nm BaF₂, 2.7 nm Ca, 150 nm Al sequentially on top of the emitting layer. After encapsulating the device in the glass cap with a UV curable resin, the current-voltage-luminescence (*I-V-L*) characteristics were obtained with a Keithley 238 source-measure unit and a Photo Research PR650 spectrophotometer.

As Fig. 2(a) shows, we compared the device power efficiency for the devices using A–E as a HIL. The device with composition D with the highest workfunction (5.7 eV) showed the highest efficiency value (6.87 lm/W, 9.23 ± 0.102 cd/A for six devices) while the device with composition A (i.e., Baytron P H) with the lowest workfunction (5.05 eV) showed the lowest efficiency value (3.28 lm/W, 6.68 ± 0.108 cd/A for six devices). When we compared the efficiency for the A–D using the same Baytron P H, the power efficiency tended to depend on the workfunction of the A–D compositions. We also compared with the device with the composition E (i.e., Baytron P AI4083) which has been mostly used as a HIL in polymer LEDs. Although the device showed the maximum power efficiency of 5.72 lm/W or the maximum current efficiency of 7.90 cd/A, it is lower than that of the device with composition D. Figure 2(b) shows the comparison of *I-V-L* charac-

TABLE II. Calculated dipole moments, ionization potential (IP) and deprotonation energy (DP) of the end groups obtained by density-functional theory calculations.

End groups	Dipole (neutral) (Debye)	Dipole (deprotonated) (Debye)	IP (eV)	DP (kcal/mol)
CH ₂ CH ₂ SO ₃ H	3.395	4.935	-8.287	336.3
CH ₃ -O-CH ₂ CH ₂ SO ₃ H	2.681	8.154	-7.424	332.8
(CH ₃) ₂ CH-O-CH ₂ -(CH ₃)CH-O-CH ₂ CH ₂ SO ₃ H	3.807	19.522	-6.943	332.6
CF ₂ CF ₂ SO ₃ H	2.800	6.248	-9.316	316.0
CF ₃ -O-CF ₂ CF ₂ SO ₃ H	2.578	10.107	-9.248	314.4
(CF ₃) ₂ CF-O-CF ₂ -(CF ₃)CF-O-CF ₂ CF ₂ SO ₃ H	2.719	21.940	-9.264	314.3
Ph-SO ₃ H ^a	4.361	8.116	-7.549	332.5
(CH ₃) ₂ CH-Ph-SO ₃ H	3.950	13.310	-7.252	333.3

^aPh=phenyl.

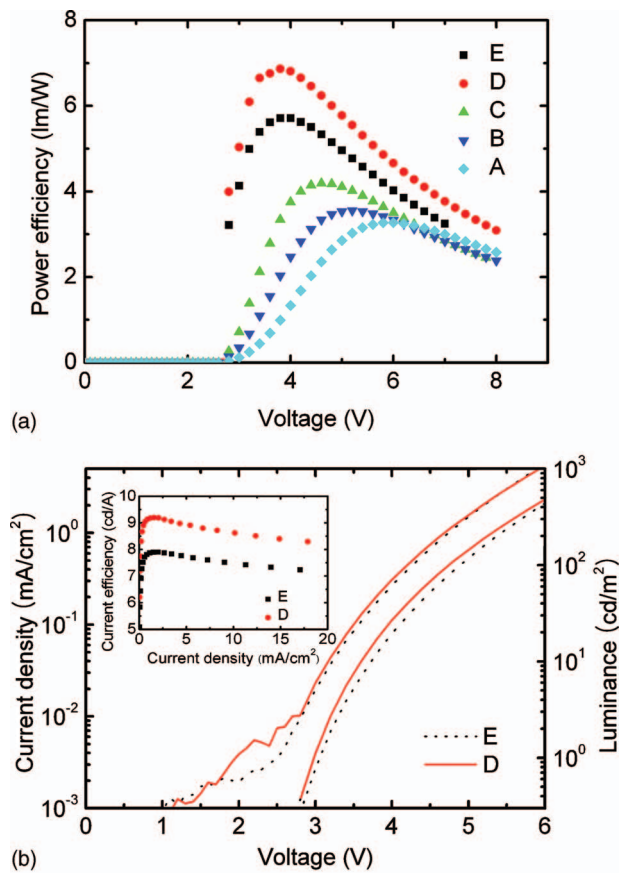


FIG. 2. (Color) (a) Power efficiencies of the devices using A–E compositions as a HIL. (b) The I - V - L characteristics of devices using D compared with the device using E. The inset shows the current efficiency of the devices using D and E.

teristics of the two devices using D and E. Despite the lower film conductivity of D (2.00×10^{-4} S/cm) than that of E (6.06×10^{-4} S/cm), the device with D showed slightly lower operating voltages and higher device efficiency as the inset of Fig. 2(b) shows. Since the device of our blue emitting polymer has electron-rich characteristics, the I - V characteristics can be much more dominated by the electrons rather than holes. Therefore, the more favorable hole injection from the HIL to the emitting layer can result in higher device efficiency.

We also tested the device lifetime of the device using A–E as a HIL at initial luminance 700 cd/m^2 (see Fig. 3) after 15 min aging at 700 cd/m^2 . Although the driving current of the device using B at 700 cd/m^2 was the highest among the device using A–E, the half lifetime was the longest. This indicates that the compositions including perfluorinated ionomers can be one of the promising hole-injection buffer materials for enhancing the device lifetime. However, as the content of PFI increased in the compositions, the lifetime tended to decrease. We are still under investigation on this. We do not also exclude the possibility of the adverse effect of impurities in the solution on the device lifetime because we have used the PFI solution without any further purification as received from the supplier. We believe that the fluorocarbon sulfonic acids in the compositions can be effectively employed to improve the device lifetime since the fluorocarbon has intrinsically a good chemical stability and

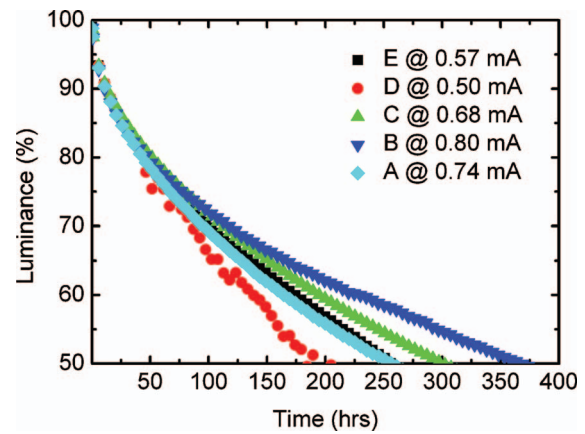


FIG. 3. (Color) The luminance decay of the devices using A–E as a HIL with the function of time. The initial luminance was 700 cd/m^2 .

hydrophobicity. In fact, our HIL materials are less sensitive to the moisture relative to the conventional PEDOT/PSS. We are now still under further investigation about the exact mechanism of the lifetime enhancement.

In summary, we introduce hole-injecting conducting polymer compositions with perfluorinated ionomers which improves the device efficiency and the lifetime. Although the conventional PEDOT/PSS exhibited relatively low workfunction levels of ~ 5.0 – 5.2 eV, one of our compositions (i.e., D) showed a very high workfunction level (5.7 eV). As a result, the device efficiency of the device using D was improved (6.87 lm/W or 9.23 cd/A) compared with the conventional PEDOT/PSS (i.e., A and E). Our device using B showed $\sim 45\%$ improvement of device lifetime relative to those using A and E. Therefore, these compositions using fluorocarbon sulfonic acid can be one of the promising materials as a HIL for enhancing the device efficiency and the lifetime.

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