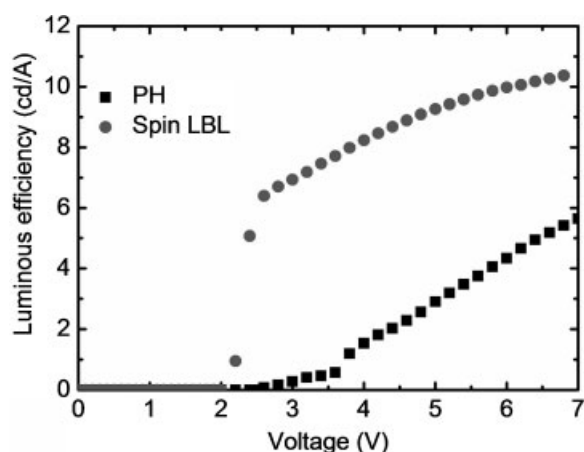


# Layer-by-Layer Spin Self-Assembled Hole Injection Layers Containing a Perfluorinated Ionomer for Efficient Polymer Light-Emitting Diodes

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Deposition of hole injection layers including a perfluorinated ionomer has been demonstrated using layer-by-layer spin self-assembly for enhanced device efficiency and lifetime in PLEDs. We show that the LBL spin self-assembled thin films enable to control work functions of indium-tin oxide anodes by changing the PFI concentration and that a resulting green-emitting device has an enhanced luminescence efficiency and 18 times longer half lifetime than a device using a conventional HIL. We also fabricate a gradient of energy levels by the LBL self-assembly of the PFI that results in a work function of 5.74 eV, which can be used to improve carrier injection even for an emitting layer whose ionization potential is over 5.7 eV.



## Introduction

Achieving a charge balance by controlling carrier injection and transport has been one of the most interesting studies to enhance luminous efficiency and operational lifetime of organic/polymeric light-emitting diodes (LEDs).<sup>[1,2]</sup> Difference in energy levels between working electrodes and emitting materials in organic or polymer LEDs, and a resulting Schottky energy barrier to carrier injection have provoked to develop numerous approaches to match work

functions of electrodes with electron affinity ( $E_A$ ) and ionization potential ( $I_P$ ) of the emitting materials. For balanced injection of electrons and holes and efficient exciton formation, multilayered device structures have been suggested with modifying cathode and anode sides by introducing hole/electron injection<sup>[3–6]</sup> or transport layers.<sup>[7,8]</sup>

Of particular interest in this communication is to improve hole injection performance at indium-tin oxide (ITO) anode by engineering the hole injection layer (HIL). The most popular HIL has been poly(3,4-ethylene dioxythiophene) (PEDOT) doped with polystyrene sulfonate (PSS) as it enables to provide stable, conductive contact with the ITO surface and to enhance device efficiency by their work functions typically in between the work

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function of the ITO ( $\approx 4.7$ – $5.0$  eV) and the ionization potential [ $I_p$ , the negative of the highest occupied molecular orbital (HOMO)] of emitting materials.<sup>[9]</sup> However, the work functions of the polymers are relatively low compared to the  $I_p$  of the emitting materials. For example, well-known commercial HIL materials, Baytron P series from H. C. Starck, GmbH, which are composed of PEDOT and PSS, have work functions of  $\approx 5.0$ – $5.2$  eV<sup>[9]</sup> while the  $I_p$  of light-emitting polyfluorenes is typically above 5.5 eV; thus the HIL is still a limiting factor for efficient device performance.

In this communication, we investigate the controllability of a perfluorinated ionomer (PFI) on the work functions of ITO anode when the PFI was layer-by-layer (LBL) spin self-assembled with PEDOT:PSS and a polycation (Scheme 1). We have recently been interested in the capability of the PFI for energy level control when the ionomer is mixed with PEDOT:PSS in different ratios and coated onto ITO surfaces. From our density-functional theory calculations, it was presumed that the fluorination of hydrocarbon sulfonic acids (PSS) resulted in increase of  $I_p$  levels and higher dipole moment than those of PSS when the sulfonic acids were deprotonated.<sup>[10]</sup> Thus, work functions of the ITO electrode could be adjusted by mixing PEDOT:PSS with the PFI, followed by spin coating on the ITO surface. Using the LBL spin self-assembly, we intend to precisely control the deposition of HILs with a specific energy level. Furthermore, we attempt to make a gradient of these controllable energy levels as ideal hole injection can be achieved if holes hop over graded energy levels organized from an anode to an emitting layer. This concept has also been demonstrated by assembling PEDOT:PSS with varying doping levels<sup>[11]</sup> or semiconducting nanocrystals with differing energy gaps by size control.<sup>[12]</sup>

The LBL self-assembly of polyelectrolyte multilayers, which was rediscovered in the early 1990s by Decher and Hong,<sup>[13,14]</sup> is a powerfully versatile technique to deposit thin films with a fine control over compositions, thickness and properties for numerous applications including

optoelectronics,<sup>[15]</sup> bio/chemical sensors,<sup>[16]</sup> energy-related devices,<sup>[17]</sup> and drug delivery.<sup>[18]</sup> Furthermore, when the technique is combined with spin-assembly as demonstrated by Char and coworkers<sup>[19,20]</sup> and Wang and coworkers,<sup>[21]</sup> it provides less interdiffusion of matters between deposited layers in a time-saving and more well-organized way, which is a big advantage for real-device fabrication. In this work, using the LBL spin self-assembly, we deposited ultrathin multilayer films of a polycation, poly(allylamine hydrochloride) (PAH), and anionic PEDOT:PSS:PFI mixtures on ITO surfaces with adjusting PFI concentration in the anionic solution mixtures from 0 to 0.1 wt.-% and investigated the work function controllability of the resulting ITO anodes and device performance.

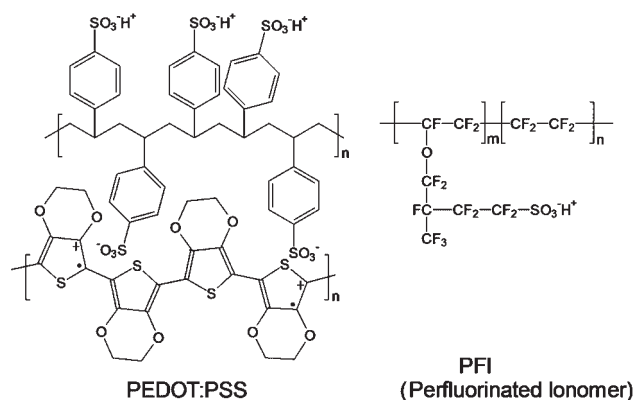
## Experimental Part

### Materials

A 1.18 wt.-% aqueous dispersion of PEDOT:PSS (Baytron PH in which the molar ratio of the monomer units is 1:2.5) was purchased from H. C. Starck, GmbH. A PFI (5 wt.-% in water/alcohol), PAH (MW  $\approx 70$  kDa), and organic solvents were purchased from Aldrich Chemical Co. and used as received. A green-emitting polyfluorene derivative (LUMATION 1300 series Green Polymer,  $\overline{M}_n = 64$  kDa,  $\overline{M}_w = 150$  kDa, HOMO =  $-5.55$  eV, lowest unoccupied molecular orbital =  $-3.05$  eV) was supplied by Dow Chemical Company.

### Hole Injection Layer Assembly

ITO-coated glass substrates (surface resistivity  $\approx 9 \Omega \cdot \text{sq}^{-1}$ ) were sonicated in dichloroethane, methanol, and isopropyl alcohol for 15 min consecutively, and dried at  $70^\circ\text{C}$  for 30 min. The substrates were treated under ultraviolet/ozone for 15 min right before spin coating. The LBL spin self-assembly was carried out by alternating spin coating of polyelectrolytes starting from a 10 mmol PAH solution and using 0.05–0.1 wt.-% PEDOT:PSS:PFI solutions. The mixture solutions of PEDOT:PSS:PFI were prepared by diluting the original solutions of PEDOT:PSS and PFI with deionized water to 0.05 and 0.1 wt.-%, respectively, followed by mixing both solutions and by sonicating the resulting solutions for 30 min. PFI concentrations were varied from 0 to 0.1 wt.-% in the anionic polymer mixtures. For the spin self-assembly that was conducted in a class 10 cleanroom, polyelectrolyte solutions (2–4 mL) filtered by  $0.45 \mu\text{m}$  pore-sized PVDF syringe filters were applied onto the ITO-glass substrates to fully cover the surfaces and spun at 2500 rpm for 20 s. After spin-assembling polyelectrolytes, the substrates were thoroughly rinsed twice with copious deionized water at the identical spin conditions. After assembling multilayers of polyelectrolytes, the substrates were dried at  $90^\circ\text{C}$  for 1 h in vacuum, and baked at  $200^\circ\text{C}$  on a hot plate for 10 min in an ambient atmosphere before measuring contact angles, atomic force microscopy (AFM) images, and work functions of the ITO substrates.



■ Scheme 1. Chemical structures of polymers.

### Polymer Light-Emitting Diode (PLED) Fabrication

For comparison, two different kinds of HIL films, PEDOT:PSS (Baytron PH) and LBL films of PEDOT:PSS:PFI and PAH were deposited on top of ITO (work function 4.9 eV) in air by spin coating and dried as described above. Then, the films were baked on the hotplate in N<sub>2</sub> glove box at 200 °C for 10 min. The green-emitting polyfluorene derivative dissolved in toluene was spin-coated upon the HIL layers to obtain an emitting layer with 80 nm thickness, which was subsequently baked at 130 °C for 15 min. The 5 nm Ba and 150 nm Al cathode layers were sequentially deposited on the emitting layer under vacuum below  $5 \times 10^{-7}$  torr. The PLED devices were encapsulated with a glass lid by using a UV curable epoxy resin.

### Characterizations

Contact angle values were obtained by averaging four measurements using a goniometer to trace changes of surface properties with varying PFI concentrations. Surface morphologies, roughness, and assembled film thickness were characterized by using a surface profilometer and an AFM (Veeco Instruments, Model Dimension 3100) equipped with a carbon nanotube tip. Work functions of the modified ITO substrates were measured at an atmospheric pressure using an ultraviolet photoelectron spectrometer for usage in air (Surface Analyzer, Model AC-2, Riken-Keiki Co., Japan). Current-voltage-luminescence (*I-V-L*) characteristics were obtained with a Keithley 238 source-measure unit and a Photo Research PR650 spectrophotometer. Device lifetime was recorded starting at initial luminance 2 000 cd · m<sup>-2</sup> by using the McScience Polaronix™ OLED Lifetime Test System.

### Results and Discussion

In assembling LBL multilayer thin films, it is supposed that both PEDOT:PSS and PFI have negative charges and form ionic bonding with the polycation, PAH, based on electrostatic interactions, enabling the deposition of thin films on surfaces, together with other attractive interaction forces such as hydrophobic and secondary interactions. As for the PEDOT:PSS, PEDOT is doped with PSS and can be dispersed in water by the excess sulfonic acid groups due to non-stoichiometric mixing, assuming particulate aqueous dispersion with negatively charged surface character.<sup>[22]</sup> The same negative surface charges are also expected for PFI. The conformation of PFI in solution highly depends on solvents because the ionomer has both strongly hydrophobic CF<sub>2</sub> groups and hydrophilic sulfonic acids. Since the PFI solution is not a true solution but a dispersion in a powerful solvent mixture (water/1-propanol/2-propanol/methanol/petroleum ether = 45:22.5:22.5:5:5), the structure of the dispersion might be controlled by adjusting the solvent mixing ratio.<sup>[23,24]</sup> Water interacts with the sulfonic acid group while hydroxyl and hydrophobic methylene/methyl groups in organic solvents can solvate

fluoroether and perfluorinated moieties. It is presumed that ionic sulfonic acid groups go outward on the surface while hydrophobic perfluorinated groups are associated into the core of the particulate dispersion as water content increases and hydrophobic alcohol portion decreases. We intended to maximize the sulfonic acid groups on PFI particulate surfaces by diluting the original 5 wt.-% PFI solution with solely water to 0.1 wt.-%, which resulted in PFI dispersion with 98.9% water. PAH, which is a weak polybase and its degree of ionization is pH-dependent, is used without controlling solution pH and ionic strength. This means the solution pH in a range of 3.0–3.5 where primary amines of polymer chains are fully ionized.<sup>[25,26]</sup>

For a good control over energy levels by varying the concentration of PFI in a thin film structure, an LBL assembly assisted by a spinning process is preferred. Spin-assembled LBL polyelectrolyte multilayers provide highly ordered layer structures as the technique does not allow a time enough for polyelectrolyte chains to diffuse into the preadsorbed layer structures. In contrast, significant interdiffusion of chains and consequent fuzzy interlayer structures are representative characteristics of LBL multilayers assembled via a dipping process. As demonstrated by X-ray reflectivity characterization of multilayers composed of polyelectrolytes and quantum dots,<sup>[19,20]</sup> spin-assembled LBL multilayers present thinner layers due to spreading out of polymer chains under centrifugal and air shear forces, and discrete interfaces between layers. When PEDOT:PSS and PFI are assembled with PAH via the spin-assisted LBL process, one can expect well-organized gradient of PFI through the thin film structure.

In this work, the anionic mixtures of PEDOT:PSS and PFI were encoded as PEDOT:PSS:PFI-*N* in which the number *N* (*N* = 1, 2, 3, 4, and 5) represent a mixing ratio with a specific PFI portion varying from 0 to 0.1 wt.-% (Table 1). Six bilayers of PEDOT:PSS:PFI-*N* and PAH that were denoted as [PAH/PEDOT:PSS:PFI-*N*]<sub>6</sub> were assembled to first evaluate the work functions at a specific PFI concentration. As an example, [PAH/PEDOT:PSS:PFI-1]<sub>6</sub> is a six-bilayer assembly of PAH and the anionic mixture with 0 wt.-% PFI. Then, another six bilayers with grading PFI concentrations, [PAH/PEDOT:PSS:PFI-*G*]<sub>6</sub>, were assembled. In this assembly, the gradient of PFI concentrations was achieved by using the anionic mixture with the mixing ratio number *N* for the *N*th bilayer. The anionic mixture with the mixing ratio number 5 (0.1 wt.-% PFI) was once more applied to the sixth bilayer to ensure a full covering of the surface by PFI, which might block migration of metal ions (In and Sn) decomposed from an ITO electrode during device operation and thus increase device lifetime.

Varying water contact angle values explicitly reflected the PFI concentration in the [PAH/PEDOT:PSS:PFI-*N*]<sub>6</sub> thin films. As summarized in Table 1, the contact angle values

**Table 1.** LBL multilayer thin film structures assembled with PEDOT:PSS, PFI and PAH, and contact angle variation of the thin films.

LBL spin self-assembled thin film structure	Baytron PH:PFI wt.-% in anionic polymer solution mixtures	Static contact angle (water probe)
[PAH/(PEDOT:PSS:PFI-1)] <sub>6</sub>	0.05:0	62.7°
[PAH/(PEDOT:PSS:PFI-2)] <sub>6</sub>	0.038:0.025	66.9°
[PAH/(PEDOT:PSS:PFI-3)] <sub>6</sub>	0.025:0.05	79.6°
[PAH/(PEDOT:PSS:PFI-4)] <sub>6</sub>	0.013:0.075	87.3°
[PAH/(PEDOT:PSS:PFI-5)] <sub>6</sub>	0:0.1	101.6°
[PAH/(PEDOT:PSS:PFI-G <sup>a</sup> )] <sub>6</sub>	PFI wt.-% in layers: 1 <sup>st</sup> = 0, 2 <sup>nd</sup> = 0.025, 3 <sup>rd</sup> = 0.05, 4 <sup>th</sup> = 0.075, 5 <sup>th</sup> = 0.1, 6 <sup>th</sup> = 0.1	1 <sup>st</sup> = 50.4°, 2 <sup>nd</sup> = 56.6°, 3 <sup>rd</sup> = 74.1°, 4 <sup>th</sup> = 65.5°, 5 <sup>th</sup> = 95.0°, 6 <sup>th</sup> = 98.2°

<sup>a</sup>) Gradient of PFI concentrations.

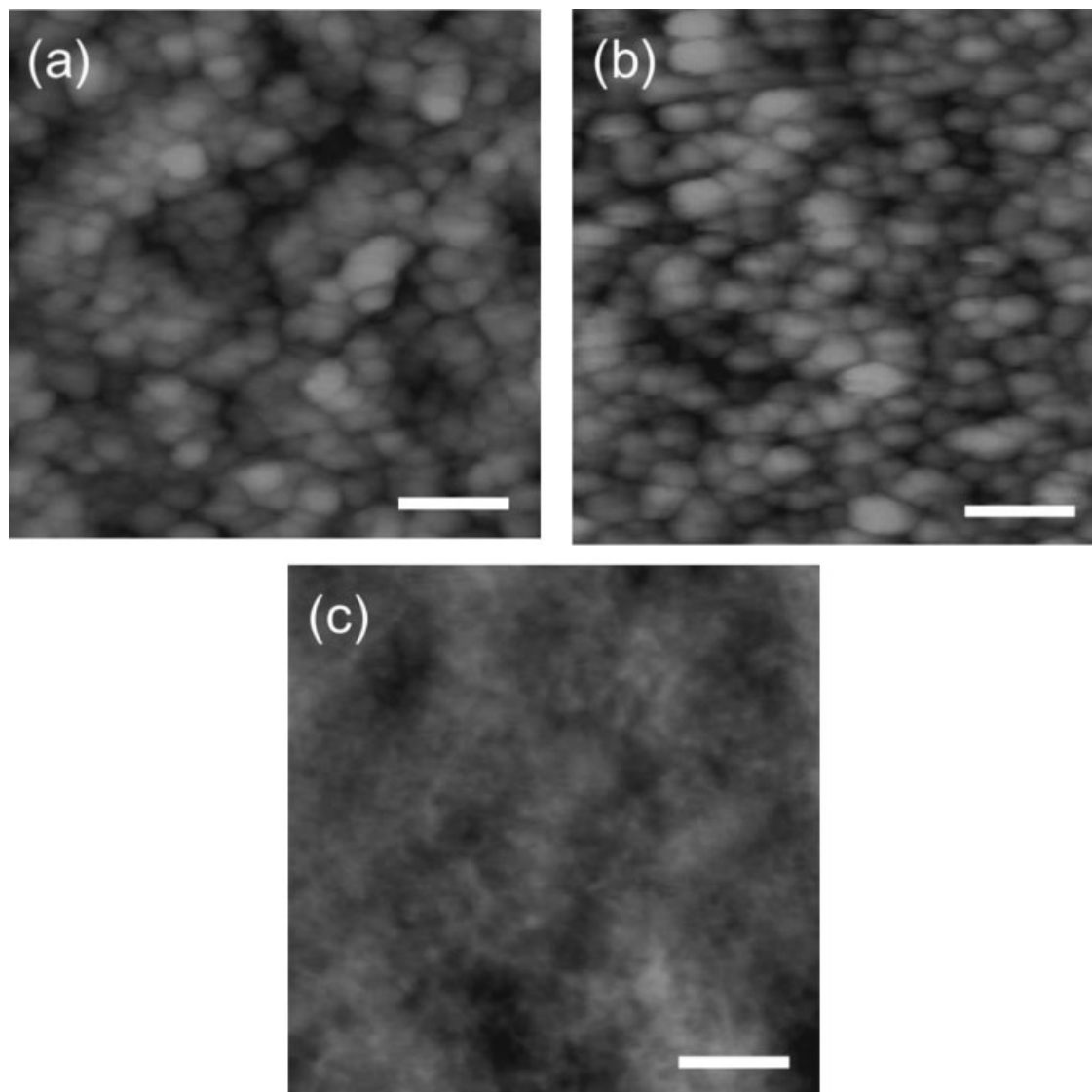
of LBL assemblies with a specific PFI concentration increased from 62.7 to 101.6° with PFI portion increasing from 0 to 0.1 wt.-% in anionic solution mixtures. For the [PAH/PEDOT:PSS:PFI-G]<sub>6</sub>, water contact angle values increased with depositing bilayers from 50.4 to 98.2° representing the varying PFI concentrations, but were a little lower than [PAH/PEDOT:PSS:PFI-5]<sub>6</sub> thin films with homogeneous PFI concentrations. Also, the values showed an irregular transition from the third to the fourth bilayer in which the contact angle after the fourth bilayer deposition was lower than that after the third bilayer deposition. These results indicate that a bilayer coating might not completely cover the surface being affected by the previously deposited layers. It was reported that in the cases of spin-assembled LBL thin films composed of nanoparticles and polyelectrolytes the particles with a diameter below 10 nm can fully cover the surface.<sup>[19,20]</sup> In contrast, particles with over 20 nm diameters cannot completely cover the surface and newly deposited particles might fill up empty spaces of the previously deposited particle layers.<sup>[27]</sup> Aqueous dispersion of PEDOT:PSS:PFI is not hard sphere like inorganic nanoparticles, but the particulates of the dispersion might have a diameter over 20 nm as later shown in AFM results, so we think that a similar style deposition might occur. Although there seems to exist the imperfect covering of an anionic mixture in a bilayer deposition with a specific PFI concentration, the increasing contact angles with LBL deposition are relatively well matched to those of homogeneous thin films, proving a gradient of PFI concentrations in the thin film structure and that the covering is reasonably complete.

Surface morphologies and thin film thickness studied using AFM technique show noticeable images. Figure 1(a) and 1(b) are representative surface images in a height mode after assembling six bilayers of PEDOT:PSS:PFI and PAH with 0 wt.-% PFI [Figure 1(a)] and 0.1 wt.-% PFI

[Figure 1(b)]. In both cases, a few tens of nanometer-sized polymer aggregates were formed on the surface. The exact sizes of the aggregates evaluated after correcting effects<sup>[28]</sup> from the radius of the carbon nanotube tip (5 nm) were in the range of 21–38 nm in both the samples. Interestingly, the aggregates in the same size range were formed in all polyelectrolyte assemblies in this work, irrespective of the mixing ratio in the anionic mixtures. It is presumed that the dilution of the original PEDOT:PSS and PFI solutions to 0.1 wt.-% and sonication results in particulate dispersions of polymers with anionic surface character and with a few tens of nanometers diameter. A comparison to the PEDOT:PSS:PFI thin film coated from a denser solution supports this presumption. When the original PEDOT:PSS (1.18 wt.-%) and PFI (5 wt.-%) solutions were mixed with each other in 1:1 volume ratio (3.09% of solid content) and spun on an ITO glass substrate at 2 500 rpm giving about a 50 nm thick thin film, we could not observe such aggregates of polymers, as shown in Figure 1(c). Thin film depositions with increasing layer numbers were monitored by scanning surfaces scratched by a blade using the AFM and a profilometer as the thin films coated on ITO-glass substrates were not appropriate for ultraviolet absorption or ellipsometry experiments. For all the six-bilayer samples, a bilayer thickness measured after each deposition step was about 5 nm and the total thin film thicknesses were 30 ± 2.3 nm with surface roughness in the range of 1.7–2.2 nm, which show regular deposition of LBL thin films.

Work function levels investigated by photoelectron spectroscopy illustrated in Figure 2 show a clear controllability, increasing with PFI concentration. For the homogeneous thin films, when 0 wt.-% PFI was used ([PAH/PEDOT:PSS:PFI-1]<sub>6</sub>), the work function was 5.01 eV, which coincides with the value known for Baytron PH (PEDOT:PSS).<sup>[9]</sup> The homogeneous thin film

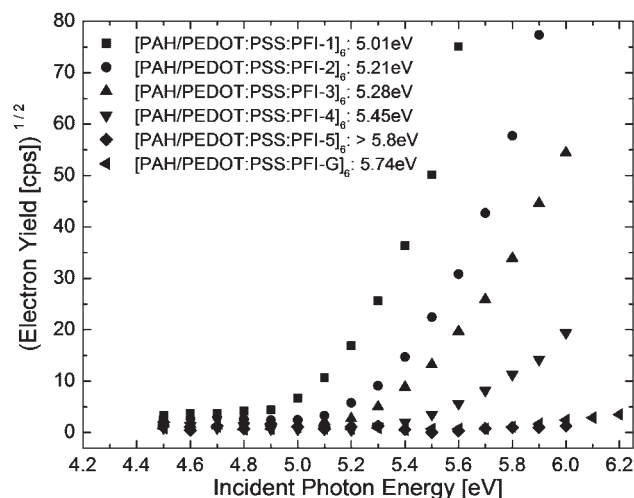




**Figure 1.** AFM images in a height mode: (a) [PAH/PEDOT:PSS:PFI-1]<sub>6</sub> of which the anionic part is 0.05 wt.-% PEDOT:PSS, (b) [PAH/PEDOT:PSS:PFI-5]<sub>6</sub> of which the anionic part is 0.1 wt.-% PFI, and (c) a PEDOT:PSS:PFI thin film coated from a 1:1 volume mixture of 1.18 wt.-% PEDOT:PSS and 5 wt.-% PFI solutions, which indicates 3.09 wt.-% of a dense polymer solution. The scale bar is 100 nm and Z-range is 30 nm.

([PAH/PEDOT:PSS:PFI-*N*]<sub>6</sub>) that resulted in controlled work functions with increasing PFI concentrations became an insulating layer when 0.1 wt.-% PFI was used, which is usual as the thickness of the insulating materials is around 30 nm. A remarkable result was obtained when grading PFI concentrations were applied with each bilayer deposition ([PAH/PEDOT:PSS:PFI-*G*]<sub>6</sub>). The high work function level of 5.74 eV is not the value that can be gained when a pure thin PFI layer ( $\approx 5$  nm) is coated on the ITO, which is around 5.5 eV,<sup>[10]</sup> and should originate from the gradient of PFI concentration and consequently controlled work function levels.

To prove the potential usefulness of the LBL thin films as HILs, we fabricated the green-emitting PLEDs using an LBL spin self-assembled film, [PAH/(PEDOT:PSS:PFI-3)]<sub>6</sub>, as an HIL layer. The original PEDOT:PSS (Baytron PH) was also spin-coated and used for comparison. The device can have electron-dominant characteristics because there is apparently no electron injection barrier from Ba cathode (work-function 2.7 eV) to the emitting layer (LUMO – 3.05 eV) and the electron mobility of the material is higher than hole mobility.<sup>[29]</sup> Figure 3(a) shows the luminous efficiency versus voltage characteristics of the PLEDs. It is found that the luminous efficiency of the device using the spin

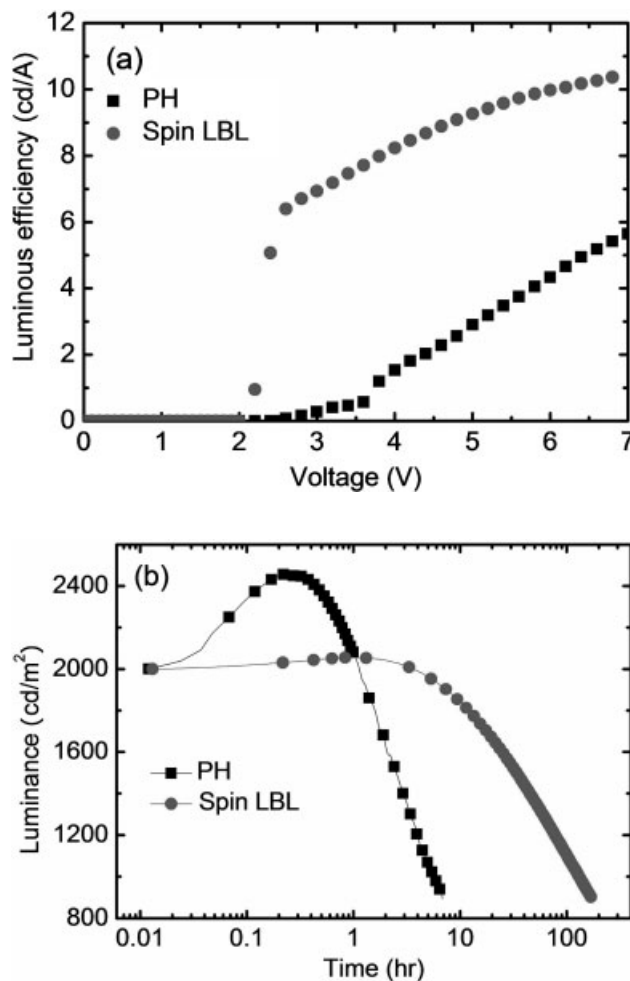


**Figure 2.** Work functions of ITO-glass substrates coated with [PAH/(PEDOT:PSS:PFI-*N*)]<sub>6</sub> thin films where *N* = 1, 2, 3, 4, and 5, and [PAH/(PEDOT:PSS:PFI-G)]<sub>6</sub> where G indicates grading PFI concentrations.

self-assembled [PAH/(PEDOT:PSS:PFI-3)]<sub>6</sub> film ( $10.4 \text{ cd} \cdot \text{A}^{-1}$  at 7 V) is much better than that of the device using the spin-coated PEDOT:PSS ( $5.64 \text{ cd} \cdot \text{A}^{-1}$  at 7 V). This is because of the fact that the spin-assembled LBL film has an appropriate work function (5.28 eV) between that of the ITO electrode ( $\approx 4.7\text{--}5.0$ ) and the  $I_p$  level of the emitting material (5.55 eV) to facilitate the hole injection from the anode. We also tested the device lifetime at an initial luminance of  $2000 \text{ cd} \cdot \text{m}^{-2}$ . It was observed that the device lifetime was also greatly improved compared to the device using the spin-coated Baytron PH film as shown in Figure 3(b). The half lifetime of the device using the LBL spin self-assembled HIL was about 18 times longer than that using the Baytron PH. One interesting thing to note is that the luminance of the device using the spin-coated Baytron PH film shows an initial overshoot within 1 h, which can be attributed to the imbalance of charge carriers and thus accumulation of dominant carriers (i.e., electrons) inside the devices. When we used the spin-assembled film, the overshooting phenomenon disappeared due to the improved balance of the charge carriers for recombination.

## Conclusion

The LBL spin self-assembly of anionic PEDOT:PSS and PFI with differing PFI ratio demonstrated a capability to modify the work function of an anode and to enhance the device efficiency and lifetime in PLEDs. Due to large  $I_p$  levels and large dipole moments originating from deprotonated hetero fluoro sulfonic acids in PFI, it was possible to



**Figure 3.** (a) The device efficiency and (b) the lifetime using an LBL spin self-assembled [PAH/(PEDOT:PSS:PFI-3)]<sub>6</sub> film on comparison with the device using the spin-coated PEDOT:PSS (Baytron PH).

control the work functions of the anode at a specific level which greatly improved hole injection to an emitting layer and thus the device efficiency and lifetime. Furthermore, the LBL assembly approach was a convenient way to deposit a HIL with a gradient of energy levels which resulted in a work function of 5.74 eV and might maximize hole injection even for emitting materials with an  $I_p$  level above 5.7 eV, which has been a great challenge. The work regarding the gradient of energy levels and device fabrication is our ongoing study and we believe the LBL spin-assisted assembly approach to deposit HILs including PFI is greatly advantageous for achieving improved device efficiency and lifetime. Moreover, our approach to tune the work function of the charge injection contacts can be useful to improve the charge injection in other electronic devices.

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