Communication

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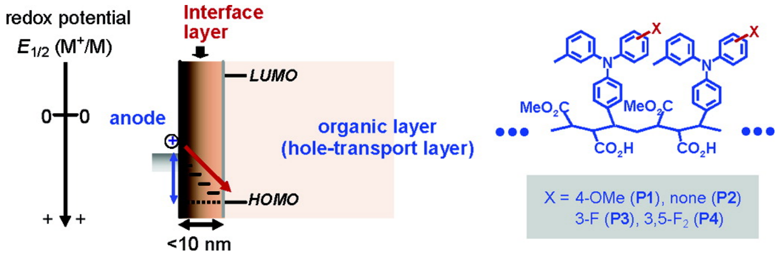

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Designing Interfaces That Function to Facilitate Charge Injection in Organic Light-Emitting Diodes

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Molecular engineering at an electrode surface is a challenging subject to chemists in the field of organic microelectronics.[1] Especially in organic light-emitting diodes (OLEDs), to tune the electronic properties at an anode surface has been a crucial issue because electronic profiles at the anode/organic interface strongly affect electron/hole injection fluence and recombination of the charge carriers that are central factors for providing efficient OLEDs.[2] In this communication, we wish to propose a new strategy for designing interfaces that provide *stepped electronic profiles* (Figure 1), which leads to remarkable facilitation of hole mobility from the anodes to the organic layers.[3]

The basic concept of our approach depends on polymeric layer-by-layer (LbL) assembly for anode modifications. This technique is a nanoscale film-forming system of sequentially adsorbed polymeric materials.[4] We previously demonstrated that the polymeric LbL assembly was a useful tool for fabricating anode interface layers that function to promote the interfacial cohesion in OLEDs.[5] Basically, the most fascinating nature of the polymeric LbL technique is that a precise control over component distribution can be easily performed in the vertical direction from the substrate surface. On the basis of this feature, we have attempted to extend our original approach to construct *stepped electronic profiles* at the anode/organic interface, by sequential deposition of systematically designed electroactive polymers in order of their redox abilities.

A series of alternating copolymers of monomethyl maleate with triarylamine (TAA)-functionalized vinyl monomers were employed in this study. The chemical structures of the copolymers used (**P1**−**P4**) are shown in Figure 2. These are regarded as *dual-functionalized* copolymers consisting of two modules. The monomethyl maleate unit allows the polymers to be LbL film-forming, where the carboxylic acid group acts as an interlayer cross-linking moiety, while the TAA-functionalized monomer unit is an electroactive functionality capable of hole transport. These polymers possess different TAA functionalities with regard to electron affinity of the substituents (X) on the aryl rings. This allows for the tuning of the redox potential of the polymers (Figure S1): $E_{1/2}(M^+/M)$ vs Ag^+/Ag: **P1**, 0.57 V; **P2**, 0.75 V; **P3**, 0.87 V; **P4**, 0.96 V. This tuning is important to optimize the energy differences between the highest occupied molecular orbital (HOMO) of the anode interface layer and the energy level of the adjacent materials, one is with the Fermi level of the anode and the other the HOMO of the organic layer (which is usually a hole transport layer) to control hole injection.

Figure 3 outlines the steps in the present film-preparation approach. Pretreated substrates (ITO or quartz) having amine-bearing surfaces were initially immersed in a 2-butanone solution of the polymer (1 mM) at room temperature for 10 min and then treated with a toluene solution of ethylenediamine (25 mM) at room temperature for 5 min. The repetitive two-step process (denoted hereafter as "cycle") was used to laminate the polymers onto the substrate surface, where a driving force of the polymer lamination is an ionic or a hydrogen-bond interaction, between the carboxylic acid group of the polymers and ethylenediamine. Finally, the deposited polymer films were converted to covalently bound counterparts via heat-induced condensation reactions between the preassociated carboxy acid−amine functions.

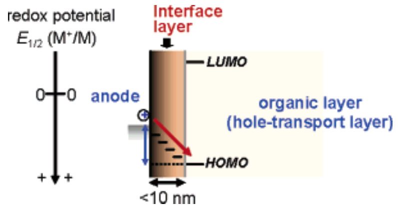

Figure 1. A basic concept of the present approach regarding an energetic scheme at an anode/organic interface.

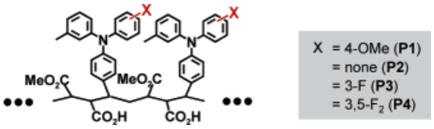

Figure 2. Chemical structures of the polymers used in this study.

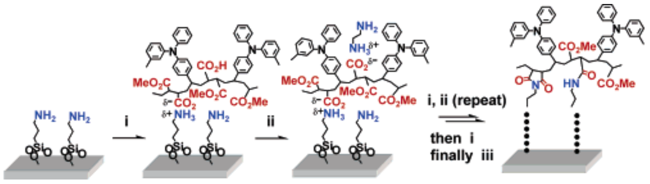

Figure 3. Schematic outline of the preparation of polymeric LbL multilayer films: (i) deposition of a polymer; (ii) deposition of ethylenediamine; (iii) thermally induced covalent bond formation.

That there was LbL fabrication of the polymers on quartz plates was demonstrated by successive UV−vis electronic absorption measurements (Figure S2). Efficiency of the stepwise film growth was slightly different among the polymers, which increases in the order **P4** < **P3** < **P2** ≤ **P1** (Figure S3). On the basis of the linearity of the absorbance change, the two-dimensional areas occupied per the TAA units are estimated to be 0.44 (**P1**)−0.65 (**P4**) nm^2 per deposition cycle. These values appear to be rather small in comparison with the size of a triphenylamine framework (0.74 nm^2, viewed as a cylinder), suggesting that the TAA units are densely assembled in the polymer multilayer films. The thickness of these films was found to be increased by 1.0−1.5 nm per deposition cycle, based on X-ray reflectivity measurements (Figure S4).

Device performances employing the polymeric LbL films as anode interface layers were investigated for conventional TPD/Alq OLEDs. Figure 4 shows representative examples of current density, luminance, and external quantum efficiency as a function of operating voltage, for the devices with the LbL films prepared via four deposition cycles of **P1**−**P4**. Functionalization with the LbL films of **P1** and **P2** revealed large enhancement in current and luminance levels in the OLEDs, compared to those with a bare

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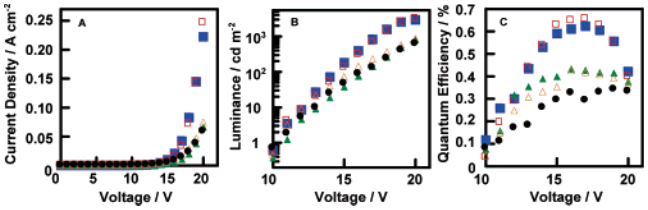

Figure 4. (A) Current density, (B) luminance, and (C) forward external quantum efficiency as a function of operating voltage for OLED devices (ITO/TPD/Alq/Al) with or without anode interface layers (four deposition cycles): (●) bare ITO; (■) **P1**; (□) **P2**; (▲) **P3**; (△) **P4**.

ITO anode. Furthermore, forward external quantum efficiency of the device with the films of **P1** and **P2** reached 0.62 and 0.65%, respectively, a large improvement over that of the bare ITO-based device of 0.32%. On the other hand, only small effects were observed on the OLED performances in the cases of the anode interface layers of **P3** and **P4**. Figure S5 shows plots of current density (A) and luminance (B) versus deposition cycles of the polymer films when applying a voltage of 20 V. There is a sharp contrast in OLED performances between the devices with the films of **P1** and **P2** and those with the films of **P3** and **P4**.

To get the insight underlying the contrasting behavior of the OLEDs, microstructural investigation for the ITO/TPD interface was performed under thermal stress.[6] Figure S6 shows SEM images of the annealed TPD films (50 nm) on the bare or functionalized ITO electrodes (four cycles of the **P2** deposition). No significant dewetting was observed for the TPD films in contact with the **P2** films, unlike the case with the bare ITO electrodes. All the LbL films prepared by using other polymers were as much effective as the **P2** films to prevent decohesion of the TPD films, regardless of the number of deposition cycles. These results clearly indicate that all of the polymer films equally enhance the ITO/TPD interfacial stability.

On the other hand, the contrasting OLED characteristics can be explained by different types of electronic profiles at the ITO/TPD interfaces among the devices. By means of atmospheric photoelectron spectroscopy, the bare ITO exhibited a surface work function of 4.80 eV, but the electrodes functionalized with the polymer films changed the values to 5.16, 5.36, 5.59, and 5.76 eV for **P1**, **P2**, **P3**, and **P4**, respectively. The former two values are smaller than the ionization potential (I_p) value of the vacuum-deposited TPD film (5.44 eV), while the latter two are apparently opposite cases. These results suggest that electronic profiles of the anode/organic interfaces are crucial to OLED characteristics, where **P1** and **P2** are mediating the hole mobility, but **P3** and **P4** are blocking. Note that, as shown in Figure S5, the values of current and luminance sharply drop over six deposition cycles even with the **P1** or **P2** films, probably due to the partial insulating effect of relatively thicker films.

On the basis of the above-mentioned fundamental properties of the polymer films, interface layers showing stepped electronic profiles were fabricated at the anode surface. The film was initially prepared by sequential deposition of each two-cycle process of **P1** and **P2**. Figure S7A shows spectrophotometric changes for the LbL films, revealing the successive increase of absorbance following the deposition cycles. Of particular interest is that the functionalized ITO electrode with this heterodeposited film exhibited a surface work function of 5.37 eV, while that with the initial two-cycle film of **P1** showed a value of 5.14 eV (Figure S8A). It is clearly suggested that the interface layer having a two-step energy level was successfully constructed on the anode surface. As shown in Figure 5, the TPD/Alq OLED device with this functionalized anode exhibited appreciably reduced turn-on voltage and higher luminous intensities, which were greater than those of the devices with the single polymer−component interface layers (compare to Figure 4). These results strongly indicate that this heterodeposited polymer film functions to enhance hole injection from the anode, through the facilitation of energy level matching at the interfaces of the ITO/(stepped interlayer)/TPD.

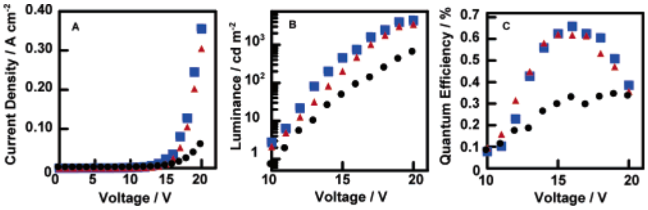

Figure 5. (A) Current density, (B) luminance, and (C) forward external quantum efficiency as a function of operating voltage for OLED devices (ITO/TPD/Alq/Al) with or without anode interface layers: (●) bare ITO; (■) four deposition cycles with a **P1−P1−P2−P2** sequence; (▲) three deposition cycles with a **P1−P2−P3** sequence.

Finally, it is of crucial interest to note that the OLED performance was also significantly improved by anode functionalization with the heterodeposited film with a **P1−P2−P3** sequence (Figure 5). This is certainly an unexpected result since the polymer film of **P3** blocks hole injection at the ITO/TPD interface (vide supra). An interesting observation was provided from the surface work function of 5.46 eV for the modified ITO with this heterodeposited film (Figure S8B), which is significantly lower than that with the **P3**-only film. This value is close to that of the TPD film. This finding would be related to an inherent nature of the LbL technique that offers a nanoscale blending system with polymeric interpenetration,[7] thus leading to fabrication of a *graded* layer structure having a *graded* electronic profile. Works are currently underway to further investigate heterodeposited polymer films, along with optimization of their effects on OLED characteristics. In this manner, the present LbL technique offers a rational and versatile way to enhance OLED performances, which is adjustable depending on the energetic scheme of devices by rational design of polymer structure and layer sequence.

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Supporting Information Available: Experimental details, syntheses and CVs of **P1−P4**, UV−vis spectra, X-ray reflectivity data, and atmospheric photoelectron spectra of the LbL films, and SEM images of TPD films on the modified electrodes. This material is available free of charge via the Internet at http://pubs.acs.org.

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