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Improved electron injection in polymer light-emitting diodes using anionic conjugated polyelectrolyte

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We report improved performance in polymer light-emitting diodes incorporating conjugated polyelectrolytes as an electron injection layer (EIL). When we introduce water soluble conjugated polymers, poly[9,9'-bis(4-sulfonatobutyl)fluorene-*co-alt*-1,4-phenylene] (anionic PFP), between the aluminum (Al) cathode and emissive layer, the devices show an increased electroluminescence efficiency with a lowered turn-on voltage. We believe the mobile Na⁺ ions in the EIL layer directly influences the device efficiency by forming a low work function layer at the interface between the EIL and Al cathode, thereby facilitating the electron injection into the emissive layer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2989133]

Electroluminescent (EL) devices based on conjugated polymers continue to be of interest as potential elements for flexible displays.¹⁻⁴ Although encouraging progress has been made in recent years, injection from the electrodes into the luminescent conjugated polymers continues to be a problem. The mismatch between the work function of the metallic electrode (cathode) and the lowest occupied molecular orbital energy level of the semiconducting polymer controls charge injection into the devices, thereby limiting the device efficiency.⁵⁻⁷ One approach is to use a low work function metal as the cathode. However, since low work function metals are highly reactive to ambient atmosphere, this approach complicates the fabrication process and requires hermetically sealed packaging in order to achieve satisfactory operating lifetimes.^{8,9}

In attempts to replace the cathode with higher work function metals with better stability, for example, with aluminum (Al), many studies were carried out with the goal of modification in the cathode/polymer interface. In particular, the insertion of an inorganic or organic electron injection layer (EIL)/transport layer between the cathode and emissive layer can provide an intermediate step for facilitating electron injection.¹⁰⁻¹² One example is the use of lithium fluoride (LiF). When incorporated into polymer light-emitting diodes (PLEDs), the LiF layer improves the device performance by increasing the electron attenuation length, by suppressing the interfacial reactions of the metal electrode with emissive layer during the cathode evaporation, and/or by reducing the barrier height of the electron injection through formation of a low work function interfacial layer at the cathode.^{10,13-15}

The recent research using cationic systems¹⁶⁻¹⁸ implies that anionic conjugated polyelectrolytes might offer several interesting opportunities for use in polymer-based optoelectronic devices. In light-emitting electrochemical cells (LECs), the mobile ions enable redox doping and the formation of ohmic contacts.¹⁹⁻²¹ Moreover, a polyelectrolyte from

this class of materials can also be used to form the EIL in PLEDs. The hydrophilic nature of the solvents used to process the conjugated polyelectrolytes enables solution casting as an EIL without disrupting the underlying hydrophobic emissive layer.²²

In this contribution, we report the use of an anionic blue-emitting poly(fluorene-*co*-phenylene) derivative as an efficient EIL in PLEDs. By using this material as an EIL with an Al electrode, we have observed that the devices exhibit almost one order of magnitude increase in brightness compared with similar devices fabricated without this EIL.

The molecular structure of the anionic conjugated polyelectrolyte, poly(9,9'-bis(4-sulfonatobutyl)fluorene-*co-alt*-1,4-phenylene) (anionic PFP), is shown in Fig. 1(a). As synthesized, the polymer contains sodium as the charge compensating counterions (i.e., PFP-Na). Ion exchange can be achieved by protonation of the polymer with HCl followed by addition of a suitable base with the cation of interest. The

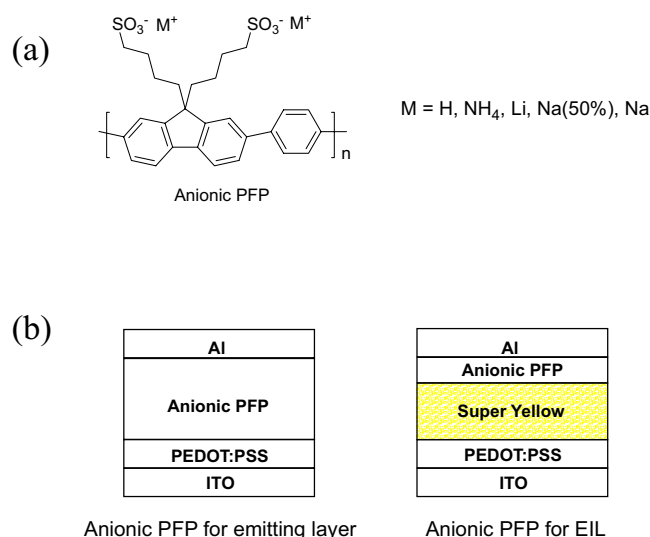


FIG. 1. (Color online) (a) Molecular structure of anionic PFP, and (b) schematic structure of devices used in this work.

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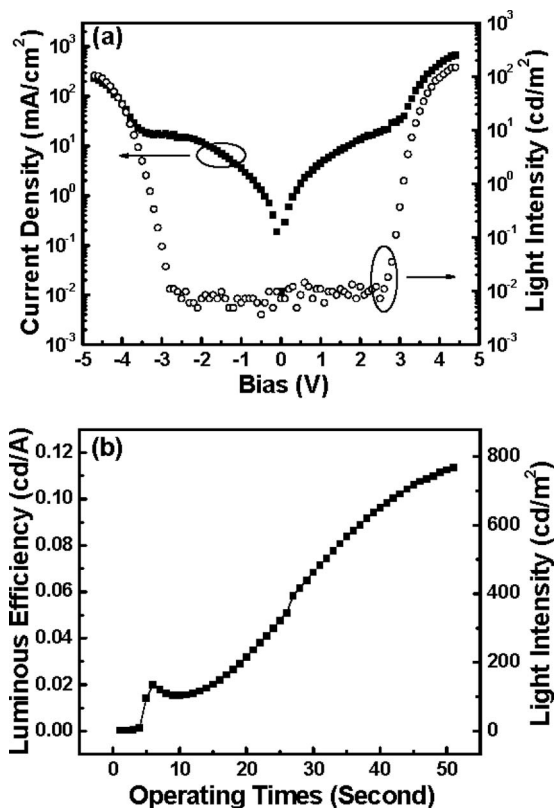


FIG. 2. (a) Current-luminance-voltage characteristics, and (b) efficiency of devices with a configuration of ITO/PEDOT:PSS/emitting layer/Al with PFP-Na as the emitting layer.

anionic conjugated polyelectrolyte PFP-Na is soluble in water, but poorly soluble in alcohols. To prepare homogeneous films on top of the hydrophilic luminescent polymer layer, a solvent mixture containing 20% water, 40% methanol, and 40% isopropanol was used.

In order to investigate the performance of these polyelectrolytes as active materials in LECs, we fabricated devices with PFP-Na as the emitting layer, indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/anionic PFP/Al. Figure 2(a) shows the current density-voltage-luminance (J - V - L) characteristics of the device under both forward and reverse bias conditions. The turn-on voltages for appreciable current injection and visible light emission are around 3 V for a forward bias scan (0–5 V) and –3 V for a reverse bias scan (0 to –5 V), after initially biasing at 5 and –5 V, respectively, for 10 s for ion redistribution. Note that the turn-on voltages are very close to the band gap of anionic PFP (3 eV). In addition, under a constant bias of 5 V for 50 s, the luminance increases to approximately 800 cd/m², as shown in Fig. 2(b). This time dependence proves that ion motion is involved in the device operation, and governs the device performance.

Typically, the efficiencies of LEDs containing conjugated polyelectrolytes are lower than those of the devices using neutral conjugated polymers. However, as the emission layer, we find that the PFP-Na devices turn on at lower voltage than the poly(dioctylfluorene) (PFO) devices fabricated in the same device structure. For example, the turn-on voltage of the PFO devices using Al was 8 V [5 V for barium (Ba):Al cathode]. In contrast, PFP-Na with an Al cathode exhibits substantially lower turn-on voltage around 3 V. This

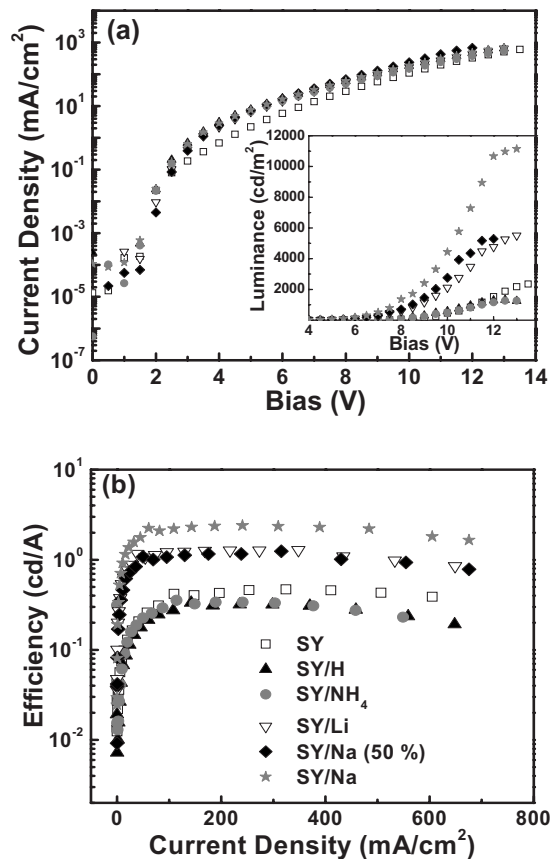


FIG. 3. (a) Current-voltage and luminance-voltage characteristics, and (b) efficiency of five devices with a configuration of ITO/PEDOT:PSS/emitting layer/EIL/Al with SY as the emitting layer.

observation is consistent with the formation of an ohmic contact for electron injection induced by the *in situ* doping characteristic of the LEC.

In addition to fabricating single layer LECs with PFP-Na, we also investigated the EIL function of this class of anionic conjugated polyelectrolytes using the following device structure: ITO/PEDOT:PSS/SY/anionic PFP/Al, where SY stands for the superyellow polymer supplied by Covion Co. The data are shown in Fig. 3. The results indicate that the devices with the PFP-alkali metal cations show better device performance with lower turn-on voltages, higher maximum luminance, and higher luminous efficiencies at fixed current densities as compared to the devices without the EIL. In particular, the devices using PFP-Na exhibit a brightness of approximately 11 000 cd/m² at 12 V, which is almost one order of magnitude higher than that of the devices without the EIL (1500 cd/m² at 12 V). Moreover, the device efficiency of PFP-Na, 2.40 cd/A, is better than that of PFP-Li, 1.25 cd/A. For the nonmetallic cations such as the ammonium salt (PFP-NH₄) and protonated (PFP-H) species, there is no appreciable increase in the device efficiency (η_{eff}) obtained from the EIL ($\eta_{\text{eff}} < 1.0$ cd/A). These observations demonstrate the importance of the specific cation in the EIL for improving electron injection into the PLED devices. The devices with the PFP-Na EIL exhibit best device performance. We attribute this to the higher LEC effects in the metallic cation polyelectrolytes as compared to the nonmetallic cation polyelectrolytes, thereby lowering the injection barrier effectively in the metallic cation polyelectrolyte devices. Moreover, the better water solubility of PFP-Na than

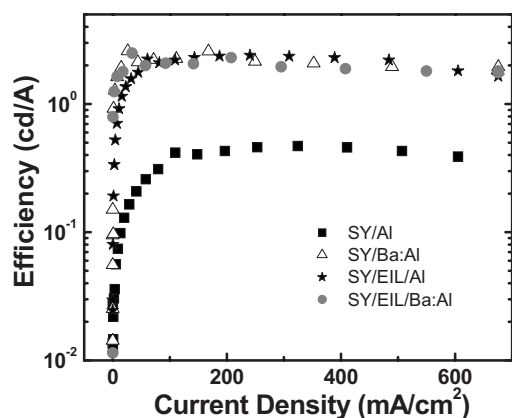


FIG. 4. Efficiency of four devices with a configuration of ITO/PEDOT:PSS/emitting layer/Al, ITO/PEDOT:PSS/emitting layer/EIL/Al, ITO/PEDOT:PSS/emitting layer/Ba/Al and ITO/PEDOT:PSS/emitting layer/EIL/Ba/Al with sodium anionic PFP as the EIL and SY as the emitting layer.

PFP-Li results in higher concentration of the Na cation, and therefore better device performance for the PFP-Na devices.

Finally, we compare the performance of devices made using different Na⁺ concentrations. The device using 100% sodium PFP as an EIL exhibits an efficiency nearly twice that of a 50% sodium PFP (50% deprotonation) device; the efficiency increases from 1.27 to 2.40 cd/A, as shown in Fig. 3(b). Thus, the concentration of the mobile Na⁺ ions in the EIL layer directly influences the device efficiency. The enhanced LEC effects in the polyelectrolyte EIL with higher concentration of Na⁺ cation improve the device performance by effectively lowering the injection barrier.

One of the main objectives of utilizing an EIL in the PLED architecture is to enable the replacement of low work function, highly reactive metals [for example, calcium (Ca) or Ba as the cathode material] with a higher work function, more stable Al cathode. Therefore, the performances of the devices with and without PFP-Na EIL, both with Ba/Al and with Al as cathodes are compared in Fig. 4 using four different device structures: ITO/PEDOT:PSS/SY/Al (device 1), ITO/PEDOT:PSS/SY/Ba/Al (device 2), ITO/PEDOT:PSS/SY/EIL/Al (device 3), and ITO/PEDOT:PSS/SY/EIL/Ba/Al (device 4). For device 3, the EIL forms a low work function injection layer at the Al cathode, resulting in device performance comparable to that obtained from device 2 (Ba cathode without the EIL). For device 3, the turn-on voltage is 2.5 V and the maximum luminance increases to over 10 000 cd/m². In contrast, there is no obvious EIL effect in devices fabricated with the Ba/Al electrode. Device 4 with the EIL and with Ba/Al cathode shows only a slight increase in current density, luminance, and luminous efficiency (with no change in turn-on voltage) compared to device 2. These observations indicate that the Ba/Al cathode already maximizes the device performance by facilitating the electron injection into the devices without any benefit from the introduction of an EIL.

In summary, we have introduced various anionic conjugated polyelectrolytes into electroluminescent devices either as the emissive layer or as an EIL. As an emissive layer, the device with PFP-Na exhibits a brightness of 800 cd/m² at 5 V. Moreover, a low turn-on voltage and increased EL efficiency were observed in devices fabricated with PFP-Na as the EIL and Al as the cathode, with a maximum efficiency of 2.4 cd/A, an increase by a factor of five over similar devices without the EIL.

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