Control of Cationic Conjugated Polymer Performance in Light Emitting Diodes by Choice of Counterion

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Introduction

Conjugated polyelectrolytes (CPs) contain a π-delocalized backbone and groups capable of ionizing in high dielectric media.[1] These materials are starting to find use in optically amplified biological assays,[2] electrochromic devices,[3] single component light emitting electrochemical cells,[4] and the fabrication of multilayer light emitting diodes (LEDs).[5,6] Their solubility in polar solvents allows fabrication of multilayer devices by solution casting methods in combination with neutral conjugated polymers.[7] In this strategy, one alternates the polarity of the casting solvents to minimize disturbance of underlying layers.

The use of CPs as an electron transport (or injection) layer (ETL) in polymer LEDs[8] is particularly intriguing.[7,9] Their charged nature allows one to circumvent often quoted guidelines for optimizing charge injection into organic semiconductors that rely on matching the semiconductor LUMO with the electrode work function.[10] It has been proposed[7] that the insertion of charged or polar groups between the cathode and the emissive layer results in a positive interfacial dipole that effectively lowers the work function of metals such as Al or Au[11] and results in a lowering of injection barrier heights at the interface.[12] However, the orientation and dynamics of charged groups at the metal/polymer interface remain poorly understood.

In this contribution we provide the synthesis of poly([(9,9-bis-(6′-*N,N,N*-trimethylammonium)-hexyl)fluorene]bromide) (**PF-Br**, see Scheme 1). Bromide exchange with different counterions yields ETL materials that substantially improve LED performance. Furthermore, the luminous efficiencies of the devices are dependent on the chemical nature of the anion.

Scheme 1 shows the synthesis of **PF-Br**. Suzuki polymerization of **1** with **2**[13] yields the neutral precursor **PF**$_\text{N}$. Subsequent reaction with NMe$_3$ results in greater than 95% quaternization and the formation of **PF-Br**. Bromide exchange is carried out by adding an excess of a salt with the counterion of interest into a **PF-Br** methanol solution with vigorous stirring. After solvent removal, the resulting solid is washed several times with deionized water to afford **PF-X** (where X corresponds to the compensating anion, Scheme 1). X-ray photoelectron spectroscopy (XPS) confirms greater than 95% Br$^-$ exchange.

We chose to fabricate LEDs using poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as the emissive layer because it is an excellent singlet emitter and because of its extensive previous characterization and ease of purification.[14] The MEH-PPV was deposited from toluene on a PEDOT treated ITO surface. Subsequently, a 10 nm film of **PF-X** was spun-coated from a 2 mg/mL solution in methanol. Finally, an Al layer or a Ba/Al bilayer was evaporated to serve as the cathode. Figure 1a shows

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Scheme 1. Synthesis of **PF-X**^{a}
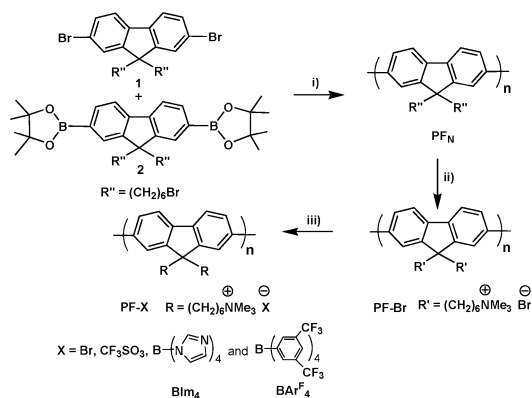
^{a} Conditions: (i) Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$, toluene, reflux, 24 h; (ii) NMe$_3$; (iii) NaX, methanol.
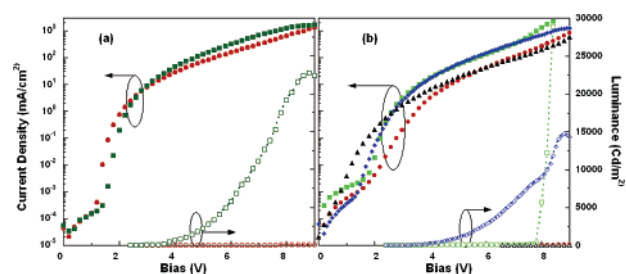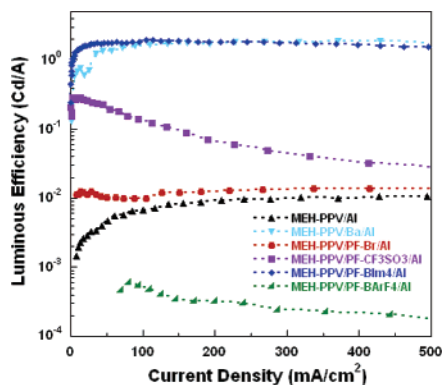

Figure 1. *J-L-V* characteristics of LEDs: (a) MEH-PPV/Al (red circles) and MEH-PPV/Ba/Al (green squares); (b) device configuration ITO/PEDOT/MEH-PPV/**PF-X**/Al showing **PF-Br** (red circles), **PF-CF$_3$SO$_3$** (green squares), **PF-BIm$_4$**,(blue diamonds), and **PF-BArF$_4$** (black triangles).

the current density-luminance-voltage (*J-L-V*) characteristics of control devices with Ba or Al cathodes, but no **PF-X**. Consistent with previous literature work,[9,15] the better match of the Ba work function ($\varphi = 2.7$ eV) with the MEH-PPV LUMO (2.9 eV) results in an ohmic contact for electron injection and LEDs with higher luminance (23000 cd/m² at 9 V) than these with Al cathodes ($\varphi = 4.3$ eV, 100 cd/m² at 9 V). Figure 1b compares the device characteristics with **PF-X**/Al cathodes. These data show that for **PF-Br** and **PF-BArF$_4$**, the *J-L-V* curves do not provide an improvement relative to the MEH-PPV/Al device. However, with **PF-CF$_3$SO$_3$** or **PF-BIm$_4$**, the *J-L-V* characteristics are substantially improved, with turn on voltages (the point at which 0.1 cd/m² is observed) at the band gap energy of MEH-PPV (2.2 eV).

Examination of the luminous efficiencies provides for a simple comparison of how X influences device characteristics. As shown in Figure 2, the efficiencies up to 500 mA/cm² can be ranked in the order (**PF-BArF$_4$**/Al) < Al ≈ (**PF-Br**/Al) < (**PF-CF$_3$SO$_3$**/Al) < Ba ≈ (**PF-BIm$_4$**/Al). The efficiencies of devices fabricated with

Figure 2. Luminous efficiency vs current density characteristics for different cathodes: **PF-BAr$^F_4$**/Al (green), Al (black), **PF-Br**/Al (red), **PF-CF$_3$SO$_3$**/Al (purple), Ba (light blue), and **PF-BIm$_4$**/Al (blue).
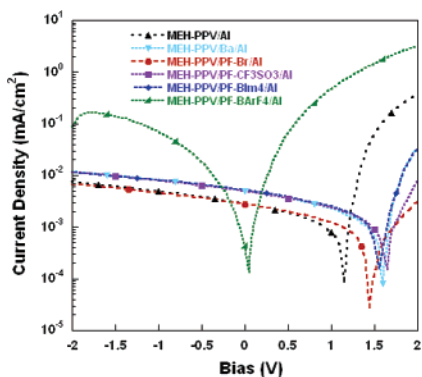
Figure 3. Photovoltaic characteristics of devices with configuration ITO/PEDOT/MEH-PPV/ETL/Al.

PF-BIm$_4$/Al are comparable to those with a Ba cathode. At the other extreme, **PF-BAr$^F_4$**/Al yields devices that are less efficient than those with Al cathodes. Both **PF-BIm$_4$** and **PF-BAr$^F_4$** have identical polymer backbones. Thus, the difference in performance is not due to differences in electrode work function/semiconducting polymer LUMO energy levels. The efficiencies of **PF-Br**/Al and **PF-CF$_3$SO$_3$**/Al are intermediate. We note that a similar dependence on X is observed when MEH-PPV is replaced with poly[2-(4-3′,7′-dimethyloctyloxy)phenyl-*p*-phenylenevinylene] (DMO−PPV, see Supporting Information).

Photovoltaic (PV) measurements were performed to obtain the open circuit voltage (V_{oc}) across the devices used to collect the data in Figure 2.[16] In these experiments, an external potential is applied to the device under constant illumination.[17] Minimum current is measured at the point where the external bias cancels V_{oc}.[18] Since the anode is identical for all devices, the V_{oc} is primarily influenced by the effective work function of the cathode. As shown in Figure 3, the V_{oc} difference between Ba and Al devices (0.45 V) is consistent with previous literature reports.[16] The V_{oc} obtained with **PF-CF$_3$SO$_3$**/Al, Ba and **PF-BIm$_4$**/Al cathodes are close in value (1.65, 1.60, and 1.55 V, respectively), followed by **PF-Br**/Al (1.45 V) and Al (1.15 V). Remarkably, we observe a V_{oc} of close to zero for **PF-BAr$^F_4$**/Al. The data in Figure 3 provide compelling evidence that the nature of X bears a direct impact on the effective potential at the cathode interface. It should be noted that similar improvements in device performance were obtained using an amino-terminated conjugated polymer as the ETL.[7]

In summary, the performance of CPs as the ETL in LEDs is strongly influenced by the charge-compensating ions. From a practical perspective, it is possible to find suitable species that allow the use of a higher work function and thus more stable metals, such as Al, and achieve efficiencies similar to those obtained with Ba. However, several basic science questions remain poorly answered. Comparison of **PF-CF$_3$SO$_3$**/Al, Ba, and **PF-BIm$_4$**/Al reveals obvious inconsistencies between V_{oc} and the luminous efficiencies. One possibility is that the charge mobility in **PF-CF$_3$SO$_3$** is substantially lower than that in **PF-BIm$_4$**/Al. Note also that the increase of luminance for devices with **PF-CF$_3$SO$_3$** is very sudden (Figure 1b), suggesting that heating the device results in changes of polymer morphology and/or ionic redistribution under stronger applied fields. The near zero V_{oc} measured with **PF-BAr$^F_4$**/Al is also difficult to understand at the present moment. There is also little known on how the different counterions may modify the internal CP/emissive layer interface. Despite these uncertainties, the work described herein demonstrates that the simple procedure of ion exchange can be used to modify the device function of conjugated polyelectrolytes. Current efforts are aimed at elucidating the structure/function relationships via structural, synthetic, and device fabrication studies.

Supporting Information Available: Synthetic details, XPS analysis, absorption and PL spectra, LED fabrication and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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