

Conjugated polyelectrolytes for organic light emitting transistors

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We report on solution-processed light emitting field-effect transistors (LEFETs) that incorporate symmetric high work function (WF) source and drain metal electrodes. A key architectural design is the incorporation of a conjugated polyelectrolyte (CPE) electron injection layer atop the emissive layer. The device structure also comprises a hole-transporting layer underneath the emissive layer. Both holes and electrons are injected from stable, high WF metal through the CPE layer leading to electroluminescence near the electron-injecting electrode. With the benefits of the simplicity in device fabrication, the LEFETs incorporating CPEs are interesting structures for integrated organic optoelectronic devices. © 2010 American Institute of Physics. [doi:10.1063/1.3467856]

Organic light-emitting field-effect transistors (LEFETs) are an emerging class of optoelectronic devices that combine the electrical switching functionality of a field-effect transistor (FET) with the capability of light generation typical of organic light-emitting diodes.^{1–11} Due to this unique combination of properties, LEFETs have potential applications in the fabrication of simplified pixels for flat panel displays, optical communication devices, and electrically driven organic lasers.^{12–16}

Injection and transport of both electrons and holes are important requirements for generating electroluminescence in LEFETs. Efficient injection of both carriers has been accomplished by using electrodes made from low and high work function WF metals.^{4,7,17} This choice of metals arises from the contact properties at the organic semiconductor/metal interfaces, which limit carrier injection. Low WF metals such as Ca (Ref. 7) and Mg (Ref. 4) can be used for facilitating electron injection. However, the complexity of evaporating two different electrodes provides a barrier for widespread implementation of these devices.

We demonstrate herein that it is possible to fabricate LEFETs using symmetric, stable and high WF metal electrodes (namely, Ag) deposited atop a very thin conjugated polyelectrolyte (CPE) layer. The CPE layer is introduced to circumvent electron injection barriers¹⁸ and leads to balanced injection, excellent brightness and a great simplification of

the fabrication of these devices. Figure 1(a) shows the chemical structures used in this study. Poly[9'9-bis × [6' (N,N,N-trimethylammonium) hexyl] fluorene-*alt*-*co*-1,4-phenylene] with tetrakis(imidazolyl)borate (PFN⁺BIm₄⁻) counterions was chosen as the CPE, and poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT-C14) as a *p*-type semiconductor that is introduced adjacent to the gate dielectric.¹⁹ As the emissive layer, we employed a phenyl-substituted poly(para-phenylene vinylene) copolymer (superyellow; SY).^{7,17}

CPE function was tested within LEFET devices with the architecture shown in Fig. 1(b): Si/SiO₂/PBTTT-C14/SY/PFN⁺BIm₄⁻/Ag. Their fabrication begins with spin coating ~65 nm of PBTTT-C14 from a chlorobenzene solution onto a SiO₂ surface, followed by thermal annealing. Subsequently, SY films of 100 nm thickness were spin-coated from toluene. The resulting PBTTT-C14/SY bilayers were annealed at 200 °C for 30 min. Films of PFN⁺BIm₄⁻ with different thicknesses were then deposited by spin-casting from 0.02% or 0.5% (w/v) methanol solutions. The 0.5% solutions provided layers on the order of 20 nm, as determined by atomic force microscopy while the 0.02% solutions were too dilute to modify measurably the device thickness. Nonetheless, these conditions have been previously shown to allow accumulation of CPEs atop a hydro-

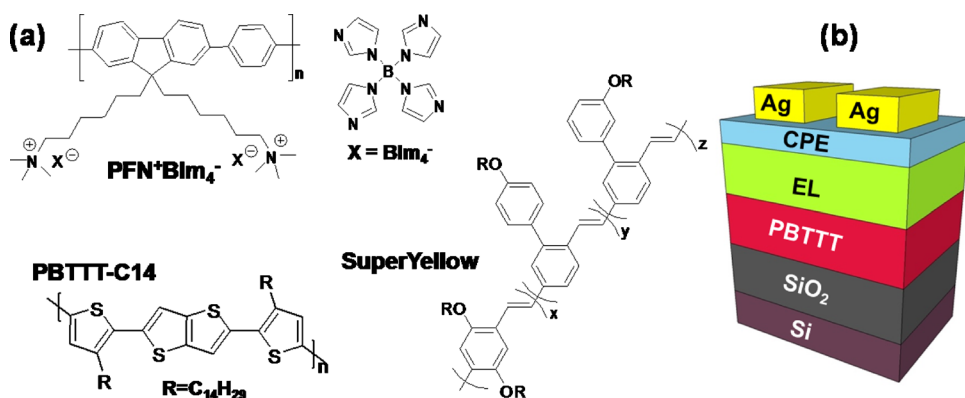


FIG. 1. (Color online) (a) Chemical structures and (b) LEFET test device.

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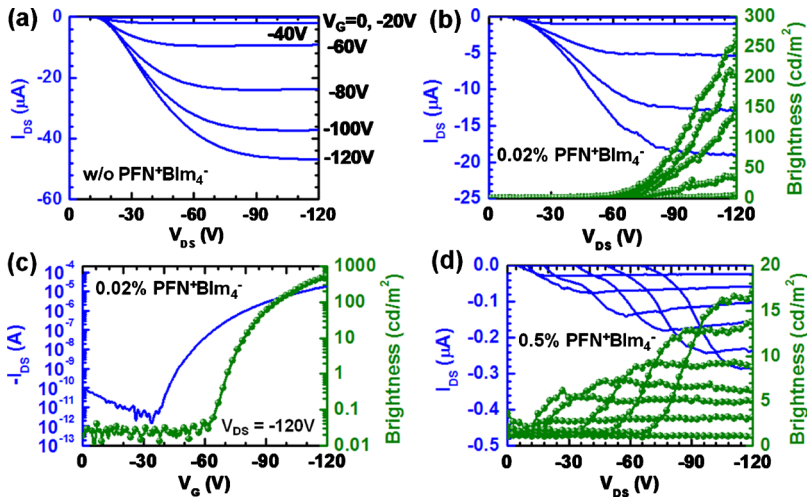


FIG. 2. (Color online) (a) Output characteristic of a control device. Electrical (solid line) and optical (circle) (b) output and (c) transfer characteristics of LEFETs with a PFN⁺BIm₄⁻ layer deposited from 0.02% methanol solutions. (d) Device characteristics of LEFETs with a 20 nm PFN⁺BIm₄⁻ layer deposited from 0.5% solutions. V_G was scanned from 0 to -120 V at intervals of -20 V.

phobic polymer semiconductor and thereby to introduce an organized dipole layer at the interface.²⁰ The final step in device construction involves thermal evaporation of 100 nm Ag electrodes.

Current-voltage-luminescence characteristics were measured under a nitrogen atmosphere by using a Keithley 4200 system and a Hamamatsu photomultiplier (PMT). The photocurrent in the PMT was collected to determine brightness and luminescence efficiency for the effective light emitting area. This analysis has been described in more detail previously.¹⁷ The width of the emission area was determined by imaging the light emission zone by optical microscope attached with a digital camera. The image was analyzed by taking an integrating profile across the image channel region. The width of emission zone was measured by taking of full width of half maximum and was ~ 3.0 μm .

Figure 2 compares the characteristics of various devices. A baseline measure was obtained by examination of a control device with no PFN⁺BIm₄⁻ layer underneath the Ag electrodes, i.e. Si/SiO₂/PBTTC-14/SY/Ag. Typical *p*-type transistor behavior is observed for this device structure, as shown by the drain current (I_{DS}) versus source drain voltage (V_{DS}) curves at various negative gate voltages (V_G) in Fig. 2(a). No light emission could be measured under these conditions. Switching the gate potential leads to no current, indicating that there is no electron current across the channel. Figures 2(b) and 2(c) show the output and transfer characteristics of a device fabricated by using the 0.02% PFN⁺BIm₄⁻ solution in methanol. FET characteristics are observed with saturation behavior; analysis of these curves yields a mobility (μ) of ~ 0.02 $\text{cm}^2/\text{V s}$ and a current on/off ratio ($I_{\text{on}}/I_{\text{off}}$) of $\approx 10^8$. More significantly, emission of light corresponding to the SY layer is observed with these devices. As shown by the brightness cd/m^2 versus V_{DS} plots, the brightness increases with V_{DS} and V_G and then saturates. This LEFET exhibits a maximum brightness 520 cd/m^2 and an efficiency of 0.08 cd/A [Fig. 2(c)]. Examination of the output characteristics of the LEFETs with the 20 nm PFN⁺BIm₄⁻ layer obtained with the more concentrated solution [Fig. 2(d)] reveals unusual dependence of threshold voltage and saturation behavior and low I_{DS} values. Such a situation is not desirable and is likely due to redistribution of electric fields due to ion motion within the PFN⁺BIm₄⁻ layer, although the exact mechanism remains poorly understood. Despite these uncertainties, proper management of the CPE thickness can cir-

cumvent these undesirable characteristics, as shown in Fig. 2(b).

A magnified optical image of the working device is shown in Fig. 3. Light emission is observed adjacent to the negative biased electrode, which we assign as the drain (D) electrode. This region of emission indicates the charge carrier recombination zone. In addition, the position of light emission is found to be *independent* of the applied voltage.

Taking the above observations into account, we propose the mechanism for operation of these LEFETs shown in Fig. 4. Under negative V_G , the injection probability for the holes from the Ag electrode into the highest occupied molecular orbital (HOMO) of SY (4.8 eV),¹⁷ and subsequently into the HOMO of PBTTC-14 (5.1 eV) (Ref. 19) is higher than that of electrons. These conditions lead to the accumulation of holes near the gate insulator/PBTTC-14 interface and the transistor operates in hole accumulation mode. Incorporating a thin CPE layer leads to the introduction of an interfacial dipole with the positive pole pointing toward the polymer layer and the negative pole toward the metal.²⁰ Such an orientation raises the effective WF of the electrode, thereby causing a reduction in the electron injection barrier into the lowest unoccupied molecular orbital of SY (2.4 eV), as shown in Fig. 4(b). Under these circumstances, holes moving across the channel recombine with electrons in the SY layer, leading to light emission adjacent to the drain electrode. Efficient electron injection from the CPE/Ag electrode is thus an essential criterion for light emission, even though electron transport along the channel is negligible.

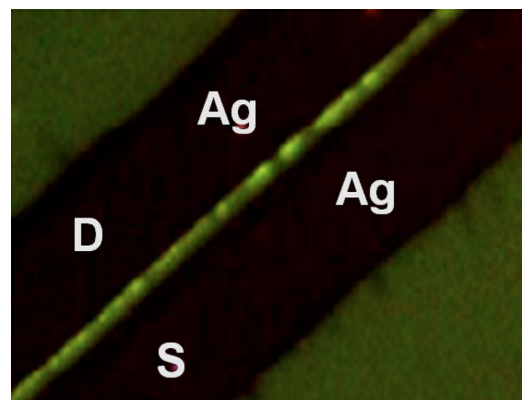


FIG. 3. (Color online) A photograph of an operating LEFET.

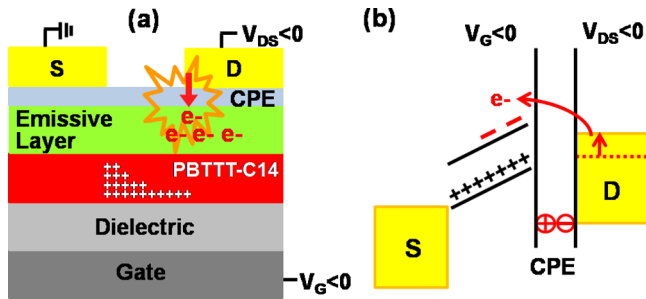


FIG. 4. (Color online) (a) Schematic of a LEFET on a three component layered architecture. (b) A model of electron injection from the drain electrode modified by the presence of an interfacial dipole layer. The emissive layer corresponds to SY.

In conclusion, we disclose a new strategy for simplifying the fabrication of LEFET devices with excellent performance by using CPEs that effectively modulate charge injection, provided that the thickness is sufficiently thin to avoid possible field redistribution effects. We propose that the thin CPE layers introduce ordered dipoles at the metal/organic semiconductor interface that modify the energy levels and facilitate electron injection. Furthermore, the use of high WF metals for electron and hole injection opens the opportunity of designing LEFETs that are less sensitive to environmental degradation.

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¹M. Muccini, *Nature Mater.* **5**, 605 (2006).

²H. Sirringhaus, N. Tessler, and R. H. Friend, *Science* **280**, 1741 (1998).

³A. Hepp, H. Heil, W. Weise, M. Ahles, R. Schmechel, and H. von Seg-

gern, *Phys. Rev. Lett.* **91**, 157406 (2003).

⁴T. Takenobu, S. R. Bisri, T. Takahashi, M. Yahiro, C. Adachi, and Y. Iwasa, *Phys. Rev. Lett.* **100**, 066601 (2008).

⁵K. Yamane, H. Yanagi, A. Sawamoto, and S. Hotta, *Appl. Phys. Lett.* **90**, 162108 (2007).

⁶C. Rost, S. Karg, W. Riess, M. A. Loi, M. Murgia, and M. Muccini, *Synth. Met.* **146**, 237 (2004).

⁷J. S. Swensen, C. Soci, and A. J. Heeger, *Appl. Phys. Lett.* **87**, 253511 (2005).

⁸F. Cicoira, C. Santato, A. Dadvand, C. Harnagea, A. Pignolet, P. Bellutti, Z. Xiang, F. Rosei, H. Meng, and D. F. Perepichka, *J. Mater. Chem.* **18**, 158 (2008).

⁹J. Zaumseil, R. H. Friend, and H. Sirringhaus, *Nature Mater.* **5**, 69 (2006).

¹⁰E. C. P. Smits, S. Setayesh, T. D. Anthopoulos, M. Buechel, W. Nijssen, R. Coehoorn, P. W. M. Blom, B. de Boer, and D. M. de Leeuw, *Adv. Mater.* **19**, 734 (2007).

¹¹T. Oyamada, H. Uchiuzou, S. Akiyama, Y. Oku, N. Shimoji, K. Matsushige, H. Sasabe, and C. Adachi, *J. Appl. Phys.* **98**, 074506 (2005).

¹²G. Tsiminis, Y. Wang, P. E. Shaw, A. L. Kanibolotsky, I. F. Perepichka, M. D. Dawson, P. J. Skabara, G. A. Turnbull, and I. D. W. Samuel, *Appl. Phys. Lett.* **94**, 243304 (2009).

¹³A. R. Brown, A. Pomp, C. M. Hart, and D. M. de Leeuw, *Science* **270**, 972 (1995).

¹⁴C. Ulbricht, B. Beyer, C. Friebe, A. Winter, and U. S. Schubert, *Adv. Mater.* **21**, 4418 (2009).

¹⁵H. Kajii, T. Taneda, and Y. Ohmori, *Thin Solid Films* **438–439**, 334 (2003).

¹⁶M. C. Gwinner, S. Khodabakhsh, M. H. Song, H. Schweizer, H. Giessen, and H. Sirringhaus, *Adv. Funct. Mater.* **19**, 1360 (2009).

¹⁷E. B. Namdas, P. Ledochowitsch, J. D. Yuen, D. Moses, and A. J. Heeger, *Appl. Phys. Lett.* **92**, 183304 (2008).

¹⁸C. V. Hoven, A. Garcia, G. C. Bazan, and T.-Q. Nguyen, *Adv. Mater.* **20**, 3793 (2008).

¹⁹I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, and M. F. Toney, *Nature Mater.* **5**, 328 (2006).

²⁰J. H. Seo, G. Andrea, B. Walker, S. Cho, A. Garcia, R. Yang, T.-Q. Nguyen, A. J. Heeger, and G. C. Bazan, *J. Am. Chem. Soc.* **131**, 18220 (2009).