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Separating Ion and Electron Transport: The Bilayer Light-Emitting Electrochemical Cell

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Light-emitting devices based on electroluminescent (EL) organic materials offer a plethora of desirable advantages, such as conformable and extremely thin form factors, sharp contrast in displays, and, as recently shown, high luminous efficacy.[1,2] High-performance small displays based on organic light-emitting diodes (OLEDs) have been commercialized,[3] but the current drawback that hinders their introduction into low-cost and large-area applications is that they comprise either a vacuum-processed and therefore expensive active material (small-molecule OLEDs) or a reactive, low-work-function cathode (polymer OLEDs).

An alternative organic EL device, the light-emitting electrochemical cell (LEC), can in contrast simultaneously be fabricated from solely solution-processed materials and utilize stable, high-work-function materials for both electrodes.[2,4] These attractive features stem from the fact that these devices allow both electron and ion transport,[5−10] and polymer LECs typically comprise an intimate blend of a luminescent and semiconducting conjugated polymer (CP) and an ion-conducting electrolyte as the active material.[11−13] Following the application of a voltage, the ions are first redistributed to the electrode interfaces[14] and then allow electrochemical doping and p−n junction formation within the CP, so the electrons and holes can move through high-conductivity doped regions before forming excitons that can recombine radiatively at the p−n junction.[5,15] Despite these important advantages, the interest in LECs has remained limited, as the stability during operation has been unsatisfying for most applications (although promising results in the context of improved operational lifetime have been presented recently).[16−19] Two culprits that result in the limited stability of polymer LECs are the typical employment of a thermodynamically unstable blend of a hydrophobic CP and a hydrophilic electrolyte as the active material[20] and the coexistence of reactive species on the CP (dopants and excitons) with an electrolyte having limited chemical and electrochemical stability during operation.[19,21,22]

Here we introduce a novel bilayer device structure (see Figure 1a) that addresses both these problems, as the phase separation between the CP and the electrolyte is maximized and stabilized by design and most of the electrolyte component (the excess ions and the ion-solvating material) is separated from the CP during operation. Moreover, our results further reveal that the distinct spatial separation of the major ion transport (see Figure 1b,c) and the electron transport (see Figure 1d) leads to desirable device characteristics in the form of a decreased turn-on time and improved light emission.

The planar LECs were fabricated on glass substrates onto which Au electrodes with an interelectrode gap of 300 μm were deposited by thermal evaporation through a shadow mask. The bilayer film structure was formed by spin-coating first a 5 g/L solution of superyellow (SY, Merck) in toluene onto the Au electrodes (layer thickness 120 nm) and then a 10 g/L solution of electrolyte in acetonitrile on top of the dry SY layer (layer thickness 180 nm). The electrolyte comprised poly(ethylene oxide) (PEO) and KCF_3SO_3 in a 1.35:0.25 mass ratio. In a separate atomic force microscopy study, the SY layer was demonstrated to exhibit a very flat surface and to be completely inert toward the acetonitrile solution; thus, the interface between the SY and the electrolyte layers is effectively planar. The blend LECs were fabricated by spin-coating a blend solution comprising SY, PEO, and KCF_3SO_3 in a 1:1.35:0.25 mass ratio on top of the Au electrodes. Device fabrication took place in a N_2-filled glovebox, and characterization was performed in a high-vacuum optical-access vacuum chamber at $p < 1 \times 10^{-6}$ mBar and $T = 360$ K.

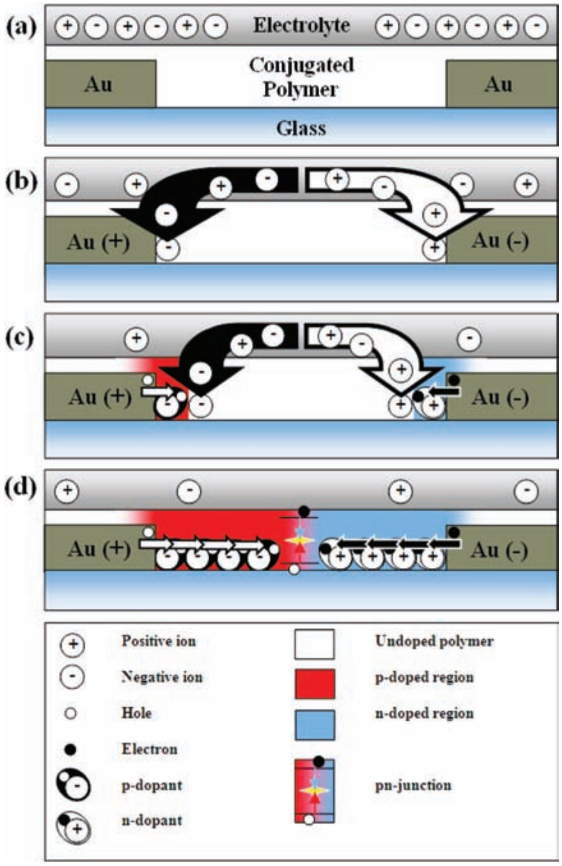

Figure 1. Schematic operation of the bilayer LEC. (a) Pristine device structure. (b) Initial ion transport and formation of the electric double layer. (c) Electronic charge injection and initial formation of doping next to the electrodes. (d) Steady-state operation with light emission from the p−n junction.

Figure 2 presents three panels of sequential photographs. Two of these were recorded during the operation of a bilayer device as probed from the electrolyte side (a) and through the glass substrate (b) the third was recorded during the operation of a blend device (c). The appearance and growth of dark regions correspond to electrochemical doping formation (p-type originating at the positive anode and n-type at the negative cathode) as the UV-excited fluorescence of SY is

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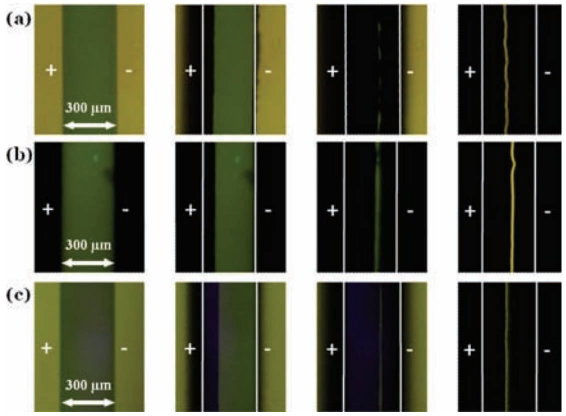

Figure 2. Fluorescence probing of planar devices during operation at $V = 5$ V and $T = 360$ K. The device in (a) and (b) is a bilayer LEC, as probed from (a) the electrolyte side and (b) the CP/glass side (see Figure 1 for a schematic of the bilayer device structure). The device in (c) is a "conventional" blend LEC. The devices in their pristine states are presented in the first photograph in each panel, and the appearance of dark regions (with quenched fluorescence) in the subsequent photographs corresponds to electrochemical doping. The light-emitting p−n junction is clearly visualized in the last photograph in each panel.[23]

sensitively quenched by doping. We call attention to the fact that both p- and n-type doping are observed during the operation of the bilayer devices and more importantly that a light-emitting p−n junction eventually forms in the middle of the gap (see the last photograph in each panel), which proves the functionality of the bilayer concept.

A comparison between panels (a) and (b) in Figure 2 reveals a very similar doping progression and p−n junction formation process, independent of whether the primarily probed SY layer is in direct contact with the electrolyte (a) or as far removed from the electrolyte as possible (b). This observation demonstrates that the doping penetrates all the way through the SY layer in the bilayer device and that the ions that facilitate the doping indeed can leave the electrolyte phase and enter the SY phase during the doping process. The latter is relevant in the context of a long-term debate regarding the operation of LEC devices, as it has been questioned whether the ions do enter the CP phase.[5,15,24,25]

We choose to define the turn-on time as the time at which the p−n junction is initially formed (although the light-emission intensity continues to increase for some time as a reflection of continued doping until ion depletion sets in).[26,27] It is highly interesting to note that the turn-on time for the bilayer devices is *shorter* by a factor of 2 than that for the blend devices ($\sim$13 vs $\sim$25 s). This observation implies that the main ion transport in a bilayer device during turn-on takes place within the electrolyte phase, as schematically outlined in Figures 1b,c, and that the subsequent ion insertion into and ion motion within the SY phase is not a significantly limiting kinetic factor, despite the fact that the interfacial area between the SY and electrolyte phases is minimized in the bilayer structure. The prerequisites for long-range ion transport in the blend device, with its characteristic interpenetrating SY/electrolyte network morphology,[28] are less appealing, as the long-range motion of ions is hindered by the intimate coexistence of SY domains within the active material, which forces the ions to pursue nonstraight and dwindling paths toward the electrode interfaces/doping fronts. Moreover, the current at turn-on is higher (by a factor of 2), and the subsequent light emission from the p−n junction is distinctly brighter in the bilayer devices than in the blend devices. We propose that these observations can at least partially be attributed to a similar effect, since the electron transport (and the related exciton formation rate at the p−n junction) within the "pure" doped SY layer in the bilayer device can be expected to be more efficient than that within the doped SY layer in the blend device, which is "contaminated" by a significant amount of intermixed electronically insulating electrolyte.

We also calculated the "nominal" doping concentrations in the bilayer and blend devices using a previously published procedure.[21,29] We found that the nominal p-type/n-type doping concentrations are 0.06/0.09 dopants per average repeat unit in the bilayer devices and 0.18/0.19 dopants per average repeat unit in the blend devices. We note that the former value is slightly lower than previously published results on blend devices based on smaller-bandgap CPs, while the latter value is higher.[21,29] Considering further that similar SY-based devices have been demonstrated to operate well outside the electrochemical stability window of the $\{\mathrm{PEO} + \mathrm{KCF_3SO_3}\}$ electrolyte during doping and light emission,[19] it seems reasonable to state that the higher nominal doping concentration in the blend devices is an artifact that originates from a combination of doping of SY and side reactions involving the electrolyte. The latter are suppressed in the bilayer device configuration by the spatial separation of a significant fraction of the electrolyte (the excess ions and the ion-solvating material) from the reactive species on the conjugated polymer (excitons and dopants) during operation. In this context, it is interesting to note that the operational lifetime (here defined as the time at which the current has dropped to half its maximum value) is improved by a factor of $\sim$2 in the bilayer devices.

To conclude, we have introduced a bilayer light-emitting electrochemical cell structure in which the ion- and electron-transport channels are separated, allowing the utilization of electrolyte/electroluminescent material combinations with mutually incompatible solubilities. We have further shown that this novel concept can lead to improved device operation.

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References

(1) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lussem, B.; Leo, K. *Nature* **2009**, *459*, 234.
(2) Yu, Z.; Hu, L.; Liu, Z.; Sun, M.; Wang, M.; Gruner, G.; Pei, Q. *Appl. Phys. Lett.* **2009**, *95*, 203304.
(3) Tseng, F. M.; Cheng, A. C.; Peng, Y. N. *Technol. Forecasting Social Change* **2009**, *76*, 897.
(4) Matyba, P.; Yamaguchi, H.; Eda, G.; Chhowalla, M.; Edman, L.; Robinson, N. D. *ACS Nano* **2010**, *4*, 637.
(5) Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.
(6) Slinker, J. D.; Rivnay, J.; Moskowitz, J. S.; Parker, J. B.; Bernhard, S.; Abruna, H. D.; Malliaras, G. G. *J. Mater. Chem.* **2007**, *17*, 2976.
(7) Costa, R. D.; Pertegas, A.; Orti, E.; Bolink, H. J. *Chem. Mater.* **2010**, *22*, 1288.
(8) Edman, L. *Electrochim. Acta* **2005**, *50*, 3878.
(9) Sun, Q. J.; Li, Y. F.; Pei, Q. B. *J. Disp. Technol.* **2007**, *3*, 211.
(10) Marcilla, R.; Mecerreyes, D.; Winroth, G.; Brovelli, S.; Yebra, M. d. M. R.; Cacialli, F. *Appl. Phys. Lett.* **2010**, *96*, 043308.
(11) Alem, S.; Gao, J. *Org. Electron.* **2008**, *9*, 347.
(12) Leger, J. M.; Rodovsky, D. B.; Bartholomew, G. R. *Adv. Mater.* **2006**, *18*, 3130.
(13) Hu, Y. F.; Gao, J. *J. Am. Chem. Soc.* **2009**, *131*, 18236.
(14) Lin, F.; Walker, E. M.; Lonergan, M. C. *J. Phys. Chem. Lett.* **2010**, *1*, 720.
(15) Matyba, P.; Maturova, K.; Kemerink, M.; Robinson, N. D.; Edman, L. *Nat. Mater.* **2009**, *8*, 672.
(16) Shao, Y.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2007**, *19*, 365.
(17) Fang, J. F.; Matyba, P.; Edman, L. *Adv. Funct. Mater.* **2009**, *19*, 2671.
(18) Bolink, H. J.; Cappelli, L.; Coronado, E.; Grätzel, M.; Orti, E.; Costa, R. D.; Viruela, P. M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2006**, *128*, 14786.
(19) Sandström, A.; Matyba, P.; Edman, L. *Appl. Phys. Lett.* **2010**, *96*, 053303.
(20) Cao, Y.; Yu, G.; Heeger, A. J.; Yang, C. Y. *Appl. Phys. Lett.* **1996**, *68*, 3218.
(21) Fang, J.; Matyba, P.; Robinson, N. D.; Edman, L. *J. Am. Chem. Soc.* **2008**, *130*, 4562.
(22) Wågberg, T.; Hania, P. R.; Robinson, N. D.; Shin, J. H.; Matyba, P.; Edman, L. *Adv. Mater.* **2008**, *20*, 1744.
(23) In ref 19, we reported that we could not detect light emission from similar blend devices driven at low voltages. Here we show in Figure 2c that this is indeed possible, and we attribute this to an improved vacuum in the test chamber and the employment of a very long exposure time for the detecting camera.
(24) deMello, J. C.; Tessler, N.; Graham, S. C.; Friend, R. H. *Phys. Rev. B* **1998**, *57*, 12951.
(25) Pei, Q.; Heeger, A. J. *Nat. Mater.* **2008**, *7*, 167.
(26) Robinson, N. D.; Fang, J. F.; Matyba, P.; Edman, L. *Phys. Rev. B* **2008**, *78*, 245202.
(27) Fang, J.; Yang, Y.; Edman, L. *Appl. Phys. Lett.* **2008**, *93*, 063503.
(28) Shin, J. H.; Dzwilewski, A.; Iwasiewicz, A.; Xiao, S.; Fransson, A.; Ankah, G. N.; Edman, L. *Appl. Phys. Lett.* **2006**, *89*, 013509.
(29) Shin, J. H.; Robinson, N. D.; Xiao, S.; Edman, L. *Adv. Funct. Mater.* **2007**, *17*, 1807.

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