

## General method to solution-process multilayer polymer light-emitting diodes

Shin-Rong Tseng, Shi-Chang Lin, Hsin-Fei Meng, Hua-Hsien Liao, Chi-Hung Yeh, Huan-Chung Lai, Sheng-Fu Horng, and Chain-Shu Hsu

Citation: *Applied Physics Letters* **88**, 163501 (2006); doi: 10.1063/1.2192574

View online: <http://dx.doi.org/10.1063/1.2192574>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/88/16?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Solution-processed conjugated polymer organic p - i - n light-emitting diodes with high built-in potential by solution- and solid-state doping](#)

*Appl. Phys. Lett.* **95**, 213303 (2009); 10.1063/1.3257979

[High-efficiency blue multilayer polymer light-emitting diode based on poly\(9,9-dioctylfluorene\)](#)

*J. Appl. Phys.* **101**, 084510 (2007); 10.1063/1.2721830

[Improved performances of organic light-emitting diodes with metal oxide as anode buffer](#)

*J. Appl. Phys.* **101**, 026105 (2007); 10.1063/1.2430511

[High-efficiency light-emitting diodes using neutral surfactants and aluminum cathode](#)

*Appl. Phys. Lett.* **86**, 083504 (2005); 10.1063/1.1865327

[Color-tunable multilayer light-emitting diodes based on conjugated polymers](#)

*Appl. Phys. Lett.* **84**, 1195 (2004); 10.1063/1.1645983

---

The advertisement features a dark blue background with white and orange text. At the top left, it reads 'NEW! Asylum Research MFP-3D Infinity™ AFM' in large white letters, followed by 'Unmatched Performance, Versatility and Support' in orange. On the right, the Oxford Instruments logo is shown with the tagline 'The Business of Science®'. Below the text are four images: a textured surface, a brown patterned surface, a grid of small squares, and the MFP-3D Infinity AFM instrument itself. Text descriptions are placed around these images: 'Stunning high performance' next to the textured surface, 'Simpler than ever to GetStarted™' next to the brown patterned surface, 'Comprehensive tools for nanomechanics' next to the grid of squares, and 'Widest range of accessories for materials science and bioscience' next to the AFM instrument.

## General method to solution-process multilayer polymer light-emitting diodes

Shin-Rong Tseng, Shi-Chang Lin, and Hsin-Fei Meng<sup>a)</sup>

*Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*

Hua-Hsien Liao, Chi-Hung Yeh, Huan-Chung Lai, and Sheng-Fu Horng

*Department of Electric Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China*

Chain-Shu Hsu

*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*

(Received 31 August 2005; accepted 13 March 2006; published online 17 April 2006)

An intermediate liquid buffer layer is introduced to overcome the dissolution problem of solution-processed multilayer conjugated polymer light-emitting diodes. This method can be applied to arbitrary combinations of polymers with no restriction on solvents. As an example, a hole-blocking layer is successfully spin coated on the common *p*-type emissive polymer layers. One green- and two blue-emitting polymers are chosen as the emissive layers. The electron-hole balance and efficiency are significantly improved by the addition of hole-blocking layer. The electroluminescence efficiency can be increased up to nine times, while the luminance up to seven times. In particular, 1.5 cd/A is obtained for deep blue emission from poly(9,9-dioctyl-fluorene) with 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene spin coated as the hole-blocking material. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192574]

Recently organic light-emitting diodes (OLED) have been demonstrated to reach nearly 100% internal quantum efficiency by employing triplet emitters and multilayer structures,<sup>1,2</sup> which usually include emissive, carrier transport, and carrier blocking layers. In general, a multilayer structure is required in order to balance the electron and hole currents. Although there have been impressive improvements in the carrier balance of polymer light-emitting diodes (PLED) by molecular design,<sup>3,4</sup> the efficiency is still far below OLEDs. The main reason for this problem is that the solution process itself causes dissolution between spin-coated or ink-jetted polymer layers.<sup>5–8</sup> This unfortunately means that the advantage of separating different functions such as charge injection, charge transport, and light emission into different layers cannot be used to improve PLED efficiency. Some efforts have been devoted to fabricate multilayer PLEDs by developing new materials such as cross-linkable polymers<sup>9</sup> and water/methanol-soluble copolymers.<sup>10</sup> But these methods are only restricted to specific polymers combined with specific solvents. Until now, there is no general and reliable method to fabricate arbitrary all-solution-processed multilayer PLED. In this letter, we report a new liquid buffer layer (BL) method which successfully prevents the dissolution between solution-processed polymer layers and completely removes the material and solvent restrictions.

The material of the BL must be a viscous nondissolvent liquid with relatively low boiling point. The viscosity is directly related to the protection capability. Before depositing the next polymer layer over an existing soluble polymer surface, the BL is first spin coated. The next layer is then spun on top of the liquid surface of the BL. Because the viscosity

of the BL is much higher than the usual solvent, the next layer will initially float over the BL instead of mixing with it. The polymer underneath is therefore protected by the BL against the solvent of the next layer. During the spinning most of the solvent of the next layer and part of the liquid BL are evaporated, resulting in a double-layer structure with possibly some residue of the BL in between. The residual BL is removed in the following baking in vacuum. Therefore, besides the high viscosity, low boiling point and small molecule weight of BL are also important for easy removal by baking. If the boiling point is much higher than the polymer's melting temperature, the required high baking temperature could damage the emissive polymer. The protection capability of many kinds of BL materials against various typical solvents such as xylene, toluene, and chloroform are studied as follows. Figure 1(a) shows the steps. First, a polymer layer 1 (L1) is spin coated on the substrate and baked in

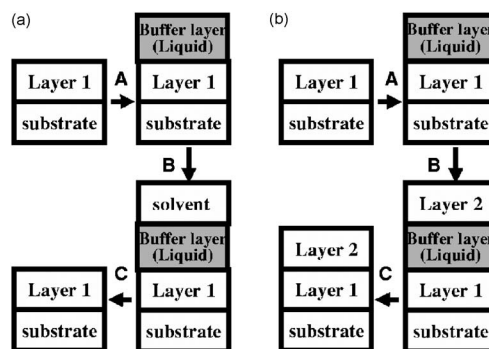


FIG. 1. (a) Test of BL protection capability by pure solvent. The viscous buffer layer and solvent are consecutively spin coated on layer 1 (A and B). Baking (C) moves both liquids. (b) Double-layer fabrication flow using BL. (A) The liquid BL is spin coated on L1, (B) L2 is quickly spin on the liquid BL, and (C) BL is removed by baking the device in vacuum.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: meng@mail.nctu.edu.tw

TABLE I. The BL protection capability test. The test flow is shown in Fig. 1(a). The viscosity and boiling point of each BL material are shown. Although the viscosity of 1,2-propylene glycol is low at room temperature, it increases rapidly when cooled down to 0 °C. Glycerol has good protection capability as 1,2-propylene glycol, but its high boiling point is unfavorable for removal by baking.

Layer 1 thickness (nm) <sup>a</sup>	200			200			180			106			103 (PFO)		
Buffer material <sup>b</sup>	B1			B2			B3			No buffer			B3		
Boiling point (°C)	290			188			128			...			128		
Viscosity ( $\eta$ /mPa s)	934 (25 °C)			248 (0 °C)			0.508 (25 °C)			...			0.508 (25 °C)		
Solvent <sup>c</sup>	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Final thickness (nm)	200	200	200	200	200	200	60	60	70	20	20	20	22	22	22

<sup>a</sup>L1 is BP105 except the last column.

<sup>b</sup>B1: glycerol, B2: 1,2-propylene glycol, and B3: *n*-octane.

<sup>c</sup>A: xylene, B: toluene, and C: chloroform.

vacuum at 120 °C for 40 min. After spinning the BL on L1, we spin the pure solvent on the liquid surface immediately. The temporary layer structure is substrate/L1/BL/solvent. After the evaporation of solvent and BL in air, we compare the L1 film thickness before and after the BL/solvent process. BL protection capability can be measured as the smallness of L1 thickness reduction. LUMINATION<sup>®</sup> BP105 from the Dow Chemical Company light-emitting polymer (LEP) is chosen to be the test L1 material due to its high solubility in all common solvents. The dissolution for any other polymer under the same situation can only be less than BP105. The film thicknesses are measured by a Kosaka ET4000 surface profiler. Table I summarizes the results. Due to the high viscosity derived from hydrogen bonding, glycerol and 1,2-propylene glycol both have excellent protection capability. Even for the strong solvents such as chloroform, they can perfectly protect L1 from the dissolution. On the contrary, *n*-octane has poor viscosity and the protection capability is not so good. Interestingly 1,2-propylene glycol combines the unique properties of high viscosity at 0 °C (248  $\eta$ /mPa s) and low boiling point (188 °C), which are crucial for the protection and subsequent removal of BL as stated above. Because the viscosity of 1,2-propylene glycol decreases with temperature dramatically, it is applied as buffer before cooling to 0 °C.

The next step is to see whether the next polymer layer L2 can be spin coated on L1 using the BL method. Below 1,2-propylene glycol is always used as the BL and BP105 is chosen to be both L1 and L2. The process flow is shown in Fig. 1(b). Ideally the final total thickness is the sum of the thicknesses of L1 and L2 as they are individually spin coated on the substrate. Under the protection of the BL, the thickness difference between the double layer and the sum of L1 and L2 is less than 7 nm. The BL is therefore proved successful to fabricate a polymer multilayer structure without dissolution. Obviously this can be applied to arbitrary L1 and L2 in any solvent. Using this new method it becomes possible to make many kinds of multilayer PLEDs, which include not only poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole-transport layer (HTL), and emission layer (EML) but also other functional layers such as hole-blocking layer (HBL), electron-blocking layer (EBL), as well as electron transport layer (ETL) in order to optimize device efficiency.

Below we demonstrate some multilayer PLEDs with improved efficiency using this buffer layer method. Many emissive conjugated polymers are *p* type, and the hole mobility is two or three orders larger than electron mobility. We therefore consider the device structure indium tin oxide (ITO)/PEDOT:PSS/EML/HBL/cathode to block the hole current

and improve the device efficiency. Three typical *p*-type polymers are used as EML, including poly(9,9-dioctyl-fluorene) (PFO, EA/IP=3/5.8 eV) (purchased from American Dye Source), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(*N*-(4-sec-butylphenyl)diphenylamine))] (TFB,EA/IP=2.3/5.3 eV) (purchased from American Dye Source), and poly[(2-(4-(3,7-dimethyloctoxy)phenyl)-3-phenyl-1,4-phenylenevinylene)-co-(2,5-dimethoxy-1,4-phenylenevinylene)] (DPOC10-DOMe-PPV, EA/IP=3.2/5.6 eV) (synthesized in our laboratory). EA and IP are electron affinity and ionization potential respectively. For HBL, we choose 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene (TPBI, EA/IP=2.7/6.7 eV) with good electron transport characteristic and large IP to block holes. With the unusually large IP, TPBI is commonly used as the HBL in OLEDs by evaporation.<sup>11</sup> The structure of the device without HBL is glass/ITO/PEDOT:PSS/EML/LiF/Ca/Al, and the baking condition of EML is 180 °C for TFB and 120 °C for the other EML for 40 min in vacuum. The structure of the device with HBL is glass/ITO/PEDOT:PSS/EML/HBL/LiF/Ca/Al, and the baking condition

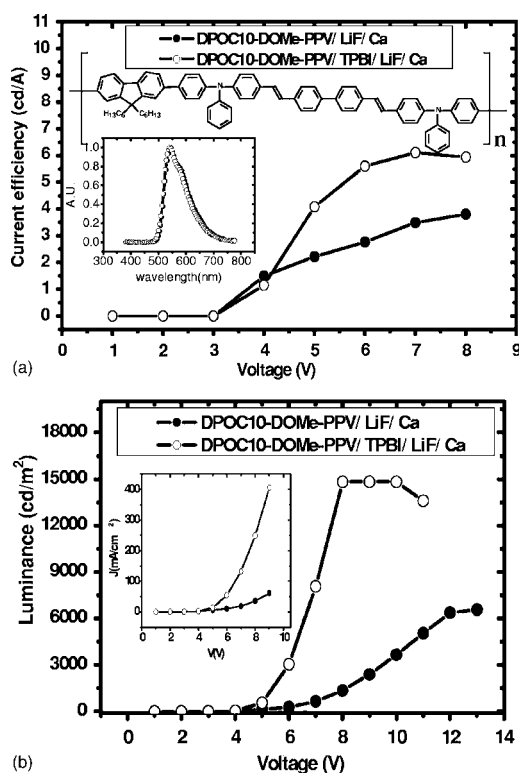


FIG. 2. The performances of DPOC10-DOMe-PPV LED (solid circle) and DPOC10-DOMe-PPV/TPBI LED (open circle). The chemical structure of DPOC10-DOMe-PPV is shown.

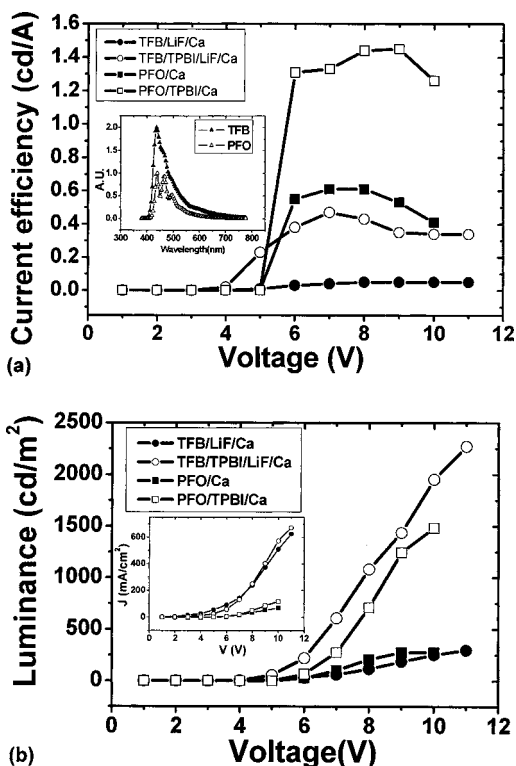


FIG. 3. The performances of PFO LED (solid circle), PFO/TPBI LED (open square), TFB LED (solid circle), and TFB/TPBI LED (open circle). The EL spectra are normalized to 2 for TFB device (solid triangle) and 1 for PFO (open triangle) for clarity.

of EML is the same as the devices without HBL. After the HBL is spin coated on the EML using BL method, the devices are baked in vacuum for 60 min at 200 °C for DPOC10-DOMe-PPV and 120 °C for the other EML. Then the devices are coated with LiF/Ca/Al cathodes and packaged in the glove box. The electroluminescence (EL) spectra and current-luminance-voltage ( $I$ - $L$ - $V$ ) characteristics are measured by a Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter.

The first example is green DPOC10-DOMe-PPV as EML and TPBI as HBL, both dissolved in toluene. The DPOC10-DOMe-PPV thickness is 120 nm without TPBI and 80 nm with TPBI (30 nm). The maximum luminance is increased from 6367 to 14820 cd/m<sup>2</sup>, which is shown in Fig. 2. The device efficiency is enhanced from 3.89 to 6.11 cd/A. For blue polymers, the  $I$ - $L$ - $V$  curves of PFO PLED with and without TPBI HBL are shown in Fig. 3. Both PFO and TPBI are dissolved in toluene. The PFO thickness is 130 nm without TPBI and 60 nm with TPBI (45 nm). The maximum luminance is again significantly improved from 278 to 1483 cd/m<sup>2</sup>, and the current does not become smaller. The current efficiency is enhanced from 0.61 to 1.45 cd/A. It is the highest record in the literature for unfiltered PFO.<sup>10,12,13</sup> An even more dramatic case is TFB, also shown in Fig. 3. TFB is dissolved in xylene and TPBI is dissolved in chloroform. The TFB thickness is 86 nm and the TPBI thickness is 35 nm. The maximum luminance is en-

hanced from 298 to 2271 cd/m<sup>2</sup>, and the current efficiency from 0.05 to 0.47 cd/A. The general feature of all the devices is that the HBL significantly improves the efficiency and luminance while the current remains about the same. The turn-on voltage is also remarkably reduced for all devices with HBL. The lifetime and uniformity of the bilayer devices are not degraded relative to the single-layer ones, indicating complete removal of the buffer liquid by annealing. The above results not only open the possibility of all-solution-processed multilayer PLEDs through buffer layer method but also show that the LED thus made indeed significantly exceeds the conventional single-layer device for three typical green and blue emissive polymers. This method is very easy to apply and does not involve any process other than spin coating and baking. There is no need to design and synthesize new functional materials. One can simply choose the combinations of existing materials with desired properties as long as they can be dissolved in some solvent.

In conclusion we develop a buffer layer method to fabricate all-solution-processed multilayer polymer devices and use this method to improve the efficiency of PLED as an example. To serve as a buffer layer, the material must be a nondissolvent liquid with high viscosity in order to protect the underneath layer. On the other hand it must have low boiling point and small molecular weight for easy removal by baking. 1,2-propylene glycol appears to be the best choice. This method can be applied to not only multilayer PLEDs but also other solution-process multilayer polymer devices such as solar cells which also need multilayer structure to increase the efficiency.

This work is supported by the National Science Council of the Republic of China and the Excellence Project of the ROC Ministry of Education.

<sup>1</sup>C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000).

<sup>2</sup>M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.* **79**, 156 (1996).

<sup>3</sup>X. Gong, W. Ma, J. C. Ostrowski, G. C. Bazan, D. Moses, and A. J. Heeger, *Adv. Mater. (Weinheim, Ger.)* **16**, 615 (2004).

<sup>4</sup>W. Sotoyama, T. Satoh, N. Sawatari, and H. Inoue, *Appl. Phys. Lett.* **86**, 153505 (2005).

<sup>5</sup>S. R. Forrest, *Nature (London)* **428**, 911 (2004).

<sup>6</sup>C. C. Huang, H. F. Meng, G. K. Ho, C. H. Chen, C. S. Hsu, J. H. Huang, S. F. Horng, B. X. Chen, and L. C. Chen, *Appl. Phys. Lett.* **84**, 1195 (2004).

<sup>7</sup>Z. L. Li, H. F. Meng, S. F. Horng, C. S. Hsu, L. C. Chen, and S. M. Chang, *Appl. Phys. Lett.* **84**, 4944 (2004).

<sup>8</sup>G. K. Ho, H. F. Meng, S. C. Lin, S. F. Horng, C. S. Hsu, L. C. Chen, and S. M. Chang, *Appl. Phys. Lett.* **8**, 4576 (2004).

<sup>9</sup>Z. Liang and O. M. Cabarcos, *Adv. Mater. (Weinheim, Ger.)* **16**, 823 (2004).

<sup>10</sup>W. Ma, P. K. Iyer, X. Gong, B. Liu, D. Moses, G. C. Bazan, and A. J. Heeger, *Adv. Mater. (Weinheim, Ger.)* **17**, 274 (2005).

<sup>11</sup>T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S. C. Lo, and P. L. Burn, *Appl. Phys. Lett.* **82**, 4824 (2003).

<sup>12</sup>K. H. Weinfurter, H. Fujikawa, S. Tokito, and Y. Taga, *Appl. Phys. Lett.* **76**, 2502 (2000).

<sup>13</sup>D. Neher, *Adv. Mater. (Weinheim, Ger.)* **22**, 1022 (2001).