

Enhanced emission efficiency in organic light-emitting diodes using deoxyribonucleic acid complex as an electron blocking layer

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Enhanced electroluminescent efficiency using a deoxyribonucleic acid (DNA) complex as an electron blocking (EB) material has been demonstrated in both green- and blue-emitting organic light-emitting diodes (OLEDs). The resulting so-called BioLEDs showed a maximum luminous efficiency of 8.2 and 0.8 cd/A, respectively. The DNA-based BioLEDs were as much as 10× more efficient and 30× brighter than their OLED counterparts. © 2006 American Institute of Physics. [DOI: 10.1063/1.2197973]

The next frontier in organic electronic and photonic devices is the use of biomaterials, either naturally occurring or artificially produced, based on biological methods. Biomaterials with unusual properties not easily replicated in conventional organic or inorganic materials can provide another degree of freedom in terms of device design and produce enhancements in device performance.¹ Furthermore, natural biomaterials are a replenishable resource and are inherently biodegradable.

We report on the use of deoxyribonucleic acid (DNA) as an integral element of organic light-emitting diodes (OLED). Devices that incorporate DNA thin films as electron blocking layers (EBL), so-called BioLEDs, produce significant increases in luminance and luminous efficiency. This is illustrated in the photographs of Fig. 1 where photoemission from green- and blue-emitting conventional OLEDs is compared to DNA-containing BioLEDs. All devices were identically processed (with the exception of the DNA layer) and have the same active area of $2 \times 2 \text{ mm}^2$. The effect of blocking electron flow is to enhance the probability of radiative electron-hole recombination, leading to increased device luminous efficiency and luminance. Adamovich *et al.* first noted^{2,3} the use of EBL layers in OLEDs to prevent electron-hole recombination from occurring in adjacent hole transport layers (HTL).

DNA-based BioLEDs previously reported^{4,5} have incorporated DNA-based thin films as hosts for lumophores indicating the feasibility of the concept, but without significant improvement in device performance over conventional OLEDs. Hirata *et al.* have investigated⁶ the properties of DNA as a charge transport layer in several device configurations elucidating their properties through their effect on the device current-voltage (*I-V*) characteristics.

The DNA used in this study is processed⁷ from naturally occurring salmon sperm DNA (saDNA), a waste product of the salmon fishing industry. DNA is converted to a DNA-lipid complex by a cationic surfactant reaction,⁸ resulting in a compound that is soluble in polar organic solvents but insoluble in water. This allows the formation of thin films by casting or spin coating. We have utilized the reaction⁹ with

cetyltrimethylammonium (CTMA) to form a DNA-CTMA complex from which thin films were produced. This process has been utilized in investigations of DNA-CTMA as an electro-optical material.^{10,11} DNA-CTMA molecular weight reduction is performed by sonication to aid thin film formation and reduce electrical resistivity.¹² For devices reported here, the final DNA-CTMA molecular weight is $\sim 145\,000 \text{ Da}$, which is equivalent to 220 base pairs and an average molecular length of 75 nm. The electrical resistivity of separately fabricated DNA-CTMA thin films is $\sim 10^7 \Omega \text{ cm}$.

The energy level diagram of the green-emitting BioLED is shown in Fig. 2. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the organic materials are shown along with the work functions of the metal layers. The green BioLED structure consists of the following layers: indium tin oxide (ITO) anode; PDOT [poly(3,4-ethylenedioxythiophene)] doped with PSS [poly(4-styrenesulfonate)] hole injection layer (HIL); DNA-CTMA electron blocking layer (EBL);

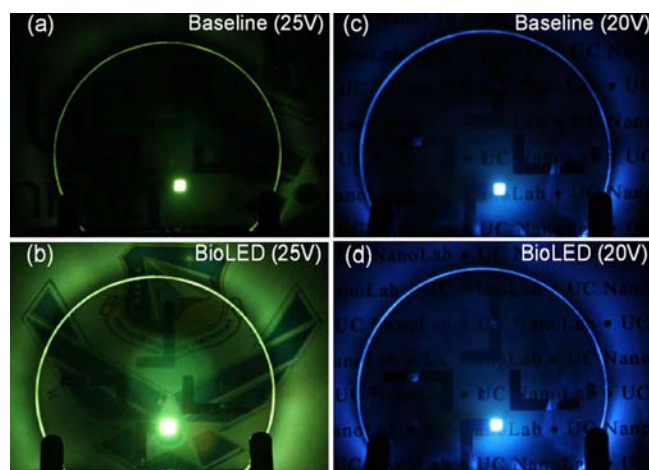


FIG. 1. (Color online) Photographs of EL emission from several devices: (a) green Alq_3 baseline OLED at 25 V (707 mA/cm^2)— 590 cd/m^2 , 0.35 cd/A ; (b) green Alq_3 BioLED with DNA EBL at 25 V (308 mA/cm^2)— $21\,100 \text{ cd/m}^2$, 6.56 cd/A ; (c) blue NPB baseline OLED at 20 V (460 mA/cm^2)— 700 cd/m^2 , 0.14 cd/A ; (d) blue NPB BioLED with DNA EBL at 20 V (200 mA/cm^2)— 1500 cd/m^2 , 0.76 cd/A . The device emitting area is $2 \times 2 \text{ mm}^2$.

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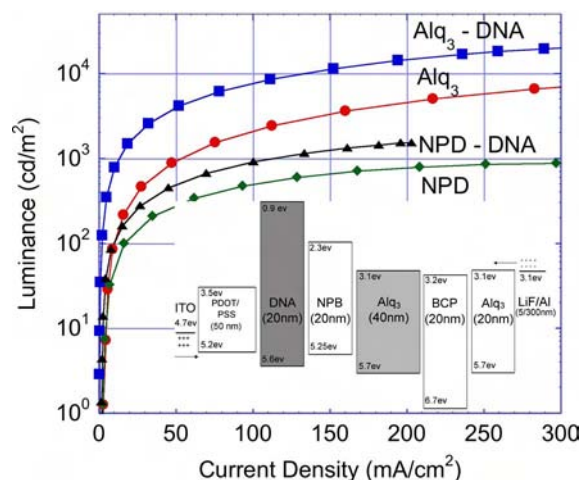


FIG. 2. (Color online) Luminance vs current density in green Alq_3 and blue NPB EL devices with and without DNA EBL. The inset shows an energy level diagram in a green-emitting (Alq_3) DNA BioLED structure.

NPB [*N,N'*-bis(naphthalene-1-yl)-*N,N'*-bis(phenyl) benzidine)] hole transport layer (HTL); Alq_3 [tris-(8-hydroxyquinoline) aluminum] emitter layer (EML); BCP [2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline] hole blocking layer (HBL); Alq_3 electron transport layer (ETL); LiF electron injection layer (EIL); and Al cathode. The blue BioLED structure did not contain the Alq_3 EML, thus forcing electron-hole recombination and related photoemission to occur in the NPB layer. For comparison, OLEDs were fabricated with no EBL (baseline device) or with EBLs using common electro-optic polymers [PMMA (polymethylmethacrylate) or PVK (polyvinyl carbazole)].

The energy level diagram in Fig. 2 intuitively shows that DNA-CTMA will act as an EBL in the device. With a LUMO level⁶ of 0.9 eV electrons in the NPB layer will experience an energy barrier of 1.4 eV. The DNA-CTMA HOMO level⁶ of 5.6 eV should not inhibit hole transport. Long distance hole transfer has also been reported for DNA in solution.¹³ PVK has a LUMO level of 2.3 eV and a HOMO level of 5.8 eV, which does not suggest that the material will effectively block electrons. The PMMA LUMO and HOMO levels are not reported, but the energy gap is estimated at 5.6 eV from the optical absorption of the mate-

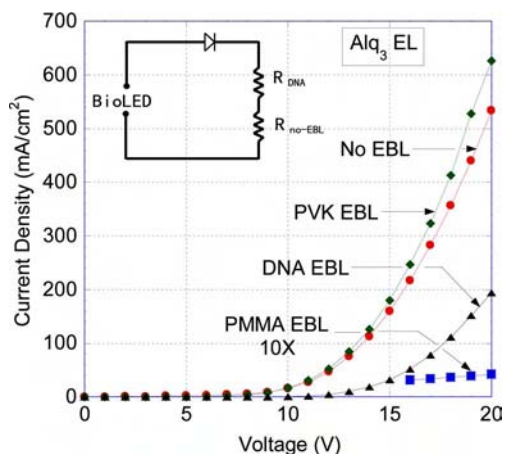


FIG. 3. (Color online) Current density vs voltage in green Alq_3 LEDs: baseline device, DNA EBL, PVK EBL, PMMA EBL. The inset shows a simple equivalent circuit for the DNA EBL device.

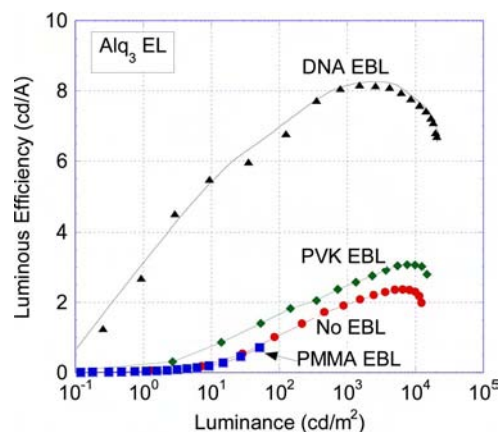


FIG. 4. (Color online) Luminous efficiency vs luminance in Alq_3 EL devices: baseline device, DNA EBL, PVK EBL, and PMMA EBL.

rial. Such a wide energy gap suggests that PMMA could be a charge blocking material.

A PDOT/PSS HIL (50 nm) is spin deposited onto the ITO (80 nm) anode. Next (for the BioLED structures), DNA-CTMA dissolved into butanol is spin deposited (20 nm) on top of the PDOT/PSS HIL. The difference in DNA molecule length and film thickness suggests that most DNA chains lie in the plane of the film, hence perpendicular to current flow. For EBL material comparison in OLED structures, PMMA or PVK were substituted for DNA-CTMA. PMMA dissolved in cyclopentanone and PVK dissolved in chlorobenzene are spin deposited to a thickness of ~ 20 nm. The remaining layers were deposited by molecular beam deposition at pressures $\sim 1 \times 10^{-7}$ Torr. For the blue BioLED and OLED structures the NPB layer is 40 nm.

Figure 2 shows the luminous performance of blue (NPB emitting) and green LEDs for the BioLED and baseline OLED structures. The benefit of using DNA-CTMA as the EBL is clear for both blue and green LEDs. Comparing luminance at a current density of 200 mA/cm^2 , the green BioLED achieves $15\,000 \text{ cd/m}^2$, whereas the baseline device reaches only 4500 cd/m^2 . Similarly, the blue BioLED has a luminance of 1500 cd/m^2 at 200 mA/cm^2 [Fig. 1(d)], while the corresponding baseline device reaches only $\sim 800 \text{ cd/m}^2$. The highest luminance of $\sim 21\,000 \text{ cd/m}^2$ was achieved by the green BioLED at a bias of $\sim 310 \text{ mA/cm}^2$ [Fig. 1(b)].

The current density versus voltage (J - V) curves in forward bias for the green (Alq_3 emitting) OLEDs as a function of EB material are shown in Fig. 3. Under reverse bias, a current rectification ratio of $>20\times$ at $\pm 20 \text{ V}$ is measured and no light emission is observed. PVK is a commonly used conductive polymer that acts as a HTL in this device structure as shown by the increase in current as compared to the device with no EB material. Conversely, since PMMA is electrically insulating, the current is greatly reduced when it is used as the EB material. DNA is reported^{14–17} to act as a semiconductor material, which accounts for the fact that there is charge transport through the device, but at a lower current than the device without DNA-CTMA. A simple equivalent circuit for the BioLED (DNA EBL) is shown in the inset of Fig. 3, which isolates the series resistance associated with the DNA layer (R_{DNA}) and the series resistance ($R_{\text{no-EBL}}$) due to all the other layers as measured in the no-EBL LED case. By comparing the J - V slope after turn-on for

the two devices R_{DNA} of $\sim 300 \Omega$ is calculated. This corresponds to a DNA-CTMA resistivity of $\sim 6 \times 10^6 \Omega \text{ cm}$.

The luminous efficiency of the green (Alq_3) devices with various EB layers is shown as a function of luminance in Fig. 4. The DNA-CTMA increases the efficiency by a factor of $\sim 2\text{--}10\times$ over devices with PVK, PMMA, and no EBLs. It is clear that an EBL with a low LUMO level of $\sim 1 \text{ eV}$ is preferred to block electrons, along with a HOMO level matching that of common hole transport materials (5.3 eV). Of all the materials tested, DNA-CTMA matches these criteria the closest.

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¹M. A. Strosio and M. Dutta, *Proc. IEEE* **93**, 1772 (2005).

²V. Adamovich, J. Brooks, A. Tamayo, A. Alexander, P. Djurovich, B. D'Andrade, C. Adachi, S. Forrest, and M. Thompson, *New J. Chem.* **26**, 1171 (2002).

³V. Adamovich, S. Cordero, P. Djurovich, A. Tamayo, M. Thompson, B. D'Andrade, and S. Forrest, *Org. Electron.* **4**, 77 (2003).

⁴N. Kobayashi, S. Umemura, K. Kusabuka, T. Nakahira, and H. Takashi, *J. Mater. Chem.* **11**, 1766 (2001).

⁵T. Koyama, Y. Kawabe, and N. Ogata, *Proc. SPIE* **4464**, 248 (2002).

⁶K. Hirata, T. Oyamada, T. Imai, H. Sasabe, C. Adachi, and T. Kimura, *Appl. Phys. Lett.* **85**, 1627 (2004).

⁷L. Wang, J. Yoshida, and N. Ogata, *Chem. Mater.* **13**, 1273 (2001).

⁸K. Tanaka and Y. Okahata, *J. Am. Chem. Soc.* **118**, 10679 (1996).

⁹L. Wang, J. Yoshida, and N. Ogata, *Chem. Mater.* **13**, 1273 (2001).

¹⁰J. Grote, N. Ogata, D. Diggs, and F. K. Hopkins, *Proc. SPIE* **4991**, 621 (2003).

¹¹J. Grote, J. Hagen, J. Zetts, R. Nelson, D. Diggs, M. Stone, P. Yaney, E. Heckman, C. Zhang, W. Steier, A. Jen, L. Dalton, N. Ogata, M. Curley, S. Clarson, and F. K. Hopkins, *J. Phys. Chem. B* **108**, 8584 (2004).

¹²E. Heckman, J. Hagen, P. Yaney, J. Grote, and F. K. Hopkins, *Appl. Phys. Lett.* **87**, 211115 (2005).

¹³T. Takada, K. Kawai, M. Fujitsuka, and T. Majima, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 14002 (2004).

¹⁴H. Fink and C. Schonenberger, *Nature (London)* **398**, 407 (1999).

¹⁵D. Porath, B. Bezryadin, S. de Vries, and C. Dekker, *Nature (London)* **403**, 635 (2000).

¹⁶L. Cai, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* **77**, 3105 (2000).

¹⁷A. Yu. Kasumov, M. Kociak, S. Gueron, B. Reulet, V. T. Volkov, D. V. Klinov, and H. Bouchiat, *Science* **291**, 280 (2001).