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Pure DNA as an Efficient Electron Blocking Layer

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*We report on fabrication and characterization of polymer light emitting diode by using a thin film of pure deoxyribonucleic acid as electron blocking layer (EBL). A thin film of phosphorescent Ir(ppy)$_3$ luminophore, embedded in the poly(*N*-vinylcarbazole) (PVK)/2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) is used as emission layer. The obtained BioLED shows a good stability and its luminous efficiency is improved by* ca *40% as compared to the case without EBL. The result shows that using the DNA layer one can either improve the OLED brightness at the same current density or operate at a significantly lower current density with the same brightness than without it.*

Keywords OLED; BioLED; deoxyribonucleic acid; luminance; luminous efficiency; PVK; PBD

Introduction

The electroluminescence phenomenon, in which electron and holes, with corresponding energies, recombine in a photoluminescent layer giving light emission was first reported in early fifties by A. Bernanose and co-workers [1–2]. The observation was done in a layer containing acridine orange luminophore (3-*N*,3-*N*,6-*N*,6-*N*-tetramethylacridine-3,6-diamine), embedded in cellulose or cellophane by applying an AC electric field to a thin film. Since that time the field of organic light emitting devices (OLEDs) has known an immense development. This is motivated by high potential of practical applications as light sources for display as well as for lighting, as OLEDs exhibit an excellent external conversion efficiency from electric current into light. Principally two kind of molecules are used as luminophores: small molecules (SLED) like tris(8-hydroxyquinolinato)aluminium (Alq_3) [3] or polymers (PLEDs) [4].

In the first case the emission layer is obtained by vacuum evaporation while in the case of polymers this is got by a solution casting method. Both approaches show some advantages and drawbacks. The main advantage of using polymers is the possibility of mass and cheap large area displays fabrication by solution casting or making very small

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pixels using the inkjet technique. Numerous studies were done on optimization of OLED's performances by introducing electron (ETL) and hole (HTL) transporting layers to improve the current/photons conversion efficiency.

Recently Steckl and co-workers [5] (see also Hagen et al. [6]), and later Chen et al. [7], have shown that introducing to the OLED structure an DNA based electron blocking layer (EBL) increases its brightness as well as the lifetime. Both research teams used N,N0-bis(naphthalen-1-yl)-N,N0-bis(phenyl)-benzidine (NPB) as blue light emitting molecule. As EBL both groups used DNA modified by reaction with a surfactant: cetyltrimethyl ammonium (Steckl et al. [5]) or an aromatic one (Chen et al. [6]). However to make reaction of surfactant with DNA, and to decrease the DNA resistivity, it is necessary to decrease the molecular mass of DNA what is done by sonication. This method is a brutal one and may lead to breaking of DNA molecule with formation of new species. In fact, in our practice, we observed browning of DNA due to sonication made for a longer time period or with a higher sonication energy. Steckl et al. included also two layers of tris(8-hydroxyquinolinato) aluminium (Alq3): one for green emission and the second as electron transporting layer (ETL), while Chen et al. [6]). used this molecule to make just an ETL.

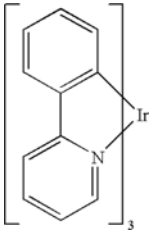
In this paper we report on realization of a BioLED using a thin layer ($\sim$10 nm) of pure deoxyribonucleic acid (DNA) as EBL. It does not require its sonication. By spin coating of water solution of DNA one obtains robust, homogenous thin films on PEDOT:PSS layer. The DNA conductivity, few orders of magnitude larger than that of DNA-surfactant complex is high enough to do not alter I-V characteristics of BioLED. The fabrication technology is simpler with another advantage of not using organic solvents which may alter the OLED structure. The observed luminance efficiency is *ca* 40% larger with EBL in comparison to the OLED without it.

Materials

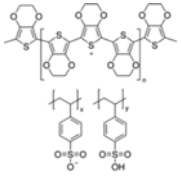
In our approach as active luminophore we used a phosphorescent lanthanide organometallic molecule: iridium (III) complex tris(2-phenylpyridine) iridium ($Ir(ppy)_3$), known for its high luminescence quantum efficiency [8–10]. The luminophore was purchased from American Dye Source, Inc. and used as supplied. To avoid quenching effect the molecule was incorporated in poly(*N*-vinylcarbazole) (PVK), mixed with 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) [11–12], 0.30 wt%. It allows thin film formation by solution casting. The high internal conversion quantum efficiency of phosphorescent $Ir(ppy)_3$ luminophore is due to the formation of both singlet and triplet excitons and their very effective radiative recombination. For a similar dye bis(2-phenylpyridine)iridium (III) acetylacetonate Ir(acac)(ppy) EQ \s\do5(2), embedded in 3-phenyl-4-(1′-naphthyl-5-phenyl)-1,2,4-triazole matrix Adachi et al. [13] found it to be close to 100%. As anode we used indium tin oxide (ITO) thin layer (work function of 4.7 eV [14]), deposited on glass substrate and as cathode a vacuum deposited thin film of aluminium, coated with a thin layer of LiF (effective work function $\sim$3.1 eV). The LiF layer reduces the work function of aluminium and enhances the electron injection [15–16]. The chemical structures of used molecules and polymers are shown in Table 1.

The HOMO and LUMO energies of the used materials, together with the corresponding layers thicknesses are shown in Fig. 1. The cited energies originate from Clevios website [17] (PEDOT:PSS), Steckl et al. [5] (DNA), D'Andrade et al. [17] (PVK), Chang et al. [19] and Chen et al. [20] (PBD), respectively. Comparison of the relative positions of the energy levels allows to expect very good conditions for the hole injection into the emissive

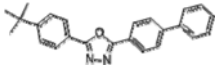
Table 1. Chemical structures of molecules and polymers used in this study



Ir(ppy)3 (Tris[2-phenylpyridinato-C^2,*N*]iridium(III))

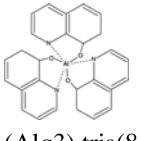


PEDOT:PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

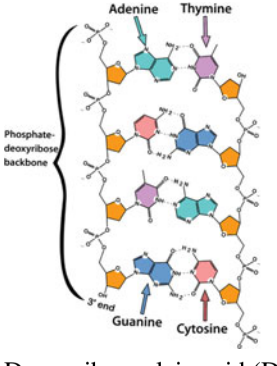


PBD (2-(4-*tert*-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole)

PVK (polyvinyl carbazol)



(Alq3) tris(8-hydroxyquinolinato) aluminium



Deoxyribonucleic acid (DNA) (http://www.google.fr/search?q=chemical+structure+of+dna&tbm=isch&tbo=u&source=univ&sa=X&ei=09qUU5uGEMGr0QWGioCACQ&ved=0CC0QsAQ&biw=884&bih=337)

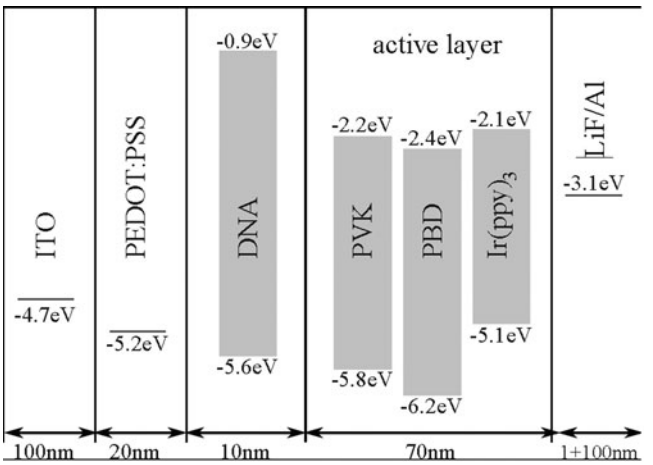


Figure 1. Energetic levels diagram of materials used for BioLED fabrication. For details see text.

layers and slightly worse conditions for electron injection. Moreover the high value of DNA LUMO level ensures the electron blocking, and its low HOMO level favours the hole injection.

DNA used in this study was supplied by Naoya Ogata, Ogata Research Laboraory, Ltd., Chitose, Japan. It was extracted from the waste produced by the salmon processing industry. Its molecular mass is *ca* 10^8 Da. The biopolymer was used as supplied. For the sake of comparison another OLED was fabricated without the DNA EBL layer.

BioLED Fabrications

The studied BioLED was fabricated using the following procedure: first on the ITO coated glass substrate a thin layer of the diluted 1:2 solution with methanol the well-known conducting polymer mixture of poly(3,4-ethylenedioxythiophene) (PEDOT) with poly(styrene sulfonate) (PSS) (PEDOT:PSS), purchased at Clevios was deposited by spinning. Before deposition the solution was filtered with a 0.22 μm pore diameter PVDF filter (ROTH). The substrate rotation speed was of 2000 rpm. Then the deposited film was annealed at 200°C for 10 minutes. It makes the PEDOT:PSS layer insoluble in water, allowing the deposition of DNA biopolymer by the solution casting. Thin layer of pure DNA alone and of PVK–PBD (70/30 wt%), doped with 2 wt% of $Ir(ppy)_3$ complex were deposited subsequently by spin coating too after filtering the solutions before the deposition with a 0.45 μm pore size PTFE filter. The angular rotation speed used was of 2 000 rpm for both depositions. Then a very thin LiF layer (1 nm) was predeposited by vacuum sublimation, followed by deposition of Al electrode using the same technique. The thickness of the layers was independently measured with DektakXT profilometer (Bruker). The spectral distributions of electroluminescence were recorded using MicroHR spectrometer and a CCD camera 3500 (Horriba Jobin Yvon). The diode luminance and the colour of the emitted light were measured with the Minolta CS-200 camera. The I-V characteristics were obtained by means of the Keithley 2400 Source Measure Unit.

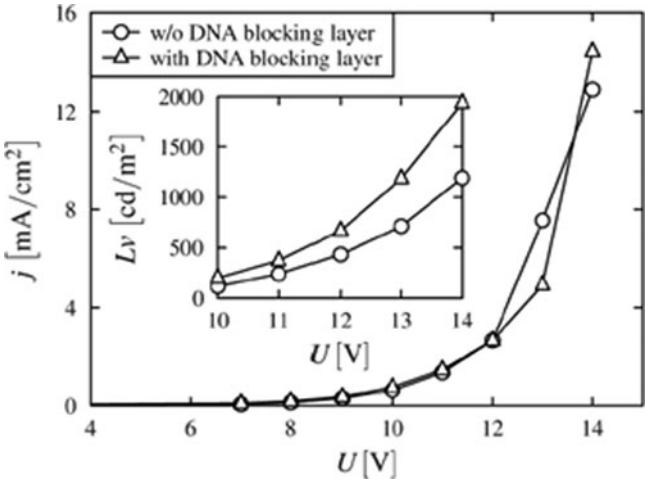


Figure 2. Current density (j) vs voltage (V) for studied PLEDs with and w/o DNA electron blocking layer. Inset shows luminance (Lv) dependency on applied voltage for both fabricated PLEDs.

Experimental Procedure and Results

The I-V characteristics were obtained by means of the Keithley 2400 Source Measure Unit. The measured current density-voltage characteristics of both diodes are displayed in Fig. 2. They exhibit a typical behaviour for organic diodes in the voltage range from 6 to 14V. It is worth to notice that the diodes with and without DNA blocking layer have similar current densities at the given voltage. Inset in Fig. 2 displays the measured luminance versus the applied voltage. One can see that the luminance values are significantly higher for BioLED than for OLED with the same structure but without the DNA layer. For the driving voltage of 14 V the BioLED luminance is about 40% larger than that of OLED.

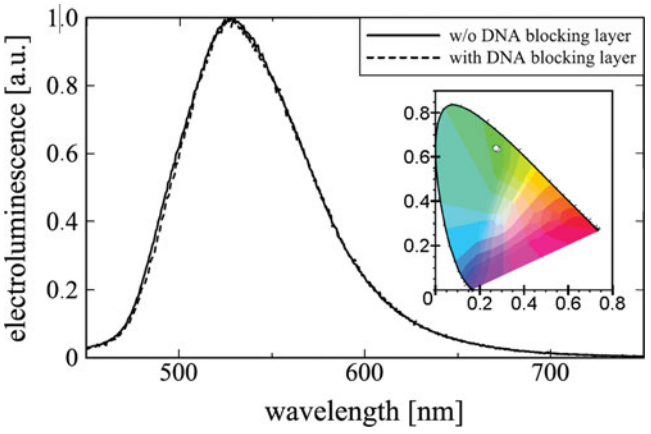


Figure 3. Normalized emission spectra of the two studied PLEDs: (PVK/PBD)+Ir(ppy) EQ \s\do5(3) (solid line), (PVK/PBD)+Ir(ppy) EQ \s\do5(3) + DNA blocking layer (thickness ca. 10 nm – dashed line). Inset: shows the CIE 1931 chromaticity diagram with the colour coordinates obtained from the emission spectra.

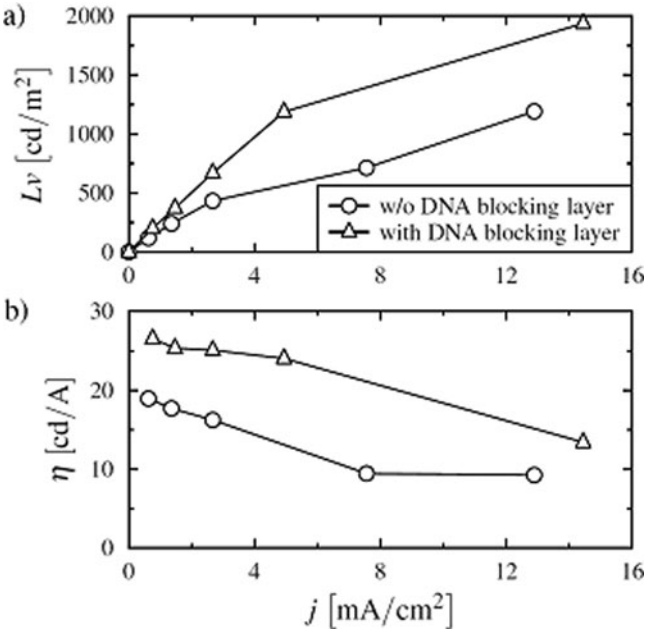


Figure 4. Luminance (a) and Luminous efficiency (b) *vs* current density for device with and w/o DNA blocking layer.

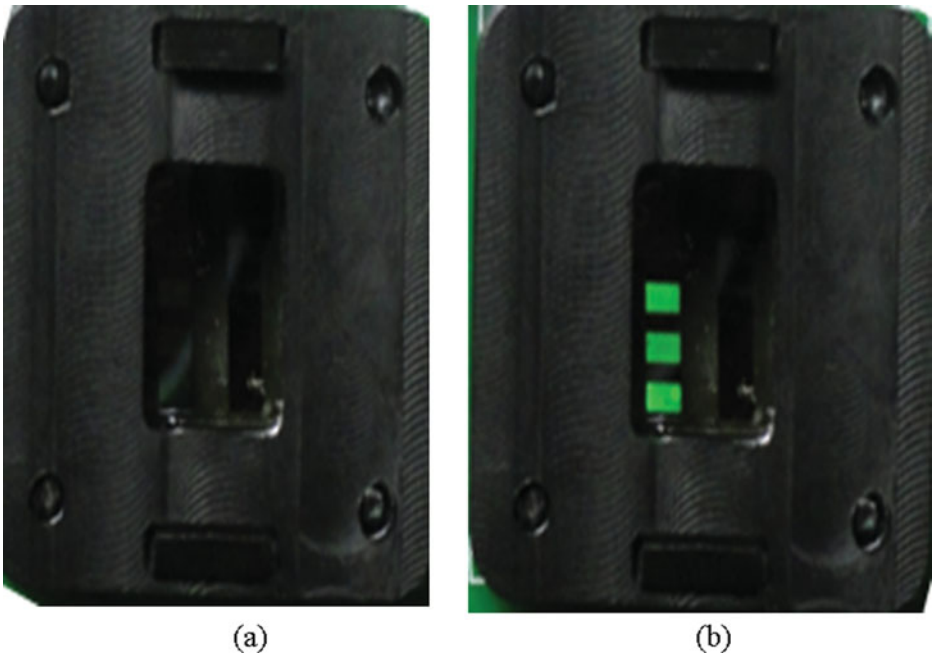


Figure 5. Photo of three simultaneously deposited BioLEDs without (a) and with applied driving voltage (b)

Figure 3 shows the normalized electroluminescence spectra of the studied BioLED (dashed line) and of PLED. Both overlap showing that the DNA layer practically does not alter the emission spectrum of $Ir(ppy_3)$ molecule. Insert to this figure shows the CIE 1931 chromaticity diagram [20] with the colour coordinates obtained from the emission spectra, which are almost identical for both LEDs.

An important parameter used for the evaluation of the performance of the LED is the observed luminance versus the current density flowing through the diode. For both devices they are displayed in Fig. 4a. It is seen that with increasing current density for both LEDs the luminance is increasing too, as expected. However this increase is significantly faster for BioLED than for OLED. For current densities higher than 4 mA/cm^2 the luminance is approximately two times larger for the device with DNA blocking layer than without it. Basing on the luminance-current density characteristics (Fig. 4a) we have calculated the luminous efficiencies for both diodes, which are shown in Fig. 4b. For both types of diodes the largest values of luminous efficiency (18 and 26 Cd/A for PLED and BioLED, respectively) were obtained for the current density of *ca.* 1 mA/cm^2. It means that the BioLED luminous efficiency is about 40% higher than for the diode without EBL. This result shows an effective electron blocking, increasing in this way the probability of e-h recombination with an emission of photon. A photo of three simultaneously deposited and operating BioLEDs without (a) and with (b) applied driving voltage is shown in Fig. 5.

Conclusions

The present study confirms interest which presents DNA supramolecule material for application in photonics and in electronics [22]. We show that a BioLED realized with a pure DNA electron blocking layer permits to have 40% higher luminance efficiency for the same current density than the same LED without EBL. It is an important gain allowing to realize a significant economy of energy in a large scale use of these light sources, particularly in large area lighting. The layer is easy to deposit by solution casting on large surfaces and adding it to the structure should not be expensive as DNA is an ecological material obtained from the waste produced by the food processing industry, thus can be cheap. Also the higher efficiency allows using this BioLED with lower current density, not only economising the energy but also increasing its operation time.

The present study shows also that the pure DNA layer acts as an effective electron blocker. As consequence the electrons are forced to remain in the emissive layer giving a higher probability of exciton formation. This principle can be used in other devices, like photovoltaic cells where blocking electrons and/or electron holes may result in decrease of electron-hole recombination, thus higher conversion efficiency. Compared to DNA-surfactant case using DNA alone simplifies the technological process. It is easier to modify its electrical conductivity by adapting the molecular mass [22]. Using DNA may present also an important technological advantage in ink jet technologies because of its insolubility in organic solvents, which are usually used for deposition of other active or passive layers. The studied BioLED luminance efficiency may be still improved by the optimisation of EBL thickness.

The result is also important for its energy conservation aspects as the use of organic light emitting diodes market is expected to grow rapidly, with first large screen TVs present already on the market [23]. They offer not only lower energy consumption, but also a better, 180 degrees vision, better resolutions and also significantly lower weigh. The curved screen technology proposed by Samsung gives 3D vision without the necessity of using special image registration systems and glasses [24]. An important revolution is expected also to

come in the everyday lighting: house, office, streets, buildings, etc. giving more comfort, flexibility and energy conservation.

Although in the present study we used DNA and wet technology for DNA thin film deposition, an improvement in technology can come from using of nucleobases [25], which can be deposited by the vacuum sublimation technique.

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