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Development and Characterization of Bio-White Polymer Light-Emitting Diodes

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An efficient white polymer light-emitting diode (WPLED) with stable Commission Internationale de l'éclairage (CIE) coordinates is fabricated. A blue electroluminescence (EL)-emitting conductive polymer [poly(9,9-di-n-hexyl-fluorenyl-2,7-diyl)], PHF is used as a host for red [*Bis*(1-phenyl-isoquinoline)(acetylacetonate)iridium(III)], $Ir(piq)_2(acac)$ and green [iridium(III)*tris*(2- (4-tolyl)pyridinato-N,C^2)], $Ir(mppy)_3$ phosphorescent dyes. Although efficient triplet energy transfer is not possible in the green phosphorescent dye, the self-trapping mechanism is utilized for the emission of EL in the green region while an efficient triplet exciton energy transfer from the host to the red dye is utilized for EL in the red wavelength region. Concentrations of the three constituents are optimized to obtain pure white light of appropriate CIE coordinates. An efficient electron-blocking layer based on a biomaterial (salmon-DNA) is also incorporated in the WPLED to improve the device performance. The WPLED shows three distinguished peaks for the primary colors and achieved a maximum luminance and luminous efficiency of 350 cd/m^2 and 0.86 cd/A, respectively.

Keywords : Conductive polymers, phosphorescent dye, self-trapping mechanism, salmon-DNA, electron-blocking layer, bio-white emission

生体白色高分子発光素子の開発と特性

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赤色発光する[Bis(1-phenyl-isoquinoline)(acetylacetonate)iridium(III)], $Ir(piq)_2(acac)$および緑色発光する[iridium(III)-*tris*(2-(4-tolyl)pyridinato-N,C^2)], $Ir(mppy)_3$ 燐光色素をゲスト材料とし，ホスト材料には青色電界発光する導電性高分子, poly(9,9- di-n-hexyl-fluorenyl-2,7-diyl), PHF を使用して白色発光の高分子電界発光素子の開発を試みた。発光色を国際照明委員会（Commission Internationale de l'éclairage, CIE）が策定した CIE 座標を有する効率的な白色高分子電界発光素子（WPLED）を作製した。三重項エネルギー移動は, PHF から $Ir(piq)_2(acac)$へ効率よく起こるが, $Ir(mppy)_3$ の発光は電極から注入された電子および正孔の自己捕獲機構に基因している。純粋な白色発光を得るため, CIE 座標から濃度を最適化した。ここで提案する電界発光素子では, 鮭の白子から抽出した DNA を脂質 cetyltrimethyl ammonium chloride, CTMA と結合してポリイオンコンプレックスを作製し, 電子ブロッキング層として陽極側に製膜した。白色発光素子の発光スペクトルは, 赤領域で 612 nm, 緑領域で 514 nm そして青領域で 430 nm 付近に分離された三つの発光ピークを示す。試作した電界発光素子の最大輝度は 350cd/m^2, 発光効率は 0.86cd/A であった。

キーワード：導電性高分子, 燐光色素, 電子状態, 自己捕獲機構, 鮭の DNA, 電子ブロッキング層, 生体白色発光

1. Introduction

For the past few years, a large number of workers [1-10] are engaged in the development of white organic light-emittingdiodes (WOLEDs). Almost all of them use low molecular-weight organic materials (LMWOM) such as 1, 4, 5, 8 *N*-pentamethyl-carbazole (PMC) for emission of blue electroluminescence (EL) and as a host for red and green phosphorescent dyes. PMC produces singlet excitons (S_1) and triplet excitons (S_3) in the ratio of 1:3 [11]. While S_1 are utilized for blue EL emission, the S_3 are utilized for producing red and green EL from phosphorescent dyes. The internal quantum efficiency of the device is therefore close to 100%. However, LMWOM being insoluble in common organic solvents cannot be spin coated and has to be vacuum evaporated. Not only vacuum evaporation is an expensive, but also it is not possible to deposit large area films by this technique and therefore this method of fabricating WOLED is not commercially viable. White polymer light-emitting diodes (WPLEDs) based on blue EL-emitting conductive polymers using

red and green dyes as fluorescent dopants have low efficiencies as compared to WOLEDs because the red and green emitting fluorescent dyes cannot utilize S_3 from the host polymer. The internal quantum efficiency of such a device cannot exceed 25%. In order to utilize S_1 as well as S_3 to produce high efficiency WOLED, one can on principle use three basic color components R, G, and B as phosphorescence dyes. However, blue phosphorescent dyes are unstable and hence such a device has a very low operating life [12].

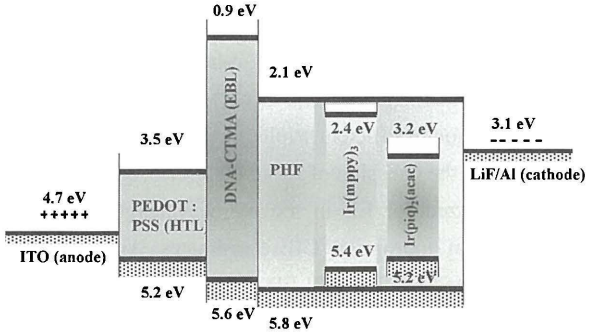


Fig. 1. Energy level diagram for the Bio-WPLED.

An ideal solution to be used therefore will be a combination of blue-emitting conductive polymer such as poly(9,9-di-*n*-hexyl-fluorenyl-2,7-diyl), (PHF) as host doped with red and green phosphorescent dyes. In such a system all the S_1 and S_3 can be utilized by the fluorescent PHF and phosphorescent dyes, respectively. Hence, the internal quantum efficiency of such a device can approach 100%. However, the difficulty in this is that all the available green phosphorescent dyes have S_3 energy level higher than that of the blue-emitting conductive polymers. As an example S_3 energy level of PHF is 2.15 eV [13] while that of the green phosphorescent dyes is higher (e.g., for $Ir(mppy)_3$, S_3 level is 2.4 eV [14]) and thus S_3 energy cannot flow from former to later. However, the S_3 energy levels of the red dyes (for $Ir(piq)_2(acac)$, S_3 level is 2.0 eV [15]) are lower than that of the blue conductive polymer PFO and the S_3 energy transfer from PFO can excite the red dyes easily. In this study, an attempt has been made to fabricate a polymer-based white LED structure. Although the host is still a conductive polymer PHF, the green dye iridium(III)*tris*(2-(4-tolyl)pyridinato-N,C^2) ($Ir(mppy)_3$) produces EL in green region, not by the S_3 energy transfer but due to self-trapping mechanism in the green dye itself. This is because the LUMO level of this dye is unusually low 2.4 eV and HOMO level is very high 5.4 eV [14], as shown in Fig. 1. Most of the electrons injected from cathode and holes injected from anode are therefore trapped in the dye molecules and can easily produce singlet and triplet excitons in the dye itself, producing EL in the green region. If the concentration of green dye in the host is appropriate, optimum EL intensity from the green and red dyes can be obtained to produce white light of correct Commission Internationale de l'e´clairage (CIE) coordinates. A very significant point to be taken into consideration is that the concentration of the green dye in PHF is very important because not only it produces EL by self-trapping but exciton energy may also be transferred from PHF and green dye to the red dye due to the process of incomplete Forster resonance energy transfer.

Recently, biomaterials are also being used in conductive polymer-based devices to bring into being a new field called bioelectronics [16, 17]. In our previous study, we have successfully improved the device performance of the MEH-PPV and PHF-based polymer light-emitting diodes using salmon-deoxyribonucleic acid (sDNA) [17]. We have used cetyltrimethylammonium (CTMA) to form sDNA-CTMA complex, which is soluble in organic solvents and hence used to form films by the spin cast technique. An electron-blocking layer (EBL) based on sDNA-CTMA is also incorporated in the WPLED and the device is now called bio-white polymer light-emitting diode (Bio-WPLED).

The EBL helps in balancing the charge carriers by blocking electrons due to its very low LUMO level, which enhances the recombination probability of electrons and holes in the emissive layer and hence enhancing the efficiency of the device [17]. The Bio-WPLED shows three primary distinguished color peaks for blue (~430 nm), green (~514 nm), and red (~612 nm). The CIE coordinates become stable at higher voltages and are well within the white region, making the device suitable for the flat panel display technology. The maximum efficiency of this Bio-WPLED is found to be 0.86 cd/A, whereas the blue Bio-PLED fabricated in our previous study showed maximum efficiency of ~0.062 cd/A [17]. The CIE coordinate are found to be (0.30, 0.34) at ~34 V which are closest to the pure white region (0.33, 0.33).

2. Experimental

Figure 2 shows the molecular structures of materials used in the present work. The blue-emitting conductive polymer PHF was procured commercially from Sigma.Aldrich (St. Louis, MO, USA). The green [$Ir(mppy)_3$] and red Bis(1-phenyl-isoquinoline) (acetylacetonate)iridium(III) [($Ir(piq)_2(acac)$)] phosphorescent dyes were purchased from American Dye Source (Quebec, Canada). An aliquot of 10 mg/ml PHF was made in chlorobenzene. To this solution red and green dyes were added in the concentrations of 0.2 and 0.8% w/w, respectively. These concentrations were obtained by trial- and error to obtain best possible EL spectrum. The solution was homogenized using an ultrasonicator and spin coated on a patterned ITO-coated glass (having sheet resistance ~15Ω/□), keeping the spin rate 2000 rpm for 30 s. Before coating the emissive layer, a PEDOT:PSS layer was spin coated on the ITO. This layer acts as a hole transporting layer and also smoothens the uneven surface of the ITO [18].

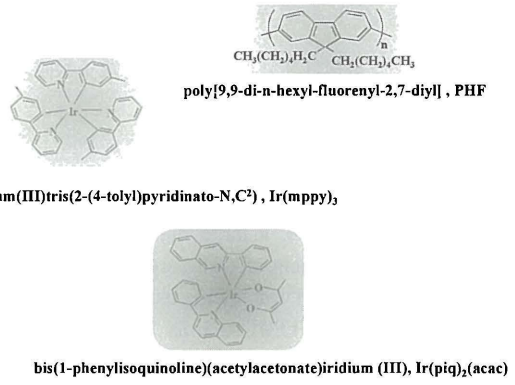


Fig. 2. molecular structures of materials used in the present

A thin layer of DNA-CTMA complex was also coated on the PEDOT:PSS layer to be act as an EBL. A buffer layer of LiF 10 nm thick was vacuum evaporated on the active layer, which reduces the potential barrier at the polymer/Al interface [19]. On the buffer layer, aluminum cathode contacts of 100 nm thick were vacuum evaporated at a rate of 0.6 nm/s. A shadow mask was used for the deposition of the cathode resulting in the devices area of 2 mm×2 mm. The current voltage characteristics of the device were measured with the help of a Keithley Source Meter (Model: SMU 2400). The luminance intensity of EL was measured using Minolta LS 100 luminance meter. EL spectrum and CIE coordinates were measured by spectral flux measurement system, Labsphere (model: CSLMS 1011). All the measurements were carried out in air at room temperature without any device encapsulation. The schematic for the Bio-WPLED used is shown in **Fig. 3**.

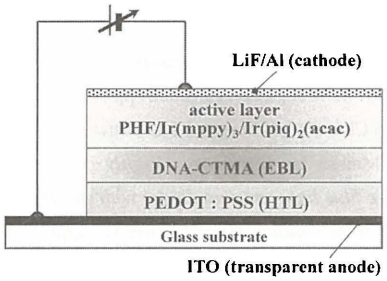


Fig. 3. Schenatic of layers arrangement used for Bio-WPLED.

3. Results and discussion

〈3·1〉 Basic properties of Bio-WPLED

The luminance (L), current density (J), and bias voltage (V) characteristics for the Bio-WPLED are shown in **Fig. 4**. The turn on voltage is found to be ~21 V. Maximum luminance achieved is ~350 cd/ m^2 at a bias voltage of 34 V, above this voltage the device performance starts deteriorating.

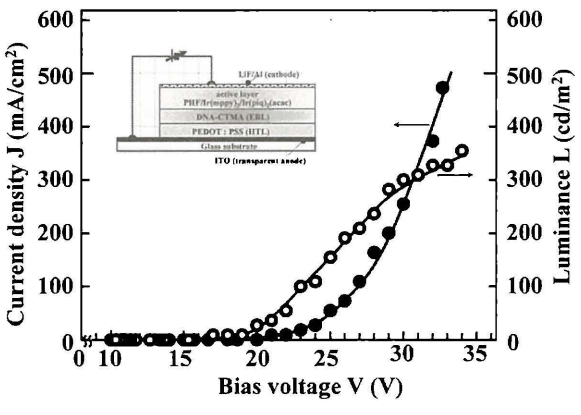


Fig. 4. Current density (J)-, and Luminance (L) -bias voltage (V) characteristics for the Bio-WPLED.

〈3·2〉 EL spectra of Bio-WPLED

The EL spectra for different bias voltages of the fabricated Bio-WPLED are shown in **Fig. 5**. It is found that till 24 V no significant red emission is observed but green emission is still prominent, showing the existence of the charge trapping mechanism in the green dye. As the voltage is increased beyond 25 V, the red emission becomes significant. At ~32 V, all the three primary color peaks become considerable and remain constant till 34 V.

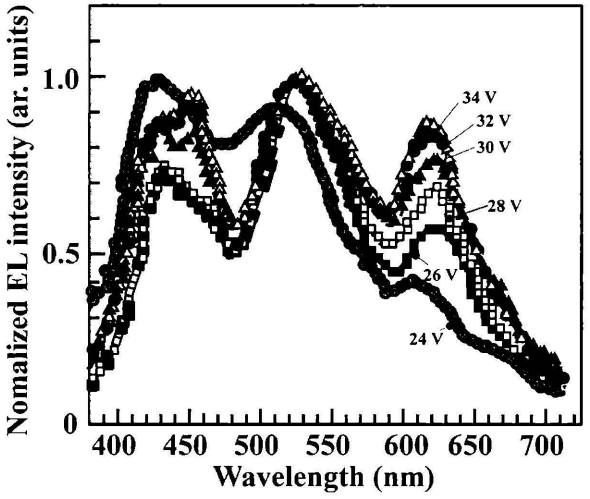
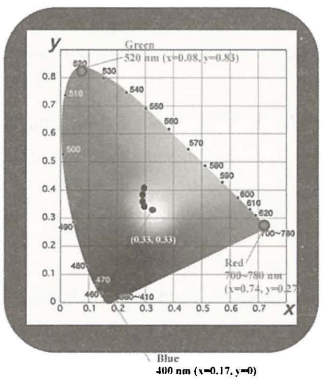


Fig. 5. EL spectra of the Bio-WPLED for different bias voltages.

〈3·3〉 CIE coordinates of Bio-WPLED

Corresponding CIE coordinates of the Bio-WPLED at different bias voltages are shown in **Fig. 6**. The CIE coordinates remain stable above 32 V and are well within the white region. At higher voltages charge trapping mechanism in the green dye starts saturating thus saturation in the green peak takes place while blue and red peaks simultaneously increase and grow to be comparable to the green peak. However, increasing the red dye concentration may enhance the efficiency of the device but in that case the spectrum will experience a huge shift toward the red wavelength region. The concentration of the constituents is optimized carefully to get the best-balanced EL spectrum and hence the appropriate CIE coordinates.



CIE coordinates
26 V (0.28, 0.38)
28 V (0.29, 0.40)
30 V (0.29, 0.36)
32 V (0.30, 0.34)
34 V (0.30, 0.34)

Fig. 6. CIT coordinates of the Bio-WPLED and their chromaticity diagram.

〈3·4〉 Luminous efficiency of Bio-WPLED

Luminous and power efficiencies for the Bio-WPLED are shown in **Fig. 7**. Maximum luminous and power efficiency for

the Bio-WPLED are achieved to 0.86 cd/A and 0.12 lm/W, respectively, at a typical luminance intensity of 54 cd/m^2.

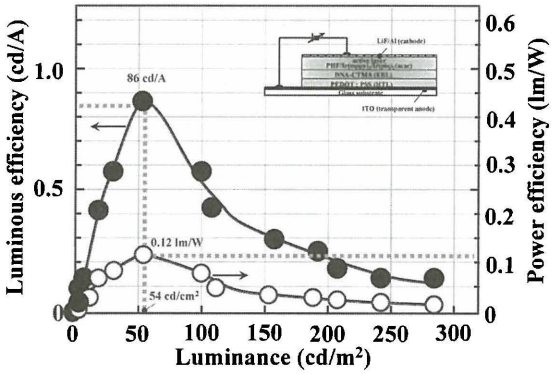


Fig. 7. Luminous efficiency and power efficiency for the Bio-WPLED fabricated.

4. Conclusion

Self-trapping mechanism in the green phosphorescent dye has been utilized for producing EL by trapping holes and electrons in the dye itself. The concentrations of red and green phosphorescent dopants in the host PHF have been optimized to fabricate a Bio-WPLED of appropriate CIE coordinates. An EBL based on bio-material (DNA) was also incorporated in the device structure to enhance the device performance. The device possesses stable CIE coordinates at higher voltages with EL spectrum, showing all the three peaks of the primary colors are necessary for the generation of the white light.

References

[1] X.-M.Wu, Y.-L.Hua, S.-G.Yin, L.-J.Zhang, Y.Wang, Q.-C.Hou, and J.-M.Zhang, "*Influence of dopant concentration on electroluminescent performance of organic white-light-emitting device with double-emissive-layered structure*", Chinese Phys.Lett., **25**, No.1 (2008) pp.294-297.

[2] A.Kumar, P.K.Bhatnagar, P.C.Mathur, M.Husain, S.Sengupta, and J.Kumar, "*Temperature and electric-field dependences of hole mobility in light-emitting diodes based on poly[2-methoxy-5-(2-ethylhexloxy)-1,4-phenylene vinylene]*", J.Appl.Phys., **98**, Issue 2 (2005) 024502 (3pages).

[3] A.Kumar, P.K.Bhatnagar, P.C.Mathur, K.Tada, and M.Onoda, "*Optical characterization of MEH-PPV/Alq$_3$ composite films*", J.Mater.Sci., **40**, N.40 (2005) pp.3849-3851.

[4] F.Guo and D.Ma, "*High efficiency white organic light-emitting diodes based on double recombination zone*", Opt.Mater., **28**, Issue 8-9 (2006) pp.966-969.

[5] Y.W.Ko, C.-H.Chung, J.H.Lee, Y.-H.Kim, C.-Y.Sohn, B.-C.Kim, C.-S.Hwang, Y.-H.Song, J.Lim, Y.-J.Ahn, G.-W.Kang, N.Lee, and C.Lee, "*Efficient white organic light emission by single emitting layer* ", Thin Solid Films, **426**, Issue 2-1 (2003) pp. 246-249.

[6] G.Lei, X.Yi, L.Duan, L.Wang, and Y.Qui, "*Multilayer white organic light-emitting diodes with a single host material*", Semicond.Sci.Technol., **21**, No.10 (2006) pp.1455-1458.

[7] S.-H.Yang, M.-H.Liu, and Y.-K.Su, "*Stable and highly bright white organic light-emitting diode based on 4,4',4"-tris(N-30methylphenyl-N-phenyl-amino)-triphenylamine*", J.Appl.Phys., **100**, Issue 8 (2006) 083111 (3pages).

[8] G.Li and J.Shinar, "*Combinatorial fabrication and studies of bright white organic light-emitting devices based on emission from rubrene-doped 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl*", Appl.Phys.Lett., **83**, Issue 26　(2003) 5359 (3 pages).

[9] J.-H.Niu, W.-L.Li, H.-Z.Wei, M.-T.Li, W.-M.Su, Q.Xin, Z.-Q.Zhang, and Z.-Z.Hu, "*White organic light-emitting diodes based on bis(2-methyl-8-quinolinolato) (para-phenylphenolato)alminium(III) doped with tiny red dopant*", J.Phys.D: Appl.Phys., **38**, No.8 (2005) pp.1136-1139.

[10] Z.Q.Gao, C.S.Lee, I.Bello, and S.T.Lee, "*White light electroluminescence from a hole-transporting layer of mixed organic matrials*", Synth. Met., **111-112** (2000) pp.39-42

[11] A.Fischer, S.ChénaisS, S.Forget, M-C.Castex, D.Adès, A.Siove, C.Denis, P.Maisse, and B.Geffroy, "*Highly efficient multilayer organic pure blue light emitting diodes with substituted carbazoles compounds in the emitting layer*", J.Phys.D: Appl.Phys., **39**, No.5 (2006) pp.917-922.

[12] C.-L.Lee, R.R.Das, J.-J.Kim, "*Polymer based blue electrophosphorescent light emitting devices*", Curr.Appl.Phys., **5**, Issue 4 (2005) pp.309-313.

[13] F.-C.Chen, G.He, and Y.Yang, "*Triplet exciton confinement in phosphorescent polymer light-emitting diodes*", **82**, Issue 7 (2003) pp.1006-1008.

[14] X.Yang, D.Neher, D.Hertel, and T.K.Däubler, "*Highly efficient single-layer polymer electrophosphorescent devices*", Adv.Mater., **16**, Issue 2 (2004) pp.161-166.

[15] Y.-Y.Lyu, J.Kwak, W.S.Jeon, Y.Byun, H.S.Lee, D.Kim, C.Lee, and K.Char, "*Highly efficient red phosphorescent OLEDs based on nano-conjugated silicon-cored spirobifluorene derivatives doped with Ir-compolexes*", Adv.Funct.Mater., **19**, Issue 3 (2009) pp.420-427.

[16] J.A.Hagen, W.Li, A.J.Steck, and J.G.Grote, "*Enhanced emission efficiency in organic light-emitting diodes using deoxyribonucleic acid complex as an electron blocking layer*", Appl.Phys.Lett., **88**, Issue 17 (2006) 171109 (3 pages).

[17] D.Madhwal, S.S.Rait, A.Verma, A.Kumar, P.K.Bhatnagar, P.C.Mathur, M.Onoda, "*Increased luminescence of MEH-PPV and PFO based PLEDs by using salmon DNA as an electron blocking layer*", J.Lumin., **130**, Issue 2 (2010) pp.331-333.

[18] F.Huang, Y.-J.Cheng, Y.Zhang, M.S.Liu, and A.K.-Y.Jen, "*Crosslinkable hole-transporting materials for solution processed polymer light-emitting diodes*", J.Mater.Chem., **18**, Issue 38 (2008) pp.4495-4509.

[19] H.Yoshihara, Y.Tanaka, S.Tanaka, M.Kitagawa, H.Kusano, and H.Kobayashi, "*Effect of thin LiF layers in multi-layered PVCz polymer LEDs*", Curr.Appl.Phys., **5**, Issue 1 (2005) pp.27-30.

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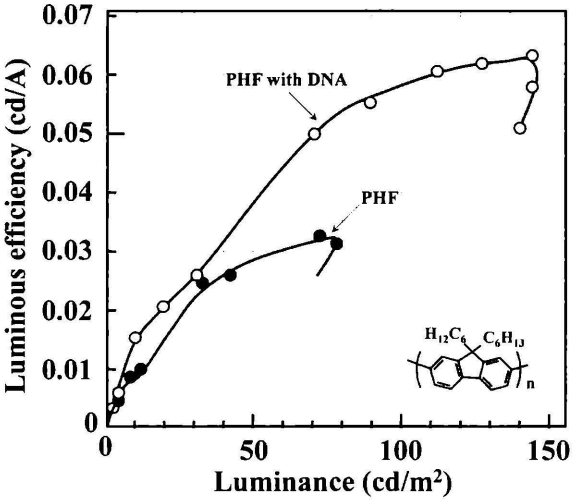
Mitsuyoshi Onoda was born in Okayama prefecture, Japan on August 19, 1951. He received the B. Eng. and M. Eng. degrees in Electrical Engineering from Himeji Institute of Technology, in 1975 and 1977, respectively. He received the Dr. Eng. Degree in Electrical Engineering from Osaka University, in 1983. He is now a Professor of University of Hyogo. He has been mainly engaged in research of electronic properties and applications of organic materials. In 1994, he studied as a visiting scientist at Professor Alan G. MacDiarmid (passed away on February 7, 2007.: received the Nobel Prize in Chemistry in 2000) office of University of Pennsylvania. Professor Onoda is a member of the Institute of Electrical Engineers of Japan, the Institute of Electronics, Information and Communication Engineers, the Japan Society of Applied Physics, the Society of Polymer Science, Japan, Japanese Liquid Crystal Society, and the Institute of Electrical and Electronics Engineers, Inc. (IEEE).

Appendix

1 PHF based PLED by using salmon DNA as an electron blocking layer

It may be mentioned that the transport mechanism in DNA-CTMA complex may be quite different from that of the free DNA, and also the orientation of DNA molecules in the CTMA complex may be completely random. In that case the explanation of a high potential barrier for electrons in EBL due to its low LUMO level may not be valid. However, using OLED structures, K. Hirata *et al.* ("*Electroluminescence as a probe for elucidating electrical conductivity in a deoxyribonucleic acid-cetyltrimethyl-ammonium lipid complex layer*", Applied Physics Letters, Volume 85, Issue 9 (2004) pp.1627-1629.) have examined the carrier transport mechanism of a DNA-CTMA lipid complex. It was concluded by them that though the DNA-CTMA layer basically possesses abilities to transport both holes and electrons, there is preferentially hole transport due to a shallow LUMO level, which prohibits an electron injection from an adjacent carrier transport layer. It was further concluded by these authors that the origin of electrical conduction in this layer is due to DNA strands, and the nonconjugated CTMA (lipid) does not contribute to the charge transport. In our case the thickness of the DNA-CTMA layer is tailored to the molecular width of DNA (~20 nm). The length of the DNA chains is also reduced to ~70 nm so that these chains do not intermingle with each other during spin coating. For this purpose, sonication process of DNA solution has been perfonned for longer durations (2 h). These processing constraints enable all the molecules of sDNA to lie on the plane of the film. Hence in this case the molecular orbital theory for explaining the electron blocking in terms of high potential barrier for electrons at the polymer-DNA interface due to its low LUMO level is valid.



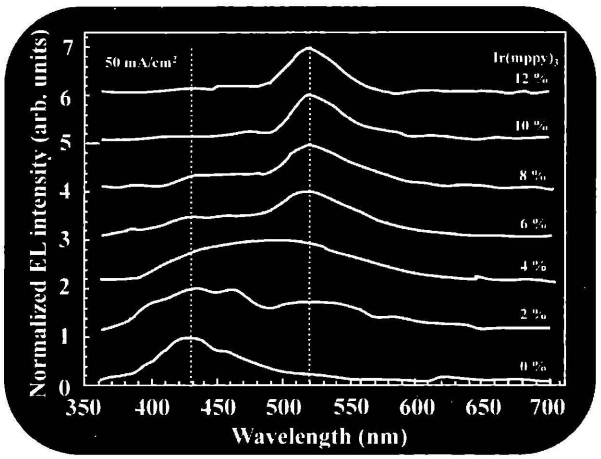
Appended chart 1: Liminous efficiency for the PHF based PLEDs.

The luminous efficiency (luminance／current) for the PHF based PLEDs is shown in Appended chart 1. The effect of sDNA EBL is quite significant for the device. The luminance for simple PHF based PLED have been increased by introducing sDNA as the EBL in between the anode and emissive layers. This increase is found to be about two times in case of PHF devices. Attempts are being made to further enhance the luminance by improving the orientation of sDNA molecules in the EBL layer with the help of an optimized annealing process.

2. Self-trapping mechanism in green phosphorescent dye-doped PLED

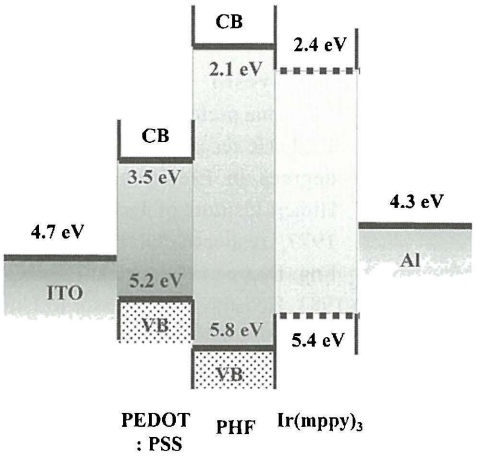
The EL performances of the PLEDs fabricated for various concentrations of the green phosphorescent dye (0–12%) in PHF are shown in Appended chart 2. For the sake of comparison, the same current density of 50 mA/cm^2 is used to drive all the PLEDs. It is found that with an increase in the green dye concentration, EL emission in the green wavelength region (~514 nm) increases significantly. When the concentration of the green phosphorescent dye is > 6 %, the emission in the green wavelength region overshoots the blue emission. The main possible reason for this green EL is due to the trapping of charge carriers in the green phosphorescent dye due to the self-trapping mechanism. Electrons injected from the cathode and holes from the anode in PHF get trapped in the dye molecules and, hence, can easily form excitons in the green phosphorescent dye itself. These excitons further decay radiatively to produce EL in the green wavelength

region. As the concentration of the green phosphorescent dye in PHF increases, the probability of charge trapping also increases, as seen in Appended chart 2.



Appended chart 2: EL spectra of the PLEDs fabricated using PHF + $Ir(mppy)_3$ (0-12 %) composite fiulms as the active emissive layers (a fixed current density of 50 mA/cm^2 is used to drive all the diodes.

It is clear from Appended chart 3 that the electrons from the host PHF can easily fall into the LUMO of the green phosphorescent dye since the LUMO level of the green phosphorescent dye is 2.4 eV, and is aligned well below that of the PHF (2.1 eV). The electrons have a very high probability to get trapped in the green dye molecules. Similarly, the HOMO levels of $Ir(mppy)_3$ and PHF are 5.4 and 5.8 eV, respectively (J. J. Park *et al.*, "*Small molecule interlayer for solution processed phosphorescent organic light emitting device*, Organic Electronics, Volume 10, Issue 1 (2009) pp.189-193., U. Scheff and D. Neher, *Polyfluorenes*, Advances in Polymer Science Volume 212 (2008, Springer, Berlin) making it favorable for hole trapping.



Appended chart 3: Energy level diagram for the PLEDs fabricated.