

Uniform dispersion of triplet emitters in multi-layer solution-processed organic light-emitting diodes

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ABSTRACT

The influence of the iridium complex solubility on the efficiency of multi-layer solution-processed organic light-emitting diode is demonstrated by synthesized orange triplet iridium complexes with the same core. The solubility of the iridium(III) bis(4-phenylthieno[3,2-c]pyridinato-*N,C*′) acetylacetonate is increased and uniform dispersion of iridium complex in polymer host poly(vinylcarbazole) is achieved by *tert*-butyl and *n*-hexyl group modification. Blade coating technique is utilized to achieve tri-layer structures with a polymer hole-transporting layer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(*N*-(4-*s*-butylphenyl))diphenylamine)], a host-guest emissive layer, and small-molecule hole-blocking layer 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene. The efficiency as high as 20 cd/A is achieved for orange-emitting device.

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1. Introduction

Organic light-emitting diode (OLED) is a rapidly emerging technology for semiconductor lighting and display. In the past it is divided into two classes: the small-molecule light-emitting diode by high-cost vacuum-evaporation deposition and polymer light-emitting diode by low-cost solution process. So far the light-emission efficiency of small-molecule diodes are significantly higher than the one of polymer diodes with two major reasons. One is that the former can be easily made to contain three or more layers for electron and hole current balance. The other is that the emissive layer of the former can be made as a host material with guest emitter molecules uniformly dispersed by co-evaporation. Without uniform dispersion the luminance will be reduced by self-quenching in the emitter aggregates and undesired host emission will result from poor energy transfer to the emitters. Both the multi-layer structure and uniform emitter dispersion have been difficult to realize by solution process in polymer light-emitting diodes. Recently there have been great efforts to combine the advantages of low-cost solution process and the multi-layer device design. Cross-linking molecules are used for both the hole-transporting and emissive layers [1]. The material design and synthesis are however quite complicated. Solution-processed emissive layers were

combined with vacuum-deposited hole-blocking and electron-transporting layers, [2] with emitters modified to enhance the dispersion with the host [3]. The fabrication cost is still limited by the vacuum deposited layers. Very recently a blade coating technique is developed for multi-layer deposition of arbitrary organic semiconductors by solution process [4]. Efficiency of the multi-layer device made by blade coating was shown to be close the one of vacuum-deposited devices [5]. The uniform dispersion of the triplet emitters in polymer host is however still a major problem. Indeed most of the triplet emitters are iridium complexes with poor solubility in organic solvents. Uniformly dispersed host-guest emissive layer in combination with all-solution-processed multi-layer structure remain a challenge for an ideal organic light-emitting diodes. Furthermore the effect of solubility of the guest emitters on the device performance remain unknown.

In this work we develop a series of four orange triplet iridium complexes with the same core but various chemical modifications for better solubility and application in multi-layer solution-processed OLED. The first one iridium(III) bis(4-phenylthieno[3,2-c]pyridinato-*N,C*′)acetylacetonate (PO-01) is originally designed for vacuum deposition, [6,7] the second one iridium(III) bis(4-*p*-tolylthieno[3,2-c]pyridinato-*N,C*′)acetylacetonate (PO-01-m) has a methyl group added to the ligand, and the third one iridium(III) bis(4-(4-*t*-butylphenyl)thieno[3,2-c]pyridinato-*N,C*′)acetylacetonate (PO-01-TB) has a *tert*-butyl group added to the ligand, and the fourth one iridium(III) bis(4-(4-*n*-hexylphenyl)thieno[3,2-c]pyridinato-*N,C*′)acetylacetonate (PO-01-Hex) has a *n*-hexyl group add to the ligand. These four

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emitters are mixed with polymer host to form the emissive layer. Blade coating technique is used to make tri-layer structures with a polymer hole-transporting layer, a host-guest emissive layer, and small-molecule hole-blocking/electron-transporting layer. Dissolution is minimal in this coating method. As expected the *tert*-butyl group significantly improve the solubility of the iridium complexes in organic solvent. Accordingly the efficiency of the devices made of the third and the fourth emitter are much higher than the first two with poor solubility. The efficiency of orange light-emitting diodes with PO-01-TB and PO-01-Hex reach 20 cd/A with LiF/Al cathode, while the efficiency of the other two is below 5 cd/A. Efficiency of 16 cd/A is reached for PO-01-TB with CsF/Al cathode without electron-transporting layer. The combination of good emitter dispersion and multi-layer design give high efficiency solution-processed organic light-emitting diodes with the stable LiF/Al cathode.

2. Experimental

The chemical structures of the four orange triplet emitters PO-01, PO-01-m, PO-01-TB, and PO-01-Hex are shown in Fig. 1(a). PO-01 has been used in vacuum deposited organic light-emitting diodes with high efficiency [6,7]. It has a poor solubility below 0.5 wt% in chlorobenzene. In order to enhance the solubility a methyl group is added to the ligand in PO-01-m. The solubility is however basically the same, implying that methyl group is not enough to achieve the good solubility and dispersion with host polymer. To further improve the solubility a *tert*-butyl group is added in PO-01-TB, and a *n*-hexyl group is added in PO-01-Hex. The solubility of PO-01-TB in chlorobenzene increases from less than 0.5 wt% to over 1.5 wt%, and the solubility of PO-01-Hex in chlorobenzene dramatically increases to over 3 wt%. The synthesis of the emitter molecules will be described elsewhere.

PLED based on four orange triplet emitters (PO-01, PO-01-m, PO-01-TB, and PO-01-Hex) are fabricated. The triplet emitter is doped into poly(vinylcarbazole) (PVK,

Mw = 1,100,000) host blended with *N,N'*-diphenyl-*N,N'*-(bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine) (TPD) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD). TPD and PBD are functional materials to enhance carrier transporting ability. PVK is purchased from Sigma Aldrich, TPD and PBD are purchased from Luminescence Technology Corporation. The emission layer (EML) is a blend of various materials. The weight blending ratios are PVK:PBD:TPD:triplet emitter = 61:24:9:6 for investigating the effect of chemical structure of the three emitters on the device performance. Devices based on PO-01-TB emitter have the weight blending ratios PVK:PBD:TPD:PO-01-TB = 65:24:9:2, 61:24:9:6, and 57:24:9:10. Devices are fabricated on patterned and cleaned indium tin oxide (ITO) glass substrate. A layer of 500 Å poly-(3,4-ethylenedioxythiophene)doped with poly-(styrenesulfonate) (PEDOT:PSS, CLEVIOSTTM P CH8000) is spin coated and annealed at 100 °C for 40 min in vacuum. Polymer layers other than PEDOT:PSS are fabricated by blade and spin coating which has been demonstrated to be a successful method to achieve polymer multi-layer structure. The gap of the blade coater is 60 μm. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(*N*-(4-*s*-butylphenyl)diphenylamine)] (TFB) solution (1 wt%) is bladed on top of PEDOT:PSS and immediately spined at 4000 rpm to form a TFB layer of 200 Å. TFB is then annealed at 180 °C for 40 min in vacuum. TFB (Mw = 197,000, American Dye Source) is used as the hole-transporting layer (HTL), as well as the electron blocking layer (EBL). Afterward, a 70 nm EML is formed on TFB by blade and spin coating. The emission layer is then annealed at 80 °C or 100 °C in vacuum. The annealing time are 30 and 60 min as the annealing temperature is 80 °C. As for the 100 °C annealing temperature, the annealing time are 20 and 30 min. Another layer of 20 nm 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene (TPBI) is then formed by blade and spin coating on emission layer without annealing for the devices use LiF(1 nm)/Al(100 nm) as cathode. The TPBI solution is prepared in methanol (0.5 wt%). Devices with CsF(2 nm)/Al(100 nm) cathode but without TPBI layer are also fabricated for comparison. All the devices are packaged in the glove box. The film thickness is measured by the Kosaka ET4000 Surface Profiler. The EL efficiency is measured by the Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter.

3. Results and discussion

The energy levels of the materials used in the devices are shown in Fig. 1(b). TFB is for hole transport and electron blocking. TPBI is for electron transport and hole blocking. The characteristics of the devices with the three iridium complexes as the emitter are shown in Fig. 2. For PO-01 and PO-01-m with poor solubility the current efficiency is only about 5 cd/A. There are however some interesting differences between these two emitters. The residual blue emission from TPD in the host is stronger in PO-01 device than in PO-01-m device, suggesting the dispersion of the latter is better than the former presumably due to the addition of the methyl group. The luminance and current density of PO-01 is much lower than the ones of PO-01-m, probably due to the formation of large aggregates of the PO-01 molecules which act as carrier traps. For devices with PO-01-TB and PO-01-Hex, both the efficiency are raised dramatically to about 20 cd/A as shown in Fig. 2(b). The residual blue emissions from the host become invisible as shown in the inset of Fig. 2(c), strongly indicating that the high efficiency are due to the uniform dispersion of the PO-01-TB and PO-01-Hex in the host. Both the solubility of PO-01-TB and PO-01-Hex are high enough and hence the self-quenching in the emitter aggregates is reduced and the host excitons can always transfer to a nearby emitter molecule. Since the performances of the devices with PO-01-TB and PO-01-Hex are similar, in all the results below PO-01-TB is

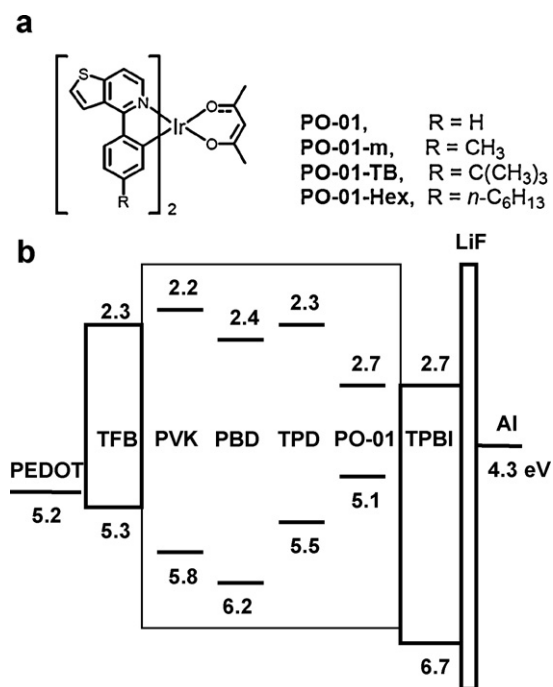


Fig. 1. (a) Chemical structures of the four emitters PO-01, PO-01-m, PO-01-TB, and PO-01-Hex. (b) Schematic energy level diagram of the device. Electron affinity and ionization potential of materials used in this work are also shown. Numbers are given in eV.

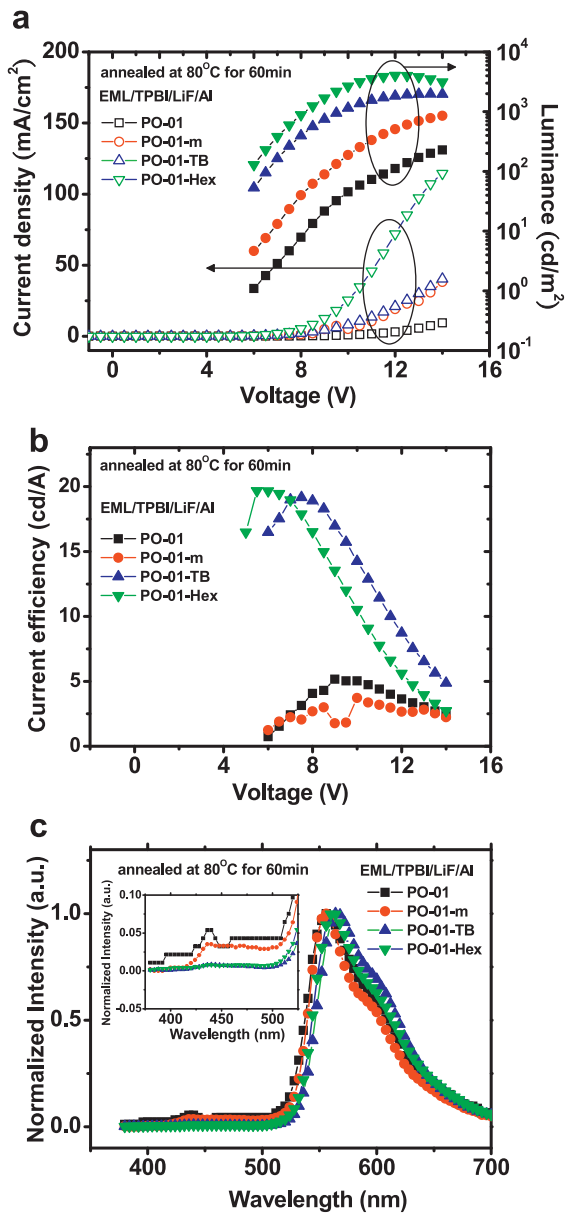


Fig. 2. The performance of PLED including PO-01 (square), PO-01-m (circle), PO-01-TB (triangle), and PO-01-Hex (inverted triangle) in emission layer. (a) The current density and luminance. (b) The current efficiency. (c) The EL spectrum. The inset shows the enlarged spectrum around 450 nm.

used as the emitter. In Fig. 3(a) and (b) the host-to-emitter weight ratio is varied. The weight ratios of the electron-transporting PBD and hole-transporting TPD are fixed at 24% and 9% respectively. The ratio of the emitter increases from 2% to 10% with the corresponding decrease of the PVK host polymer ratio. In Fig. 3(b) it is shown that the efficiency is low for 2% of emitter in the host because balance between negative and positive charges changes due to the changes of LUMO/HOMO on the blends. For devices with 6% and 10% of emitters the efficiency is roughly the same except for the low voltage region where 6% device is better. The luminance is higher for the 10% device. The fact that high efficiency and luminance can be kept up to 10% of emitters suggests a good mixing of the iridium complex with *tert*-butyl modification and the polymer host. In addition to the tri-layer devices with TFB/EML/TPBI/LiF/Al structure we also make bi-layer devices with TFB/EML/CsF/Al structure. CsF/Al cathode is known to have a good electron injection property without electron-transporting layer. In Fig. 3(c) and (d) it is

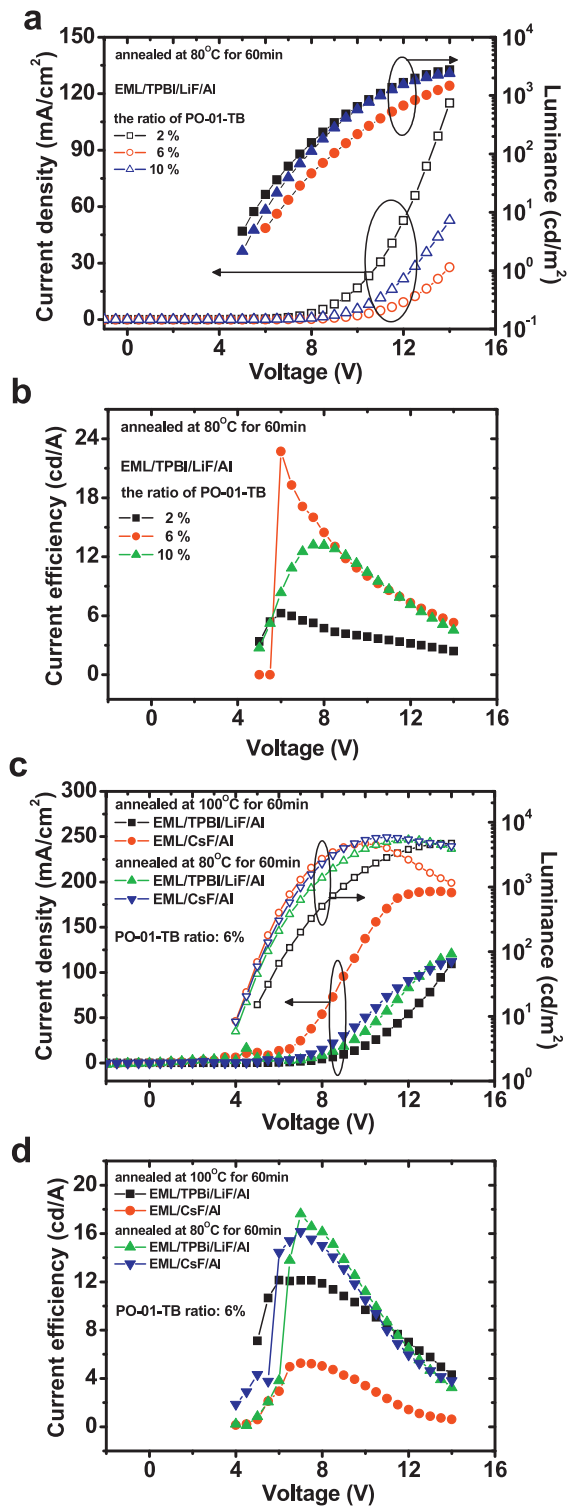


Fig. 3. The performance of the tri-layer PLED with various host-to-emitter ratio. Square represents 2% PO-01-TB, circle represents 6% PO-01-TB, and triangle represents 10% PO-01-TB. (a) The current density and luminance. The device structure of tri-layer PLED is ITO/PEDOT:PSS/TFB/EML/TPBI/LiF/Al. (b) The current efficiency. The performance of the bi-layer PLED and tri-layer PLED under different annealing condition. The device structure of bi-layer PLED is ITO/PEDOT:PSS/TFB/EML/CsF/Al. The ratio of PO-01-TB is fixed at 6%. (c) The current density and luminance. Square and circle represent the EML in bi-layer and tri-layer PLED is being annealed at 100°C for 60 min. Triangle and inverted triangle represent the EML in bi-layer and tri-layer PLED is being annealed at 80°C for 60 min. (d) The current efficiency.

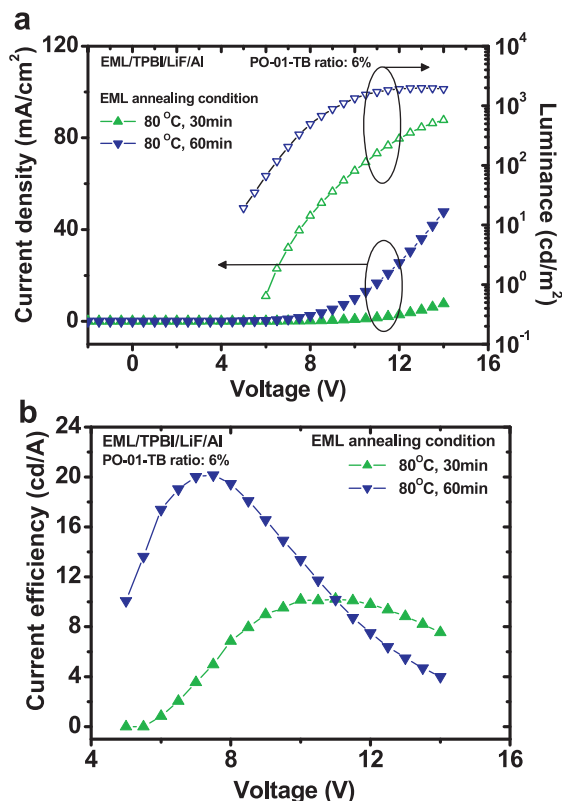


Fig. 4. The performance of tri-layer PLED with various annealing condition. Triangle and inverted triangle represent the EML is being annealed at 80 °C for 30 and 60 min, respectively. The ratio of PO-01-TB is fixed at 6%. (a) The current density and luminance. (b) The current efficiency.

shown that these two structures give similar device performances. For real applications LiF/Al cathode is much more practical than CsF/Al cathode because of the strong water-absorbing tendency of CsF. The combination of multi-layer blade coating method and the highly soluble triplet emitter therefore give a tri-layer polymer light-emitting diodes with structures similar to vacuum-deposited OLED and same stable cathode of LiF/Al. The annealing condition

of the emissive layer turns out to be crucial to the device performance. In Fig. 4 it is shown that at 80 °C the efficiency is reduced from 20 cd/A with 60 min annealing to only 10 cd/A with 30 min annealing, suggesting long annealing time is required to form a stable morphology of the emissive layer which contains as many as five different materials.

4. Conclusion

In conclusion, three triplet iridium complexes with the same core are synthesized to demonstrate the influence of the complex solubility on the efficiency of multi-layer solution-processed organic light-emitting diode. The *tert*-butyl and *n*-hexyl group modified iridium complex possess high solubility which make them can be uniformly dispersed in polymer host. Tri-layer structures with a polymer hole-transporting layer TFB, a host-guest emissive layer, and small-molecule hole-blocking layer TPBI is achieved by blade coating technique. With the electron-transporting layer TPBI and LiF/Al cathode, the current efficiency of 20 cd/A is achieved. For the device with CsF/Al cathode but without TPBI, the efficiency of 16 cd/A is obtained. With the easy blade coating and high efficiency, large-area solution-processed display and lighting is expected.

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References

- [1] N. Rehmman, C. Ulbricht, A. Köhnen, P. Zacharias, M.C. Gather, D. Hertel, E. Holder, K. Meerholz, U.S. Schubert, *Adv. Mater.* 20 (2008) 129.
- [2] Y. Tao, Q. Wang, C. Yang, K. Zhang, Q. Wang, T. Zou, J. Qin, D. Ma, J. Mater. Chem. 18 (2008) 4091.
- [3] C. Huang, C.G. Zhen, S.P. Su, Z.K. Chen, X. Liu, D.C. Zou, Y.R. Shi, K.P. Loh, J. Organomet. Chem. 694 (2009) 1317.
- [4] S.R. Tseng, H.F. Meng, K.C. Lee, S.F. Horng, *Appl. Phys. Lett.* 93 (2008) 153308.
- [5] J.D. You, S.R. Tseng, H.F. Meng, F.W. Yen, I.F. Lin, S.F. Horng, *Org. Electron* 10 (2009) 1610.
- [6] K.H. Shen, S.T. Yeh, H.L. Huang, I.H. Shen, M.T. Chu, T.S. Shieh, U.S. Patent, 7445857 (2008).
- [7] K.H. Shen, S.T. Yeh, H.L. Huang, I.H. Shen, M.T. Chu, T.S. Shieh, T.W. Patent, 1242999 (2004).