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2014 Chinese Phys. Lett. 31 097801

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Efficient Phosphorescent Organic Light Emitting Diodes Using F₄TCNQ as the Indium-Tin-Oxide Modification Layer *

JIAO Bo(焦博), ZHU Xiao-Bo(朱晓博), WU Zhao-Xin(吴朝新)**, YU Yue(于跃), HOU Xun(侯洵)

Shaanxi Key Laboratory of Photonics Technology for Information, Department of Electronic Science and Technology, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049

(Received 30 June 2014)

A phosphorescent organic light emitting diode by using tetrafluorotetracyanoquinodimethane (F₄TCNQ) as the indium-tin-oxide modification layer and 4,4'-bis(carbazol-9-yl)biphenyl (CBP) as the hole transporting layer is reported. CBP doped with a green phosphorescent dopant, tris(2-(p-tolyl)pyridine) iridium(III) (Ir(mppy)₃) is used as the emission layer in this device, and the maximum current efficiency of 31.3 cd/A is achieved. Furthermore, low efficiency roll-off of 10.4% is observed with device luminance increasing from 100 cd/m² (29.7 cd/A) to 10000 cd/m² (26.5 cd/A). It is demonstrated that a charge-generation area is formed at F₄TCNQ/CBP interface, which will benefit hole injection into the hole transporting layer. Moreover, use of the CBP hole transporting layer will benefit the low efficiency roll-off by broadening triplet exciton formation, as well as by avoiding accumulation of unbalanced carrier at the hole transporting layer/emission layer interface.

PACS: 78.60.Fi, 68.37.Ps, 73.61.Ph

DOI: 10.1088/0256-307X/31/9/097801

Phosphorescent organic light emitting diodes (PhOLEDs) have attracted considerable interest due to their potential application of nearly 100% internal quantum efficiency.^[1] However, PhOLEDs still suffered from the strong efficiency roll-off at high brightness, which was typically ascribed to the influence of triplet-triplet annihilation^[2,3] and triplet-polaron quenching.^[4,5] Typically, nearly 30% efficiency roll-off can be observed with luminance increasing from 100 cd/m² to 10000 cd/m² for PhOLEDs,^[6–8] which seriously limits their application in high luminance fields such as lighting. Thus many strategies were developed to reduce the efficiency roll-off of PhOLEDs. Recently, it has been demonstrated that efficiency roll-off of PhOLEDs can be reduced by using a special inorganic modification layer such as MoO₃^[9] and InCl₃^[10] for indium-tin-oxide (ITO) which is a widely used transparent anode. Generally, it was believed that those inorganic modification materials play an important role in enhancement of the hole injection by increasing the work function of ITO.^[10,11]

Tetrafluorotetracyanoquinodimethane (F₄TCNQ) was typically used as a p-type dopant to increase the hole transporting property of organic semiconductor material, such as *N-N'*-diphenyl-*N-N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPB).^[12,13] In this study, it is demonstrated that the introduction of F₄TCNQ as the anode modification layer can not only enhance the efficiency of the PhOLEDs but also significantly reduce the efficiency roll-off of PhOLEDs at high luminance when CBP is used as hole transporting layer (HTL). This performance enhancement, in general, is ascribed to lowering hole-injection barrier induced by electron transfer from anode to the F₄TCNQ layer.^[14,15] In this study, a novel scheme based on charge-generation effect is demonstrated. It is found that a charge-generation area is built at the F₄TCNQ/CBP interface, which will benefit hole in-

jection into CBP HTL.

All devices used in this study were fabricated by vacuum thermal evaporation. The 100-nm-thick ITO-coated glass with a sheet resistance of 25 Ω/\square was used as substrates. Emission area of the device was about 12 mm². Device fabrication process as well as measurement method is in accord with our previous work.^[16–18] To study the influence of F₄TCNQ thickness on device performance, devices with structures of ITO/F₄TCNQ (*x* nm)/CBP (40 nm)/CBP:Ir(mppy)₃ (20 nm, 10 vol%)/1,3,5-tris (N-phenylbenzimidazole-2-yl) benzene (TPBi) (40 nm)/Cs₂CO₃ (2 nm)/Al(100 nm) were fabricated, where *x* are 0 nm (device A), 5 nm (device B), 10 nm (device C), and 15 nm (device D) respectively (see Fig. 1(a)). Here a 40-nm-thick undoped CBP layer was used as HTL, a 20-nm-thick CBP layer doped with Ir(mppy)₃ was used as the emission layer (EML), and TPBi was used as the electron transporting layer. The luminance-voltage-current (*L-V-J*) characteristics as well as the efficiency performance of devices A–D are shown in Figs. 1(b) and 1(c) respectively. In device A without the F₄TCNQ layer, hole is the minority carrier and electron is the majority carrier due to the huge injection barrier between the Fermi level *E_f* of ITO and the highest occupied molecular orbital (HOMO) level of CBP, just as shown in the energy diagram of Fig. 1(a). When a F₄TCNQ layer is inserted into the ITO/CBP interface, as shown in Fig. 1(b), conduction current (or the luminance) at the same driven voltage increases dramatically. This strong performance enhancement demonstrates that the F₄TCNQ layer can effectively enhance the minority carrier injection, which will benefit hole-electron balance in EML and enhance device efficiency. Just as shown in Fig. 1(c), the maximum current efficiency (corresponding power efficiency) of devices A–D are 14.4 cd/A (3.6 lm/W), 20.6 cd/A (8.3 lm/W), 31.3 cd/A (19.1 lm/W), and 26.3 cd/A (11.6 lm/W), respectively. Device C with

*Supported by the National Basic Research Program of China under Grant Nos 2013CB328705, the National Natural Science Young Foundation of China under Grant Nos 61106123 and 61275034, and the Natural Science Basic Research Plan in Shaanxi Province of China under Grant No 2012JQ8001.

**Corresponding author. Email: zhaoxinwu@mail.xjtu.edu.cn

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10-nm-thick F₄TCNQ exhibits the highest efficiency performance.

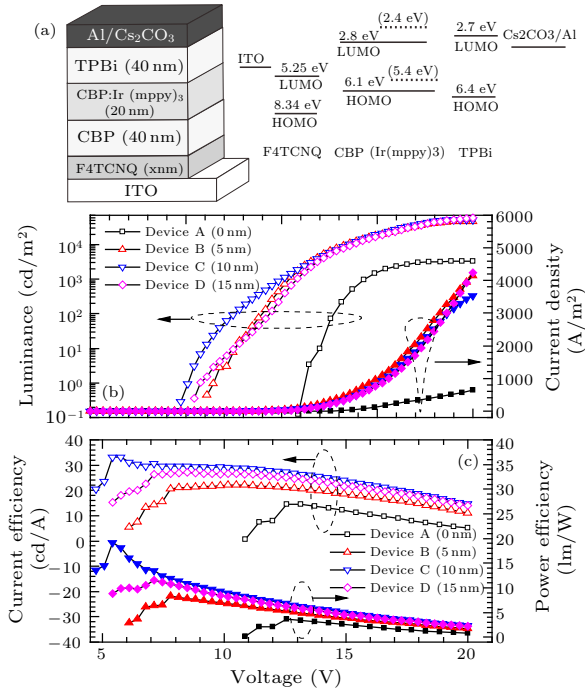


Fig. 1. (a) Configurations of PhOLEDs with different thicknesses of the F₄TCNQ modification layer, where x is 0 nm, 5 nm, 10 nm, and 15 nm for devices A–D, respectively. Energy diagram of PhOLEDs with the F₄TCNQ modification layer is also exhibited. (b) The L – V – J characteristics of devices A–D, respectively. (c) The efficiency performance of devices A–D, respectively.

To understand the influence of F₄TCNQ thickness on the performance of PhOLEDs, morphology of ITO substrates modified by the F₄TCNQ layer with different thicknesses were studied by using AFM. The thickness of the F₄TCNQ layer was varied from 0 nm to 15 nm. It can be found from Fig. 2(b) that 5-nm-thick F₄TCNQ can not cover the ITO surface uniformly. Thus the rms value of ITO surface dramatically increases from 1.225 nm to 5.745 nm when the 5-nm-thick F₄TCNQ layer is deposited on bare ITO surface. When the thickness of the F₄TCNQ layer is increased to 10 nm, as shown in Fig. 2(c), surface coverage becomes nearly 100%. Thus the surface roughness decreases to 4.186 nm. When the F₄TCNQ thickness is further increased to 15 nm, as shown in Fig. 2(d), island-type growth mode of F₄TCNQ is exhibited, and surface becomes rougher (rms=7.492 nm). These findings are in agreement with previous reports on deposition process of the F₄TCNQ film.^[15] Generally, it is believed that the increase of F₄TCNQ coverage will increase the work function of ITO surface, which will benefit hole injection from ITO anode to HTL.^[14,15] However, the influence of F₄TCNQ/HTL interface on the performance of PhOLEDs was seldom reported. Since the increase of F₄TCNQ coverage on ITO substrate will improve the F₄TCNQ-CBP contact at F₄TCNQ/CBP interface as well as decrease the ITO-CBP contact, the thickness-dependent phenomenon indicates that the F₄TCNQ/CBP interface may also play an important role for the PhOLEDs performance.

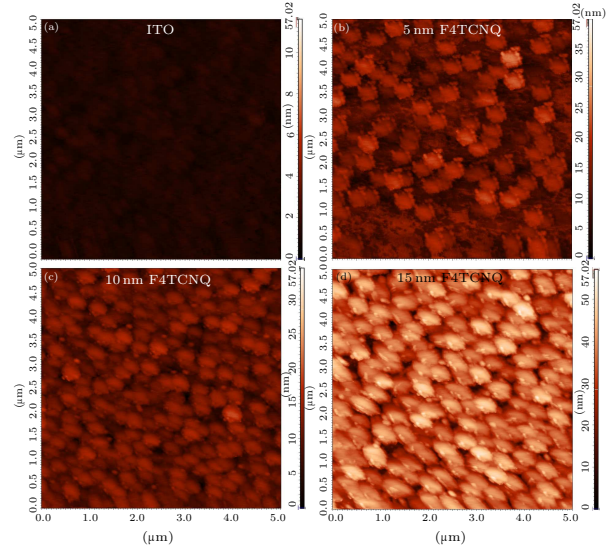


Fig. 2. AFM images of surface of ITO substrates modified by F₄TCNQ with thickness varied from 0 nm to 15 nm: (a)–(d) corresponding to 0 nm (rms=1.225 nm), 5 nm (rms=5.745 nm), 10 nm (rms=4.186 nm), 15 nm (rms=7.492 nm), respectively. The ranges of Z coordinates of all the above four images are set in the identical range from 0 nm to 57 nm for easy comparison (scan size: $5 \times 5 \mu\text{m}^2$).

To obtain a primary insight into the role of F₄TCNQ/CBP interface in the PhOLEDs, four devices (devices E, F, G, and H) were fabricated. Their respective configurations are shown in Fig. 3(a). Device E with structure of ITO/NPB (60 nm)/Al (100 nm) is a typical hole-only device due to low hole injection barrier between E_f of ITO and the HOMO of NPB (5.5 eV), as well as high electron injection barrier between E_f of Al (4.3 eV) and the lowest unoccupied molecular orbital (LUMO) of NPB (2.4 eV). When a 5-nm-thick NPB layer doped with 10 vol% Cs₂CO₃ is inserted into ITO/NPB interface (i.e., device F with structure of ITO/NPB:Cs₂CO₃ (5 nm, 10 vol%)/NPB (60 nm)/Al (100 nm)), as shown in Fig. 3(b), current is dramatically suppressed, which demonstrates that the 5-nm-thick NPB:Cs₂CO₃ layer can effectively block the hole injection for ITO anode. Thus for device G with structure of ITO/NPB:Cs₂CO₃ (5 nm, 10 vol%)/CBP (60 nm)/Al (100 nm), hole injection from ITO anode can be neglected due to the strong hole-blocking property of the NPB:Cs₂CO₃ layer. When a 10-nm-thick F₄TCNQ layer is inserted into NPB:Cs₂CO₃/CBP interface of device G (i.e., device H with structure of ITO/NPB:Cs₂CO₃ (5 nm, 10 vol%)/F₄TCNQ (10 nm)/CBP (60 nm)/Al (100 nm)), however, the conduction current was significantly enhanced, which indicates that a charge generation area is formed due to the insertion of the F₄TCNQ layer. The ultra low HOMO of F₄TCNQ, just as shown in Fig. 1(a), indicates its strong electron accepting property. Taking the driven voltage polarity (i.e., ITO as anode, and Al as cathode), the charge generation area can not be formed in NPB:Cs₂CO₃/F₄TCNQ interface, while be built in F₄TCNQ/CBP interface. Due to the strong electron accepting property of F₄TCNQ, charge transfer from CBP HOMO to F₄TCNQ LUMO will occur when the CBP layer is deposited on F₄TCNQ sur-

face, just as shown in the inset of Fig. 3(b), which is similar to the p-type doping process of F₄TCNQ in organic semiconductor.^[3,12,19,20] Then, driven by the applied voltage, electron transported to ITO anode through F₄TCNQ layer, as well as hole injected into CBP layer, which will benefit the device performance enhancement of devices B, C and D.



Fig. 3. Configurations of devices E, F, G and H (a), and their current density-voltage characteristics (b). Inset of (b) is the energy diagram of ITO/F₄TCNQ/CBP structure. The arrow represents the charge transfer process from CBP HOMO to F₄TCNQ LUMO.

Table 1. Current efficiency (CE) at a luminance of 100 cd/m² and 10000 cd/m², power efficiency (PE) at a luminance of 100 cd/m² and 10000 cd/m², and driven voltage for devices C, I and J at a luminance of 100 cd/m², i.e. V₁₀₀.

| | CE _{100/1000} (cd/A) | PE _{100/1000} (lm/W) | V ₁₀₀ (V) |
|----------|-------------------------------|-------------------------------|----------------------|
| Device C | 29.7/26.5 | 12.5/6.3 | 7.4 |
| Device I | 18.2/13.6 | 10.3/3.0 | 9.4 |
| Device J | 21.6/13.0 | 6.7/3.1 | 6.7 |

In traditional OLEDs design, NPB was widely used as HTL.^[17] Furthermore, F₄TCNQ has been demonstrated as an efficient anode buffer layer for fluorescence OLEDs based on NPB HTL.^[21] Thus influence of the F₄TCNQ modification layer on device performance of PhOLEDs by using NPB as HTL was also studied. As shown in Fig. 4, two devices with the structures of ITO/NPB (30 nm)/CBP (10 nm)/CBP:Ir(mppy)₃ (20 nm, 10 vol%)/TPBi (40 nm)/Cs₂CO₃ (2 nm)/Al (100 nm) (device I) and ITO/F₄TCNQ (10 nm)/NPB (30 nm)/CBP (10 nm)/CBP:Ir(mppy)₃ (20 nm, 10 vol%)/TPBi (40 nm)/Cs₂CO₃ (2 nm)/Al(100 nm) (device J) were fabricated respectively. For easy comparison with performance of the device by using CBP as HTL, the performance of device C is also shown in Fig. 4. As shown in Fig. 4(b), device J using F₄TCNQ as the modification layer, as well as NPB as HTL, exhibits the lowest driven voltage among devices C, I, and J. For example, at the luminance of 100 cd/m², the driven voltage of those three devices are 7.4 V (device C), 9.4 V (device I), and 6.7 V (device J)

(from Table 1). A possible reason is that, compared to the HOMO of CBP, the HOMO of NPB is closer to the LUMO of F₄TCNQ, which leads to the charge transfer from NPB to F₄TCNQ easier than that from CBP to F₄TCNQ. Thus F₄TCNQ/NPB interface exhibits stronger charge generation ability than F₄TCNQ/CBP interface at the same driven voltage. For the performance of device efficiency, however, device C with the F₄TCNQ modification layer, as well as CBP HTL, exhibits the highest efficiency among devices C, I, and J. For example, the maximum current efficiency (corresponding power efficiency, corresponding luminance) of devices C, I, and J are 31.3 cd/A (16.1 lm/W, 15 cd/m²), 19.6 cd/A (7.6 lm/W, 12 cd/m²), and 23.3 cd/A (13.7 lm/W, 11 cd/m²), respectively. Furthermore, the efficiency roll-off of device C is markedly decreased compared to that of devices I and J. As shown in Table 1, the efficiency roll-off of device C with the luminance increased from 100 cd/m² to 10000 cd/m² is 10.4% (29.7 cd/A at 100 cd/m² and 26.5 cd/A at 10000 cd/m²), while that of devices I and J are 25.2% (18.2 cd/A and 100 cd/m² and 13.6 cd/A at 10000 cd/m²) and 39.8% (21.6 cd/A and 100 cd/m² and 13.0 cd/A at 10000 cd/m²), respectively.

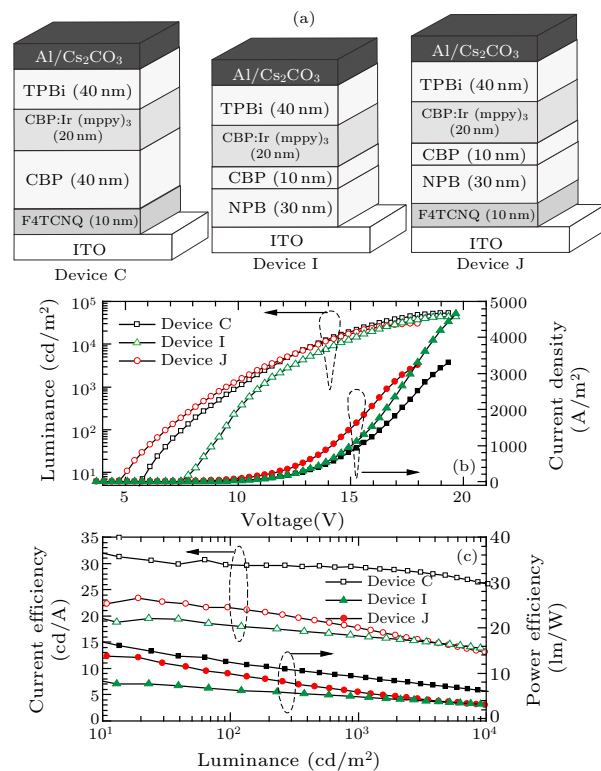


Fig. 4. Configurations of devices C, I, and J (a). The L-V-J characteristics (b) and efficiency performance (c) of devices C, I, and J respectively.

It has been demonstrated that CBP is a bipolar material. Both the hole mobility and electron mobility of CBP are of the order of 10⁻³ cm²V⁻¹s⁻¹.^[22] Due to the better charge generation property of F₄TCNQ/CBP interface, CBP can be directly used as HTL in device C. Thus the triplet exciton formation region of device C should include CBP HTL as well as CBP:Ir(mppy)₃ EML. However, for devices I and

J using NPB as HTL, the triplet exciton formation region was restricted to EML due to the strong electron blocking property of NPB.^[23] As demonstrated by Baldo *et al.*,^[2] larger exciton formation region of device C will benefit its low efficiency roll-off by decreasing triplet-triplet annihilation. Moreover, CBP HTL will also avoid the accumulation of unbalanced carrier at HTL/EL interface. As shown in Fig. 5(a), the electroluminescence spectrum of device C without NPB HTL is stable with the increase of driven current. However, for devices I and J with NPB HTL, as shown in Figs. 5(b) and 5(c), the increase of NPB fluorescence around 450 nm can be observed when the driven current is increased. Since more excess electrons will transport into the NPB layer with the increase of driving current, the increase of NPB fluorescence indicates the existence of unbalanced holes that are accumulated at NPB/CBP interface, which has been demonstrated as an important source for significant efficiency roll-off.^[3]

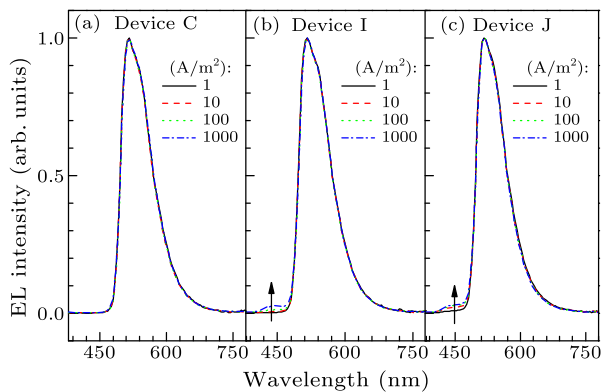


Fig. 5. The EL spectra of devices C, I, and J as a function of current density ((a)–(c)), respectively

In summary, a PhOLEDs with F_4TCNQ as the ITO modification layer and CBP as the HTL is developed. Low efficiency roll-off of 10.4% when the device luminance is increased from 100 cd/m^2 to 10000 cd/m^2 , as well as the max current efficiency of 31.3 cd/A , is achieved. It is demonstrated that the use of the F_4TCNQ modification layer will build a charge-generation region at the F_4TCNQ /CBP interface, which will enhance the hole injection into

the CBP HTL. Furthermore, using CBP as the HTL instead of NPB will benefit the low efficiency roll-off by enlarging the triplet exciton formation region and avoiding accumulation of unbalanced carriers at HTL/EL interface.

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