Eur. Phys. J. B **59**, 151–154 (2007)
DOI: 10.1140/epjb/e2007-00282-4

THE EUROPEAN PHYSICAL JOURNAL B

Charge tunneling and cross recombination at organic heterojunction under electric fields

S.Y. Yang[a], X.L. Zhang, Z.D. Lou, and Y.B. Hou

Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, P.R. China

Received 13 May 2007 / Received in final form 25 August 2007

Abstract. Electroluminescence (EL) of bilayer organic light-emitting diodes based on 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) were reported. The EL spectra of bilayer device ITO/TPD/PBD/Al consist of monomolecular emission from TPD, exciplex emission and charge carriers cross recombination at the TPD/PBD interface. By varying the thickness of each organic layer while keeping the thickness of the whole device constant, three kinds of bilayer devices were fabricated and their EL and photoluminescence spectra were compared with each other, and our experimental data show that charge tunneling and cross recombination coexist at the TPD/PBD interface, and these two processes compete with each other under high electric fields.

PACS. 73.20.-r Electron states at surfaces and interfaces – 73.40.-c Electronic transport in interface structures – 74.78.Fk Multilayers, superlattices, heterostructures – 77.84.Jd Polymers; organic compounds

1 Introduction

Organic electroluminescent devices have remarkable processing and performance advantages for large-area flat panel displays. Multilayer electroluminescence (EL) devices are often employed to balance charge injection and improve efficiency in organic light-emitting devices (OLEDs) [1,2]. The key device processes of OLEDs, charge recombination and charge separation, occur at the heterojunction between two molecules [3,4]. Exciplex formation will form at the solid interface between a hole-transporting layer (HTL) and an electron-transporting layer (ETL), where there is a significant spatial overlap between the lowest unoccupied molecular orbitals (LUMOs) of the constituent species [5], which is clearly the case for conjugated organics, whose LUMOs are highly delocalized π orbitals. Exciplex emission and electroplex emission between 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) molecules were reported [6–8]. As an example, the EL spectra of double-layer OLEDs based on TPD and PBD molecules incorporated in bisphenol-A–polycarbonate matrix were believed to consist four emission bands $\lambda_1 = 400$ nm (emission of TPD), $\lambda_2 = 480$ nm (exciplex emission at the TPD/PBD interface), $\lambda_3 = 550$ nm (electroplex emission in strongly disordered regions) and $\lambda_4 = 690$ nm (from the trapping of the e-h heteropairs in a disordered environment) [6]. As we know, the EL spectra of bilayer or multilayer devices usually depend on both the thickness of each organic layer and applied voltages [9]. Then, it is essential to know the detailed process of charge carriers at the organic heterojunction interface when electric field changes in each layer.

For different organic components, the charge carriers process at the organic heterojunction interface is different under electric fields [10]. In this paper, we choose TPD as HTL and PBD as ETL to reveal the detailed process of charge carriers at the TPD/PBD interface under different electric fields by varying the thickness of each organic layer while keeping the thickness of the whole device constant. By comparing with the EL and photoluminescence (PL) spectra of single-layer devices ITO/TPD/Al and ITO/PBD/Al, we found charge carriers tunneling and cross recombination compete with each other in bilayer device ITO/TPD/PBD/Al under high electric fields, and the EL spectra are different for three kinds of bilayer devices.

2 Experimental details

Both TPD and PBD are bought from J&K-ACROS company without further purification. TPD film was firstly thermally evaporated under high vacuum of 2.6×10^{-4} Pa onto the ITO substrate (sheet resistance of 10 Ω/square) which was thoroughly cleaned by scrubbing, ultrasonic and irradiation in a UV-ozone chamber, consequentially

---

[a] e-mail: `syyang@bjtu.edu.cn`

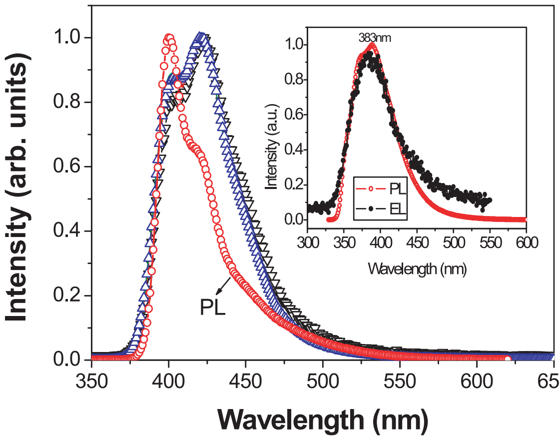

Fig. 1. Normalized EL spectra of single-layer device ITO/TPD(105 nm)/Al at different applied voltages and its normalized PL spectrum at the excitation wavelength of 325 nm. The inset shows the normalized EL and PL spectra of single-layer device ITO/PBD(110 nm)/Al.

PBD film at a rate of 0.1 nm/s, and then cathode Al was evaporated to complete the devices. The thickness of organic layer was measured with a surface profilometer (XP-2, AMBIOS). The EL and PL spectra were measured with Spex Fluorolog-3 spectrometer (Jobin Yvon) at room temperature in air.

3 Results and discussions

Firstly, we fabricated single-layer devices ITO/TPD/Al and ITO/PBD/Al. The normalized EL spectra of single-layer device ITO/TPD(105 nm)/Al at different applied voltages and its normalized PL spectrum under the excitation wavelength of 325 nm are shown in Figure 1. From here, one can see that the EL spectra, maximizing at around 420 nm with a shoulder emission peak at 400 nm, are very different from its PL spectrum which maximizes at 400 nm with a shoulder emission peak at ~420 nm. The emission peak at ~420 nm is from vibrational sideband [11]. The ratio of emission intensity at 400 nm to that at 420 nm ($I_{400\text{ nm}}/I_{420\text{ nm}}$) firstly increases with applied bias and then decreases again. Also, the normalized EL and PL spectra of single-layer device ITO/PBD(110 nm)/Al are shown in the inset of Figure 1. From here, one can see that the EL spectrum of device ITO/PBD(110 nm)/Al resembles its PL spectrum maximized at 389 nm with a little shoulder peak at 372 nm.

And then, we fabricated bilayer device ITO/TPD(70 nm)/PBD(70 nm)/Al (device A) and its normalized EL spectra at different applied voltages are shown in Figure 2. From here, one can see that the EL spectra peak at ~470 nm with a shoulder peak at ~400 nm. The relative emission intensity at ~400 nm increases with applied voltages and, to a certain applied bias, another emission at ~420 nm appears and it gradually increases with applied voltages. The emissions at 400 nm and 420 nm are from TPD (see the EL spectra of ITO/TPD/Al in Fig. 1). It is worthy to note that the emission at ~470 nm is a top-flat and broad emission band, and it is natural for one to believe that it should combine two or more emission components.

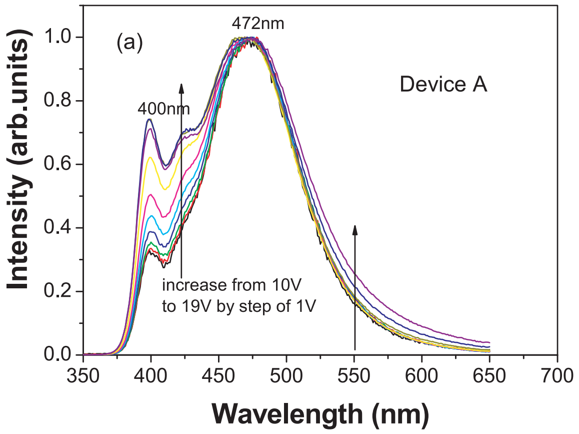

Fig. 2. Normalized EL spectra of bilayer device ITO/TPD(70 nm)/PBD(70 nm)/Al at different applied voltages.

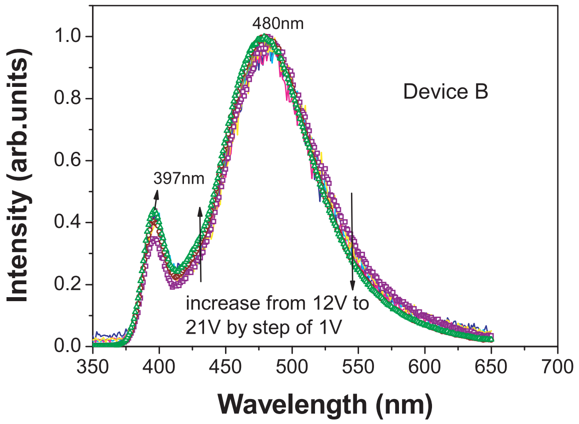

Fig. 3. Normalized EL spectra of bilayer device ITO/TPD(45 nm)/PBD(100 nm)/Al at different applied voltages.

In order to know how many emission components it includes, we changed the thickness of each organic layers while keeping the thickness of the whole device constant and made devices ITO/TPD(45 nm)/PBD(100 nm)/Al (device B) and ITO/TPD(100 nm)/PBD(45 nm)/Al (device C). The normalized EL spectra of device B and device C at different applied voltages are shown in Figures 3 and 4, respectively. From Figure 3, one can see that the normalized EL spectra are almost insensitive to the applied voltages, maximizing at ~480 nm with a shoulder emission at ~400 nm, and all of them consist of monomolecular emission of TPD and exciplex emission formed at the TPD/PBD interface. From Figure 4, one can see that the relative emission intensity from TPD increases significantly with increasing applied voltages, and gradually four emission peaks at ~400 nm, ~420 nm, ~460 nm and ~480 nm can clearly be observed. From these experimental data, we believe that emission peak

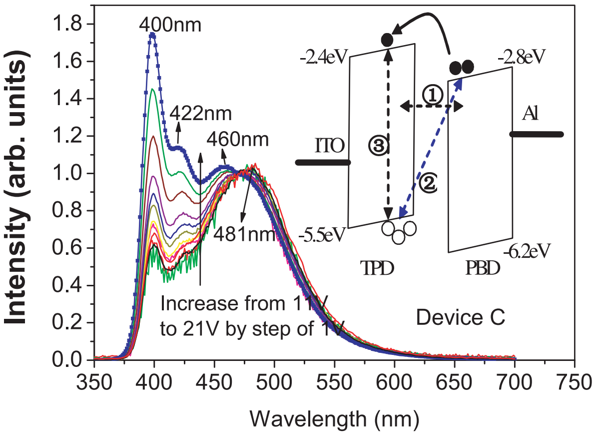

Fig. 4. Normalized EL spectra of device ITO/TPD(100 nm)/PBD(45 nm)/Al at different applied voltages. Note: the EL spectra of device C is normalized at 470 nm. The inset shows the energy diagram of organic heterostructure TPD/PBD under high electric fields, and the relaxation pathways ①, ② and ③ correspond to 480 nm, 460 nm and 400 nm emission band, respectively.

at around 480 nm origins from the exciplex emission at the TPD/PBD interface, as reported in reference [6]. The emission at around 460 nm is the result of cross recombination of electrons in the LUMO of PBD with holes in the highest occupied molecular orbital (HOMO) of TPD [8]. From the EL spectra of these three bilayer devices, it is obvious that both exciplex emission and charge carriers across recombination compete with each other under high electric fields.

It is easy to understand the above phenomena with the energy diagram of bilayer device ITO/TPD/PBD/Al. As shown by the inset in Figure 4, the HOMOs and LUMOs of TPD and PBD are 2.4 eV and 5.5 eV, 2.8 eV and 6.2 eV [8,12,13], respectively. Being the high injection barrier for holes (0.7 eV) at the TPD/PBD interface, parts of holes will be blocked by PBD and accumulate at the TPD/PBD interface. Similarly, some electrons will be blocked by TPD and accumulate at the TPD/PBD interface. More electrons transport from LUMO of PBD into LUMO of TPD since electrons injection barrier is lower than holes injection barrier at the TPD/PBD interface. Therefore, electrons in LUMO of PBD took part into two processes simultaneously: some electrons tunnel into LUMO of TPD and some electrons across recombine with holes in the HOMO of TPD at the TPD/PBD interface. As a result, the former process results to both monomolecular emission in TPD bulk (relaxation pathway ③) and (TPD*PBD)-type exciplex emission (relaxation pathway ①) at the TPD/PBD interface, and the later process results to the emission of charge cross recombination (relaxation pathway ②). Naturally, these radiation processes compete with each other under high electric fields. Generally speaking, the charge density inside the bulk of bilayer OLEDs is controlled by interfacial charge accumulation and the response time is determined by the time required to accumulate a significant fraction of the capacitor charge [14,15]. Interfacial charge accumulation enhances the field in the cell compartment adjacent to the contact at which minority carriers are injected. This gives rise to enhanced minority carrier injection and explains why efficient bilayer LEDs can be fabricated even with aluminum as the cathode material [16]. For device A, the amount of charge carriers accumulated at the TPD/PBD interface increases with applied voltage, sequentially the electric field in the device bulk redistributes [17] and the electric field in PBD layer gets higher than that in TPD layer, and the increased electric field in PBD layer will make its charge carrier mobility to increase dramatically. In this way, more and more electrons tunnel into TPD and encounter with holes to form excitons in TPD bulk, therefore, monomolecular emission of TPD gets more and more intense; For device B, electrons tunneling from LUMO of PBD into LUMO of TPD is dominant and, as a result, charge carriers cross recombination is not obvious and the relative emission intensity from TPD (~400 nm) to that of exciplex emission (~480 nm) almost keeps constant; For device C, electric field changes dramatically with increasing applied voltages, and more electrons tunnel into TPD layer and form excitons in TPD layer, therefore, monomolecular emission from TPD bulk increases dramatically with increasing applied biases (as shown in Fig. 4), and charge carriers cross recombination gradually gets more and more intense.

Therefore, the spectra will become top-flat and broad band emission at 470 nm when the emission intensity at around 460 nm almost equals to that at around 480 nm, just as the case of EL spectra of device A (see Fig. 2). However, most electrons tunnel through the TPD/PBD interface and the exciplex emission is dominant for device B (see Fig. 3), therefore, only the emission maximized at around 480 nm can clearly be observed. The ratio of emission intensity of exciplex emission to that of monomolecular emission is not insensitive with increasing applied voltages. For device C (see Fig. 4), it is clear that the relative emission intensity at 480 nm to that at 460 nm gradually decreases with increasing applied voltages, and monomolecular emission of TPD gets more and more intense under high electric fields. For further comparison, Figure 5 shows the normalized EL spectra of these three bilayer devices at the same applied voltage of 18 V. Obviously, the emission at 470 nm can be decomposed to two emissions at 460 nm and 480 nm. Also, the PL spectra of devices A, B and C are shown in the inset of Figure 5. From here, one can see that their PL spectra are different from each other and, the monomolecular emission of TPD always appears in their spectra. On the other hand, it is worthy to note that there is an obvious shoulder emission at around 550 nm in the PL spectrum of device B, and it was designed as an "electroplex" emission in reference [6]. As we know, an electroplex refers to a particular emission species, and it distinguishes from exciplex in that an electroplex only occurs under high electric fields, but an exciplex occurs under both photoexcitation and high electric fields [18]. From here, it can be drawn that this emission around 550 nm is also an "exciplex" emission instead

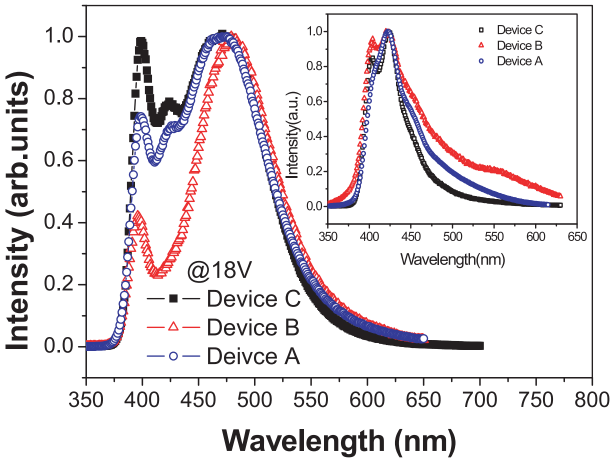

Fig. 5. Normalized EL spectra of bilayer devices A, B and C under the same applied voltage of 18 V. The inset shows the normalized PL spectra of bilayer devices A, B and C under the excitation wavelength of 325 nm.

of "electroplex" emission by its definition [18], and the detailed information is under investigation.

4 Conclusions

In summary, we have observed charge tunneling and cross recombination at the TPD/PBD interface by studying the EL spectra of bilayer device ITO/TPD/PBD/Al. The EL spectra of bilayer device ITO/TPD/PBD/Al consist of monomolecular emission of TPD, (TPD*PBD)-type exciplex emission and charge carriers cross recombination at the TPD/PBD interface. By varying the thickness of each organic layer while keeping the thickness of the whole device constant, in this way, to change the electric field distribution in each organic layer, we have observed charge tunneling (resulting to monomolecular emission of TPD and (TPD*PBD)-type exciplex emission) competes with charge carriers cross recombination at the TPD/PBD interface, and it results to different EL characteristics for these bilayer OLEDs.

This project was supported by the National Natural Science Foundation of China (60406006, 60777025 and 10434030), the Beijing Natural Science Foundation (2062019), the "973" National Key Basic Research Special Foundation of China (2003CB314707), the Program for New Century Excellent Talents in University (NCET) and Beijing NOVA program for Science and Technology (2006B20).

References

1. C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987)
2. C. Adachi, S. Tokito, T. Tsutsui, S. Saito, Jpn J. Appl. Phys. **27**, L713 (1988)
3. B.K. Crone, P.S. Davids, I.H. Campbell, D.L. Smith, J. Appl. Phys. **87**, 1974 (2000)
4. H.J. Snaith, A.C. Arias, A.C. Morteani, C. Silva, R.H. Friend, Nano Lett. **2**, 1353 (2002)
5. A. Horvath, K.L. Stevenson, Coord. Chem. Rev. **153**, 57 (1996)
6. G. Giro, M. Cocchi, J. Kalinowski, P. Di Marco, V. Fattori, Chem. Phys. Lett. **318**, 137 (2000)
7. J. Kalinowski, M. Cocchi, P. Di Marco, W. Stampor, G. Giro, V. Fattori, J. Phys. D **33**, 2379 (2000)
8. S.Y. Yang, X.L. Zhang, Y.B. Hou, Z.B. Deng, X.R. Xu, J. Appl. Phys. **101**, 096101 (2007)
9. S.Y. Yang, Z.J. Wang, Z. Xu, X.H. Chen, Y.B. Hou, X.R. Xu, Chin. Sci. Bull. **45**, 1623 (2000)
10. S.Y. Yang, D. Liu, Y. Jiang, F. Teng, Z. Xu, Y. Hou, X.R. Xu, Eur. Phys. J. B **52**, 329 (2006)
11. A.J. Campbell, D.D.C. Bradley, J. Laubender, M. Sokolowski, J. Appl. Phys. **86**, 5004 (1999)
12. H. Ogawa, R. Okuda, Y. Shirota, Appl. Phys. A **67**, 599 (1998)
13. Z.L. Zhang, X.Y. Jiang, S.H. Xu, T. Nagatomo, O. Omoto, Chin. J. Lumin. **16**, 281 (1995) (in Chinese)
14. D.V. Khramtchenkov, V.I. Arkhipov, H. Bässler, J. Appl. Phys. **79**, 9283 (1996)
15. D.V. Khramtchenkov, V.I. Arkhipov, H. Bässler, J. Appl. Phys. **81**, 6954 (1997)
16. J. Pommerehne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch, J. Daub, Adv. Mater. **7**, 551 (1995)
17. S.Y. Yang, Z.J. Wang, Z. Xu, Y.B. Hou, X.R. Xu, Chem. Phys. **274**, 267 (2001)
18. T. Granlund, L.A.A. Petterson, M.R. Anderson, O. Inganäs, J. Appl. Phys. **81**, 8097 (1997)