Electrochemiluminescence Studies of Phosphorescent Dopant and Host Molecules of Polymer Light-emitting Diodes

Wang, Dongdong[a](王栋东)   Wu, Zhaoxin*,[b](吴朝新)   Hou, Xun[b](侯洵)

[a] School of Science, Xi'an Jiaotong University, Xi'an, Shannxi 710049, China
[b] Key Laboratory for Physical Electronics and Devices of the Ministry of Education, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, Shannxi 710049, China

Electrochemiluminescence (ECL) from tris(2-phenylpyridine)irdium [Ir(ppy)$_3$] was investigated following cross reaction of its anion with oxidized poly(*N*-vinyl-carbazole) (PVK) and its cation with reduced 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD). Both cross reactions show Ir(ppy)$_3$ emission and the cross reaction of $PVK^{+\bullet}/Ir(ppy)_3^-$ showed the highest ECL intensity. The comparisons of the reaction enthalpy and the energy of Ir(ppy)$_3$ light emitting shows that reaction between $PVK^{+\bullet}$ and $Ir(ppy)_3^-$ is energy sufficient to populate metal-to-ligand charge transfer (MLCT) excited singlet (3.04 eV) of Ir(ppy)$_3$, while the reaction between $Ir(ppy)_3^+$ and $PBD^{-\bullet}$ is energy efficient to populate MLCT excited triplet (2.4 eV). The ECL result in solution reveals that the energy released from charge transfer between the Ir(ppy)$_3$ and PVK or PBD is sufficient to produce the excited state of Ir(ppy)$_3$ in solid polymer light-emitting diodes (PLEDs) based on PVK∶PBD hosts doped by Ir(ppy)$_3$. These results obtained will provide further insight into charge-transfer excitation in PLEDs.

Keywords electrochemiluminescence, organic electroluminescence, electron-transfer reaction, charge-transfer excitation

Introduction

Electrochemiluminescence (ECL) is a well-known method for generating light: electrochemically generated radical ions undergo a homogenerious electron transfer to produce the excited state that releases excited energy as light.[1,2] ECL has been long of interest because it can provide a simple light production mechanism for various applications and some insight into light-emitting mechanism.[3] ECL can be observed from both organic and inorganic compounds such as 5,6,11,12-tetraphenylnaphacene[4] and transition metal complexes Ru(II) chelates,[5,6] which were extensively used for sensitive or selective detection reagents in analytical chemistry.[7] Recently, the materials investigated for ECL study[8] have been expanded to the light-emitting materials used in OLEDs (organic light-emitting diodes) which are extensively investigated subject since it was reported by Tang and VanSlyke[9] and considered to be the candidate for the next generation light source and flat panel displays. By using solution contacts for one of electrodes [*e.g.* ITO/MEH-PPV (poly(2-methoxy-5-(2'-methylhexyloxy)-1,4-phenylene vinylene))/acetonitrile, 0.4 mol/L tetrabutylammonium tetrafluorborate, Bu_4NBF_4], Richter's studies[7] showed that there was connection between ECL and the condensed-phase properties of MEH-PPV. Anderson *et al.*[8] investigated the electrochemical characteristics of hole- and electron-transport materials, as well as molecular dopants for OLEDs, and found that the ECL reactions $DIQA^{-\bullet}/DIQA^{+\bullet}$, $DIQA^{+\bullet}/Alq_3^{-\bullet}$ and $DIQA^{-\bullet}/TPD^{+\bullet}$ all produced emission spectra from $DIQA^{*s}$ state which were identical to emission spectral response seen from OLEDs. These ECL reactions described in solution provide much valuable informations for understanding these materials and electroluminescence (EL) process in OLEDs and therefore, it is expected that ECL are likely to provide a direct means for characterizing and optimizing the condensed-phase electrochemical reactions that lead to emissive state production.[3]

Recently, several literatures[2,10,11] reported ECL behaviours of cyclometalated Iridium complexes which are effective phosphorescent dopants in OLEDs. These reports focused mostly on annihilation reaction of Iridium complexes themselves or co-reaction with coreactant. The ECL behaviours from cross reactions between Iridium (Ir) complex and PVK [poly(*N*-vinyl-carbazole)] or PBD [2-(4-biphenylyl)-5-(-4-*tert*-butyl-phenyl)-1,3,4-oxadiazole] are still not to be investigated, while the study on such system is very significant. To the best our knowledge, although Iridium (Ir) complex doped PVK∶PBD as light-emitting layer is one kind of prevailing device architecture in the fields of PLEDs and

---

* E-mail: zhaoxinwu@mail.xjtu.edu.cn; Tel.: 0086-029-82664867 ; Fax: 0086-029-82664867
Received October 7, 2009; revised December 21, 2009; accepted April 15, 2010.
Project supported by Ministry of Science and Technology of China (973 Program No. 2006CB921602), the Ministry of Education of China (Key Program No. 107100) and the Technology Program of Shaanxi Province (No. 2006K04-c25).

the charge-trapping induced excitation of dopants, which is similar to the electron-transfer reaction of ECL process in solution, was the dominant mechanism for light emission in these devices,[12,13] the detailed charge-transfer process occurring among the component of these materials of PLEDs is still not well understood. It is expected to well know the process so as to optimize these condensed-phase redox process and achieve better device performance.

In the paper, we investigated the ECL process from electron-transfer reaction between the ionic states of tris(2-phenylpyridine)irdium [Ir(ppy)$_3$] and the ionic species of PVK or PBD. We hope that the results obtained will provide further insight into charge-transfer excitation in PLEDs.

Experimental

Cyclic voltammetric experiments and ECL studies were performed on the electrochemical and chemiluminescent analyzer (MPI-A). A three-electrode cell was used, which consists of a carbon disk (r=3.0 mm) working electrode, a platinum wire counter electrode and an Ag/AgNO$_3$ (0.01 mol/L) reference electrode. Prior to each experiment, the carbon disk electrode was polished with alumina paste. For electrochemical and ECL measurements, millimolar concentrations of the molecules along with 0.1 mol/L tetrabutylammonium perochlorate (TBAP) were dissolved in dry degassed *N*,*N*,-dimethyl-methamide (DMF). During the ECL experiments, the potential of the working electrode was stepped between potential limit established to lie from 0.02 to 0.14 V beyond the potentials needed to reduce or oxidize the target molecules. ECL emissions were observed during the second reactant generation step in the course of a triple-step-potential sequence.[14,15] To measure the spectral response of the ECL process, narrow bandpass interference filters with a wavelength range from 400 to 700 nm were placed under the cell and used to determine the ECL emission spectrum.

The PLEDs for EL measure were fabricated with the structure indium tin oxide (ITO)/PVK∶PBD (7∶3): Ir(ppy)$_3$(5%)/LiF/Al. A blend of PVK, PBD, and Ir(ppy)$_3$ in chlorobenzene solution was spin-coated on top of the film of ITO on the glass substrate. The spin-coated film was about 70 nm-thick measured with an ellipsometer, and the cathode of the device, LiF (0.8 nm)/Al(100 nm), was deposited by vacuum thermal evaporation. EL spectra were recorded by a spectrophotometer (PR-650) and photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (JY-Fmax-4).

Results and discussion

Figure 1 shows chemical structure of Ir(ppy)$_3$ and PBD, and their cyclic voltammetry in 0.1 mol/L TBAP-DMF solution. The peak potential is a mean value for three-time measurements. The oxidation of Ir(ppy)$_3$ proceeds by one electron process[16] and its oxidation wave shows a peak potential of +0.36 V. The reduction wave of Ir(ppy)$_3$ shows a peak potential of −2.68 V. From Figure 1a, the redox states of Ir(ppy)$_3$ are chemically stable on the time scale of seconds. The reduction wave of PBD with a peak potential of −2.34 V shows an i_a/i_c of 1.17 (Figure 1b), indicating that anion radical of PBD is stable on the time scale of seconds, while the oxidation peak is not observed in our experiment due to the unstability of PBD radical cation. The similar results were reported by Keszthelyi *et al*.[17] for a related compound, 2,5-diphenyl-1,3,4-oxadiazole. The oxidation of PVK is a chemically irreversible process[18] and the peak potential for PVK oxidation is about +0.79 V vs. Ag/Ag$^+$.

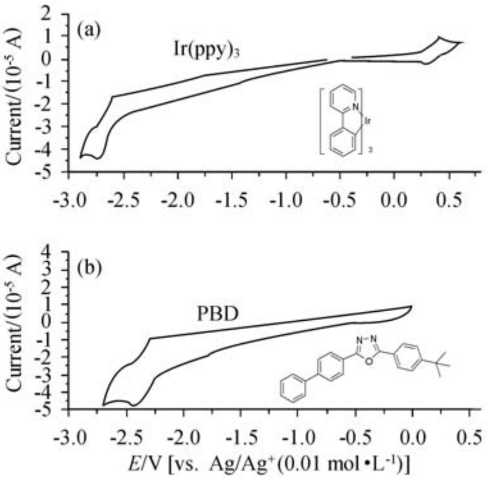

Figure 1 Chemical structure and cyclic voltammogram of (a) Ir(ppy)$_3$ and (b) PBD in 0.1 mol/L TBAP-DMF solution. The reference electrode is Ag/AgNO$_3$ (0.01 mol/L), [Ir(ppy)$_3$]=0.1 mmol/L, [PBD]=0.1 mmol/L, scan rate=100 mV.

In PLEDs based on PVK∶PBD doped by Ir(ppy)$_3$, the holes were injected into the hole-transporting material PVK to form radical cation state, which is similar to the electrochemically oxidized process in solution, and the electrons were injected into PBD to form radical anion state, which is similar to electrochemically reduced process. In addition, when the injected holes or electrons transport jumpily between the PVK or PBD molecules,[19] they can be trapped by Ir(ppy)$_3$ molecules to form cation or anion states of Ir(ppy)$_3$ due to its ionization potentials and the electron affinity located inside the band gap of PVK and PBD.[20] Thus the excited state of Ir(ppy)$_3$ can be presumably produced by electron-transfer reactions as follows:

$$\mathrm{Ir(ppy)}_3^- + \mathrm{Ir(ppy)}_3^+ \rightarrow \mathrm{Ir(ppy)}_3 + \mathrm{Ir(ppy)}_3^* \qquad (1)$$

$$\mathrm{PVK}^{+\bullet} + \mathrm{Ir(ppy)}_3^- \rightarrow \mathrm{PVK} + \mathrm{Ir(ppy)}_3^* \qquad (2)$$

$$\mathrm{PBD}^{-\bullet} + \mathrm{Ir(ppy)}_3^+ \rightarrow \mathrm{PBD} + \mathrm{Ir(ppy)}_3^* \qquad (3)$$

Therefore, the ECL investigation below focuses on the reactions above.

Figure 2 shows the ECL emission spectrum obtained from the cross reaction in Eq. (2), EL spectrum from PLEDs and the photoluminescence (PL) spectrum of Ir(ppy)$_3$ in PMMA (polymer methyl methacrylate) film. In Figure 2, there is about 25 nm difference between ECL emission spectrum produced by the reaction in Eq. (2) and EL (PL) in the intensity maxima. It should be noted that the spectral response of ECL process was obtained by narrow bandpass interference filters, and the 25 nm difference is the experiment error resulting from narrow bandpass interference filters. Regardless of experiment error, the spectrum shape produced in ECL is similar to that in EL, indicating both emission from the same excited state, namely, metal-to-ligand charge transfer (MLCT) triplet state.[11] As for cross reaction in Eq. (3) and annihilation reaction in Eq. (1), the emission spectra obtained are the same as the reaction in Eq. (2). These ECL results suggest that the three reactions can induce population of MLCT triplet state of Ir(ppy)$_3$.

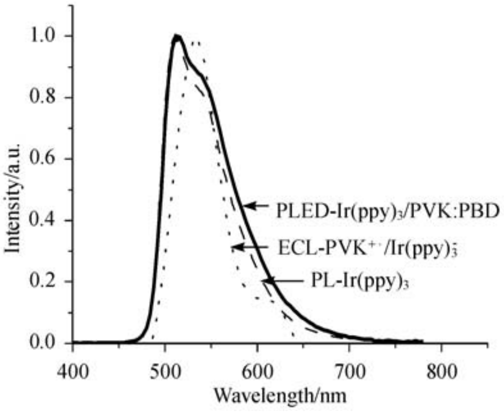

Figure 2 ECL response spectra for triplet potential step experiments. ECL emission spectra for solution containing PVK (0.5 mg/mL) and 0.5 mmol/L Ir(ppy)$_3$ (dot line), EL spectra of PLEDs based on PVK : PBD doped by 5% Ir(ppy)$_3$ (solid line) and PL spectra of 5% Ir(ppy)$_3$ doped PMMA film (dash line).

Figures 3a and 3b show the ECL emission intensity vs. time profile in the presence of Ir(ppy)$_3$ alone and mixed solution containing Ir(ppy)$_3$ and PBD, respectively. The potential for Ir(ppy)$_3$ solution was stepped from $+0.50$ to -2.70 V, exclusively forming Ir(ppy)$_3^+$ and Ir(ppy)$_3^-$, and for mixed solution the electrode was stepped from $+0.50$ to -2.40 V, only producing Ir(ppy)$_3^+$ and PBD$^{-\bullet}$. In Figures 3a and 3b, the ECL emission intensity (integral of emission across the intensity spectrum) from reaction in Eq. (1) is 1.5

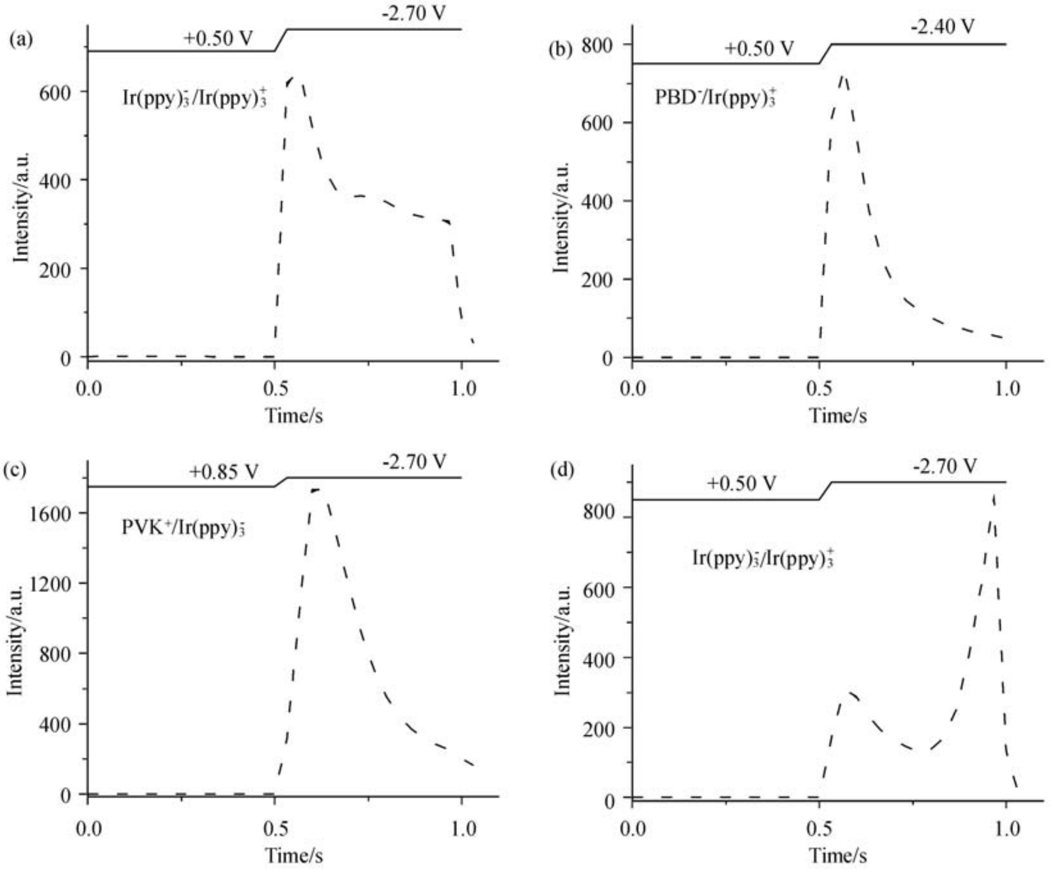

Figure 3 ECL emission intensity vs. time profiles for triplet potential step experiments in the presence of (a) 1 mmol/L Ir(ppy)$_3$, (b) mixed solution containing Ir(ppy)$_3$ (0.5 mmol/L) and PBD (0.5 mmol/L), (c) mixed solution involving Ir(ppy)$_3$ (0.5 mmol/L) and PVK (0.5 mg/mL) in which potential is stepped from $+0.85$ to -2.70 V, and (d) mixed solution involving Ir(ppy)$_3$ (0.5 mmol/L) and PVK (0.5 mg/mL) in which the potential is stepped from $+0.50$ to -2.70 V.

times higher than that of reaction in Eq. (3), which means that more photons are released from the reaction in Eq. (1). The comparisons of the reaction enthalpy (calculated according to the equation in reference[21]) and the energy of Ir(ppy)$_3$ emitted light can determine whether the reaction is energy-efficient S-routes or energy-deficient T-routes processes. The reaction enthalpy for reaction in Eq. (1) is *ca.* 2.88 eV, indicating that the energy released is sufficient to populate the triplet state of Ir(ppy)$_3$ directly (2.40 eV).[22] As for cross reaction in Eq. (3), the enthalpy is about 2.54 eV. It appears marginally sufficient to populate the triplet state. The higher ECL emission intensity from reaction in Eq. (1) may be a result from higher reaction enthalpy.

Figure 3c shows the ECL emission intensity vs. time profile in the presence of Ir(ppy)$_3$ and PVK. The electrode is stepped from $+0.85$ V to -2.70 V, producing $\text{PVK}^{+\bullet}$ and Ir(ppy)_3^-, as well as Ir(ppy)_3^+. It suggests that the reaction in Eq. (1) may also operate when the electrode is swept to potential where the cross reaction in Eq. (2) occurs. As shown in Figure 3c, the ECL intensity from PVK/Ir(ppy)$_3$ was the highest among the three reactions and its intensity was nearly twice that of reaction in Eq. (1). However, one question is whether the reaction in Eq. (2) is a major contribution to light emission in PVK/Ir(ppy)$_3$. In order to clarify the question, we observed the ECL emission intensity from this system when potential is stepped from $+0.50$ V to -2.70 V, in which only reaction in Eq. (1) contributes to light emission. It was found that its ECL intensity (shown in Figure 3d) was about one third of the intensity that the electrode was stepped from $+0.85$ to -2.70 V. Thus, it can be concluded that the major contribution to light emission is from reaction in Eq. (2). Moreover, the enthalpy change from electron-transfer reaction in Eq. (2) is about 3.31 eV. It means that the energy released from the reaction is sufficient to populate the MLCT singlet state of Ir(ppy)$_3$ (3.04 eV) directly,[23] and subsequently, the MLCT singlet state may cross the MLCT triplet state, emitting phosphorescence.

We now move to discuss the charge-trapped induced excitation of Ir(ppy)$_3$ in PLEDs. It has been ever reported that the energy released from charge-transfer process in the condensed phase would be comparable to that observed in solution, with differences arising due to difference in energies of stabilization of the oxidized and reduced forms of these molecules in solution versus the solid thim film.[8] Thus, the electrochemical measurements give us simple approach to estimate the lower limit to the energy value in condensed phase.[8,24] For PLEDs based on PVK/PBD doped by Ir(ppy)$_3$, the ECL result shows that both cross reactions $\text{PVK}^{+\bullet}/\text{Ir(ppy)}_3^-$ and $\text{Ir(ppy)}_3^+/\text{PBD}^{-\bullet}$ may induce the production of Ir(ppy)$_3$ excited state, meaning that charge-transfer processes between the Ir(ppy)$_3$ and PVK or PBD in PLEDs are energy sufficient to produce the excited state of Ir(ppy)$_3$. Notably, the energy released from charge transfer between PVK and Ir(ppy)$_3$ is significantly beyond the energy to excite Ir(ppy)$_3$ as excited triplet state, which means that some of energy was lost by intersystem crossing. As for charge transfer between Ir(ppy)_3^- and Ir(ppy)_3^+, the probability of forming Ir(ppy)$_3$ excited state is little in condensed phase. This is because the charge transfer is typically limited to a maximum distance of 0.5—1 nm[24] in solid PLEDs, while a mean intermolecular distance of emitter is beyond 3 nm when the emitter was molecularly dispersed in the carbazole homopolymer at a mass ratio of 3%—8%.[25]

conclusion

ECL from annihilation reaction of Ir(ppy)$_3$, cross reaction of $\text{PVK}^{+\bullet}/\text{Ir(ppy)}_3^-$ and $\text{Ir(ppy)}_3^+/\text{PBD}^{-\bullet}$ was investigated in DMF solution. Three reactions show emission of MLCT triplet state of Ir(ppy)$_3$ and the cross reaction of $\text{PVK}^{+\bullet}/\text{Ir(ppy)}_3^-$ shows the highest ECL intensity among the reactions which is related with high reaction enthalpy. The ECL described in solution show that both charge-transfer processes [$\text{PVK}^{+\bullet}/\text{Ir(ppy)}_3^-$, and $\text{Ir(ppy)}_3^+/\text{PBD}^{-\bullet}$] are energy sufficient to produce excited triplet state of Ir(ppy)$_3$ in PLEDs and this explains why the PLEDs based on PVK/PBD doped by Ir(ppy)$_3$ show excellent device performances.

Acknowledgement

We greatly appreciate associate professor Qi honglan and Zhang yu for kind help in electrochemical measurements (School of Chemistry and Materials Science, Shaanxi Normal University).

References

1 Hercules, D. M. *Science* **1964**, *145*, 808.

2 Kim, J. I.; Shin, I.-S.; Kim, H.; Lee, J.-K. *J. Am. Chem. Soc.* **2005**, *127*, 1614.

3 Armstrong, N. R.; Wightman, R. M.; Gross, E. M. *Ann. Rev. Phys. Chem.* **2001**, *52*, 391.

4 Bezman, R.; Faulkner, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 6324.

5 Tokel, N. E.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862.

6 McCord, P.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *318*, 91.

7 Richter, M. M.; Fan, F.-R. F.; Klavetter, F.; Heeger, A. J.; Bard, A. J. *Chem. Phys. Lett.* **1994**, *226*, 115.

8 Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S.; Jabbour, G.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R.; Armstrong, N. *J. Am. Chem. Soc.* **1998**, *120*, 9646.

9 Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

10 Shin, I.-S.; Kim, J. I.; Kwon, T.-H.; Hong, J.-I.; Lee, J.-K.; Kim, H. *J. Phys. Chem. C* **2007**, *111*, 2280.

11 Kapturkiewicz, A.; Chen, T.-M.; Laskar, I. R.; Nowacki, J.

Electrochem. *Commun*. **2004**, *6*, 827.

12 Gong, X.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv*. *Funct*. *Mater*. **2003**, *13*, 439.

13 Gong, X.; Ostrowski, J. C.; Bazan, G. C.; Moses, D.; Heeger, A. J. *Adv*. *Mater*. **2004**, *16*, 615.

14 Faulkner, L. R. *J*. *Electrochem*. *Soc*. **1975**, *122*, 1190.

15 Faulkner, L. R. *J*. *Electrochem*. *Soc*. **1977**, *124*, 1724.

16 Bruce, D.; Richter, M. M. *Anal*. *Chem*. **2002**, *74*, 1340.

17 Keszthelyi, C.; Tachikaw, H.; Bard, A. J. *J*. *Am*. *Chem*. *Soc*. **1972**, *94*, 1522.

18 Xia, H.; L, M.; Lu, D.; Zhang, C. B.; Xie, W. J.; Liu, X. D.; Yang, B.; Ma, Y. G. *Adv*. *Funct*. *Mater*. **2007**, *17*, 1757.

19 Auweraer, M. V.; Schryver, F. C.; Borsenberger, P. M. *Adv*. *Mater*. **1994**, *6*, 199.

20 Kolosov, D.; Adamovich, V.; Djurovich, P.; Thompson, M. E.; Adachi, C. *J*. *Am*. *Chem*. *Soc*. **2002**, *124*, 9945.

21 Wu, J. M. *Chem*. *Rev*. **2008**, *108*, 2506.

22 Gregor, S.; Sebastian, R.; Thomas Conrad, R.; Karsten, W.; Karl, L. *Adv*. *Funct*. *Mater*. **2009**, *19*, 1319.

23 Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J*. *Am*. *Chem*. *Soc*. **2001**, *123*, 4304.

24 Shaheen, S. E.; Kippelen, B.; Peyghambarian, N.; Wang, J. F.; Anderson, J. D.; Mash, E. A.; Lee, P. A.; Armstrong, N. R.; Kawabe, Y. *J*. *Appl*. *Phys*. **1999**, *85*, 7939.

25 Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stossel, P.; Brunner, K. *J*. *Am*. *Chem*. *Soc*. **2004**, *126*, 7718.

(E0910071 Zhao, X.)