



# Suppression of phase separation through blending of electron transporting materials in polymer electrophosphorescent devices

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## ABSTRACT

Herein, we report the concentration effect of an electron transporting material, 1,3-bis((4-tert-butyl-phenyl)-1,3,4-oxadiazolyl) phenylene (OXD-7), on the performance of polymer electrophosphorescent devices. From the phase mode images of atomic force microscopy, we observed that phase separation between the host material and the triplet dopants was suppressed in the photoactive film while the concentration of OXD-7 was increased. Correspondingly, the single-layer blue light-emitting device with the best external quantum efficiency of 7.9% was achieved. We attributed the device enhancement to the improved compatibility between the host and the phosphorescent molecules after the addition of OXD-7 molecules.

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## 1. Introduction

Polymer light-emitting diodes (PLEDs) are attracting much attention owing to their potential applications in flexible flat-panel displays and the next-generation lighting systems [1–5]. They have advantages of low costs, flexibility, and low fabrication temperature. For enhancing the light-emitting efficiency, phosphorescent molecules are often employed as dopants in the devices [6–10]. The triplet (phosphorescent) dopants, which usually consist of heavy metals for inducing the heavy-metal effect, allow triplet excitons generated upon the charge recombination become emissive by coupling the triplet states with singlet ones. Therefore, the internal quantum efficiency of the devices can be ideally improved as high as ~100% because of the harvesting of both singlet and triplet excitons [6–10].

Aside from the triplet dopants, however, some reports also demonstrated that the electron transporting materials might also play important roles in such polymer electrophosphorescent devices [11–14]. For example, the performance of the blue devices using 1,3-bis((4-tert-butyl-phenyl)-1,3,4-oxadiazolyl)phenylene (OXD-7) as the electron transporting molecules is superior than that of the device using 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD) [14]. Particularly, the reason is due to the higher triplet energy of OXD-7, which can result in better confinement of triplet excitons on the dopants [15,16].

The purpose of this work is to systematically investigate the functions of the electron transporting material, OXD-7, in the

devices. We observed that the OXD-7 molecules not only can help to confine the triplet excitons on the dopants [14–16] but can also improve the morphology of the emitting layer. The severe phase separation between different components was effectively inhibited while the concentration of OXD-7 was optimized. As a result, the single-layer blue-emitting devices with a high efficiency up to 7.9% (17.1 cd/A) has been achieved.

## 2. Experimental

### 2.1. Device fabrication and materials

The chemical structures and the energy levels of the materials used in this study are illustrated in Fig. 1 [17–22]. The light-emitting devices were fabricated on pre-cleaned indium tin oxide (ITO)-coated glass substrates. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was firstly spin-coated onto the ITO substrates, which were pretreated by UV ozone. After baking of the PEDOT:PSS layer at 120 °C for 1 h to remove the solvent, the emitting layer, consisting of a host polymer, poly(vinylcarbazole) (PVK), an electron transporting material, OXD-7, and iridium dopants, were spin-coated on top of the PEDOT:PSS layer from chlorobenzene inside a glove box and then annealed at 120 °C for 15 min. The phosphorescent dopant used in this work was either iridium bis[2-(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>]picolate (Flrpic, blue emission) in device A, B, C, and D or iridium bis[2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>]acetylacetonate [Btp<sub>2</sub>Ir(acac), red emission] in device E, F, G, and H. The dopant concentration was controlled as 10 wt% respect to the weight of PVK in all the devices. The weight ratios of the materials in the devices are

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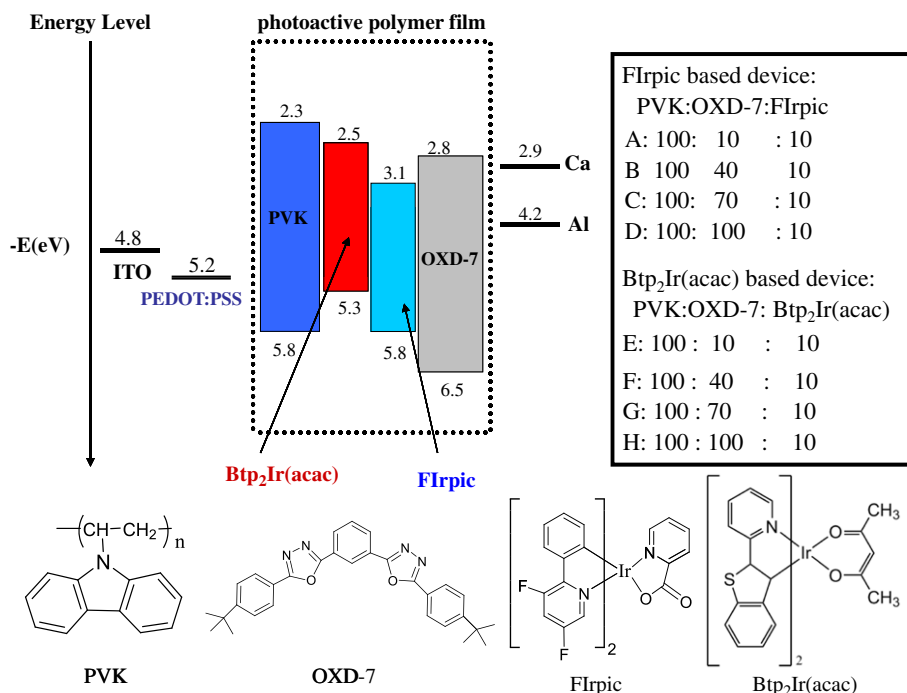


Fig. 1. Energy levels and the chemical structures of the materials used in this work.

summarized in Fig. 1. Finally, the samples were transferred to a thermal evaporator in a nitrogen atmosphere for metal deposition. The devices have the following device structure: ITO/PEDOT:PSS/PVK:OXD-7:iridium dopants/Ca(50 nm)/Al(100 nm).

## 2.2. Device measurements

The thicknesses of the active layers of different devices were almost identical, which were confirmed by using Alpha stepper. The device electrical characteristics were measured by a Keithley 2400 source measure unit and a Keithley 2000 digital multimeter with a calibrated Si photodiode. The emission spectra were obtained using a PR650 spectrascan colorimeter. Surface morphology of different thin films was measured using a Digital Instrument Dimension 3100 atomic force microscope (AFM).

## 3. Results and discussions

### 3.1. Electrical characteristics of blue-emitting devices

The current density–electric field ( $J$ – $E$ ) characteristics of the devices containing different concentrations of OXD-7 are shown in Fig. 2(a). Originally, we expected that the current density increased with the concentration of OXD-7 (in weight ratio with respect to PVK) because the electron transporting nature of OXD-7 should improve the electron conduction in the devices. However, the result in Fig. 2(a) clearly indicates that the current density decreased with the concentration of OXD-7. Because the concentration of Flrpic was identical for all the devices, we suspect that the addition of OXD-7 increased the charge trapping probability. From the energy levels shown in Fig. 1, we realized that the electron-charge trapping should occur at Flrpic dopants. Therefore, the trapped charges could form space charges, leading to higher driving voltages. In addition, from the device brightness–electric field ( $B$ – $E$ ) characteristics (Fig. 2(b)), we observed that the brightness increased while the concentration of OXD-7 increased from 10 to 70 wt%, and then decreased while the concentration was 100 wt%. The current efficiency of device A was only

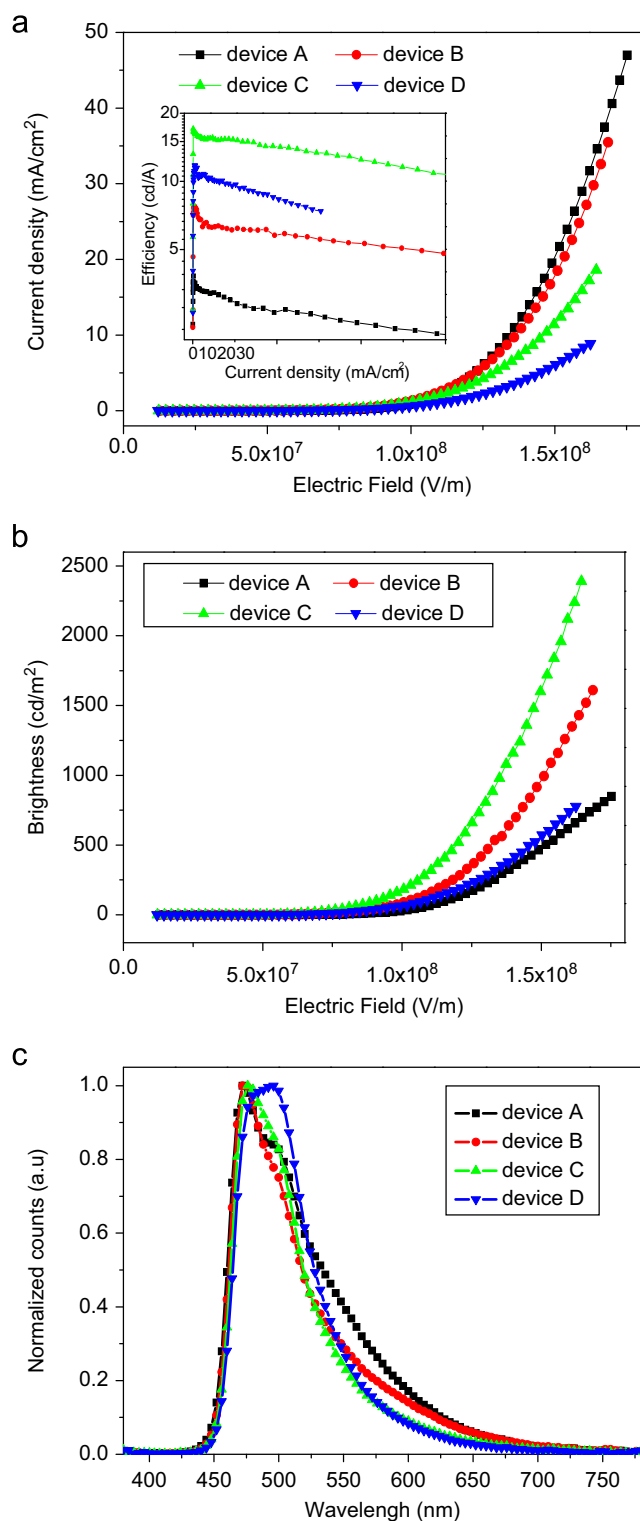
3.93 cd/A (the inset of Fig. 2(a)). On the other hand, the efficiency of device C was significantly enhanced up to 17.1 cd/A (7.9%). At such concentration of OXD-7, the device probably had the best charge balance, thereby resulting in the highest device efficiency. The electrical properties of the PLEDs were summarized in Table 1.

Fig. 2(c) shows the electroluminescence (EL) spectra of the blue devices containing different concentrations of OXD-7 in the light-emitting layers. Device A had the largest full width at half maximum (FWHM) of the EL peak among the EL devices, suggesting that Flrpic molecules aggregated seriously in the device [19]. On the other hand, the FWHM of the emission spectra of device C was much narrower. Note that device C exhibited the highest efficiency among those of the devices containing different amount of OXD-7. The results indicated that the distribution of Flrpic molecules in the emissive layer was more even while the concentration of OXD-7 was 70 wt% (device C). In addition, the gradual red-shift of the EL spectra with increase in OXD-7 concentration was probably due to the shift of the recombination zone. Such optical effect has been reported previously [23, 24].

### 3.2. Morphological analysis

From the above results, we suspect that the addition of OXD-7 in photoactive layer could effectively optimize the blend thin film morphology, such as diminishing the serious phase separation between host and dopant or reducing the degree of aggregation of Flrpic molecule. While the dopants supposedly dispersed much better, the “effective” dopant concentration would increased, leading to more efficient charge trapping and therefore, lowers current density at certain bias (Fig. 2(a)). Consequently, the improved charge balance and/or increased recombination probability resulted in a higher device efficiency.

To further confirm the above assumption, the morphology of the photoactive polymer films was examined using AFM (Fig. 3). The insets to Fig. 3 display the corresponding height mode images of the thin films containing different concentrations of OXD-7. We could not find any difference in these high-mode images. The root-mean-square (rms) surface roughness was 0.470, 0.580, 0.578, 0.562 nm



**Fig. 2.** (a) The current density–electric field ( $J$ – $E$ ) and (b) brightness–electric field ( $B$ – $E$ ) curves of the blue electrophosphorescent devices prepared with different concentrations of OXD-7. (c) The electroluminescent spectra of the devices blended with different concentrations of OXD-7. The inset to figure (a) displays plots of the luminescence efficiency as a function of current density.

for the films containing 10, 40, 70, and 100 wt% OXD-7, respectively. On the other hand, while we further examined the phase mode images, we observed significant morphological changes while different amount of OXD-7 was incorporated in the light-emitting layers. As in Fig. 3(a), the thin film containing 10 wt% OXD-7 exhibited

**Table 1**

Characterization of the device performance and the corresponding light-emitting thin films (phase-mode surface roughness).

Device	Dopant	OXD-7 concentration <sup>a</sup>	Efficiency (cd/A)	Roughness <sup>b</sup> (degree)
A	Flrpic	10	3.83	25.486
B	Flrpic	40	7.79	18.09
C	Flrpic	70	17.10	5.36
D	Flrpic	100	11.28	7.21
E	Btp <sub>2</sub> Ir(acac)	10	3.05	0.397
F	Btp <sub>2</sub> Ir(acac)	40	2.96	0.369
G	Btp <sub>2</sub> Ir(acac)	70	2.65	0.412
H	Btp <sub>2</sub> Ir(acac)	100	2.06	0.443

<sup>a</sup> Weight percentage respect to the weight of PVK.

<sup>b</sup> Obtained from the results of atomic force microscopy.

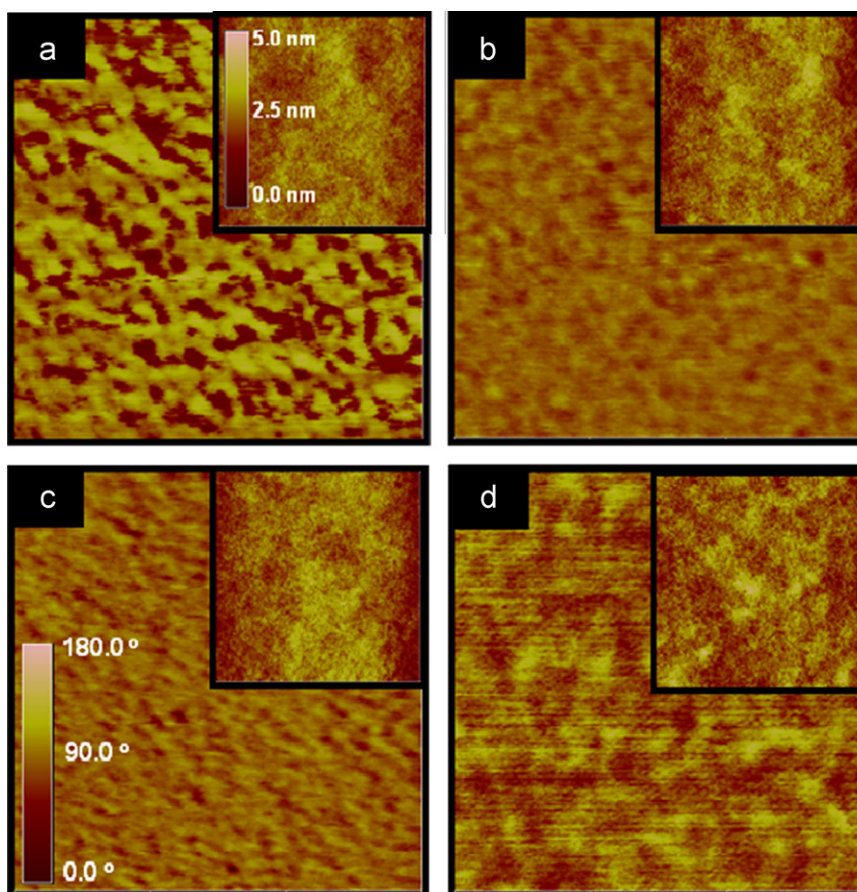
apparent phase separation, which could be attributed to the segregation between PVK and Flrpic molecules. The phase mode roughness was as high as 25.486°. On the other hand, the thin film became more uniform while more OXD-7 was blended (Fig. 3(b) and (c)). The roughness decreased to 18.09° and 5.36° while the concentration of OXD-7 was 40 and 70 wt%, respectively. However, the roughness slightly increased again to 7.21° while the concentration of OXD-7 was further increased to 100 wt% (Fig. 3(d)). Therefore, we deduced that the addition of OXD-7 can inhibit the phase separation between the PVK and Flrpic molecules.

The results of the AFM images in the phase mode indeed consisted very well with those of the device electrical properties and also the electroluminescence (EL) spectra while the weight concentration of OXD-7 was changed gradually. The OXD-7 molecules behaved not only as an electron transporting material, but also as a “binder”, which could inhibit the phase separation of the other components in the light-emitting layers. Because of the presence of F atoms, the Flrpic molecules have very strong dipoles. The difference in polarities between PVK and Flrpic molecules resulted in significant phase separation [25]. On the other hand, although OXD-7 also contains some electron withdrawing atoms, such as O and N atoms, which lead to polar bonds, the bulky terminal *t*-butyl groups at the other side of the molecules exhibited nonpolar properties. As a result, the “ambipolar”-nature of OXD-7 molecules could improve the compatibility between PVK and Flrpic molecules [25,26].

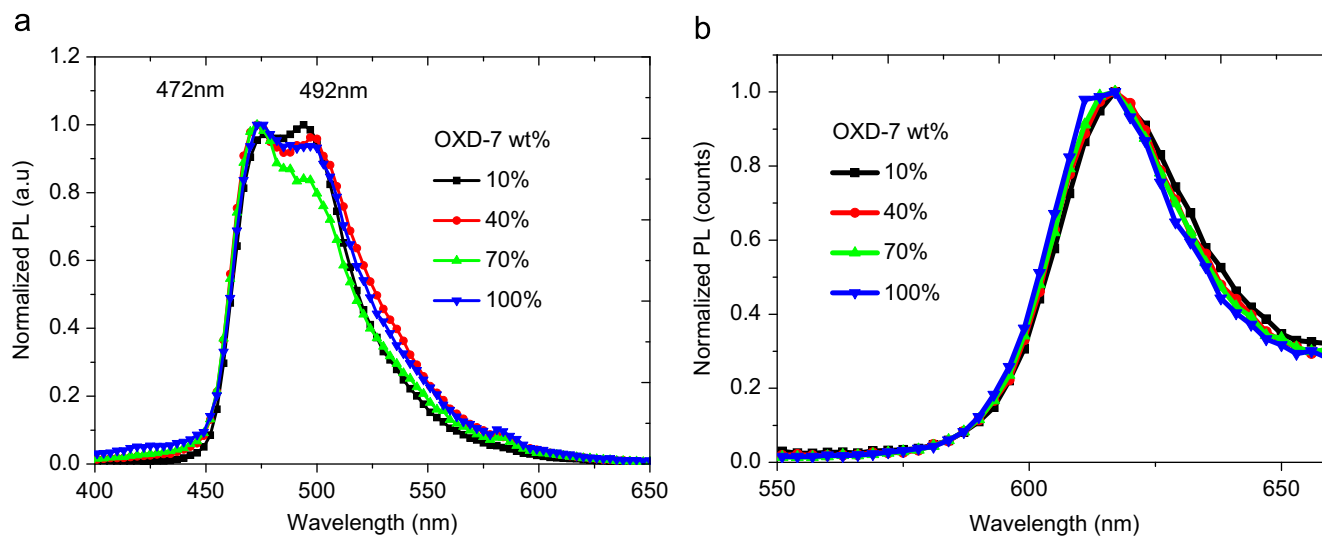
The photoluminescence (PL) spectra of the phosphorescent-dye-doped thin films were further investigated to understand the degree of aggregation for triplet dopants in the emissive layers. As shown in Fig. 4, we observed a similar trend with that of the absorption spectra (Fig. 2(c)). The PL of Flrpic-doped films consisted of two peaks at 472 and 492 nm. Meanwhile, the intensity of the peak at 492 nm became higher with the decrease in OXD-7 weight ratio from 70% to 10%. Because the pronounced PL shoulder at 492 nm suggested that the aggregation states of the triplet dopants [25], this phenomenon indicates that optimized OXD-7 concentration would indeed inhibit the aggregation of Flrpic molecules. This result is consistent with the conclusion deduced from the EL spectra (Fig. 2(c)) and the AFM phase images (Fig. 3).

### 3.3. Investigation of the performance of red-emitting devices

To further verify the above assumption, the other red-color triplet molecule, Btp<sub>2</sub>Ir(acac), was used as the dopant. The performances of the red devices were also summarized in Table 1 (device E, F, G, and H). As we can see, the device E containing 10 wt% OXD-7 exhibited the highest efficiency; the efficiency decreased with increase in OXD-7 concentration. We, therefore, investigated the phase mode images of the light-emitting thin films containing



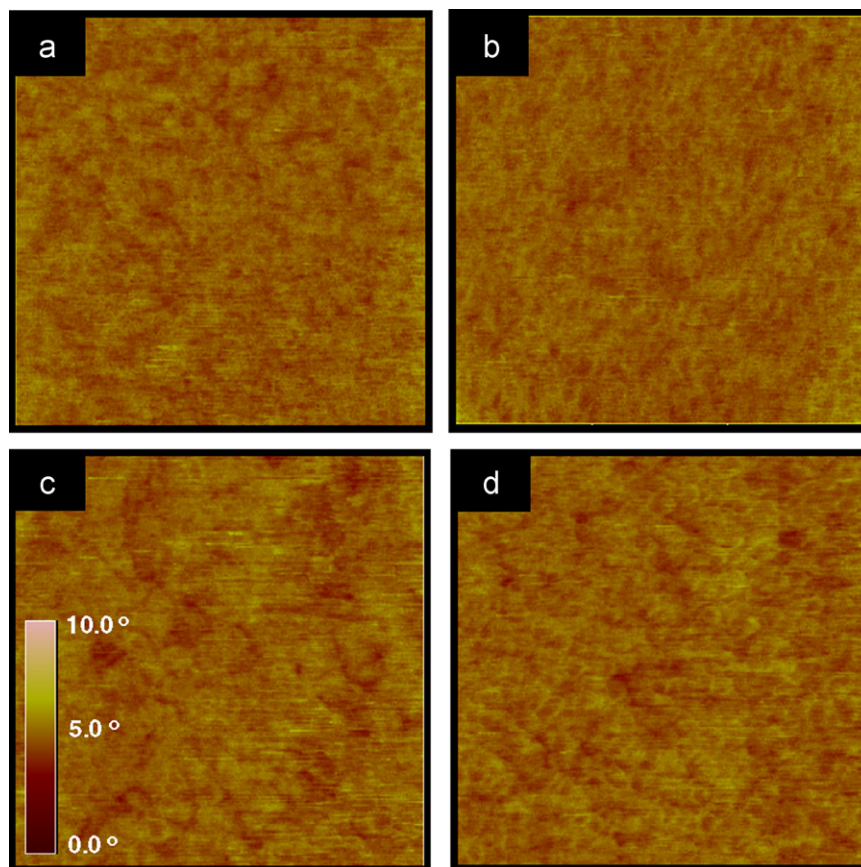
**Fig. 3.** The phase-mode AFM images ( $3 \mu\text{m} \times 3 \mu\text{m}$ ) of the polymer films prepared at OXD-7 concentrations of (a) 10; (b) 40; (c) 70; (d) 100 wt%. The insets show the corresponding height mode images. The dopants used were Flrpic.



**Fig. 4.** Normalized PL spectra of (a) Flrpic and (b) Btp<sub>2</sub>Ir(acac) devices containing various OXD-7 weight percentages.

different amount of OXD-7 (Fig. 5). The roughness for each condition was similar ( $\sim 0.4^\circ$ ) and only slightly increased from  $0.397^\circ$  to  $0.443^\circ$  while the OXD-7 concentration was increased from 10 to 100 wt%. Therefore, we could expect that the phase separation was not the major factor determining the red-emitting device efficiency. Further, the normalized PL spectra of red-emissive layers were also plotted in Fig. 4(b). While various weight percentages of OXD-7 were blended into the red-emissive layer, no significant PL spectral

change was observed. These results were obviously different from those in which the dopant material used was Flrpic. As shown in Fig. 1, unlike Flrpic dopants, Btp<sub>2</sub>Ir(acac) molecules do not contain any strong electron withdrawing groups. Its polarity is rather similar to that of PVK. Therefore, no series phase separation was observed. On the other hand, the addition of OXD-7 slightly induced the phase separation, probably resulting in degraded device performance (Table 1).



**Fig. 5.** The phase-mode AFM images ( $3\ \mu\text{m} \times 3\ \mu\text{m}$ ) of the polymer films prepared at OXD-7 concentrations of (a) 10; (b) 40; (c) 70; (d) 100 wt%. The dopants used were  $\text{Btp}_2\text{Ir}(\text{acac})$ .

#### 4. Conclusion

We have demonstrated that the performance of polymer electrophosphorescent devices can be enhanced through optimization of the concentration of OXD-7 in the emission layer. The enhancement mechanism was found to be relative to the improved compatibility between PVK and Irpic molecules and better thin film morphology. We anticipate that the dual functions of OXD-7 organic materials could be further applied to other organic devices where the active layer encountering problems of phase separation.

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