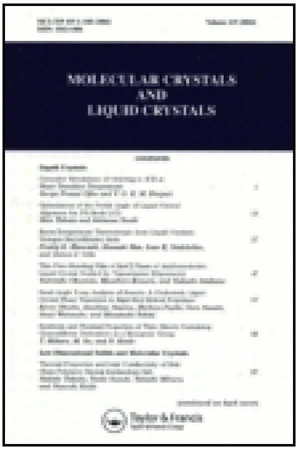

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Phosphorescent Polymer Light-Emitting Devices Doped with Red Iridium (III) Bis(2-phenyl-Isoquinoine)-(2-acetyl-cyclohexane) Complex

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*Devices with a configuration of ITO/PEDOT/Ir-PIQCH (10 wt%) in Polymer/BAlq (30 nm)/Alq_3(20 nm)/LiF (1 nm)/Al (120 nm) were fabricated. In the emitting layer, three different polymers, poly(*N*-(2-ethyhexyl)-3,6-dibromocarbazole-*alt*-aniline) (P(3,6-EHCZ-*alt*-Al)) (**1**), poly(bis[6-bromo-*N*-(2-ethylhexyl)-carbazole-3-yl-*alt*-aniline] (P(Bis-EHCZ-*alt*-Al)) (**2**) and poly(*N*-(2-ethyhexyl)-2,7-dibromo-carbazole-*alt*-aniline) (P(2,7-EHCZ-*alt*-Al)) (**3**) were used as a host material, respectively, and new cyclometalated red phosphorescent iridium complex with phenyl-isoquinoline and 2-acetyl-cyclohexanone ligands (Ir-PIQCH) was employed as a guest material. Surface morphology of thin emitting films fabricated by spin-coating from the dilute solution was studied by using 3D optical analyzer. The average roughness of the surface was measured in the range of 1-2 nm to show the films uniformly formed. From the electroluminescent measurement, a red electrophosphorescence was observed with emission peak at approximately 620 nm, 624 nm or 632 nm for Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) (**1**), Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (**2**) or Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (**3**) device.*

Keywords: carbazole; electroluminescence; guest; host polymer; phosphorescence; PLED

INTRODUCTION

Organic electrophosphorescent light-emitting devices have attracted much attention because of their high efficiency [1–4]. Spin statistics

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predicted that the operation of organic light-emitting devices (OLEDs) generated spin-symmetric triplet and spin-antisymmetric singlet with the ratio of 3:1 [5,6]. Since a radiative decay from triplet (phosphorescence) was spin forbidden and often very inefficient, electroluminescence only could be obtained from fast radiative decay of singlet excitons (fluorescence) [7]. In the OLEDs, therefore, even with 100% efficiency of the singlet emission, the maximum internal quantum efficiency could arrive at 25%. Further experiments revealed, in π-conjugated polymers, that the internal electroluminescence quantum efficiency could be as high as 50% or even higher, which was attributed to delocalization nature in charged particles of π-conjugated polymers [8,9]. Even though the singlet ratio in π-conjugated polymers might be higher than the prediction by spin statistics, triplet excitons were still waste. Strong spin-orbit coupling of heavy metal ions was found to allow an efficient intersystem crossing between singlet and triplet excited states, rendering high harvesting light not only from singlet but also from triplet. Therefore, 100% internal quantum efficiency could be achieved theoretically [10]. This provided the possibility to design the efficient OLEDS by utilization of organometallic emitters. Of many researches on organometallic emitters, cyclometalated iridium complexes have been considered to be very efficient emissive dopants due to relatively short lifetime of its triplet state [1,2,5,11].

Polymer light-emitting devices (PLEDs) were known to have the potential of being used economically with large-area because of the easy processing such as spin-coating, screen printing, or inkjet printing method at room temperature [9,12]. Polymeric materials exhibited another potential for flexible displays fabricated on plastic film to realize roll to roll coating [13]. To achieve a full-color display based on phosphorescent PLEDs (PhPLEDs), red phosphorescent complexes became very important to be developed with suitable host polymers. Chen *et al.* [14] reported phosphorescence emission from an iridium complex blended into PVK host. Zhu *et al.* [12] reported red emitting phosphorescence from iridium (III) bis(2-(1-naphthalene)pyridinato-C2',N) acetylacetone blended into CNPPP as a host material with PVK as a hole-transporting layer, and maximum luminance efficiency of 0.47 cd/A at the brightness of 40 cd/m^2.

In this paper, we report on our efforts in fabricating red PhPLEDs by blending an red phosphorescent iridium (III) bis(2-phenyl-isoquinoine)(2-acetyl-cyclohexane) (Ir-PIQCH) complex with three different host polymers, P(3,6-EHCZ-*alt*-Al) (***1***), P(Bis-EHCZ-*alt*-Al) (***2***) and P(2,7-EHCZ-*alt*-Al) (***3***), respectively, as an emitting layer. Three polymers had wide band gaps with higher HOMO energy, which afforded the polymers with qualification as good hole-transporting and host materials. Morphological characteristics of the thin emitting layers such as surface roughness and thickness were studied by using 3D optical analyzer. Electrophosphorescent properties of the devices were also presented.

EXPERIMENTAL

Materials

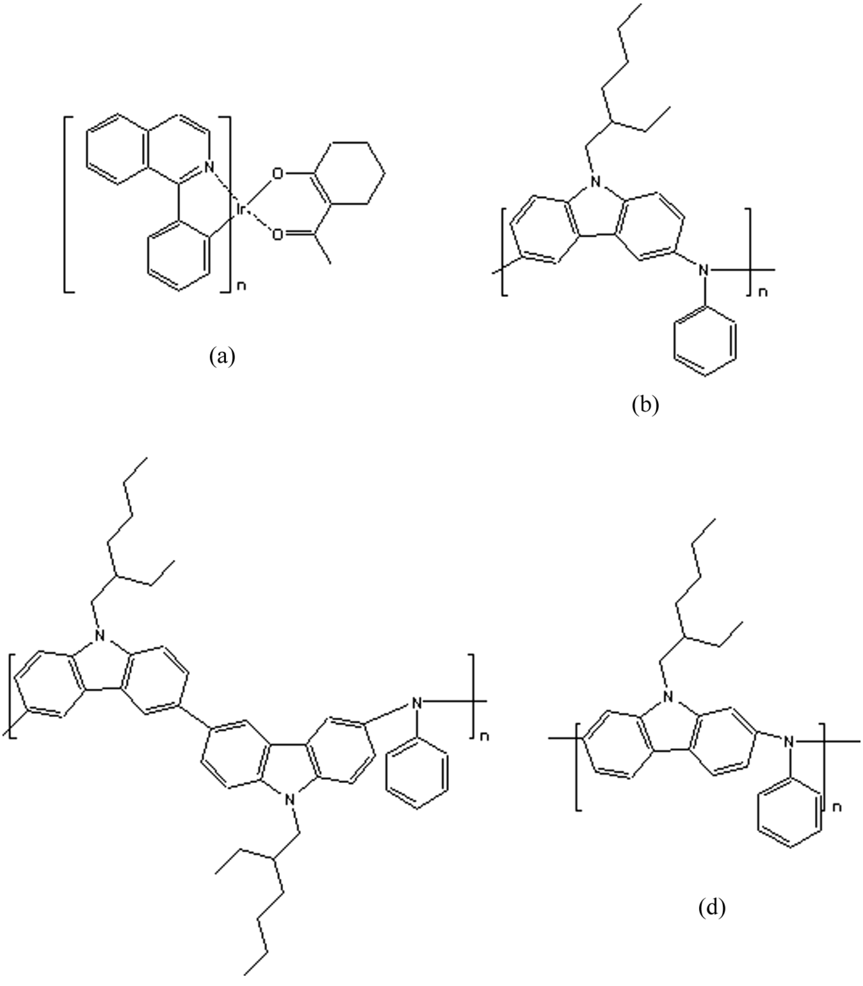
PEDOT was received from LG Electronics Co. Bis(2-methyl-8-quinolinato)-4-phenlphenolate aluminum (BAlq), tri(8-hydroxylquinolate)-aluminum (Alq_3) and lithium fluoride (LiF) were obtained from Tokyo Kasei Co., and used as received. Aluminum (99.99%) was purchased from CERAC, USA. Indium-tin oxide (ITO) coated glass with a sheet resistance of $50\,\Omega/\square$ was obtained from Sin'an SNP Co. Host polymers, P(3,6-EHCZ-*alt*-Al) (***1***), P(Bis-EHCZ-*alt*-Al) (***2***) and P(2,7-EHCZ-*alt*-Al) (***3***) were synthesized and characterized according to the literature reported previously [15]. A phosphorescent dopant, iridium (III) bis(2-phenyl-isoquinoine)(2-acetyl-cyclohexane) (Ir-PIQCH), was synthesized according to the published paper [16]. The chemical structures of both host polymers and the dopant have been presented in Figure 1.

Fabrication of Phosphorescent PLEDs

ITO coated glass was cut into 5.0 cm × 5.0 cm, and electrode area was prepared by photo-etching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) solution. Hole injecting layer was spin-coated from 1 wt% PEDOT solution in isopropyl alcohol onto ITO substrate in two steps: 1,000 rpm for 10 s and 2,000 rpm for 10 s, then baked on a hot plate at 80°C for 5 min. 1 wt% solution of Ir-PIQCH-doped polymers in 1,1,2,2-tetrachloroethane (TCE), after filtration using MFS filter (0.45 μm pore size), was spin-coated at 1,200 rpm for 10 s and dried at 100°C for 10 min. to remove the residual solvent. Doping level of 10% (w/w) was kept in all cases. Subsequently, a thin hole-blocking layer of BAlq (30 nm), a thin electron transporting layer of Alq_3 (20 nm), a thin electron-injecting layer LiF (1 nm) and a thin capping layer Al (120 nm) as a cathode were successively deposited over the spin-coated polymer film under a base pressure $<10^{-6}$ torr.

Characterization

UV-Visible absorption spectra were obtained by using Shimadzu UV-2100. Photoluminescence (PL) spectra excited by He-Cd laser at



(a)

(b)

(c)

(d)

FIGURE 1 Chemical structures of (a) guest dopant and host polymers: (b) P(3,6-EHCZ-*alt*-Al), (c) P(Bis-EHCZ-*alt*-Al), and (d) P(2,7-EHCZ-*alt*-Al).

325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The thickness and the image of surface morphology of spin-coated films were measured by using 3D optical instrument (Nano view E-1000) via WSI mode with Nikon Japan 5X lens. Electroluminescence (EL) spectra were measured by using Spectroscan PR 650 (Photoresearch Inc). Current and luminescence vs. voltage

profiles were obtained by using dc power supply connected Model 8092A Digital Multimeter and luminance meter (Minolta LS-100).

RESULTS AND DISCUSSION

Physical, Optical and Electrochemical Properties

Structures of carbazole/triarylamine-based alternating copolymers prepared by Pd-catalyzed polycondensation are presented in Figure 1. All alternating copolymers were synthesized in high yields. According to their structures, P(3,6-EHCZ-*alt*-Al) (***1***) possessed basic structure of alternating carbazole/triarylamine polymers, in which triarylamine moiety was linked to 3,6-disubstituted carbazole groups. P(Bis-EHCZ-*alt*-Al) (***2***) contained two 3,6-disubstituted carbazole groups linked with triarylamine groups. P(2,7-EHCZ-*alt*-Al) (***3***) was consisted of triarylamine moiety linked to 2,7-disubstituted carbazole groups. *N*-2-Ethylhexyl group on the carbazole in the main chain of all alternating copolymers was introduced to impart high solubility in common organic solvent, which was required for spin-coating solution process. Therefore, the copolymers exhibited excellent solubility in common organic solvent such as toluene, benzene, chloroform, TCE, and THF. Results on physical properties of synthesized alternating copolymers such as molecular weight, molecular weight distribution, and decomposition temperature are summarized in Table 1. The polymers showed molecular weight ($\overline{M}_n$) of 3,000 g/mole ~ 6,000 g/mole with molecular weight distribution of 1.16 ~ 1.60. The thermal properties of the copolymers were determined by using TGA and DSC measurement. All the polymers showed good thermal stability with decomposition temperature (T_d) over 400°C. In DSC measurement, no melting temperature and obvious glass transition temperature could be

TABLE 1 Physical and Photophysical Properties of Polymers

Polymers	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	T_d (°C)[a]	$\lambda_{max,UV}$ (nm) Solution	$\lambda_{max,UV}$ (nm) film	$\lambda_{max,PL}$ (nm) Solution	$\lambda_{max,PL}$ (nm) film	Bandgap energy (eV)[b]	HOMO (eV)[c]	LUMO (eV)[d]
1	6,000	1.30	442	309	310	452	453	2.91	−5.19	−2.28
2	3,000	1.16	467	304	320	442	451	3.06	−5.25	−2.19
3	3,500	1.60	416	374	420	423	469	3.07	−5.11	−2.04

[a] Temperature at 5 wt% loss based on the initial weight.

[b] Calculated from the crosspoint of UV-Vis and PL spectra.

[c] Measured by a RIKEN Keiki AC-2.

[d] Estimated from the HOMO and bandgap energy.

observed below 400°C, suggesting those polymers were virtually amorphous polymeric materials.

Optical properties such as UV-Visible absorption maximum ($\lambda_{\mathrm{max,UV}}$) and PL emission maximum ($\lambda_{\mathrm{max,PL}}$) are also summarized in Table 1. Figure 2 shows UV-Visible absorption spectra of Ir-PIQCH in solution (S) and in film (F). The absorption peaks of Ir-PIQCH, appeared at 300 nm, 362 nm, 487 nm, and 563 nm in the solid films, were slightly red-shifted in comparison with those in solution, respectively. The intensive peak at 300 nm of Ir-PIQCH was assigned to the allowed singlet π-π^* transition of bis(2-phenyl-isoquinoine) ligand. Weaker absorption peaks at 487 nm and 563 nm of Ir-PIQCH were assigned to singlet and triplet metal ligand charge transfer (MLCT) transition, respectively [12]. The spin-forbidden transition ^{3}MLCT at 487 nm was gained by mixing higher spin-allowed transition ^{1}MLCT through the strong spin-orbit coupling of iridium [12]. As presented in Figure 2, host polymers presented maximum PL emission peaks at 452 nm for P(3,6-EHCZ-*alt*-Al) (***1***), 442 nm for P(Bis-EHCZ-*alt*-Al) (***2***), and 423 nm for P(2,7-EHCZ-*alt*-Al) (***3***) with narrow bandwidth [15]. Overlap between UV-Visible absorption of guest dopant Ir-PIQCH and PL emission of host polymers was obviously observed. It appeared that such overlap in host-guest system afforded a condition required for the energy transfer from host material to guest material in PhOLED [9,17].

3D optical measurement was used to analyze the thickness and morphology of the spin-coated thin films. The thickness of the films

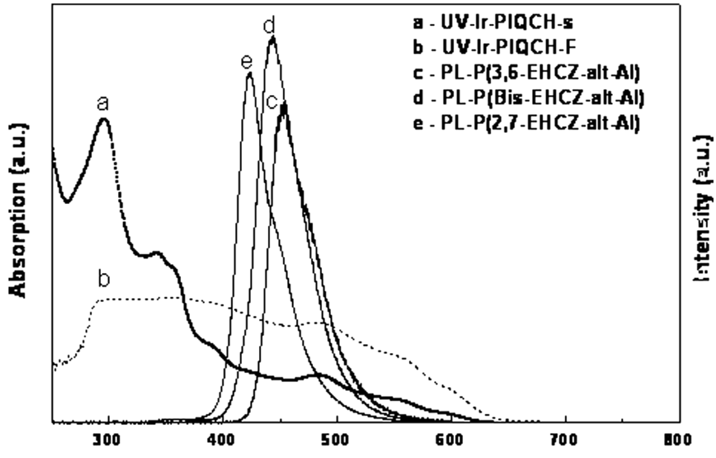
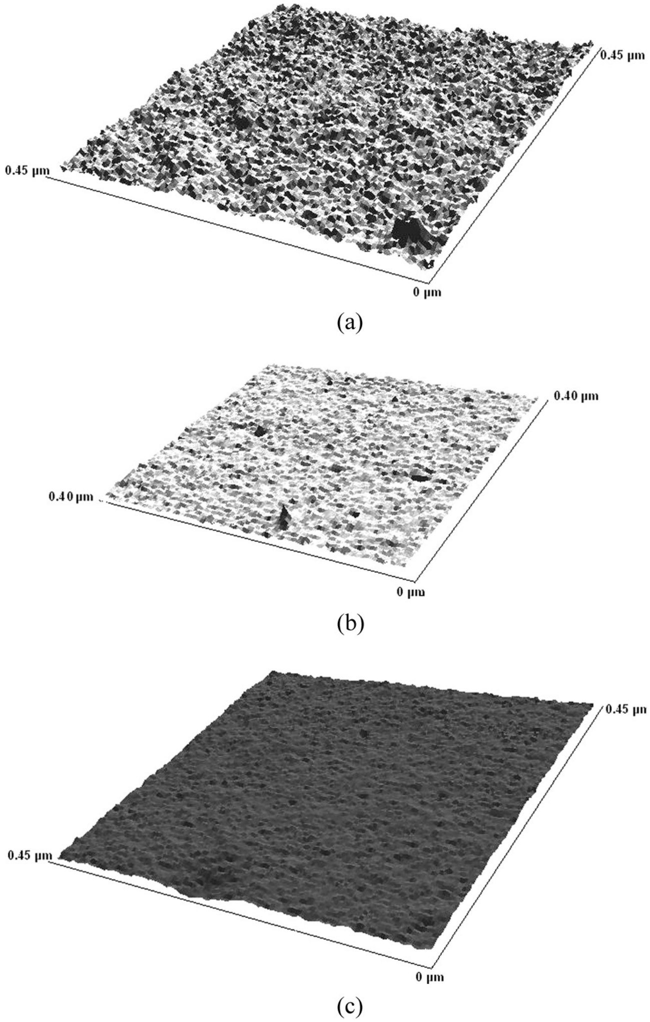


FIGURE 2 UV-visible absorption spectra of Ir-PIQCH complex in the solution and in the film, and PL emission spectra of polymers.

was measured to be 75 nm for Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) (***1***), 60 nm for Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (***2***), and 120 nm for Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (***3***) films, respectively. The images of surface morphology of films were shown in Figure 3. It



(a)

(b)

(c)

FIGURE 3 Image of the surface morphology of the spin-coated films. (a) Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) film (Ra: 1.70 nm; Rq: 2.19 nm; Rt: 9.55 nm), (b) Ir-PIQCH doped P(Bis-EHCZ- *alt*-Al) film (Ra: 1.17 nm; Rq: 1.49 nm; Rt: 11.40 nm), and (c) Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) film (Ra: 1.00 nm; Rq: 1.30 nm; Rt: 8.00 nm).

was well known [18] that the interfacial morphology between stacked thin layers in the devices definitely affected on the electroluminescent characteristics. Figure 3 exhibited compact and homogeneous state of spin-coated emitting layers. The average root-mean-square (rms) roughness of the surface measured was about 1–2 nm in films, giving the evidence that the films were uniformly formed by spin-coating process.

From photophysical study, band gap and HOMO energy levels of the polymers were measured as follows; 2.91 eV and −5.19 eV for P(3,6-EHCZ-*alt*-Al) (***1***), 3.06 eV and −5.25 eV for P(Bis-EHCZ-*alt*-Al) (***2***), and 3.07 eV and −5.11 eV for P(2,7-EHCZ-*alt*-Al) (***3***). These wide band gap and high HOMO energy levels seem to afford the polymers to have dual qualification both as a hole-transporting materials and a host matrix for a red and/or green phosphorescent dopant. In this paper, we preliminary study on the feasibility of these materials for host matrix as well as hole-transporting layer in red PhPLEDs.

Electroluminescent Properties

Figure 4 shows electrophosphorescent properties of the devices. Electrophosphorescence of the devices were observed with the emission peak at approximately 620 nm in Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) (***1***), 624 nm in Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (***2***), and 632 nm in Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (***3***) devices, respectively. The EL emission peaks of the devices with Ir-PIQCH doped

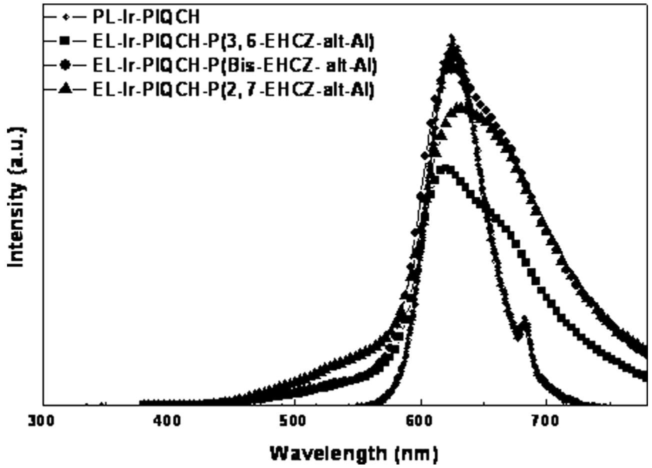
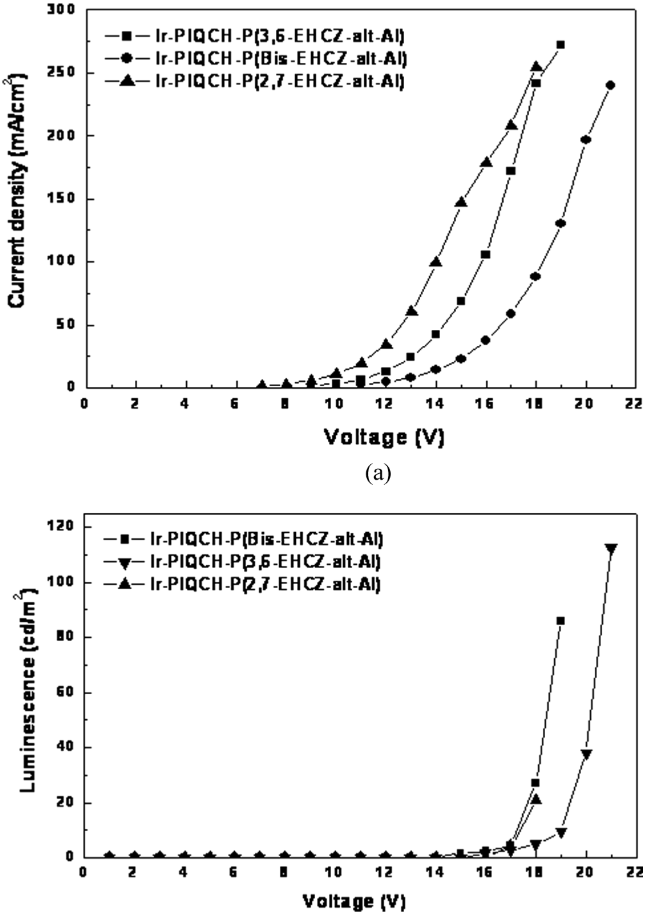


FIGURE 4 PL spectra of Ir-PIQCH and EL spectra of the devices.

P(3,6-EHCZ-*alt*-Al) (***1***) and Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (***2***) were the same as maximum PL emission peak of Ir-PIQCH, but the maximum EL emission peak of the device with Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (***3***) showed about 10 nm red shift. No emission peaks from host polymers were observed for devices, implying an effective energy transfer from host polymers to Ir-PIQCH complex.

Figure 5 (a) and (b) present current density-voltage (*I*-*V*) and luminescence-voltage (*L*-*V*) curves of the devices. From Figure 5 (b),



(a)

(b)

FIGURE 5 (a) Current density-voltage (*I*-*V*) and (b) luminescence-voltage (*L*-*V*) curves of the devices.

the maximum luminescence was measured to be 86 cd/m^2 for Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) (***1***), 113 cd/m^2 for Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (***2***), and 21 cd/m^2 for Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (***3***) devices. The Commission International de L'Eclairage (CIE) coordinates for the devices were (x = 0.60, y = 0.37) for Ir-PIQCH doped P(3,6-EHCZ-*alt*-Al) (***1***), (x = 0.62, y = 0.37) for Ir-PIQCH doped P(Bis-EHCZ-*alt*-Al) (***2***), and (x = 0.52, y = 0.42) for Ir-PIQCH doped P(2,7-EHCZ-*alt*-Al) (***3***) devices.

CONCLUSIONS

Three different types of conjugated copolymers with wide band gap and balanced HOMO energy levels were synthesized in an effort to fabricate the reduced layers in PhOLED structure, since they could simultaneously afford the dual functions both as a hole-transporting layer and host matrix in an emitting layer. PhOLEDs were fabricated with a configuration of ITO/PEDOT/Ir-PIQCH (10 wt%) in Polymer/BAlq (30 nm)/Alq$_3$(20 nm)/LiF (1 nm)/Al (120 nm). In the devices, the emitting layer was prepared by using spin-coating process with the red phosphorescent Ir-PIQCH dopant as the guest material in a host matrix polymer; P(3,6-EHCZ-*alt*-Al) (***1***), P(Bis-EHCZ-*alt*-Al) (***2***) or P(2,7-EHCZ-*alt*-Al) (***3***). The morphology of the films prepared by spin-coating process was studied to show the films uniformly formed. Red electrophosphorescence were observed with emission peaks at 620 nm and 624 nm, appearing at the same as PL emission of Ir-PIQCH complex and confirming an effective energy transfer from polymers to Ir-PIQCH complex. Although the device structure of PhOLEDs could not be optimized in this research, the preliminary study on device performance of PhOLEDs showed better performance of P(3,6-EHCZ-*alt*-Al) (***1***) and P(Bis-EHCZ-*alt*-Al) (***2***) as hole-transporting/host matrix in the emitting layer.

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