Original Research Paper

White Electroluminescence Obtained from a Polymer Light-Emitting Diode Containing Two Phosphorescent Iridium(III) Complexes in an Emitting Layer

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(Received February 23, 2010 : Accepted March 15, 2010)

Abstract

Aimed at fabrication of a solution-processed white polymer light-emitting diode (PLED), novel phosphorescent bis-cyclometalated Ir(III) complexes were developed: bis [2-(3,5-bis(trifluoromethyl)phenyl)pyridinato-N,C20] iridium (III) (2,2,6,6-tetramethylheptane-3,5-dionate-O,0) (1) and bis [2-(dibenzo[b,d]furan-4-yl)quinolinato-N,C60] iridium (III) [1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dionate-O,0] (2). The complex 1 exhibited bluish-green photoluminescence (PL) at 475 and 507 nm with a quantum yield (ΦPL) of 0.91 (toluene, rt), and 2 showed red PL at 610 nm with ΦPL of 0.77 (toluene, rt). Using these phosphorescent complexes, PVCz-based PLEDs were fabricated (PVCz : poly(N-vinylcarbazole)), of which structures were ITO (150 nm)/PEDOT:PSS (40 nm)/PVCz : PBD : 1 (or 2) (100 nm)/CsF (1.0 nm)/Al (250 nm). The PLEDs containing 1 and 2 exhibited bluish-green and red electroluminescence (EL), respectively, in similar regions to their PL. These results indicated that the combination of these complexes as co-dopants should yield white luminescence. Indeed, the PLED containing both of 1 and 2 in a PVCz emitting layer was fabricated. When the ratio of PVCz : PBD : 1 : 2 was adjusted to 10 : 3.0 : 1.2 : 0.012 (wt/wt/wt/wt), white EL with a CIE chromaticity coordinate of (0.364, 0.378) was obtained with maximum luminance of 4200 cd m⁻² at 13.0 V, affording maximum current efficiency of 4.9 cd A⁻¹ at 7.0 V, maximum power efficiency of 2.4 lm W⁻¹ at 6.0 V, and maximum external quantum efficiency of 2.4 % at 7.0 V.

Key-words : Bis-cyclometalated iridium (III) complex, White electroluminescence, Polymer light-emitting diode, Organic light-emitting diode

1. Introduction

For the last two decades, organic light-emitting diodes (OLEDs) have been attracting great attention because their device characteristics such as self-emission, fast response, simple device structure, low driving voltage and availability of various emission colors are potentially applicable to flat-panel displays as well as illumination devices. Especially, OLED-based illuminating applications are expected to replace conventional fluorescence tubes that are subjected to environmental issues, and thus, white OLEDs are eagerly investigated by lots of researchers. White electroluminescence (EL) is obtained from the emission covering the whole visible region, and either combination of three RGB emitters or two RB emitters is usually employed. The high-performance white OLEDs so far reported are composed of multi-stacked emitting layers fabricated by vapor deposition. This strategy has an advantage in achieving high luminous efficiency and color stability. From the industrial viewpoint, however, solution-processed OLEDs are more favored because of efficient use of materials as well as availability of large area printing.

In order to obtain high performance white OLEDs, it is also necessary to use phosphorescent materials as emitters. In general, electrically generated excitons
are statistically divided into 25% of singlet and 75% of triplet. Thus, the nature of emission from pure singlet excitons of fluorescent materials limits the internal quantum efficiency ($\eta_{int}$) of EL to 25% at most. Taking into consideration that the light extraction efficiency of EL from an OLED device is at most ca. 20%, the upper limit of the external quantum efficiency ($\eta_{ext}$) of fluorescent OLEDs is only 5%\(^7\). On the other hand, phosphorescent materials can harvest both of singlet and triplet excitons: that is, $\eta_{ext}$ of 100% is theoretically possible via intersystem crossing, and thus, the upper limit of $\eta_{ext}$ of phosphorescent OLEDs is four times more efficient than that of fluorescent OLEDs. With this respect, a lot of efforts have been directed to development of phosphorescent materials suitable as emitters in OLEDs\(^{22-27}\).

In this study, we report the polymer-based light-emitting diode (PLED) consisting of poly(N-vinylcarbazole) (PVCz) doped with bluish green and red phosphorescent Ir (III) complexes as co-dopants. This device is fabricated by solution processing, and white EL is obtained by tuning the ratio of the co-dopants.

2. Experimental

2.1 Materials

For preparation of 3,5-bis(trifluoromethyl)phenylpyridine (3,5-btfppy-H and dbfq-H, starting materials (2-iodopyridine, 1-chloroquinoline, and aryboronic acids) and palladium catalysts Pd(PPh\(_3\))\(_2\)Cl\(_2\) and Pd(PPh\(_3\))\(_4\) were purchased and used without purification. THF was dried over LiAlH\(_4\) and distilled just before use. For preparation of the µ-chloro-bridged Ir(III) dimers (3,5-btfppy)\(_2\)Ir(µ-Cl)\(_2\)Ir(3,5-btfppy)\(_2\) and (dbfq)\(_2\)Ir(µ-Cl)\(_2\)Ir(dbfq)\(_2\) and the cyclometalated complexes 1 and 2, 2-ethoxyethanol was used as a solvent, which was recently purchased and freshly opened. For characterization of the prepared materials, \(^1\)H NMR spectra were obtained on a Jeol LA-400 spectrometer (400 MHz) using TMS as an internal standard (0.00 ppm). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Shimadzu AXIMA-CFR plus spectrometer using sinapinic acid as a matrix. Elemental analysis was carried out on a Yanako CHN CORDER MT-3 analyzer.

An aqueous solution of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS, Clevios P VP AI 4083) was purchased from H.C. Starck Corporation. PVCz (M\(_w\) = 25000 ~ 50000) was purchased from Sigma-Aldrich Co. and purified by precipitation from THF into methanol. 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and CsF were purchased from Tokyo Chemical Industry Co. Ltd and Wako Pure Chemical Industries, respectively. An Al wire was purchased from Nilaco Corporation. The pre-patterned ITO-glass substrate with a sheet resistance of 10 \(\Omega\) was purchased from Sanyo Vacuum Industries.

2.2 Synthesis of 2-\((3,5\text{-bis(trifluoromethyl)}\text{-phenyl})\text{pyridine (3,5-btfppy-H)}\)

This compound was prepared by the improved method of the reported procedure\(^{28}\). To a mixture of 3,5-bis(trifluoromethyl)phenylboronic acid (650 mg, 2.50 mmol), 2-iodopyridine (450 mg, 2.19 mmol), and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (87.7 mg, 0.125 mmol) in benzene (8 mL) were added 3.1 M potassium carbonate (8 mL) and ethanol (4 mL). Then, the mixture was heated at 70 °C for 24 h under nitrogen. After cooling, chloroform (30 mL) and water (30 mL) were added and insoluble materials were removed by filtration. The filtrate was moved to a separation funnel, and the organic layer was separated. The aqueous layer was extracted with chloroform (30 mL × 2). All the organic layers were combined, washed with water (100 mL × 2) and sat. brine (100 mL), and dried over anhydrous MgSO\(_4\). The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform as eluent to afford a white solid of the title compound in 91% yield (583 mg, 2.00 mmol). The \(^1\)H NMR data is comparable to the literature\(^{28}\) : \(^1\)H NMR (400 MHz, CDCl\(_3\)) $\delta$ 7.34-7.38 (m, 1H), 7.81-7.87 (m, 2H), 7.92 (s, 1H), 8.49 (s, 2H), 8.75 (d, \(J = 4.4\) Hz, 1H). : MALDI-TOF MS m/z 291 ([M]+).

2.3 Synthesis of 2-\((\text{dibenzo}[b,d]\text{furan-4-yl)}\text{quinoine (dbfq-H)}\)

To a mixture of 2-chloroisouquinoline (1.80 g, 11.0 mmol) and Pd(PPh\(_3\))\(_4\) (403 mg, 0.432 mmol) in 1,2-dimethoxyethane (50 mL) were added a solution of dibenzo[b,d]furan-4-y1boronic acid (2.32 g, 10.9 mmol) in ethanol (50 mL) and 2.0 M sodium carbonate (50 mL). Then, the mixture was heated at 90 °C for 44 h under nitrogen. After cooling, ethyl acetate (50 mL) and water (100 mL) were added and insoluble materials were removed by filtration. The filtrate was moved to a separation funnel, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (30 mL × 3). All the organic layers were combined, washed with water (100 mL × 2) and sat. brine (100 mL × 2), and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform as eluent to afford a white solid of the title compound in 81% yield (2.61 g, 8.83 mmol) : \(^1\)H NMR (400 MHz, CDCl\(_3\)) $\delta$ 7.39 (dt, \(J = 1.2\) Hz and 7.5 Hz, 1H), 7.47-7.60 (m, 3H), 7.66 (d, \(J = 8.1\) Hz, 2H), 8.18 (s, 1H), 8.58 (s, 1H), 8.95 (s, 1H), 9.66 (d, \(J = 7.7\) Hz, 1H), 10.85 (dd, \(J = 7.7\) Hz and 11.4 Hz, 1H). : MALDI-TOF MS m/z 341 ([M]+).
1H), 7.76 (dt, J = 1.2 Hz and 7.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 8.00-8.08 (m, 2H), 8.23 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.44 (dd, J = 1.2 Hz and 7.5 Hz, 1H), 8.52 (dd, J = 1.2 Hz and 8.4 Hz, 1H); MALDI-TOF MS m/z 295 ([M]+). Anal. Calcd for C₂H₂Ir₂NO : C 85.40 ; H 4.44 ; N 4.74. Found : C 85.65 ; H 4.57 ; N 4.75.

2.4 Synthesis of (3,5-bis(3H-2H)pyridinato-N,C2)-Iridium(III) (3)

To a solution of 3,5-bis(3H-2H)pyridinato-N,C2-Ir (500 mg, 1.56 mmol) in 2-ethoxyethanol (27 mL) was added a solution of IrCl₃·3H₂O (275 mg, 0.780 mmol) in water (8 mL), and the mixture was heated at 110°C for 20 h. After cooling, water (100 mL) was added, and the precipitate was collected by filtration. The obtained precipitate was washed with ethanol and hexane to obtain the titled compound as a yellow solid in 94% yield (600 mg, 1.47 mmol). This material was highly insoluble, and thus, used in the next reaction without further purification.

2.5 Synthesis of (2-ethylanthracene)(3,5-bis(3H-2H)pyridinato-N,C2)-Iridium(III) (4)

To a solution of 2-ethylanthracene (0.395 g, 1.03 mmol) and 2-ethoxyethanol (25 mL) was added a solution of IrCl₃·3H₂O (184 mg, 0.522 mmol) in water (8 mL), and the mixture was heated at 120°C for 22 h. After cooling, water (100 mL) was added, and the precipitate was collected by filtration. The obtained precipitate was washed with CHCl₃ and hexane to obtain the titled compound as a red solid in 64% yield (270 mg, 0.165 mmol). This material was highly insoluble, and thus, used in the next reaction without further purification.

2.6 Synthesis of bis[2-(3,5-bis(trifluoromethyl)phenyl)pyridinato-N,C2]-Iridium(III) (5)

A mixture of (3,5-bis(3H-2H)pyridinato-N,C2)-Ir(µ-Cl)Ir(3,5-bis(3H-2H)pyridinato)₂ (180 mg, 0.11 mmol), dipivaloylmethane (41 mg, 0.22 mmol) and Na₂CO₃ (96 mg, 0.906 mmol) in 2-ethoxyethanol (33 mL) was heated at 100°C for 1.5 h under nitrogen. The solvent was removed by distillation under reduced pressure, and then CHCl₃ (50 mL) was added. The organic layer was washed with water (50 mL × 3) and sat. brine (50 mL), and dried over anhydrous Na₂SO₄. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1:1, v/v) as eluent to afford a yellow solid. Further purification by recrystallization from chloroform/hexane afforded the titled compound as a yellow solid in 87% yield (186 mg, 0.195 mmol); 1H NMR (400 MHz, CDCl₃) δ 0.76 (s, 18H), 5.40 (s, 1H), 7.01 (t, J = 7.2 Hz, 2H), 7.52 (s, 2H), 7.78 (t, J = 8.2 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 8.02, (d, J = 5.6 Hz, 2H), 8.06 (s, 2H); MALDI-TOF MS m/z 956 ([M]+). Anal. Calcd for C₅₀H₃₅F₂₃IrN₂O₂ : C 46.49 ; H 3.27 ; N 2.93. Found : C 46.48 ; H 3.30 ; N 2.96.

2.7 Synthesis of bis[2-(dibenzo[b,d]furan-4-yl)quinoxalino-N,C2]-Iridium(III) (6)

A mixture of (2-ethylanthracene)(3,5-bis(3H-2H)pyridinato-N,C2)-Iridium(III) (400 mg, 0.245 mmol), 1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dione (400 mg, 0.781 mmol) and Na₂CO₃ (200 mg, 1.44 mmol) in 2-ethoxyethanol (60 mL) was heated at 100°C for 3 h under nitrogen. The solvent was removed by distillation under reduced pressure, and then CHCl₃ (150 mL) was added. Insoluble materials were filtered off, and the filtrate was evaporated. The residue was dried and then purified by silica gel column chromatography using chloroform/hexane (4/1, v/v) as eluent to afford a red solid. Further purification by recrystallization from ethanol/hexane afforded the titled compound as a red crystal in 51% yield (323 mg, 0.250 mmol); 1H NMR (400 MHz, CDCl₃) δ 0.86 (t, J = 7.3 Hz, 6H), 0.92 (t, J = 7.3 Hz, 6H), 1.26-1.35 (m, 4H), 1.38-1.48 (m, 4H), 1.52-1.64 (m, 4H), 1.70-1.77 (m, 4H), 3.92 (t, J = 7.3 Hz, 2H), 3.93 (t, J = 7.3 Hz, 2H), 5.84 (s, 1H), 6.62-6.68 (m, 4H), 7.07-7.14 (m, 6H), 7.25-7.31 (m, 4H), 7.34 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 7.3 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H), 8.48 (d, J = 8.8 Hz, 2H), 9.24 (d, J = 8.8 Hz, 2H); MALDI-TOF MS m/z 1292 ([M]+). Anal. Calcd for C₇₃H₆₇IrN₂O₈ : C 67.83 ; H 5.22 ; N 2.17. Found : C 67.82 ; H 5.29 ; N 2.15.

2.8 Spectroscopic measurements

UV-vis absorption and PL spectra were measured on a Shimadzu UV-3100 spectrophotometer and a Jasco FP-6600 spectrofluorometer, respectively, using a quartz cell. PL lifetimes were obtained on a Horiba FluoroCube lifetime spectrometer system, using LED light sources. PL quantum yields were obtained on a Hamamatsu Photonics C9920 PL quantum yield measurement system. The sample solutions for optical and photophysical measurements were deaerated by argon bubbling followed by complete sealing, and the analyses were carried out immediately after sample preparation.

2.9 Fabrication of PLEDs

The PLEDs were prepared according to the following procedure. The pre-patterned ITO-glass substrate was routinely cleaned by ultrasonic treatment in an aqueous detergent solution, distilled water, methanol, chloroform, hexane, and then boiling isopropanol. The ITO-glass substrate was then air-dried. A hole injection layer of PEDOT:PSS (40 nm) was first spin-coated on the UV-O₃ treated ITO layer, and then dried at 120°C for
1 h under air. A mixture of PVCz, PBD and the Ir(III) complex in toluene was filtered through a 0.2 μm Millipore Co. and then spin-coated onto the PEDOT:PSS layer under an argon atmosphere. A profilometer (KLA Tencor P-15) was used to measure the thickness of the films. Thereafter, CsF (1.0 nm) as an electron injection layer and aluminum (250 nm) as a cathode were successively deposited in vacuum (ca. 1.0 × 10⁻⁴ Pa) onto the organic layers through a shadow mask. The thicknesses of the CsF and Al layers were in situ monitored using a QCM crystal thickness deposition monitor. Finally, the PLED was covered with a glass cap and encapsulated with a UV-curable epoxy resin under an argon atmosphere to prevent oxidation of the cathode and the organic layer. The area of the emitting part was 10 (2 × 5) mm². Fabrication of the PLED described above was carried out in a dehydrated glove box filled with argon, except for fabrication of the PEDOT:PSS layer. The final structure of the PLED was ITO (150 nm)/PEDOT:PSS (40 nm)/PVCz : PBD : Ir(III) complex (100 nm)/CsF (1.0 nm)/Al (250 nm). The device performance of the fabricated PLEDs was monitored at room temperature, using a Hamamatsu Photonics C-9920-11 organic EL device evaluating system.

3. Results and discussion

3.1 Synthesis of phosphorescent Ir(III) complexes

The synthesis of Ir(III) complexes 1 and 2 was carried out according to the conventional method for preparation of heteroleptic cyclometalated Ir(III) complexes[29,30] as shown in Scheme 1. The cyclometalating ligands 2-(3,5-bis(trifluoromethyl)phenyl)pyridine (3,5-btffppy-H) and 2-(dibenzo[b,d]furan-4-yl)quinoxline (dbfq-H) were prepared by the Suzuki-Miyaura cross-coupling reactions of the corresponding arylboronic acids with 2-iodopyridine or 2-chloroquinoline. The obtained 3,5-btffppy-H and dbfq-H were subsequently reacted with IrCl₃ to afford μ-chloro-bridged Ir(III) dimers (3,5-btffppy)₂Ir(μ-Cl)₂Ir(3,5-btffppy)₂ and (dbfq)₂Ir(μ-Cl)₂Ir(dbfq)₂, respectively. The precursor (3,5-btffppy)₂Ir(μ-Cl)₂Ir(3,5-btffppy)₂ was reacted with dipivaloylmethane (dpm-H) in 2-ethoxyethanol in the presence of Na₂CO₃ to afford 1 in 87% yield. In a similar way, 2 was prepared by the reaction of (dbfq)₂Ir(μ-Cl)₂Ir(dbfq)₂ with 1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dione (bdbp-H) in 51% yield. For the preparation of 2, the synthesis of bdhp-H was previously reported[21]. The structures of 1 and 2 were identified by ¹H NMR and MALDI-TOF mass spectra as well as elemental analyses.

![Scheme 1](image1.png)

![Scheme 2](image2.png)

Fig. 1 UV-vis absorption and photoluminescence spectra of 1 and 2 in CHCl₃ at rt. [Ir(III) complex] = 15 μM.

3.2 Optical properties

In Fig. 1 are shown UV-vis absorption spectra of 1 and 2 in CHCl₃ at room temperature. The spectral data are summarized in Table 1. In the UV-vis spectrum of 1, strong structured absorption bands at 240-300 nm are observed, which are assigned to C=N ligand-centered (LC) π-π* transitions. The next low-energy transition at 300-400 nm can be assigned to the spin-allowed metal-to-ligand charge transfer (MLCT). In the UV-vis spectrum of 2, strong absorption bands at 240-400
nm are assigned to the LC π-π* transitions in both of C*+N and O*+O ligands. The absorption band of the extensively conjugated bdbp ligand is intense enough to mask the 1MLCT transition band. For both of 1 and 2, the absorption bands with comparable intensities are observed next to the the 1MLCT transitions (>400 nm for 1 and >450 nm for 2). These transitions are assigned to the spin-forbidden 3MLCT transitions. The relatively large intensities of the 3MLCT transition bands indicate effective mixing of the 3MLCT level with the 1MLCT due to the strong spin-orbit coupling caused by the iridium center29,31.

Photoluminescence (PL) spectra of 1 and 2 are also shown in Fig. 1. These spectra were obtained for deaerated CHCl₃ solutions at room temperature. Bluish-green emission was observed for 1, of which PL maxima (λₚℓ) were observed at 475 and 507 nm. Using an integral sphere, the PL quantum yield (Φₚℓ) was also determined as 0.67 (CHCl₃, rt). For 2, bright red emission was observed (λₚℓ = 610 nm), accompanied by Φₚℓ of 0.50. The Φₚℓs were more enhanced in toluene : 0.91 and 0.77 for 1 and 2, respectively. The PL lifetimes of 1 and 2 were also measured for CHCl₃ solutions, exhibiting single-exponential decays to afford τₚℓ = 1.21 μsec (γ² = 1.08) and 0.76 μsec (γ² = 1.10) for 1 and 2, respectively. These results indicate that the observed PL spectra were phosphorescent. Such short phosphorescent lifetimes should suppress triplet-triplet annihilation in phosphorescent PLEDs32. One can see that PL emission color of 1 is a complementary color of PL color of 2. Therefore, the combination of 1 and 2 should be a good candidate of co-dopants for a white OLED.

### 3.3 Electroluminescent properties of PLED

Next, PLEDs containing our Ir (III) complexes as emitting dopants were fabricated, and their EL properties were investigated. We selected PVCz as a host polymer because it is one of good hole-transporting polymers with high hole mobility33 and often used for dye-doped PLED systems3,5,7,8,11,34. For a hole injection layer, commercially available PEDOT:PSS was used. As shown in Fig. 2, we designed the PVCz-based PLED, of which structure is ITO (150 nm)/PEDOT:PSS (40 nm)/EML (100 nm)/CsF (1.0 nm)/Al (250 nm).

The emitting layer (EML) consists of PVCz containing the Ir (III) complex and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD, an electron transporting material). On fabrication of PLED by the solution technique, an emitting dopant must be molecularly dispersed in a host polymer to obtain a pinhole-free thin film. Both of 1 and 2 exhibited good solubility in toluene, and the homogeneous thin film with 100 nm thickness was obtained when a mixture of PVCz, PBD, and ITO (150 nm)/Al (250 nm).

![Fig. 2 Device structure of PLED containing 1 or 2 as an emitting dopant. PVCz/PBD/Ir (III) complex = 10/3.0/1.2 (wt/wt/wt).](image)

![Fig. 3 J-V-L curves of PLEDs containing 1 (a) and 2 (b).](image)
2 as emitting dopants. The device performance of both PLEDs is also summarized in Table 2. As the increasing voltage was applied to the PLED containing 1, bluish-green emission corresponding to the Commission Internationale de l’Eclairage (CIE) chromaticity coordinate of \((x, y) = (0.190, 0.391)\) was observed, showing the emission maxima \(\lambda_{\text{EL}}\) at 476 and 509 nm, as shown in Fig. 4a. The maximum luminance \(L_{\text{max}}\) of 2600 cd m\(^{-2}\) was obtained at the applied voltage of 13.0 V. This bluish-green-emitting PLED exhibited the current efficiency \((\eta_j)_{\text{max}}\) of 4.6 cd A\(^{-1}\) at 7.0 V, the power efficiency \((\eta_p)_{\text{max}}\) of 2.1 lm W\(^{-1}\) at 7.0 V, and the external quantum efficiency \((\eta_{\text{ext}})_{\text{max}}\) of 2.0% at 7.0 V. On the other hand, the PLED containing 2 exhibited bright red emission at 610 nm (Fig. 4b), showing the CIE chromaticity coordinate of \((0.641, 0.366)\). For this red EL, \(L_{\text{max}}\) of 23300 cd m\(^{-2}\) was obtained at 19.5 V, and the PLED exhibited \(\eta_j)_{\text{max}}\) of 7.4 cd A\(^{-1}\) at 14 V, \((\eta_p)_{\text{max}}\) of 2.0 lm W\(^{-1}\) at 10.0 V and \((\eta_{\text{ext}})_{\text{max}}\) of 5.3% at 13.5 V.

### 3.4 Fabrication of white PLED

From the results obtained above, the superimposition of the bluish green and red EL spectra in Fig. 4 indicates that the combination of 1 and 2 as phosphorescent co-dopants for PLED is expected to yield broadened visible EL spectrum, that is, white EL. Indeed, we next fabricated the PLED containing both of 1 and 2 in the PVCz emitting layer. The device structure was the same as that of the PLED with a single emitting dopant discussed above, where the ratio of PVCz : PBD : 1 : 2 was adjusted to 10 : 3.0 : 2 : 0.012 (wt/wt/wt/wt). When the voltage was applied, the PLED began to emit at 6.0 V, affording the EL spectrum with the CIE chromaticity coordinate of \((0.336, 0.386)\) (Fig. 5). As the applied voltage was increased, the emission peak at ca. 605 nm was slightly enhanced. According to the spectral changes, the CIE chromaticity coordinate was also slightly shifted as shown in Fig. 7 and finally reached \((0.364, 0.378)\) at 13.0 V, where \(L_{\text{max}}\) of 4200 cd m\(^{-2}\) was obtained. This chromaticity coordinate is very close to the ideal white coordinate of \((0.33, 0.33)\) as shown in Fig. 8. The EL performance is summarized in Table 3. The present white PLED exhibited \((\eta_j)_{\text{max}}\) of 4.9 cd A\(^{-1}\) at 7.0 V, \((\eta_p)_{\text{max}}\) of 2.4 lm W\(^{-1}\) at 6.0 V and \((\eta_{\text{ext}})_{\text{max}}\) of

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Device performance of PLED</th>
</tr>
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<tbody>
<tr>
<td>(V_{\text{max}}) / V</td>
<td>4.5</td>
</tr>
<tr>
<td>(L_{\text{max}}) / cd m(^{-2})</td>
<td>2600 [@13.0 V]</td>
</tr>
<tr>
<td>((\eta_j)_{\text{max}}) / cd A(^{-1})</td>
<td>4.6 [@7.0 V]</td>
</tr>
<tr>
<td>((\eta_p)_{\text{max}}) / lm W(^{-1})</td>
<td>2.1 [@7.0 V]</td>
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<tr>
<td>((\eta_{\text{ext}})_{\text{max}}) / %</td>
<td>2.0 [@7.0 V]</td>
</tr>
<tr>
<td>CIE ((x, y))</td>
<td>((0.190, 0.391))</td>
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<tr>
<td>(\lambda_{\text{EL}}) / nm</td>
<td>476, 509</td>
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*The maximum values of luminance \((L_{\text{max}})\), current efficiency \((\eta_j)_{\text{max}}\), power efficiency \((\eta_p)_{\text{max}}\), and external quantum efficiency \((\eta_{\text{ext}})_{\text{max}}\) for PLEDs. The values in parentheses are the voltages at which they were obtained.

*Obtained at the voltage where \(L_{\text{max}}\) was observed.
and in an emitting layer in toluene at rt. And second, good solubility in an emitting layer is potentially applicable to 100/1 wt/wt co-dopant system of an illumination device.

2.4 b1-%T5IFWBMVFTJOQBSFOUIFTFTBSFUIFWPMUBHFTBUXIJDIUIFZXFSFPCUBJOFEa

Table 3 EL performance of white PLED containing 1 and 2 in an emitting layer (1/2 = 100/1, wt/wt).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Device performance of White PLED</th>
</tr>
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<tbody>
<tr>
<td>( V_{T_{\text{max}}} ) / V</td>
<td>4.0</td>
</tr>
<tr>
<td>( I_{\text{max}} ) / cd m(^{-2})</td>
<td>4200 (at 13.0 V)</td>
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<tr>
<td>( \eta_{\text{max}} ) / cd A(^{-1})</td>
<td>4.9 (at 7.0 V)</td>
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<td>( \eta_{\text{max}} ) / lm W(^{-1})</td>
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<tr>
<td>( \eta_{\text{ext}} ) / %(^{\circ})</td>
<td>2.4 (at 7.0 V)</td>
</tr>
<tr>
<td>CIE (x, y)(^{\circ})</td>
<td>(0.364, 0.378)</td>
</tr>
</tbody>
</table>

2.4% at 7.0 V. From these results, the PLED with the co-dopant system of 1 and 2 is potentially applicable to an illumination device.

4. Conclusions

We developed a pair of novel phosphorescent bis-

cyclometalated Ir(III) complexes for fabrication of a white-emitting OLED. The complexes 1 and 2 exhibited bluish green and red PL, respectively. These phosphorescent materials exhibited two special properties worth noting. First, these complexes possess high PL quantum yields: the \( \Phi_{\text{PLS}} \) are 0.91 for 1 and 0.77 for 2 in toluene at rt. And second, good solubility of these complexes in organic solvents and polymer materials enabled us to fabricate solution-processed OLED. Using these complexes as emitting dopants, PVCz-based PLEDs were fabricated, and an EL spectrum corresponding to PL was obtained for each dopant: CIE chromaticity coordinates of (0.190, 0.391) and (0.641, 0.366) were obtained for 1 and 2, respectively, at the voltages yielding the maximum luminance. Taking into consideration that the white region lies between these two coordinates, it is expected that the co-dopant system employing 1 and 2 should yield white EL. Indeed, the PLED containing these dopants in a single PVCz emitting layer at the ratio of 1/2 100/1 (wt/wt) emitted white with a chromaticity coordinate of (0.364, 0.378). Thus, these results reveal that the bis-cyclometalated Ir(III) complexes developed here are good candidates of phosphorescent dopants for white PLED. The present white PLED showed current efficiency of 4.9 cd A\(^{-1}\) at 7.0 V, power efficiency of 2.4 lm W\(^{-1}\) at 6.0 V and external quantum efficiency of 2.4% at 7.0 V. The device performance should be further improved by exploring better carrier-transporting/injecting materials as well as polishing up the device structure.

References

発光層中に2種のりん光性イリジウム(Ill)錯体を含む高分子電界発光素子から得られる白色発光

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(2010年2月23日受付；2010年3月15日受理)

要 旨

溶液塗布法による高分子電界発光素子（PLED）の開発を目的として、りん光性ビシンクロメタル化イリジウム（III）錯体、ビス[2-(3,5-ビス(トリフルオロメチル)フェニルビリジナト-N,C)]イリジウム（III）[2,2',6,6'-テトラメチルスピリブン-3,5-ジオニーナート-O,O](1)およびビス[2-ジベンゼン[b,d]フラン-4-イル]ビリジナト-N,C)]イリジウム（III）[1,3-ビス(3,4-ジブチルフェニル)プロパン-1,3-ジオニーナート-O,O](2)を新規合成した。錯体1はトルエン溶液中において、発光極大発光475 nmおよび507 nm、発光量子収率0.91を有する青緑色発光を示した。また、錯体2は、発光極大発光610 nm、発光量子収率0.77を有する赤色発光を示した。これらのりん光素子を電界発光素子とし、ポリビルカルバゾール（PVCz）をホストドライバーとするPLEDを作製した（素子構造：ITO（150 nm）／PEDOT：PSS（40 nm）／PVCz／PBD：1（or 2）（100 nm）／CSF（1.0 nm）／Al（250 nm））。錯体1および錯体2を発光ドライバーとするPLEDは、それぞれ溶液中と同様な青緑色および赤色の発光到達を示した。これらの結果から、共ドライバーとして錯体1と錯体2を組み合わせることによって発光特性が得られた。実際、ポリビルカルバゾール層中に錯体1と錯体2の両方を含むPLEDを製造し、組成比を制御することによって発光特性が変化した。