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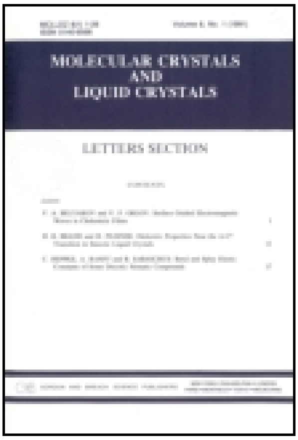

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Green and Reddish-Orange Light-Emitting Electrochemical Cells Using Cationic Iridium (III) Phenanthroline Complexes

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Green and Reddish-Orange Light-Emitting Electrochemical Cells Using Cationic Iridium (III) Phenanthroline Complexes

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A new series of cationic heteroleptic iridium(III) complexes with phenanthroline based-ancillary ligands, namely, [Ir(ppy)$_2$(dmphen)]PF$_6$, [Ir(ppy)$_2$(dbphen)]PF$_6$ and [Ir(ppy)$_2$(dpphen)]PF$_6$ (ppy is 2-phenylpyridine, dmphen is 2,9-dimethyl-1,10-phenanthroline, dbphen is 2,9-dibutyl-1,10-phenanthroline, dpphen is 2,9-diphenyl-1,10-phenanthroline and PF$_6$ is hexafluorophosphate) have been synthesized and characterized by various spectroscopic methods. These synthesized complexes were used for the fabrication of single component light-emitting electrochemical cells (LECs). The electroluminescent devices were evaluated on the basis of electroluminescence properties and the effect of substituents on the phenanthroline ligands tune the emission color of the complexes.

Keywords Cationic iridium complex; electroluminescence properties; light-emitting electrochemical cells; optoelectronic devices

Introduction

Solid-state light-emitting electrochemical cells (LECs) are a promising type of electroluminescent device for display and lighting application [1–4]. LECs offer a number of advantages over traditional organic light-emitting diodes(OLEDs), in particular simpler architectures and production. LECs contain only single light-emitting layer, which can be easily processed from solutions [1]. Furthermore, charge injection in LECs is insensitive to the workfunction of the cathode material, thus permitting use of air-stable metals as the cathodes. Therefore, their encapsulation does not have to be as rigorous as that with OLEDs. These characteristics make LECs the simplest kind of electroluminescent devices.

The first solid-state LEC device was based on a polymer blend containing a light-emitting polymer, an ion-conductiong polymer and an inorganic salt [2]. More recently, LECs based on iTMCs have received more attention because of their several advantages over conventional polymer-based LECs. For iTMCs-based LECs, no inorganic salt or ion-conductiong polymer are needed because iTMCs are intrinsically ionic. Besides, iTMCs show good thermal and photophysical stabilities.

Most of the iTMC materials reported in the literature are based on ruthenium, osmium, copper, and iridium complexes. Among these complexes, iridium complexes are interesting

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*Address correspondence to Prof. Young Son Choe, Department of Chemical Engineering, Pusan National University, Jang-jeon-Dong, Geumjeong-Gu, Pusan 609-735, Korea (ROK). Tel.: (+82)51-510-3562; Fax: (+82)51-512-8634. E-mail: choe@pusan.ac.kr candidates in terms of color tuning because of the pronounced ligand-field-splitting effects. For this reason, iridium complexes have drawn increased attention as electroluminescent materials in Itmc-LECs in the past few years [5–9].

In this study, new iridium complexes with phenanthroline based ancillary ligands have been synthesized. LECs based on these complexes were fabricated and investigated in terms of their emission color and electroluminescent properties.

Experimental

General Comments

All reagents and solvents were purchased from Sigma-Aldrich, while $IrCl_3 \cdot H_20$ hydrate was purchased from Alfa-aesar. Luminescent material was prepared from 2-phenylpyridine as cyclometallated ligand and iridium trichloride by Nonoyama reaction to form tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)diiridium followed by addition of ancillary ligand which is a phenanthroline derivative, and ion exchange with ammonium hexafluorophosphate [10]. All reactions were carried out under nitrogen.

Synthesis

Synthesis of tetrakis(2-phenylpyridine-C2,N')(μ-dichloro)diiridium. The precursor of ionic transition metal complex was synthesized according to the literature [11,12]. Iridium trichloride hydrate (0.388 g, 1.1 mmol) dissolved in distilled water (10 ml) was added to 2-phenylpyridine (0.371 g, 2.4 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed for 24 h under nitrogen gas, and then cooled down to room temperature. The yellow solid was collected on a membrane filter. The resulting precipitate was washed with ethanol (120 ml) and dissolved in dichloromethane (97 ml) and filtered to remove residual inorganic salts. Hexanes (13 ml) were added to the filterate, which was then reduced by evaporation to 50 ml, and cooled down to give crystals of $[Ir(ppy)_2Cl]_2$, then filtered by membrane filter and dried in an vacuum oven for 12 h. Yield: 0.2737 g (46%).

Synthesis of $[Ir(ppy)_2(dmphen)]PF_6$ (complex 1). $[Ir(ppy)_2Cl]_2$ (0.069 g, 0.064 mmol) and 2,9-dimethyl-1,10-penanthroline (0.027 mg, 0.128 mmol) were heated to reflux in an ethylene glycol solution (20 ml) for 16 h. The mixture was transferred into a separation funnel with water (90 ml) and washed through three extractions with diethyl ether (60 ml). A concentrated solution of ammonium hexafluorophosphate in water was slowly added into the aqueous layer, yielding a colored suspension. The precipitate was collected by filtration [13]. Yield: 0.098 g (89%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.46 (d, J = 8.28 Hz, 2H), 8.04 (s, 2H), 7.95 (d, 8.24 Hz, 2H), 7.77 (t, 7.76 Hz, 2H), 7.67 (d, 7.92 Hz, 2H), 7.61 (d, 8.26 Hz, 2H), 7.44 (d, 5.36 Hz, 2H), 6.91 (t, 8.42 Hz, 2H), 6.86 (t, 7.00 Hz, 2H), 6.80 (t, 8.15 Hz, 2H), 6.15 (d, 8.57 Hz, 2H), 2.14 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 168.4, 165.7, 149.9, 149.2, 148.5, 143.5, 139.6, 138.6, 132.1, 130.6, 130.4, 128.5, 127.8, 125.3, 123.3, 122.8, 120.3, 28.1.

$[Ir(ppy)_2(dbphen)]PF_6$ (complex 2) and $[Ir(ppy)_2(dpphen)]PF_6$ (complex 3) were synthesized according to the similar methods with that of complex 1. Complex 2: $[Ir(ppy)_2Cl]_2$ (0.07 g, 0.065 mmol) and 2,9-dibutyl-1,10-penanthroline (0.04 g, 0.137 mmol). Yield: 0.112 g (82%).^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.49 (d, 8.43 Hz, 2H), 8.23 (s, 2H), 7.94 (d, 7.95 Hz, 2H), 7.75 (t, 8.94 Hz, 2H), 7.68 (d, 8.44 Hz, 2H), 7.65 (d, 9.10 Hz, 2H), 7.42 (d, 8.03 Hz, 2H), 6.98 (t, 8.40 Hz, 2H), 6.84 (t, 7.36 Hz, 2H), 6.79 (t, 8.3 Hz, 2H), 6.14

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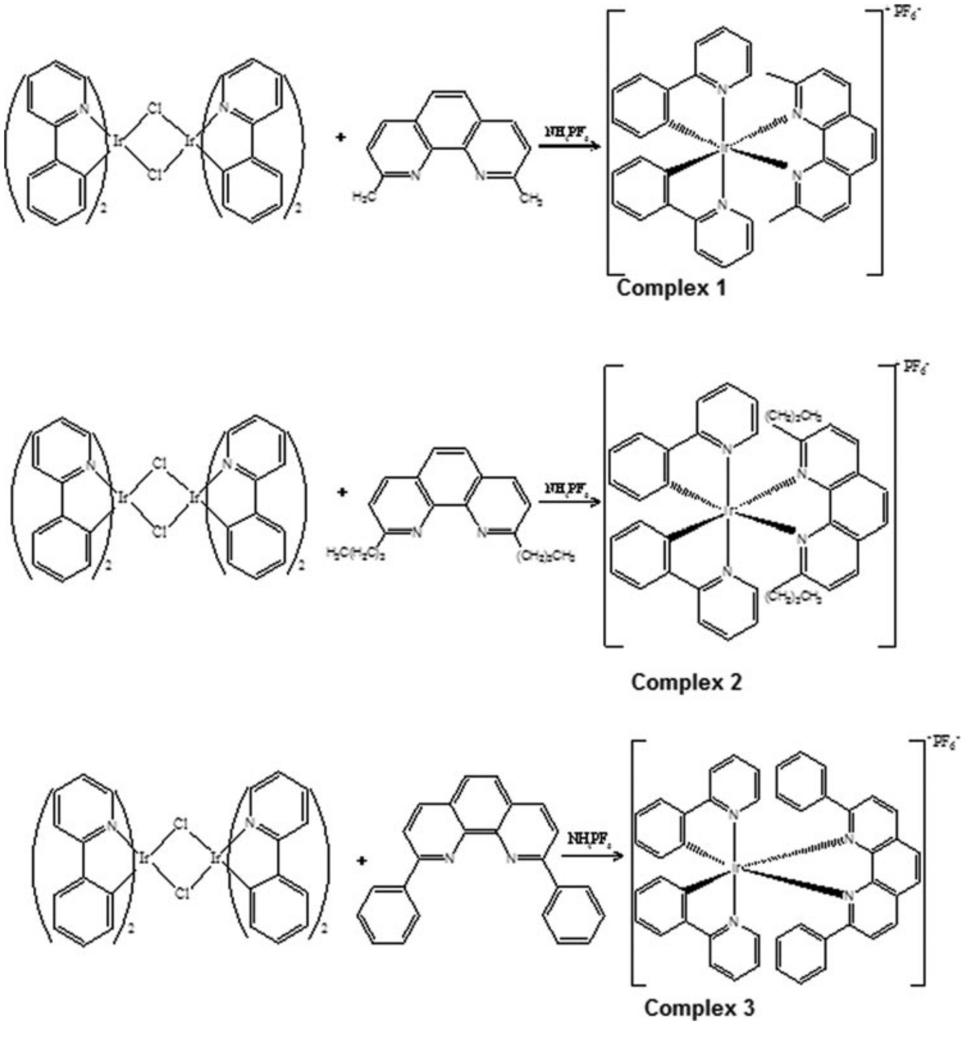
(d, 8.47 Hz, 2H), 2.73–2.6 7(m, 4H), 1.25–1.17 (m, 4H), 0.88–0.81 (m, 4H), 0.66 (t, 7.09 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 169.7, 168.2, 149.8, 148.3, 147.9, 143.3, 139.4, 138.5, 131.9, 130.6, 130.1, 127.6, 126.3, 125.1, 122.9, 122.7, 120.1, 39.6, 32.7, 22.9, 13.9.

Complex 3: $[Ir(ppy)_2Cl]_2$ (0.70 g, 0.065 mmol) and 2,9-diphenyl-1,10-penanthroline (0.043 g, 0.130 mmol). Yield: 0.1g (78.5%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.61 (d, 8.23 Hz, 2H), 8.23 (s, 2H), 7.74 (t, 7.53 Hz, 2H), 7.66 (d, 5.27 Hz, 4H), 7.64 (d, 3.14 Hz, 2H), 7.62 (d, 3.46 Hz, 2H), 7.09 (d, 7.79 Hz, 2H), 7.03 (t, 5.91 Hz, 2H), 6.93 (t, 6.18 Hz, 2H), 6.76 (t, 7.68 Hz, 2H), 6.58 (s, 4H), 6.53 (t, 7.23 Hz, 2H), 6.20 (t, 8.47 Hz, 2H), 5.24 (d, 7.73 Hz, 2H) ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 168.9, 166.7, 150.4, 147.3, 139.0, 138.4, 131.2, 130.1, 129.6, 128.8, 128.6, 128.2, 127.4, 124.6, 122.2, 121.3, 120.2.

The synthetic routes of the complexes are shown in Scheme 1.



Scheme 1. The synthetic routes and structure of iridium complexes: Complex 1: $[Ir(ppy)_2(dmphen)]PF_6$, Complex 2: $[Ir(ppy)_2(dbphen)]PF_6$ and Complex 3: $[Ir(ppy)_2(dpphen)]PF_6$

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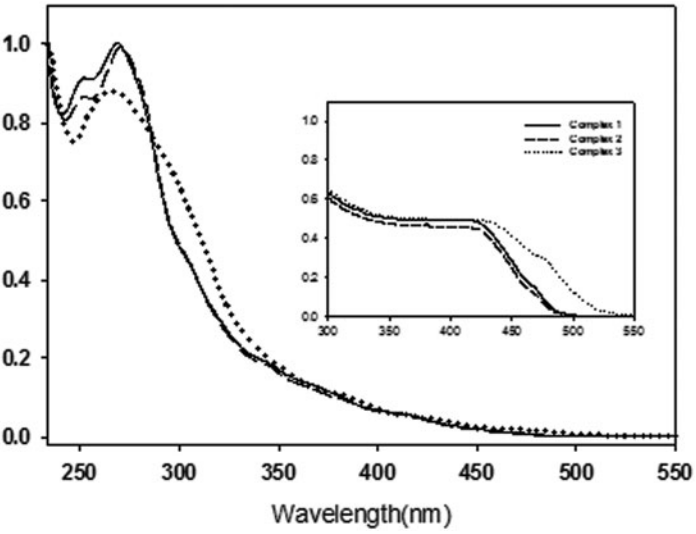

Figure 1. Absorption spectra for complexes in dilute CH_3CN solutions (10^{-5}M). The inset shows the absorption spectra of the complexes in dilute CH_3CN solutions (10^{-3}M) in the range from 300 to 550 nm.

Fabrication of LEC Devices

PEDOT:PSS was purchased from HC-Starck and solvents used were obtained from Aldrich. ITO-coated glass substrates were extensively cleaned in mixed alcohol (isopropyl alcohol, ethyl alcohol and acetone, 1:1:1 by volume ratio) by ultrasonication 45 min and dried in an oven for an hour. PEDOT:PSS buffer layer was spin-coated on to the ITO glass at 2000 rpm for 20 s and annealed on hot plate for an hour at 130 °C under vacuum. Solid film of

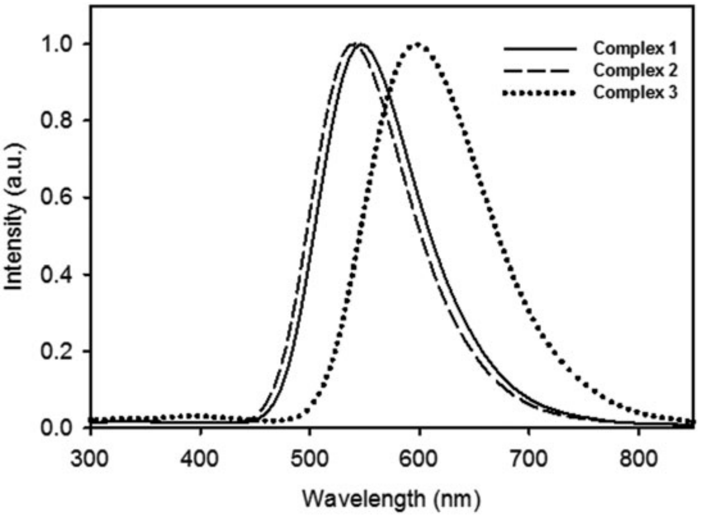

Figure 2. Photoluminescence emission spectra for complex 1, 2 and 3 in CH_3CN solution (10^{-3}M)

Table 1. Photophysical and electrochemical characteristics of complexes

complex	Emission λ_{max} (nm)	E_{ox} [V]	E_{red} [V]	ΔE_{redox}
$[Ir(ppy)_2(dmphen)]PF_6$	546	1.02	−1.52	2.54
$[Ir(ppy)_2(dbphen)]PF_6$	540	1.02	−1.54	2.56
$[Ir(ppy)_2(dpphen)]PF_6$	602	1.02	−1.44	2.46

luminous layer were obtained by spinning from acetonitrile solution using concentration of 20 mg/ml and annealed on hot plate for 20 min at 80 °C under vacuum. Then, a 100 nm thick aluminum cathode was evaporated on top under a vacuum. The deposition rate was controlled by 3.0∼7.0Å/s.

Measurements

^{1}H and ^{13}C NMR spectra were collected on a Bruker 500 MHz spectrometer. UV-vis absorption specta were recorded on 8453 UV-visible Agilent spectrophotometer. PL spectra were measured with an F-7000 FL spectrophotometer. Cyclic voltammetry was obtained using a potentiostat/galvanostat (Iviumstat) voltametric analyzer using 10^{-3} M solution of CH_3CN at a scan rate of 100 mV/s at room temperature. A glassy carbon was used as the working electrode, a platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. The supporting electrolyte was 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and ferrocene was used as internal standard. The current density and luminance versus voltage characteristics were recorded using a Keithley 2400 source meter and calibrated with silicon photodiode. An Avantes luminance spectrometer was used to measure the EL spectrum and CIE coordinates.

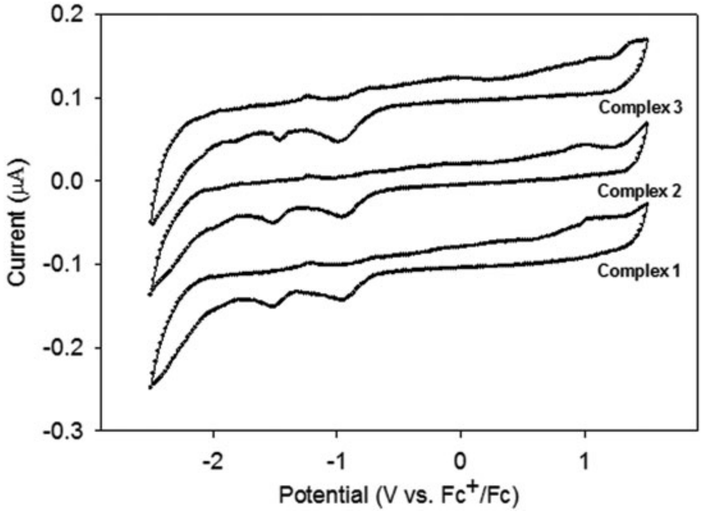

Figure 3. Cyclic voltammogramms of the data for complex 1, 2 and 3 in dilute CH_3CN solutions containing 0.1M Bu_4NPF_6 as supporting electrolyte. Potentials were recorded versus Fc^+/Fc (Fc is ferrocene)

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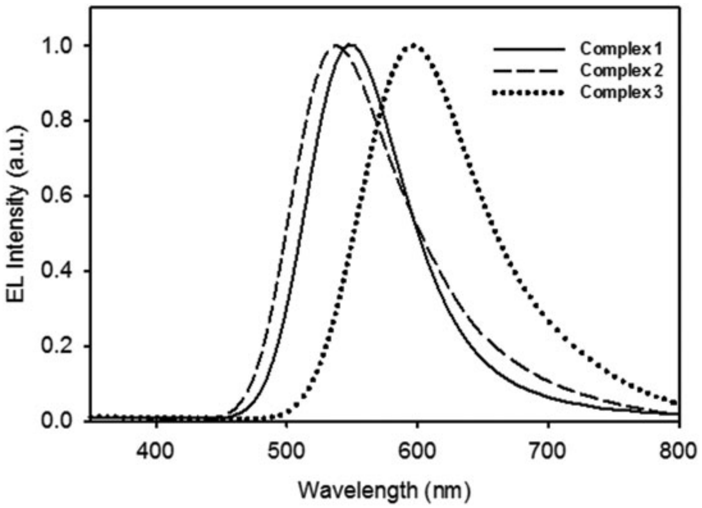

Figure 4. Electroluminescence (EL) spectra of LECs based on the complex 1, 2, and 3

Results and Discussion

The UV-vis absorption spectra of the complexes in CH_3CN solutions are shown in Fig. 1. The intense absorption bands in the region of 250–300 nm can be attributed to spin-allowed π-π^* ligand-centered (LC) transitions typically involving the excitation of electrons from filled π to vacant π^* orbitals of the cyclometalated ppy and phen ligands. The relatively weak absorption bands from 300 nm extending to the visible region correspond to metal-to-ligand charge-transfer transitions (MLCT, arising from the excitation from the filled t_{2g} orbital of the Ir ion to the vacant π^* orbital of the phen ligand) and ligand-to-ligand charge-transfer transitions (LLCT) [17,18].

Figure 2 exhibits the photoluminescence (PL) spectra of complexes in CH_3CN solution. As shown from Fig. 2 and Table 1, the PL spectra of complex 1 and 2 are peaked at 546 nm and 540 nm, located in the green region. The PL spectrum of complex 3 is significantly red-shifted about 60 nm with respect to the ionic iridium complexes with alkyl substitution on phenanthroline ring. All complexes have the same cyclometalated ligands, therefore, the results demonstrate that the presence of phenyl substituents on the phenanthroline ligand causes more stabilization of LUMO compared to the alkyl substituted phen ligand and capability to tune the emission color of the cationic iridium complex through the modification of ancillary ligands.

Figure 3 shows the electrochemical behaviors of the synthesized complexes with ferrocene as the internal standard and the redox potentials are listed in Table 1. As for three complexes, the oxidation potentials (1.02V) are nearly the same, which can be assigned to the oxidation of Ir center and the cyclometalated ligand. Whereas the complexes exhibit reversible reduction peaks at −1.52, −1.54 and −1.44 V for complex 1, 2 and 3, respectively, which are mainly contributed to the reduction of ancillary ligand [14–16]. Especially, the lower LUMO of complex 3 (−1.44 V) respect to complex 2 (−1.54 V) indicate that the LUMO are significantly stabilized by the ancillary ligand. The HOMO-LUMO gaps of these complexes are 2.54, 2.56 and 2.46V, respectively. A narrower energy gap observed in complex 3 than the other two complexes results in a red-shifted light emission.

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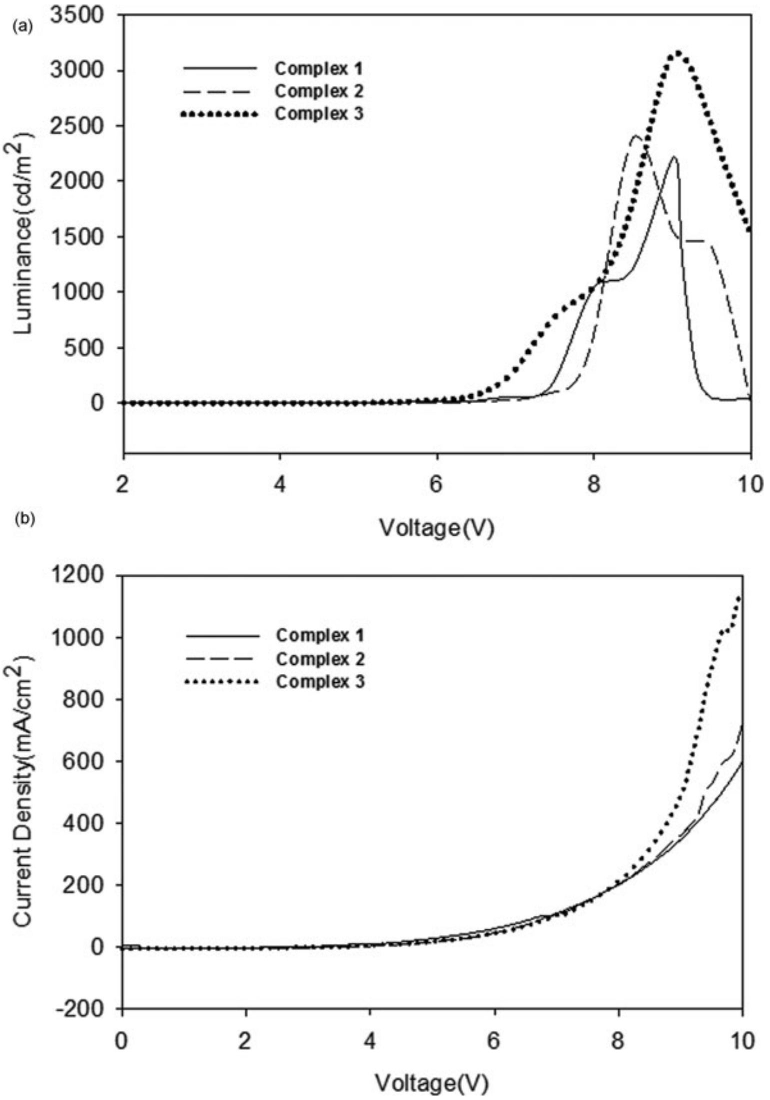

Figure 5. a) Luminance and b) current density versus voltage curves of the LECs based on complex 1, 2 and 3 as pristine luminous layer.

To investigate the electroluminescence (EL) properties of the cationic iridium complexes, LECs with device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)(PEDOT:PSS)/cationic iridium complexe/Al were fabricated, where the PDOT:PSS layer is inserted as anode buffer layer to smoothen the anode surface and facilitate hole injection [19]. Figure 4 shows electroluminescence (EL) emission spectra of the LEC devices, these EL spectra are quite similar to the PL spectra of the cationic iridium complexes (Fig. 2). LECs based on complex 1 and 2 exhibited green light with CIE coordinates of (0.41, 0.55) and (0.37, 0.57) for complex 1 and 2, respectively. The device based on complex 3 gave reddish-orange electroluminescence ($\lambda_{max} = 600$ nm) with CIE coordinates of (0.55, 0.44). The red shift of EL spectra of the device based on

Table 2. The detailed electrical characteristics of LEC devices

Active material	EL_{max} (nm)	CIE	Maximum luminance, voltage	Maximum current density
$[Ir(ppy)_2(dmphen)]PF_6$	551	(0.41, 0.55)	2207 cd/m^2, 9 V	600 mA/cm^2
$[Ir(ppy)_2(dbphen)]PF_6$	537	(0.37, 0.57)	2397 cd/m^2, 9 V	725 mA/cm^2
$[Ir(ppy)_2(dpphen)]PF_6$	600	(0.55, 0.44)	3137 cd/m^2, 8.5 V	1150 mA/cm^2

complex 3 is attributed to the chemical modifications of phenanthroline ligands. The results demonstrate that the the lowest unoccupied molecular orbital (LUMO) located on the ancillary ligand is decreased by phenyl substituents on the phenanthroline ancillary ligand, resulting in narrower HOMO-LUMO energy gap than devices based on complex 1 and 2.

To investigate EL properties of the devices based on these complexes, luminance and current density were measured against voltage from 0 to 10 V. As shown in Fig. 5, both the luminance and current density of the devices increase slowly upon applying increasing bias to the devices, which is a typical feature of LECs. This reflects the mechanism of device operation for which the PF_6^- counter-ions have to reach the interface of the electrodes, which enhances the charge-injection process [2,20]. The rapid increase in current density above 6.0 voltage is due to the fast migration of mobile ions towards the electrodes leading to the rapid injection of electrons and holes. The luminance also increases with the voltage due to the ion migration which lowers the injection barrier for electron and hole. Even though high luminance is obtained with increasing voltage, reaching a maximum value and then diminishes because of more extensive exciton quenching [21]. Detailed electrical characteristics of the LEC devices are summarized in Table 2. The total device performances of complex 3 are evidently better than those of complex 1 and 2. The current density for device based on complex 3 is higher than that obtained from the devices based on other complexes. Similarly, the maximum luminance of 3137 cd/m^2 at 9 V is obtained for device based on 3, which is significantly higher than that for device based on complex 1and 2, and it undergoes slow decomposition with voltage after reaching a maximum. It is believed that the luminance, current density and stability of the LEC could be further enhanced by modifying the complex, such as by attaching bulky and hydrophobic side groups onto the ligands. These bulky groups act as physical barriers that protect the negative charge injected in cationic iridium complex. This shielding is a clear impediment to the entrance of water molecules, which render the complex through water-based chemical reactions, and it sterically hinders a close overlapping of ligands, thus reducing the possibility for nonradiative intermolecular charge recombination [22].

Conclusions

In summary, we investigated the influence of substituents attached to phenanthroline based ancillary ligands on the photophysical and electroluminescent properties of Ir(III) complexes. Three cationic iridium complexes, $[Ir(ppy)_2(dmphen)]PF_6$ (complex 1), $[Ir(ppy)_2(dbphen)]PF_6$ (complex 2) and $[Ir(ppy)_2(dpphen)]PF_6$ (complex 3) have been synthesized and fully characterized. With dpphen as the ancillary ligands, $[Ir(ppy)_2(dpphen)]PF_6$ has significantly stabilized LUMO orbitals and, therefore, show much red-shifted emission spectra with respect to the other complexes. These complexes have been used as the single active component in simple double-layer LEC devices employing air-stable electrodes. With increasing size of the side groups, the luminance and

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current density of devices increased. LECs based on $[Ir(ppy)_2(dpphen)]PF_6$ gave a high luminescence of 3137 cd/m^2 at 9 V. Our work suggests that the light emission of cationic iridium complexes can easily tuned by substituting attached groups on ancillary ligands, and the complex with large bulky groups greatly improves the luminance and the stability of the LECs employing them.

Acknowledgments

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