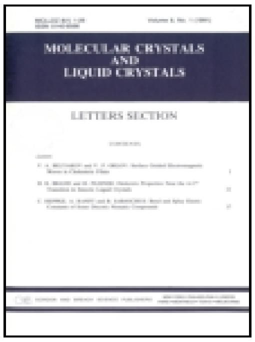

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Synthesis and Photophysical Properties of Cationic Iridium Complexes using Oxazoline based Ancillary Ligands for Lighting Applications

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In this study, we report the design, synthesis and characterization of two new cationic iridium(III) complexes employing oxazole based ancillary ligand, namely, and [Ir(ppz)$_2$(mbdiho)]PF$_6$ (Complex 1) and [Ir(dfppy)$_2$(mbdiho)]PF$_6$ (Complex 2) and its use in light-emitting electrochemical cells (LECs). The design is based on 2-phenylpyrazole (ppz) and 2-(2,4-difluorophenyl)pyridine (dfppy) as cyclometalating ligands and 2,2-Methylenebis[3a,8a-dihydro-8H-indeno[1,2]oxazole] (mbdiho) as ancillary ligand. The effect of substituents in the cyclometalating ligands on the photophysical and electrochemical properties of the complexes has been investigated. The synthesized complexes were used for the fabrication of LEC devices and studied their electroluminescent properties. The complexes incorporated LECs resulted in a higher luminance of 2820 cd m^{-2} and current efficiency of 1.04 cd A^{-1} for Complex 2 than Complex 1. Our work suggests that the light emission of cationic iridium complexes can easily tuned by the substituents present on the cyclometalating ligands which resulted in yellow and green emission for LECs based on Complexes 1 and 2, respectively.

Keywords Iridium complexes; Photophysical properties; Electrochemical properties; Electroluminescence.

1. Introduction

Light-emitting electrochemical cells (LECs) are a promising type of lighting device, which have received greater attention both in research and industry owing to their potential applications in display and lighting devices [1–5]. Compared with conventional organic light-emitting diodes (OLEDs) with multilayered stack structure and low work-function cathodes, LECs possess simpler device architecture which came from the single active component, solution processed fabrication, the possibility of using air-stable electrodes and non-rigorous encapsulation processes [3–10]. Since, LECs consists of mobile ionic species in the active layer which migrate and accumulate at the surface of electrodes under an external bias and assist the injection of charges followed by their recombination.

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The luminescent materials commonly utilized in LECs are either ionic transition metal complexes (iTMCs) or polymer in combination with inorganic salt (PLECs). The concept of LEC was started from polymer material which comprised a blend of light-emitting polymer, an ion-conducting polymer and an inorganic salt [1]. More recently, LECs based on iTMC have received much more consideration than PLECs owing to the phosphorescent nature of the former. In case of iTMC-LECs, iTMCs can support all the three necessary processes for electroluminescence, namely: injection of charge carriers, carrier transport, and emissive recombination [8–13]. Besides, iTMCs exhibit good thermal and photophysical stabilities. The first iTMC- LEC was based on ionic ruthenium(II) complex, reported in 1996 by Rubner et al [2]. Thereafter, a large number of iTMCs were reported for LEC applications, which are based on ionic Ru(II), Cu(I) and Os(II) complexes. However, these complexes incapable to tune emission colors in the short-wavelength region owing to their low ligand–field splitting energies (LFSEs). Besides, LECs based on these complexes resulted low luminescent efficiencies and thus limit their application in LEC devices. In 2004, Slinker et al. studied the example of a LEC based on an ionic Ir(III) complex, which emitted yellow light with a peak brightness of 300 cdm^{-2} and a peak power efficiency exceeding 10 lm W^{-1} under 3 V [4]. Thereafter, tremendous efforts have been performed on LECs employing cationic iridium complexes to tune the light emission to shorter wavelength region [14–24]. LECs based such cationic iridium complexes exhibited high luminescent efficiency and versatile emission colors compared to other metal complexes due to their high ligand-field splitting energies (LFSEs). However, the color turning to green, blue and red is highly desirable since mixing of these colors produce white which is very crucial for practical display and lighting applications

Herein, we report the synthesis, characterization and optoelectronic properties of two new cationic iridium(III) complexes containing oxazoline based ancillary ligands, namely, [Ir(ppz)$_2$(mbdiho)]PF$_6$ (Complex 1) and [Ir(dfppy)$_2$(mbdiho)]PF$_6$ (Complex 2) where ppz is 2-phenylpyrazole, dfppy is 2-(2,4-difluorophenyl) pyridine, mbdiho is 2,2-Methylenebis[3a,8a-dihydro-8H-indeno[1,2]oxazole]. LECs have been fabricated utilizing both complexes which show yellow and green emission for Complexes 1 and 2, respectively. Our work suggests that the light emission of cationic iridium complexes can easily tuned by substituents present on cyclometalating ligands.

2. Experimental Section

2.1. Materials and Methods

All the materials and solvents for the synthesis of iridium(III) complexes were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz FT-NMR spectrometer and measured relative to the residual CD_2Cl_2 solvent with tetramethylsilane as an internal standard. Elemental analyses were performed on an Elementar Vario EL CHN elemental analyzer. Absorption spectra were carried out using an 8453 UV–Vis Agilent spectrophotometer with a 1 cm path length quartz cell. Photoluminescence (PL) spectra were obtained on F-7000 FL spectrophotometer. Cyclic voltammetry (CV) curves were recorded in a potentiostat/galvanostat (Iviumstat) voltametric analyzer using a 10^{-3} M solution of CH_3CN at room temperature. The electrolytic cell consists of a glassy carbon as the working electrode, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The redox potentials were corrected toward to the ferrocenium/ferrocene (Fc^+/Fc) couple which was as an internal standard. The HOMO/LUMO energies and the energy gap (E_{gap}) of the complexes were calculated using the empirical relations [25, 26], $E_{HOMO} = [–e(E_{ox\ (vs.\ Ag/AgCl)} – E_{1/2\ (Fc/Fc+\ vs.\ Ag/AgCl)})] – 4.8$ eV; $E_{LUMO} = [–e(E_{red} – E_{1/2})] – 4.8$ eV and $E_{gap} = E_{HOMO} – E_{LUMO}$ (where E_{HOMO} is the energy of the highest occupied molecular orbital, E_{LUMO} is the energy of the lowest unoccupied molecular orbital, E_{ox} and E_{red} are the respective oxidation and the reduction potentials, $E_{1/2\ (Fc/Fc+\ vs.\ Ag/AgCl)}$ is the reduction potential of ferrocene which was found to be 0.43 V.

2.2. *Fabrication and Characterization of LEC Devices*

LEC devices were fabricated by spin-coating onto the ITO substrate which were cleaned in ethanol, acetone and isopropyl alcohol using an ultrasonic cleaner for 40 min. Prior to the deposition of the active layer, the PEDOT:PSS layer was spin coated onto the cleaned ITO substrate at a rate of 2000 rpm for 20 s and then baked at 120° for 30 min under vacuum. The PEDOT:PSS layer was used as hole injecting layer material as well as to smoothen the ITO surface. The solutions of complexes 1 and 2 were then spin-coated onto ITO/PEDOT:PSS layer and baked at 80° for 1h. The active layers of the complexes were prepared from an acetonitrile solution using 20 mg of the complexes in 1 mL of acetonitrile solutions. Finally, a 100 nm thick aluminum (Al) cathode was thermally evaporated on top using a shadow mask under high vacuum. The resulting device had the structure of ITO/PEDOT: PSS/iTMC/Al. The electroluminescent properties of devices were determined using Keithley characterization systems. The current density and luminance versus voltage sweeps were measured using a Keithley 2400 source meter and calibrated with silicon photodiode. An Avantes luminance spectrometer was used to measure the EL spectrum and IE coordinates.

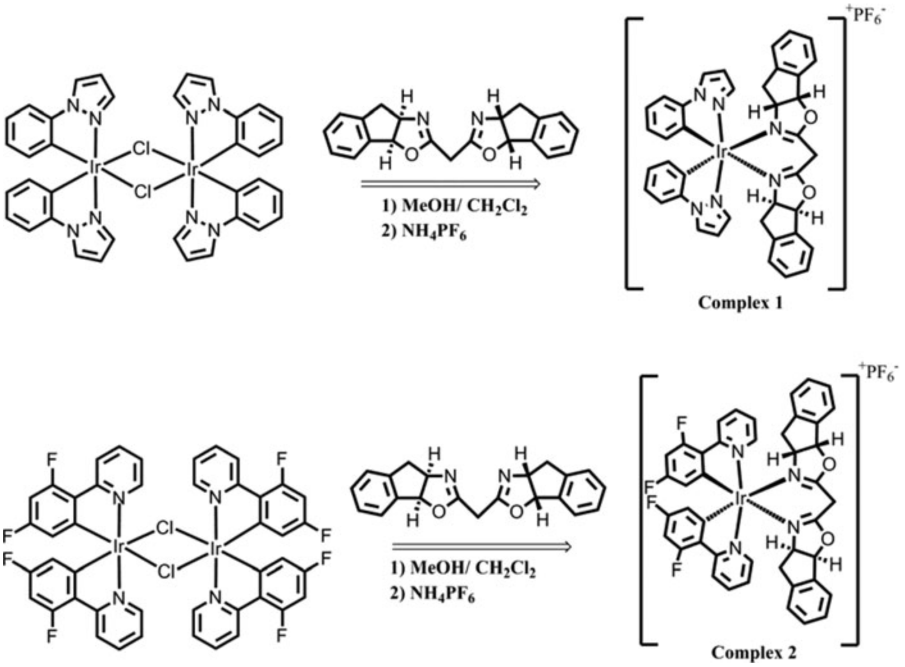
2.3. *Synthesis of the Dimeric Iridium Complexes*

In the first step, iridium trichloride hydrate (1.0 mmol) with 2.5 equivalents of the cyclometalating ligands, for instance 2-(2,4-difluorophenyl)pyridine (dfppy) or 2-phenylpyrazole (ppz), were dissolved in a mixture of 2-ethoxyethanol and water (3:1 v/v). The solution was refluxed for 24 h and cooled at room temperature [27, 28]. The yellow precipitate obtained were filtered out and washed with water, ethanol and hexane. The survival was dried under vacuum at 80° for 24 h.

2.4. *Synthesis of $[Ir(X)_2(mbdiho]PF_6$ (X = ppz, dfppy)*

The dichloro-bridged iridium complex $[Ir(X)_2Cl]_2$ (ppz: 0.1 mmol, 103 mg and dfppy: 0.1 mmol, 121mg) and 2,2-Methylenebis[3a,8a-dihydro-8H-indeno[1,2]oxa zole] (0.22 mmol, 72 mg) were dissolved in a mixture of CH_2Cl_2 (15 ml) and MeOH (15 ml) for 16 h under nitrogen. The reaction mixture was then cooled to room temperature and solid NH_4PF_6 (62 mg, 1.5 mmol) was added to it and stirred for 1 h at room temperature. The solvent was evaporated under vacuum to yield a yellow suspension. The crude product obtained was then recrystallized by using CH_2Cl_2/n-hexane, to give compound as yellow solids, namely, $[Ir(ppz)_2(mbdiho)]PF_6$ (Complex 1, 153 mg, 79%) and $[Ir(dfppy)_2(mbdiho)]PF_6$

(Complex 2, 143 mg, 81%). The synthetic routes with structures of cationic iridium complexes are shown in Scheme 1.



Scheme 1. The synthetic routes and structures of the cationic iridium complexes.

Complex 1: ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.87 (d, J = 8.5 Hz, 1H), 8.65 (d, J = 8.3 Hz, 1H), 8.76–8.45 (m, 4H), 8.32 (d, J = 7.1 Hz, 1H), 8.04 (d, J = 7.5 Hz, 2H), 7.93–7.80 (m, 2H), 7.32–6.84 (m, 4H), 6.70–6.63 (m, 2H), 5.86–5.83 (m, 2H). ^{13}CNMR (126MHz, CD_2Cl_2) δ (ppm) :167.5, 167.4, 164.8, 164.7, 160.3, 160.1, 159.7, 159.6, 150.6, 150.5, 149.1, 148.5, 139.7, 139.3, 137.9, 137.2, 130.7, 129.1, 128.9, 128.5, 128.4, 128.3, 126.8, 126.7, 126.5, 126.3, 124.8, 124.3, 123.6, 123.4, 116.5, 115.4, 112.8, 99.0, 87.4, 79.5, 30.1, 28.1, 28.0. Anal. Calcd (%) for $C_{39}H_{32}N_6O_2PF_6Ir$: C 49.11, H 3.38, N 8.81; Found: C 49.21, H 3.30, N 8.95.

Complex 2: ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.80 (d, J = 8.6 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.42–8.32 (m, 2H), 8.10 (d, J = 5.1 Hz, 1H), 7.93–7.60 (m, 4H), 7.32-6.88 (m, 4H), 6.68–6.63 (m, 2H), 5.86–5.83 (m, 2H). ^{13}CNMR (126MHz, CD_2Cl_2) δ (ppm): 168.3, 167.7, 156.5, 151.3, 148.3, 147.0, 145.0, 143.8, 130.5, 130.2, 130.1, 129.3, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 126.5, 126.1, 126.0, 123.7, 123.3, 88.7, 87.7, 53.5, 54.1, 53.3. Anal. Calcd (%) for $C_{43}H_{30}N_4O_2PF_{10}Ir$: C 49.29, H 2.89, N 5.35; Found: C 49.38, H 2.99, N 5.37.

3. Results and Discussion

3.1. Photophysical Properties

The absorption spectra of the complexes in acetonitrile solutions (10^{-5} M) and neat thin films at room temperature are shown in Fig. 1. The UV–visible absorption spectra of both complexes show similar absorption bands both in solution and film state (Fig 1 (a)

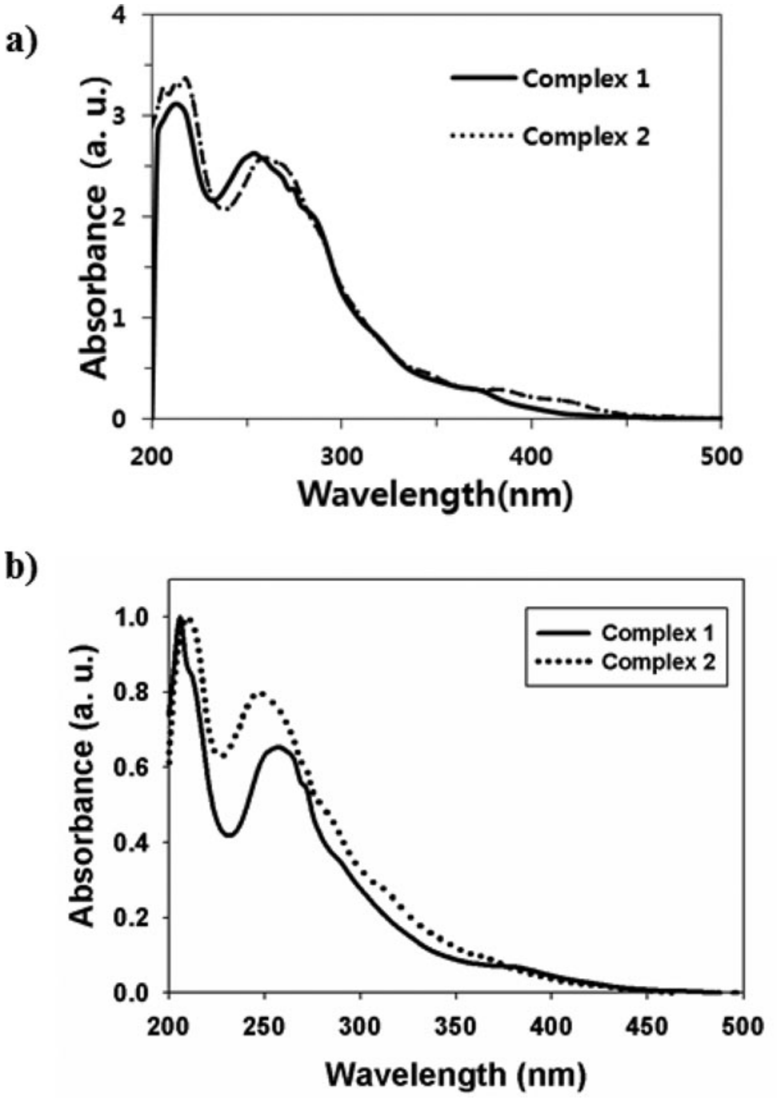


Figure 1. UV-visible absorption spectra of cationic iridium complexes in (a) acetonitrile solutions (10^{-5} M) and (b) neat thin film at room temperature.

with a broad and an intense absorption bands in the UV region, ranging from 230 to 350 nm attributed to the spin-allowed ligand-centered (LC) $^1\pi$–π^* transitions of ligands. Less intense absorption bands are observed from 350 nm to 450 nm, which correspond to excitations to spin–allowed metal–to–ligand charge-transfer (^{1}MLCT), spin–forbidden metal–to–ligand charge-transfer (^{3}MLCT), ligand–to–ligand charge–transfer (^{3}LLCT and ^{1}LLCT) and ligand-centered (LC) $^3\pi$–π^* transitions of the complexes [29].

The room temperature photoluminescence (PL) emission spectra of complexes in solution and neat films are shown in Fig. 2. The PL spectra of both complexes in solution show vibronically structured emission peaks with emission maxima at 485 nm and a shoulder at 514 nm for Complex 1 and that of Complex 2 are at 463 nm and 490 nm,

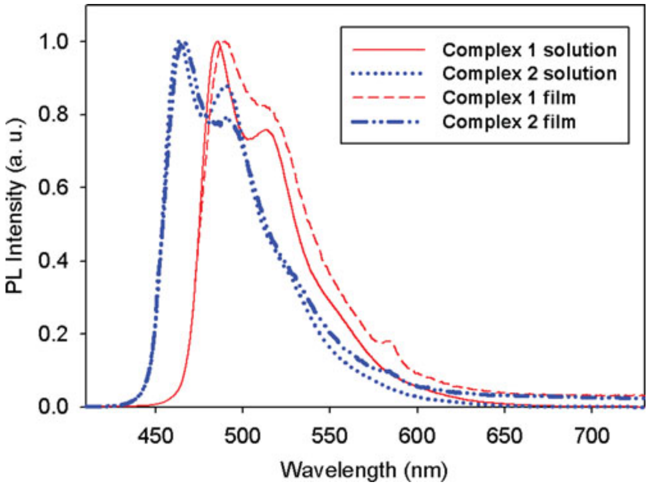


Figure 2. Photoluminescence (PL) emission spectra of cationic iridium complexes in acetonitrile solution and neat thin film.

respectively. Compared to complex 1, the emission spectrum of complex 2 is blue shifted by 24 nm due to the presence of electron withdrawing fluorine atoms on complex 2. These structured emission peaks of complexes indicate that the emissive excited states have LC $^3\pi$–π^* character rather than ^{3}MLCT or ^{3}LLCT characters [29, 30]. The emission spectra of neat films of the complexes resemble the emission spectra in solution with vibronically structured peaks at 489 and 515 nm for Complex 1, whereas those of Complex 2 at 466 and 492 nm. However, the film PL spectra of the complexes are broadened and red shifted by ~4 nm compared to PL spectra in solution.

3.2. Electrochemical Properties

The electrochemical properties of cationic iridium complexes were studied by cyclic voltammetry and the redox potentials are summarized in Table 1. Fig. 3 depicts the cyclic voltammograms of the complexes which shows an irreversible oxidation peak at 1.11 and 1.38 V for complex 1 and 2, respectively, due to the oxidation of Ir (III) to Ir (IV). The reduction peaks of the complexes are at –1.63 for complex 1 and –1.58 V for complex 2 which resulted from the reduction of ancillary ligand. The HOMO and the LUMO energies of the complexes were calculated from the corresponding oxidation (E_{ox}) and reduction

Table 1. Photophysical and electrochemical properties of cationic iridium complexes

	Absorption	PL λ_{max} (nm)		Electrochemical data	
Complex	λ [nm]	Solution	Film	E_{ox} [V]	E_{red} [V]
1	209, 257, 278, 317, 374	485, 514	489, 515	1.11	−1.63
2	218, 260, 287, 347, 386	463, 490	466, 492	1.38	−1.58

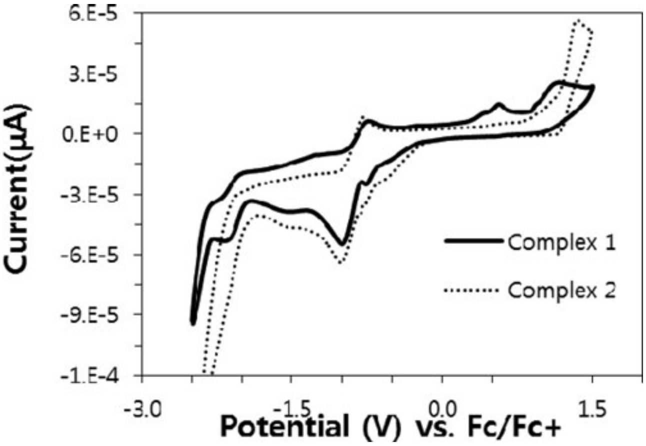


Figure 3. Cyclic voltammograms of the complexes in acetonitrile solution (10^{-3} M). The potentials were recorded versus Fc^+/Fc (ferrocene).

(E_{red}) potentials and the HOMO–LUMO gap of 2.74 eV and 2.96 eV were calculated for Complex 1 and 2, respectively.

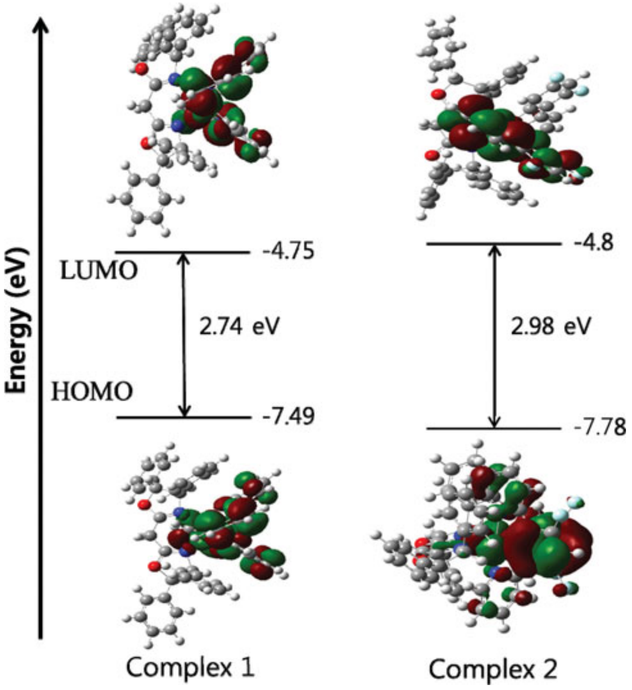


Figure 4. The energy and electron density contours calculated for the HOMO and the LUMO of complexes 1 and 2 in the ground state.

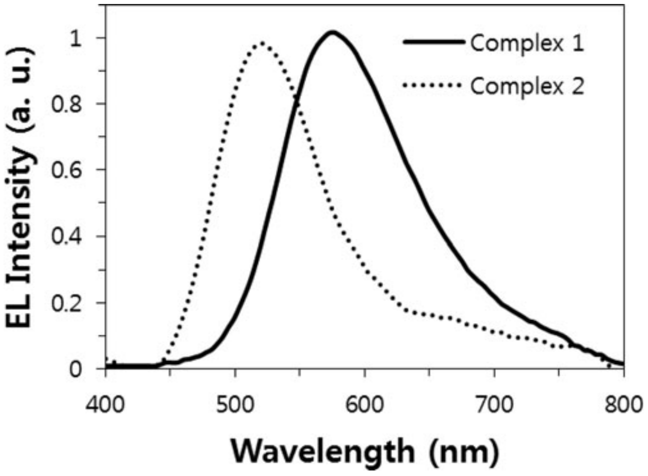


Figure 5. Electroluminescence (EL) spectra of LECs based on cationic iridium complexes.

3.3. DFT Calculations

Density functional theory (DFT) calculations were performed in order to investigate the nature of the excited states, thereby rationalizing the photophysical and electrochemical behaviors of the cationic iridium complexes using Gaussian 09 suite of programs. The geometries of the complexes were optimized by using B3LYP functional and the Ir atom was treated by the LANL2DZ basis set while all the other atoms were treated by 6-31G(d,p) basis set. The energy and electron density contours calculated for the HOMO and the LUMO of both complexes in the ground state are displayed in Fig. 4. The electron density distribution of the HOMO of both complexes resides on the t_{2g} orbitals of iridium ion and phenyl π orbitals of cyclometalated ligands while the LUMO of both complexes lies on the π^* orbital of ancillary ligand.. From the HOMO and LUMO energy values, the energy gaps of 2.74 and 2.98 eV are obtained for complex 1 and 2 respectively, which is consistent with the energy values obtained from experimental values.

3.4. Electroluminescent Properties of LECs

LECs were fabricated with the device structure of ITO/PEDOT:PSS (40 nm)/iTMC (75 nm)/Al. The electroluminescence (EL) spectra of LECs incorporating cationic iridium complexes are shown in Fig. 6. The EL spectra for both devices show unstructured band which does not show any similarity with the PL spectra of corresponding iridium complexes in acetonitrile solutions. LECs based on these complex 1 gave yellow emission color with an emission maximum at 567 nm and that of Complex 2 resulted in green emission color with at 512 nm. The CIE color coordinates are (0.46, 0.49) and (0.38, 0.50) for Complex 1 and 2, respectively.

The voltage dependent luminance and current density curves of LECs are shown in Fig. 6 and 7, respectively. The luminance and the current density of the devices increase slowly with voltage, which are typical characteristics of LECs [1, 4]. The sluggish nature of LECs at the early stage of bias arises from the slow migration of PF_6^- ions. The device performances are summarized in Table 2. LECs based on complex 1 resulted in a maximum luminance of 2115 cd m^{-2}, current density of 220 mA cm^{-2} and current efficiency of 0.96

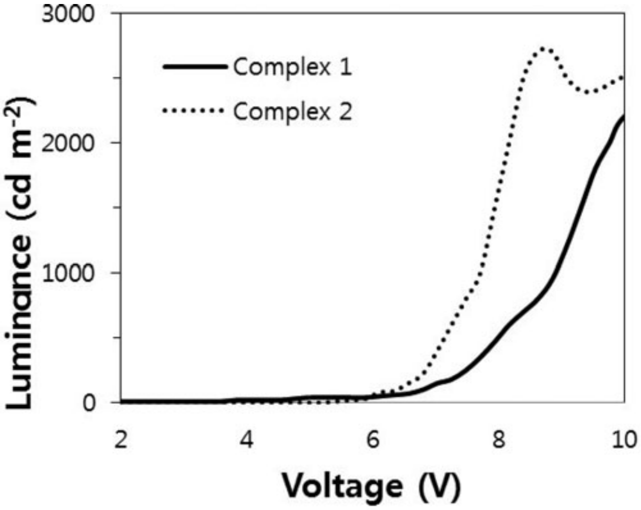


Figure 6. Luminance versus voltage curves of LECs based on cationic iridium complexes.

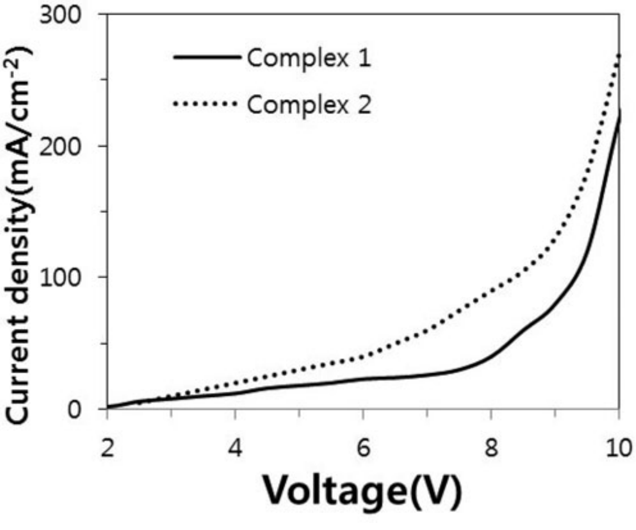


Figure 7. Current density versus voltage curves of LECs based on cationic iridium complexes.

Table 2. The detailed electrical characteristics of LECs based on cationic iridium complexes

Complex	EL λ_{max} (nm)	CIE (x,y)	L_{max} (cd m^{-2})	Maximum current density (mAcm^{-2})	Maximum current efficiency (cd A^{-1})
1	567	(0.46, 0.49)	2115 (10V)	220 (10V)	0.96
2	512	(0.38, 0.50)	2820 (10V)	270 (10V)	1.04

cd A^{-1}. The device fabricated using complex 2 exhibited a maximum luminance, current density and current efficiency of 2820 cd $m^{-2,}$ 270 mA cm^{-2}, and 1.04 cd A^{-1}, respectively. The lower luminance and current efficiencies of LECs based on complex 1 are unbalanced charge injection and their recombination.

Conclusions

Two new cationic iridium complexes were synthesized for the fabrication of LEC devices using oxazoline based ancillary ligand and studied their structural, photophysical and electrochemical properties. The photophysical properties of the complexes were significantly tuned by the substituents present on the cyclometalated ligands. The emission spectrum of Complex 1 in acetonitrile solution shows structured emission peaks at 485 and 514 nm, which is located in blue-green region while for Complex 2, which is located in the blue region with peak and shoulder emissions at 463 and 490 nm, respectively. However, LECs incorporating these complexes emitted yellow and green electroluminescence for Complex 1 and 2, respectively. Moreover, LECs based on Complex 2 resulted in a higher luminance of 2820 cd m^{-2} and current efficiency of 1.04 cd A^{-1} than Complex 1 which are 2115 cd m^{-2} and 0.96 cd A^{-1}, respectively.

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