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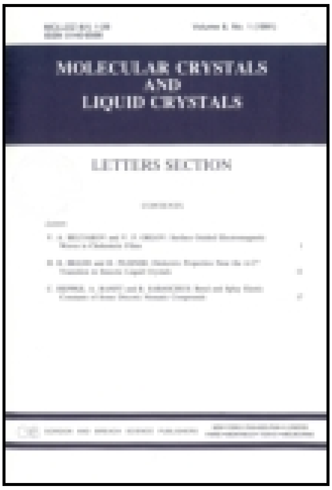

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Characteristics of Light Emitting Electrochemical Cells Using Cationic Iridium(III) Complexes with Imidazole Based Ancillary Ligand

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Two cationic heteroleptic iridium(III) complexes with imidazole based ancillary ligands, namely, [Ir(ppz)$_2$(Hpyim)]PF$_6$ and [Ir(dfppy)$_2$(Hpyim)]PF$_6$ (where ppz is 1-phenylpyrazole, dfppy is 2-(2,4-difluorophenyl)pyridine, Hpyim is 2-(1H-Imidazol-2yl)pyridine and PF$_6^-$ is hexafluorophosphate) have been synthesized and characterized by various spectroscopic methods and studied their photophysical and electrochemical properties. Solid-state light-emitting electrochemical cells (LECs) were fabricated using the synthesized complexes and resulted in green electroluminescence through the particular selection of cyclometalated ligands.

Keywords Light-emitting electrochemical cells; cationic iridium complex; optoelectronic devices; electroluminescence properties

1. Introduction

Ionic transition metal complexes (iTMCs) have been used as electroluminescent materials and have potential applications in various fields especially in optoelectronic devices [1–8]. Light emitting electrochemical cells (LECs) are the optoelectronic devices which produce light under the application of an external bias and considered as promising technology for display and light-emitting purposes. LECs are classified according to the nature of luminescent material which is based on polymer materials and those employing iTMCs. LECs containing ionic species have several advantages over traditional multilayered organic light-emitting diodes (OLEDs) such as simple device structure, solution processed fabrication, air sensitive electrode materials, non-encapsulated device structure and cost effective.

The first solid-state LEC device was proposed by Heeger which was based on a polymer blends containing a light-emitting polymer, an ion-conducting polymer and an inorganic salt [9]. More recently, LECs based on iTMCs have received more attention over conventional polymer-based LECs. The ionic nature of iTMCs makes it soluble in polar solvents and it doesn't require an additional inorganic salt or ion-conducting material for the fabrication of LEC devices. Besides, iTMCs show good thermal and photophysical stabilities.

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Most of the iTMC materials reported in the literatures which are based on ruthenium [10–12], osmium [13–14], copper [15–16] but they are incapable of tuning the emission color to blue region due to their limited ligand-field splitting energies (LFSEs) and hence they are not favorite candidates for LEC applications. More recently, iTMCs based on iridium have drawn increased attention owing to their large LFSEs and exhibit high efficiency, thermal and chemical stability and tunable emission colors [17–19].

Herein, two cationic iridium complexes with imidazole based ancillary ligands have been synthesized. Green light-emitting LECs were fabricated based on these complexes and their electrical properties were studied. Our work reveals that cationic iridium complexes with imidazole based ancillary ligands are promising candidate to tune the emission color to blue region.

2. Experimental

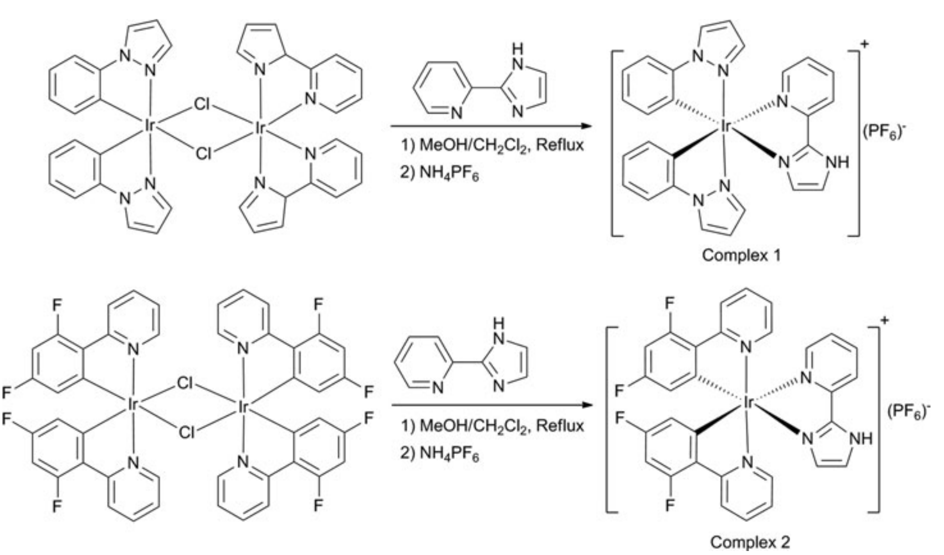
2.1. Materials and Methods

All reagents and solvents were purchased from Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity Inova 500 MHz FT-NMR spectrometer and measured relative to residual CD_2Cl_2 solvent with tetramethylsilane as an internal standard. Elemental analyses were carried out in Elementar Vario EL CHN elemental analyzer. UV-visible absorption spectra were obtained using 8453 UV-visible Agilent spectrophotometer. Photoluminescence (PL) emission spectra were recorded with an F-7000 FL spectrophotometer. Voltammetric measurements were performed in a potentiostat/galvanostat (Iviumstat) voltametric analyzer using 10^{-3} M solution of complexes in CH_3CN at a scan rate 100 mVs^{-1}. The electrolytic cell consists of a glassy carbon as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN solutions and the redox potentials were recorded against ferrocenium/ferrocene (Fc^+/Fc) couple as an internal standard.

2.2. Synthesis of Cationic Iridium Complex

The synthesis of cationic iridium complexes $[Ir(ppz)_2(Hpyim)]PF_6$ (complex 1) and $[Ir(dfppy)_2(Hpyim)]PF_6$ (complex 2) were synthesized by the reaction of cyclometalated iridium(III) chloro-bridged dimer with the imidazole based ancillary ligand followed by an ion exchange reaction from Cl^- to PF_6^- [20–21]. The synthetic routes of the complexes are shown in Scheme 1.

2.2.1. Synthesis of $[Ir(ppz)_2(Hpyim)]PF_6$ (complex 1). $[Ir(ppz)_2Cl]_2$ (154 mg, 0.15 mmol) and 2-(1H-Imidazol-2-yl)pyridine (45 mg, 0.31 mmol) were heated to reflux in a mixture of CH_2Cl_2 (15 ml) and MeOH (15ml) for 16 h under nitrogen. The yellow solution obtained was cooled to room temperature and solid ammonium hexafluorophosphate (98 mg, 0.6 mmol) was added to it. The reaction mixture was stirred at room temperature for 1 h and the solvent was evaporated under vacuum. The crude product obtained was dissolved in dichloromethane, filtered to remove the inorganic impurities and then precipitated with hexane by adding it to the filtrate. The precipitate was collected by filtration. Yield: 106 mg (45%). ^{1}H NMR (500 MHz, CD_2Cl_2) : 13.4 (s, NH), 8.44 (d, 7.99 Hz, 1H), 8.11 (dd, 3.85, 3.14 Hz, 2H), 8.02 (dd, 6.90,1.65 Hz, 2H), 7.3 (m, 7.35 $\sim$ 7.25, 5H), 7.02 (d, 1.32 Hz, 1H),



Scheme 1. The synthetic routes and structures of iridium complexes: Complex 1: [Ir(ppz)$_2$ (Hpyim)]PF$_6$, Complex 2: [Ir(dfppy)$_2$(Hpyim)]PF$_6$.

6.99 (d, 2.27 Hz, 1H), 6.9 (m, 6.89~6.81, 4H), 6.54 (dd, 2.47,5.19 Hz, 2H). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) : 156.8, 151.4, 140.1, 138.8, 134.1, 134.0, 128.9, 127.3, 127.2, 127.0 126.7, 126.4, 126.3, 123.5, 123.3, 122.7, 122.2, 108.5. Anal. Found (%): C 40.68, H 2.79, N 12.83. Anal. Calcd for C$_{26}$H$_{21}$N$_7$PF$_6$Ir: C 40.63, H 2.75, N 12.76.

2.2.1. Synthesis of [Ir(dfppy)$_2$(Hpyim)]PF$_6$ (complex 2). It was synthesized according to the similar methods with that of complex 1 with [Ir(dfppy)$_2$Cl]$_2$ (122 mg, 0.1 mmol) and 2-(1H-Imidazol-2-yl)pyridine (32 mg, 0.22 mmol). Yield: 126 mg (73%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) : 11.79 (s, NH), 8.3 (d, 8.31Hz, 1H), 8.1 (d, 7.96 Hz, 2H), 7.8

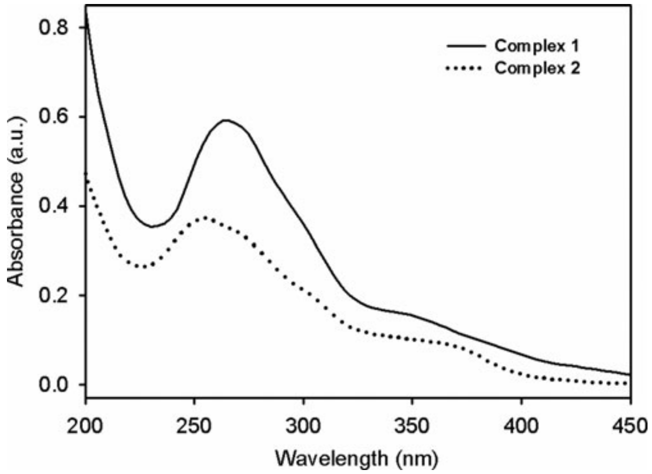


Figure 1. Absorption spectra of complexes in acetonitrile solution (10^{-5} M).

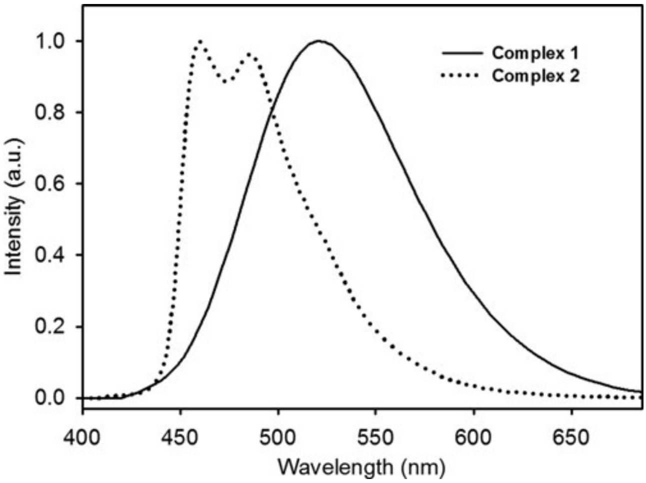


Figure 2. Photoluminescence (PL) emission spectra ($\lambda_{ex} = 410$ nm) of the cationic iridium complexes in CH_3CN solution (10^{-5} M).

(m, 7.84~7.80, 1H), 7.1 (m, 7.09~7.02, 4H), 7.65 (d, 5.74Hz, 1H), 7.54 (d, 1.58 Hz, 2H), 7.4 (m, 7.40~7.36, 3H), 6.6 (m, 6.61~6.53, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2) : 164.8, 160.5, 155.3, 155.2, 150.9, 149.4, 140.5, 139.3, 139.2, 128.3, 127.4, 124.0, 123.9, 123.8, 123.7, 123.0, 122.8, 114.5, 99.2. Anal. Found (%): C 41.80, H 2.28, N 8.26. Anal. Calcd for $C_{30}H_{19}N_5PF_{10}Ir$: C 41.77, H 2.22, N 8.12.

2.3. Fabrication and Characterization of LEC Devices

LEC devices were fabricated using poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS) as buffer layer and cationic iridium complexes as luminous layer. Prior to the deposition of active layer, the pre-patterned indium tin oxide (ITO) glass plates were sufficiently cleaned using ultra sonication in a mixture of ethanol, acetone, and isopropyl alcohol for 30 min followed by UV-ozone treatment. After spin coating the PEDOT:PSS layer, it was annealed at 140°C for 10 min. The luminous layer was prepared by dissolving the complex in acetonitrile solution (20 mg mL^{-1}), kept inside the shaking incubator for 24 h and then filtered using 0.1 μm PTFE-filter. The filtered complex solution was then spin coated on the top of ITO/PEDOT:PSS layer at 2000 rpm at 20 s and then baked at 80°C for 1 h. Finally, the substrates were transferred into a vacuum chamber where aluminum cathode was deposited by thermal evaporation method. The luminance and current density versus voltage sweeps of the devices were measured using a Keithley 2400 source meter and calibrated with a silicon photodiode. An Avantes luminance spectrometer was used to measure the EL spectrum and CIE coordinates.

3. Results and Discussion

3.1. Photophysical Properties

The UV-Vis absorption spectra of complexes in acetonitrile solution are shown in Fig. 1. The complex displays highly intense and broad absorption band below 330 nm in the ultraviolet region, which is assigned to the spin allowed $^1\pi-\pi^*$ transitions of the ligands

Table 1. Photophysical and electrochemical characteristics of cationic iridium complexes

Complex	Absorbance λ_{max} (nm) (εx10^4 $M^{-1}cm^{-1}$)	Emission maximum λ_{max} (nm)	Electrochemical data E_{ox} [V]	 E_{red} [V]
Complex 1	266 (5.9), 359 (1.4)	521	1.02	−2.12
Complex 2	255(3.7), 376 (0.7)	459, 485	1.13	−2.09

(^{1}LC). The weak absorption bands from 335 nm extending to visible region corresponds to the spin-allowed and spin-forbidden metal-to-ligand charge-transfer (^{1}MLCT and ^{3}MLCT) and spin-forbidden ligand-centered (^{3}LC) transitions provided by the strong spin-orbit coupling of Ir(III) atom [22].

The room temperature photoluminescence (PL) emission spectra of complexes in acetonitrile solution are displayed in Fig. 2. The emission spectrum complex 1 shows a broad and structure less peak with a maximum centered at 521 nm which corresponding to the light emission in the green region. This featureless emission band indicates that the emission is associated with the excited states of ^{3}MLCT or ^{3}LLCT. In case of complex 2, a vibronic structure develops with the peak emissions at 459 and 485 nm corresponds to the emission in the blue-green region, indicates that the emissive excited states contain LC $^3\pi-\pi^*$ character [23]. Compared to other reported iridium complexes, [Ir(ppz)$_2$(Me-phen)]PF$_6$ (558 nm) [4] and [Ir(dfppy)$_2$(dtb–bpy)]PF$_6$ (512 nm) [24] containing same kind of cyclometalated ligands (where dtb–bpy is 4,4′–di–tert–butyl–2,2′–dipyridyl and Me–phen is 5-methyl-1,10-phenanthroline), the PL emission spectra of complex 1 and 2 are largely blue shifted indicating that imidazole based ancillary ligand is a better candidate to tune emission color of LEC devices through the LUMO destabilization.

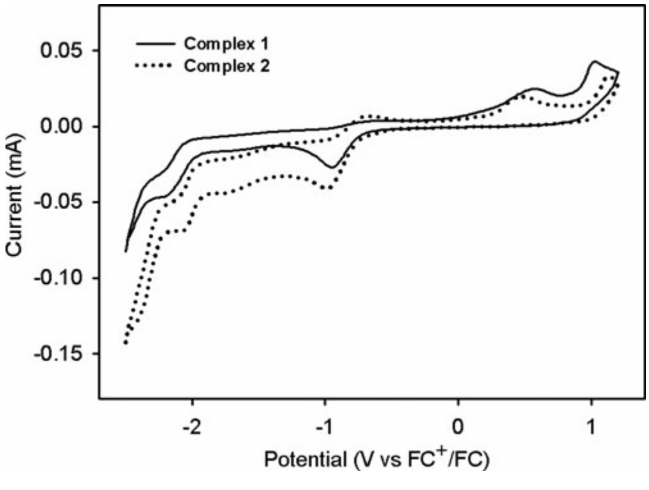


Figure 3. Cyclic voltammograms of the cationic iridium complexes in CH$_3$CN solution (10^{-3} M). The potentials were recorded versus Fc$^+$/Fc.

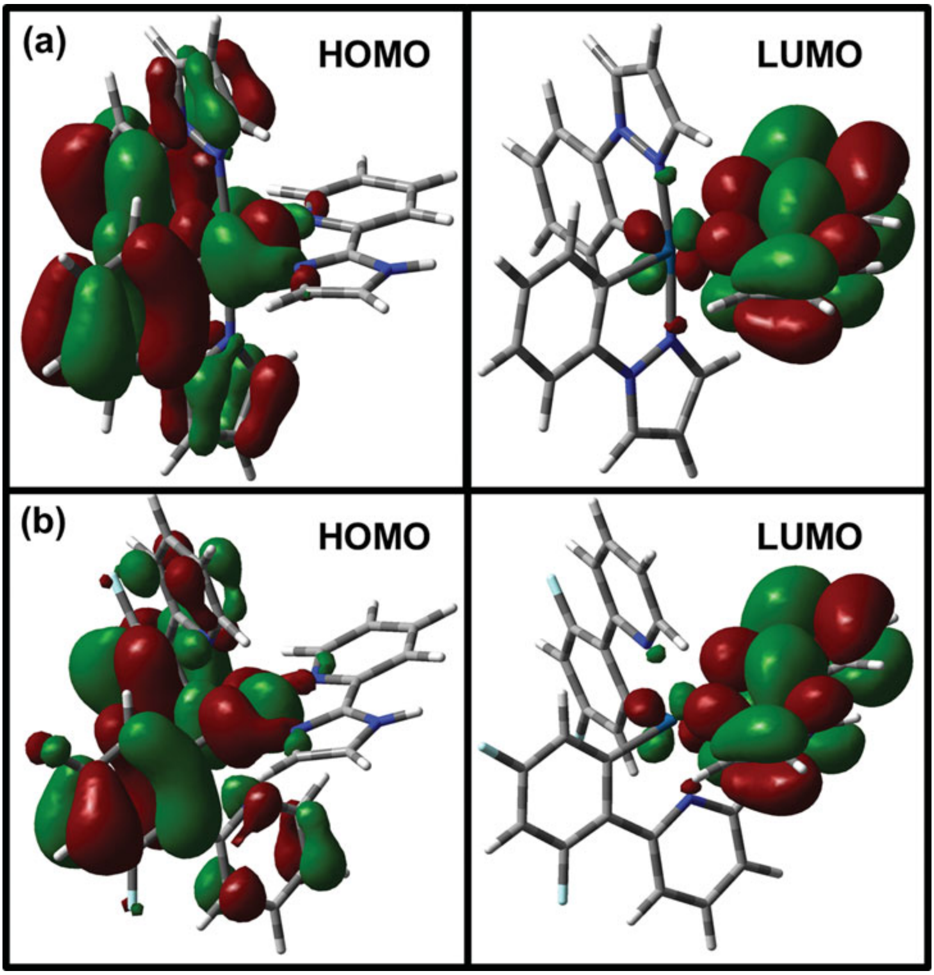


Figure 4. The optimized geometry together with molecular surfaces of the cationic iridium complexes in the ground state: (a) complex 1 and (b) complex 2 with HOMO and LUMO orbitals.

3.2. Electrochemical Properties

The electrochemical properties of complexes were investigated by cyclic voltammetry and the redox potentials are listed in Table 1. Figure 3 depicts the cyclic voltammograms of the complexes which shows an irreversible oxidation peaks at 1.02 and 1.13 V for complex 1 and 2, respectively which resulted from the oxidation of Ir(III) to Ir(IV). The oxidation potential of complex 2 was anodically shifted by 110 mV indicates the stabilization of HOMO arising from the presence of electron withdrawing fluorine atoms on the cyclometalated ligand (dfppy) which reduces the electron density around the iridium center. Similarly, the complexes shows irreversible reduction peaks at −2.12 and – 2.09 V for complex 1 and 2, respectively which occurs on the ancillary ligand where the LUMOs of the complexes are located. The higher HOMO-LUMO energy gap of 3.22 eV is obtained for complex 2 than complex 1 (3.14 eV) assuring blue shift in emission color complex 2 than complex 1.

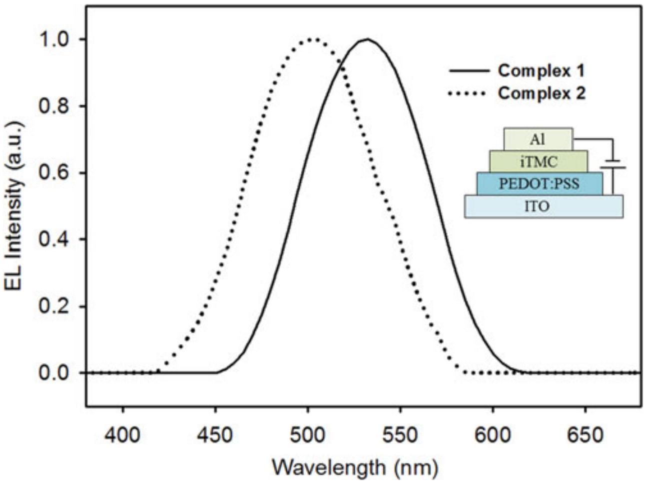


Figure 5. Electroluminescence (EL) spectra of the devices based on cationic iridium complexes. The inset shows the configuration of LEC device.

3.3. DFT Calculations

Quantum chemical density functional theory (DFT) calculations were simulated on the above complex to gain insight into the photophysical properties. DFT calculations were performed by Gaussian 09 suite of programs and the geometry of the complex was optimized by using B3LYP functional. The Ir atom was treated by the LANL2DZ basis set while all the other atoms were treated by 6–31G(d,p) basis set. Figure 4 displays the optimized geometry together with molecular surfaces of complexes in ground state. The HOMO of both the complexes resides on the phenyl groups of cyclometalated ligands and iridium ion with energies of −7.85 and −8.14 eV, while the LUMO of the complex is located on the ancillary ligand with no contribution from central metal atom with energies of −4.86 and −5.05 eV for complex 1 and 2, respectively. The LUMO+1 of both complexes still reside on the ancillary ligand but the LUMO+2 reside on phenyl groups of cyclometalated ligand and central iridium ion. The HOMO−1 and HOMO−2 orbitals of both complexes all reside on the phenyls groups of cyclometalated ligands and iridium ion unlike complex 1 which does not have any contribution from central iridium ion. The theoretically calculated HOMO−LUMO energy of the complexes are 2.99 and 3.08 eV for complex 1 and 2, respectively. The increased energy gap of complex 2 confirms a blue shift in emission properties when passing from complex 1 to complex 2.

LECs were fabricated for the purpose of studying the electroluminescent properties of the devices with the device structure of ITO/PEDOT:PSS/iTMC/Al. The electroluminescent (EL) spectra of the resulting devices are shown in Fig. 5. The EL spectra of the LEC device based on both complexes shows broad and unstructured peaks with the difference in emission maxima of 27 nm only. The EL spectrum of complex 1 resembles the PL spectrum in acetonitrile solution with an emission maximum at 530 nm corresponds to the light emission in the green region. However, the EL spectrum of complex 2 shows an emission maximum at 503 nm. Unlike the PL spectrum, the unstructured shape of EL emission band of complex 2 reveals that the light emission is associated from MLCT states in thin solid film. The device based on both complexes gave green light with CIE coordinates of (0.29, 0.48) and (0.31, 0.44) for complex 1 and 2, respectively.

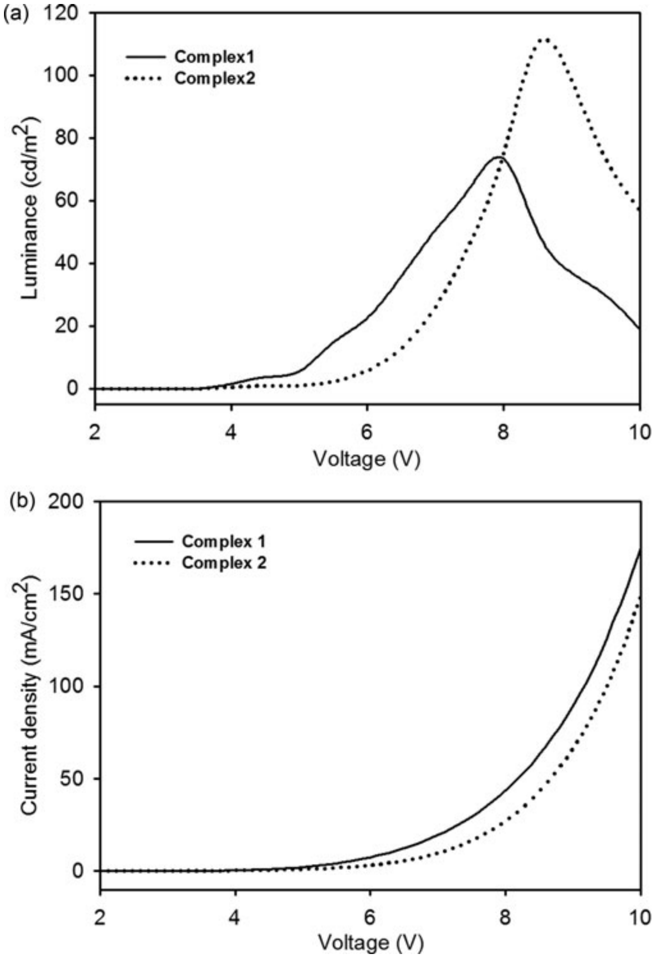


Figure 6. (a) Luminance and (b) current density versus voltage curves of the LECs based on complexes 1 and 2.

The electrical properties of the LEC devices were illustrated by plotting the luminance and current density versus voltages as shown in Fig. 6 and summarized in Table 2. The Fig. 6 shows that the luminance and current density of all the devices increases slowly with voltage due to the slow migration of PF_6^- ion towards electrode under an external electric field [25–26]. Compared to complex 2, the turn on voltage of complex 1 is less and the luminance intensity increases with increasing voltage. The lower turn

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

Active material	EL_{max} (nm)	CIE coordinates	Maximum luminance	Maximum current density
Complex 1	530	(0.29, 0.48)	73 cd/m^2	174 mA/cm^2
Complex 2	503	(0.31, 0.44)	110 cd/m^2	148 mA/cm^2

on voltage of complex 1 arises from the faster mobility of the mobile ions towards the electrode surface. Even though the luminance of both complexes increases with voltage, it reaches a maximum value and then decreases the intensity of luminance due to their limited stability with voltages. The increase in voltage induces the fast displacement of ions toward the electrodes and results a strong interfacial electrical field at the electrode surface thereby facilitating enhanced carrier injection. These charge carriers transport and their more balanced carrier recombination eventuates high luminance of 73 cd/m^2 and 110 cd/m^2 and the maximum current density of 174 mA/cm^2 and 148 mA/cm^2 for complex 1 and 2, respectively. LECs based on complex 1 and 2 gave a peak current efficiency of 0.26 cd/A and 0.27 cd/A, respectively.

4. Conclusions

Light-emitting electrochemical cells using a cationic iridium complex with imidazole based ancillary ligand were fabricated and their electroluminescent properties were investigated. The LECs based on these complexes emitted green electroluminescence with maximum luminance of 73 cd/m^2 and 110 cd/m^2 were resulted for complex 1 and 2, respectively.

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References

[1] Slinker, J., Bernards, D., Houston, P. L., Abruna, H. D., Bernhard, S., & Malliaras, G. G. (2003). *Chem. Commun.*, *19*, 2392.

[2] Slinker, J. D., Rivnay, J., Moskowitz, J. S., Parker, J. B., Bernhard, S., Abruna, H. D., & Malliaras, G. G. (2007). *J. Mater. Chem.*, *17*, 2976.

[3] Sunesh, C. D., Chandran, M., Mathai, G., & Choe, Y. S. (2013). *Opt. Mater.*, *35*, 407.

[4] Sunesh, C. D., Mathai, G., Cho, Y. R., & Choe, Y. S. (2013). *Polyhedron.*, *57*, 77.

[5] Baranoff, E., Bolink, H. J., Constable, E. C., Delgado, M., Nazeeruddin, M. K., Neuburger, M., Orti, E., Schneider, G. E., Tordera, D., Walliser, R. M., & Zampese, J. A. (2013). *Dalton. Trans.*, *42*, 1073.

[6] Slinker, J. D., Gorodetsky, A. A., Lowry, M. S., Wang, J. J., Parker, S., Rohl, R., Bernhard, S., & Malliaras, G. G. (2004). *J. Am. Chem. Soc.*, *126*, 2763.

[7] Nazeeruddin, M. K., Wegh, R. T., Zhou, Z., Klein, C., Wang, Q., Angelis, F. D., Fantacci, S., & Gratzel, M. (2006). *Inorg. Chem.*, *45*, 9245.

[8] Costa, R. D., Ortı′, E., Bolink, H. J., Graber, S., Housecroft, C. E., & Constable, E. C. (2010). *J. Am. Chem. Soc. 132*, 5978.

[9] Pei, Q. B., Yu, G., Zhang, C., Yang, Y., & Heeger, A. J. (1995). *Science.*, *269*, 1086.

[10] Bolink, H. J., Cappelli, L., Coronado, E., & Gavina, P. (2005). *Inorg. Chem. 44*, 5966–5968.

[11] Kalyuzhny, G., Buda, M., McNeill, J., Barbara, P., & Bard, A. J. (2003). *J. Am. Chem. Soc. 125*, 6272–6283.

[12] Lyons, C. H., Abbas, E. D., Lee, J. K., & Rubner, M. F. (1998). *J. Am. Chem. Soc. 120*, 12100–12107.

[13] Gao, F. G., & Bard, A. J. (2002). *Chem. Mater. 14*, 3465–3470.

[14] Hosseini, A. R., Koh, C. Y., Slinker, J. D., Torres, S. F., Abruna, H. D., & Malliaras, G. G. (2005). *Chem. Mater. 17*, 6114–6116.

[15] Armaroli, N., Accorsi, G., Holler, M., Moudam, O., Nierengarten, J. F., Zhou, Z., Wegh, R. T., & Welter, R. (2006). *Adv. Mater. 18*, 1313–1316.
[16] Zhang, Q., Zhou, Q., Cheng, Y., & Wang, L., Ma, D., Jing, X., Wang, F. (2006). *Adv. Funct. Mater. 16*, 1203–1208.
[17] Costa, R. D., Ortı′, E., Bolink, H. J., Graber, S., Housecroft, C. E., & Constable, E. C. (2011) *Chem. Commun.*, *47*, 3207–3209.
[18] Costa, R. D., Ortí, E., Tordera, D., Pertegás, A., Bolink, H. J., Graber, S., Housecroft, C. E., Sachno, L., Neuburger, M., & Constable, E. C. (2011). *Adv. Energy Mater. 1*, 282–290.
[19] He, L., Duan, L., Qiao, J., Zhang, D., Wang, L., & Qiu, Y. (2011). *Chem. Commun. 47*, 6467–6469.
[20] Nonoyama, M. (1974). *Bull. Chem. Soc. Jpn. 47*, 767–768.
[21] Sprouse, S., King, K. A., Spellane, P. J., & Watts, R. J. (1984). *J. Am. Chem. Soc. 106*, 6647–6653.
[22] Tamayo, A. B., Garon, S., Sajoto, T., Djurovich, P. I., Tsyba, I. M., Bau, R., & Thompson, M. E. (2005). *Inorg. Chem. 44*, 8723–8732.
[23] Lowry, M. S., Hudson, W. R., Pascal, R. A., & Bernhard, S. (2004). *J. Am. Chem. Soc. 126*, 14129–14135.
[24] Bolink, H. J., Coronado, E., Costa, R. D., Lardiés, N., & Ortí, E. (2008). *Inorg. Chem. 47*, 9149–9151.
[25] Slinker, J. D., Gorodetsky, A. A., Lowry, M. S., Wang, J. J., Parker, S., Rohl, R., Bernhard, S., & Malliaras, G. G. (2004). *J. Am. Chem. Soc. 126*, 2763–2767.
[26] He, L., Duan, L., Qiao, J., Wang, R., Wei, P., Wang, L. D., & Qiu, Y. (2008). *Adv. Funct. Mater. 18*, 2123–2131.