



Electroluminescent properties of yellow light-emitting electrochemical cells based on a cationic iridium complex and the effect of ionic liquids incorporation in an active layer

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ABSTRACT

A cationic iridium complex $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ was synthesized, in which ppz is 1-phenylpyrazole and dmphen is 5,6-dimethyl-1,10-phenanthroline, and characterized by spectroscopic and photophysical methods. Light-emitting electrochemical cells (LECs) were fabricated using the resulting complex and their electroluminescent properties were investigated. LECs based on $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ gave a yellow electroluminescence of 4052 cd m^{-2} at 9.0 V. Furthermore, the luminance of the devices was constructively tuned by doping ionic liquids (ILs) into the light emitting layer. The addition of ILs resulted in enhanced luminance of the devices at shorter turn-on voltages indicating its great potential for display and lighting applications. Among the three employed ILs, BMIMPF₆ showed best performance in terms of luminance of 3850 cd m^{-2} at 6.5 V.

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1. Introduction

Recently, light-emitting electrochemical cells (LECs) have received considerable attention as electroluminescent devices for the applications in full color displays and solid-state lighting devices [1,2]. LECs are optoelectronic devices consisting of a single active component of either ionic transition metal complex (iTMC) or inorganic salt incorporated conjugated polymer sandwiched between two metal electrodes [2–4]. LECs offer great advantages over multi-layered organic light-emitting diodes (OLEDs), such as simple device architecture, the use of air stable electrode materials and cost effectiveness. The concept of LEC devices was put forward by Heeger in 1995, which was based on conjugated polymer together with an ion-conducting polymer and an inorganic salt [3]. The initial reports on LECs based on iTMC dates back to those based on ionic ruthenium complex containing 4,7-diphenyl-1,10-phenanthroline ligand with sulfonate groups on the para position of both the phenyl group [5]. Thereafter iTMCs have been found exhibiting better performance than polymer based LECs due to the phosphorescent nature of transition metal complexes and showed high electroluminescent (EL) efficiency. Moreover, the mobile ions present on the iTMC itself can perform all the necessary roles of charge injection, charge transport and emissive recombination for electroluminescence.

Among the iTMCs reported for LEC applications, phosphorescent iridium complexes (Ir-iTMCs) are very attractive owing to the larger

spin-orbit coupling of central iridium(III) ion [6,7]. Slinker et al. reported the foremost solid state LEC based on ionic iridium complex, bis(2-phenylpyridine)(4,4'-di-tert-butyl-2,2'-dipyridyl)-iridium(III) hexafluorophosphate which shows an emission in the yellow region of visible spectrum [6]. Since then, tremendous research is going on the synthesis of Ir-iTMCs through the structural modification of organic ligands for the fabrication of LEC devices exhibiting high luminance, efficiency and tunable light emission in addition to the thermal and electrochemical stability [8–17].

Recently, Dumur et al. has reported a yellow light emitting LECs using iridium soft salt through the combination of cationic and anionic iridium complex. The yellow light emission (λ_{max} 553 nm) obtained from the device had Commission Internationale de L'Eclairage (CIE) coordinates of (0.43, 0.54) and displayed higher turn-on voltage with a maximum luminance of 1114 cd m^{-2} at 9.3 V [18]. Hence in the purpose of improving the brightness and turn on voltage of yellow LECs towards lighting applications, herein we are reporting a highly luminescent LECs based on a cationic iridium complex $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$, using 5,6-dimethyl-1,10-phenanthroline ancillary ligand. Density functional theory (DFT) calculations were performed on the synthesized complex and have calculated the electronic energy levels for the optimized geometry. LECs fabricated using the as synthesized $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ as light-emitting layer resulted in yellow light emission (λ_{max} 555 nm) with lower turn-on voltage and a maximum luminance of 4052 cd m^{-2} at 9.0 V. Three different ILs which are 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIMPF₆), and 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIMPF₆) were

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separately added to the light-emitting layer in order to promote the ionic conductivity of the active material and the electroluminescent properties of the fabricated devices were investigated and compared.

2. Experimental details

2.1. Materials and methods

All reagents and solvents were purchased from Aldrich and used without further purification. ^1H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Varian Unity Inova 500 MHz FT-NMR spectrometer and measured relative to residual CD_2Cl_2 solvent with tetramethylsilane as internal standard. Elemental analysis was carried out in Elementar Vario EL CHN elemental analyzer. Absorption spectrum was obtained using 8453 UV–visible Agilent spectrophotometer. Photoluminescence (PL) emission spectra were performed in a de-aerated acetonitrile solution at an excitation wavelength of 420 nm using Hitachi F-7000 Fluorescence spectrophotometer equipped with 150 W xenon lamp. The measurements were recorded in a 1 cm path length quartz cell, with a wavelength scan speed of 1200 nm/min. The surface morphology of the films was investigated using a dynamic force microscopy (DFM), model L – Trace II; SII Nano Technology Inc., operated on a non-contact mode with cantilever type SI-DF40.

2.2. Synthesis of $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$

The chloro-bridged dimeric iridium complex $[\text{Ir}(\text{ppz})_2\text{Cl}]_2$ (154 mg, 0.15 mmol) and 5,6-dimethyl-1,10-phenanthroline (69 mg, 0.33 mmol) in CH_2Cl_2 (15 ml) and MeOH (15 ml) were refluxed under nitrogen for 16 h. 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 2 h and the solvent was evaporated under vacuum. The resulting yellow solid was dissolved in dichloromethane and the insoluble inorganic impurities were filtered out, and then diethyl ether was slowly layered onto the filtrate yielding crystalline yellow solid (235 mg, 0.53 mmol, 94%). ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.75 (d, $J = 8.8$ Hz, 2H), 8.43 (d, $J = 4.9$ Hz, 2H), 8.14 (d, $J = 2.9$ Hz, 2H), 7.81 (d, $J = 8.5$ Hz, 2H), 7.38 (dd, $J = 1.2, 7.9$ Hz, 2H), 7.15–7.11 (m, 4H), 6.97–6.93 (m, 4H), 6.47–6.43 (m, 4H), 2.86 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 150.6, 143.2, 138.5, 135.7, 133.9, 133.2, 127.6, 127.4, 126.5, 124.1, 124.0, 118.2, 117.9, 112.3, 108.6, 15.9. Anal. Found (%): C 46.28, H 3.14, N 10.21. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_6\text{PF}_6\text{Ir}$: C 46.21, H 3.15, N 10.10.

2.3. Fabrication and characterization of LEC devices

The electroluminescent iridium complex was dissolved in acetonitrile solution using the concentration of 20 mg ml^{-1} . Three different ILs were separately added to the emissive layer at 1:1 molar ratio of iTMC:IL and stirred for 24 h. Prior to the fabrication of the LECs, the ITO glass substrates as anode were sufficiently cleaned using sonication in a mixture of ethanol, acetone, and isopropyl alcohol in 1:1:1 v/v ratio for 30 min followed by UV-ozone treatment for 20 min. A thin film of poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS) as buffer layer was spin coated on the ITO substrate at 2000 rpm for 20 s and baked at 140°C for 10 min. The iTMC:IL films were then spin-coated above the buffer layer and baked at 80°C for 1 h. Aluminum cathode was thermally evaporated above the active layer using a shadow mask under high vacuum. The electroluminescent properties of the resultant devices were performed using Keithley characterization systems. The current density and luminance versus voltage sweeps 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

The room temperature absorption and photoluminescence (PL) emission spectra of $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ in acetonitrile solution are shown in Fig. 1. The absorption spectrum of the phosphorescent iridium complex shows an intense absorption bands below 350 nm in the ultraviolet region resulting from the spin-allowed $^1\pi\text{-}\pi^*$ transitions of the ligands. The less intense absorption band around 378 nm can be attributed to the spin-allowed metal-to-ligand charge-transfer ($^1\text{MLCT}$), ligand-to-ligand charge-transfer ($^1\text{LLCT}$) and spin-forbidden ligand-centered (^3LC), $^3\text{MLCT}$ and $^3\text{LLCT}$ transitions of the complex.

As shown in Fig. 1, the PL emission spectrum of the complex shows a broad and featureless emission band in acetonitrile solution. Fig. 1 displays the emission spectra of the complex containing three different ionic liquids are same as that of the complex, indicating that ionic liquids have no significant effects on the photophysical properties of the complex. The unstructured emission peak at room temperature is attributed to the emission from $^3\text{MLCT}$ rather than ^3LC transition state [19,20]. The broad emission band of the complex shows the PL maximum at 555 nm corresponding to light emission in the yellow region. In addition, the PL spectra of complex and that containing three different ILs at various temperatures were also measured and compared with those at room temperature. The emission spectra at higher temperatures were found the same as those observed at room temperature, revealing that the complex does not exhibit any thermochromic behavior.

In order to study the effect of solvatochromism, the emission spectra of the cationic iridium complex in various solvents with different polarities were measured and shown in Fig. 2. As shown in Fig. 2, a red shift in emission maximum is observed with increasing polarity from dichloromethane to dimethyl sulfoxide (DMSO) at room temperature. However, the difference in emission maximum is only 23 nm from dichloromethane to DMSO. The red shift of emission maximum in more polar solvent is due to the positive solvatochromic effect of the solvent that causes the stabilization of molecule in the excited state than the ground state.

The molecular and electronic structural studies of $[\text{Ir}(\text{ppz})_2(\text{dmphen})]^+$ was stimulated and constructed by DFT calculations. All the 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

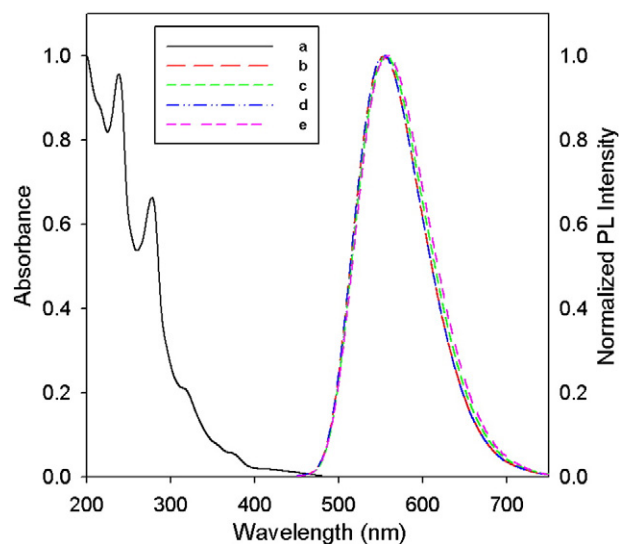


Fig. 1. (a) UV–vis absorption spectrum of $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ and photoluminescence (PL) emission spectra of (b) $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$, (c) $[\text{Ir}(\text{ppz})_2(\text{dmphen})]\text{PF}_6$ mixed with BMIMPF₆, (d) EMIMPF₆, and (e) HMIMPF₆.

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