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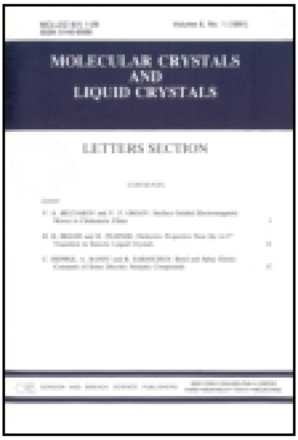

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A cationic iridium complex with tetrafluoroborate (BF_4^-) as anion was synthesized and characterized for its potential application in display and solid state lighting devices. Light-emitting electrochemical cells (LECs) based on this complex displayed yellow electroluminescence with CIE coordinates of (0.50, 0.49). The imidazolium ionic liquids such as $BMIMBF_4$ and $EMIMBF_4$ were separately added to the light-emitting layer of the devices and their effects on the electroluminescent properties were studied. The presence of smaller BF_4^- ion effectively facilitates the charge injection from the electrodes and hence results in rapid increase of luminance and current density of the devices with voltages.

Keywords Cationic iridium complex; electrical properties; light-emitting electrochemical cells; thin films

1. Introduction

Light-emitting electrochemical cells (LECs) containing ionic transition metal complex (iTMC) with d^6, d^8, and d^{10} electronic configurations have attracted widespread interest owing to their potential application in full color display and lighting devices [1–3]. LECs consist of a single layer of electroluminescent material, which can be easily fabricated from solution process. They render great advantages over multilayered organic light-emitting diodes (OLEDs), such as the use of air stable electrodes, cost-efficiency and simple device architecture. The first solid state LEC reported in 1995 was based on polymer blend, which consists of a conjugated polymer, an ion conducting polymer and an inorganic salt [1]. The iTMCs based LECs are more prominent over the polymer based LECs due to its ionic nature and hence obviate the use of the inorganic salt as well as the ion conducting material [4–6]. Among the reported iTMCs based LECs, iridium complexes have attracted increasing interest because of the larger spin-orbit coupling of heavy iridium atom. As a result, they exhibit tunable emission colors through the meticulous selection of organic ligands. Furthermore, the heteroleptic iridium complexes can be easily synthesized and smoothly

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applied to display devices affording high luminance and efficiency at low operating voltages [2–13].

LECs based on cationic iridium complex, $[Ir(ppy)_2(dtbbpy)]PF_6$ (where ppy is 2-phenylpyridine, dtbbpy is 4,4'-di-*tert*-butyl-2,2'-bipyridine and PF_6^- is hexafluorophosphate anion) was first reported by Slinker et *al*. in 2004 which emits orange light (581 nm) in acetonitrile solution [7]. Since then, tremendous research has been performed using iridium complexes with various organic ligands and achieved high efficiency and versatile emission colors [5,10–11]. Recently, Chen and co-workers demonstrated sky-blue and blue-green LECs based on cationic iridium complexes using 1,2,4-triazole-pyridine as the ancillary ligand and exhibited maximum brightness of 430 cd m^{-2} at 5 V [11]. Dumur and co-workers reported LEC devices using iridium complex with 4,4'-dinonyl-2,2'-bypyridine as the ancillary ligand with a maximum brightness of 1223 cd m^{-2} at 6.3 V [14]. In all these complexes, PF_6^-, which is a larger ion, serves as the counter anion which caused the device to operate at higher voltage. A smaller size of the counter anions is crucial for reducing the turn-on voltage and to increase the luminance of the LEC devices at low operating voltages. Recently, our group has reported an iridium complex based LEC with PF_6^- as counter anion which exhibited a high luminance of 5199 cd m^{-2} at 9.0 V [12]. Considering the aforementioned facts and as a continuum to our previous work [12] we thought it worthwhile to device an iridium complex with a smaller counter ion, BF_4^- that can produce electric double layer at electrode surface faster than large counter anion, PF_6. Hence herein, we report the synthesis and photophysical properties of a cationic iridium complex, $[Ir(ppz)_2(dphen)]BF_4$, with smaller mobile counter anion and their performance in LEC devices. Two different ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) were separately added to the light-emitting layer of the device at 1:1 molar ratio of iTMC:IL and their electroluminescent properties were also studied and compared.

2. Experimental

2.1. *Materials and Methods*

All reagents and solvents were purchased from Aldrich and used without further purification. ^1H 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 analysis was carried out in Elementar Vario EL CHN elemental analyzer. UV-visible absorption spectrum was obtained using 8453 UV-visible Agilent spectrophotometer. PL spectrum was recorded with an F-7000 FL spectrophotometer.

2.2 *Synthesis of Cationic Iridium Complex*

The cyclometalated iridium(III) chloro-bridged dimer $[Ir(ppz)_2Cl]_2$ (ppz = 1-phenylpyrazole) was prepared using iridium trichloride hydrate and 1-phenylpyrazole in a 3:1 v/v mixture of 2-ethoxyethanol and water and refluxed for 24 h according to the previously reported procedures [15,16].

2.2.1. Synthesis of $[Ir(ppz)_2(dphen)]BF_4$. The chloro-bridged dimeric iridium complex $[Ir(ppz)_2Cl]_2$ (123 mg, 0.12 mmol) and 4,7-diphenyl-1,10-phenanthroline (88 mg, 0.26 mmol) were dissolved in CH_2Cl_2 (15 ml) and MeOH (15 ml). The mixture was refluxed under nitrogen for 12 h and the yellow solution obtained was cooled to room

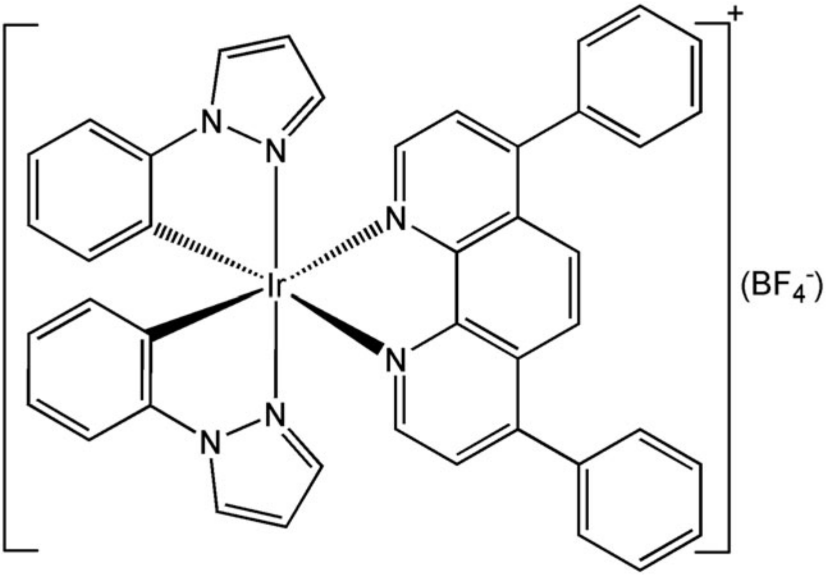

Figure 1. Chemical structure of cationic iridium complex with 4,7-diphenyl-1,10-phenanthroline as ancillary ligand and tetrafluoroborate as counter anion.

temperature and solid ammonium tetrafluoroborate (52 mg, 0.5 mmol) was added to it. The reaction mixture was stirred at room temperature for 1 h and the solvent was evaporated under vacuum. The product obtained was dissolved in dichloromethane, filtered to remove the unwanted inorganic impurities, and then precipitated with hexane. The crude material obtained was purified by column chromatography (Merck Alox 90; CH_2Cl_2 changing to CH_2Cl_2/MeOH, 100:2) yielding the desired product as yellow solid (156 mg, 0.17 mmol, 73%). The chemical structure of the cationic iridium complex is shown in Fig. 1. ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.50 (d, J = 5.2 Hz, 2H), 8.13 (d, J = 3.1 Hz, 2H), 7.66 (d, J = 5.1 Hz, 2H), 7.61–7.54 (m, 4H), 7.33 (d, J = 7.1 Hz, 2H), 7.26 (d, J = 2.93 Hz, 2H), 7.11–7.07 (m, 4H), 6.98–6.92 (m, 4H), 6.54 (t, 5.1 Hz, 1H), 6.48–6.46 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 151.6, 150.8, 148.3, 143.5, 139.0, 135.8, 130.3, 129.9, 129.7, 129.4, 127.2, 126.9, 126.5, 123.6, 121.7, 111.7, 108.7. Anal. Found (%): C 56.25, H 3.45, N 9.34. Anal. Calcd for $C_{42}H_{30}N_6BF_4Ir$: C 56.19, H 3.37, N 9.36.

2.3. Fabrication and Characterization of LEC Devices

LEC devices were fabricated using poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) as buffer layer and [Ir(ppz)$_2$(dpphen)]BF$_4$ as luminous layer. The pre-patterned indium tin oxide (ITO) glass plates were sufficiently cleaned using ultra sonication in mixture of ethanol, acetone, and isopropyl alcohol for 30 min followed by UV-ozone treatment.

The thin film of PEDOT:PSS was spin coated onto the ITO glass plates and baked at 140 °C for 10 min. The luminous layer of the complex (20 mg mL^{-1}) containing different ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) at a molar ratio of 1:1 were spin coated from the acetonitrile solutions and baked at 80 °C for 1 h. Thereafter, the substrates were

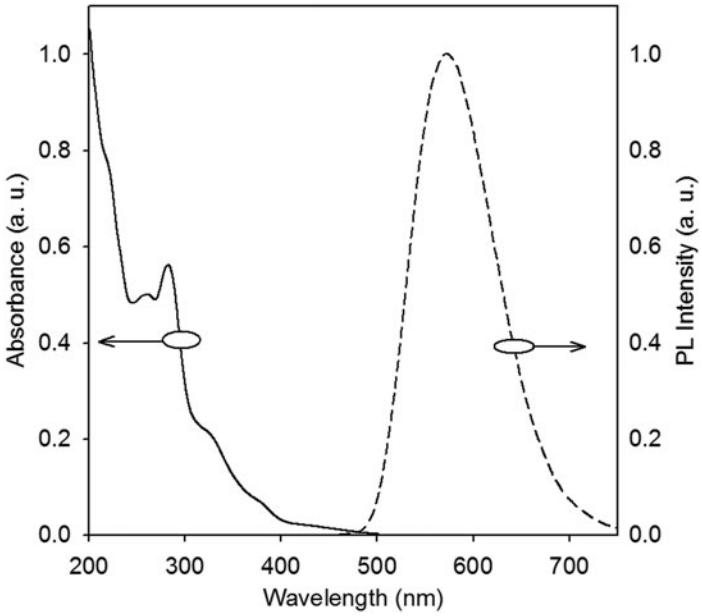

Figure 2. Absorption and photoluminescence (PL) emission spectra of cationic iridium complex in acetonitrile solution.

transferred into a vacuum chamber where aluminum cathode was thermally evaporated. The luminance 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

The UV-Vis absorption and photoluminescence (PL) emission spectra of the cationic iridium complex in acetonitrile solution are depicted in Fig. 2. The complex displays highly intense absorption bands up to 350 nm in the ultraviolet region due to the spin allowed $^1\pi$-π^* transitions of the ligands (^{1}LC). These large molar absorbance bands accompanied by less intense bands from 350 nm extending to the 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 [17–18]. The photoluminescence (PL) emission spectrum of complex in acetonitrile solution is displayed in Fig. 2. The PL spectrum is obtained by exciting the complex by an excitation wavelength of 430 nm. As shown in Fig. 2, the complex shows a broad and unstructured emission band at room temperature with an emission maximum centered at 572 nm corresponding to the light emission in the yellow region. This featureless emission band is attributed to the MLCT character in the excited state of the iridium complex.

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

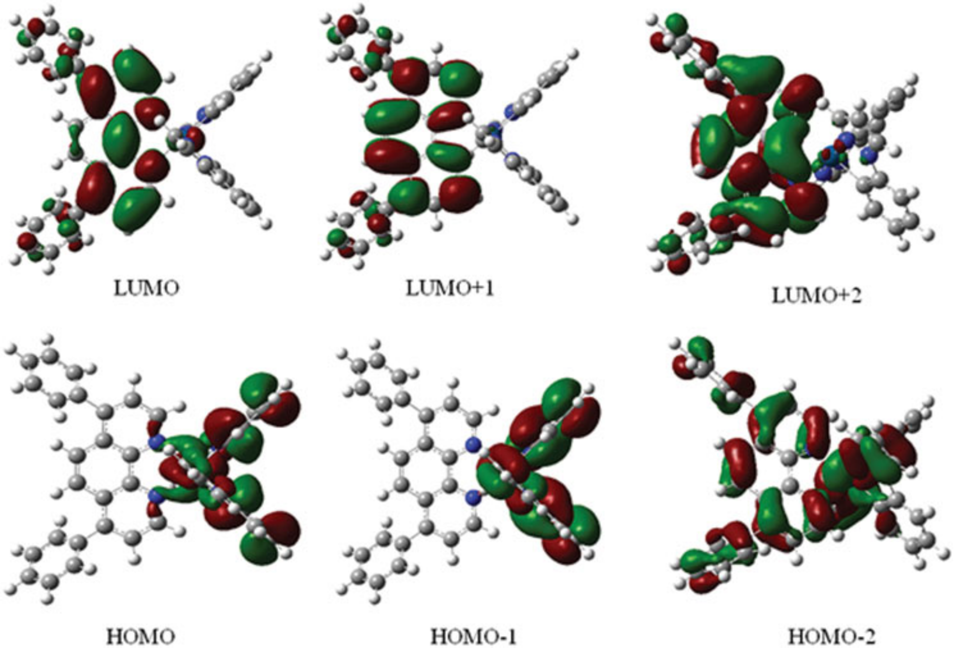

Figure 3. The optimized geometry together with molecular surfaces of $[Ir(ppz)_2(dpphen)]^+$.

set while all the other atoms were treated by 6–31G(d,p) basis set. Figure 3 displays the optimized geometry together with molecular surfaces of $[Ir(ppz)_2(dpphen)]^+$ in ground state. As shown in Fig. 3, the HOMO of the complex resides in phenyl groups of both ppz cyclometalated ligands and iridium ion, while the LUMO of the complex is localized on the ancillary ligand. The LUMO+1 and LUMO+2 orbitals still reside on the ancillary ligand whereas the HOMO-1 orbital is located on cyclometalated ligand and iridium ion as its HOMO orbital. However, the HOMO-2 orbital shows different molecular surfaces which reside on the ancillary ligand and iridium atom. The calculated HOMO and LUMO energy of the complex is 3.03 eV.

LECs were fabricated for the purpose of studying the electroluminescent properties of the devices with the device structure ITO/PEDOT:PSS/iTMC:IL (1:1)/Al. The role of PEDOT:PSS is to smoothen the electrode surface and it serves as a hole conducting material. The active layer consists of a blend of iTMC and ionic liquid (IL) in 1:1 molar ratio spin coated from acetonitrile solution. Ionic liquids were added to the iridium complex in order to enhance the performance of the devices owing to their high intrinsic ionic conductivities. The electroluminescent (EL) spectra of the resulting devices are shown in Fig. 4. The EL spectra of all the LEC devices with and without ILs are broad and unstructured peaks which resembles the PL spectrum in acetonitrile solution. The EL spectrum of the pristine device displays yellow electroluminescence with a maximum emission at 579 nm corresponding to the CIE coordinates of (0.50, 0.49).The addition of ILs blue shift the emission spectrum to yellowish-green region ($\lambda_{max} = 566$ nm) with CIE coordinates of (0.46, 0.53) compared to pristine device which is attributed to the light emission from higher lying excited states. Similar blue shift was reported for the LEC devices based on iridium complex by the addition of ionic liquid [19].

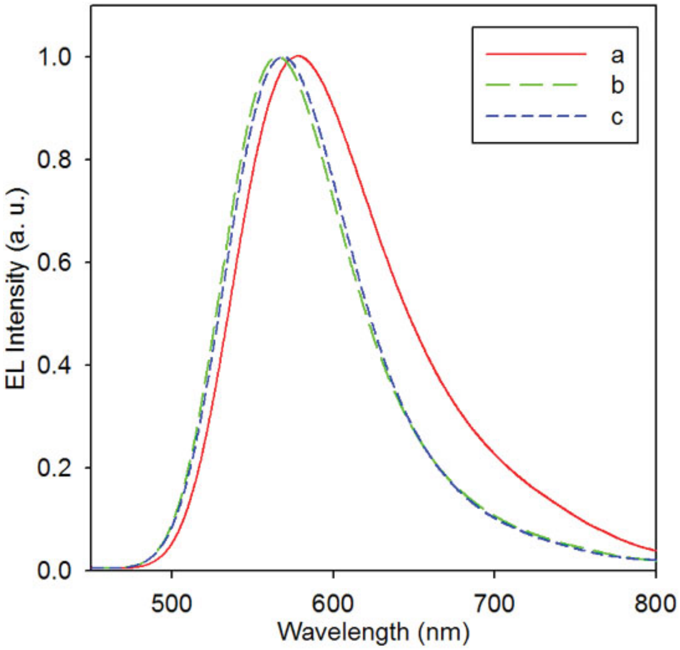

Figure 4. Electroluminescence spectra of LECs employing iTMC (a), iTMC + BMIMBF$_4$ (b), and iTMC + EMIMBF$_4$ (c) as electroluminescemt materials.

The electrical properties of the LEC devices were illustrated by plotting the luminance and current density versus voltages as shown in Fig. 5. The electrical characteristics of devices with and without ILs are summarized in Table 1. The Fig. 5 shows that the luminance and current density of all the devices increases rapidly with voltage due to fast migration of BF$_4^-$ ion towards electrode under a bias. It is noted that, the luminance of

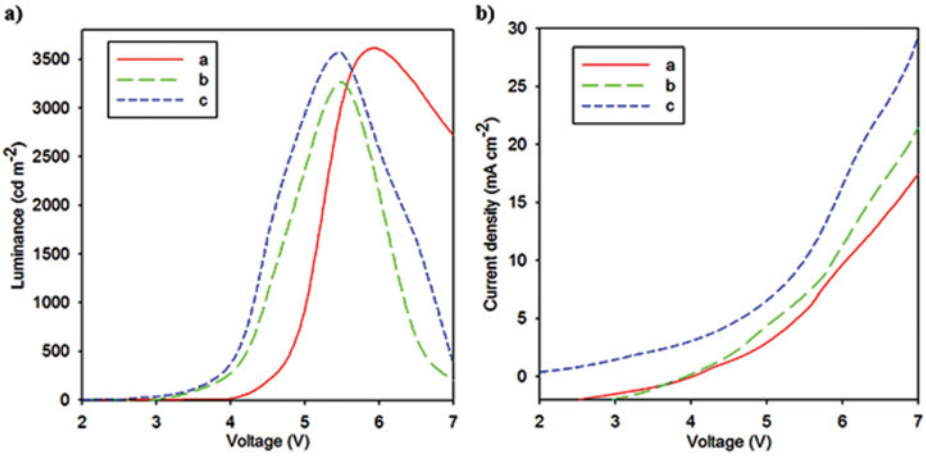

Figure 5. (a) Luminance and (b) current density versus voltage curves of LECs containing iTMC (red), iTMC + BMIMBF$_4$ (green), and iTMC + EMIMBF$_4$ (blue) as electroluminescent materials.

Table 1. The detailed electrical characteristics of LECs based on cationic iridium complex

Active material	EL_{max} (nm)	CIE coordinates	Maximum luminance, voltage	Maximum current density, voltage
$[Ir(ppz)_2(dpphen)]BF_4$	579	(0.50, 0.49)	3605 cd m^{-2}, 6.0 V	17.45 mA cm^{-2}, 7.0 V
$[Ir(ppz)_2(dpphen)]BF_4$ + $BMIMBF_4$	566	(0.46, 0.53)	3267 cd m^{-2}, 5.5 V	21.46 mA cm^{-2}, 7.0 V
$[Ir(ppz)_2(dpphen)]BF_4$ + $EMIMBF_4$	567	(0.47, 0.52)	3563 cd m^{-2}, 5.5 V	29.29 mA cm^{-2}, 7.0 V

pristine device begins to increase from 3.5 V, reaches a maximum of 3605 cd m^{-2} at 6 V and then decreased. The rapid increase in luminance is due to the fast displacement of BF_4^- anions toward the anode 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 at low operating voltages. Blending the complex with different ionic liquids improves the luminance of the devices with a turn-on voltage at 3 V. This is because of the high intrinsic ionic conductivities of ILs as well as its ability to suppress the quenching of iTMCs in active layer [6,20]. The addition of IL enhances the ionic conductivity of the active material and also provides extra BF_4^- ions, thereby resulting in the faster movement of BF_4^- towards the electrode surfaces which reduces the electron/hole injection barriers. Consequently, the injected charge carriers undergo more balanced recombination leading to lower turn-on voltage and high luminance. In our previous work, we have fabricated an LEC with the same iridium complex with PF_6^- as the anion where it yielded a max luminance at higher voltage only [12]. Moreover, the turn on voltage with the PF_6^- was found to be as higher as 5 V while the current study with the BF_4^- anion resulted in a low turn on voltage of 3.5 and 3 V respectively for pristine device and the device containing ILs due to its comparatively smaller size. Among the ionic liquids added, $EMIMBF_4$ showed higher luminance of 3563 cd m^{-2} at 5.5 V than the device containing $BMIMBF_4$. Even though higher luminance is obtained at lower voltage due to the fast migration of BF_4^- ions, the device stability was deteriorated by the addition of ILs and also by the use of smaller counter anion because of the faster migration of BF_4^- ions leading to a more extensive exciton quenching [21].

4. Conclusions

Light-emitting electrochemical cells using a cationic iridium complex containing BF_4^- ion were fabricated and their electroluminescent properties were investigated. LECs based on this complex generate yellow electroluminescence of 3605 cd m^{-2} at 6.0 V. The incorporation of two different ILs into the light-emitting layer of the devices resulted in the luminance of 3267 and 3563 cd m^{-2} for $BMIMBF_4$ and $EMIMBF_4$ respectively at 5.5 V. In conclusion, the addition of ionic liquids enhanced the faster migration of the smaller counter anion which resulted in high luminescence and lower turn-on voltage for the LEC devices.

Acknowledgments

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