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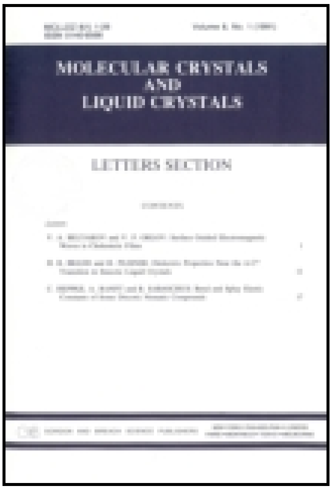

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Light Emitting Electrochemical Cells Based on Ionic Iridium Complexes and Ionic Conductor Blend as the Active Layer

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Recently, light emitting electrochemical cells (LECs) have received considerable attention for their application in display and lighting applications. In this manuscript we put forward a study of cationic iridium complex and ionic conductor blend as the active layer of light emitting electrochemical cells. Tetrabutylammonium triflate functions as an ionic conductor. We have synthesized iridium metal complex using phenanthroline based ancillary ligands and studied light emitting properties of the devices in pristine as well as ionic conductor blends. Current density, luminescence plots were well studied against applied bias and on comparison, the devices with ionic liquids showed better performance.

Key words Light emitting electrochemical cells; ionic-transition metal complex; electroluminescence; ionic-conductor; photoluminescence; phenanthroline ligands.

Introduction

In recent years, among the various type of solid-state light emitting devices, light-emitting electrochemical cells (LECs) have been considered successful in attracting the attention of worldwide researchers to an appreciable extent [1–4]. LECs are considered as a potential device for display and lighting applications owing to their peculiar electroluminescent properties. On comparison with organic light emitting diodes (OLEDs), they have numerous advantages including the simplicity in device structure, solution processability, and insensitivity towards electrode materials, which all contribute to reduce the cost of production [1]. The presence of mobile ions in active layers make the device insensitive towards the work function of electrode materials and hence enable LECs the use of inert metals (such as Au, Ag or Al) as cathode. In OLEDs, metals with lower work function are used as electrode materials and this makes it a necessity to undergo encapsulation to protect the device from air and moisture.

The prototype of light emitting electrochemical cells was introduced by A. J. Heeger in 1995 which revolutionized the research of organic electronic materials. First LEC employed a blend of conjugated polymer, an ion conducting polymer and a metallic salt as

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*Address correspondence to Youngson Choe, Department of Chemical Engineering, Pusan National University, Jang-jeong Dong, Geum-jeong Gu, Busan 609-735, South Korea. Tel.: +8251-510-3562; Fax: +8251-512-8634. E-mail: choe@pusan.ac.kr the active material [2]. In 1996, LECs based on ionic transition metal complexes (iTMC) were introduced by Rubner *et al.* who employed ruthenium complexes as active material which was accepted widely among organic electronics researchers [5]. Light emitting electrochemical cells based on iTMC has several advantages due to intrinsic ionic nature over the polymer based devices which includes the use of single material as the active layer. However, in conjugated polymer based LEC materials, because of its inherent electrical neutrality, supporting electrolyte and inorganic ions must be used for smooth charge injection which triggers phase separation in most occasions. The iTMCs are potentially efficient due to phosphorescent nature and their synthesis is comparatively simple along with relatively easy purification [6–8]. In case of fluorescent dye molecules, emissions were induced from the singlet excited state which represent a small fraction of the total excited state population whereas the phosphorescent materials are capable of achieving improved light efficiencies by harvesting both singlet and triplet excited states [9]. Moreover, the thermal and photophysical stabilities of iTMCs are remarkable and show the potential as a future lightening material.

Slinker *et al.* in 2004 was the first to put forward metal complexes based on iridium for light emitting applications [10]. Even though most of the recent literature reports focused on iTMCs are based on ruthenium, osmium, copper, and iridium complexes, materials based on iridium are particularly interesting in terms of color tuning owing to the pronounced ligand-field-splitting effects [11–15]. In this study, light emitting electrochemical cells based on these complexes were fabricated and electroluminescent properties were investigated. The cationic iridium complexes used in this study are $Ir[(ppy)_2(dbphen)]PF_6$ and $Ir[(ppy)_2(dpphen)]PF_6$. LECs were fabricated using as synthesized $Ir[(ppy)_2(dbphen)]PF_6$ resulted in green emission (λ_{max} 540 nm) with a lower turn on voltage and maximum luminescence of 2100 cd/m^2 at 9.0 V. Device based on $Ir[(ppy)_2(dpphen)]PF_6$ also emits green light (λ_{max} 540 nm) with a maximum luminescence 3150 cd/m^2 at 9.0V. In order to improve the device performance, tetrabutylammonium triflate ion conductor was incorporated with active layer and the performance was evaluated.

Experimental

Materials and Device Fabrication

All reagent were purchased from Sigma Aldrich, Alfa-Aeser while PEDOT:PSS obtained from HC Stark Germany. All reagents were used as received without further purification. The architecture of LECs used in this study was depicted in Figure 1. Ionic iridium complexes with phenanthroline derivatives as the ancillary ligands have been synthesized

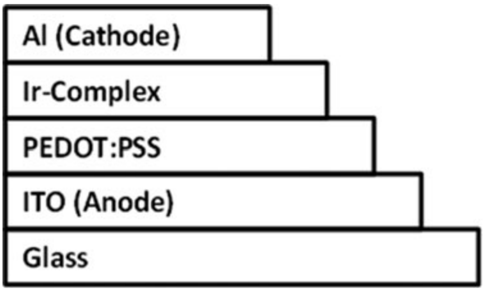

Figure 1. Device structure of light emitting electrochemical cells.

and the structures of iTMCs used was portrayed in Figure 2. Complexes were 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 the addition of ancillary ligand which is a derivative of phenanthroline followed by ion exchange with ammonium hexafluorophosphate [16]. ^{1}H and ^{13}C NMR were recorded on a Bruker 500 MHz spectrometer. UV-visible absorption spectra were measured on 8453 UV-visible Agilent spectrophotometer. PL spectra were obtained from F-7000 FL spectrophotometer. The current density, luminescence and voltage characteristics of the LEC device were measured using a Keithley 2400 source meter calibrated with silicon photodiode. An Avantes luminence spectrometer was used to record EL spectrum and CIE coordinates.

ITO-coated glass were extensively cleaned in a mixture of alcohol (isopropyl alcohol, and ethyl alcohol) and acetone in 1:1:1 ratio by ultrasonication for 45 minutes and dried in vacuum oven at 100°C for 1 h. PEDOT:PSS buffer layer was spin coated on ITO at spin rate of 2000 rpm for 20 s and annealed on a hot plate at 130°C under vacuum. Thin film of luminous layer was then spin coated on top of annealed PEDOT:PSS layer using the complex solution in acetonitrile at a concentration 20 mg/ml and again dried on under vacuum at 80°C for 20 min. Then a thin layer of aluminium (thickness 100 nm) cathode was vacuum deposited on top of luminous layer under ultra-vacuum with a deposition rate of 3.0~0.7 Å/s.

Synthesis

Tetrakis(2-phenylpyridine-C^2,N′)(μ-dichloro)diiridium

The precursor of ionic transition metal complexes was synthesized following procedure reported elsewhere [17, 18]. Iridium trichloride hydrate (0.39 g, 1.1 mmol) dissolved in distilled water (10 ml) was added to 2-phenylpyridine (0.37 g, 2.4 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed under nitrogen for 24 h and then cooled down to room temperature. The yellow solid was collected by filtration and the precipitate was thoroughly washed with ethanol and re-dissolved in dichloromethane. The residual inorganic salt precipitated was removed by filtration and to the filtrate, n-hexane was added. The mixture was concentrated under vacuum and cooled down to give crystals of $[Ir(ppy)_2Cl]_2$, which

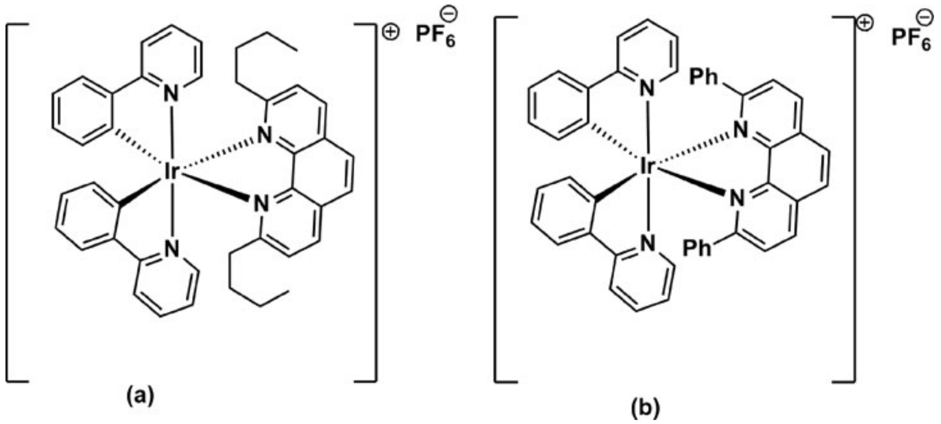

Figure 2. Structure of iTMC (a) $[Ir(ppy)_2(dbphen)]PF_6$, (b) $[Ir(ppy)_2(dpphen)]PF_6$.

was again filtered and dried under vacuum for overnight to yield 0.27 g of yellow crystals. Yield (46%).

[Ir(ppy)$_2$(dbphen)]PF$_6$ (Complex 1)

To a mixture of tetrakis(2-phenylpyridine-C^2,N′)(μ-dichloro)diiridium (1) (0.07 g, 0.06 mmol) and 2,9-dibutyl-1,10-phenanthroline (0.04 g, 0.14 mmol) were added 20 ml ethylene glycol and refluxed under nitrogen for 16 h. The cooled reaction mixture was then added to water and extracted three times with ether to remove ethylene glycol. A concentrated solution of ammonium hexaflurophosphate in water was slowly added into the aqueous layer, yielding a colored suspension, which was separated by filtration [19] and dried under vacuum at 80°C for 24 h to give the title product with a yield of 82%. (500 MHz, CD_2Cl_2) d: 8.49 (d, J = 8.43 Hz, 2H), 8.23 (s, 2H), 7.94 (d, J = 7.95 Hz, 2H), 7.75 (t, J = 8.94 Hz, 2H), 7.68 (d, J = 8.44 Hz, 2H), 7.65 (d, J = 9.10 Hz, 2H), 7.42 (d, J = 8.03 Hz, 2H), 6.98 (t, J = 8.40 Hz, 2H), 6.84 (t, J = 7.36 Hz, 2H), 6.79 (t, J = 8.3 Hz, 2H), 6.14 (d, J = 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) d: 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.

[Ir(ppy)$_2$(dpphen)]PF$_6$ (Complex 2)

Syntheis procedure for Complex 2 is same as that of Complex 1. In case of this complex, $[Ir(ppy)_2Cl]_2$ (0.7 g 0.07 mmol) and 2,9-diphenyl-1,10-phenanthroline (0.04g, 0.14 mmol) were used to yield 0.10 g (78.5%) of complex 2. ^{1}H NMR (500 MHz, CD_2Cl_2) d: 8.61 (d, J = 8.23 Hz, 2H), 8.23 (s, 2H), 7.74 (t, J = 7.53 Hz, 2H), 7.66 (d, J = 5.27 Hz, 4H), 7.64 (d, J = 3.14 Hz, 2H), 7.62 (d, J = 3.46 Hz, 2H), 7.09 (d, J = 7.79 Hz, 2H), 7.03 (t, J = 5.91 Hz, 2H), 6.93 (t, J = 6.18 Hz, 2H), 6.76 (t, J = 7.68 Hz, 2H), 6.58 (s, 4H), 6.53 (t, J = 7.23 Hz, 2H), 6.20 (t, J = 8.47 Hz, 2H), 5.24 (d, J = 7.73 Hz, 2H) ^{13}C NMR (126 MHz, CD_2Cl_2) d: 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.

Results and Discussion

The UV-vis absorption spectra of the complex solution in acetonitrile are shown in Figure 3. An intense absorption band found between 250–300 nm was 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 cyclometallated ligands. Absorption observed beyond 300 nm to the visible region were relatively weak owing to metal-to-ligand charge-transfer transitions (MLCT, arising from the excitation from the filled t_{2g} orbital of Iridium ion to the vacant π^* orbital of the phen ligand) and ligand-to-ligand charge-transfer transitions (LLCT) [20, 21].

Photoluminescence (PL) emission spectra of complex solution in acetonitrile were displayed in Figure 4. The PL spectra of complexes 1 and 2 have shown a maximum at 540 and 600 nm respectively which was in the green region. PL spectrum of complex with aryl substitution on phenanthroline was red shifted (60 nm) with respect to that of complexes with alkyl substitution. All complexes have same cyclometallated ligands, therefore the results demonstrate that presence of aryl substituents causes more stabilization to LUMO

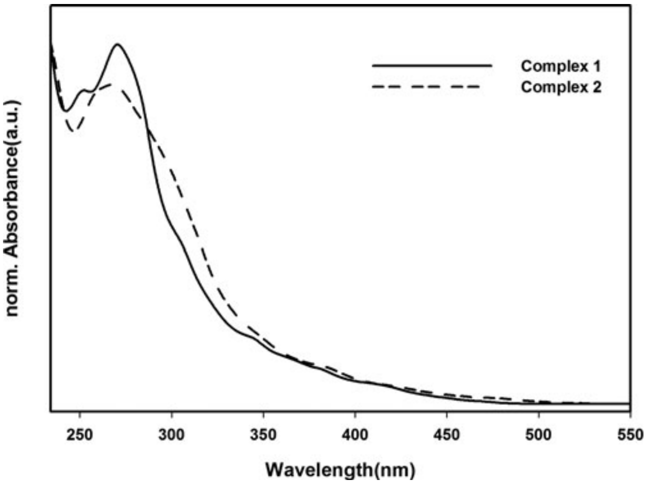

Figure 3. UV-Visible absorption spectra of complex solutions in acetonitrile.

on comparison to alkyl groups and thereby induces red shift. This allows tuning the emission color of cationic iridium complexes through modification of the ancillary ligands.

To study electroluminescence (EL) properties, the light emitting electrochemical cells were fabricated using complexes with the structure indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)(PEDOT:PSS)/cationic iridium complex/Al. The buffer layer of PEDOT:PSS were incorporated between ITO and active layer to smoothen the anode and to facilitate hole injection [22]. Figure 5 shows electroluminescence (EL) emission spectra of the light emitting electrochemical cells. The EL spectra are similar to that of PL spectra of the complex solutions in acetonitrile. LECs based on complexes 1 and 2 exhibited green light with CIE coordinates (0.37,0.57) and (0.55,0.44) respectively. Complex 2 electroluminesence rather red shifted to that of Complex 1, which was attributed to the chemical modifications on the penanthroline ligands. It is believed

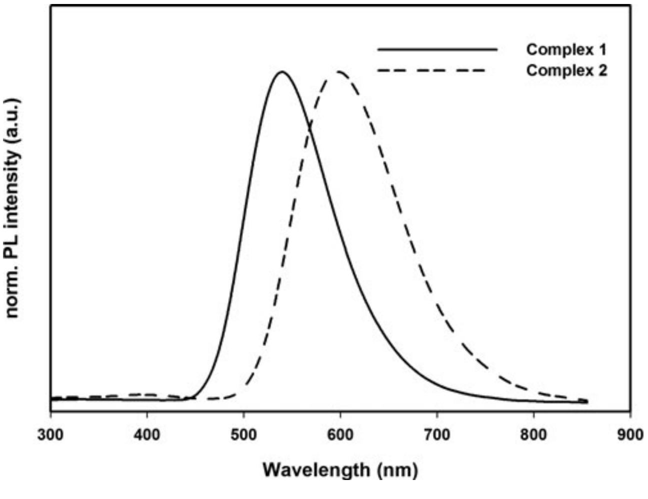

Figure 4. Photoluminescence spectra of complex solutions in acetonitrile.

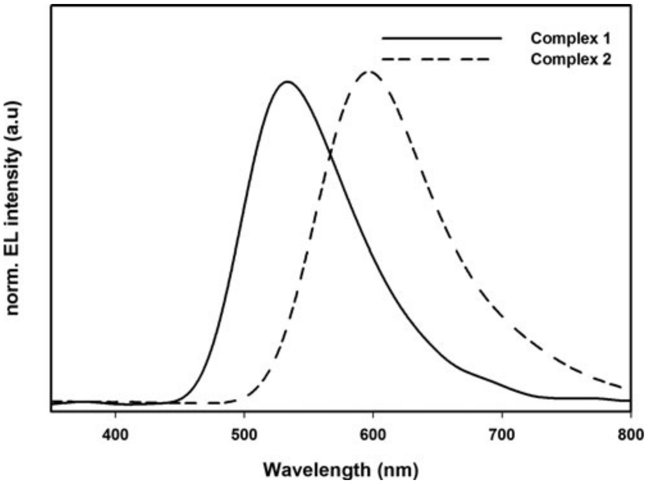

Figure 5. Electroluminescence spectra of LECs using complexes 1 and 2 as the active material.

that the lowest unoccupied molecular orbital (LUMO) located on the ancillary ligands was stabilized by the phenyl substituents on the phenanthroline ligand, resulting in the greater reduction of the energy of HOMO and LUMO than the device based on Complex 1. In order to improve the device performance, an ion conductor TBAOTf was blended with iTMC and active layer was fabricated. The emission color of the device was unaffected by the presence of ionic conductor whereas the electrical conductivity of the device improved as expected.

To study the electrical properties of these complexes, luminescence and current density were measured against voltage from 0–10V. From Figure 6 and 7, it is observed that both luminance and current density of the devices rise slowly on the application of an increasing forward bias to the devices which is a typical characteristics of light emitting electrochemical cells. The presence of ion conductor (TBOTf) dramatically changed the

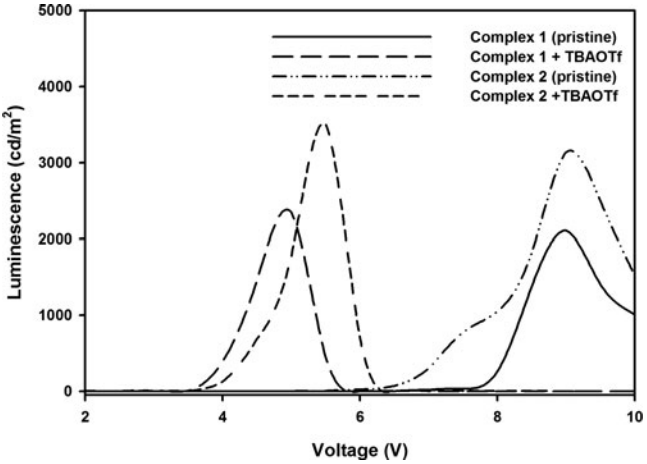

Figure 6. Luminescence versus voltage curves of LECs based on complexes 1 and 2 with and without ionic conductor (TBAOTf).

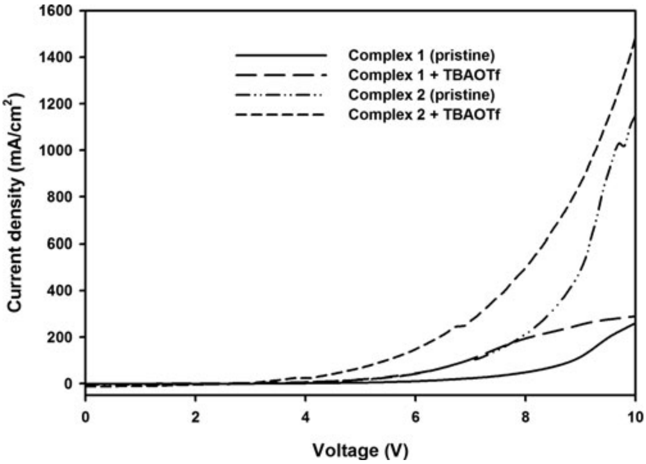

Figure 7. Current density versus voltage curves of LECs based on complexes 1 and 2 with and without ionic conductor (TBAOTf).

electro-optical properties of both complexes by producing more ions in the active material which thereby facilitates more easy thin film conduction. This observation supports the operation mechanism of the devices, where the first step on application of forward bias is the rearrangement of ions in the devices towards the respective electrodes which enhances the charge injection process [23]. The exponential enhancement in the current density above 6.0 V is due to the formation of electrical double layer and whereby accelerating the charge injection and production of both charge carriers (electron and holes). The luminance also increases with respect to voltages due to the increased charge injection and thereby generating the p-i-n junction where the electron and holes recombine to form excimers which de-excite their energy in the form of light. Even though high luminance is obtained by increasing voltage, after reaching a maximum, luminance then gradually decrease due to the more extensive exciton quenching [24]. When we compare all device performances, device with complex and ion conductor are evidently better than the devices based on pristine complexes. The device based on Complex 1 give maximum luminance of 2100 cd/m^2 whereas Complex 2 gives 3150 cd/m^2 at 9.0 V. On the addition of ion conductor, device based on Complex 1 gives maximum luminescence at 3100 cd/m^2 at 5.0 V whereas Complex 2 give 3500 cd/m^2 at 5.5 V. The highest current efficiency of 1.9 cd/A and 0.6 cd/A has achieved for complex 1 and 2 respectively, while the addition of ionic conductor to the active layer enhanced current efficiency to 3.0 cd/A (complex 1) and 2.6 cd/A (complex 2). 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 on to the ligands. These bulky groups act as the physical barrier that protects the negative charge injected in the iridium complexes. This hydrophobic shielding also hinders the attack of moisture and thus diminishes the possibility of non-radiative intermolecular charge recombination [25].

Conclusion

In summary, we investigated the influence of ionic conductor (TBAOTf) on the active layer of ionic iridium based light emitting electrochemical cells. We have synthesized two cationic iridium complexes named $[Ir(ppy)_2(dbphen)]PF_6$ (Complex 1) and $[Ir(ppy)_2(dpphen)]PF_6$

(Complex 2) and characterized by spsectroscopic and electroluminescent instrumental methods. With phenyl groups in the ancillary ligand, Complex 2 has significantly stabilized LUMO orbital, and therefore, it shows more red shifted emission spectra than Complex 1. These complexes have been used as the emissive materials in LEC employing air stable devices. With the incorporation of ionic conductor material, devices based on both complexes dramatically showed better electro-optical properties. Our work put forward a simple way of enhancing the device properties by introducing ionic conductor materials in the active layer of LEC and thereby tune the electrical properties of iTMC based light emitting electrochemical cells.

Funding

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