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Iridium-based light-emitting electrochemical cells containing ionic liquids in the luminous layer

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ABSTRACT

To fabricate transition metal complex-based LECs (light-emitting electrochemical cells), ([Ir(ppy)$_2$(5,6-dime-1,10-phenthroline)]PF$_6$ was synthesized and used as a luminous material and ILs (ionic liquids) were incorporated into a luminous layer, in which two types of ionic liquid were used; 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$). ILs were added to a [Ir(ppy)$_2$(5,6-dime-1,10-phenthroline)]PF$_6$ luminous layer to improve ionic conductivity and light intensity. Both ILs significantly increased the current density and luminance. Due to the small molecule of BF$_4^-$, turn-on time was reduced and ionic conductivity was increased. However, the device stability was sacrificed. High current efficiency of 34.5 cd/A was investigated at 7 V of BMIMPF$_6$-doped luminous layer. The LECs based on [Ir(ppy)$_2$(5,6-dime-1,10-phenthroline)]PF$_6$ gave yellow emission color when ILs were added into light-emitting layer, and no significant change of color has been found in this study.

1. Introduction

Among the electroluminescent devices, solid-state light-emitting electrochemical cells (LECs) are promising alternatives to replace organic light-emitting devices (OLEDs). In their simplest film-type configuration, conducting polymers or ionic transition metal complexes are placed between two electrodes [1–3]. When the external electric field is applied, mobile ions existing in luminous layer lower the energy barrier, so LECs are insensitive to work function of electrodes [1]. Over the several benefits of LECs, a few critical drawbacks have been occurred. Due to slow mobility of mobile ions in the luminous layer, slow response time was exhibited. For improving ion conductivity in conductive polymeric materials, ionic liquids (ILs) can be used by simply adding to active materials. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$) is a widely used ionic liquid because of its high conductivity and stability [4].

ILs are attractive because of their chemical, physical or electrical properties such as low volatility, non-flammability, high ionic conductivity and liquid-phase stability at high temperature [5]. The LECs containing ILs exhibit much faster response and much higher power efficiency than those of identical devices which are not containing ILs in the luminous layer. LECs containing ionic liquids based on imidazolium salt as electrolytes showed fast response and operation stability [6]. Implying small counterions like BF$_4^-$ instead of PF$_6^-$, rather fast turn-on time can be predictable because mobile ions carry holes and electrons [7].

In this study, [Ir(ppy)$_2$(5,6-dimephen)]PF$_6$ was synthesized as a luminous material [8]. Ir complex was mixed with ILs to fabricate devices with the structures of ITO/PEDOT:PSS/[Ir(ppy)$_2$(5,6-dimephen)]PF$_6$:1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$)/Al and ITO/PEDOT:PSS/[Ir(ppy)$_2$(5,6-dimephen)]PF$_6$:1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$)/Al, where the PEDOT:PSS layer was added to smooth the anode surface and the ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$), were added to the luminous layer to shorten the response time of LECs. PEDOT:PSS is widely used as a buffer layer as well as a hole injection layer in OLEDs and photovoltaic cells. It enhances hole-injection from the anode and smoothen the surface between ITO and luminous layer [9].

2. Experimental

2.1. Preparation of luminous material

Iridium trichloride hydrate (298.58 g/mol, anhydrous base), 2-phenylpyridine (155.20 g/mol), 5, 6-dimethyl-1,10-phenanthroline (208.26 g/mol) and two types of ionic liquids; 1-butyl-3-methylimidazolium hexafluorophosphate (284.18 g/mol) and 1-butyl-3-methylimidazolium tetrafluoroborate (226.02 g/mol) were purchased from Aldrich. Luminous material was prepared

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from 2-phenylpyridine as cyclometalated 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 phenanthroline derivative, and ion exchange with ammonium hexafluorophosphate. Iridium complex[iridium(2-phenylpyridine)$_2$(5,6-dimethyl-1,10-phenanthroline)]hexafluorophosphate and each of ionic liquids were dissolved in acetonitrile (20 mg/ml, 99.5% pure, Katayama Chemical Co. Ltd.) by stirring at 40 °C for 1 h with a molar ratio of 4:1, respectively. The solution was filtrated through Micropore (pore-size: 20 nm) syringe filter.

2.2. Synthesis of tetrakis(2-phenylpyridine-C^2,N′)(μ-dichloro)diiridium

The precursor, ionic transition metal complex, was synthesized according to the literature [8,10]. Iridium trichloride hydrate (0.5 g, 1.229 mmol) dissolved in water (13 ml) was added to 2-phenylpyridine (0.974 g, 6.276 mmol) in 2-ethoxyethanol (39 ml). The mixture was refluxed for 24 h under nitrogen gas, and then cooled down to room temperature, the yellow solid was collected on a membrane filter. The resulting precipitated was washed with ethanol (77.5 ml) and acetone (77.5 ml) and dissolved in dichloromethane (97 ml) and filtered to remove residual inorganic salts. Toluene (32 ml) and hexanes (13 ml) were added to the filterate, which was then reduced by evaporation to 50 ml, and cooled down to give crystals of $[Ir(ppy)_2Cl]_2$. Yield: 0.3221 g (42%) ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 9.25 (d, J = 5.0 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.56 (dd, J = 7.8 Hz, 1H), 6.83 (m, 2H), 6.60 (t, J = 7.8 Hz, 1H), 5.87 (dd, J = 7.8 Hz, 0.8, 1H) [8].

2.3. Synthesis of bis(2-phenylpyridine-C^2,N′)(5,6-dimethyl-1,10-phenanthroline-N,N′)iridium(III) hexafluorophosphate

A yellow suspension of tetrakis(2-phenylpyridine-C^2,N′)(μ-dichloro)diiridium(III) (0.100 g, 0.0933 mmol, 1 equiv.) and 5,6-dimethyl-1,10-phenanthroline(0.0389 g, 0.1866 mmol, 2 equiv.) were dissolved in CH_2Cl_2–MeOH(15 ml, 2:1, v/v) and refluxed at 45 °C for 5–6 h. The orange solution obtained was cooled to room temperature, and a 10-fold excess of ammonium hexafluorophosphate was added into it. The reaction mixture was stirred for 15 min and cooled to give yellow suspension [11]. Yield: 0.1439 g (90%) ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.78 (d, J = 5.00 Hz, 2H), 8.32 (d, J = 5.00 Hz, 2H), 8.00 (d, J = 10.00 Hz, 2H), 7.81 (m, 6H), 7.34 (d, J = 5.0 Hz, 2H), 7.16 (t, J = 7.5 Hz, 2H), 7.03 (t, J = 7.5 Hz, 2H), 6.87 (t, J = 8.33 Hz, 2H), 6.46 (d, J = 5.0 Hz, 2H), 5.36 (d, J = 5.0 Hz, 2H), 2.90 (s, 6H) [11].

2.4. Device fabrication and characterization

ITO-patterned glass substrates were cleaned by ultrasonication. Prior to the deposition of active layer, PEDOT:PSS as a buffer layer material was spin-coated on to the ITO glass and annealed on the hot plate for an hour at 120 °C under vacuum. Luminous layer materials containing ionic iridium complex and ionic liquids were spin-coated from acetonitrile solution (20 mg/ml) and annealed on the hot plate under vacuum. Then, aluminum electrode was deposited on to the top of the substrate. The thickness of electrode was 100 nm and the deposition rate was controlled by 3.0–7.0 Å/s. ^{1}H spectra were recorded on 500 MHz superconducting FT-NMR Spectrometer (Unity-Inova 500). Absorption spectra of thin films was measured using UV–vis spectrometer (Lambda 20, Perkin Elmer) in the range of 250–800 nm. Photoluminescence intensity was measured using photoluminescence spectrometer (Labram HR-800, Horiba Co.). Ionic conductivity of luminous layer was measured by a four-point probe (CMT-SR1000N). Atomic force microscopy (L-trace II with nanonavi, Sii NanoTechnology Inc.) was used in contact mode with 1 Hz scan speed to analyze the surface morphology and roughness at room temperature.

3. Results and discussion

Three types of LECs were fabricated; a LEC without using ILs in the luminous layer, a LEC containing 4:1 molar ratio of Ir

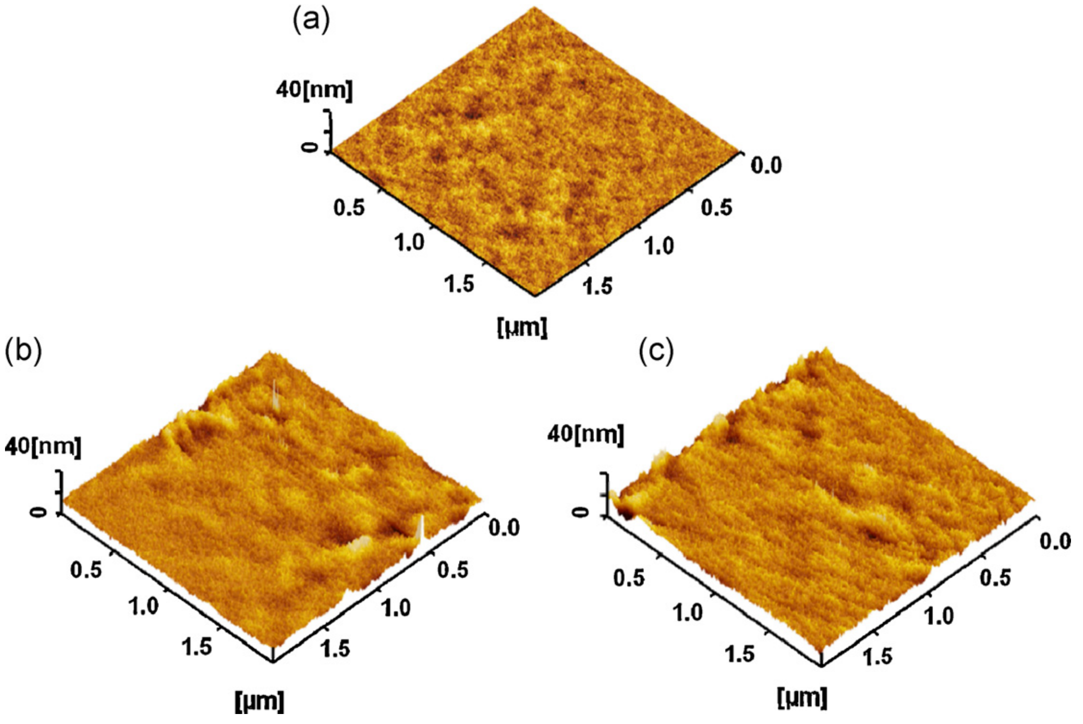

Fig. 1. AFM images of LECs with the luminous layer of (a) $[Ir(ppy)_2(5,6\text{-dimephen})]PF_6$, (b) $[Ir(ppy)_2(5,6\text{-dimephen})]PF_6$ containing $BMIMPF_6$, and (c) $[Ir(ppy)_2(5,6\text{-dimephen})]PF_6$ containing $BMIMBF_4$.