



Flexible blue-green and white light-emitting electrochemical cells based on cationic iridium complex



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ABSTRACT

In this paper, we demonstrated a simple solution fabrication route to realize flexible single layer light-emitting electrochemical cells (LEC) by employing cationic iridium complexes. The flexible LEC show the efficiency as high as 10.71 cd/A at 5 V and 9.8 cd/A at 7 V for blue-green and white electroluminescence, respectively. Bending test was also performed for the as-fabricated flexible LEC, and they exhibited an excellent light-emitting stability during the multiple mechanical bending at a 10 mm curvature radius.

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1. Introduction

Recently, light-emitting electrochemical cells (LEC) based on ionic iridium can be used as new-type display and lighting sources because of their excellent characteristics [1–3]. In comparison with organic light-emitting diodes (OLEDs), LEC are solution processable, and do not rely on air-sensitive charge-injection layers or are insensitive to the work function of electrodes [4,5]. There are two types of LEC that could be named by employing the luminescent material, i.e., namely polymer-LEC (PLEC) [6–8] and ionic transition metal complex (iTMC)-LEC [7–13]. Nowadays, the ionic biscyclo-metallated iridium (III) complexes are used generally in iTMC-LEC [11,14]. Iridium (III) complexes in terms of their short excited-state lifetimes, high thermal stability, excellent color tuning through changing its' structure and high photoluminescence quantum yields have emerged as the promising materials for LEC applications [15–22]. However, high efficiency blue LEC is rarely reported and it is desired for white light emission. In addition, although some promising progress involving cationic iridium complexes to realize LEC have been reported in recent years, highly efficient flexible LEC are still very scarce and extremely desired.

Generally, the ligands of cationic iridium complexes can be divided into cyclometalated ligand (C^N) and ancillary ligand (N^N). The lighting color of the device can be controlled by adding functional substituent groups on the cyclometalated ligand, whereas the efficiency and lifetime of device can be improved by introducing steric hindrance groups on the ancillary ligand. The cyclometalated and ancillary ligands can be separately substituted with electron withdrawing and electron donating groups in heteroleptic complexes, which enables deliberate control over the excited state [23]. Therefore, in this work, we demonstrate the simple solution method to fabricate high efficiency blue-green and white flexible LEC. The blue-green flexible LEC could be realized by employing cationic iridium complex with 1-(2,4-difluorophenyl)-1H-pyrazole (dfppz) as the cyclometalated ligand and 2-(5-methyl-2-phenyl-2H-1,2,4-triazol-3-yl)pyridine (Mptz) as the ancillary ligand on flexible indium-tin-oxide (ITO) coated polyethylene terephthalate (PET) substrate. High efficiency of 10.72 cd/A at 5 V was achieved for the blue-green LEC with Commission International De l'Eclairage (CIE) coordinates of (0.25, 0.48). By doping a small amount of red-emitting ionic complex into the blue-green LEC, white LEC were fabricated with CIE coordinates of (0.43, 0.42), a color rendering index (CRI) up to 80 and a peak current efficiency of 9.8 cd/A at 7 V.

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2. Experimental details

2.1. Synthesis of the iridium (III) complexes

The cationic iridium complexes used in this study were $[\text{Ir}(\text{dfppz})_2 \text{Mptz}]\text{PF}_6$ (denoted as complex B1) and $[\text{Ir}(\text{pq})_2 (\text{Mptz})]\text{PF}_6$ (denoted as complex R1). Fig. 1 (a) shows the chemical structures of the cationic iridium complexes. In case of complex B1, the cyclometalated chloride-bridged dimers were synthesized by refluxing $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with the corresponding cyclometalated ligand (1-(2,4-difluorophenyl)-1H-pyrazole, dfppz) in the mixture of 2-ethoxyethanol and water. The synthesis of complex R1 was similar to that of complex B1 except that the organometalated dimmer 1-(2,4-difluorophenyl)-1H-pyrazole (dfppz) was replaced with 1-phenylisoquinoline (pq).

2.2. Fabrication and characterization of LEC devices

The stacking device structure consists of Al(100 nm)/Complexes/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/ITO/PET, as shown in Fig. 1(b). The flexible ITO/PET substrate was purchased from Csgolding in Shenzhen, China with sheet resistance of 300 Ω/sq . Prior to device fabrication, ITO electrodes coated on PET substrate were patterned using scotch tape followed by etching in ferric chloride (FeCl_3) and diluted hydrochloric acid to form $5 \times 10 \text{ mm}^2$ active light-emitting area. Then, the patterned substrate was cleaned with ultrasonic treatment for 20 min sequentially in acetone, ethanol, deionized water and dried in oven. Subsequently, oxygen plasma treatment was performed for 10 s to improve the contact angle before PEDOT:PSS was spin-coated on ITO/PET substrate at 3000 rpm for 50 s. The spin-coated PEDOT:PSS layer was annealed on a hot plate at 120 $^\circ\text{C}$ for 30 min in ambient conditions [15,20,24,25]. The light-emitting mixture was prepared by dissolving 20 mg/ml cationic iridium complexes and 10 mg/ml 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM- PF_6) in 1 ml acetonitrile. The white light-emitting mixture was the mixed solutions of complexes B1 and R1 and BMIM- PF_6 . The mixture was stirred for 2 h at room temperature before spin coating on top of PEDOT:PSS layer at 3000 rpm for 50 s, and heated at 70 $^\circ\text{C}$ for 30 min in ambient conditions. Finally, an aluminum cathode (100 nm) was thermally evaporated in vacuum chamber below 3×10^{-3} Pa.

The electroluminescence (EL) and photoluminescence (PL) spectra of the as-fabricated LECs were recorded with Hitachi F-4600 fluorescence spectrophotometer. Luminance intensity and CIE coordinates were measured using Topcon SR-3A spectroradiometer. Current-voltage (I - V) and current-time (I - t) measurements were performed by using semiconductor characterization system (Keithley 4200-SCS). All tests were carried out in ambient conditions.

3. Results and discussion

It's believed that the LEC could be fabricated for better performance with device structure as shown in Fig. 1(b) by applying the optimum experimental parameters. Detailed electrical characteristics of the LEC are summarized in Table 1. PL and EL spectra of the blue-green LEC were conducted as shown in Fig. 2(a). The EL spectrum is red-shift to 503 nm in comparison with the PL spectrum of the light-emitting layer. Bolink et al. have reported the similar phenomenon, the reason might be attributed to the change of complex molecule's environment that yielded the change of excited states [26,27]. The device based on complex B1 emitted light in the blue-green region with CIE coordinates $x = 0.25$ and $y = 0.48$.

As shown in Fig. 2(b), at 5 V, it required 23 min for complex B1 to reach a maximum brightness of 36.5 cd/m^2 with a peak current efficiency of 10.72 cd/A . Meanwhile, it required 12.6 min for complex B1 to reach a maximum brightness of 90 cd/m^2 with a peak current efficiency of 10.71 cd/A at 6.5 V, then decay with time. Both the current density and brightness increase gradually with time at first, then decay after reaching its maximum value at a constant voltage, which is a typical characteristic of LECs [28]. Before the current reaches a steady value, the injection rate may keep increasing due to unbalanced carrier injection induced by the high electron mobility of the iridium complexes, which would lead to exciton quenching [29]. Furthermore, it also could be related to the degradation of the emissive material during the LEC operation [10,29]. As bias voltage increases, the mobile ions in the active layer will move faster and accumulate near the electrode interface, which facilitates formation of ohmic contacts with the electrodes. Thus, the device response will be shortening at a higher bias voltage, consequently leading to higher current density and higher brightness. However, the improved performance is obtained at the expense of device stability. As shown in Table 1, the device lifetime (time to reach half of the maximum luminance) decreased to 38 min at 6.5 V as it is possible associated with the stability of the light-emitting materials [30].

On the basis of the efficient blue-green LEC, white LEC was fabricated by doping the red-emitting complex R1 into the active layer. The device structure is ITO/PEDOT:PSS/ $[\text{Ir}(\text{dfppz})_2 \text{Mptz}]\text{PF}_6$: $[\text{Ir}(\text{pq})_2 (\text{Mptz})]\text{PF}_6$:BMIM PF_6 (molar ratio 1:X:0.2)/Al. As shown in Fig. 3, we can adjust the doping concentration of complex R1 to change the relative intensity of red component. With the reduction of the concentration of complex R1, the CIE is shifted towards the blue region. When the molar ratio between complex B1 and complex R1 is 1:0.0167 (device 1.67%), white light emission with the CIE coordinates of (0.42,0.43) is obtained, which is closest to white light. So this doping concentration is selected for achieving white emission. Fig. 4(a) shows the EL spectrum of the white LEC, along with the PL spectrum of the light-emitting layer. The relative intensity of the red component to the blue one in the PL spectrum is

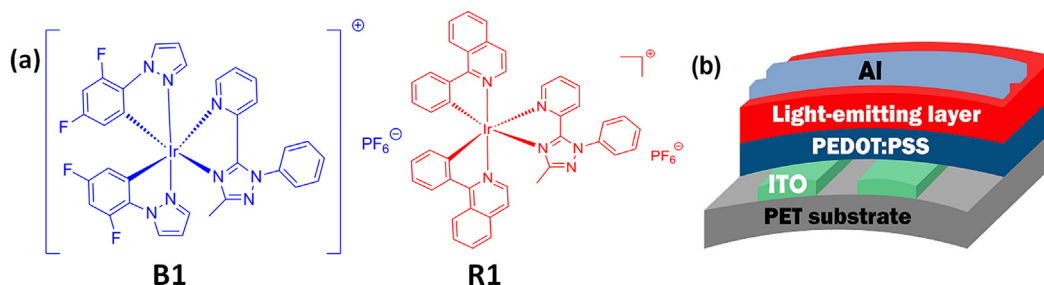


Fig. 1. (a) Chemical structure of the cationic iridium complexes. (b) Configuration schematic of the as-fabricated LEC.

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