Organic Electronics 11 (2010) 1185–1191

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Highly efficient solution-processed blue-green to red and white light-emitting diodes using cationic iridium complexes as dopants

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ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 16 April 2010
Accepted 19 April 2010
Available online 27 April 2010

Keywords:
Organic light-emitting diode
Solution process
Cationic iridium complex
White light emission

ABSTRACT

Using cationic iridium complexes as dopants and poly(*N*-vinylcarbazole) as host, highly efficient blue-green to red and white organic light-emitting diodes (OLEDs) have been fabricated by a solution process. In single-layer devices, electron-trapping by complexes dominates the device performance. Complexes with cyclometalated 2-phenylpyridine ligands show better device performance compared with those containing cyclometalated 2-(2,4-difluorophenyl)pyridine ligands. With the addition of an electron-transporting/exciton-blocking layer, the devices show improved performances, achieving peak current efficiencies of 24.3, 25.3, 20.5, and 4.2 cd A^{-1} for the blue-green, green, yellow, and red electroluminescence, respectively. White OLEDs have been fabricated by co-doping blue-green and red-emitting complexes, attaining a peak current efficiency of 20.7 cd A^{-1}. Thus, cationic iridium complexes can be used as dopants in solution-processed OLEDs, as well as in light-emitting electrochemical cells, to achieve highly efficient blue-green to red and white electroluminescence.

1. Introduction

Cationic iridium complexes have been attracting widespread interest in recent years because of their easy preparation process, rich photophysical and electrochemical properties, and good solubility in polar solvent or even in aqueous media. In the field of organic electronics, cationic iridium complexes have been widely used as emitting complexes in light-emitting electrochemical cells (LECs) [1–7]. Using carefully designed cationic iridium complexes, highly efficient blue-green to red and white LECs have been obtained [2–5]. Nevertheless, the active layers of LECs are comprised of neat complexes, which lead to severe excited-state quenching [6,7]. Moreover, LECs suffer from slow response and limited device stability compared with conventional organic light-emitting diodes (OLEDs) [1–4].

In OLEDs, mostly neutral iridium complexes are used as dopants dispersed in host matrices [5]. Both singlet and triplet excitons are harvested by the phosphorescent iridium complexes. For this reason, nearly 100% internal quantum efficiency can be achieved [5]. However, cationic iridium complexes, despite possessing high phosphorescent efficiencies, tunable light emission color, and excellent redox stability, have seldom been used as dopants in OLEDs [8–11]. Severe excited-state quenching that occurs in LECs is expected to be significantly suppressed when cationic iridium complexes are used as dopants in OLEDs. In addition, fast electroluminescent (EL) response will be achieved when cationic iridium complexes are used as dopants in OLEDs, because the migration of ions, as is the case in LECs, is no longer necessary in OLEDs. Plummer et al. reported yellow-emitting polymer OLEDs with a peak current efficiency of 22.5 cd A^{-1} using a cationic iridium complex as the dopant [8]. Wong et al. reported yellow-emitting, multi-layered, small-molecule OLEDs using sublimable cationic iridium complexes as dopants [9]. These devices showed a peak current efficiency of 19.7 cd A^{-1} [9]. Byun et al. reported red-emitting polymer OLEDs with a peak current efficiency of 12.6 cd A^{-1} using a zwitterionic

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doi:10.1016/j.orgel.2010.04.018

iridium complex as the dopant [10]. Recently, we reported blue-green-emitting polymer OLEDs using cationic iridium complexes as dopants [11]. The devices showed a peak current efficiency of 20.2 cd A^{-1} [11]. Nevertheless, a systematic evaluation of the use of cationic iridium complexes in OLEDs has not been reported, and white OLEDs using cationic iridium complexes as emitters have not yet been explored.

In this paper, a systematic investigation on blue-green to red and white OLEDs is carried out using cationic iridium complexes as dopants and poly(*N*-vinylcarbazole) (PVK) as the host. These cationic iridium complexes have been previously developed and used in highly efficient LECs [7,12]. Due to the low sublimability of cationic iridium complexes, light-emitting layers of OLEDs have been deposited from cost-effective solution processes.

2. Experimental

2.1. Materials

The cationic iridium complexes (Scheme 1): Irdf-pyim, Ir-pzpy, Irdf-pybi, Ir-pyim, Ir-pybi, and Ir-qlbi, which are blue-green-emitting (489 nm), blue-green-emitting (475 nm), green-emitting (528 nm), yellow-green-emitting (554 nm), orange-emitting (588 nm), and red-emitting (627 nm) in CH_3CN solutions, were prepared in the laboratory and crystallized from CH_2Cl_2/hexane before use [7,12]. Poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate) (PEDOT:PSS) was purchased from H.C. Starck, Inc. PVK was purchased from TCI, Inc. And 1,3-bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]benzene (OXD-7), 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBI), and bis(2-methyl-dibenzo[f,h]quinoxalinato-*N*,C2′)-iridium(III)(acetylacetonate) [Ir(MDQ)$_2$(acac)] were purchased from Nichem Fine Technology Co., Ltd. All materials were used as received without further purification.

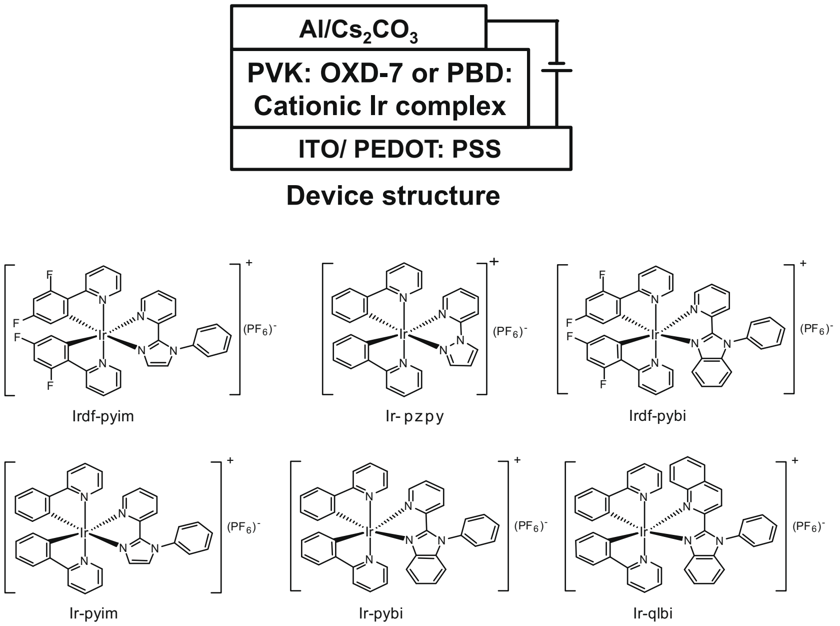
2.2. Fabrication and characterizations of OLEDs

Indium–tin-oxide (ITO) substrates with a sheet resistance of 15 Ω/□ were sufficiently cleaned by ultrasonication in detergent and deionized water and then treated with UV-zone before use. The PEDOT:PSS layer was spin-coated in air and baked at 200 °C for 10 min. The light-emitting layer was spin-coated onto the PEDOT:PSS-coated substrates from 1,2-dichloroethane solutions of PVK:OXD-7 or PBD:cationic iridium complexes in a nitrogen-filled glove box. The coated substrates were annealed at 80 °C for 30 min. The substrate was transferred to an evaporation chamber integrated with the glove box. TPBI was evaporated at a rate of 1–2 Å/s under a pressure of 4×10^{-4} Pa. The Cs_2CO_3/Al bilayer cathode was evaporated at rates of 0.2 and 10 Å/s for Cs_2CO_3 and Al, respectively, under a pressure of 1×10^{-3} Pa. The current–voltage–brightness characteristics of the devices were characterized with a Keithley 4200 semiconductor characterization system. The EL spectra were collected with a Photo Research PR705 spectrophotometer. All measurements were performed in an ambient atmosphere without encapsulations.

3. Results and discussion

3.1. Single-layer devices

Cationic iridium complexes, which emit light ranging from blue-green to red, are shown in Scheme 1. The detailed photophysical and electrochemical characteristics of the complexes have been presented in previous studies



Scheme 1. OLED device structure and the cationic iridium complexes.