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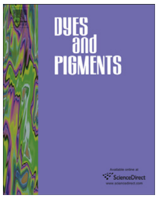

Efficient yellow-green organic light-emitting diodes based on sublimable cationic iridium complexes

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ABSTRACT

Three new yellow-emitting cationic iridium complexes have been prepared, and the photophysical and electrochemical properties have been investigated. These cationic iridium complexes have excellent thermal stability and can be thermally vacuum-sublimed as phosphorescent dyes for the fabrication of efficient organic light-emitting diodes. The devices based on these complexes give yellow-green electroluminescences with Commission Internationale de L'Eclairage coordinates of (0.38, 0.58), (0.37, 0.58), (0.38, 0.58). The maximum current efficiencies of devices based on these complexes are 20.2, 23.7 and 21.5 cd A^{-1} that corresponds to maximum external quantum efficiencies of 6.3%, 6.8% and 6.5%, respectively.

1. Introduction

In the recent years, phosphorescent cyclometalated iridium(III) complexes have attracted more and more interest in the field of optoelectronics due to their high quantum efficiency, short lifetime of triplet excited states and broad range of emission colors [1]. Iridium(III) complexes can be divided into two classes: (i) the neutral complexes with molecular formula $[Ir(C\hat{}N)_3]$ [2–4] or $[Ir(C\hat{}N)_2(L\hat{}X)]$ ($C\hat{}N$ and $L\hat{}X$ stand for cyclometalated ligand and anionic ancillary ligand, respectively) [5–8] and (ii) cationic iridium(III) complexes $[Ir(C\hat{}N)_2(N\hat{}N)]^+$ containing neutral bidentate ancillary ligands [9]. The former class of iridium(III) complexes have high quantum yields and their emission wavelengths and excited-state lifetimes can be tuned by changing the cyclometalated ligands. Most of the OLEDs based on these complexes were fabricated by vacuum deposition due to their good volatility. As for the latter case, the ionic character makes them quite soluble in polar solvents, which enable solution process to form the film for solid-state light-emitting electrochemical cells (LECs) containing only a single emissive layer [10]. LECs offer several advantages such as very simple device architectures, being independent of the thickness of the active layer and being used with air-stable electrodes. However, these devices suffer from a slow response and severe excited-state quenching in the active layers compared with conventional OLEDs [11–14]. Therefore, they are indeed difficult to be used in full-color flexible panel displays which require fast switching. Such drawbacks in LECs can be significantly suppressed by doping the phosphors in the polymer host materials as the emissive layer as well as using an extra functional layer in solution-processed OLEDs. Consequently, by using cationic iridium(III) complexes as emissive phosphors, blue, red, green, yellow and near-infrared OLEDs have been realized [15–20]. Most of these kind of devices commonly exhibit low luminance and efficiency due to the inferior compatibility of cationic iridium complex guest with hydrophobic polymer hosts, which could hinder the development of their widespread applications. It is expected that the

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performance of OLEDs based on cationic iridium complexes can be significantly relieved as the dopants are deposited by a vacuum-evaporable method. However, the intrinsic ionic nature of cationic iridium complex can result in their poor volatility and severe thermal degradation during vacuum evaporation. The volatility of cationic iridium complexes can be improved by enhancing molecular structural rigidity. Wong et al. reported OLEDs with sublimable cationic iridium complexes with rigid pyridinylfluorene derivatives as dopants, which gave yellow light emission with a maximum luminance efficiency of 20 cd A^{-1} and a quantum efficiency of 7% [19]. As far as we know, other than the foregoing accounts there were no other reports on OLEDs based on cationic iridium dopants by thermally vacuum-sublimed method.

In this work, three novel cationic iridium complexes were synthesized by using 2-phenylpyridine as the main ligand and biscarbazole substituted 4,5-diazafluorene derivatives as the ancillary ligand. The bipolar ancillary ligands comprise two electron-donating carbazole units and an electron-accepting 4,5-diazafluorene group, and were even used as hosts for highly efficient blue phosphorescent OLEDs [21]. Such cationic iridium complexes have excellent thermal stability and can be thermally evaporated under vacuum without significant decomposition in phosphorescent OLED fabrication.

2. Experimental

2.1. General experiments

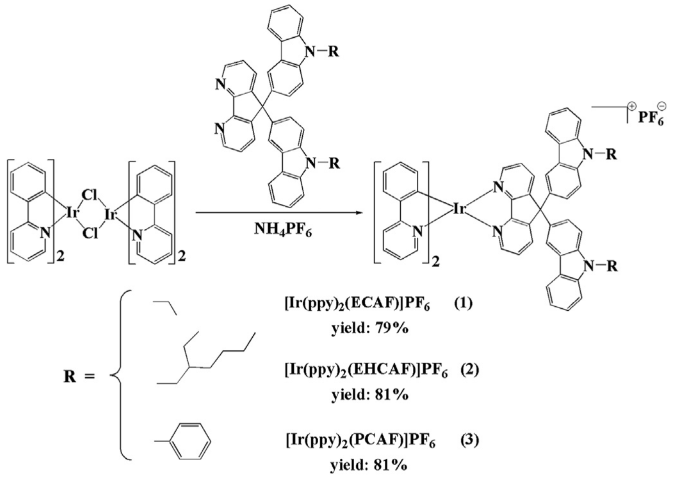
All reactants and solvents were used as received, and were purified or dried by standard methods when required. All reactions were monitored using precoated thin-layer-chromatography plates (0.20 mm with fluorescent indicator UV254). ^{1}H NMR spectra were recorded on a JEOL JNMECA600 NMR spectrometer with tetramethylsilane [$Si(CH_3)_4$] as the internal standard. Mass spectrometry (MS) was performed with an Esquire-LC_00136 mass spectrometer. Elemental analysis for carbon, hydrogen, and nitrogen was determined on an Exeter Analytical CE-440 elemental analyzer. The dimeric iridium(III) intermediate $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ and diimine ligands ECAF (9,9-bis(9-ethylcarbazol-3-yl)-4,5-diazafluorene), EHCAF (9,9-bis(9- ethylhexylcarbazol-3-yl)-4,5-diazafluorene) and PCAF (9,9-bis(9-phenylcarbazaol-3-yl)-4,5-diazafluorene) were prepared according to the literature procedure [21,22]. Absorption spectra were recorded with a UV–vis spectrophotometer (Agilent 8453) and photoluminescent (PL) spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The excited state lifetimes of the complexes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. Absolute PL quantum efficiency at room temperature were measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in DMF solutions (1×10^{-3} M) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was $n\text{-}Bu_4NPF_6$ (0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with argon for 10 min before measurements.

2.2. Fabrication and characterization of OLEDs

Indium-tin-oxide (ITO) substrates with sheet resistance of 10 Ω sq^{-1} were sufficiently cleaned using chemical and UV-ozone methods before the deposition of the organic layers. The poly-(3,4-ethylenedioxythiophene:poly-(styrene sulfonate) (PEDOT:PSS) layer was spin-coated onto the ITO substrate in air and baked at 120 °C for 30 min. The transporting material of TCTA (4,4′,4″-tri(9-carbazoyl)triphenylamine) film (15 nm) was then deposited on the hole-injecting layer. The phosphor (10 wt%) and CBP (4,4′-bis(9*H*-carbazol-9-yl)biphenyl) host were co-evaporated to form 30 nm emitting layer from two separate sources. Then, TmPyPb (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene) (50 nm), LiF (0.5 nm), and Al (100 nm) were evaporated, respectively. The organic layers were laminated in the above sequence under 6×10^{-4} Pa at a rate of 0.5–1 Å s^{-1} without breaking vacuum between each vacuum-deposition process. The layer thickness was monitored in situ using a quartz crystal oscillator. The luminance–voltage–current density characteristics were measured with a PR655 spectrometer and a Keithley 2400 programmable voltage–current source. The current efficiency and external quantum efficiency characteristics were calculated from electrical parameters, electroluminescent (EL) spectra and luminance. All measurements of the devices were carried out in ambient atmosphere without further encapsulations.

2.3. Syntheses

The ancillary ligands ECAF, EHCAF and PCAF were synthesized



Scheme 1. The synthetic route of iridium complexes **1**–**3**.

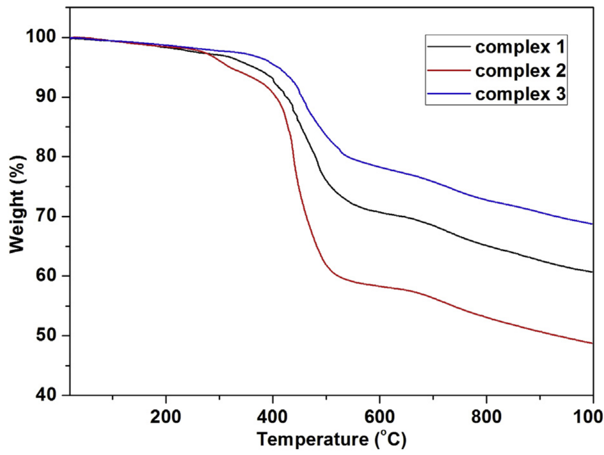


Fig. 1. The TGA curves of complexes **1**–**3**.