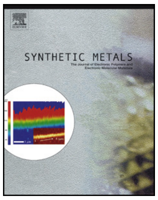
Synthetic Metals 175 (2013) 68–74

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

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



Synthesis and characterization of white light-emitting polyfluorene-based copolymers containing new red iridium complex in the main chain

Woosum Cho[a], N.S. Karthikeyan[a], Siwon Kim[b], Suhkmann Kim[b], Yeong-Soon Gal[c], Jae Wook Lee[d,*], Sung-Ho Jin[a,*]

[a] Department of Chemistry Education, Graduate Department of Materials Chemistry, and Institute for Plastic Information and Energy Materials, Pusan National University, Busan 609-735, Republic of Korea
[b] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea
[c] Polymer Chemistry Lab., Kyungil University, Hayang 712-701, Republic of Korea
[d] Department of Chemistry, Dong-A University, Busan 604-714, Republic of Korea

ARTICLE INFO

Article history:
Received 20 February 2013
Received in revised form 24 April 2013
Accepted 29 April 2013
Available online 5 June 2013

Keywords:
Polymer light-emitting diodes
Phosphorescence
Iridium complex
White emission
Polyfluorenes

ABSTRACT

We report the synthesis of single chain white light-emitting polyfluorene (PF)-based copolymers containing a novel red iridium complex ($(CVz\text{-}PhQ)_2IrdbmBr$), benzothiadiazole (BT), and 2,5-bisphenyl-1,3,4-oxadiazole (OXD) segments. The resulting copolymers were highly soluble in common organic solvents and could be easily spin-coated onto an indium-tin oxide (ITO)-coated glass substrate to obtain high quality optical thin films. The weight-average molecular weight (M_w) and polydispersity of the copolymers were $(17.5–36.3) \times 10^4$ and 1.54–1.65, respectively. We fabricated white polymer light-emitting diodes (WPLEDs) in ITO/PEDOT:PSS/PVK/copolymer/CsF/Ca/Al, both with and without the poly(9-vinylcarbazole) (PVK) interlayer. By carefully controlling the concentrations of the low-energy-emitting species in the resulting copolymers, white light-emission with contributions from each of the three primary colors was achieved. By incorporating 2 mol% of an electron transporting material, OXD, as a comonomer into the copolymer backbone and inserting a PVK interlayer, the external quantum efficiency (EQE) and luminance efficiency (LE) of the WPLEDs were enhanced. The turn-on voltages of the copolymers were in the range of 5.5–7.5 V, and the maximum EQE and LE were 1.79% and 1.89 cd/A with CIE coordinates of (0.32, 0.34), which are close to the standard for white light emission.

1. Introduction

Since their initial discovery by Kido and coworkers in 1994, white organic light-emitting diodes (WOLEDs) and white polymer light-emitting diodes (WPLEDs) have attracted promising attention and interest both academically and industrially [1–4]. Particularly, WPLEDs have been the subject of intensive investigation in recent years because of their unique advantages such as backlighting for liquid crystal displays and next generation lighting sources [5–7]. Despite the high performance of small molecule WOLEDs, WPLEDs are superior for the fabrication of large area displays using inexpensive solution processing techniques [8–10]. Various methods have been adopted to realize white light-emission. The general approach to obtain WPLEDs is to blend fluorescent or phosphorescent dyes into a polymer matrix [11–13] or to use polymer blending systems, such as blending red, green, and blue light-emitting polymers or blue and orange light-emitting polymers [14,15]. However, these blending systems may suffer intrinsic limitations of efficiency and stability because of possible phase separation and color shift with the applied voltage. To address these issues, WPLEDs using a single polymer with broad emission covering the whole visible region from 400 nm to 700 nm as emitting layer have recently been developed [16–20]. Liu et al. reported the first single polymer with simultaneous blue, green, and red emission for white emission with a luminance efficiency (LE) of 1.59 cd/A and Commission Internationale de L'Eclairage (CIE) coordinates of (0.34, 0.34) [21]. In the past few years, various efforts have been made to improve WPLEDs with single emitting polymer materials [22–24].

Phosphorescence imparted by heavy metal complexes has played a vital role in raising the efficiency of OLEDs [25–28]. Phosphorescent emitters of heavy metal complexes, which can harvest both singlet and triplet excitation emissions and elevate the internal quantum efficiency of the devices up to 100% theoretically, have been used to produce high performance WPLEDs [29–31]. Among the transition metal complexes, iridium (Ir) complex yields very high efficiency when doped into the polymer matrix. The high ligand field strength of the carbon atom bonding to the Ir atom

---

* Corresponding authors. Tel.: +82 51 510 2727; fax: +82 51 581 2348.
E-mail addresses: jlee@donga.ac.kr (J.W. Lee), shjin@pusan.ac.kr (S.-H. Jin).

0379-6779/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.synthmet.2013.04.029

provides high emission energy, which potentially covers the entire visible light range from blue to red.

Polyfluorenes (PFs) are very promising materials for light-emitting materials because of their high photoluminescence (PL) efficiency and high thermal stability. Consequently, PFs can be used as both the host and the blue emitter in WPLEDs [32,33]. The emission spectra of PF-based polymers have been tuned to cover the entire visible region by incorporating electron deficient comonomers [34]. Hence, we incorporated the benzothiadiazole (BT) unit into the PF backbone as a green emitter.

On the other hand, we have previously reported the synthesis and characterization of a series of carbazole–phenylquinoline (Cz–PhQ) main ligand-based red Ir(III) complexes with high quantum yields and appropriate lifetimes. Among them, $(\text{Et-Cz–PhQ})_2\text{Ir(acac)}$ gives an external quantum efficiency (EQE) of 4.08% and an LE of 4.31 cd/A with CIE coordinates of (0.65, 0.34) [35]. These results encouraged us to further link $(\text{Et-CVz-PhQ})_2\text{Ir(acac)}$ to the PF main chain via chemical bonds, with the aim of designing white light-emitting phosphorescent polymers.

The occurrence of charge trapping on Ir(III) complexes and of unmatched highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) to the electrodes among the polymers has often resulted in unbalanced holes and electrons in the emitting layer, with low resulting efficiencies. To solve these problems, carrier transporting moieties have been chemically incorporated into the main chain of PFs. Many research groups have introduced electron transport moieties into the main or side chains of π-conjugated polymers. Among the most widely used electron transport moieties are aromatic 1,3,4-oxadiazole (OXD) derivatives, which have high electron affinities that facilitate electron transport and injection. We have incorporated the OXD unit into the PF backbone to increase the electron injection and transportation into the emitting layer.

The poly(3,4-ethylenedioxythiophene):poly(4-stylenesurfonate) (PEDOT:PSS) layer has already been proven to be a successful and efficient hole injection layer [36]. However, it still does not provide a fully ohmic contact to a number of OLEDs. For enhancing the hole injection, several conjugated and non-conjugated polymeric materials have been tried as an interlayer [37]. In general, conjugated polymers are difficult to use in printing process due to their solubility issues in several organic solvents [38]. However, non-conjugated polymers such as poly(9-vinylcarbazole) (PVK) have found favor due to their hole transport chemical units that have been attributed as improving hole injection [39–41]. Therefore, the use of high molecular weight PVK interlayer is advantageous, as it forms a dense film that remains stable and well preserved when the emissive layer is spin-coated on top of it [38].

Herein, we report a new series of white emission PFs both with and without the electron transport molecule, 2,5-bisphenyl-1,3,4-oxadiazole (OXD) unit, in the main chain. Their photophysical properties and resulting device performance are discussed in detail. By incorporating 2 mol% of an OXD segment into the PF backbone and inserting a PVK interlayer, we obtained a maximum EQE of 1.79%, and maximum LE of 1.89 cd/A with the CIE coordinates of (0.32, 0.34).

2. Experimental

2.1. Materials and characterization

9-Ethyl-3-(4-phenylquinolin-2-yl)-9H-carbazole (1), 2,7-bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2,yl)-9,9-dioctylfluorene (M2) and 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (M4) were synthesized according to the literature procedures [35,42,43]. 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (M3) and PVK (M_w: 1,100,000) were obtained from Aldrich Chemicals. All the manipulations involving air sensitive reagents were performed under nitrogen atmosphere. The solvents were of analytical grade and were purified by routine procedures before being used. All column chromatography was performed using silica gel (250–430 mesh, Merck) as the stationary phase in a column.

^{1}H NMR spectra were recorded on a 600 MHz Agilent NMR spectrometer and $CDCl_3$ was used as the solvent at 298 K. The chemical shifts were reported in ppm. Electronic absorption spectra were obtained on a JASCO V-570 UV spectrophotometer with baseline correction and normalization carried out using Origin 7.0 software. Emission spectra were recorded for dilute solutions at 298 K by a Hitachi F-4500 fluorescence spectrophotometer. The solid-state emission measurements were carried out by supporting each film on a quartz substrate that was mounted to receive front-face excitation at an angle of less than 45°. Each polymer film was excited with several portions of visible light from a xenon lamp. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) using a PL gel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and then calibrated with polystyrene standards. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851, DSC 822 analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) experiments were performed with a CHI-600C electrochemical analyser at a potential scan rate of 100–150 mV/s at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, an auxiliary electrode and a nonaqueous $Ag/AgNO_3$ reference electrode. The solvent used in all CV experiments was anhydrous acetonitrile and the supporting electrolyte was nitrogen-saturated 0.1 M solution of tetrabutylammoniumtetrafluoroborate (Bu_4NBF_4). Each polymer film was coated on a Pt disk electrode (0.2 cm^2) by spinning the electrode from the polymer solution (10 mg/mL).

2.2. Synthesis of 1,3-bis(p-bromophenyl)propane-1,3-dione (dbmBr) (3) [44]

A mixture of ethyl *p*-bromobenzoate (2.3 g, 10 mmol) and sodium hydride in oil dispersion (60%, 0.53 g, 22 mmol) in dry THF (30 mL) was heated to 60 °C. *p*-Bromoacetophenone in dry THF (20 mL) was added dropwise to the reaction mixture and stirred for 24 h. The reaction mixture was poured into water and then neutralized with hydrochloric acid. The resulting precipitate was recrystallized from ethanol to give pale yellow needle like crystals (3.1 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.7 (s, 1H), 7.6 (d, 4H), 7.8 (d, 4H); ^{13}C NMR (600 MHz, $CDCl_3$): δ (ppm) 194.23, 136.37, 131.52, 130.18, 128.34, 52.33.

2.3. Synthesis of $(\text{CVz-PhQ})_2\text{Ir(dbmBr)}$ (M5)

The cyclometalated Ir(III) chloride bridged dimer (2) was synthesized by the method reported by Nonoyama [45]. 9-Ethyl-3-(4-phenylquinolin-2-yl)-9H-carbazole (Et-Cz–PhQ) (1) (4 g, 10.36 mmol) and $IrCl_3\ H_2O$ (1.6 g, 45.6 mmol) were added to a mixture of 2-ethoxyethanol and water (130 mL, 3:1, v/v). The reaction mixture was stirred at 140 °C for 20 h and a brown precipitate was obtained after cooling to room temperature. The precipitate was collected and washed with deionized water and methanol. Subsequently, the cyclometalated Ir(III) chloride bridged dimer (2) was dried under vacuum to give a brown solid. The cyclometalated Ir(III) chloride bridged dimer (2) (2 g, 9 mmol) and 1,3-bis(*p*-bromophenyl)propane-1,3-dione (dbmBr) (3) (0.93 g, 24 mmol) were mixed with sodium carbonate (1.036 g, 97 mmol) in 1,2-dicholoroethane (100 mL). The mixture was refluxed at 100 °C for