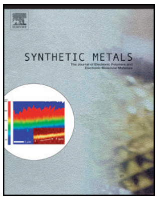
Synthetic Metals 190 (2014) 1–7

Contents lists available at ScienceDirect

Synthetic Metals

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



White polymer light emitting diode materials introducing dendritic quinoxaline derivative: Synthesis, optical and electroluminescent properties

Ho Jun Song[a,b], Gyo Jic Shin[b], Kyung Ho Choi[b], Sangkug Lee[b], Doo Kyung Moon[a,*]

[a] *Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea*
[b] *Cungcheong Regional Division IT Convergence Material R&D Group, Korea Institute of Industrial Technology, 89 Yangdaegiro-gil, Ipjang-myeon, Seobuk-gu, Cheonan-si, Chungcheongnam-do 331-822, Republic of Korea*

ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form 3 January 2014
Accepted 7 January 2014
Available online 13 February 2014

Keywords:
Dendritic derivative
Quinoxaline
Conjugated polymer
WPLED

ABSTRACT

Copolymers including dendritic-quinoxaline (DTQ1G, DTQ2G) (<0.1 mol%) as dopant derivative have been synthesized on a polyfluorene (PF) backbone based on the Suzuki coupling reaction. The UV–vis spectra of polymers showed similar behaviors in the solution and on the film. However, PL spectra were similar to that of PF in solution, but the peak around 590 nm increased as the amounts of DTQ1G and DTQ2G were increased in the casting film. In thin film, the intensities of the dendritic TQ monomers increased with the generation number of the dendrons. In case of PFDTQ2G03, the luminous efficiency and power efficiency were 0.66 cd/A and 0.29 lm/W, respectively with a maximum brightness of 3792 cd/m^2. The CIE coordinates of PFDTQ1G05 and PFDTQ2G10 were (0.33, 0.30) and (0.35, 0.34) close to the pure white coordinates of (0.33, 0.33).

1. Introduction

For the past decades, π-conjugated polymer has been applied to diverse applications such as organic light-emitting diodes (OLEDs) [1–6], organic photovoltaic cells (OPVs) [7–9], organic thin-film transistors (OTFTs) [10–12], and liquid crystal application (LC) [13]. In particular, polymer light-emitting diodes (PLED) present advantages in large-area fabrication methods, such as ink-jet and screen printing with solution processes. As a result, the material has drawn great attention as a next-generation material to replace vacuum deposition with small molecules. Thanks to its convenience and flexibility, polymer film has been popular in the flexible display sector [8,14].

A number of studies have been focusing on PLED materials in various colors since the development of poly(phenylenevinylene) in 1990 [15]. It has been reported that polyfluorene (PF) [16], poly(phenylenevinylene) (PPV) [17], and poly(methoxy, ethylhexyloxy phenylenevinylene) (MEH-PPV) [18] are the representative blue-emitting, green-emitting, and orange and red-emitting materials, respectively. Full-color displays have been enabled by such polymers [4,8].

Recently, there have been more studies on white polymer light-emitting diodes (WPLED) that introduced diverse chromophores to the blue emitting material, PF. If chromophore is introduced to a PF backbone, aggregation and excimers are suppressed. As a result, effective energy transfer occurs in such materials. Therefore, high-efficiency WPLEDs can be realized [19,20]. Recently, we introduced a small amount of low-band-gap chromophore (<0.3 mol%) to a PF backbone and had it copolymerized. Depending on the dopant mol ratio, various color changes (white, green, yellow, etc.) could be detected with high efficiency [5].

The electron-deficient quinoxaline derivative is a leading orange-emitting chromophore. Due to thermal and electrochemical stability and high PL and EL efficiency, the quinoxaline derivative has been widely used in white and orange light-emitting polymers [21–23]. In addition, the quinoxaline derivative can be easily tuned in structure with high solubility. Therefore, electronic characteristics can be changed by introducing various substituents [24,25].

Recently, there have been many studies on the introduction of dendritic derivative, which has superior quantum efficiency characteristics because dendritic derivative reduce the formation of excimers and the aggregation of emitters [26]. The dendrons not only protect the polymer rods from both aggregation and degradation but also improve PL quantum yields [27]. Therefore, if the dendritic derivative is introduced to the quinoxaline derivative, emitter may show effective emitting property.

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* Corresponding author. Tel.: +82 2 450 3498; fax: +82 2 444 0765.
E-mail address: dkmoon@konkuk.ac.kr (D.K. Moon).

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http://dx.doi.org/10.1016/j.synthmet.2014.01.019

In this study, 0.03–0.1 mol% of dendritic quinoxaline derivative was adopted as dopant with an orange emitter and PF as a host. To improve PL quantum yields and aggregation of emitters, the dendritic quinoxaline derivative was introduced to the PF backbone. The Forster energy transfer was investigated, as well as the charge trapping and charge balance effects between host and dopant, and the optimum mol concentration for effective white-emitting polymer was realized.

2. Experiment

2.1. Instruments and characterization

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere. Solvents were dried by standard procedures. Column chromatography was performed with the use of silica gel (230–400 mesh, Merck) as the stationary phase. ^{1}H NMR spectra were performed in a Bruker ARX 400 spectrometer using solutions in $CDCl_3$, and chemical concentrations were recorded in units of ppm with TMS as the internal standard. Electronic absorption spectra were measured in chloroform using a HP Agilent 8453 UV–vis spectrophotometer. Photoluminescent spectra were recorded by a Perkin Elmer LS 55 luminescence spectrometer. Cyclic voltammetry experiments were performed with a Zahner IM6eX Potentionstat/Galvanostat. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a nonaqueous Ag/AgCl reference electrode at the scan rate of 50 mV/s. The solvent in all experiments was acetonitrile and the supporting electrolyte was 0.1 M tetrabutyl ammonium-tetrafluoroborate. TGA measurements were performed on a NETZSCH TG 209 F3 thermogravimetric analyzer. All GPC analyses were made by using THF as the eluant and polystyrene standard as the reference.

2.2. EL device fabrication and characterization

The fabricated device structure was ITO/PEDOT:PSS/polymer/BaF_2/Ba/Al. All of the polymer light-emitting diodes were prepared using the following device fabrication procedure. Glass/indium tin oxide (ITO) substrates [Sanyo, Japan ($10\,\Omega/\gamma$)] were sequentially patterned lithographically, cleaned with detergent, and ultrasonicated in deionized water, acetone and isopropyl alcohol. Then, the substrates were dried on a hotplate at 120 °C for 10 min and treated with oxygen plasma for 10 min in order to improve the contact angle just before the film coating process. Poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P 4083 Bayer AG) was passed through a 0.45-μm filter before being deposited onto ITO at a thickness of ca. 32 nm through spin-coating at 4000 rpm in air, and then dried at 120 °C for 20 min inside a glove box. The light-emitting polymer layer was then deposited onto the film by spin coating a polymer solution in chlorobenzene (1.5 wt.%) at a speed of 1000 rpm for 30 s on top of the PEDOT:PSS layer. The device was thermally annealed at 90 °C for 30 min in a glove box. The device fabrication was completed by depositing thin layers of BaF_2 (1 nm), Ba (2 nm) and Al (200 nm) at pressures less than 10^{-6} Torr. The active area of the device was 9.0 mm^2. Finally, the cell was encapsulated using UV-curing glue (Nagase, Japan). EL spectra, Commission Internationale de l'Eclairage (CIE) coordinates, current–voltage, and brightness–voltage characteristics of devices were measured with a Spectrascan PR670 spectrophotometer in the forward direction, and a computer-controlled Keithley 2400 under ambient conditions.

2.3. Materials and synthesis of monomers

All reagents were purchased from Aldrich, Acros or TCI companies. All chemicals were used without further purification. The following compounds were synthesized following modified literature procedures: 4,4′-(5,8-bis(5-bromothiophen-2-yl)quinoxaline-2,3-diyl)diphenol [28], (5-(bromomethyl)-1,3-phenylene)bis(oxy)bis(methylene)dibenzene and (5,5′-(5-(bromomethyl)-1,3-phenylene)bis(oxy)bis(methylene)bis(benzene-5,3,1-triyl))tetrakis(oxy)tetrakis(methylene)tetrabenzene [29].

2.3.1. Synthesis of 2,3-bis(4-(3,5-bis(benzyloxy)benzyloxy)phenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (DTQ1G)

4,4′-(5,8-bis(5-Bromothiophen-2-yl)quinoxaline-2,3-diyl)diphenol (0.2 g, 0.31 mmol), (5-(bromomethyl)-1,3-phenylene)bis(oxy)bis(methylene)dibenzene (0.3 g, 0.78 mmol), K_2CO_3 (0.43 g, 3.13 mmol), and N,N-dimethylformamide (DMF) (15 mL) were placed in a 250 mL two-neck round-bottom flask, and then, this mixture was stirred at 90 °C for 24 h. The reaction mixture was extracted using chloroform/brine, and then, the organic layer was separated and concentrated. The product was purified using column chromatography using dichloromethane as the eluent. The product yield was 49% (0.19 g). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): 8.03 (t, 2H), 7.85 (d, 1H), 7.66 (t, 4H), 7.57 (t, 2H) 7.42–7.29 (m, 20H) 7.18 (d, 1H) 6.98 (t, 4H) 6.70 (s, 4H) 6.58 (s, 2H) 5.04 (s, 12H). Anal. Calcd. for: $C_{70}H_{52}Br_2N_2O_6S_2$: C, 67.74; H, 4.22; N, 2.26; O, 7.73; S, 5.17. Found: C, 72.36; H, 4.53; N, 2.45; O, 8.94; S, 5.63.

2.3.2. Synthesis of 2,3-bis(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (DTQ2G)

4,4′-(5,8-bis(5-Bromothiophen-2-yl)quinoxaline-2,3-diyl)diphenol (0.3 g, 0.46 mmol), (5,5′-(5-(bromomethyl)-1,3-phenylene)bis(oxy)bis(methylene)bis(benzene-5,3,1-triyl))tetrakis(oxy)tetrakis(methylene)tetrabenzene (0.94 g, 1.17 mmol), K_2CO_3 (0.64 g, 4.69 mmol), and N,N-dimethylformamide (DMF) (15 mL) were placed in a 250 mL two-neck round-bottom flask, and then, this mixture was stirred at 90 °C for 24 h. The reaction mixture was extracted using chloroform/brine, and then, the organic layer was separated and concentrated. The product was purified using column chromatography using dichloromethane as the eluent. The product yield was 32% (0.31 g). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): 8.04 (t, 2H), 7.85 (d, 1H), 7.67 (t, 4H), 7.58 (t, 2H) 7.38–7.28 (m, 40H) 7.18 (d, 1H) 7.00 (t, 4H) 6.66 (s, 12H) 6.54 (s, 6H) 4.99 (s, 28H). Anal. Calcd. for: $C_{126}H_{100}Br_2N_2O_{14}S_2$: C, 72.41; H, 4.82; N, 1.34; O, 10.72; S, 3.07. Found: C, 74.88; H, 4.94; N, 1.41; O, 11.56; S, 3.18.

2.4. Polymerization

Reaction monomers, $(PPh_3)_4Pd(0)$ (1.5 mol%) and Aliquat 336 were dissolved in a mixture of toluene and an aqueous solution of 2 M K_2CO_3. The solution was refluxed for 72 h with vigorous stirring in nitrogen atmosphere, and then excess amounts of bromobenzene, as an end capper, were added and stirring continued for 12 h. The whole mixture was poured into methanol. The precipitate was filtered off, and purified with methanol, acetone, hexane, chloroform in soxhlet.

2.4.1. PFDTQ1G03

9,9-Dioctylfluorene-2,7-dibromofluorene (0.499 equiv.), 2,2′-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.5 equiv.), 3-bis(4-(3,5-bis(benzyloxy)benzyloxy)phenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (*DTQ1G*) (0.0003 equiv.); Yield: 0.16 g (38%); ^{1}H NMR (400 MHz; $CDCl_3$;