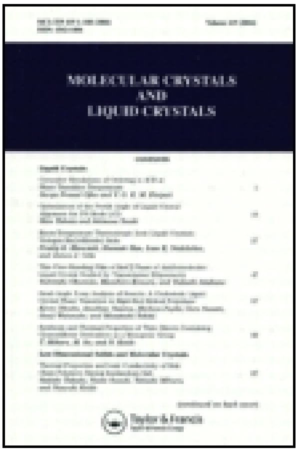

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Synthesis and Optical Properties of Light-Emitting Polyfluorene Derivatives

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The emitting-polymers, Polyfluorene (PF) and Poly(fluorene-benzothiadiazole-quinoline) [PF-BT-QL], have been synthesized by the Suzuki coupling reactions. The properties of polymers were characterized using UV-Vis spectroscopy, GPC, DSC, TGA, Photoluminescence (PL), Fluoresence (FL), Electroluminescence (EL) spectroscopy. The synthetic polymers were soluble in common organic solvents and easily spin-coated onto the indium-tin oxide (ITO)-coated glass substrates. Light-emitting devices (LEDs) with ITO/PEDOT:PSS/polymer/LiF/Al configuration were fabricated, and the devices using copolymers showed red shift EL spectra relative to that of PF. The turns on voltages of copolymers were lower than that of PF.

Keywords Light-emitting polymer; polyfluorene; polymer light-emitting diode

Introduction

In polymer light-emitting diodes (PLEDs), polyfluorenes are promising candidates as blue emitters due to their high photoluminescence quantum efficiencies (PLQEs) as solid films [1], their excellent solubility and film-forming ability, and the ease of controlling their properties via facile substitution in the 9,9-position of the fluorene unit [2–4]. In addition, chemical modifications on main chain, side chain, and chain end of PFs allow elaborate tuning of emission color covering the whole visible range (blue, green, yellow, red, and white), enhancement of device performance, and improvement of long-term operational stability. On the other hand, various types of chain conformation and chain stacking of PFs permit relatively easy physical manipulation for identical purposes as the chemical methods. In this study, new single-polymer electroluminescent systems containing three individual emission species polyfluorenes as a blue host, 2,1,3-benzothiadiazole unit as a green dopant

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and phenylene derivative units as a red dopant on the main chain were synthesized and characterized. The emitting polymers, polyfluorene and poly(fluorene-benzothiadiazole-quinoline) [PF-BT-QL], were synthesized, characterized and fabricated into devices.

Methods

1. *Synthesis of Polymer*

The synthetic route is shown in Figure 1, 1,4-dibromo-2,5-bis(8-quinolinyl)benzene **(4)**, 2,7-dibromo-9,9-di-n-octylfluorene **(5)**, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene **(7)**, 4,7-dibromo-2,1,3-benzothiadiazole **(8)**

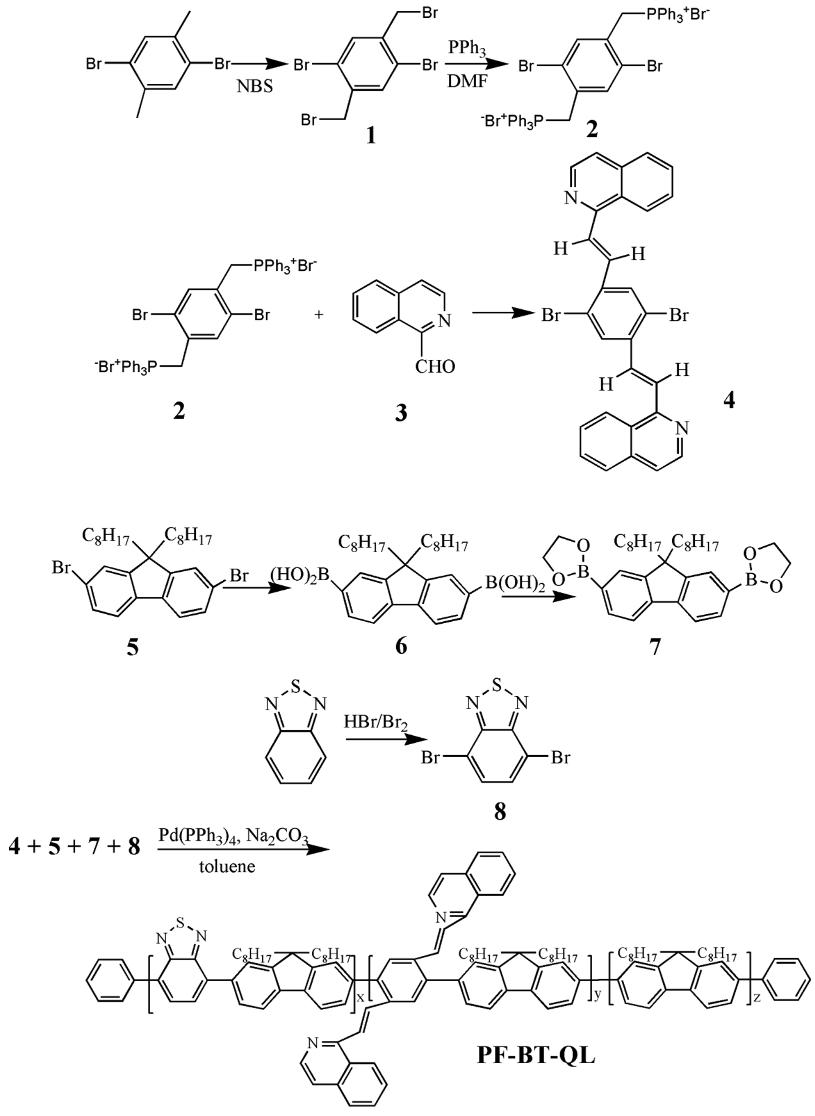

Figure 1. The synthetic route of monomers and polymers.

were synthesized. Suzuki coupling polymerization reaction with **(4)**, **(5)**, **(7)** and **(8)** were conducted in biphasic system (toluene/aqueous Na_2CO_3) with $Pd(PPh_3)_4$ as a catalyst precursor. The reaction were kept stirring at reflux temperature for 3 days. Then, phenyl boronic was added to reduce the heavy atom affecting which quenched fluorescence [5].

2. *Fabrication of Light-Emitting Devices*

In this study, the devices were fabricated with ITO/PEDOT:PSS/polymer/LiF/Al structures. Indium tin oxide (ITO)-coated glass was ultrasonically cleaned sequentially for 15 min in 2% sonicating solution, water, acetone, and 2-propanol. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode Each polymer solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (5 wt%) in tetrahydrofuran. LiF and aluminum contacts were formed by vacuum deposition at pressures below 10^{-6} Torr. The active sections of the devices were then covered with an epoxy resin and allowed to dry so that the active regions were shielded from oxygen exposure during device testing. The devices were tested using photospectrometer to a Keithley 238 and Minolta LS-100 as the luminance detector.

Results and Discussion

All polymers could be fully dissolved in common organic solvents, such as chloroform, toluene, and THF. The crude polymers were redissolved in a certain amount of THF, which was added drop-wise to methanol so as to precipitate the high molar mass polymers. The fractioned high molar mass polymers were separated by filtration and dried in vacuum oven. The molecular weights determined by gel permeation chromatography (GPC) are summarized in Table 1.

The optical properties of polymers, absorption (UV-vis), fluorescence (FL) and photoluminescence (PL) are summarized in Figure 2. A broad absorption band was observed with λ_{max} value at 390 nm, which can be attributed to the π-π^* transition of the conjugated backbone; correspondingly, a slight shoulder observed above 400 nm can be attributed to the fluorene unit [6]. The optical band gaps of polymers were 2.95, and 2.50 eV corresponding to PF, and PF-BT-QL, respectively, which were calculated from the onset of UV-vis spectra.

From the FL spectra obtained upon excitation at 390 nm of polymers, the PF has a strong emission band at 404 nm and flat after 430 nm. It is possible that the

Table 1. Average molecular weights for Polyfluorene [PF] and Poly(fluorene-benzothiadiazole-quinoline) [PF-BT-QL]

	$\overline{M}_w{}^a$ (g mol^{-1})	$\overline{M}_n{}^a$ (g mol^{-1})	PDI^b
PF	40000	20000	2.0
PF-BT-QL	1600	1100	1.4

$^a\overline{M}_w \approx$ weight-averaged molecular weight; $\overline{M}_n \approx$ number-averaged molecular weight.

^{b}Polydispersity index (PDI)) $= \overline{M}_w/\overline{M}_n$.

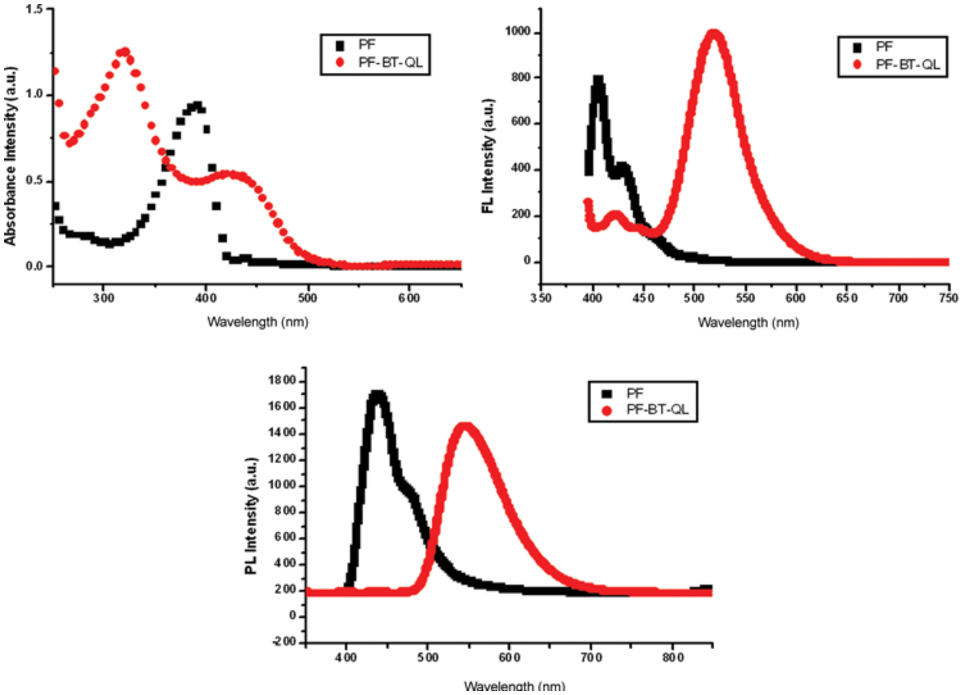

Figure 2. Optical properties of polymers.

shoulder arises earlier due to the coupling reaction between the fluorene and vinylene units to form a new electronic state with a lower energy [7], while, PF-BT-QL exhibited a broad peak at about 520 nm.

From the PL spectra of the polymers, the major emission band of PF appeared at 436 nm with a strong shoulder at a slightly longer wavelength (+30 nm). Again, the shoulder likely arose from electronic coupling between the fluorene and vinylene moieties, while PF-BT-QL exhibited a broad peak at about 540 nm. As the results, copolymer showed red-shifted emission in comparison to the homopolymer.

The electrochemical properties and HOMO and LUMO energy levels of PF and PF-BT-QL were investigated using cyclic voltammetry (CV). The measurement was performed in a solution of n-Bu_4NPF_6 (0.1 M) and polymers (20 mg) in dried CH_2Cl_2 at a scan rate of 50 mV/s at room temperature under the protection of argon. A glassy carbon electrode, a platinum electrode and an Ag/Ag^+ electrode were used as the working electrode, the counter electrode and the quasi-reference electrode respectively. As shown in Figure 3, PF and PF-BT-QL exhibit quasi-irreversible oxidation processes. The E_{HOMO} was calculated according to an empirical equation as follows [8]:

$$E_{HOMO} = -(4.44 + E_{onset})\ (eV)$$

and the E_{gap} was estimated from absorption onset of the polymers, thus, E_{LUMO} was calculated using the equation,

$$E_{LUMO} = E_{HOMO} + E_{gap}$$

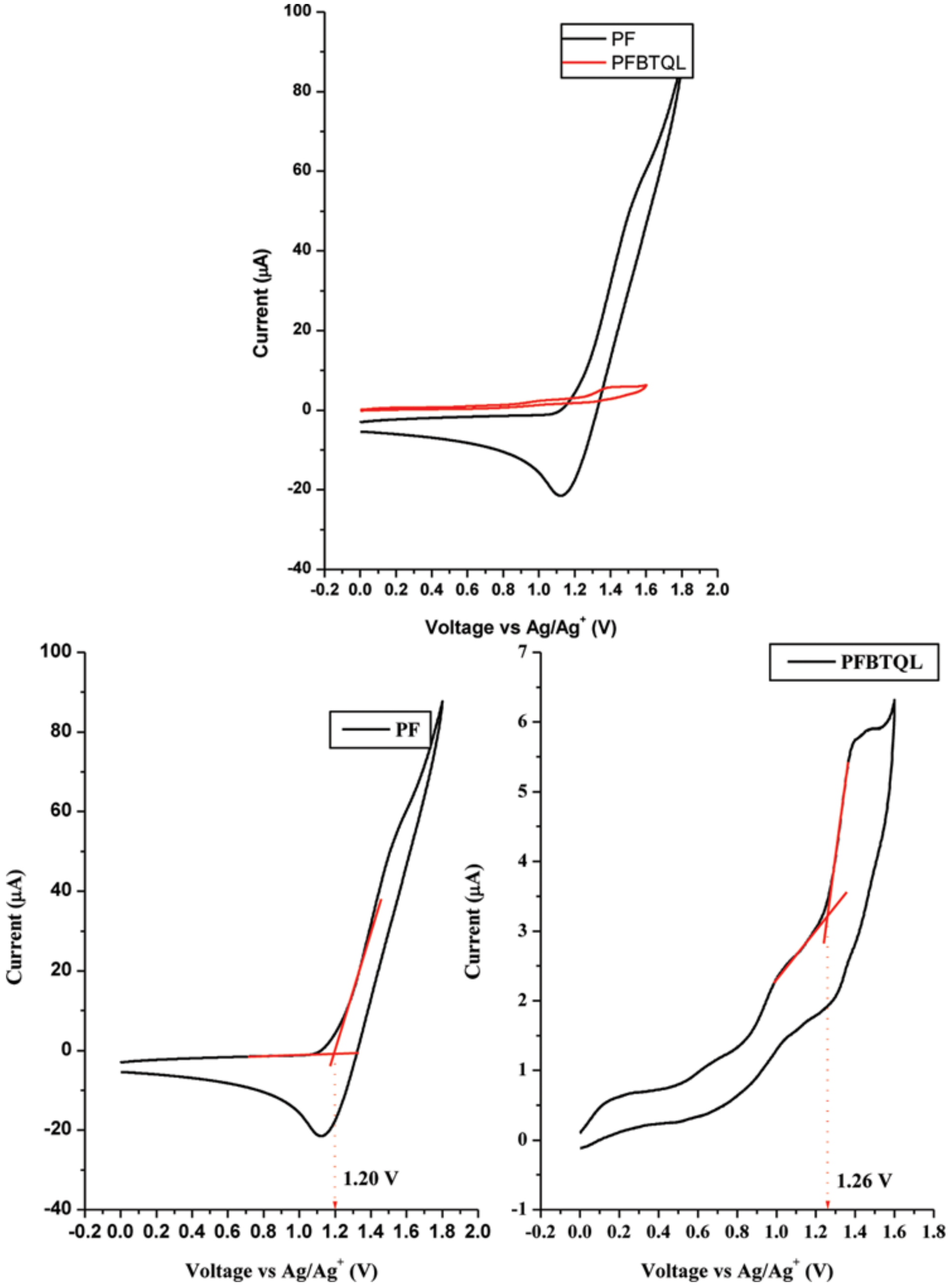

Figure 3. Cyclic voltammogram of polymers in CH_2Cl_2 with 0.1 M of n-Bu_4NPF_6 at a scan rate of 50 mV/s.

The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} are summarized in Table 2. So the oxidation process at about 1.21 V corresponds to the removal of electrons from fluorene core generating radical dications.

Table 2. The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} of polymers

	E_{onset} (V)	E_{HOMO} (eV)	E_{gap} (eV)	E_{LUMO} (eV)
PF	1.20	5.64	2.95	2.69
PF-BT-QL	1.26	5.70	2.50	3.20

E_{HOMO} decreased and E_{LUMO} increased for copolymers, which indicated more difficulty in hole or electron (charge) injection.

Light-emitting diode devices were fabricated in order to test the current-voltage-luminescence and lifetime properties of the polymers to determine their viability for use in organic optoelectronic devices. On the basis of the band gap/energy level of the polymers, an ITO(150 nm)/PEDOT:PSS(40 nm)/polymer(80 nm)/LiF(0.5 nm)/Al(150 nm) device configuration was found suitable.

Figure 4 shows EL spectra of PLEDs device. The EL spectra of PF devices exhibited blue peaks at 440 nm and extra peaks at about 465 nm. This indicated that, at 440 nm, it was originated from a radiative decay process of singlet excitons in PF molecules. The EL spectra of copolymers were similar to the PL spectra, which indicated that the same energy transfer was involved in EL and PL. It was reasonable to propose that the result was due to an energy transfer from high energy state fluorene moiety to the low energy state quinoline and benzothiadiazole moieties. As the results, the transferred excitons decayed through radiative recombination in quinoline and benzothiadiazole and exhibited the red-shifted emission in comparison to the homopolymer. The EL intensity of PF was higher than that of PF-BT-QL copolymer at the same voltage applied. The lower luminance in the copolymer is probably due to the efficient energy transfer from PF to quinoline

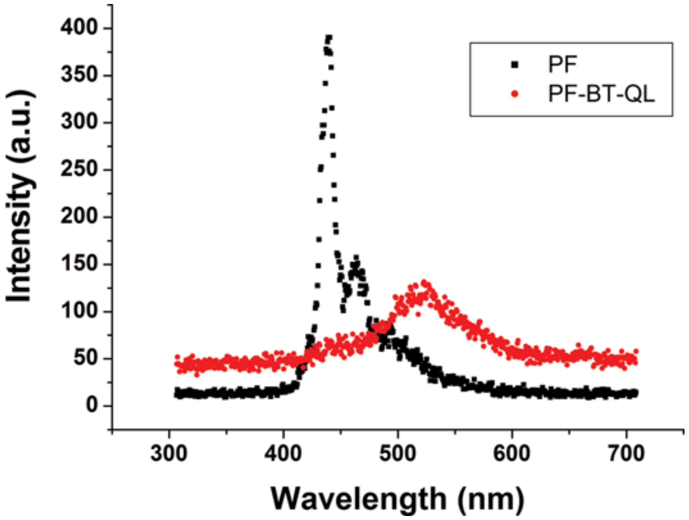

Figure 4. Electroluminescence spectra of polymers which have ITO/PEDOT:PSS/polymer/LiF/Al configuration.

Table 3. The performances of PLEDs

Device	λ_{em} (nm)	CIE (x,y)	Turn on voltage (V)
PF	440,465	0.17, 0.11	10
PF-BT-QL	517	0.28, 0.44	5

and benzothiadiazole unit. Thus, because of the red shift and the relatively lower luminance in PF-BT-QL, the luminance of copolymer was lower than the real blue emission with high luminance.

The performances of PLED are shown in Table 3. The CIE coordinates of devices and their emission color of the devices are shown in Figure 5. By changing the molar ratios of these monomer units, the electroluminescence spectra can be adjusted to white-light emission.

Though the difference in turn-on voltages will lead to a disparity in current density and brightness at a particular voltage, another attribute to consider would be the slopes of the I-V and L-V curves. These are indicative of the rates at which the current and brightness are increasing. Figures 6(a) and 6(b), both current and electroluminescence vs voltage data exhibit readily observable increases in the slopes of PF-BT-QL from PF. A higher slope indicates either efficient charge injection, higher charge mobility, or a combination of both. The threshold voltage of PF-BT-QL was lower than that of PF.

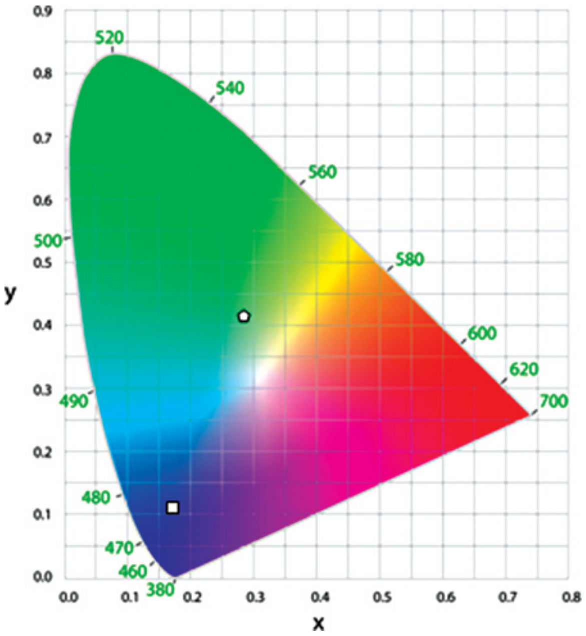

Figure 5. CIE coordinates of PF(□), and PF-BT-QL (◇) devices.

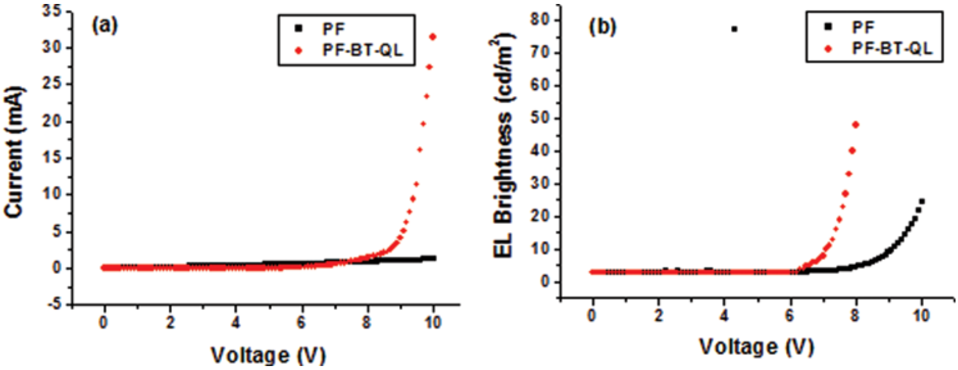

Figure 6. (a) Current-voltage (I-V) (b) luminance-voltage (L-V) characteristics of polymers with ITO/PEDOT:PSS/polymer/LiF/Al configuration.

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