

SYNTHESIS, OPTICAL AND ELECTROCHEMICAL CHARACTERIZATION OF ANTHRACENE AND BENZOTHIADIAZOLE-CONTAINING POLYFLUORENE COPOLYMERS

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ABSTRACT. New solution-processable, anthracene- and benzothiadiazole-containing polyfluorene copolymers (**P1-P3**) have been synthesized and characterized. The preparation and characterization of the corresponding blue light-emitting devices are also reported. Polymers **P2** and **P3** show high photoluminescence efficiency while polymer **P2** does not show any significant light emission up to 8.0 V. The results show the need for balance of electron and hole transport in polymer light emitting diodes.

KEY WORDS: Anthracene, Benzothiadiazole, Polyfluorene copolymers, Photoluminescence, Light emitting diode

INTRODUCTION

There has been a great deal of interest in both the academia and industries in light emitting polymeric materials after the pioneering work of Burroughes *et al.* [1] using poly(*p*-phenylene vinylene) (PPV) as green polymer light emitting diode (PLED) on positive bias potential application [2, 3]. Since then different polymers including various derivatives of poly(*p*-phenylene vinylene) [4-10], poly(*p*-phenylene) (PPP) [11-14], polyfluorenes [15-18] and polythiophenes [19-26] have been investigated as active layers in PLEDs. Several review papers have also been published in the area [27-32].

A desired requirement in all PLEDs is the simultaneous supply of electrons and holes to the active light emitting polymer layer sandwiched between two electrodes. Most electroactive conjugated polymers studied are mainly either electron transporting (n-type) or hole transporting (p-type) and do not combine the required property of balanced electron and hole transport. Hence, several studies have been done to solve this problem. One approach is to use a low work function metal such as calcium to improve the electron injection. However, the drawback in such devices is the instability of low work function metals such as calcium towards air [33]. Another approach is to use a bilayer or a multilayer structure where an electron transporting or hole transporting polymer or both are introduced in a bilayer or multilayer configuration [34]. Such devices give improved performances, even though the fabrication procedures are difficult.

Here we report the synthesis and characterization of anthracene- and benzothiadiazole-containing polyfluorene copolymers with different electron and hole injection properties.

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EXPERIMENTAL

Optical, thermal and electrochemical measurements

Absorption spectra were recorded using a Lambda 9 Spectrophotometer (Perkin-Elmer). Photoluminescence (PL) and electroluminescence (EL) spectra were recorded using a FluoroMax-2 Spectrofluorometer. The quantum yield of fluorescence (Φ_{PL}) was determined using the relative method by comparing the areas of the fluorescence spectra in dilute solutions of the standard and the sample. 9,10-Diphenylanthracene ($\Phi_{\text{PL}} = 0.91$ in ethanol) and quinine sulfate ($\Phi_{\text{PL}} = 0.54$ in 0.1 M H_2SO_4) were used as reference substances. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using SDT Q 600 (simultaneous DSC-TGA) instrument and the glass transition (T_g) and decomposition temperatures (T_d) were determined.

Cyclic voltammetry experiments were carried out using CHI600A Electrochemical Analyzer. A conventional three-electrode system consisting of glassy carbon disk (3.0 mm in diameter) as a working electrode, a silver wire quasi reference electrode directly placed into the electrolyte solution and a platinum wire as counter electrode were used. The polymer films were deposited on working electrodes by solvent casting. The glassy carbon electrode was polished and rinsed with water, acetone, and acetonitrile. A 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile was used as supporting electrolyte. Nitrogen gas was bubbled through the solution for 20 min and bubbled over the solution throughout the experiment. The potential of the quasi reference electrode was corrected to the Ag/AgCl reference electrode by measuring the ferrocene/ferrocenium redox couple in the supporting electrolyte-solvent system, which was set to 0.433 V vs Ag/AgCl.

LED fabrication and characterization

Indium-tin-oxide (ITO) coated on glass substrates were cleaned with acetone and further cleaned with a mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume) for 5 min at 85 °C. PEDOT-PSS (Grade EL) was spin-coated on top of the ITO anode, followed by 5 min annealing at 120 °C. The polymers were spin coated from chloroform solutions on top of the PEDOT-PSS. The cathodes were made by evaporating LiF (0.5 nm)/Al (60 nm) in vacuum $\sim 10^{-6}$ Torr. The diodes were defined by a mask with an active area of 4 mm².

Electrical properties, radiometric and external quantum efficiency of PLEDs were characterised using a photodetector, a Hamamatus silicon photodiode (1010BR), an electrometer (Keithley 617) and a picoammeter (Keithley 485). All preparations and characterisations were carried out in ambient atmosphere.

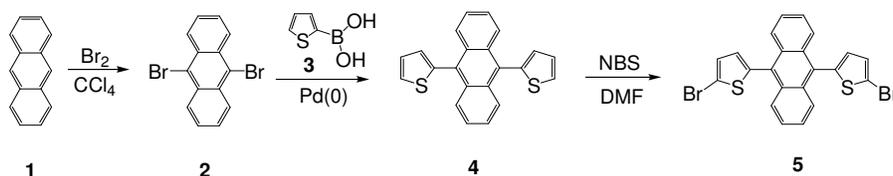
RESULTS AND DISCUSSION

Synthesis of monomers

The syntheses of the monomeric sub-units mainly involved preparation of boronate esters, boronic acids and dibromides from their respective aromatic precursors following established literature procedures [35-38]. Schemes 1-3 depict the syntheses of the monomers and the polymers.

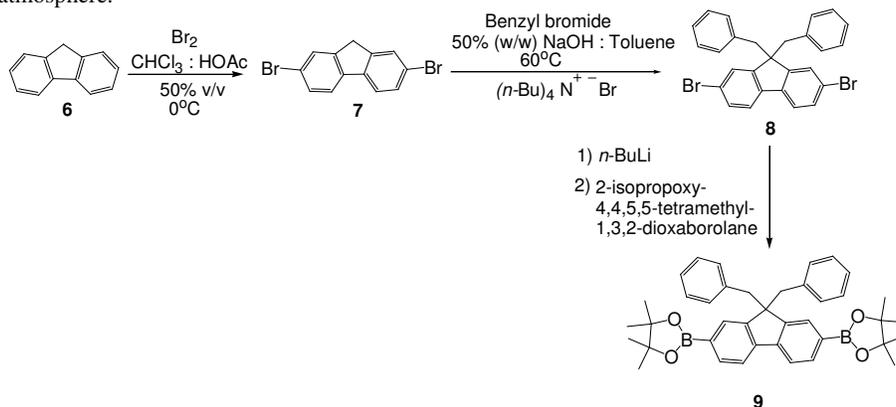
The synthesis of 9,10-bis(5-bromo-2-thienyl anthracene) (**5**) was accomplished by bromination of 9,10-bis(2-thienyl)anthracene (**4**) using NBS (*N*-bromosuccinimide) under inert atmosphere (Scheme 1). The 9,10-bis(2-thienyl)anthracene **4** was initially synthesised by a

palladium(0)-catalyzed Suzuki-type coupling reaction between 9,10-dibromoanthracene (**2**) and 2-thiophene boronic acid (**3**) using tetrakis(triphenylphosphine)palladium(0) as the catalyst. The 2-thiopheneboronic acid used in this reaction was synthesized from 2-bromothiophene using *n*-BuLi and tributylborate in dry THF under nitrogen atmosphere at -78°C .



Scheme 1. Syntheses of 9,10-bis(5-bromo-2-thienyl anthracene) (**5**).

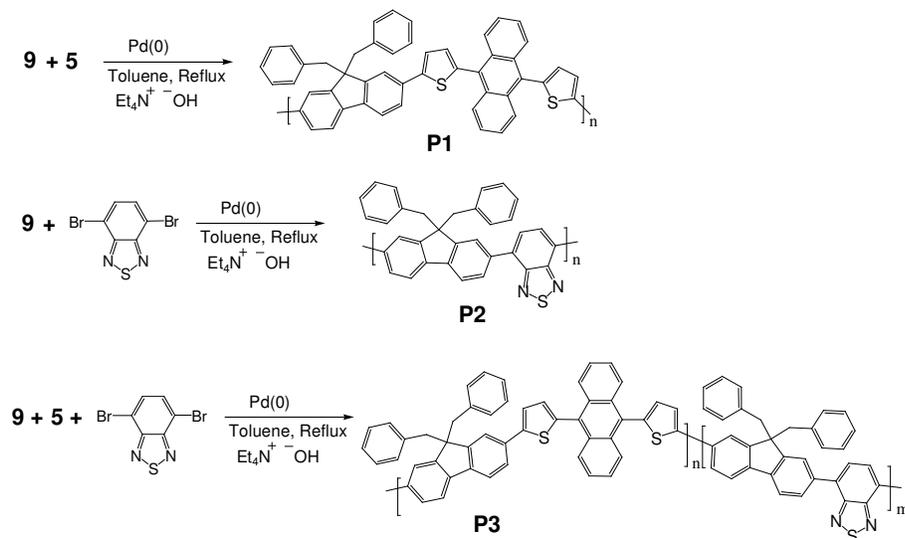
The other monomeric sub-unit 2,7-bis(4'',4'',5'',5''-tetramethyl-1',3',2'-dioxaborolane-2-yl)-9,9-dibenzylfluorene (**10**) was prepared from 2,7-dibromo-9,9-dibenzylfluorene (**8**) and 2-isopropoxy-4',4',5',5'-tetramethyl-1,3,2-dioxaborolane by means of *n*-BuLi in dry THF at -78°C under nitrogen atmosphere (Scheme 2). The synthesis of the 9,9-dibenzyl-2,7-dibromofluorene was achieved by an efficient phase-transfer catalysis reaction from 2,7-dibromofluorene (**6**) and benzyl bromide, where tetrabutylammonium bromide was used as phase transfer catalyst, in 50% w/w aqueous NaOH: toluene solution under nitrogen atmosphere.



Scheme 2. Synthesis of 2,7-bis(4'',4'',5'',5''-tetramethyl-1',3',2'-dioxaborolane-2-yl)-9,9-dibenzylfluorene (**9**).

Synthesis of the copolymers

The monomers obtained by the routes described above were subsequently polymerized using a modified Suzuki coupling reaction following previously published procedure [39] with tetrakis(triphenylphosphine)palladium(0) as catalyst and tetraethylammonium hydroxide as base (Scheme 3). This and similar Suzuki coupling reactions had been extensively used to synthesize fluorene-containing copolymers, due to their considerably faster rates and production of high molecular weight polymers [36].



Scheme 3. Syntheses of the copolymers.

Poly[5,5''(9',10'-di-2,2''-thienylanthracene)-*alt*-2,7-(9,9-dibenzylfluorene)] (**P1**) was prepared beginning with 2,7-bis(4'',4'',5'',5''-tetramethyl-1',3',2'-dioxaborolane)-2'-yl-9,9-dibenzylfluorene (**9**) and 9,10-bis(5'-bromo-2'-thienyl)anthracene (**5**) using a freshly prepared tetrakis(triphenylphosphine)Pd(0) catalyst and tetraethylammonium hydroxide base under nitrogen atmosphere. After three hours of reaction the polymer was precipitated from methanol as yellowish-green solid, which was soluble in chloroform.

Poly[2',1',3'-benzothiadiazole-*alt*-2,7-(9,9-dibenzylfluorene)] (**P2**) was prepared in a similar manner as **P1**, from 2,7-bis(4'',4'',5'',5''-tetramethyl-1',3',2'-dioxaborolane)-2'-yl-9,9-dibenzylfluorene (**9**) and 4,7-dibromo-2,1,3-benzothiadiazole using tetrakis(triphenylphosphine)Pd(0) and tetraethylammonium hydroxide under nitrogen atmosphere. The polymer was precipitated from methanol to give greenish solid, which was also soluble in chloroform.

Poly[5,5''(9,10-di-2,2''-thienylanthracene)-*alt*-2,7-(9,9-dibenzylfluorene)-*alt*-[2',1',3'-benzothiadiazole-*alt*-2,7-(9,9-dibenzylfluorene)] (**P3**) was prepared beginning with 2,7-bis(4'',4'',5'',5''-tetramethyl-1',3',2'-dioxaborolane)-2'-yl-9,9-dibenzylfluorene (**9**), 9,10-bis(5-bromo-2-thienylanthracene) (**5**), and 4,7-dibromo-(2,1,3)-benzothiadiazole with tetrakis(triphenylphosphine)Pd(0) and tetraethyl ammonium hydroxide under nitrogen atmosphere. After three hours of polymerization and a similar workup this reaction gave a greenish-yellow solid, which was soluble in chloroform.

The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the copolymers were very low ranging from 849 to 2075 and 1250 to 4651, respectively, with polydispersity indices (PDI) ranging from 1.37 to 2.24. These data are summarized in Table 1.

Table 1. Molecular weights and thermal properties of the polymers.

Polymer	M_w	M_n	PDI	T_d (°C)	T_g (°C)
P1	1250	849	1.47	296	97
P2	1704	1241	1.37	341	98
P3	4651	2075	2.24	350	101

The thermal stabilities of the polymers were evaluated by thermogravimetric analyses (TGA) under a nitrogen atmosphere. The data are summarized in Table 1. All copolymers exhibited good thermal stabilities up to 296-350 °C. Differential scanning calorimetry (DSC) measurements were also performed on all copolymers. The DSC data are reported in Table 1.

The UV-Vis absorption, PL, EL spectra and cyclic voltammograms (CVs) of polymers **P1-P3** are shown in Figures 1 and 2. The polymers were characterised using cyclic voltammetry according to the method described by Bredas *et al.* [40], commonly expressed as $I_p(\text{HOMO}) = -(E_{\text{on}}^{\text{ox}} + 4.4)$ eV and $E_a(\text{LUMO}) = -(E_{\text{on}}^{\text{red}} + 4.4)$ eV. $E_{\text{on}}^{\text{ox}}$ and $E_{\text{on}}^{\text{red}}$ are the onset potential values in volts for oxidation and reduction processes against the Ag/AgCl reference electrode. The absorption and emission maxima, the band gaps and PL efficiencies (from chloroform solutions of the polymers) and the electrochemical data of **P1-P3** are summarized in Tables 2 and 3. The data show that the absorption maxima of polymers **P2** and **P3** are more red-shifted than those of polymer **P1**. Moreover, polymer **P1** shows lesser photoluminescence quantum yield as compared to polymer **P2** and **P3**.

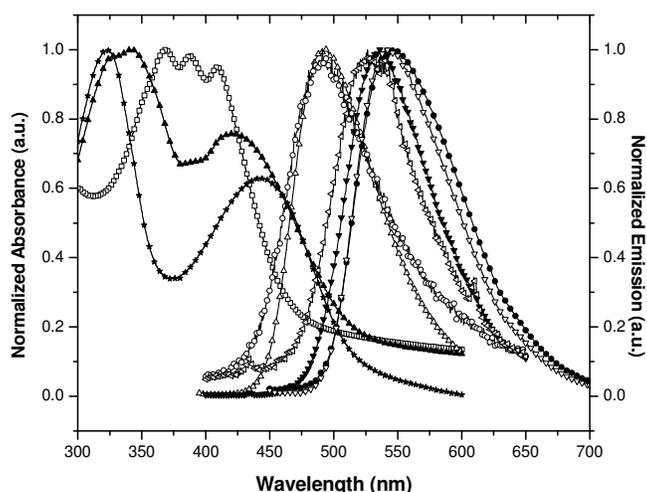


Figure 1. UV-Vis absorption spectra of polymers **P1** (○), **P2** (★) and **P3** (▲); photoluminescence emission of polymers **P1** (△), **P2** (▽) and **P3** (●); and electroluminescence emission of polymers **P1** (○), **P2** (◁) and **P3** (▼) in the solid state.

Table 2. Optical absorption and emission properties of polymers **P1-P3**.

Polymer	$\lambda_{\text{on}}/\text{nm}$	$E_g^{\text{op}}/\text{eV}$	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{max}}^{\text{PL}}/\text{nm}$	$\lambda_{\text{max}}^{\text{EL}}/\text{nm}$	Φ_{PL}
P1	473	2.62	387	492	492	0.02
P2	544	2.28	440	544	528	0.50
P3	519	2.39	420	547	533	0.42

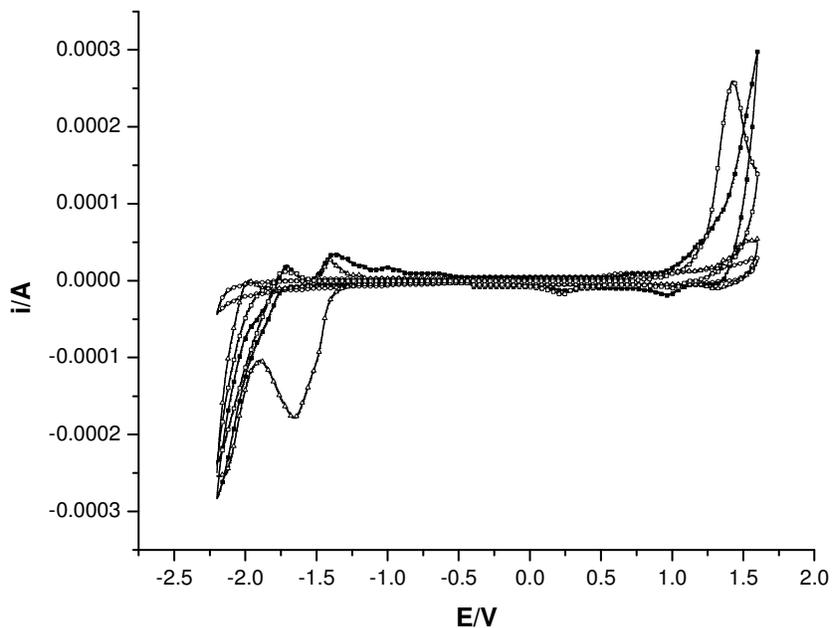


Figure 2. Cyclic voltammogram of background (o), polymers **P1** (□), **P2** (△) and **P3** (■) casted on a glassy carbon disk electrode in $\text{Bu}_4\text{NFB}_4/\text{AcN}$ supporting electrolyte/solvent system at 100 mV/s.

Table 3. Summary of the electrochemical data for **P1**, **P2**, and **P3**.

Polymer	$E_{\text{onset}}^{\text{red}}/\text{V}$	$E_{\text{onset}}^{\text{ox}}/\text{V}$	$E_{\text{LUMO}}/\text{eV}$	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{g}}^{\text{sc}}/\text{eV}$
P1	-1.87	1.05	-2.63	-5.55	2.92
P2	-1.32	1.12	-3.18	-5.62	2.50
P3	-1.73	1.00	-2.77	-5.50	2.73

The current density-voltage (J-V) characteristics of the PLED devices (ITO/PEDOT-PSS/polymer/LiF (0.5 nm)/Al(60 nm)) fabricated out of polymers **P1**-**P3** are shown in Figure 3. As shown in the insert in Figure 3, all polymers show a rectification of about one order of magnitude at ± 5 V. Figure 4 shows the light intensity versus the applied potential of polymers **P1**-**P3**. Polymer **P3** shows a more pronounced increase in light intensity after 3.5 V than polymer **P1**. Polymers **P2** and **P3** show higher photoluminescence quantum yields than polymer **P1**. Polymer **P2** does not show any light emission due to its higher LUMO as shown in Table 3 leading to a larger barrier to electron injection and imbalance of charges needed for emission of light. The light emission in polymer **P1** is smaller than that of polymer **P3** due to its low photoluminescence quantum yield. Hence, these data show that high photoluminescence quantum efficiency as well as balance of oppositely charged charge carriers is needed for a good performance of single-layer polymer light emitting diodes.

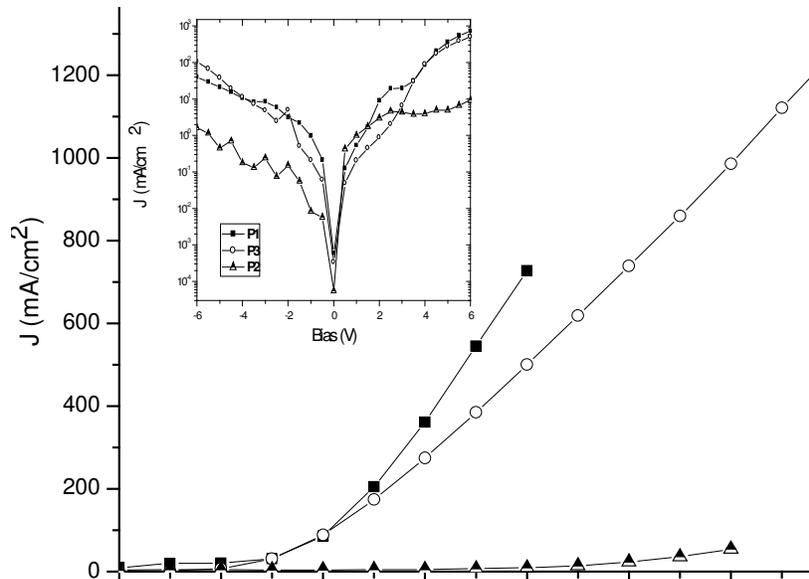


Figure 3. Current density-voltage characteristics under forward and reverse bias for polymers **P1** (■), **P2** (▲) and **P3** (○). Insert shows the rectification behaviour.

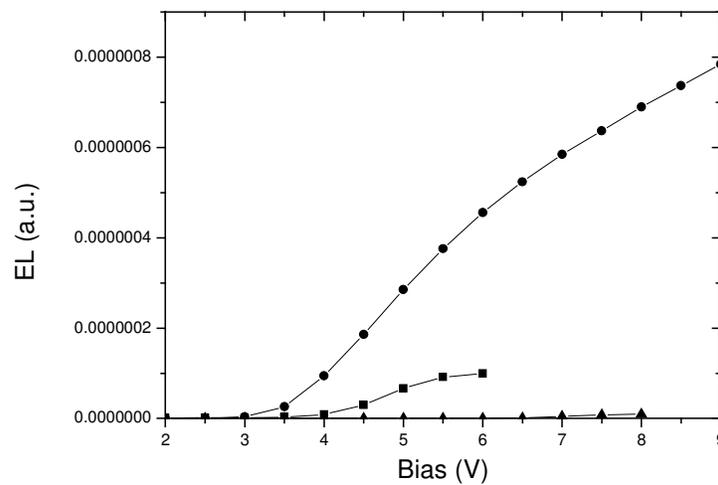


Figure 4. Light intensity *versus* the applied potential of polymers **P1** (■), **P2** (▲) and **P3** (●).

CONCLUSIONS

Three copolymers (**P1-P3**) containing anthracene and benzothiadiazole units that are soluble in chloroform were prepared by a modified Suzuki-type reaction using tetrakis(triphenylphosphine)palladium(0) as a catalyst and tetraethylammonium hydroxide as a base. The optical, electrochemical and light emitting characteristics have been investigated. Blue light emissions were observed at about 3.5 V in polymers **P1** and **P3** with a more pronounced intensity for polymer **P3**.

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