

# Emission color tuning of new fluorene-based alternating copolymers containing low band gap dyes

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## Abstract

New fluorene-based alternating copolymers (PFPhPhCN, PFPhThCN, and PFThThCN) containing different comonomers have been designed and subsequently synthesized via Pd-catalyzed Suzuki polymerization. The synthesized polymers could be well characterized by <sup>1</sup>H NMR, FT-IR, and elemental analyses. These polymers were found to be thermally stable and readily soluble in common organic solvents. The UV–vis absorption maxima of PFPhPhCN, PFPhThCN, and PFThThCN were 399, 456 and 499 nm, and the PL maxima were 484, 539 and 620 nm, respectively. The emitting color of the homopolymer, poly(9,9-dioctylfluorene-2,7-diyl) (PDOF), could be tuned by incorporating various low band gap dyes into the polymer main-chain. The absorption and emission maxima of the copolymers were varied according to the type of incorporated aromatic group (thiophene or phenylene). In particular, PFThThCN exhibited almost pure red emission (chromaticity values  $x=0.63$ ,  $y=0.37$ ). © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Color tuning; Conjugated polymers; Light-emitting diodes (LED)

## 1. Introduction

The development of electroluminescent polymers for the fabrication of full-color organic displays has given rise to intense academic and industrial research in this area. These polymers are of particular interest because their luminescence properties can be adjusted by manipulation of their chemical structures while their physical properties make them suitable for use in the spin coating and printing processes required to create large-area flat-panel displays [1–6]. Although polymer light-emitting diodes (PLEDs) have been developed to produce each of the three primary colors (red, green, and blue), to date only green and orange PLEDs meet the requirements of commercial use.

A number of polyfluorene (PF) polymers and their derivatives are the preferred polymers in light-emitting applications because of their thermal and chemical stability, good solubility in common organic solvents, and high fluorescent quantum yields in a solid state [7–9]. However, problems have been encountered due to their tendency to exhibit excimer and/or aggregated formation

as well as keto formation of the C-9 position [10], which lead to unwanted blue–green emission and fluorescence quenching.

The study of PFs is ongoing, and numerous attempts have been made to improve their performance [11–13]. Although some attempts have been made to tune the color of blue-emitting PFs, appropriate red and green emitting materials that meet the requirements for display applications have not yet been obtained, and further improvements are necessary. Recently, manipulation of the emission wavelength and band-gap of PFs to emit the whole range of visible light has been achieved through copolymerisation [14]. In particular, alternative copolymerization is preferred because of two significant advantages over the blending of a dye chromophore into the polymer matrix: (1) aggregation is prevented and (2) efficient energy transfer from the polymer to the dye chromophore easily confines the singlet excitons [15]. Thus the introduction of narrower band gap comonomers into the fluorene monomer can be utilized for color tuning [16,17].

In this study, we have systematically prepared various fluorene-based copolymers introducing different narrow band gap moieties. We then determined the relationships between the structures of these copolymers and color tuning.

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## 2. Experimental

### 2.1. Measurements

NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with tetramethylsilane as an internal reference. Mass spectra were obtained using AUTOSPEC ULTIMA spectrometer. Elemental analysis was performed using EA-1110-FISONS elemental analyzer. The number- and weight-average molecular weight of the polymer was determined by gel permeation chromatography (GPC) on Waters GPC-150C instrument using tetrahydrofuran (THF) as eluent and monodisperse polystyrene as standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymer were performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a Dupont 9900 analyzer. UV–vis spectra were measured by using a Jasco V-530 UV/vis spectrometer. PL spectra were measured by using Spex Fluorolog-3 spectrofluorometer. Cyclic voltammetry measurement was performed on an AUTOLAB/PGSTAT12 at room temperature with a three-electrode cell in a solution of Bu<sub>4</sub>NBF<sub>4</sub> (0.10 M) in acetonitrile at a scan rate of 50 mV/s. Polymer films were prepared by dipping platinum working electrodes into the polymer solutions and then air-drying. A platinum wire was used as a counter electrode and Ag/Ag<sup>+</sup> electrode as a reference electrode. Film thickness was measured with a TENCOR alpha-step 500 surface profiler.

### 2.2. Device fabrication and characterization

A hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS, Bayer Al 4083) was spin-coated onto the pre-patterned ITO anode and dried (40 nm). Polymer solution was then spin-coated onto the PEDOT:PSS layer and dried (80 nm). Ca/Al (500 nm/800 nm) cathode was vacuum-deposited onto the polymer film through shadow mask at a pressure below  $1 \times 10^{-6}$  Torr, yielding an active area of 0.04 cm<sup>2</sup>. For PLED measurements, EL spectra were obtained with a Minolta CS-1000. The current–voltage–luminance characteristics were measured with a current–voltage source (Keithley 238) and a luminescence detector (Minolta LS-100).

### 2.3. Materials

2,7-Dibromofluorene, thiophene-2-yl-acetonitrile, *N*-bromosuccinimide (NBS), 4-bromo-benzaldehyde, 5-bromo-thiophene-2-carbaldehyde, (4-bromo-phenyl)-acetonitrile, Aliquat<sup>®</sup> 336, bromobenzene, toluene (0.8%, anhydrous) were purchased from Aldrich Co. Tetrakis(triphenylphosphine)palladium(0) was purchased from DNF Solution Co., and all other reagents and solvents with analytical-grade were used during the whole experiments, and all chemicals were used without further purification. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dioctylfluorene (5) was synthesized according to the literature procedure [18].

#### 2.3.1. 5-bromo-2-thiopheneacetonitrile (1)

*N*-bromosuccinimide (7.58 g, 40.2 mmol) was added to a solution of 2-thiopheneacetonitrile (5 g, 40.0 mmol) in *N,N*-dimethylformamide (30 mL). The reaction mixture was then stirred for 5 h at room temperature. The resulting mixture was extracted with methylene chloride and brine and then dried with MgSO<sub>4</sub>. After filtering, the solvent was evaporated and the pure liquid product was obtained by column chromatography. The product yield was 74.8% (6.11 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 6.90 (d, 1H), 6.78 (d, 1H), 3.80 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 132.23, 129.92, 127.53, 116.19, 112.15, 18.62

#### 2.3.2. 2,3-Bis-(4-bromo-phenyl)-acrylonitrile (2)

To a solution of (4-bromo-phenyl) acetonitrile (3.0 g, 15.3 mmol) at RT, 150 mL of methanol and 2.83 g (15.3 mmol, 1 eq) of 4-bromo-benzaldehyde was added. The mixture was then stirred for 30 min. *t*-BuOK five spoons were added to the solution, and the resulting precipitate was stirred for 1 h. The mixture was purified by several recrystallizations in hexane to provide 3.06 g (55%) of the title product as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 7.43 (s, 1H), 7.52 (d, 2H), 7.55 (d, 2H), 7.59 (d, 2H), 7.73 (d, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 111.4, 117.3, 123.7, 125.2, 127.5, 130.7, 132.2, 132.3, 133.1, 141.0.

#### 2.3.3. 2-(4-Bromo-phenyl)-3-(5-bromo-thiophen-2-yl)-acrylonitrile (3)

The synthesis is analogous to that of 2, with 62 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 7.08 (s, 1H), 7.32 (d, 1H), 7.42 (d, 1H), 7.45–7.56 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 107.4, 117.6, 118.9, 123.4, 127.1, 130.7, 132.3, 132.5, 133.3, 133.7, 139.2.

#### 2.3.4. 2,3-Bis-(5-bromo-thiophene-2-yl)-acrylonitrile (4)

The synthesis is analogous to that of 2, with 53 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 7.06 (s, 1H), 7.34 (d, 1H), 7.44 (s, 1H), 7.47–7.56 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 107.1, 116.9, 119.0, 123.3, 126.9, 130.2, 132.2, 132.4, 133.8, 139.1.

#### 2.3.5. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dioctylfluorene (5)

It was synthesized according to the procedures outlined in the literatures [18].

#### 2.3.6. Polymerization

Into 100 mL two-neck flask were added 2.33 mmol of comonomers – 2 (0.846 g), 3 (0.860 g), and 4 (0.874 g) – and 2.28 mmol (1.5 g) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dioctylfluorene in 25 mL of anhydrous toluene. Into the mixture was transferred in a dry box 0.026 g of water soluble Pd(0) complex, tetrakis(triphenylphosphine)palladium (1 mol%). Subsequently, 2 M aqueous sodium carbonate (5.4 mL, 10.7 mmol) deaerated for 30 min and the phase transfer catalyst, Aliquat<sup>®</sup> 336 (0.092 g, 0.23 mmol) in toluene purged under nitrogen for 1 h was transferred via cannula. The reaction mixture was stirred at 100 °C for 3 days and then the excess amount of bromobenzene (0.036 g, 0.23 mmol), the end capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h.

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