



# Synthesis, characterization, optical and electrochemical properties of cyclopentadithiophene and fluorene based conjugated polymers containing naphthalene bisimide



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## ABSTRACT

Cyclopentadithiophene and fluorene based conjugated polymers containing naphthalene bisimide were synthesized through Suzuki cross-coupling polymerization. The resulting polymers exhibit good thermal stabilities and low crystallinities measured by thermogravimetric analysis and differential scanning calorimetry. The optical and electronic properties of polymers can be examined by UV–Vis spectroscopy and cyclic voltammetry. The UV–Vis absorption maxima of cyclopentadithiophene and naphthalene bisimide containing polymers showed longer wavelength than those of fluorene and naphthalene bisimide containing polymers. This is due to the stronger electron donating property of cyclopentadithiophene in the polymer backbone. The absorption maximum of cyclopentadithiophene and naphthalene bisimide containing polymers was red-shifted in comparison with those of low molecular weight analogous. Alternating polymers containing cyclopentadithiophene and naphthalene bisimide moieties showed a low band gap relative to that of the fluorene and naphthalene bisimide containing polymers presumably there is a strong charge transfer interaction between the electron-donating cyclopentadithiophene unit and the electron-accepting naphthalene bisimide.

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## 1. Introduction

Conjugated polymers exhibit fascinating electronic and optical properties that have led to application in devices such as light emitting diodes (LEDs), photovoltaic cells (PVs), plastic lasers and field effect transistors (FETs) [1–4]. It has been shown that alternating copolymers with electron rich and electron deficient units in the polymer backbone lead to smaller band gaps and higher performance in optoelectronics devices [5]. The introduction of fused-ring systems such as cyclopentadithiophenes [6], dithienopyrroles [7], dithienosiloles [8], and thienothiophenes [9] can lead to further increase in planarity and extend the conjugation of the polymer hence reduce the band gap of the polymer. A recent report on an alternating copolymer, poly[4,4-bis(hexadecyl)-4*H*-cyclopenta-[2,1-*b*;3,4-*b'*]dithiophene-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl] (PCPDTBT), showed that the polymer has high hole mobility [10] and reasonable power conversion efficiency [11].

n-Type conjugated polymers have attracted much attention owing to their high electron affinity and electron-accepting properties. Preparation of solution processable n-type conjugated polymers is a real challenge due to tedious and multistep syntheses and purifications [12]. The strong electron-withdrawing ability of the imide substituents has been employed to impart n-type characteristics to small molecule organic semiconductors [13]. In the family of arylene bisimides, two synthetic strategies are adopted to improve the stability in the presence of oxygen [14] including the introduction of fluorinated substituents at the N- and N'-termini or addition of electron-withdrawing groups to increase the electron affinity. *N,N'*-difunctionalized perylene derivatives with fluoroalkyl groups used as active layer materials in air stable n-channel field effect transistors showed high mobility in ambient atmosphere [15]. Furthermore, chemical substitution with electron-withdrawing groups is often considered as a competent approach to lower the LUMO energy level of conjugated polymers [16].

Polymers containing naphthalene bisimide (NBI) in particular have begun to attract much attention with the recent report of a soluble naphthalene bisimide–bithienyl copolymer capable of being used in printable electronics applications [17]. The research of chemical architecture is examined through the synthesis and

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characterization of a series of soluble high performance naphthalene diimide core donor–acceptor based polymers [18]. The rigidity and planarization of the polymer containing thiophene and naphthalene bisimide exhibited strong  $\pi$ – $\pi$  interactions by increasing thiophene content which lead to the effective  $\pi$ -conjugation length and enabled tuning of the band gap of the polymers.

Herein, we report the synthesis of polymers containing fused-ring systems such as cyclopentadithiophene or fluorene and naphthalene bisimide. We report a comparison of the optical and electrochemical properties of the polymers prepared via Suzuki cross-coupling reactions. In addition, the cyclopentadithiophene and fluorene were functionalized with *n*-octyl groups and naphthalene diimide was functionalized with the 2-ethylhexyl groups as the branched alkyl chain in order to increase the solubility of the resulting polymers. In this research the lowest band gap polymers contained strong donor–acceptor structures that enhance intramolecular charge transfer interactions [19]. These polymers also showed great potential for use as photo-harvesting layers in photovoltaic devices.

## 2. Experimental

### 2.1. Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker 500 MHz or 400 MHz NMR instrument. Chemical shifts are expressed in parts per million ( $\delta$ ) using residual solvent as an internal standard. Polymer molecular weights were obtained using a Waters-gel permeation chromatograph (GPC) with RI detector calibrated with low polydispersity polystyrene standards. Cyclic voltammetry for all polymers was performed at 100 mV s $^{-1}$  in a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgCl as reference electrode, platinum wire as counter electrode and polymer film on a platinum plate as the working electrode in an argon-purged anhydrous acetonitrile solution containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu $_4$ NPF $_6$ ) at room temperature. UV–Vis absorption spectra were recorded on a Jasco (V-670) UV–Vis–NIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q5000 under a heating rate of 10 °C/min and a nitrogen flow rate of 40 mL/min. Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer DSC 4000 at a heating rate and a cooling rate of 10 °C/min. Elemental analysis for C, H, N and S was undertaken using an Elementar Vario EL-III. EI mass spectra were obtained on a Finnigan MAT 95S mass spectrometer. Melting point of compounds was recorded on a MEL-TEMP 1001D melting point apparatus.

### 2.2. Materials

All chemicals and reagents were purchased from commercial sources (TCl, Alfa Aesar or Sigma Aldrich) and used without further purification unless otherwise noted. Solvents used for spectroscopic measurements were spectrograde. The monomers employed were based on cyclopentadithiophene diboronic esters **1**, fluorene diboronic esters **2** and dibromonaphthalene tetracarboxylic acid diimide **3**. The synthesis of monomers **1–3** was followed by the modification of standard procedures reported previously [18,20,21]. The details of syntheses and characterizations of monomers can be found in the [Electronic supplementary information \(ESI\)](#).

#### 2.2.1. Synthesis of alternating copolymer **4a**

2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopentadithiophene (0.131 g, 0.20 mmol), *N,N'*-bis(2-ethylhexyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide (0.130 g,

0.20 mmol) and aqueous K $_2$ CO $_3$  (2 M, 2.0 mL) were mixed in toluene (8.0 mL). After degassing, tetrakis(triphenylphosphine) palladium (10 mol%) was added under an argon atmosphere. The reaction mixture was heated at 110 °C for 48 h before cooling to room temperature. The crude polymer was collected by extraction with chloroform or dichloromethane and then the solvent was removed under vacuum. The solid was washed by Soxhlet extraction with methanol and acetone for 12 h before solubilizing in hot chloroform. The solution was dried *in vacuo* to yield a deep green powder (80 mg, 45% yield).  $^1\text{H}$  NMR (500 MHz, CDCl $_3$ ):  $\delta$  8.86 (br, s, 2H, Ar H on the naphthalene), 7.38–7.36 (br, 2H, Ar H on the cyclopentadithiophene), 4.15–4.12 (br, 4H, –CH $_2$ – next to nitrogen), 1.99–0.67 (br, 64H, alkyl chain hydrogens). 5% loss of weight temperature: 318 °C.

#### 2.2.2. Synthesis of alternating copolymer **4b**

2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopentadithiophene (0.164 g, 0.25 mmol), *N,N'*-bis(2-ethylhexyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide (0.162 g, 0.25 mmol) and aqueous K $_2$ CO $_3$  (2 M, 2.5 mL) were mixed in 1,4-dioxane (25.0 mL). After degassing, tetrakis(triphenylphosphine) palladium (10 mol%) was added under an argon atmosphere. The reaction mixture was heated at 80 °C for 48 h before cooling to room temperature. The crude polymer was collected by extraction with chloroform or dichloromethane and then dried under vacuum. The solid was washed by Soxhlet extraction with methanol and acetone for 12 h before solubilizing in hot chloroform. The solution was dried *in vacuo* to yield a deep green powder. (160 mg, 72% yield).  $^1\text{H}$  NMR (500 MHz, CDCl $_3$ ):  $\delta$  8.86 (br, s, 2H, Ar H on the naphthalene), 7.38–7.36 (br, 2H, Ar H on the cyclopentadithiophene), 4.15–4.12 (br, 4H, –CH $_2$ – next to nitrogen), 1.99–0.67 (br, 64H, alkyl chain hydrogens). 5% loss of weight temperature: 406 °C. Anal. calcd for (C $_{31}$ H $_{38}$ N $_2$ S $_2$ ) $_n$ : C 69.61, H 7.16, N 5.24, S 17.99; found C 69.44, H 7.15, N 4.94, S 17.46%.

#### 2.2.3. Synthesis of alternating copolymer **5a**

2,2'-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.129 g, 0.20 mmol), *N,N'*-bis(2-ethylhexyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide (0.130 g, 0.20 mmol) and aqueous K $_2$ CO $_3$  (2 M, 2.0 mL) were mixed in toluene (8.0 mL). After degassing, tetrakis(triphenylphosphine) palladium (10 mol%) was added under an argon atmosphere. The reaction mixture was heated at 110 °C for 48 h before cooling to room temperature. The crude polymer was collected by extraction with chloroform or dichloromethane and then dried under vacuum. The solid was washed by Soxhlet extraction with methanol and acetone for 12 h before solubilizing in hot chloroform. The solution was dried *in vacuo* to yield deep red membranes (100 mg, 46% yield).  $^1\text{H}$  NMR (500 MHz, CDCl $_3$ ):  $\delta$  8.83 (br, s, 2H, Ar H on the naphthalene), 7.96–7.95 (br, 2H, Ar H on the fluorene), 7.50 (br, 2H, Ar H on the fluorene), 7.44 (br, 2H, Ar H on the fluorene), 4.40–3.99 (br, 4H, –CH $_2$ – next to nitrogen), 2.05–0.89 (br, 64H, alkyl chain hydrogens). 5% loss of weight temperature: 352 °C.

#### 2.2.4. Synthesis of alternating copolymer **5b**

2,2'-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.161 g, 0.25 mmol), *N,N'*-bis(2-ethylhexyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide (0.162 g, 0.25 mmol) and aqueous K $_2$ CO $_3$  (2 M, 2.5 mL) were mixed in 1,4-dioxane (25.0 mL). After degassing, tetrakis(triphenylphosphine)palladium (10 mol%) was added under an argon atmosphere. The reaction mixture was heated at 80 °C for 48 h before cooling to room temperature. The crude polymer was collected by extraction with chloroform or dichloromethane and then dried under vacuum. The solid was washed by Soxhlet

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