



# Synthesis and electrochemical characterization of fluorene and benzimidazole containing novel conjugated polymers: Effect of alkyl chain length on electrochemical properties



Imge Namal<sup>a</sup>, Ali Can Ozelcaglayan<sup>a</sup>, Yasemin Arslan Udum<sup>b</sup>, Levent Toppare<sup>a,c,d,e,\*</sup>

<sup>a</sup> Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey

<sup>b</sup> Institute of Science and Technology, Department of Advanced Technologies, Gazi University, 06570 Ankara, Turkey

<sup>c</sup> Department of Polymer Science and Technology, Middle East Technical University, 06800 Ankara, Turkey

<sup>d</sup> Department of Biotechnology, Middle East Technical University, 06800 Ankara, Turkey

<sup>e</sup> The Center for Solar Energy Research and Application (GÜNAM), Middle East Technical University, 06800 Ankara, Turkey

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## ABSTRACT

The synthesis and characterization of two donor acceptor type conjugated polymers were investigated. Electrochemical properties were examined by cyclic voltammetry, spectroelectrochemistry and kinetic studies. The increase in the alkyl chain length attached to the fluorene unit was investigated in terms of electrochemical properties. The synthesis was carried out via Stille coupling of 4,7-dibromo-4'-(tert-butyl)spiro[benzo[d]imidazole-2,1' cyclohexane] and 2,5-bis(tributylstannyl)thiophene with 9,9-dihexyl-9H fluorine (P1) and 9,9-didodecyl-9H fluorene (P2) respectively. Both polymers were neutral state green polymers. They had optical band gaps of 1.55 and 1.47 eV respectively. Increasing the chain length resulted in an increase in solubility and processibility of the polymer. Polymers are multichromic, revealing colors from neutral state green to doped state blue.

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## 1. Introduction

Conducting polymers have novel properties, which encourage their usage in several applications. One of the main research areas where conjugated polymers involved is electrochromic devices [1–7]. Conducting polymers are the most popular electrochromic materials due to their relatively easy and cheap production, enhanced mechanical properties, short response time, high optical contrast, high coloration efficiency, high UV stability, independence of angle of vision and ability to control electronic properties over structural modifications [8]. Tuning the electronic character of the neutral polymer,  $\pi$ – $\pi^*$  transition peak

can be adjusted in the electromagnetic spectrum [9]. These advantages grounded the use of conjugated polymers in smart windows, optical shutters and rear view mirrors.

In search of novel electrochromic conducting polymers, the properties that the scientists interested are fast switching time, high contrast ratio, variable colors upon structural modifications and stable oxidized states [10–13]. Today, suitable polymers for electrochromic applications to overcome insolubility are being used for commercial uses in electrochromic devices. These valuable structural designs should also be used for photovoltaic device applications [14–16].

The donor acceptor theory is embraced as one of the most efficient ways to tune the band gap [17–20]. The alternating donor and acceptor units in a polymer cause broadening in valence and conduction bands. The double bond character between the donor and acceptor is very strong due to the strong resonance energy between

\* Corresponding author at: Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey. Tel.: +90 3122103251; fax: +90 3122103200.

E-mail address: [toppare@metu.edu.tr](mailto:toppare@metu.edu.tr) (L. Toppare).

the components [21]. This energy between electron rich donor and electron deficient acceptor moieties causes hybridization between the HOMO of the donor and the LUMO of the acceptor. This also causes reduction in the bond length alternation giving rise to a decrease in the band gap [22].

Thiophene and its derivatives have been widely used as donor units according to their electron rich nature. Increasing the highest occupied molecular orbital by this electron rich nature lowers the band gap.  $\pi$  conjugated materials with low band gaps are designed.

Benzimidazole is one of the benzazole derivatives. Benzazole derivatives are widely used as acceptor units. The homopolymer of benzimidazole has high thermal stability and broad absorption. The conjugated structure enables its conductivity upon doping. Due to these properties, benzimidazole can be introduced into the structure for electrochromic and solar cell applications [23]. The use of benzimidazole in the polymer structure as an acceptor is not as widely studied as other benzazole derivatives. Also polymers with pendant groups are not a commonly studied one. Due to these reasons, a benzimidazole derivative is introduced into the structure as an acceptor in this study.

Polyfluorenes are polymers with high hole mobility. Their electron mobility is low which can be improved by introducing fused structures such as benzimidazole into the structure. High quantum efficiencies are obtained in solar cell applications of fluorene containing conjugated polymers but problems like the poor solubility and low processibility lead to the introduction of alkyl chains. It is reported that physical properties are affected by altering the length of the side chains but the relationship still remains poorly understood. Therefore introduction of different alkyl chains into the fluorene structure was investigated in this study.

## 2. Materials and methods

### 2.1. Materials

All chemicals were purchased from commercial sources and used without further purification except tetrahydrofuran (THF). THF was distilled over benzophenone and Na prior to use. 4-(Tert-butyl)cyclohexanone, 9,9-dihexyl-9H fluorene and 9,9-didodecyl-9H fluorene were obtained from Sigma Aldrich. 4,7-Dibromobenzothiadiazole [24], 3,6-dibromobenzene-1,2-diamine [25], 4,7-Dibromo-4'-(tert-butyl)spiro[benzo[d]imidazole-2,1'-cyclohexane] [26] and 2,5-bis(tributylstannyl)thiophene [27] were synthesized according to the procedures published previously. The reactions are carried out under argon atmosphere unless stated otherwise.

### 2.2. Equipments

Electrochemical studies were performed using a PST050 Voltalab potentiostat. A three-electrode cell was utilized where an ITO coated glass slide was used as the working electrode. A platinum wire and an Ag wire were used as the counter and pseudo reference electrodes. The

measurements were carried out at room temperature under nitrogen atmosphere. The value of NHE is taken as  $-4.75$  eV vs. vacuum to calculate the HOMO and LUMO levels. A Varian Cary 500 Spectrophotometer was used to record the UV/Vis/nIR spectra with a scan rate of 2000 nm/min. The potentiostat/galvanostat used for the spectroelectrochemical studies was a Solartron 1285. A Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry was used in order to accomplish colorimetric measurements.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were taken on a Bruker Spectrospin Avance DPX-400 Spectrometer.  $\text{CDCl}_3$  was the solvent and the chemical shifts were recorded relative to the internal standard; tetramethylsilane (TMS). Average molecular weight was determined by gel permeation chromatography (GPC) using a Polymer Laboratories GPC 220 in tetrahydrofuran (THF).

### 2.3. Synthesis

Synthetic pathway was outlined in Scheme 1. The benzimidazole derivative was introduced into the structure of both polymers as the electron acceptor unit. Fluorene units with different pendant alkyl chains were used as electron donating moieties. For the synthetic route, benzothiadiazole was brominated and the product was reduced to diamine [24,25]. From the reaction of diamine and 4-tert-butylcyclohexanone, benzimidazole compound was produced [26]. Later dibromothiophene was stannylated to be used in Stille coupling reactions [27]. Chemical polymerizations of P1 and P2 were achieved via Stille coupling in the presence of palladium catalyst. The structures were confirmed by NMR Spectroscopy.

#### 2.3.1. Chemical polymerization for P1

One mol of 4, 7-dibromo-4'-(tert-butyl)spiro[benzo[d]imidazole-2,1'-cyclohexane] (3), 2 mol of 2,5-bis(tributylstannyl)thiophene and 1 mol of 2,7-dibromo-9,9-dihexyl-9H-fluorene were dissolved in dry THF under Ar atmosphere. The solution was heated to reflux.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (5 mol%) was added under high argon flow and the mixture was refluxed for 48 h. At the end of 48 h, the THF was removed under vacuum and the precipitate was washed with methanol, hexane and acetone respectively using soxhlett apparatus. P1 was obtained as a dark green solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.98 (m, 5H) 7.61 (m, 3H), 6.9 (s, 2H), 1.98 (t, 4H), 1.50 (m, 5H), 1.01 (s, 16H), 0.69 (m, 15H).

#### 2.3.2. Chemical polymerization for P2

One mol of 4, 7-dibromo-4'-(tert-butyl)spiro[benzo[d]imidazole-2,1'-cyclohexane] (3), 2 mol of 2,5-bis(tributylstannyl)thiophene and 1 mol of 2,7-dibromo-9,9-didodecyl-9H-fluorene were dissolved in dry THF under Ar atmosphere. After the solution was heated to reflux,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (5 mol%) was added under high argon flow. The mixture was refluxed for 48 h. At the end of 48 h, the THF was removed under vacuum and the precipitate was washed with methanol, hexane and acetone respectively using soxhlett. P2 was obtained as a dark green solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.00 (m, 5H) 7.63 (m,

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