Electrochimica Acta 109 (2013) 214–220

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The effect of para- and meta-substituted fluorine on optical behavior of benzimidazole derivatives

Merve Ileri[a], Serife O. Hacioglu[a], Levent Toppare[a,b,c,d,*]

[a] Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey
[b] Department of Biotechnology, Middle East Technical University, 06800 Ankara, Turkey
[c] Department of Polymer Science and Technology, Middle East Technical University, 06800 Ankara, Turkey
[d] The Center for Solar Energy Research and Application (GÜNAM), Middle East Technical University, 06800 Ankara, Turkey

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form 11 July 2013
Accepted 11 July 2013
Available online 26 July 2013

Keywords:
Electrochromism, Donor–acceptor,
Substitution effect, Fluorine

ABSTRACT

Design, synthesis, and electrochemical properties of two novel donor–acceptor–donor type benzimidazole and thiophene based monomers; 2-(4-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIPF**) and 2-(3-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIMF**) were highlighted. The position of fluorine as a substituent was varied from para- to meta- in order to investigate position effects on the electrochemical and optical properties of electrochemically synthesized polymers. Both polymers were p type dopable and they can be switched between orange and blue color during p-doping/dedoping. Significant improvements in the percent transmittance for **PBIMF** were observed compared to similar molecules in literature.

1. Introduction

Conjugated donor–acceptor (D–A) type polymers have drawn considerable interest due to properties like ease of processability, lightweight, high optical contrasts, fast switching times and tuning bandgap via structural modifications. These desirable properties make them more transcendent than inorganic materials [1]. On account of these advantages, conducting polymers can be used in many applications such as organic photovoltaics [2], electrochromic devices (EC) [3], organic light emitting diodes [4], organic field effect transistors [5] and sensors [6]. After detailed investigation, it is proved that bandgap has tremendous effect on electronic and optical properties of the conjugated polymers. In order to synthesize a functional polymer which is applicable in different fields, enhancing several properties with structural modification is very important. In literature different methods were used for combining desired properties in one structure such as; bandgap modification, using different substituents and combining different donor–acceptor groups [7–9].

In order to modify the bandgap of these functional materials, bond length alternation, increasing planarity, interchain effects, increasing stability of polymer with using resonance and donor–acceptor (D–A) theory can be utilized [10]. Among them, donor–acceptor theory is the most effective and commonly used method. In donor–acceptor theory, alternating electron-rich (donor) and electron-deficient (acceptor) units were combined in the polymer backbone to achieve desired bandgap. Besides, the D–A approach is not only used for obtaining low band gap polymers, but also for producing polymers with improved optical, mechanical and electronic properties [11].

Electrochromism is the reversible and visible change in transmittance or reflactance as a result of an applied voltage [12]. Characterization of electrochromic materials can be done by means of different parameters such as coloration efficiency, stability, electrochromic contrast, optical memory [13]. More importantly, an accessibility to a variety of colors by structural modification makes conjugated polymers one of the prominent EC materials.

In the literature different D–A type polymers were studied widely in order to investigate the effects of different D and A groups on the electronic and optical properties [14,15]. Recently, polymers that consist of benzothiadiazole, benzotriazole and benzimidazole as the acceptor units and derivatives of thiophene as the donor units were studied in our group [16–20]. However, derivatives of benzimidazole as the acceptor units have not been studied sufficiently up to now. Although, these benzimidazole derivatives demostrated promising and enhanced electrochemical properties, problems related to this unit are their low stability and poor electrochromic contrasts [18–20].

In this study, we have demonstrated a new class of electrochemically synthesized polymers, consisting of para- and

---

* Corresponding author at: Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey.
E-mail address: toppare@metu.edu.tr (L. Toppare).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.07.102

meta-fluorine substituted benzimidazole unit as an acceptor group and thiophene as a donor unit. Fluorine atom as a substituent has both inductive and mesomeric effects. Inductive effect will have the same influence for both position whereas, mesomeric effect will be dominant over inductive effect in para-position. In this case, depending upon the position of fluorine atom on the ring (para- or meta-) oxidation barriers will probably change. 2-(4-Fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIPF**) and 2-(3-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIMF**) were synthesized. These two novel monomers were polymerized electrochemically to obtain (**PBIPF**) and (**PBIMF**). Additionally, electrochemical, spectroelectrochemical and kinetic studies of polymers were performed.

It is worth to consider that both monomers reported in this article are novel and also the discussion on the position of fluorine atom on electronic properties will clarify substitution concept. In addition, this fluorine subtituent makes these functional polymers applicable in different fields. Herein, we introduce an approach to alter and get desired electronic properties of D–A type polymers simply by changing the position of substituents.

2. Experimental

2.1. General

All chemicals and reagents were obtained from commercial sources and used without further purification. THF was dried over sodium and benzophenone. 4,7-Dibromo-2.1.3-benzothiadiazole (**2**) and 3,6-dibromo-1,2-phenylenediamine (**3**) were synthesized according to previously published procedures [21,22]. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with TMS as the internal standard and $CDCl_3$ as the solvent. All shifts were given in ppm. Electrochemical studies were performed in a three-electrode cell consisting of an indium tin oxide (ITO) doped glass slide as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode using a Voltalab 50 potentiostat. The reference electrode was subsequently calibrated to Fc/Fc^+ (0.30 V) and the band energies were calculated relative to the vacuum level taking the value of SHE is −4.75 eV vs. vacuum. To perform the spectroelectrochemical studies of polymers Cary 5000 UV–vis spectrophotometer was used.

2.2. Synthesis of 4,7-dibromo-2-(4-fluorophenyl)-1H-benzo[*d*]imidazole (**4**)

4,7-Dibromo-2.1.3-benzothiadiazole (**2**) and 3,6-dibromo-1,2-phenylenediamine (**3**) were synthesized using previously stated procedures [21,22]. 4,7-Dibromo-2-(4-fluorophenyl)-1H-benzo[*d*]imidazole (**4**) was synthesized by the modification of a previously published procedure [23]. 3,6-Dibromo-1,2-phenylenediamine (**3**) (400 mg, 1.50 mmol) was dissolved in 4 mL acetonitrile. After hydrogen peroxide (0.8 mL, 8 mmol) was added to the mixture directly, 4-fluorobenzaldehyde (0.2 mL, 1.50 mmol) was added to the mixture drop wise. After that, ammonium cerium (IV) nitrate (90 mg, 0.16 mmol) was added to the mixture and stirred overnight at room temperature. 4,7-Dibromo-2-(4-fluorophenyl)-1H-benzo[*d*]imidazole (**4**) was purified by means of recrystallization with cold water and hexane. Compound **4** was obtained as beige solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.33 (s, 1H), 8.39 (dd, J = 3.1, 5.5, 8.6 Hz, 2H), 7.45–7.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.0, 129.9, 126.5, 125.9, 116.0, 115.8, 111.2.

2.3. Synthesis of 2-(4-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIPF**)

A solution of tributyl(thiophen-2-yl)stannane (1.010 g, 2.70 mmol) and 4,7-dibromo-2-(4-fluorophenyl)-1H-benzo[*d*]imidazole (**4**) (200 mg, 0.54 mmol) in tetrahydrofuran (40.0 mL, 0.49 mmol) was refluxed overnight under argon atmosphere with bis(triphenylphosphine)palladium (II) dichloride. The mixture was cooled and concentrated on the rotary evaporator before purification. So as to purify 2-(4-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIPF**), column chromatography technique was performed (silica gel, hexane:EtOAc 2:1) effectively. After that, the residue was subjected to preparative thin layer chromatography (silica, hexane:ethyl acetate 4:1) to purify **BIPF** completely as a yellow solid in 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 8.16 (dd, J = 1.2, 3.7 Hz, 1H), 8.04 (dd, J = 3.7, 5.2, 8.9 Hz, 2H), 7.53–7.55 (m, 1H), 7. 37–7.31 (m, 4H), 7.16–7.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 161.4, 149.0, 138.7, 127.4, 127.3, 126.6, 124.2, 123.9, 120.3, 114.8, 114.6. HRMS (EI) for $C_{21}H_{13}FN_2S_2$, calculated 377. 0582, found 377. 0557.

2.4. Synthesis of 4,7-dibromo-2-(3-fluorophenyl)-1H-benzo[*d*]imidazole (**5**)

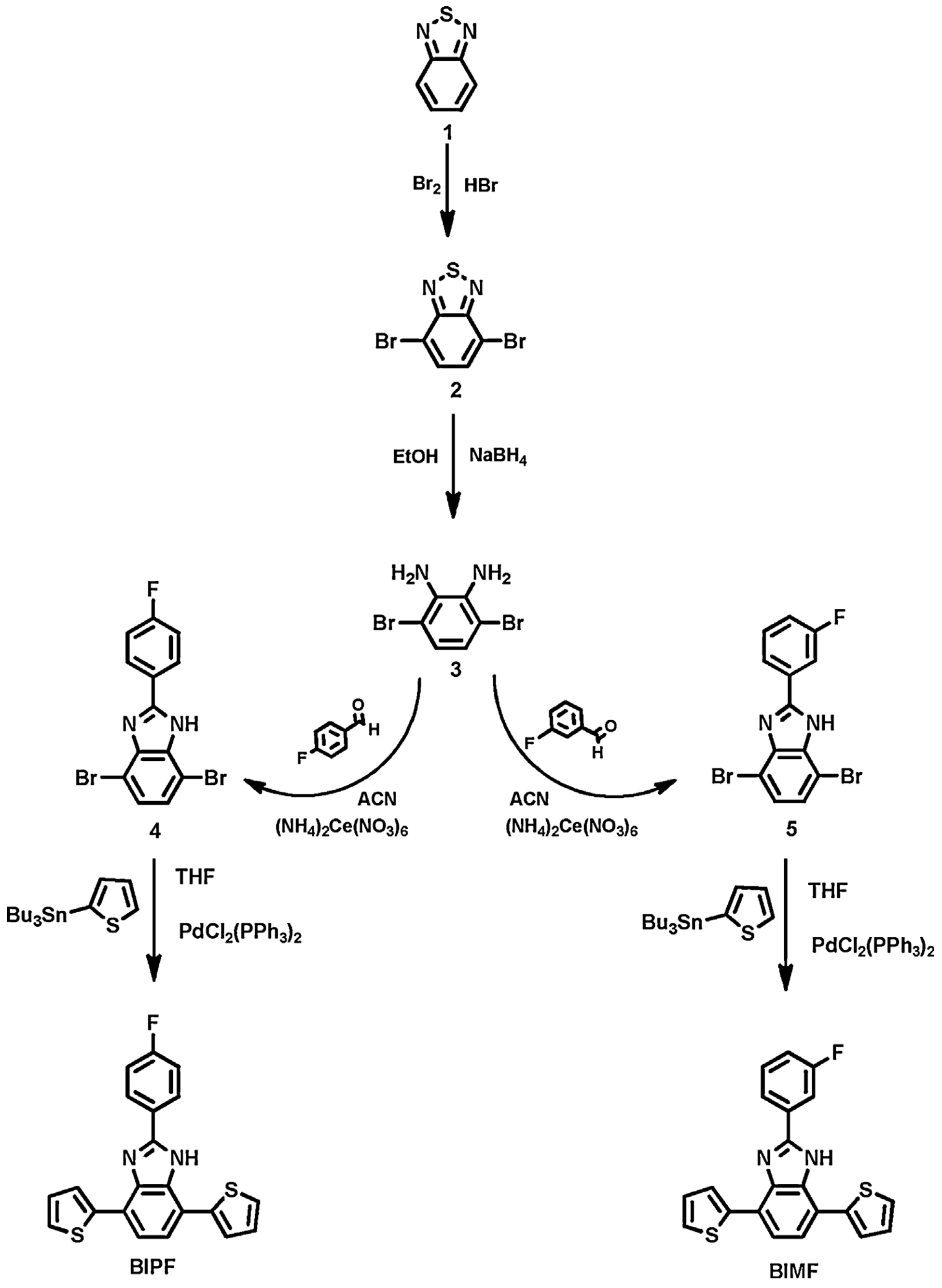
4,7-Dibromo-2-(3-fluorophenyl)-1H-benzo[*d*]imidazole (**5**) was synthesized by the modification of a previously published procedure [23]. 3,6-Dibromo-1,2-phenylenediamine (**3**) (600 mg, 2.25 mmol) was dissolved in 4 mL ACN. H_2O_2 (1.2 mL, 12 mmol) was added to the mixture directly. 3-Fluorobenzaldehyde (0.3 mL, 0.225 mmol) was added to the mixture dropwise. After that, ammonium cerium (IV) nitrate (120 mg, 0.21 mmol) was added to the mixture and stirred overnight at room temperature. Recrystallization with cold water and hexane was used in order to purify the compound **5**. As a result, compound **5** was obtained as a bejge solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.15 (m, 4H), 7.64 (dd, J = 6.6, 7.6, 14.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1, 131.0, 130.9, 126.4, 123.7, 123.6, 117.5, 117.3, 114.1, 113.9.

2.5. Synthesis of 2-(3-fluorophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[*d*]imidazole (**BIMF**)

A solution of tributyl(thiophen-2-yl)stannane (867 mg, 2.32 mmol) and 4,7-dibromo-2-(3-fluorophenyl)-1H-benzo[*d*]imidazole (**5**) (170 mg, 0.46 mmol) in tetrahydrofuran (40.0 mL, 0.49 mmol) was refluxed overnight under argon atmosphere. Bis(triphenylphosphine)palladium (II) dichloride was added to the mixture as the catalyst. The reaction was concentrated on the rotary evaporator and for purification of **BIMF** the residue was subjected to column chromatography technique (silica gel, hexane:EtOAc 3:1). After that, preparative thin layer chromatography (silica, hexane:ethyl acetate 4:1) was carried out to get **BIMF** totally as a yellow solid in 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 8.19 (dd, J = 1.1, 2.5, 3.6 Hz, 1H), 7.85–7.82 (m, 1H), 7.81–7.78 (m, 1H), 7.59–7.56 (m, 1H), 7.42–7.34 (m, 5H), 7.17–7.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 160.9, 149.2, 149.1, 139.3, 129.7, 129.6, 127.1, 124.5, 121.1, 116.4, 116.2, 113.0, 112.8. HRMS (EI) for $C_{21}H_{13}FN_2S_2$, calculated 377. 0582, found 377. 0558.



Scheme 1. Synthetic route for the monomers.

3. Results and discussion

3.1. Synthesis

The general synthetic routes toward the monomers are depicted in Scheme 1. Bromination of 1,3-benzothiadiazole with Br_2/HBr was afforded 4,7-dibromo-2.1.3-benzothiadiazole (**2**) with high yield [21]. After bromination, the reduction of this dibrominated compound (**2**) by $NaBH_4$ gave 3,6-dibromo-1,2-phenylenediamine (**3**) as described in literature [22]. In order to synthesize desired acceptor units; 4,7-dibromo-2-(4-fluorophenyl)-1H-benzo[*d*]imidazole (**4**) and 4,7-dibromo-2-(3-fluorophenyl)-1H-benzo[*d*]imidazole (**5**), the condensation of compound (**3**) with 4-fluorobenzaldehyde and 3-fluorobenzaldehyde were performed from an adapted procedure described in literature [23]. Finally, the Stille coupling of these compounds with tributyl(thiophen-2-yl)stannane [24] gave the desired monomers **BIPF** and **BIMF** (Scheme 1).

3.2. Electrochemical properties

The monomers **BIPF** and **BIMF** were electrochemically polymerized by cyclic voltammetry (CV) in order to probe the electrochemical characters of polymers. The CV was performed on indium tin oxide (ITO, 1.5 cm^2) coated glass slides with 0.1 M acetonitrile (ACN)/dichloromethane (CH_2Cl_2) (95/5, v/v) solution at several scan rates where best results were obtained with 100 mV/s. Sodium perchlorate ($NaClO_4$) and lithium perchlorate ($LiClO_4$) were used as the supporting electrolytes during electropolymerization with repeated scan

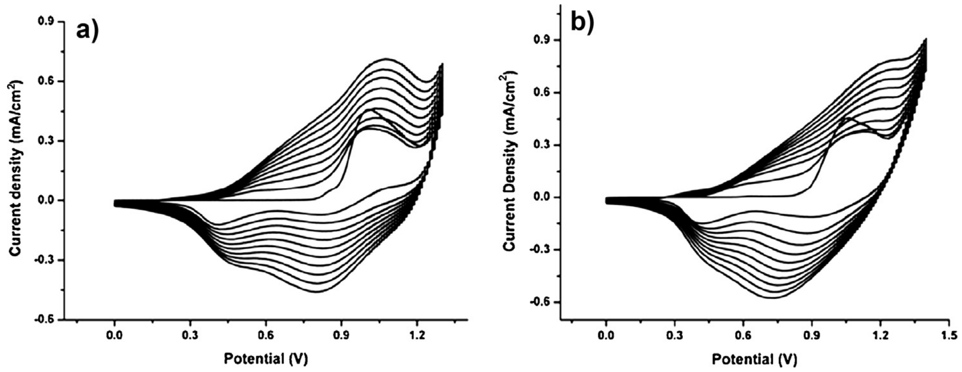


Fig. 1. Repeated potential scan polymerization of (a) **BIPF** and (b) **BIMF** at 100 mV s^{-1} in 0.1 M $LiClO_4/NaClO_4$ CH_2Cl_2/ACN (5:95, v:v) solution on an ITO electrode.

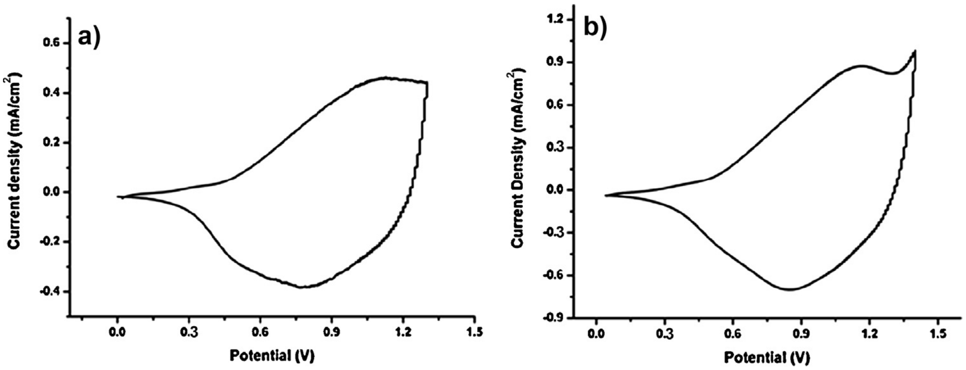


Fig. 2. Single scan cyclic voltammograms of (a) **PBIPF** and (b) **PBIMF** in a monomer free 0.1 M $LiClO_4/NaClO_4$ ACN solution.

intervals (10 scans) between 0 V and 1.3 V for **BIPF** and 0 V and 1.4 V for **BIMF** (Fig. 1).

The irreversible monomer oxidation peaks were appeared in the first cycles at 1.0 V for **BIPF** and at 1.05 V for **BIMF**. After the first cycle, observation of a new reversible redox couple with an increasing current intensity after each successive cycle proves the formation of electroactive polymer films **PBIPF** and **PBIMF** (Fig. 1).

Electrochemically synthesized polymers were subjected to CV in a monomer free solution in order to investigate the p-type and n-type doping properties of the polymers. In 0.1 M $LiClO_4/NaClO_4$/ACN solution both polymers are p-dopable with a reversible redox couple at 1.0 V/0.78 V for **PBIPF** and at 1.1 V/0.84 V for **PBIMF** vs. the Ag wire pseudo reference electrode.

The HOMO energy levels of each polymers were calculated from onset of the corresponding oxidation potentials vs. Fc/Fc^+ reference electrode (Fig. 2). Both polymers have only p-doping property hence, LUMO energy levels were calculated by using optical band gap values. As seen in Table 1 the HOMO levels were reported as −5.46 eV (**PBIPF**) and −5.54 eV (**PBIMF**) respectively.

The HOMO levels differ from each other slightly, this difference indicates the ease of oxidation of polymer films in this electrolytic medium (Table 1). This behavior can be explained by position of fluorine atom. Changing the position of fluorine unit from para- to meta- on the phenyl ring has a tremendous effect on kinetic properties as depicted in Table 2. In addition, this position change affects electrochemical and spectroelectrochemical properties significantly.

Fluorine atom as a substituent has both inductive effect (electron-withdrawing) and mesomeric effect (electron-donating). Inductive effect will have the same influence for both position whereas, mesomeric effect will be dominant over inductive effect in para-position [25]. In this case, depending upon the position of fluorine atom on the ring (para- or meta-) oxidation barriers will probably change. When resonance structures are considered, it is seen that para-substituted fluorine (**PBIPF**) could stabilize the possible cationic charge. As a result of higher ring stabilization of para-substituted one (**PBIPF**), its oxidation will be easier and its oxidation potential will be lower compared to meta-substituted derivative (**PBIMF**) which supports our results (Table 1).

Table 1
Summary of electrochemical and spectroelectrochemical properties of **PBIPF** and **PBIMF**.

	HOMO (eV)	LUMO (eV)	λ_{max} (nm)	E_g^{op} (eV)
PBIPF	−5.46	−3.55	471	1.91
PBIMF	−5.54	−3.58	440	1.96

3.3. *Spectroelectrochemistry*

The optical changes upon stepwise doping and the electrochromic properties of conjugated polymers were investigated by conducting spectroelectrochemistry studies of **PBIPF** and **PBIMF**. Both polymers were electrochemically synthesized on ITO and spectral changes were explored by UV–vis-NIR spectrometer in a monomer-free 0.1 M $NaClO_4$–$LiClO_4$/ACN solution via

Table 2
Summary of kinetic and optic studies of **PBIPF** and **PBIMF**.

	Optical contrast (ΔT%)		Switching times (s)
PBIPF	16%	475 nm	0.4
	17%	685 nm	0.4
	41%	1220 nm	0.3
PBIMF	29%	460 nm	0.7
	28%	770 nm	1.3
	73%	1265 nm	1.7

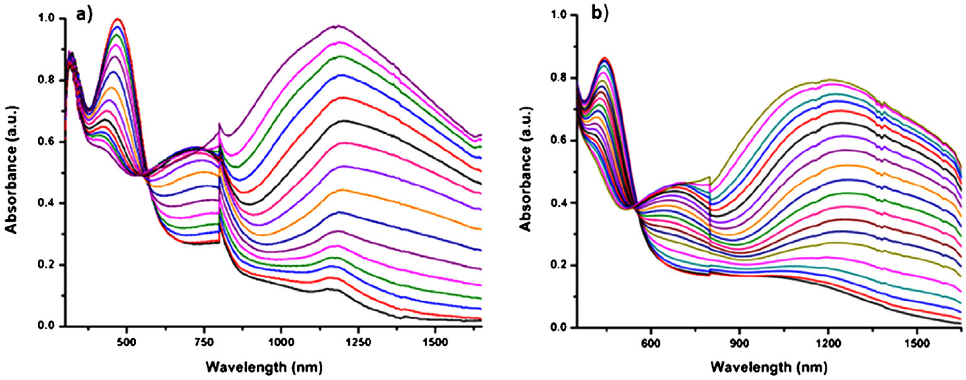


Fig. 3. Electronic absorption spectra for (a) **PBIPF** and (b) **PBIMF** films in 0.1 M $NaClO_4$–$LiClO_4$/ACN solution between 0.0 V and 1.2 V for **PBIPF**, 0.0 V and 1.15 V for **PBIMF**.

incrementally increasing applied potential between 0.0 V and 1.2 V for **PBIPF**, 0.0 V and 1.15 V for **PBIMF**. These ranges are in accordance with the CV results as given in Fig. 1.

Initially, in order to remove any trapped charge and dopant ion during electrochemical polymerization, polymer coated ITO films were reduced to their neutral state, and then stepwise oxidation was performed. During oxidation while the absorption in the visible region reached a minimum value, new absorption bands (polaron, bipolaron bands). For **PBIPF** polaronic and bipolaronic bands appear at 720 and 1180 nm respectively. These are revealed at 705 nm, 1170 nm for **PBIMF**. The normalized spectral changes occurring upon electrochemical oxidation of **PBIPF** and **PBIMF** were depicted in Fig. 3a and b in the range of 300−1650 nm.

When we compare the electronic absorption spectra of **PBIPF** and **PBIMF**, the effect of position of fluorine atom on spectroelectrochemical properties can be seen. The difference on the λ_{max} values and optical band gaps can be explained by the parameters that affect absorption spectra of conjugated polymers. In literature, it is known that these properties are widely affected by effective conjugated length and packing of resulting polymers [26].

When the position of fluorine atom was changed from meta to para, better packing was achieved in the polymer backbone which causes a shift in absorption maxima from 440 nm to 471 nm. Optical band gaps (E_g^{op}) of the **PBIPF** and **PBIMF** were calculated from the onsets of lowest energy π–π^* transitions as 1.91 eV and 1.96 eV, respectively. The λ_{max} of the **PBIPF** signifies 31 nm a red-shift when compared with λ_{max} of the **PBIMF**. To sum up, better packing for **PBIPF** will result lower energy and higher λ_{max}.

In addition, spectroelectrochemical studies of the polymer films illustrate that the film's color changed during the p-doping (oxidation) processes. Structures of **PBIPF**, **PBIMF** and their colors at their neutral and different oxidized states were demonstrated in Fig. 4a and b.

At the neutral state, both **PBIPF** and **PBIMF** have orange color. Following successive oxidation, intensity of absorption bands in the visible region steadily decrease while new absorption bands appear, and polymers have green color during oxidation. Finally, further oxidation results blue color for both polymers at fully oxidized state.

As seen in Fig. 4 there is little difference between the colors of **PBIPF** and **PBIMF**, which means that the changing position of flourine atom from para- to meta-position has a little effect on colors of corresponding polymers.

3.4. Electrochromic contrast and switching studies

The capability of a polymer to change its color rapidly between two states (neutral state and oxidized state) and illustrating a significant change are crucial properties for an electrochromic polymer. Switching time is defined as the period required for

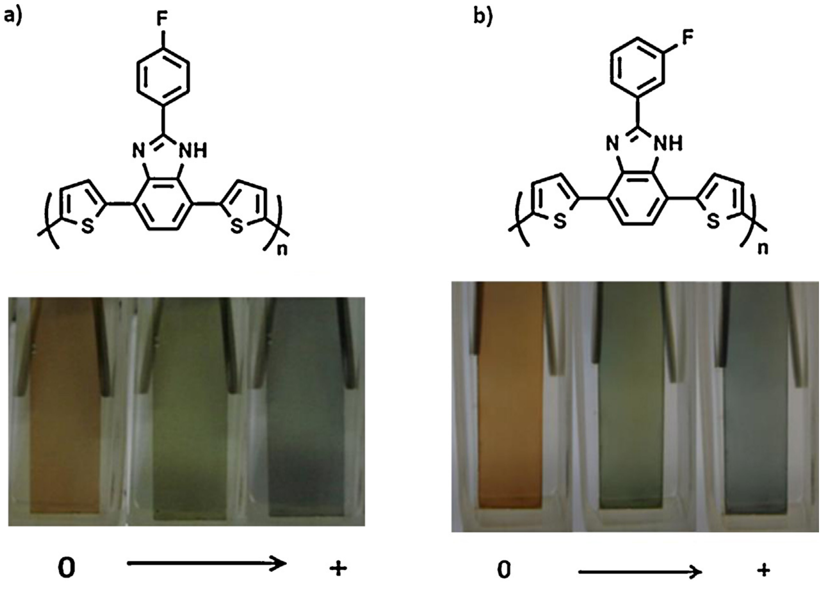


Fig. 4. Structures of the polymers and their colors at their neutral and different oxidized states.

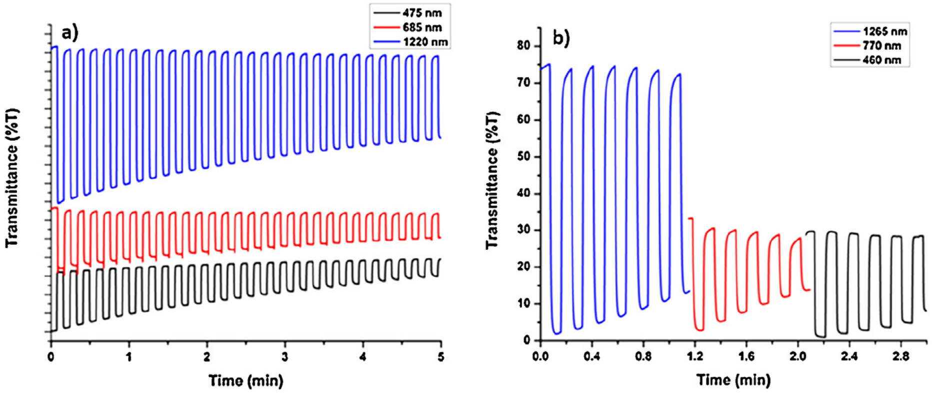


Fig. 5. Optical contrasts and switching times monitored at different wavelengths for (a) **PBIPF** and (b) **PBIMF** in 0.1 M $NaClO_4$–$LiClO_4$/ACN solution.

the color change of a material between its neutral and oxidized states. The percent transmittance changes and switching times of **PBIPF** and **PBIMF** between their fully oxidized and reduced states were investigated by applying potentials within 5 s time intervals. The kinetic studies were performed in a monomer free 0.1 M $NaClO_4$–$LiClO_4$/ACN solvent-electrolyte couple. The wavelengths at which kinetic studies performed were determined from the maximum absorbance at the spectra of polymer films.

As summarized in Table 2, **PBIPF** showed 41% transmittance change upon doping/de-doping process at 1220 nm, 17% at 685 nm and 16% at 475 nm. **PBIMF** revealed 73% transmittance at 1265 nm, 28% at 770 nm and 29% at 460 nm. Switching times were reported as 0.3 s, 0.4 s and 0.4 s for **PBIPF** and 1.7 s, 1.3 s and 0.7 s at corresponding wavelengths (Fig. 5).

Kinetic studies strongly support the argument discussed in the electrochemical studies part. As explained before, para-substituted fluorine has more ring stabilization effect on this benzimidazole derivative when compared with meta-substituted one. This effect decreases the oxidation barrier of **PBIPF** and increases its tendency to undergo a redox process which affects kinetic studies of the polymers significantly. As a result, switching times of **PBIPF** were really low when compared with **PBIMF** in all wavelengths which is consistent with our argument (Table 2).

In addition, when percent transmittance changes of **PBIMF** compared with other benzimidazole derivatives to best of our knowledge 73% is the highest one in all. To sum up, although stability of the polymers is not as good as other benzimidazole derivatives, swicthing times of **PBIPF** and percent transmittance of **PBIMF** are better compared to similar molecules [18–20].

4. Conclusion

In this study, two new benzimidazole and thiophene based polymers; **PBIPF** and **PBIMF** were synthesized, purified and characterized successfully. In order to discuss the effect of position of substituents on electrochemical properties, both para- and meta-substituted derivatives were designed. Different switching times, optical contrasts and HOMO/LUMO energy levels were observed for these two derivatives from electrochemical and spectroelectrochemical studies. Both polymer films have p-type doping property and showed electrochromic properties under applied different potentials. This makes them applicable for use in electrochromic devices. In addition, optical contrasts were enhanced by changing the position of fluorine from para- to meta- which was attributed to the better ring stabilization effect of para-substituted one. When percent transmittance changes of **PBIMF** compared with other benzimidazole derivatives from the literature to best of our knowledge 73% is the highest one. Reported results show that fluorine containing benzimidazole derivatives are multipurpose materials due to improved kinetic results and band gaps. These materials will be subject of further research interest in our group.

Acknowledgements

The authors appreciate the financial support of BAP-01-03-2013-013 and Prof. Dr. Cihangir Tanyeli for valuable discussions. We thank Cem Ozcan for the preparation of the graphical abstract.

References

[1] B.C. Thompson, P. Schottland, K. Zong, J.R. Reynolds, In situ colorimetric analysis of electrochromic polymers and devices, Chemistry of Materials 12 (2000) 1563.

[2] (a) S. Gunes, H. Neugebauer, N.S. Sariciftci, Conjugated polymer-based organic solar cells, Chemical Reviews 107 (2007) 1324;
(b) R.S. Kularatne, H.D. Magurudeniya, P. Sista, M.C. Biewer, C. Mihaela, Stefan, Donor–acceptor semiconducting polymers for organic solar cells, Journal of Polymer Science Part A: Polymer Chemistry 51 (2013) 743;
(c) Z. Li, D. Zhou, L. Li, Y. Li, Y. He, J. Liub, Q. Peng, Synthesis and characterization of copolymers based on benzotriazoles and different atom-bridged dithiophenes for efficient solar cells, Polymer Chemistry 4 (2013) 2496;
(d) J.C. Bijleveld, A.P. Zoombelt, S.G.J. Mathijssen, M.M. Wienk, M. Turbiez, D.M. Leeuw, R.A.J. Janssen, Poly(diketopyrrolopyrrole−terthiophene) for ambipolar logic and photovoltaics, Journal of the American Chemical Society 131 (2009) 16616;
(e) J.-H. Tsai, C.-C. Chueh, W.-C. Chen, C.-Y. Yu, G.-W. Hwang, C. Ting, E.-C. Chen, H.-F. Meng, New thiophene–phenylene–thiophene acceptor random conjugated copolymers for optoelectronic applications, Journal of Polymer Science Part A: Polymer Chemistry 48 (2010) 2351.

[3] (a) E. Unur, P.M. Beaujuge, S. Ellinger, J.H. Jung, J.R. Reynolds, Black to transmissive switching in a pseudo three-electrode electrochromic device, Chemistry of Materials 21 (2009) 5145;
(b) A. Balan, D. Baran, L. Toppare, Benzotriazole containing conjugated polymers for multipurpose organic electronic applications, Polymer Chemistry 2 (2011) 1029;
(c) S. Ozdemir, M. Sendur, G. Oktem, O. Doğan, L. Toppare, A promising combination of benzotriazole and quinoxaline units: a new acceptor moiety toward synthesis of multipurpose donor–acceptor type polymers, Journal of Materials Chemistry 22 (2012) 4687;
(d) C. Xua, J. Zhaoa, J. Yub, C. Cuia, Ethylenedioxythiophene derivatized polynapthalenes as active materials for electrochromic devices, Electrochimica Acta 96 (2013) 82;
(e) C. Xua, J. Zhaoa, M. Wang, Z. Wang, C. Cuia, Y. Kong, X. Zhang, Electrosynthesis and characterization of a neutrally colorless electrochromic material from poly(1,3-bis(9H carbazol-9-yl)benzene) and its application in electrochromic devices, Electrochimica Acta 68 (2012) 184.

[4] C.A. Zuniga, S. Barlow, S.R. Marder, Approaches to solution-processed multilayer organic light-emitting diodes based on cross-linking, Chemistry of Materials 23 (2011) 658.

[5] M. Horie, L.A. Majewski, M.J. Fearn, C.Y. Yu, Y. Luo, A. Song, B.R. Saundersand, M.L. Turner, Cyclopentadithiophene based polymers—a comparison of optical, electrochemical and organic field-effect transistor characteristics, Journal of Materials Chemistry 20 (2010) 4347.

[6] (a) F. Ekiz, F. Oğuzkaya, M. Akin, S. Timur, C. Tanyeli, L. Toppare, Synthesis and application of poly-SNS-anchored carboxylic acid: a novel functional matrix for biomolecule conjugation, Journal of Materials Chemistry 21 (2011) 12337;
(b) S. Demirci, F.B. Emre, F. Ekiz, F. Oguzkaya, S. Timur, C. Tanyeli, L. Toppare, Functionalization of poly-SNS-anchored carboxylic acid with Lys and PAMAM:

surface modifications for biomolecule immobilization/stabilization and biosensing applications, Analyst 137 (2012) 4254.

[7] H.-Y. Chen, S.-C. Yeh, C.-T. Chen, C.-T. Chen, Comparison of thiophene- and selenophene-bridged donor–acceptor low band-gap copolymers used in bulk-heterojunction organic photovoltaics, Journal of Materials Chemistry 22 (2012) 21549.

[8] Y. Lin, Y. Lia, X. Zhan, Small molecule semiconductors for high-efficiency organic photovoltaics, Chemical Society Reviews 41 (2012) 4245.

[9] (a) U. Salzner, Does the donor–acceptor concept work for designing synthetic metals? 1. theoretical investigation of poly(3-cyano-3′-hydroxybithiophene), Journal of Physical Chemistry B 106 (2002) 9214;
(b) P. Dutta, H. Park, W.-H. Lee, K. Kim, I.N. Kangb, S.-H. Lee, Naphtho[1, 2-*b*:5,6-*b*′]dithiophene-based conjugated polymer as a new electron donor for bulk heterojunction organic solar cells, Polymer Chemistry 3 (2012) 601.

[10] (a) Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, Synthesis of conjugated polymers for organic solar cell applications, Chemical Reviews 109 (2009) 5868;
(b) P.-M. Beaujuge, J.-R. Reynolds, Color control in π-conjugated organic polymers for use in electrochromic devices, Chemical Reviews 110 (2010) 268.

[11] A. Balan, D. Baran, L. Toppare, Benzotriazole containing conjugated polymers for multipurpose organic electronic applications, Polymer Chemistry 2 (2011) 1029.

[12] R.J. Mortimer, Electrochromic materials, Chemical Society Reviews 26 (1997) 147.

[13] A.A. Argun, P.H. Aubert, B.C. Thompson, I. Schwendeman, C.L. Gaupp, J. Hwang, N.J. Pinto, D.B. Tanner, A.G. MacDiarmid, J.R. Reynolds, Multicolored electrochromism in polymers: structures and devices, Chemistry of Materials 16 (2004) 4401.

[14] (a) B.C. Thompson, L.G. Madrigal, M.R. Pinto, T.-S. Kang, K.S. Schanze, J.R. Reynolds, Donor–acceptor copolymers for red- and near-infrared-emitting polymer light-emitting diodes, Journal of Polymer Science Part A: Polymer Chemistry 43 (2005) 1417;
(b) D.-M. Kima, K.-B. Shimb, J.I. Sona, S.S. Reddya, Y.-B. Shim, Spectroelectrochemical and electrochromic behaviors of newly synthesized poly[3′-(2-aminopyrimidyl)-2,2′:5′,2″-terthiophene], Electrochimica Acta 104 (2013) 322.

[15] (a) N. Zhou, X. Guo, R.P. Ortiz, S. Li, S. Zhang, R.P.H. Chang, A. Facchetti, T.J. Marks, Bithiophene imide and benzodithiophene copolymers for efficient inverted polymer solar cells, Advanced Materials 24 (2012) 2242;
(b) M. İçli, M. Pamuk, F. Algi, A.M. Önal, A. Cihaner, Donor–acceptor polymer electrochromes with tunable colors and performance, Chemistry of Materials 22 (2010) 4034.

[16] G. Oktem, A. Balan, D. Baran, L. Toppare, Donor–acceptor type random copolymers for full visible light absorption, Chemical Communications 47 (2011) 3933.

[17] G. Gunbas, L. Toppare, Electrochromic conjugated polyheterocycles and derivatives—highlights from the last decade towards realization of long lived aspirations, Chemical Communications 48 (2012) 1083.

[18] H. Akpınar, A. Balan, D. Baran, E.K. Ünver, L. Toppare, Donor–acceptor–donor type conjugated polymers for electrochromic applications: benzimidazole as the acceptor unit, Polymer 51 (2010) 6123.

[19] A.G. Nurioglu, H. Akpinar, M. Sendur, L. Toppare, Multichromic benzimidazole-containing polymers: comparison of donor and acceptor unit effects, Journal of Polymer Science Part A: Polymer Chemistry 50 (2012) 3499.

[20] A.C. Ozelcaglayan, M. Sendur, N. Akbasoglu, D.H. Apaydin, A. Cirpan, L. Toppare, Synthesis and electrochemical properties of a new benzimidazole derivative as the acceptor unit in donor–acceptor–donor type polymers, Electrochimica Acta 67 (2012) 224.

[21] B.A. Da Silveria Neto, A.L. SantAna, G. Ebeling, S.R. Goncalves, E.V.U. Costa, H.F. Quina, J. Dupont, Photophysical and electrochemical properties of π-extended molecular 2,1,3-benzothiadiazoles, Tetrahedron 61 (2005) 10975.

[22] Y. Tsubata, T. Suzuki, T. Miyashi, Y. Yamashita, Single-component organic conductors based on neutral radicals containing the pyrazino-TCNQ skeleton, Journal of Organic Chemistry 57 (1992) 6749.

[23] K. Bahrami, M.M. Khodaei, F. Naali, Mild and highly efficient method for the synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles, Journal of Organic Chemistry 73 (2008) 6835.

[24] S.S. Zhu, T.M. Swager, Conducting polymetallorotaxanes: metal ion mediated enhancements in conductivity and charge localization, Journal of the American Chemical Society 119 (1997) 12568.

[25] Y. Huang, M. Zhang, L. Ye, X. Guo, C.C. Han, Y. Li, J. Hou, Molecular energy level modulation by changing the position of electron-donating side groups, Journal of Materials Chemistry 22 (2012) 5700.

[26] W.A. Goedel, N.S. Somanathan, V. Enkelmann, G. Wegner, Steric effects in 3-substituted polythiophenes: comparing band gap, nonlinear optical susceptibility and conductivity of poly(3-cyclohexylthiophene) and poly(3-hexylthiophene), Macromolecular Chemistry 193 (1992) 1195.