Spray-Processable Thiazolothiazole-Based Copolymers with Altered Donor Groups and Their Electrochromic Properties

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ABSTRACT: Two novel thiazolo[5,4-d]thiazole containing donoracceptor type alternating copolymers, poly[2-(5-(2-decyl-2Hbenzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo [5,4-d]thiazole] (BTzTh) and poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)furan-2-yl)-5-(furan-2-yl)thiazolo[5,4-d]thiazole] (BTzFr) were synthesized by Stille coupling polymerization and their electrochemical and electrochromic properties were explored. Electrochemical activities of the spray-casted polymer films were determined by cyclic voltammetry. To evaluate the effect of thiophene and furan moieties on the optical properties of the copolymers, spectroelectrochemistry studies were performed. To examine the switching abilities, copolymer films were

INTRODUCTION Invention of conducting polymers¹ opened a new era in construction of organic electronics. The usefulness of this class of polymer originates since they can be tailored to be used in different applications. As an example, introducing alkyl chains to the polymer's backbone gained to obtain solubility, which is indispensable for developing low-cost and large area optoelectronic devices.²

The uncertainty in conductivity of polyfurans compare to polythiophenes was interpreted in terms of unfavorable electronic effects of the oxygen atom.³ Additionally, due to the difficulties in handling furan relative to other five-membered heterocycles and its lower stability, it is less considered as a building block than pyrrole and thiophene. However, biodegradable properties and availability of biorenewable sources of furan-based materials^{4,5} could make them more fascinating than current favorites of organic electronics.^{6,7}

Thiazolo[5,4-d]thiazole (TTz) molecule has a rigid and coplanar fused ring which ensures highly extended π -electron system. Thanks to its quite straightforward preparation starting from the corresponding aldehyde and dithiooxamide, TTz subjected to a double potential step chronoamperometry in their local maximum absorptions. Both thiazolothiazolecontaining copolymers showed multichromic properties with low band-gap values 1.7 and 1.9 eV for BTzTh and BTzFr, respectively. The decent electrochromical properties together with solution processability make them important candidates for electrochromic applications. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3901–3906

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was used to modify the target molecules to design and obtain novel structures for different purposes, such as liquid crystallines,⁸ binuclear heterocyclic ligands,⁹ biological activity,¹⁰ electroluminescence,¹¹ and fluorescent chemosensors.¹²

Because of high on/off ratio and stability against oxygen as well as their π -stacked structure leading to strong intermolecular interactions in solid state, TTz derivatives emerged recently as promising semiconductors.^{13–23} Additionally, TTz derivatives appear to be very useful as active materials in bulk heterojunction solar cells for effective charge transport. Therefore, TTz containing small molecules and conjugated copolymers were designed and synthesized for organic photovoltaics (OPVs).^{24–31}

In obtaining a low band-gap-conjugated polymer, donoracceptor (DA) approach and planarity are the two important parameters to be considered. The advantage of the absence of the H-atoms in the core of TTz molecule should enhance both stability and the planarity of the polymer when introduced this molecule into a main chain. In literature, there exists a review on thiazole-based organic semiconductors for

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organic electronics which summarizes all small molecules and polymers containing TTz molecule used in OFETs and OPVs.³² To our knowledge, electrochromic properties of TTzbased polymers never explored so far. In this study, we were interested to design and prepare two novel copolymers to investigate their optoelectronic properties using thiophene and furan as the electron rich and BTz and TTz as the electron deficient moieties to obtain a DA configuration. Chemically synthesized copolymers showed multichromic properties and fast switching times and low band-gap values, which makes them promising candidates for electrochromic device applications.

EXPERIMENTAL

Instrumentation and Materials

Electrochemical studies were performed in a three-electrode cell containing an indium tin oxide-doped glass slide (ITO, 12 Ω -cm), a platinum wire, and an Ag wire as the working, counter, and pseudo-reference electrodes, respectively with a Voltalab PST 050 potentiostat. Spectroelectrochemical and kinetic studies were conducted by Varian Cary 5000 UV-vis-NIR spectrophotometer coupled with a Solartron 1285 Potentiostat. Minolta CS-100 spectrophotometer was used for quantitative determination of the film colors coated on ITO slides. For structural characterization, $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra were recorded in CDCl3 on Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. Average molecular weight was determined by gel permeation chromatography (GPC) using a Polymer Laboratories GPC 220 in tetrahydrofuran (THF) and polystyrene as the standard.

All chemicals were purchased from Aldrich and Acros and used as they received without further purification. THF was dried before use in benzophenone/Na system. Polymerization reactions were carried out under argon atmosphere. 4,7-Dibromo-2decyl-2H-benzo[d][1,2,3]triazole,³³ 2,5-di(thiophen-2-yl)thiazolo [5,4-d]thiazole, 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiaz zole, 2,5-di(furan-2-yl)thiazolo[5,4-d]thiazole, and 2,5-bis(5bromofuran-2-yl)thiazolo[5,4-d]thiazole^{14,29} were synthesized according to the literature procedures.

Synthesis of 2,5-Bis(5-(tributylstannyl)thiophen-2-yl)thiazolo[5,4-*d*]thiazole

This monomer was synthesized using a modified procedure excerpted from the literature.¹⁹ 2,5-Bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (500 mg, 1.08 mmol) were dissolved in dry THF (50 mL) under argon atmosphere. After adjusting the temperature to -78 °C, 2.5 M solution of *n*-BuLi in hexane (1.07 mL, 2.68 mmol) were added dropwise and stirred for 2 h. SnBu₃Cl (3.21 mL, 2.62 mmol) were added in one portion to the mixture under same conditions, and the mixture was warmed up to the room temperature. Ethyl acetate (50 mL) and water (50 mL) were added. Organic layer was separated and washed with water several times and dried with MgSO₄. After removing the solvent, the residue was purified via column chromatography over Al₂O₃

(eluent: DCM:hexane (1:1)) to obtain the product (yield: 65%).

¹H NMR (400 MHz, CDCl₃, δ): 7.59 (d, ³*J* = 3.6, 2H), 7.08 (d, ³*J* = 3.6, 2H), 1.51 (m, 12H), 1.28 (m, 12H), 1.08 (t, ³*J* = 8, 12H), 0.83 (t, ³*J* = 7.6-7.2, 18H). ¹³C NMR (100 MHz, CDCl₃, δ): 162.3, 142.7, 142.6, 142.6, 136.1, 127.7, 28.9, 27.2, 13.6, 11.0.

Synthesis of 2,5-Bis(5-(tributylstannyl)furan-2-yl)thiazolo[5,4-*d*]thiazole

The monomer was synthesized using the same procedure described above with 2,5-bis(5-bromofuran-2-yl)thiazolo[5,4-d]thiazole (1.33 g, 3.0 mmol), *n*-BuLi (3.0 mL, 4.73 mmol), and SnBu₃Cl (9.0 mL, 7.35 mmol) to obtain the monomer as a dark orange oil (yield: 60%).

¹H NMR (400 MHz, CDCl₃, δ): 7.02 (d, ³*J* = 3.6, 2H), 6.62 (d, ³*J* = 3.6, 2H), 1.54 (m, 12H), 1.28 (m, 12H), 1.08 (t, ³*J* = 8, 12H), 0.84 (t, ³*J* = 7.6-7.2, 18H). ¹³C NMR (100 MHz, CDCl₃, δ): 165.5, 158.9, 153.3, 150.6, 124.1, 109.8, 28.9, 27.2, 13.7, 10.4.

General Procedure for the Synthesis of the Copolymers (BTzTh and BTzFr)

Polymers were synthesized according to the similar procedures in literature³¹ starting from respective monomers. Equal equivalents of distannylated and dibrominated compounds were dissolved in dry toluene. The mixture was purged with argon for 15 min and $Pd(PPh_3)_4$ was added. Under argon flow, the reactants were refluxed for 36 h. After removing the 90% of the solvent, the mixture was poured into the cold MeOH and filtered through a Soxhlet thimble. The polymers were washed with MeOH and hexane via Soxhlet and recovered with DCM. The ¹H NMR and GPC data of the polymers are listed below.

Poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole] (BTzTh): $M_{\rm w}$: 17,889 g mol⁻¹; $M_{\rm n}$: 8288 g mol⁻¹; $M_{\rm w}/M_{\rm n}$: 2.2. ¹H NMR (400 MHz, CDCl₃, δ: 7.91 (benzotriazole), 7.77–7.32 (thiophene), 4.70 (N—CH₂), 2.11 (CH₂), 1.50–1.22 (alkyl chain), 0.80 (CH₃).

Poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)furan-2-yl)-5-(furan-2-yl)thiazolo[5,4-d]thiazole] (BTzFr): M_{w} : 5962 g mol⁻¹; M_{n} : 1516 g mol⁻¹; M_{w}/M_{n} : 3.9. ¹H NMR (400 MHz, CDCl₃, δ : 7.79 (benzotriazole), 7.30–6.84 (furan), 4.71 (N—CH₂), 2.10 (CH₂), 1.30–1.12 (alkyl chain), 0.79 (CH₃).

RESULTS AND DISCUSSION

Monomer and Copolymer Synthesis

To synthesize the thiophene and furan-containing thiazolothiazole building blocks, corresponding aldehyde was condensed with dithiooxamide in DMF. After bromination with NBS stannylation reactions were performed using a strong base (*n*-BuLi) in an inert atmosphere. To obtain solution processable copolymers alkylated dibromobenzotriazole derivative coupled with distannylated TTz derivatives in dry toluene. Reaction times were kept as 36 h for both copolymers. After precipitating in



FIGURE 1 Cyclic voltammograms of the copolymers (a) BTzTh and (b) BTzFr.

methanol, copolymers were purified by Soxhlet extraction. Both copolymers exhibited good solubility in common organic solvents, such as chloroform, dichloromethane, and toluene (Scheme 1).

Polymer Electrochemistry

To investigate the redox potentials of the copolymers with different repeat units, cyclic voltammetry (CV) was performed. The spray-cast thin films on ITO slides were prepared from the DCM solutions (5 mg mL⁻¹) to use as the working electrode in combination with a platinum wire as the counter and an Ag wire as the pseudo reference. Figure 1 shows a set of cyclic voltammograms performed in the potential range between 0.0 and 1.6 V for BTzTh and BTzFr at a scan rate of 100 mV s⁻¹. In Table 1, electrochemical results and HOMO/LUMO energy levels of the copolymers

TABLE 1 Electrochemical and Electrochromic Properties of Thiophene and Furan Bridged Thiazolothiazole Containing

 Copolymers

	BTzTh	BTzFr
E ^{doped, ox} (V)	1.55	1.30
E ^{dedoped, ox} (V)	1.00	1.10
E ^{doped, ox} (onset) V	1.00	0.95
HOMO (eV)	-5.32	-5.27
LUMO ^a (eV)	-3.62	-3.37
Eg ^{op}	1.7	1.9
λ ^{max} (nm)	460/630/1,230	440/700/1,280
Optical contrasts (%)	10/40/65	-/35/25
Switching times (s)	2.5/0.5/0.5	-/0.6/1.8

^a LUMO energy levels calculated from subtracted optical band-gap values from HOMO levels.

are listed. HOMO levels are given relative to the vacuum level, considering that the SCE is 4.7 eV versus vacuum 34 and Fc/Fc+ is 0.35 V versus SCE. 35

All electrochemical experiments were performed in same electrolyte solution (0.1 M TBAPF₆/ACN). A reversible redox couple was observed for copolymer BTzTh at 1.55 and 1.10 V. Furan incorporated copolymer showed a lower redox couple versus the same reference electrode at 1.30 and 1.10 V in anodic region. As given in the literature, furan substitution into a polymer backbone compare to thiophene, reduces the oxidation potential since oxygen-containing furan is richer in terms of electrons. In other words, when oxygen-containing heterocycles used as the donor group in a polymer chain they reduce the HOMO energy level.³⁶



SCHEME 1 Synthetic route of the copolymers BTzTh and BTzFr [(i) dithiooxamide, DMF, reflux, 5 h; (ii) NBS, DMF, reflux, 1 h; (iii) *n*-BuLi, tributyltin chloride, THF; (iv) Pd(PPh3)4, toluene, reflux, 36 h].

HOMO levels of the BTzTh and BTzFr were calculated from the onset oxidation potentials; 1.00 and 0.95 eV, respectively. Upon replacing thiophene with furan moiety, a smaller E^{ox} onset value and a more destabilized HOMO level were found. LUMO levels were also calculated subtracting the optical band-gap values from the HOMO energy levels of the copolymers (Table 1).

Spectroelectrochemistry and Colorimetry

To figure out the relation between the redox processes and UV-vis-NIR absorptions, spectroelectrochemistry experiments were performed in the same electrolytic medium (TBAPF₆/ACN) with the same electrodes (ITO: working, platinum: counter and Ag wire: pseudo-reference) for both copolymers. Thin films (160 nm) of the copolymers were prepared utilizing the same procedure used for electrochemistry (5 mg mL⁻¹ in CHCl₃). All copolymers showed multielectrochromic nature since the absorption bands of oxidized states lie mostly in visible region.

In Figure 2, a full characterization of all bands was shown for related states via oxidation for both copolymers. UV-vis-NIR spectra for polymer films were obtained first in their fully reduced states at 0.0 V, which show different hues of orange. Color discrepancies of the copolymers were clearly characterized during sequentially stepping to higher oxidizing potentials with 0.1 V increments, which lead to the generation of polaronic and bipolaronic bands at longer wavelengths. Because of intramolecular DA electronic interactions of the neutral polymers, they have a single broad absorption bands with a maximum peak value of 460 and 440 nm for BTzTh and BTzFr, respectively. BTzTh has a 20nm redshifted broad absorption band than BTzFr. This may be attributed to thiophene having a wider absorption band compare to furan³⁷ and also the longer chain length of BTzTh than BTzFr. As the polaron bands of both copolymers were in the visible region, with a max value of 630 nm (BTzTh) and the 700 nm (BTzFr), they have a greater effect on the colors of the polymers at oxidized states. In both cases, the distinct increase in the intensities of the absorptions was started to be seen beyond their E^{ox} onset potentials as determined from CV.

As shown in Figure 2(a), intensities of the newly generated bands increased as the π - π band of BTzTh depleted. While oxidizing the polymer BTzTh, three additional intermediate film colors were observed at potentials 0.9, 1.2, and 1.3 V. Upon fully oxidation a dark blue color was observed at 1.5 V. However, for complete oxidation of BTzFr [Fig. 2(b)] a green color was observed at 1.2 V. As known, to observe the green color, presence of two bands is a must in the regions around 400 and 700 nm. During stepwise oxidation, the polaron band revealed at 700 nm of the BTzFr, and the intensity of the neutral absorption band did not decrease. At potentials 1.0 and 1.1 V, two additional colors, which are different shades of neutral and fully oxidized color tones, were determined. The more variety of the polymer film colors of BTzTh than BTzFr may be explained as the polaron band of the thiophene-containing polymer has a wider absorption range in the visible region than that of furan containing polymer. Bipolaron band of the both copolymers were generated in the low energy region with a maximum peak values at 1230 and 1280 nm for BTzTh and BTzFr, respectively.

The optical band gaps of the copolymers were calculated from their onset absorption wavelengths of the π - π * transitions. A smaller band-gap value for thiophene containing polymer (1.7 eV) was calculated than that of BTzFr (1.9 eV), which are compatible with the electrochemical results. According to both the optical and the electrochemical results, both copolymers are promising candidates for the optoelectronic device applications in organic solar cells. With the help of optical band-gap values of the copolymers, LUMO energy levels were calculated and reported in Table 1.

To report the polymer film colors (Fig. 3) quantitatively in a scientific manner, colorimetry studies were performed to define three attributes "*L*" (brightness), and two color components "*a*" (the axis extends from -a: green to +a: red) and "*b*" (the axis extends from -b: blue to +b: yellow) as defined by Commission Internationale de l'e 'Clairage (CIE). Neutral polymer film colors were given as *L*: 50.334, *a*: 40.684, and *b*: 61.332 for BTzTh and *L*: 60.516, *a*: 41.501, and *b*: 101.426 for BTzFr. Upon oxidation of the BTzTh film, color turns into blue with *b*: -30.056. During oxidation of



FIGURE 2 Electronic absorption spectra of (a) BTzTh and (b) BTzFr in TBAPF6/ACN solution.



FIGURE 3 L, a, and b values of the polymer films at different applied voltages (a) BTzTh and (b) BTzFr.

the BTzFr, a component had a more negative value, which specifies the green region. *L*, *a*, and *b* components of all states of the films of both copolymers were listed in Table 2.

Switching Studies

As explained in the spectroelectrochemistry section, both copolymers showed multichromicity with prominent color changes at different applied potentials. To define the switching speeds of the polymer films, double potential step

TABLE 2 List of *L*, *a*, and *b* Values for Polymer Films Obtained from BTzTh and BTzFr

L	а	b
50.334	40.684	61.332
38.199	19.435	65.215
38.199	-0.631	19.262
43.360	-11.234	9.427
38.021	-8.762	-30.056
60.516	41.561	101.426
58.696	26.017	76.532
69.184	-2.969	47.735
66.213	-12.543	45.590
	L 50.334 38.199 38.199 43.360 38.021 60.516 58.696 69.184 69.184	L a 50.334 40.684 38.199 19.435 38.199 -0.631 43.360 -11.234 38.021 -8.762 60.516 41.561 58.696 26.017 69.184 -2.969 66.213 -12.543

chronoamperometry studies were performed between their neutral and fully oxidized states using a UV-vis–NIR spectrophotometer at their local maximum absorption wavelengths (Fig. 4). Experiments were carried out for BTzTh at its all absorption regions whereas for the BTzFr only in its polaronic and bipolaronic regions due to almost no change in the π - π * absorption intensity. Switching times, listed in Table 1, were calculated taking 95% of a full transition of neutral fully doped states.

To evaluate the kinetic properties of the BTzTh and BTzFr, polymer films were first spray-casted on ITO-coated glass slides. Thiophene containing polymer films were consecutively stepped between neutral (0.0 V) and oxidized (1.5 V) (vs. Ag wire) in 5-s time intervals. At 460 nm, only 10% optical contrast was determined with a switching speed of 2.5 s. In longer wavelengths, a faster switching time (0.5 s) was observed at both 630 and 1230 nm with increased optical contrast values of 40 and 65%, respectively. This result shows charge transport is easier in its lower energy bands. For the furan-containing polymer, smaller optical contrast values (35% at 700 nm, 25% at 1280 nm) were observed than the thiophene containing one. These results are also consistent with their electrochemical studies. The charge loaded (area under the curve of oxidative doping) on the



FIGURE 4 Double potential step chronoamperometry studies with 5-s time intervals at local absorption maximums (a) BTzTh (0.0 and 1.5 V) and (b) BTzFr (0.0 and 1.4 V).

furan-containing polymer is lower with respect to the thiophene containing copolymer.³⁸

All switching times and percent optical transmittance differences ($\Delta \% T$) at specific wavelengths are listed in Table 1.

CONCLUSIONS

A new series of alternating DA conjugated copolymers were synthesized containing benzotriazole and thiazolothiazole unit in the main chain via Stille coupling polymerization by altering the thiophene and furan moieties. Electrochemical and electrochromic properties of the copolymers were reported. They showed low oxidation potentials and low optical band-gap values. With the help of the spectroelectrochemistry technique, we defined the redox affected color change of the polymer films. Copolymers showed multichromic properties in a small potential range. It is known that consequential variation in electrochromic performance can be rationalized with small structural modifications in polymer chain. As having suitable energy levels and multichromic properties, electrochromic and solar cell application of a branched chain-introduced BTzTh derivative is an issue in our ongoing research.

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