

## Synthesis and Spectroelectrochemistry of Dithieno(3,2-*b*:2',3'-*d*)pyrrole Derivatives

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**ABSTRACT:** New  $\pi$ -conjugated polymers containing dithieno(3,2-*b*:2',3'-*d*)pyrrole (DTP) were successfully synthesized via electropolymerization. The effect of structural differences on the electrochemical and optoelectronic properties of the 4-[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]aniline (DTP-aryl-NH<sub>2</sub>), 10-[4*H*-dithiyeno(3,2-*b*:2',3'-*d*)pirol-4-il]dekan-1-amine (DTP-alkyl-NH<sub>2</sub>), and 1,10-bis[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl] decane (DTP-alkyl-DTP) were investigated. The corresponding polymers were characterized by cyclic voltammetry, NMR (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR), and ultraviolet-visible spectroscopy. Changes in the electronic nature of the functional groups led to variations in the electrochemical properties of the  $\pi$ -conjugated systems. The electroactive polymer films revealed redox couples and exhibited electrochromic behavior. The replacement of the DTP-alkyl-DTP unit with DTP-aryl-NH<sub>2</sub> and DTP-alkyl-NH<sub>2</sub> resulted in a lower oxidation potential. Both the poly(10-(4*H*-Dithiyeno[3,2-*b*:2',3'-*d*]pirol-4-il)dekan-1-amin) (poly(DTP-alkyl-NH<sub>2</sub>)) and poly(1,10-bis(4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-4-yl) decane) (poly(DTP-alkyl-DTP)) films showed multi-color electrochromism and also fast switching times (<1 s) in the visible and near infrared regions. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40701.

**KEYWORDS:** conducting polymers; electrochemistry; optical properties

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### INTRODUCTION

In the growing field of organic materials, the synthesis and applications of  $\pi$ -conjugated organic materials have attracted intense research interest in recent years because of their beneficial optical and electronic properties and unique advantages, such as their low-cost, simple manufacturing process; light weight; and the capability of fabricating flexible large devices.<sup>1-7</sup> In recent years, the dithieno(3,2-*b*:2',3'-*d*)pyrrole (DTP) moiety received much attention, and DTP-based  $\pi$ -conjugated organic materials have been used in organic light emitting diode (OLED),<sup>8</sup> organic thin-film transistor (OTFTs),<sup>9</sup> field-effect transistor (FET),<sup>10,11</sup> and photovoltaic cells<sup>12,13</sup> and photoluminescent and electroluminescent thin films.<sup>14</sup> Substituted DTP complexes, such as poly(dithieno[3,2-*b*:2',3'-*d*]pyrrole) (polyDTP), alkyl *N*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (alkyl *N*-DTP), and poly *N*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (poly*N*-DTP) structures, have been synthesized. These

structures can be incorporated into various polymeric, oligomeric, and molecular materials to be used in OLED,<sup>8</sup> OTFTs,<sup>9</sup> FET,<sup>10,11</sup> and photovoltaic cells.<sup>12,13</sup> The synthesis of DTP derivatives is significant because of their thiophene-pyrrole-thiophene fused-ring system. Their good planar crystal structure, extended conjugation, and strong electron-donating ability, which can be very easily substituted by functional groups, make them promising materials.<sup>15-17</sup> To this end, enormous efforts have been devoted to the development of efficient molecules for new materials in the past decade. To date, the functionalization of C2, C3, and N positions of DTP have been performed, but the N position was limited to primary amine and aryl amine compounds. C2 and C3 position functionalizations were also limited because of their low reactivity (Scheme 1).

In this study, we synthesized new DTP derivatives, 4-[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]aniline (DTP-aryl-NH<sub>2</sub> or **8**),

10-[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]dekan-1-amine (DTP-alkyl-NH<sub>2</sub>), and 1,10-bis[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]decane (DTP-alkyl-DTP or **6**) via the palladium and copper amidation of 3,3'-dibromo-2,2'-bithiophene, as shown in Scheme 2. Electrochemical and optical studies of the synthesized low-band-gap polymers were performed by ultraviolet-visible (UV-vis) spectrometry and cyclic voltammetry (CV). This study was carried out with the anticipation of achieving polymers with fast switching times, high optical contrast, and more color variety compared to -aryl-NH<sub>2</sub> and -alkyl-NH<sub>2</sub> through the incorporation of alkyl-DTP into the polymeric structure.

## EXPERIMENTAL

### Chemicals

Palladium catalyst, [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] ligand, and sodium *tert*-butoxide (*t*-BuONa) were purchased from Sigma-Aldrich. 1,10-Diaminodecane, 1,4-diamine benzene compounds, CuI, K<sub>2</sub>CO<sub>3</sub>, ethyl acetate (EtOAc), dimethyl sulfoxide (DMSO), and toluene were analytical grade and were obtained from Merck.

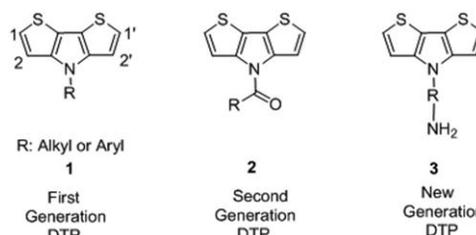
### Materials and Instrumentation

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the compounds were recorded in deuterated chloroform (CDCl<sub>3</sub>) with a 400 (100)-MHz spectrometer, and the chemical shifts are given relative to tetramethylsilane. A Voltlab 50 potentiostat was used for the investigation of the redox behavior of the electroactive monomers. The electropolymerizations were carried out in a three-electrode cell consisting of indium tin oxide (ITO)-coated glass as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo-reference electrode. The electrodeposition of the 1.10<sup>-2</sup>M monomer solution was performed with a CV technique in a 0.1M solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>)/dichloromethane (DCM)/acetonitrile (ACN) (1:2) supporting electrolyte under a nitrogen atmosphere at a scan rate of 100 mV/s. We calculated the highest occupied molecular orbital (HOMO) and lowest lying molecular orbital (LUMO) energy levels by taking the normal hydrogen electrode value to be -4.75 eV with HOMO = -(4.75 + 0.35 + E<sub>ox</sub><sup>onset</sup>) and LUMO = -(4.75 + 0.35 + E<sub>red</sub><sup>onset</sup>), where E<sub>red</sub><sup>onset</sup>, onset reduction potential; E<sub>ox</sub><sup>onset</sup>, onset oxidation potential.

UV-vis-near infrared spectra of the polymers were recorded on a Varian Cary 5000 spectrophotometer. A Minolta CS-100A Chroma meter was used for colorimetry measurements. The Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet 510 FTIR spectrometer, where the samples were dispersed in KBr. Mass analysis was carried out on a Bruker time-of-flight mass spectrometer with an electron impact ionization source.

### Synthesis of the Monomers

**Synthesis of 10-[4*H*-Dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]decan-1-amine (DTP-alkyl-NH<sub>2</sub> or **5**).** A solution of 3,3'-dibromo-2,2'-bithiophene (100 mg, 0.31 mmol), 1,10-diaminodecane (53 mg, 0.31 mmol), *t*-BuONa (65 mg, 0.67 mmol), tris(dibenzylideneacetone)dipalladium (Pd<sub>2</sub>(dba)<sub>3</sub>) (14 mg, 0.015 mmol), and (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (BINAP) (14 mg,



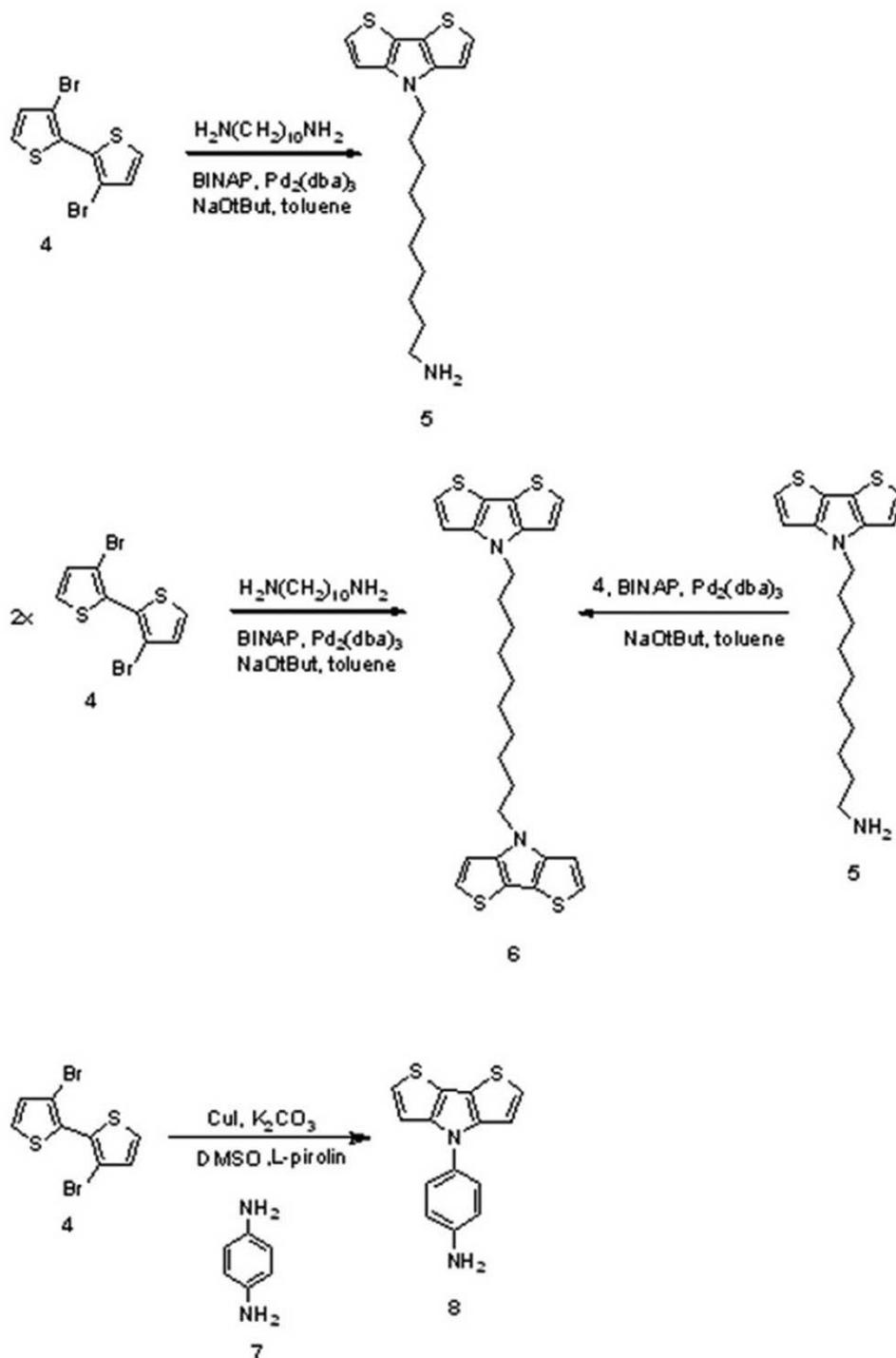
**Scheme 1.** Structures of the first-generation, second-generation, and new-generation DTPs.

0.02 mmol) in dry toluene (5 mL) was purged with a nitrogen atmosphere and stirred for 20 min at room temperature. The reaction mixture was stirred at 130°C under a nitrogen atmosphere until the 3,3'-dibromo-2,2'-bithiophene was completely consumed [as monitored by thin layer chromatography (TLC)]. After cooling, water (15 mL) was added, and the layers were separated. The water phase was extracted twice with EtOAc (2 × 30 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, evaporated, and purified by flash column chromatography. The yellow solid was obtained from hexane/CH<sub>3</sub>OH/EtOH (yield = 65 mg, 45%; mp = 145–147°C). The solution of DTP-alkyl-NH<sub>2</sub> in DCM had two absorption peaks at 235 and 295 nm.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.16 (d, *J* = 5.3 Hz, =CH, 2H), 6.99 (d, *J* = 5.3 Hz, =CH, 2H), 4.18 (t, *J* = 7.0 Hz, CH<sub>2</sub>, 2H), 2.67–2.63 (m, CH<sub>2</sub>, 2H), 1.87–1.83 (m, CH<sub>2</sub>, 2H), 1.42–1.40 (m, CH<sub>2</sub>, 2H), 1.38–1.23 (m, CH<sub>2</sub>,NH<sub>2</sub>, 14H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 145.0, 122.7, 114.6, 110.9, 47.4, 42.2, 33.9, 30.3, 29.5, 29.4, 29.4, 29.2, 27.0, 26.8. mass spectrometry (MS): [mass-to-charge ratio (*m/z*)] 334.

**Synthesis of DTP-alkyl-DTP (**6**). Procedure A.** To a 10-mL, round-bottomed flask equipped with a magnetic stirrer, 3,3'-dibromo-2,2'-bithiophene (200 mg, 0.62 mmol), 1,10-diamine decane (53 mg, 0.31 mmol), BINAP (35 mg, 0.05 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (28 mg, 0.03 mmol), and *t*-BuONa (140 mg, 1.44 mmol) were dissolved in 5 mL of dry toluene. The reaction mixture was stirred and refluxed under continuous bubbling with nitrogen for 5 days at 130°C (where no starting material was observed by TLC). The solvent was evaporated via rotary evaporation. The residue was dissolved with EtOAc (30 mL) and washed with deionized water (1 × 20 mL). The aqueous phase were again washed with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation. The crude product was purified by silica gel column chromatography (methanol). Recrystallization from dichloromethane/hexane afforded yellow crystals. The resulting yellow solid was obtained at a 78% yield (238 mg, mp = 133°C).

**Procedure B.** In a 10-mL, round-bottomed flask equipped with a magnetic stirrer, 3,3'-dibromo-2,2'-bithiophene (100 mg, 0.31 mmol) and 10-[4*H*-dithieno(3,2-*b*:2',3'-*d*)pyrrol-4-yl]decan-1-amine (103 mg, 0.62 mmol), BINAP (31 mg, 0.05 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (28 mg, 0.03 mmol), and *t*-BuONa (140 mg, 1.45 mmol) were dissolved in 4 mL of dry toluene. The reaction mixture was stirred and refluxed under continuous bubbling



**Scheme 2.** Synthesis of the DTP-alkyl-NH<sub>2</sub> (5), DTP-alkyl-DTP (6), and DTP-aryl-NH<sub>2</sub> (8) compounds. NaOtBut, sodium tert-butoxide.

with nitrogen for 5 days (where no starting material was observed by TLC). The solvent was evaporated via rotary evaporation. The residue was dissolved with EtOAc (30 mL) and washed with deionized water (1 × 20 mL). The aqueous phase was washed again with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation. The crude product was purified by silica gel

column chromatography (methanol) and dried *in vacuo*. Recrystallization from dichloromethane/hexane afforded yellow crystals. The resulting yellow solid was obtained in an 81% yield (124 mg, mp = 133°C). The solution of DTP-alkyl-DTP in DCM had two absorption peaks at 245 and 300 nm.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.11 (d, *J* = 5.3 Hz, =CH, 4H), 6.99 (d, *J* = 5.3 Hz, =CH, 4H), 4.17 (t, *J* = 7.0 Hz, CH<sub>2</sub>, 4H),

1.86–1.79 (m, CH<sub>2</sub>, 4H), 1.23–1.17 (m, CH<sub>2</sub>, 12H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 144.9, 122.7, 114.6, 110.9, 47.4, 30.3, 29.2, 29.0, 36.9. MS (*m/z*): 496.

**Synthesis of DTP-aryl-NH<sub>2</sub> (8).** In a 10-mL, round-bottomed flask equipped with a magnetic stirrer, 3,3'-dibromo-2,2'-bithiophene (100 mg, 0.308 mmol), 1,4-diamine benzene (33.37 mg, 0.308 mmol), K<sub>2</sub>CO<sub>3</sub> (85 mg, 0.616 mmol), CuI (14 mg, 0.074 mmol), and L-proline (14 mg, 0.12 mmol) were dissolved in 4 mL of DMSO. The reaction mixture was stirred and refluxed under continuous bubbling with nitrogen for 1 day at 120°C. The reaction mixture was saturated with an NaCl solution and was thereafter extracted with EtOAc (3 × 30 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation. The crude product was purified by silica gel column chromatography (methanol), and recrystallization was performed from methanol/*n*-hexane (124 mg, 81%). The resulting light green solid was obtained in a 20% yield (16 mg, mp = 175°C). The solution of DTP-aryl-NH<sub>2</sub> in DCM had two absorption peaks at 260 and 375 nm.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.37 (d, *J* = 8.6 Hz, =CH, 2H), 7.16 (d, *J* = 5.3 Hz, =CH, 2H), 7.10 (d, *J* = 5.3 Hz, =CH, 2H), 7.84 (d, *J* = 8.6 Hz, =CH, 2H), 3.84–3.78 (bs, NH<sub>2</sub>, 2H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 144.94, 144.61, 131.15, 124.51, 123.07, 115.92, 115.80, 112.08. MS (*m/z*): 270.

## RESULTS AND DISCUSSION

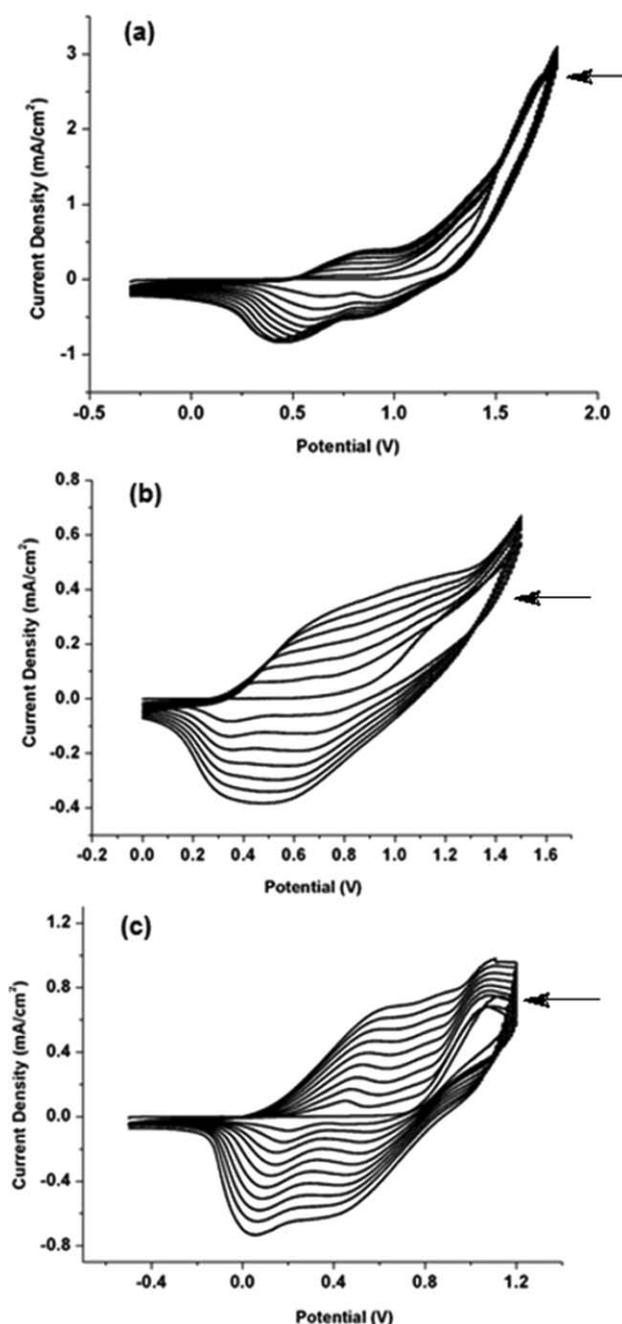
### Synthesis of the Monomers

Before the synthesis of DTP-aryl-NH<sub>2</sub>, DTP-alkyl-NH<sub>2</sub>, and DTP-alkyl-DTP via a palladium- or copper-catalyzed coupling reaction, other groups reported various alkyl (first-generation)<sup>18</sup> and acyl (second-generation)<sup>19</sup> *N*-substituted DTP molecules (Scheme 1). The presence of a few derivatives with C2, C3, and N positions limited the effective application of DTP-based materials in various devices.

In this study, we achieved the synthesis of a functionalized novel DTP-aryl-NH<sub>2</sub>, DTP-alkyl-NH<sub>2</sub>, and DTP-alkyl-DTP compounds via a palladium- and copper-coupling reaction (Scheme 2). The use of highly polar solvents, such as DMSO and DMF, led to low yields via a palladium-coupling reaction. The use of CuI, L-proline, and DMS resulted in higher yields compared to the one for palladium-coupling. The structures were confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.

### Electrochemical Polymerization of DTP-aryl-NH<sub>2</sub>, DTP-alkyl-NH<sub>2</sub>, and DTP-alkyl-DTP

The electrochemical polymerization of DTP-aryl-NH<sub>2</sub> (8), DTP-alkyl-NH<sub>2</sub> (5), and DTP-alkyl-DTP (6) were performed with a CV technique. Figure 1 displays the potentiodynamic scans of the monomer in the presence of TBAPF<sub>6</sub>/DCM/ACN (1:2) with an ITO working electrode at a scan rate of 100 mV/s. The monomer oxidation of DTP-aryl-NH<sub>2</sub> occurred at 1.7 V versus an Ag wire pseudo-reference electrode [Figure 1(a)]. After the monomer oxidation, an electroactive polymer film grew on the ITO electrode, and reversible redox peak couples of the polymer film were observed. Monomer oxidation peaks for



**Figure 1.** Repeated potential scan electropolymerization of (a) DTP-aryl-NH<sub>2</sub>, (b) DTP-alkyl-NH<sub>2</sub>, and (c) DTP-alkyl-DTP at 100 mV/s in 0.1M TBAPF<sub>6</sub>/DCM:ACN (1:2) on an ITO electrode.

DTP-aryl-NH<sub>2</sub> and DTP-alkyl-DTP were obtained at 1.3 and 1.1 V, respectively, in the first cycle of the voltammograms.

As shown in Figure 1, the monomer oxidation potential of DTP-aryl-NH<sub>2</sub> was higher than that of DTP-alkyl-NH<sub>2</sub>. The aniline group in the monomer DTP-aryl-NH<sub>2</sub> donated an electron to the pyrrole moiety and increased the aromatic stability of the fused ring. Electron delocalization lowered the potential energy of the substance and, thus, makes it more stable than any of the contributing structures. In light of this, the oxidation potential of the monomer DTP-alkyl-DTP was found to be the

**Table I.** Optoelectronic Properties of the Polymers

Polymer	Poly(DTP-aryl-NH <sub>2</sub> )	Poly(DTP-alkyl-NH <sub>2</sub> )	Poly(DTP-alkyl-DTP)
$E_m^{\text{ox}}$ (V)	1.70	1.30	1.10
$E_p^{\text{ox}}$ (V)	0.90	0.95	0.65
$E_p^{\text{red}}$ (V)	0.45	0.47	0.06
HOMO (eV)	-5.60	-5.45	-5.20
LUMO (eV)	-3.95	-3.45	-3.40
$E_g^{\text{opt}}$ (eV)	1.65	2.0	1.8
$\lambda_{\text{max}}$ (nm)	410/1060	475/1030	490/680/1040
Optical contrast (%)	14 and 32	35 and 50	45, 24, and 56
Switching time (s)	1.8 and 1.5	0.7 and 0.9	0.8, 0.5, and 0.8

<sup>a</sup>  $E_m^{\text{ox}}$  is monomer oxidation potential,  $E_p^{\text{ox}}$  is polymer oxidation potential,  $E_p^{\text{red}}$  is polymer reduction potential, and  $\lambda_{\text{max}}$  is maximum wavelength.

lowest one. As summarized in Table I, the monomer oxidation potentials decreased in the order DTP-aryl-NH<sub>2</sub> > DTP-alkyl-NH<sub>2</sub> > DTP-alkyl-DTP.

The formation of the polymer films were proven with FTIR spectroscopy. Most of the characteristic peaks of the monomers remained unperturbed after the electropolymerization of the monomers. The FTIR spectra of the monomers showed strong peaks at 692 cm<sup>-1</sup> (C-H bond deformations). The band at 692 cm<sup>-1</sup> disappeared completely, whereas the evolution of a new absorption peak at 1610 cm<sup>-1</sup> was observed. The peak at 1610 cm<sup>-1</sup> and the intense band at 1109 cm<sup>-1</sup> stood for the formation of polyconjugation and the presence of dopant anions, respectively.<sup>20</sup>

### Spectroelectrochemical and Optical Properties

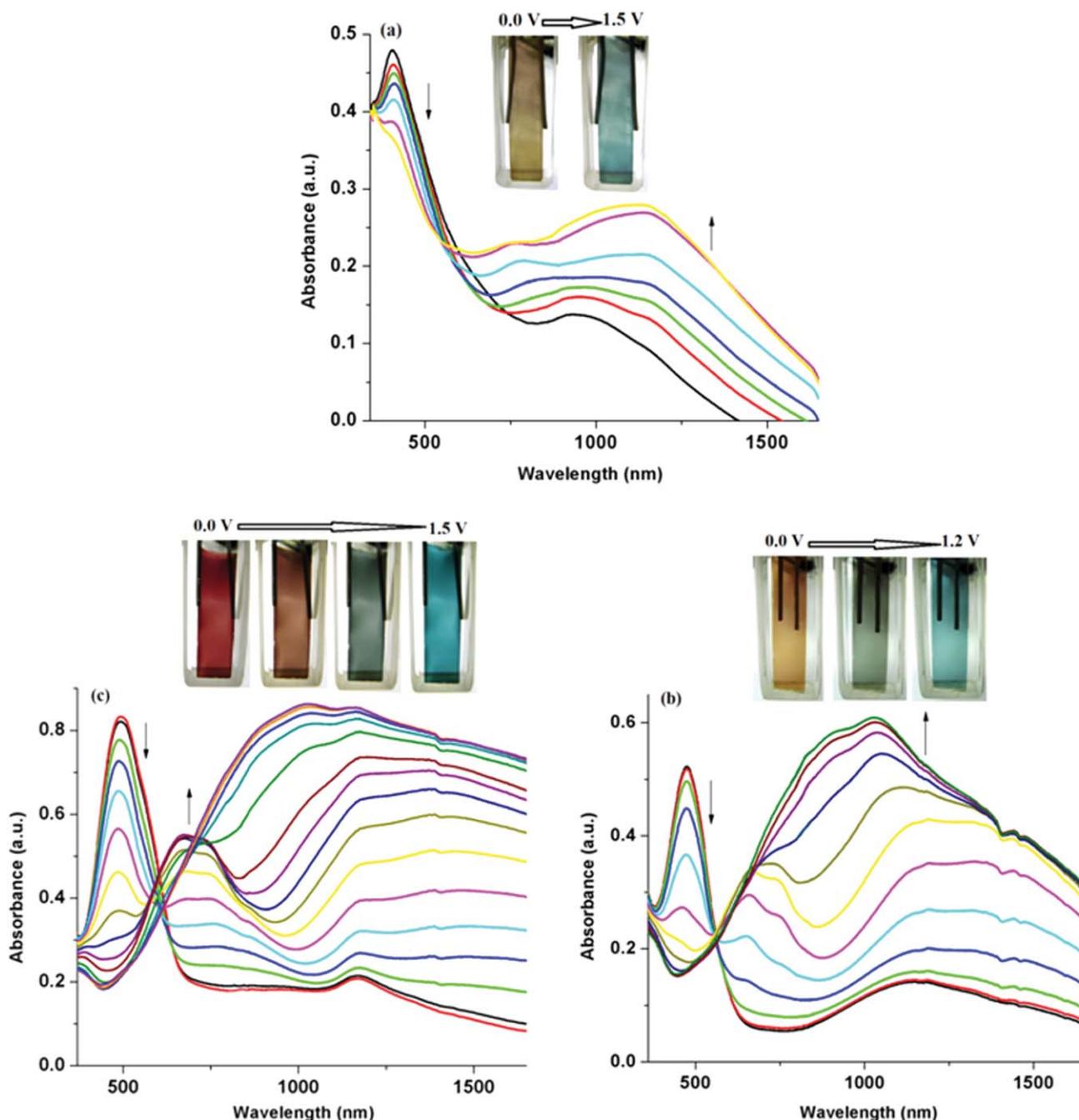
Spectroelectrochemical analysis of poly(4-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)aniline) (poly(DTP-aryl-NH<sub>2</sub>)), poly(10-(4H-Dithiyeno[3,2-b:2',3'-d]pirol-4-il)dekan-1-amin) (poly(DTP-alkyl-NH<sub>2</sub>)), and poly(1,10-bis(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl) decane) (poly(DTP-alkyl-DTP)) were studied to observe the electronic transitions when the polymer was doped. The film was coated on ITO by the electrochemical polymerization of DTP-aryl-NH<sub>2</sub>, DTP-alkyl-NH<sub>2</sub>, and DTP-alkyl-DTP (0.1M) in the presence of TBAPF<sub>6</sub>/DCM:ACN (1:2). The thickness of the conducting polymer films used for the spectroelectrochemical studies were also calculated at 0.090, 0.072, and 0.057 μm for poly(DTP-aryl-NH<sub>2</sub>), poly(DTP-alkyl-NH<sub>2</sub>), and poly(DTP-alkyl-DTP), respectively. Poly(DTP-aryl-NH<sub>2</sub>)-coated ITO was investigated by UV-vis spectroscopy in a monomer-free electrolyte medium by switching the potential between 0.0 and 1.5 V with an incremental increase in the applied potential. There was a gradual decrease in the peak intensity of the π-π\* transition when the applied potential was increased. The application of the voltage resulted in the formation of charge carrier bands. Thus, the appearance of a peak around 1060 nm was attributed to the evolution of charge carriers. The resulting UV-vis spectrum confirmed the typical bipolaronic nature of the charge carriers [Figure 2(a)]. The poly(DTP-alkyl-NH<sub>2</sub>) synthesized and characterized under same dopant-solvent conditions revealed a single broad transition at 475 nm. When the applied potential was increased, the peak

height of the interband transition was reduced, and simultaneously, a new absorption peak appeared around 1030 nm because of charge carrier band formations. On the other hand, poly(DTP-alkyl-DTP) synthesized between 0.0 and 1.5 V revealed a maximum absorption at 490 nm [Figure 2(c)]. The peak height of the interband transition was repressed, and simultaneously, a new absorption peak was observed around 680 and 1040 nm because of charge carrier band formations.

The optical and electrochemical properties of the conjugated polymers depend on the magnitude of band gap. To find an effective method to adjust the energy levels (HOMO and LUMO) of the polymers is an important goal for applied sciences. According to the literature, three different strategies can be used to design and synthesize polymers with a low band gap. The first approach is based on an increase in the stability of the quinoid form of a conjugated polymer with decreasing bond length alternation.<sup>21</sup> The second approach is based on the building of a polymer chain with alternating electron-rich (donor) and electron-deficient (acceptor) units.<sup>22</sup> The last approach is to increase the planarity of the monomer with fused-ring systems.<sup>23,24</sup> All three criteria affect the charge-transfer process and band-gap energy of the polymers. The optical band gaps of the polymers ( $E_g^{\text{opt}}$ ) were calculated from the onsets of the π-π\* transitions on the UV-vis-near infrared spectra. The band gaps of poly(DTP-aryl-NH<sub>2</sub>), poly(DTP-alkyl-NH<sub>2</sub>), and poly(DTP-alkyl-DTP) were calculated as 1.65, 2.0, and 1.8 eV, respectively. The HOMO levels of the polymers were calculated from the onset oxidation potentials. The LUMO levels of the polymers were not calculated from cyclic voltammograms because of a lack of ability in n-doping. Thus, the LUMO levels were also calculated by the subtraction of the optical-band-gap values from the HOMO energy levels of the polymers. The HOMO levels of the polymers had the same value approximately, but the LUMO level of poly(DTP-aryl-NH<sub>2</sub>) was different than the others. The lower LUMO energy level of poly(DTP-aryl-NH<sub>2</sub>) led to a lower band-gap energy compared to those of the other polymers. The data are summarized in Table I.

### Electrochromic Switching and Colorimetry of the Polymers

We monitored the switching ability of the polymers by monitoring the changes in the percentage transmittance of the polymer

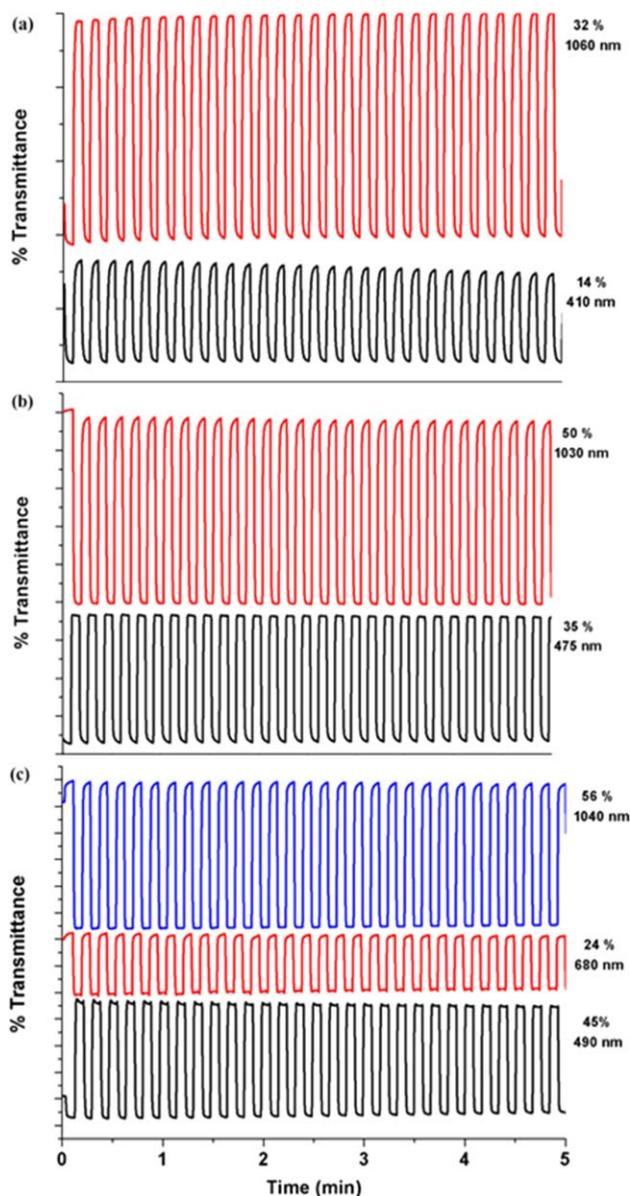


**Figure 2.** *p*-Doping spectroelectrochemistry of (a) poly(DTP-aryl-NH<sub>2</sub>) at applied potentials between 0.0 and +1.5 V, (b) poly(DTP-alkyl-NH<sub>2</sub>) at applied potentials between 0.0 and +1.2 V, and (c) poly(DTP-alkyl-DTP) at applied potentials between 0.0 and +1.5 V on an ITO-coated glass slide in a monomer-free 0.1M TBAPF<sub>6</sub>/DCM:ACN (1:2) electrolyte-solvent couple. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

while applying potential in square-wave form between its neutral and doped states with a change in transmittance at a fixed wavelength. The results are represented in Figure 3. Poly(DTP-aryl-NH<sub>2</sub>) maintained its stability for several cycles. The electrochromic contrast was calculated as the percent transmittance change ( $T\%$ ) at 410 and 1060 nm. The electrochromic polymer had a 14% optical contrast at 410 nm and a 32% optical contrast at 1060 nm [Figure 3(a)]. The switching speeds (the time required for the coloring/bleaching process) were 1.8 s at 410

nm and 1.5 s at 1060 nm for poly(DTP-aryl-NH<sub>2</sub>). The optical contrasts for poly(DTP-alkyl-NH<sub>2</sub>) were calculated as 35% at 475 nm and 50% at 1030 nm, respectively. The switching times for poly(DTP-alkyl-NH<sub>2</sub>) were 0.7 and 0.9 s, respectively [Figure 3(b)]. The replacement of the aryl-NH<sub>2</sub> and alkyl-NH<sub>2</sub> with alkyl-DTP enhanced the kinetic properties; this revealed a 45% contrast at 490 nm with an 0.8-s switching time, a 24% contrast at 680 nm with a 0.5-s switching time, and a 56% contrast at 1040 nm with an 0.8-s switching time [Figure 3(c)].

Colorimetry analysis is an important method for characterizing the colors of electrochromic polymers. The color coordinates of the electrochemically synthesized polymers were determined by colorimetry studies to obtain an accurate measurement of the colors. This method allows the accurate determination of the color for an electrochromic material. According to Commission Internationale de l'Éclairage coordinates, there are three attributes used to describe the color: luminance ( $L$ ), hue ( $a$ ), and saturation ( $b$ ).  $L$  of a material is the transmittance of light through a sample as seen by the human eye.  $a$  symbolizes the wavelength



**Figure 3.** Electrochromic switching and optical absorbance changes monitored for (a) poly(DTP-aryl-NH<sub>2</sub>) at applied potentials of 0.0 and +1.5 V, (b) poly(DTP-alkyl-NH<sub>2</sub>) at applied potentials of 0.0 and +1.2 V, and (c) poly(DTP-alkyl-DTP) at applied potentials of 0.0 and +1.5 V in 0.1M TBAPF<sub>6</sub>/DCM:ACN (1:2). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Electrochromic Properties of the Polymers

Polymer	Color <sup>a</sup>	Applied potential (V)	$L$ , $a$ , and $b$
Poly(DTP-aryl-NH <sub>2</sub> )	Brown (r)	0.0	67.87, -1.56, and 37.94
	Blue (o <sub>2</sub> )	1.2	72.10, -22.32, and -0.02
Poly(DTP-alkyl-NH <sub>2</sub> )	Dark yellow (r)	0.0	73.74, 13.81, and 6.92
	Gray (i)	0.5	70.11, -15.21, and 9.06
	Blue (o <sub>2</sub> )	1.1	75.89, -24.25, and 1.28
Poly(DTP-alkyl-DTP)	Red (r)	0.0	46.58, 53.80, and 36.94
	Dark brown (i)	0.2	50.22, 23.55, and 34.86
	Light gray (o <sub>1</sub> )	0.3	53.49, -11.36, and 13.63
	Blue (o <sub>2</sub> )	0.5	63.01, -29.65, and -6.53

<sup>a</sup>The colorimetry study results are presented for reduced (r), intermediate (i), half-oxidized (o<sub>1</sub>), and highly oxidized (o<sub>2</sub>) states.

of maximum contrast.  $b$  is the intensity of a certain color. Color changes and  $L$ ,  $a$ , and  $b$  data were given in Table II.

Poly(DTP-aryl-NH<sub>2</sub>) had a brown color at 0.0 V (reduced state) and blue color at 1.2 V (highly oxidized state). Poly(DTP-alkyl-NH<sub>2</sub>) was a multicolored polymer. The film revealed a dark yellow color in the reduced state, gray in the midstate, and a blue color in the highly oxidized state. The results of the colorimetric measurement were also ensured upon variation of the polymerization potential. Also, poly(DTP-alkyl-DTP) indicated a different multichromism. The colors of poly(DTP-alkyl-DTP) were red at 0.0 V, dark brown at 0.2 V, light gray at 0.3 V, and blue at 0.5 V (Table II).

## CONCLUSIONS

Three novel DTP-based monomers were synthesized, and their polymerizations were achieved by electrochemical techniques. The electronic and optical properties of the polymers were investigated. The corresponding polymers were characterized by CV and UV-vis spectroscopy. Changes in the structure of the polymers led to variations in their electrochemical and optical properties. The use of the DTP-alkyl-DTP unit instead of DTP-aryl-NH<sub>2</sub> and DTP-alkyl-NH<sub>2</sub> led to a lower oxidation potential. The band gap, switching times (<1 s), and multicolored electrochromism behavior of the synthesized poly(DTP-alkyl-DTP) were found to be much better compared to results found in the literature up to now for DTP-based electrochromic conducting polymers.<sup>16,25</sup> The DTP structure, which restricted the C2, C3, and N derivatives, were synthesized with DTP-

alkyl-NH<sub>2</sub>, DTP-alkyl-DTP, and DTP-aryl-NH<sub>2</sub> groups, which are key molecules for numerous derivatives.

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