Multicolored Electrochromic Cells Based On Poly(2,7-Carbazole) Derivatives For Adaptive Camouflage

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We report the synthesis and characterization of three new poly(2,7-carbazole) derivatives, namely, poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(thien-3-yl)-thieno[3,4-b]pyrazine (P1), poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(phen-1-yl)-thieno[3,4-b]pyrazine (P2), and poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(4-octylphen-1-yl)-thieno[3,4-b]pyrazine (P3), which reflect green light in their neutral state and show transmissive brown when oxidized. These two colors are compatible for adaptive camouflage for military assets. All solid-state electrochromic cells were prepared using spray-coated films of electrochromic conjugated polymer (P1−P3) as active layer. We report the development of multicolored electrochromic cells (MEC) based on the additive color mixing theory. MEC of various sizes were prepared from 2.5 × 2.5 cm, and up to 12.5 × 12.5 cm. Finally, we also describe the fabrication of a multicolored electrochromic cell with an active surface of 156 cm^2.

Introduction

During the past decades, conjugated polymers have emerged as a novel class of synthetic polymers with highly promising mechanical, optical, and electrical properties for advanced technological applications such as light-emitting diodes, photovoltaic cells, and electrochromic cells. Because electrochromism can be defined as a reversible change of the color resulting form the oxidation or the reduction of the material by electrochemical means, the development of electrochromic devices based on inorganic or organic compounds has been widely investigated by both academic and industrial laboratories. Up to now, only a few electrochromic devices have hit the market; one can think of the car's rearview mirror from Gentex Corp.[1] Like inorganic (WO_3) and organic compounds (Viologens, Prussian Blue),[2−4] conjugated polymers can show high coloration efficiencies, low operating voltage, and fast switching capabilities.[5] Moreover, the most important features of conjugated polymers are the possibilities to fine-tune the color through chemical structure modification of the conjugated backbone and to get multichromism from the same material.[6−11]

Over the past few years, conjugated polymers such as poly(3-alkylthiophene)s, poly(3,4-alkylenedioxythiophene)s, and poly(pyrazine)s have emerged as promising candidates for the development of large and flexible electrochromic devices. However, many of these electrochromic materials are obtained by simple oxidative electrochemical or chemical polymerization methods. To date, only a few electrochromic conjugated polymers allow the easy preparation of thin films of polymers by spin- or spray-coating techniques.[12−27]

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In the past few years, our group has developed several electrochromic polymers with interesting color transitions.[24] Moreover, single layer electrochromic cells have been prepared for adaptive camouflage (chameleon effect) for military assets. Recently, the fabrication of green electroactive polymers by Sonmez et al.[20] pave the way for the development of additive multicolored electrochromic devices. Up to now, only a few green-colored conjugated polymers have been reported,[20,26−33] which is mainly due to the difficulty in obtaining the absorption required in the visible region to observe a green color.

In this regard, we report here the synthesis and characterization of three new poly(2,7-carbazole) derivatives: poly[*N*-9-heptadecanyl-2,7-carbazole-alt-5,7-di(3-octylthien-2-yl)-2,3-di(thien-3-yl)-thieno[3,4-b]pyrazine (**P1**), poly[*N*-9-heptadecanyl-2,7-carbazole-alt-5,7-di(3-octylthien-2-yl)-2,3-di(phen-1-yl)-thieno[3,4-b]pyrazine (**P2**), poly[*N*-9-heptadecanyl-2,7-carbazole-alt-5,7-di(3-octylthien-2-yl)-2,3-di(4-octylphen-1-yl)-thieno[3,4-b]pyrazine (**P3**). These polymers reflect green light when they are in their neutral state and show transmissive brown when oxidized. **P1−P3** are readily soluble in most common organic solvents such as chloroform, toluene, and tetrahydrofuran. All solid-state electrochromic cells were prepared by spray-coating the conjugated polymers onto ITO-coated glass electrodes. Multicolored electrochromic cells (MEC) based on the additive color mixing theory were prepared by combining **P1−P3** with other available conjugated polymers such as poly(3-hexylthiophene) (**P3HT**) and poly(2,5-thiophene)-*alt*-(4-butyltriphenylamine) (**PT-TPA**),[24] which have color transition from red to blue and yellow to green, respectively, when they are oxidized. Finally, we report the fabrication of multicolored electrochromic cells that have different active pixel sizes and colors for adaptive camouflage.

Experimental Section

Chemicals. All chemical were purchased from Aldrich Chemical. 3-Bromothiophene was distilled prior to use. Tetrahydrofuran was distilled over potassium/benzophenone system. Toluene, acetonitrile, and propylene carbonate (99.7% anhydrous) were distilled over calcium hydride before use.

Instrumentation. NMR spectra were recorded on a Bruker AMX300 in deuterated chloroform at ambient temperature. Number-average (M_n) and weight-average (M_w) molecular weight were determined by size exclusion chromatography (SEC) with HPLC Pump using a Waters 515 Differential Refractometer. THF (HPLC grade) was the eluting solvent at a flow rate of 1 mL/min. The calibration curve was made with a series of polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TG50 under heating rate of 20 °C/min. with a nitrogen flow rate of 200 mL/min.

Electrochemical measurements were carried out using a Solartron model 1287 potentiostat. A two-compartment cell using a three-electrode assembly was used to record cyclic voltammetry. The working electrode was either platinum button or ITO-coated glass. The counter electrode was a platinum wire and 0.01 M Ag/ $AgNO_3$ (Ag/Ag^+) was used as the reference electrode. The electrolyte used was 0.1 M $TBABF_4$ in dry acetonitrile. Spectroelectrochemistry data of the polymers films were recorded on Hewlett-Packard diode-array spectrophotometer (model 8452A). The measurements were done using spray-coated films on ITO-coated glass slides (25 × 75 × 0.7 mm, 15−25 Ω/square, Delta Technologies Ltd.) using the same electrode setup used for cyclic voltammetry. Spectroelectrochemical data of the all solid-state electrochromic cells were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) using an Instek GPS-3303 laboratory DC power source.

Electrochromic polymer films were obtained by spraying solutions of the polymers (5 mg/mL in tetrahydrofuran) using a Paasche airbrush nozzle (pressure fixed at 12 PSI) onto different sizes of home patterned ITO-coated glass substrate: (25 × 75 × 0.7 mm, 15−25 Ω/square, CG-61IN-S107); (50 × 75 × 0.7 mm, 15−25 Ω/square, Delta Technologies Ltd., CG-61IN-S207); (150 × 150 × 0.7 mm, 15−25 Ω/square, Delta Technologies Ltd., CG-61IN-1507). For single layer electrochromic cells, a gel electrolyte[22] was sandwiched between the polymer-coated electrode and the bare ITO counter-electrode. For the double-layer additive electrochromic cells, three ITO electrodes were used: Two polymer-coated electrodes were separated with a double-sided ITO electrode: (25 × 75 × 0.5 mm, 5−15 Ω/square, CG-61IN-S105); (50 × 75 × 0.5 mm, 5−15 Ω/square, Delta Technologies Ltd., CG-61IN-S205); (150 × 150 × 0.5 mm, 5−15 Ω/square, Delta Technologies Ltd., CG-61IN-1505). A thin paraffin layer was used as spacer to prevent electrical shorts and the cells were sealed using an epoxy resin.

Colorimetric measurements were obtained using a Datacolor Mercury 2000 portable spectrophotometer and the color coordinates are expressed in the CIE 1931 $L^*a^*b^*$ color space. A Canon (Canon A95) digital camera was used to take photographs of the polymer electrochromic device at high resolution.

Monomer Syntheses. The following materials were purchased or prepared according to literature procedures: 3-octylthiophene,[34] 2-bromo-3-octylthiophene,[35] 2-trimethyltin-3-octylthiophene,[36] 2,5-dibromo-3,4-dinitrothiophene,[37] 3,3′-thenil,[38] benzyl (Aldrich), 4,4-octylbenzil,[39] 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9′′-heptadecanylcarbazole[40] and poly(2,5-thiophene)-*alt*-(4-butyltriphenylamine) (PTTPA),[24] and poly(3-hexylthiophene)-(P3HT) (Rieke). All the monomers were carefully purified prior to use in the polymerization reaction.

*2,5-Bis-(3-octylthien-2-yl)-3,4-dinitrothiophene (**1**).* $PdCl_2(PPh_3)_2$ (391 mg) was added to a solution of 2,5-dibromo-3,4-dinitrothiophene (8.402 g, 25.31 mmol) and 2-trimethyltin-3-octylthiophene (20.000 g, 55.69 mmol) in toluene (65 mL). The mixture was refluxed in a nitrogen atmosphere overnight. The mixture was

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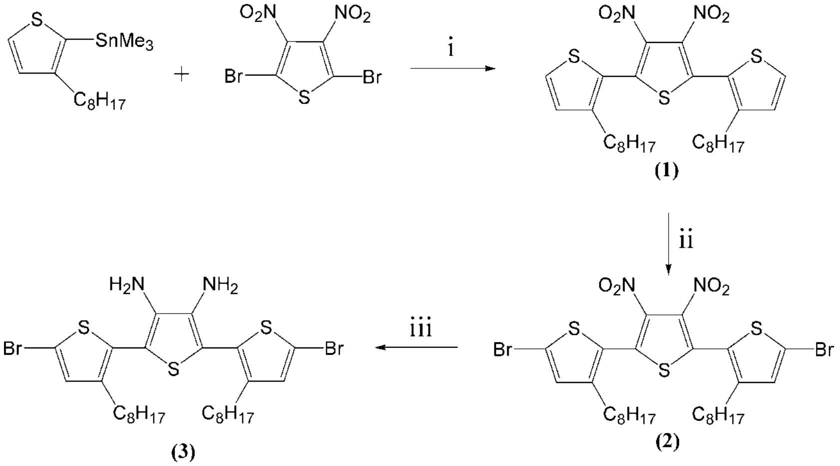
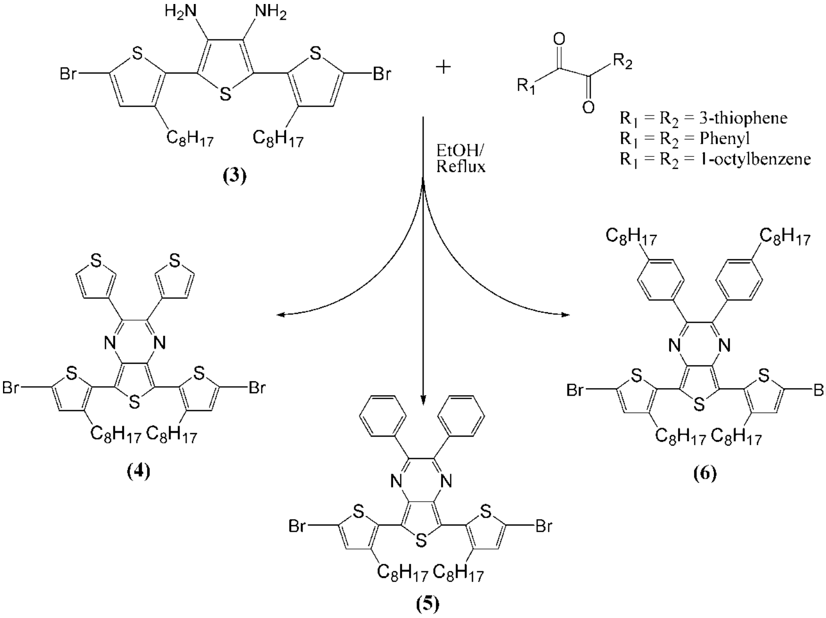
Scheme 1. Synthesis of Pyrazine Precursor



i- $PdCl_2(PPh_3)_2$/Toluene/Reflux; ii- NBS/CF_3COOH:$CHCl_3$; iii- $SnCl_2$/EtOH:HCl

Scheme 2. Syntheses of Pyrazine Derivatives



then cooled to room temperature and the solvent was removed under reduced pressure. The crude oil was chromatographed over silica gel using Hexane:EtOAc (90:10) as eluent giving the compound as an orange oil (12.570 g, 88%).^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.49 (d, 2H, $J = 5.1$ Hz); 7.03 (d, 2H, $J = 5.2$ Hz); 2.58 (t, 4H, $J = 7.4$ Hz); 1.59 (m, 4H); 1.26 (m, 20H); 0.87 (t, 6H, $J = 6.0$ and 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 146.27; 136.57; 134.76; 129.33; 129.09; 120.43; 31.86; 30.44; 29.37 (2C); 29.23; 29.20; 22.67; 14.11.

HRMS calcd for $C_{28}H_{38}N_2O_4S_3$: 558.2039. Found: 558.2034.

2,5-Bis-(2-bromo-3-octylthien-5-yl)-3,4-dinitrothiophene (*2*). NBS (2.554 g, 14.35 mmol) was added to a suspension of 2,5-bis-(3-octylthien-2-yl)-3,4-dinitrothiophene (3.845 g, 6.83 mmol) in trifluoroacetic acid:chloroform (136 mL; 1:1 v/v). The reaction mixture was kept in the dark and stirred overnight. A small portion of NBS was added until the completion of the reaction. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with brine and dried over magnesium sulfate. The crude oil was chromatographed over silica gel using hexane:EtOAc (90:10) as eluent giving orange oil (4.896 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.00 (s, 2H); 2.52 (t, 4H, $J = 7.3$ Hz); 1.56 (m, 4H); 1.25 m, 20H); 0.87 (t, 6H, $J = 6.3$ and 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 147.17; 138.74; 133.42; 132.12; 121.30; 116.76; 31.84; 30.29; 29.30 (3C); 29.14; 22.65; 14.09.

HRMS calcd for $C_{28}H_{36}Br_2N_2O_4S_3$: 718.0204.Found: 718.0195.

2,5-Bis-(2-bromo-3-octylthien-5-yl)-3,4-diaminothiophene (*3*). Tin chloride (47.570 g, 250.9 mmol) was added to a suspension of 2,5-bis-(2-bromo-3-octylthien-5-yl)-3,4-dinitrothiophene (4.733 g, 6.568 mmol) in a mixture of ethanol/hydrochloric acid (46 mL/32 mL) under inert gaz. The reaction was stirred overnight. The mixture was poured into 700 mL of KOH (25% p/v) and then extracted 3 times with ethyl acetate. The organic layers were combined and washed with brine and then dried over sodium sulfate. The crude oil was chromatographed over silica gel using Hexane: EtOAc (85:15) as eluent giving a brown oil (2.249 g, 52%). This product is very unstable and should not be stored. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.94 (s. 2H); 3.46 (m, 4H); 2.53 (t, 4H, $J = 7.4$ Hz); 1.54 (m, 4H); 1.24 (m, 20H); 0.87 (t, 6H, $J = 6.3$ and 6.8 Hz)^{13}C NMR (75 MHz, Acetone-D6, ppm): 143.72; 136.94; 132.97; 131.41; 111.47; 104.81; 32.57; 31.04; 29.93; 29.48; 23.28; 14.41 (two carbon atoms are blind by the deuterated solvent).

Scheme 3. Synthesis of Copolymers

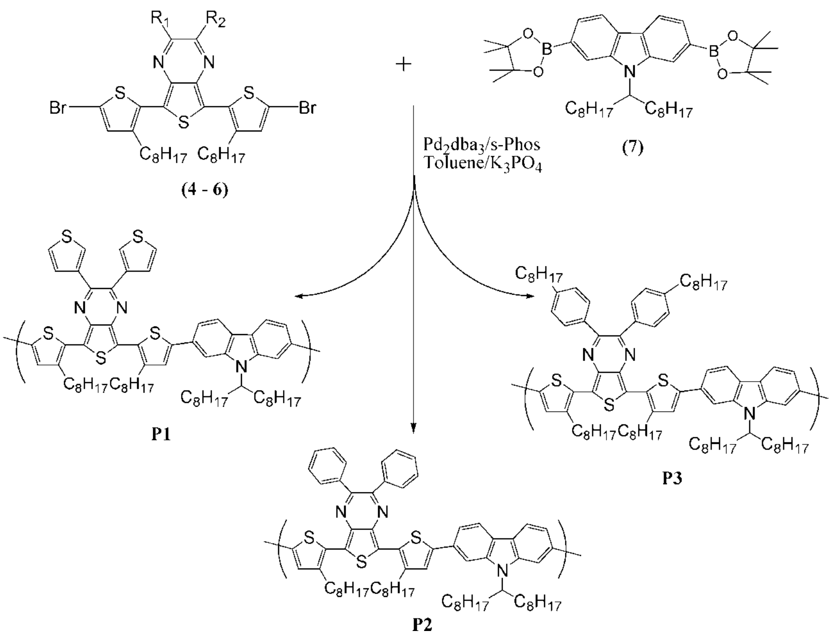


Table 1. GPC and TGA Data of Poly(carbazole) Derivatives

polymer	M_n (KDa)	M_w (KDa)	PDI	T_{dec} (°C)	E_{ox} vs SCE	E'_{ox} vs SCE
P1	27	69	2.6	414	0.77	0.49
P2	9	14	1.6	407	0.81	0.58
P3	15	20	1.3	413	0.79	0.57

*2,3-Di(thien-3-yl)-5,7-di(2-bromo-3-octylthiophene)thieno[3,4-b]pyrazine (**4**).* 3,3-Thenil (313 mg, 1.406 mmol) was added to suspension of 2,5-Bis-(2-bromo-3-octylthien-5-yl)-3,4-diaminothiophene (774 mg, 1.172 mmol) in ethanol (30 mL). The mixture was refluxed overnight. The mixture was cooled to room temperature and the solid was filtered. The solid was washed with copious amounts of cold ethanol and then dried under a vacuum. A dark purple solid was obtained. (830 mg, 84%). M.P. 110−112 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.58 (d, 2H, $J = 2.1$ Hz); 7.35 (m, 4H); 6.70 (s, 2H); 2.89 (t, 4H, $J = 7.7$ Hz); 1.71 (m, 4H); 1.41−1.27 (m, 20H); 0.88 (t, 6H, $J = 6.1$ and 6.8). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 147.74; 140.82; 140.08; 137.13; 132.00; 129.80; 129.06; 127.99; 125.30; 123.82; 114.39; 31.94; 30.71; 29.99; 29.80; 29.54; 29.34; 22.71; 14.13.

HRMS calcd for $C_{38}H_{42}Br_2N_2S_5$: 844.0318. Found: 844.0331.

*2,3-Di(phen-1-yl)-5,7-di(2-bromo-3-octylthiophene)thieno[3,4-b]pyrazine (**5**).* Benzil (269 mg, 1.281 mmol) was added to suspension of 2,5-bis-(2-bromo-3-octylthien-5-yl)-3,4-diaminothiophene (705 mg, 1.067 mmol) in ethanol (25 mL). The mixture was refluxed overnight. The mixture was cooled to room temperature and the solid was filtered. The solid was washed with a copious amount of cold ethanol and then dried under a vacuum. A dark purple solid was obtained. (699 mg, 79%). M.P. 134−135 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.56 (dd, 4H, $J = 6.3$ and 1.6 Hz); 7.36 (m, 6H); 6.98 (s, 2H); 2.91 (t, 4H, $J = 7.6$ Hz); 1.72 (m, 4H); 1.41−1.27(m, 20H); 0.88(t, 6H, $J = 7.6$ and 7.1). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 152.69; 141.02; 138.84; 137.60; 132.07; 130.13; 129.76; 129.10; 128.15; 124.25; 114.49; 31.94; 30.66; 30.06; 29.79; 29.54; 29.34; 22.71; 14.14

HRMS calcd for $C_{42}H_{46}Br_2N_2S_3$: 832.1190. Found: 832.1198.

*2,3-Di(4-octylphen-1-yl)-5,7-di(2-bromo-3-octylthiophene)thieno[3,4-b]pyrazine (**6**).* 4,4-Octylbenzil (0.685 g, 1.577 mmol) was added to suspension of 2,5-Bis-(2-bromo-3-octylthien-5-yl)-3,4-diaminothiophene (0.868 g, 1.314 mmol) in ethanol (25 mL). The mixture was refluxed overnight. The mixture was cooled to room temperature and extracted with ethyl ether 3 times. The organic layers were combined and washed with water and brine. The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. The crude oil was chromatographed over silica gel using hexane:dichloromethane (60:40) as eluent giving dark purple oil. (1.043 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.47 (d, 4H, $J = 8.0$ Hz); 7.13 (d, 4H, $J = 4$ Hz); 6.98 (s, 2H); 2.91 (t, 4H, $J = 7.3$ and 7.9); 2.62 (t, 4H, $J = 7.3$ and 7.9); 1.72 (m, 4H); 1.63 (m, 4H); 1.43−1.26 (m, 40H); 0.88 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 152.88; 144.18; 140.82; 137.62; 136.30; 132.03; 130.05; 129.92; 128.17; 123.89; 114.30; 35.86; 31.94; 31.22; 30.64; 30.09; 29.79; 29.53; 29.35; 22.71; 14.14.

HRMS calcd for $C_{58}H_{78}Br_2N_2S_3$: 1056.3694. Found: 1056.3671.

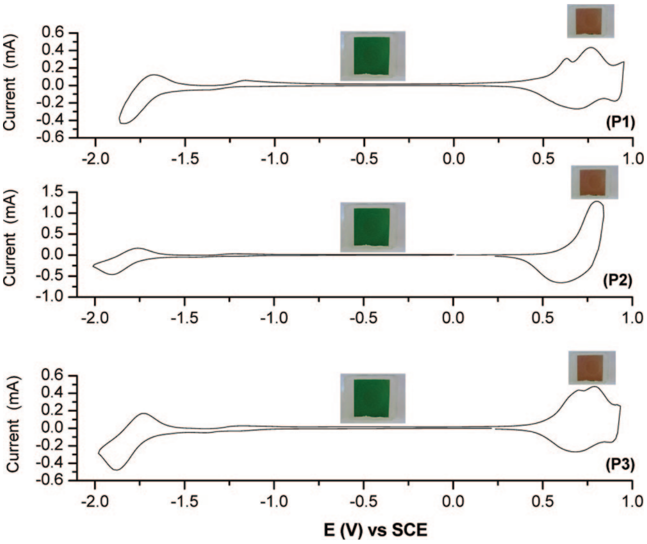


Figure 1. Cyclic voltammograms of P1−P3 on Pt button.

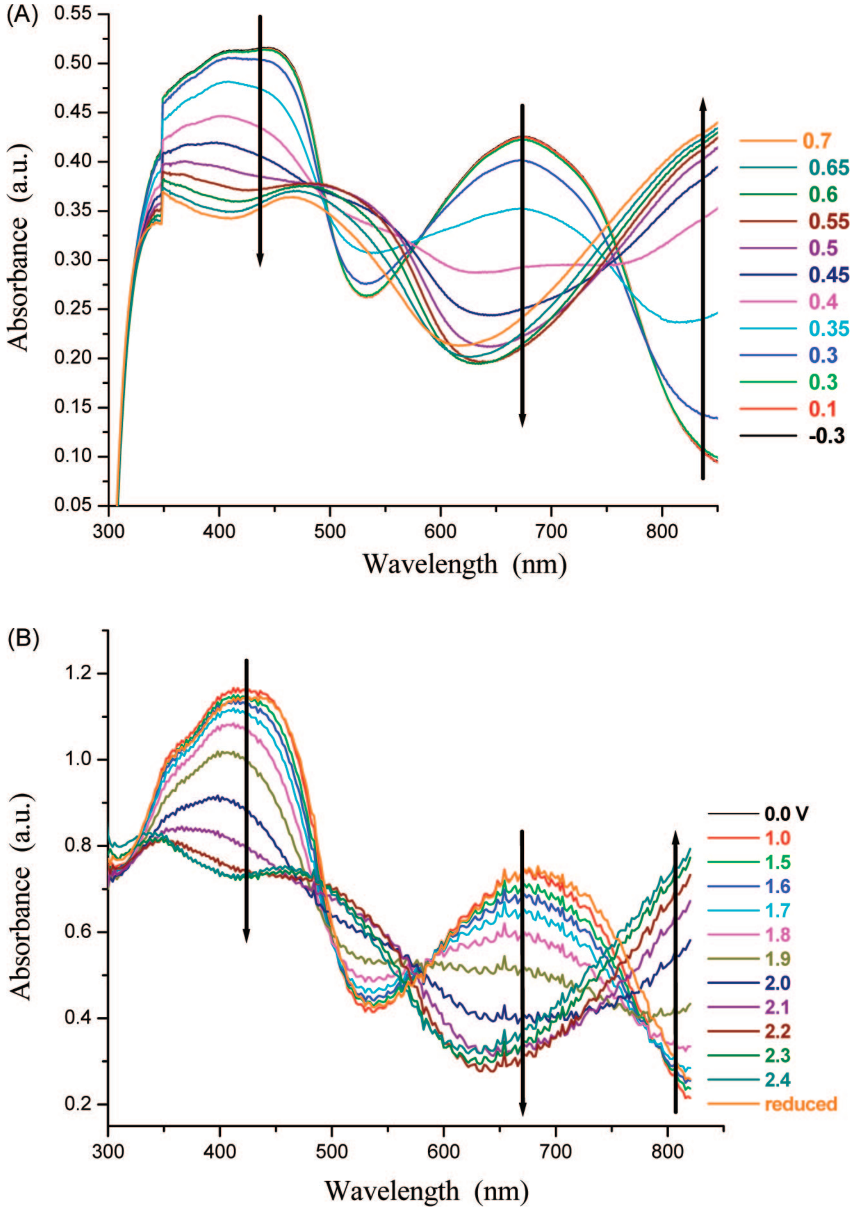


Figure 2. Spectroelectrochemistry of (A) P1 film on ITO immerged in 0.1 M $TBABF_4$ /acetonitrile (E vs Ag/Ag^+) and (B) P1 all-solid state EC using gel electrolyte (DC source).

Copolymer Syntheses. Copolymers were synthesized using Suzuki-Miyaura cross-coupling reaction using this typical procedure: To a mixture of dibromide compound (**4**−**6**) (1.00 equiv.), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9′′-heptadecanylcarbazole (**7**) (1.00 equiv.), Pd_2dba_3 (0.005 equiv.), and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.020 equiv) was added a deoxygenated mixture of toluene ([monomer = 0.1M]) and aqueous 2 M K_3PO_4 (8.00 equiv.). The mixture was vigorously stirred at 85−90 °C for 48−72 h. After the solution was cooled, the whole mixture was poured slowly into cold mixture of methanol/deionized water (10/1 in volume). The polymer was collected by filtration and washed with methanol. The solid was then washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The polymer was further purified by redissolving in chloroform and then precipitated from cold methanol prior to drying at room temperature under a high vacuum.

Poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(thien-3-yl)-thieno[3,4-b]pyrazine (**P1**). (253 mg, Y = 66%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.12 (br, 2H); 7.89 (br, 2H); 7.72 (br, 2H); 7.61 (br, 2H); 7.51 (br, 2H); 7.36 (br, 4H); 4.70 (br, 1H); 3.08 (br, 4H); 2.45 (br, 2H); 2.07 (br, 40); 1.89 (br, 4H); 1.53 (br, 4H); 1.30−1.15 (br, 42H); 0.89 (t, 6H, J = 6.8 Hz); 0.77 (t, 6H, J = 6.3 and 6.8).

Poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(phen-1-yl)-thieno[3,4-b]pyrazine (**P2**) (196 mg, Y = 51%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.12 (br 2H); 7.88 (br, 2H); 7.71 (br, 2H); 7.60 (br, 2H); 7.39 (br, 10H); 4.70 (br, 1H); 3.10 (br, 4H); 2.43 (br, 2H); 2.06 (br, 2); 1.89 (br, 4H); 1.52 (br, 4H); 1.31−1.15 (m, 40H); 0.88 (t, 6H, J = 6.7 Hz); 0.77 (t, 6H, J = 6.5 and 6.8 Hz).

Poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,7-di(3-octylthien-2-yl)-2,3-di(4-octylphen-1-yl)-thieno[3,4-b]pyrazine (**P3**). (61 mg, Y = 16%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.12 (br, 2H); 7.89 (br, 2H), 7.54 (br, 6H); 7.37 (br, 2H); 7.18 (br, 4H); 4.72 (br, 1H); 3.09 (br, 4H); 2.66 (br, 4H); 2.49 (br, 2H); 2.06 (br, 2H); 1.89 (br, 4H); 1.65−1.52 (br, 8H); 1.30−1.14 (br, 64H); 0.89 (br, 12H); 0.76 (br, 6H).

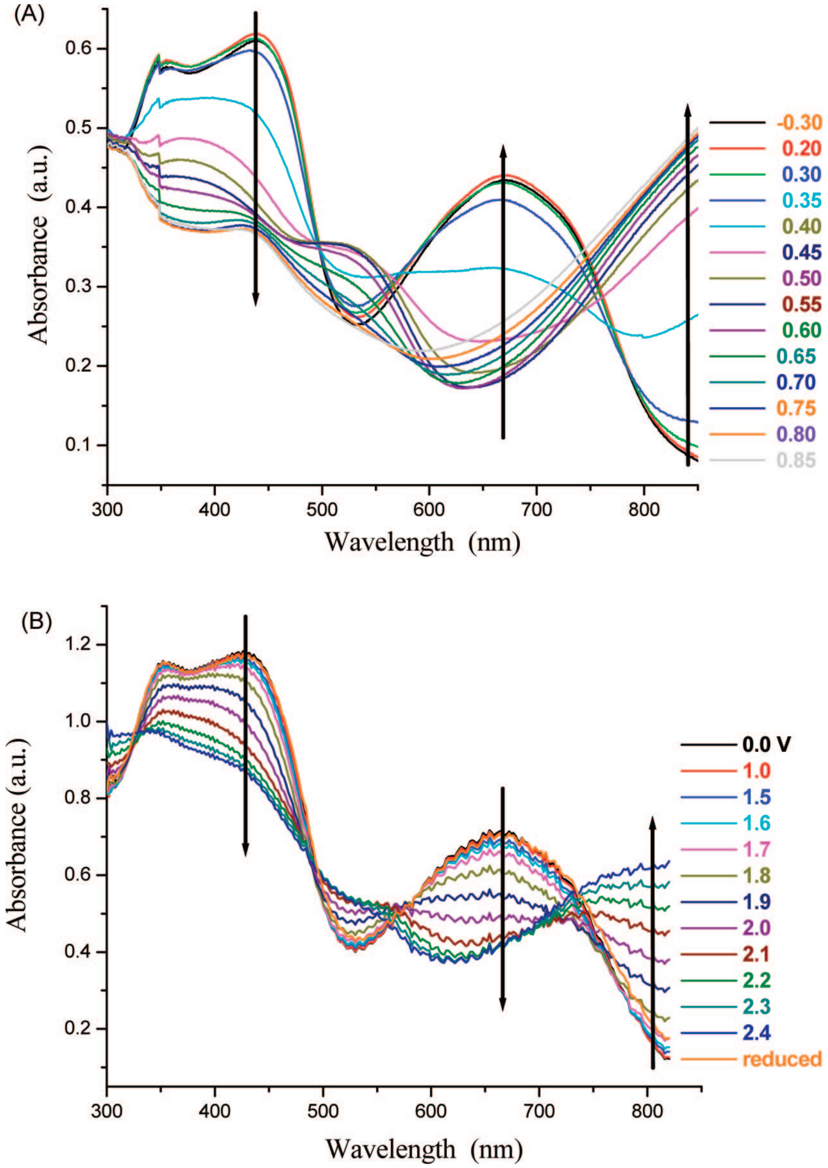


Figure 3. Spectroelectrochemistry of (A) P2 film on ITO immerged in 0.1 M TBABF$_4$ /acetonitrile (*E* vs Ag/Ag$^+$) and (B) P2 all-solid state EC using gel electrolyte (DC source).

Results and Discussion

The chemical structure and the synthetic routes to the new poly(2,7-carbazole) derivatives are depicted in Schemes 1−3. Despite the fact that Sonmez et al. have already published compound **1**,[41] to the best of our knowledge, we report for the first time the full synthetic procedure. The bromination of compound **1** was successfully carried out using NBS in a mixture of trifluoracetic acid/chloroform mixture. We have tried several times the procedure reported by Andersson et al. using NBS in DMF for related structures without any success.[28,29] We found that their procedure gave mixtures of brominated compounds that cannot be isolated from each other. Reduction of 2,5-bis-(2-bromo-3-octylthien-5-yl)-3,4-dinitrothiophene (**2**) was successfully accomplished using tin chloride in a mixture of ethanol/hydrochloric acid, giving the diamine **3**. This diamine compound had to be used right after the purification because we have observed some degradation when exposed to air. The condensation of **3** with diketones (3,3-thenil, benzil, and 4,4-dioctylbenzil) afforded compounds **4**−**6** in good yields. The 4,4-octylbenzil was chosen to improve the solubility of the resulting polymer because of the long alkyl side chains. The synthesis of **P1**, **P2**, and **P3** was accomplished by the copolymerization of compounds **4**, **5**, and **6**, respectively, with 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanyl-carbazole (**7**) using a modified Suzuki coupling reaction. Indeed, no polymerization occurred when we used the typical Suzuki coupling reaction with Pd(PPh$_3$)$_4$ in toluene/K$_2$CO$_3$. Changing the catalyst from Pd(PPh$_3$)$_4$ to in situ ligand substitution between Pd$_2$dba$_3$ and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos) led to the desired polymers (**P1**−**P3**). All polymers (soluble fraction) were obtained in moderated yield (16−81%) as green solids. They were readily soluble in chloroform, toluene, and tetrahydrofuran, which make them suitable for spin- or spray-coating techniques.

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(41) Campos, L. M.; Tontcheva, A.; Günes, S.; Sonmez, G.; Neugebauer, H.; Sariciftci, N. S.; Wudl, F. *Chem. Mater.* **2005**, *17*, 4031.

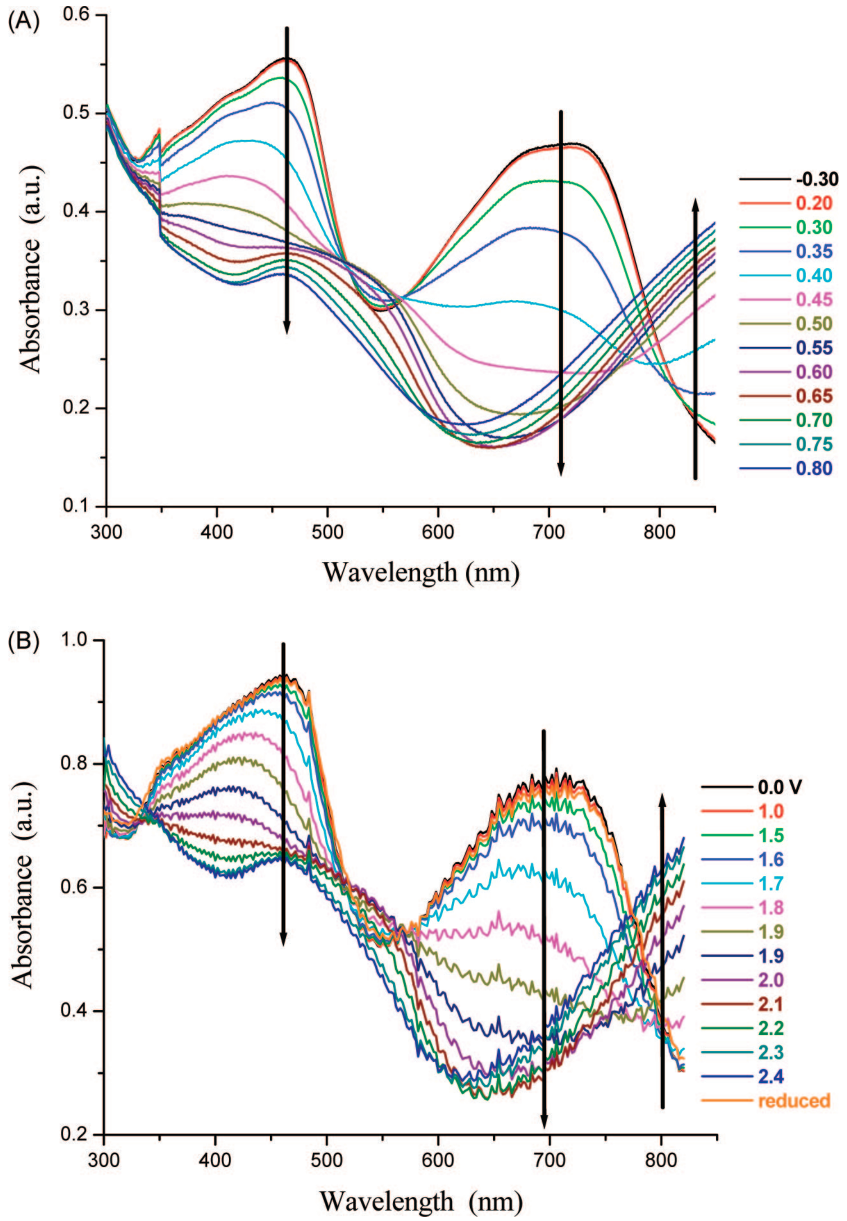

Figure 4. Spectroelectrochemistry of (A) P3 film on ITO immerged in 0.1 M $TBABF_4$ /acetonitrile (E vs Ag/Ag^+) and (B) P3 all-solid state EC using gel electrolyte (DC source).

Table 2. CIE Coordinates (Color Space Lab/D65/10°)

polymer[a]	L^*	a^*	b^*	C	h	color
P1 (n)	27.35	−16.12	2.72	16.34	170.41	green
P1 (o)	43.39	−5.45	9.13	10.63	120.81	brown
P2 (n)	29.26	−17.08	3.33	17.40	168.98	green
P2 (o)	42.60	1.46	9.81	9.92	81.56	brown
P3 (n)	28.26	−16.58	3.03	17.00	169.98	green
P3 (o)	42.83	2.46	9.51	10.92	91.56	brown
P3HT (n)	29.80	23.66	−20.70	31.43	318.82	purple
P3HT (o)	40.95	−4.83	−17.02	17.69	254.14	blue

[a] (n), Neutral; (o), oxidized.

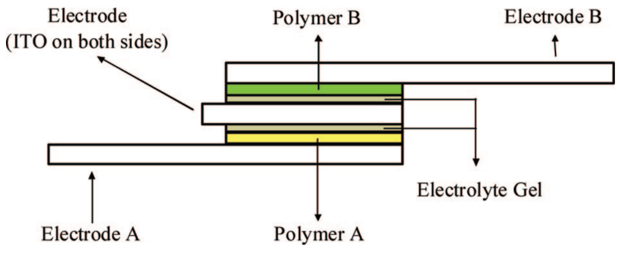

Figure 5. Multicolored electrochromic cells (MEC).

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the copolymers ranges from 9 to 27 kDa and 14 to 69 kDa, respectively, with polydispersity indexes ranging from 1.3 to 2.6. These data are summarized in Table 1. Uniform, free-standing, and flexible films can be prepared from slow evaporation of a concentrated solution. This mechanical property is important for the further development of flexible electrochromic devices. The thermal stability of the polymers was evaluated by thermogravimetric analyses (TGA) under a nitrogen atmosphere. These data are also summarized in Table 1. Most copolymers exhibit very good thermal stabilities, losing less than 5% of their weight up to 400 °C.

The electrochemical data of **P1**−**P3** are reported in Table 1. Cyclic voltammograms were obtained by casting films of polymers onto a platinum wire or by spray-coating films onto an ITO-coated glass electrode. We have observed slight shifts

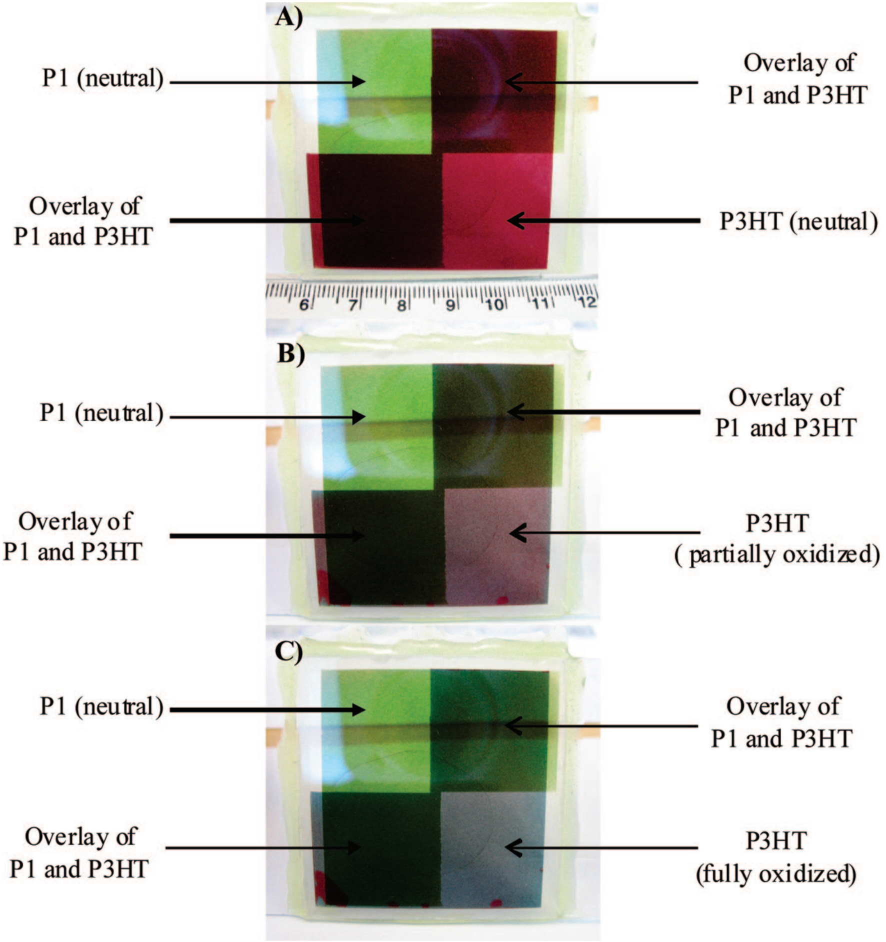

Figure 6. Example of MEC cell based on P1 and P3HT (5 cm × 5 cm).

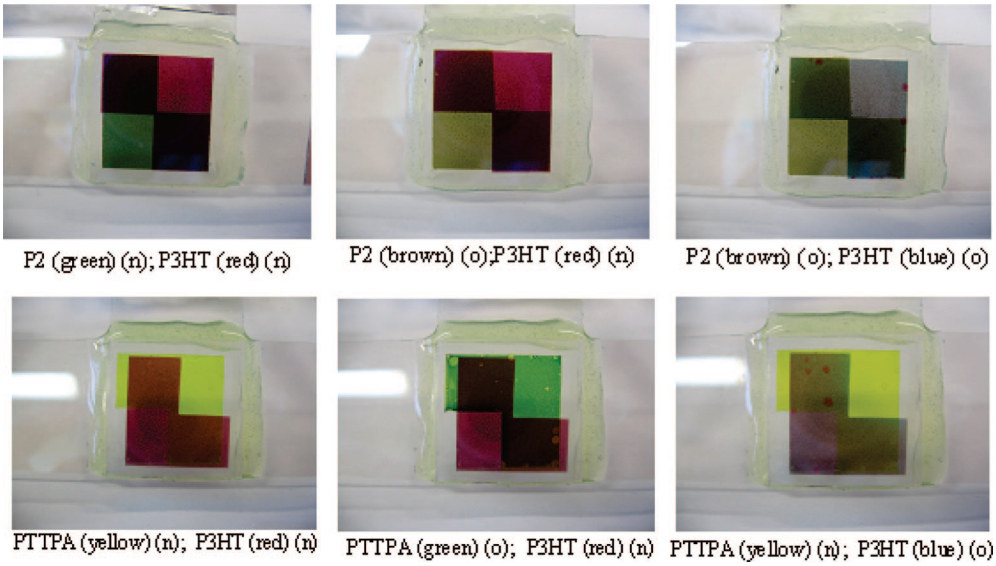
P2 (green) (n); P3HT (red) (n)
P2 (brown) (o);P3HT (red) (n)
P2 (brown) (o); P3HT (blue) (o)
PTTPA (yellow) (n); P3HT (red) (n)
PTTPA (green) (o); P3HT (red) (n)
PTTPA (yellow) (n); P3HT (blue) (o)

Figure 7. All solid-state MEC (5 × 5 cm).

toward higher oxidation potential values for films of **P1**−**P3** on ITO when compared to films on Pt disks (not shown here). This phenomenon was attributed to the large difference of resistivity between the platinum and the ITO-coated glass. As shown in Figure 1, all polymers are stable upon oxidation with potential of oxidation ranging from 0.77 to 0.81 V vs SCE. As already reported by Sonmez et al.,[17] there is a notable difference between the amounts of transferred electrons during the redox processes for pyrazine derivatives. High peak currents were obtained when **P1**−**P3** are oxidized while low peak currents were observed when the polymers were reduced. One can think that **P1**−**P3** were better electron donor than acceptor. Despite that **P1**−**P3** were used as anodic electrochromic materials, coloration from green to transmissive brown was observed during both oxidation and reduction processes.

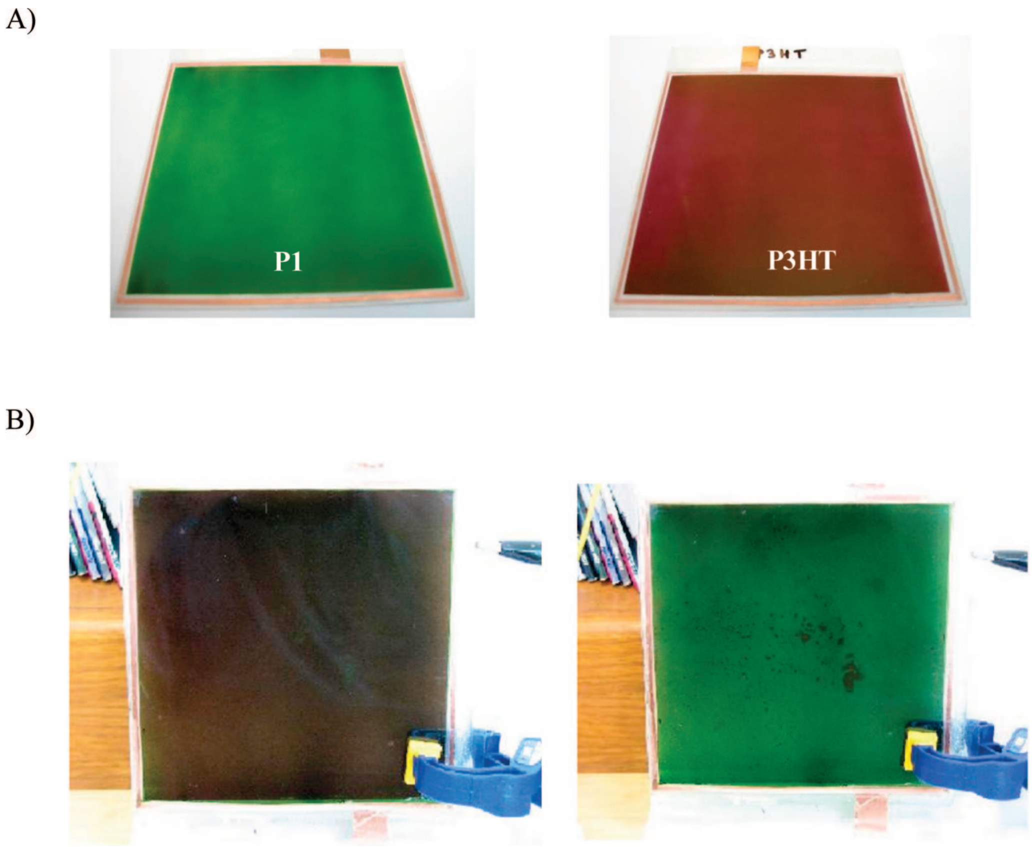

Figure 8. (A) Spray-coated film of P1 and P3HT on ITO-glass electrode (active surface of 12.5 × 12.5 cm); (B) MEC where P1 and P3HT are neutral (left) and MEC where P1 was neutral and P3HT fully oxidized (right).

Spectroelectrochemical measurements were performed on both films of polymers spray-coated onto ITO-coated glass slides immerged in electrolyte solution and on single layer electrochromic cell. The spectroelectrochemical results of **P1**−**P3** are shown in Figures 2−4. Films of **P1**−**P3** appeared green because the absorption spectra show blue and red absorption of the visible spectra and a valley centered near 530 nm. These conditions, rarely observed for neutral conjugated polymers, are required to obtain reflecting green materials. Upon oxidation, from −0.3 to 0.8 V vs Ag/Ag$^+$, we have observed a gradual depletion of the maxima of absorption in the visible region and the formation of a new absorption band in the near IR upon oxidation. Reflecting green color (neutral polymer) slowly faded away and a transmissive brown color took place when **P1**−**P3** were fully oxidized (see Table 2). These two colors meet the needs for adaptive camouflage for military assets.

Cycling stability upon oxidation of **P1**−**P3** has been performed (see the Supporting Information). A thin film of polymer was deposited on a platinum button and cyclic voltammetry was performed at speed rate of 50mV/s. The cyclic voltammograms of **P1** between −0.5 and +0.75 V vs Ag/Ag$^+$ shows a slight shift of the anodic peak (+87 mV) and a decrease of the current density of 10% after 500 cycles. For **P2**, the cyclic voltammograms between −0.5 and +0.65 V vs Ag/Ag$^+$ shows a shift of the anodic peak (+61 mV) and a decrease of 16% of the current density after 500 cycles. Finally, **P3** between −0.5 and +0.60 V vs Ag/Ag$^+$ shows a shift of the anodic peak (+111 mV) and a decrease of 18% in the current density. The slight shift of the anodic peak and the decrease of the current densities upon cycling can be attributed to a change in the film morphology or activation of new electroactive site from freshly cast polymer film upon the repetitive insertion and extraction of counterion during the oxidation process.

As shown in Figure 5, color mixing experiments were conducted using home patterned ITO-glass slides of various sizes which led to pixel sizes ranging from 1 × 1 cm to 12.5 × 12.5 cm. Polymer films of **P1**−**P3**, **P3HT**, and **PTTPA** were obtained by the spray coating technique. Once the polymer films were dried, a thin layer of conductive gel electrolyte was applied on it. Then, we used as counter-electrode a double sided ITO-glass slide sandwiched between the polymer coated electrodes. The devices were sealed using an epoxy resin. This configuration generates two individual electrochromic cells in one device where each cell can be controlled separately to effectively tune the color. However, the use of bare ITO as counter-electrode may affect the long-term stability of the electrochromic devices. An ion storage layer such as vanadium pentoxide or other electrochromic materials can be used as counter-electrode.[9,10,42] As shown in Figure 6A−C, we present a typical example of additive electrochromic cells using **P1** (green) and **P3HT** (purple) as active layers with pixel of 2.2 × 2.2 cm. The results for **P2** and **P3** were similar and not shown here. Neutral polymers (0 V) **P1** and **P3HT** reflect green and purple color respectively. The mixture of these two colors gives a dark

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(42) Fungo, F.; Jenekhe, S.; Bard, A. J. *Chem,. Mater.* **2003**, *15*, 1264.

brown pixel (Figure 6A). As **P3HT** was partially oxidized (1.5 V), the color of the polymer was changed from purple to violet. The resulting color for the overlap pixels became pale brown (Figure 6B). Finally, when **P3HT** was fully oxidized (2.4 V), its color changed to blue. The resulting color for the pixels was dark green (Figure 6C). For this device, the overall color change was dark brown to dark green. Moreover, the resulting color can be tuned by controlling the oxidation level of one or both electrochromic polymers at the same time. We have explored several combinations of polymer for additive electrochromic cell as shown in Figure 7.

Only a few examples of large electrochromic cells based on conjugated polymers are reported in the literature. Xu et al.[22] have described electrochromic devices with active surfaces of 900 cm^2, whereas Sotzing et al.[23] have reported devices with active surface of 30 cm^2, both using electropolymerized PEDOT derivatives. To the best of our knowledge, we report for the first time the fabrication of a large electrochromic cell based on the additive color mixing theory were active layers are obtained by spray-coating technique. As shown in images A and B in Figure 8, we prepared a prototype of a multicolored electrochromic cell based on **P1** and **P3HT** with an active surface of 156 cm^2. Because ITO has a high electrical resistance, we have covered the perimeter of the polymer layer with an adhesive copper tape to limit the potential drop along the surface of the active layer.[23] The copper tape was covered by a layer of paraffin to prevent electrical short. Gel electrolyte was applied manually over the polymer layers, then the double-sided ITO was inserted and the three electrodes were clamped together then the device was sealed. Removing air bubble inside the gel electrolyte was a painful process and despite the spacer layer, many of our devices have shown electrical shorts in one or both segments. As reported by Sotzing,[23] the incorporation of glass beads in the gel electrolyte seems a good way to prevent electrical shorts. As shown in Figure 8B, our device was switched from dark brown (0 V) to green (2.4 V) with switching times around 15s for both layers. Work on both devices fabrication and characterization of electrochromic cells still in progress in order to optimize the color tuning, the stability and the switching time of large devices.

Conclusion

We have prepared three poly(2,7-carbazole) derivatives that have a green color in their neutral state. Once oxidized, a transmissive brown color was observed. These two colors are compatible for adaptive camouflage for military assets. We have reported the fabrication of small multicolored electrochromic cells based on the additive color mixing theory where the color of the pixel can be tuned easily by controlling the oxidation level of the electroactive layer. Finally, we have prepared a large MEC with an active surface of 156 cm^2, where the active layers were obtained by the spray coating technique. More results on the evaluation of the devices will be published in a forthcoming publication. Finally, the performance of **P1−P3** as active layer in photovoltaic cells is under investigation.

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Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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