Multichromic Copolymers Based on 3,6-Bis(2-(3,4-ethylenedioxythiophene))-*N*-alkylcarbazole Derivatives

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ABSTRACT: Electrochemical copolymers of 2,2′-bis(3,4-ethylenedioxythiophene) (BiEDOT) and 3,6-bis-(2-(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole (BEDOT−*N*MeCz) were prepared from nine comonomer solutions of varying concentration. The monomers exhibit low peak oxidation potentials ($E_{p,m}$) that are in close proximity (BiEDOT = +0.56 V vs Ag/Ag^+, BEDOT−*N*MeCz = +0.41 V), allowing for facile copolymerization. Spectroelectrochemical analysis revealed that the neutral copolymers possess unique, broad, neutral absorbance maxima and colors ranging from blue (587 nm), to red (464 nm), to orange (429 nm), and finally to yellow (420 nm) that were comonomer concentration dependent, while stepwise oxidation showed that the copolymers pass through a green intermediate state before reaching a blue oxidized state that is concentration independent. A soluble hybrid copolymer of 3,6-bis(2-(3,4-ethylene-dioxy)thienyl)-*N*-eicosylcarbazole (BEDOT−NC_{20}Cz) was prepared via $FeCl_3$ polymerization. Molecular weights of this soluble polymer have been characterized by gel permeation chromatography (GPC) and vapor phase osmometry (VPO). Solution doping and cast film spectroelectrochemical analyses show that the copolymer has a maximum absorbance in the area of 430 nm and that upon sequential oxidation the copolymer passes though a green intermediate state before reaching the fully doped blue state. Photoluminescence experiments revealed emission maxima at 470 and 506 nm and an efficiency (ϕ_f) of 0.12.

Introduction

Molecular or polymeric materials that can be electrochemically switched between different color states as a result of an electron-transfer or redox reaction are said to be electrochromic (EC).[1] Many different classes of compounds display electrochromism and range from mixed-valence metal complexes (Prussian blue), to inorganic metal oxides (WO_3), to organic small molecules (viologens), and finally to organic conjugated polymers. Typical EC materials switch between a transparent or bleached state and a colored state, although it is not uncommon for them to switch between two color states, or in some cases between more than two color states.

A host of applications exist for conjugated polymers and copolymers that take advantage of their inherent ability to remain in either the neutral or oxidized state as well as to reproducibly switch between these states.[2] The applications can be subdivided based on the form of the conjugated polymer that is utilized. Neutral conjugated polymers are employed for semiconducting applications such as thin film transistors (TFTs)[3] and as the active material in light-emitting (pLEDs)[4] devices. The oxidized and conducting state of conjugated polymers allows their use as electrode materials for capacitors and antistatic coatings in photographic film.[5] Finally, a large number of applications exist which rely on the reproducible switching characteristics of conjugated polymers which result in color, conductivity, and volume changes. These applications include chemical sensors for a variety of analytes,[6] battery electrodes,[7] mechanical actuators,[8] drug delivery,[9] and electrochromics.[10]

Of the conjugated EC polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives represent a larger family of materials known as the poly(3,4-alkylenedioxythiophenes) or PXDOTs,[11] which have solidified their position as a dominant set of materials in conducting polymer research. PEDOT shows sufficiently high conductivity for many applications and also possesses other attractive properties that include lower oxidation potentials compared to PTh, resulting in a more stable doped (oxidized) polymer,[12] and a decreased band gap, leading to a transmissive oxidized and conducting state and a very absorptive (dark blue/purple) neutral and insulating state. Because of these characteristics, PEDOT has been commercialized as an aqueous dispersion with poly(styrenesulfonate) (PSS) as a polymeric dopant and is commonly known as PEDOT/PSS.[13]

Modification of the electrical and optical properties of conjugated polymers has been realized through the synthesis of EDOT derivatives as well as multiring or extended conjugation monomers. Extended conjugation monomers using thiophene,[14] EDOT,[15] and furan[16] have been synthesized and range from the simple example of bithiophene to complex molecules such as substituted alkoxybenzenes terminated with EDOT units, as well as fused ring systems.[17]

By linking the polymerizable EDOT moieties through the 3- and 6-positions of carbazole, EC polymers are formed that exhibit three distinct color states: a transmissive yellow neutral state, a green intermediate state, and an absorptive blue oxidized state.[18] The multichromic response displayed by these systems occurs because there is a conjugation break along the polymer chain allowing for the formation of radical cation and dication oxidized states. Carbazole-based molecules are also interesting in that a wide variety of functional groups can be attached to the carbazole nitrogen without disturbing the planarity of the carbazole fused-ring system, an important consideration when specific optical properties are desired.

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Despite the significant progress made in the arena of electrochromic polymers, the multichromic capabilities of current technology is limited. While a wide variety of EC responses (colors) are possible, they are not easily tunable. Furthermore, color gradients are only possible with the use of several individual homopolymers in laminate-type configurations. Therefore, the logical approach toward extending the utility of proven EC homopolymers, is to prepare copolymers. Different compositions of comonomers can be prepared on very small scales, to quickly assess their utility. Conversely, chemical polymerizations not only allow the preparation of large amounts of polymer but also allow for more complete characterization by traditional analytical techniques, such as molecular weight determination experiments.

Several different approaches have been developed to electrochemically synthesize pyrrole and thiophene-based copolymers. Copolymerizations between pyrrole and various *N*-arylpyrroles[19] and *N*-alkylpyrroles[20] were performed and tracked either by conductivity fluctuations or by monomer feed ratios and resulted in materials with enhanced electronic and mechanical properties. Similarly, thiophene copolymers such as those that yield self-doping and fused ring systems have been synthesized.[21−24] Work performed in our laboratory has focused on the electrosynthesis of extended conjugation systems, specifically 1,4-bis(thienyl)arylene and 3,6-bis(thienyl)-carbazole hybrid copolymers, and manipulating their electrochromic properties.[25] Applications for the copolymers presented above include soluble conductors,[26] donor−acceptor low band gap polymers,[27] sensors,[28] and electrochromics,[29] to name a few.

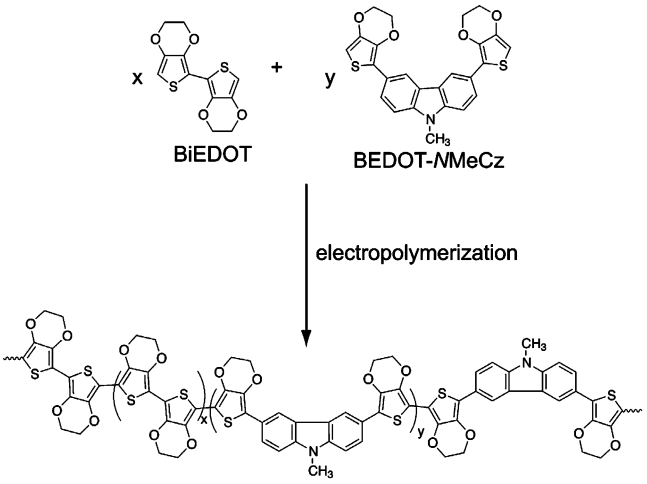
A popular and cost-effective means to produce soluble conducting polymers is oxidative polymerization with $FeCl_3$.[30−32] This mechanism[33] is very similar to that of electrochemical polymerizations. Careful use of oxidative polymerization with $FeCl_3$ provides a means to synthesize soluble electrochromic polymers when other methods present significant synthetic challenges.

Therefore, we have utilized both electrochemical and chemical techniques to synthesize tunable EC copolymers based upon the carbazole framework. The carbazole framework was chosen not only because of the three-color electrochromism the homopolymers display but also because of their low monomer oxidation potentials (+0.41 V vs Ag/Ag^+) and the added advantage of solubility imparted by *N*-alkyl substitution. An *N*-methyl-substituted carbazole monomer with terminal EDOT units has been synthesized for electrochemical copolymerization with the dimer of EDOT (BiEDOT) to form a multichromic dynamic color gradient EC copolymer. Through careful control over the comonomer concentration, continuously variable λ_{max}/band gap (E_g) copolymers have been prepared that span the visible region of the electromagnetic spectrum, leading to yellow, orange, red, purple, and blue colors. In addition, we have chemically polymerized an EDOT-terminated *N*-eicosyl-substituted carbazole monomer with $FeCl_3$ to form a soluble hybrid copolymer.

Results and Discussion

Monomer Syntheses. 3,6-Bis(2-(3,4-ethylenedioxy)-thienyl-*N*-methylcarbazole (BEDOT−*N*MeCz) and 3,6-bis(2-(3,4-ethylenedioxy)thienyl-*N*-eicosylcarbazole (BEDOT−NC_{20}Cz) were synthesized via Kumada cross-coupling reactions according to literature procedures.[18,34]

Scheme 1. Representative Copolymer Structure of BiEDOT and BEDOT−*N*MeCz.



Deprotonation of 3,6-dibromocarbazole with NaH, followed by the addition of the appropriate alkyl bromide or iodide yielded the alkylated carbazoles as off-white powders. The 3,6-dibromo-*N*RCz and $NiCl_2$(dppp) catalyst were then added to the Grignard adduct of EDOT, which was prepared by the lithiation of EDOT with butyllithium followed by quenching with magnesium bromide diethyl etherate ($MgBr_2 \cdot Et_2O$), to yield the BEDOT−*N*RCz derivatives.

2,2′-Bis(3,4-ethylenedioxythiophene) BiEDOT was synthesized via either Ullmann[35,37] coupling utilizing lithiated EDOT and copper(II) chloride or TMEDA in the presence of $Fe(acac)_3$. Following the reaction, the remaining metal salts were removed by passing the crude product through a packed silica gel column. The purified monomer was then stored under an argon blanket in a refrigerator to prevent unwanted degradation reactions from occurring.

Electrochemical Copolymerization. The oxidative electrochemical copolymerization of BiEDOT and BEDOT−*N*MeCz from 0.05 M monomer solutions in 0.1 M tetrabutylammonium perchlorate/acetonitrile (TBAP/ACN) was performed via repeated potential cycling and potentiostatic techniques. A structural representation of the reaction taking place during electrochemical copolymerization is shown in Scheme 1. If it is assumed that both BiEDOT and BEDOT−*N*MeCz oxidize at approximately the same potential, then radical cations of both monomers are formed simultaneously at the working electrode surface which then react with each other. It is expected that since both radical cations possess EDOT termini there is no preference shown between reactive species, resulting in the formation of a random copolymer. The series of coupling events would therefore lead to segments of conjugated BiEDOT separated by BEDOT−*N*MeCz units.

Initially, each of the monomers were homopolymerized, as shown in Figure 1, to confirm both their oxidation potentials and that their electrochemistry possessed adequate overlap to ensure copolymerization. To ensure successful electrochemical copolymerization, both monomers must oxidize to form their reactive radical cations at approximately the same potential. BiEDOT has a peak monomer oxidation potential ($E_{p,m}$) of +0.56 V vs Ag/Ag^+ and BEDOT−*N*MeCz has an $E_{p,m}$ of +0.41 V vs Ag/Ag^+ (from now on all potentials are reported vs this reference electrode), giving them a

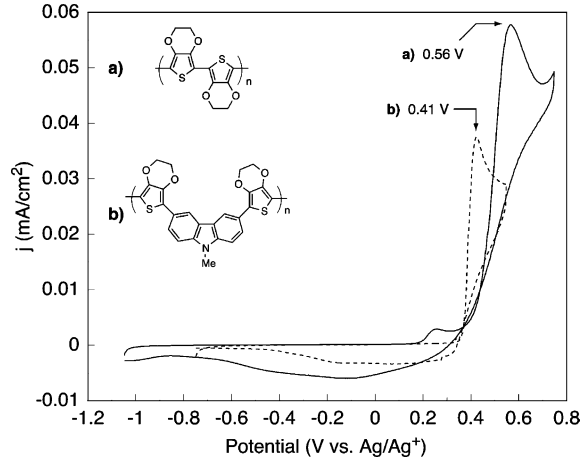


Figure 1. Initial cyclic voltammograms for 0.05 M solutions of (a) BiEDOT and (b) BEDOT−*N*MeCz in 0.1 M TBAP/CAN electrolyte on Pt disk electrodes (area = 0.02 cm^2) at scan rates of 20 mV/s.

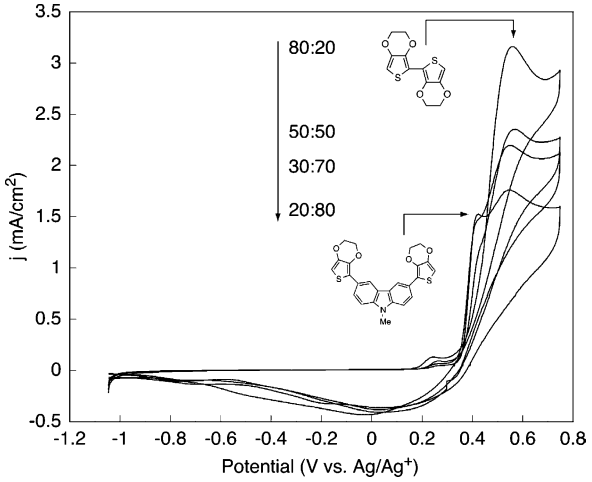


Figure 2. Initial cyclic voltammograms for varying concentration comonomer solutions of BiEDOT and BEDOT−*N*MeCz. The first number in the legend corresponds to the concentration of BiEDOT in the comonomer solution.

$\Delta E_{p,m}$ of 150 mV. The two distinct redox processes associated with the carbazole cation and dication formation in PBEDOT−*N*MeCz are clearly evident, as is the broad redox process of PBiEDOT which can be seen in Figure 3 (parts a and e). It should be noted that even after careful recrystallization, a small pre-peak in the BiEDOT electropolymerization at +0.25 V is evident and may be due to either the presence of a small amount of ter-EDOT impurity or a surface phenomenon, but does not adversely affect copolymerization or the copolymers' resultant optical properties. On the basis of these closely overlapping redox processes, nine comonomer solutions were prepared ranging from 90% BiEDOT to 90% BEDOT−*N*MeCz.

The comonomers were electrochemically polymerized by repeated potential scanning from −1.1 V to +0.75 V until a blue, electroactive polymeric film formed on the working electrode surface. Figure 2 displays the initial cycle for five comonomer solutions. It is apparent that as the BEDOT−*N*MeCz concentration increases, its monomer oxidation becomes more pronounced, while at the same time BiEDOT's monomer oxidation current decreases. This corresponds to the concurrent formation of radical cations of each monomer, allowing for their combination and subsequent copolymerization. The

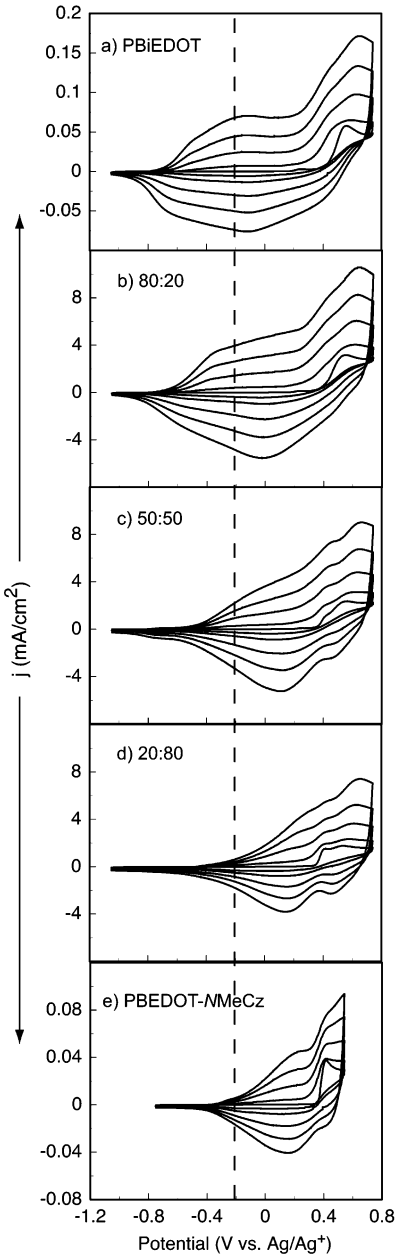


Figure 3. Electrochemical copolymerization of comonomer solutions from 0.1 M TBAP/ACN (20 mV/s), onto a Pt disk (area = 0.02 cm^2). The first number in the legend corresponds to BiEDOT concentration. Homopolymerizations of BiEDOT and BEDOT−*N*MeCz are included for comparison purposes. The first cycle, followed by the even cycles 2 through 8 are shown. The vertical dashed line indicates the approximate $E_{1/2}$ of PBiEDOT.

decreased current response for increasing BEDOT−*N*MeCz concentration could be the result of either BEDOT−*N*MeCz's broken conjugation compared to the more highly conjugated BiEDOT or to associated electron-transfer rates at the electrode surface.

Inspection of the repeated scan copolymerizations' potential−current responses compared to those of the respective homopolymers, shown in Figure 3, reveals evidence of copolymerization based upon potential shifts. The electrochemical copolymerization of three comonomer solutions, as well as the homopolymerizations of BiEDOT and BEDOT−*N*MeCz are shown, which demonstrate the shift in electrochemical character from pure

PBiEDOT (Figure 3a) to pure PBEDOT−*N*MeCz (Figure 3e). A vertical dashed line has been drawn through each electropolymerization to indicate the location of PBiEDOT's $E_{1/2}$, and to reference the shift in polymer redox process. Specifically, the polymerization of a comonomer solution that is 20% BEDOT−*N*MeCz, begins to incorporate the more positive redox process of PBEDOT−*N*MeCz, forming a material that is neither PBiEDOT nor PBEDOT−*N*MeCz. As the concentration of BEDOT−*N*MeCz is increased further to 50% and finally to 80%, the copolymer electrochemistry continues to resemble that of pure PBEDOT−*N*MeCz, while still maintaining PBiEDOT character. Furthermore, the slow positive shift in $E_{1/2}$ shows the evolution of copolymerization in that the individual redox processes of each homopolymer are no longer resolved, instead being replaced by another broad redox process that lies midway between each homopolymer's half-wave potential.

The composition of the copolymer is therefore dependent on both comonomer concentration in the polymerization media and the reactivity of their radical cations. A higher concentration of BiEDOT in the comonomer solution would result in a copolymer with larger run lengths of EDOT separated by *N*-methylcarbazole units. Conversely, a higher BEDOT−*N*MeCz concentration would result in a copolymer with a decreased content of consecutive EDOT segments. Because PBiEDOT and PBEDOT−*N*MeCz have very dissimilar electrochromic responses in the neutral state, it was expected that large color gradients would be possible through varied EDOT domain lengths.

Copolymer Electrochemistry. Following copolymerization, the surface-bound copolymer was rinsed with monomer-free electrolyte and then placed into a three-electrode cell containing 0.1 M TBAP/ACN electrolyte solution. The copolymer films were then cycled over the potential range for complete copolymer oxidation and reduction as shown in Figure 4. The oxidation of PBiEDOT domains as well as the cation and dication formation of the BEDOT−*N*MeCz domains are present in each copolymer, indicating that each monomer is being incorporated into the copolymer chain. As the concentration of BiEDOT is increased, there is a clear shift of the copolymer $E_{1/2}$ to more negative potentials. However, even in the case of an 80% BiEDOT monomer solution, the resulting copolymer still displays the cation and dication formation associated with BEDOT−*N*MeCz. The same trend is also observed for very high concentrations of BEDOT−*N*MeCz, where PBiEDOT character is still present. More importantly, there is a new, broad redox process present, centered at approximately −0.05 V, which is midway between the $E_{1/2}$'s of PBiEDOT (ca. −0.4 V) and PBEDOT−*N*MeCz (ca. +0.25 and +0.52 V, respectively) and is attributed to the copolymer. The scan rate dependence of each copolymer film was studied to determine whether the observed redox process was surface confined. Scan rate dependencies were calculated by measuring the peak anodic ($i_{p,a}$) and cathodic ($i_{p,c}$) current responses as a function of increasing scan rate. In all cases, a linear relationship was found, indicating that the electroactive centers of the copolymers are indeed electrode confined.

Copolymer Spectral Analysis. The most compelling evidence for electrochemical copolymerization can be found in the copolymer spectroelectrochemical analysis, which provides insights into electronic structure.

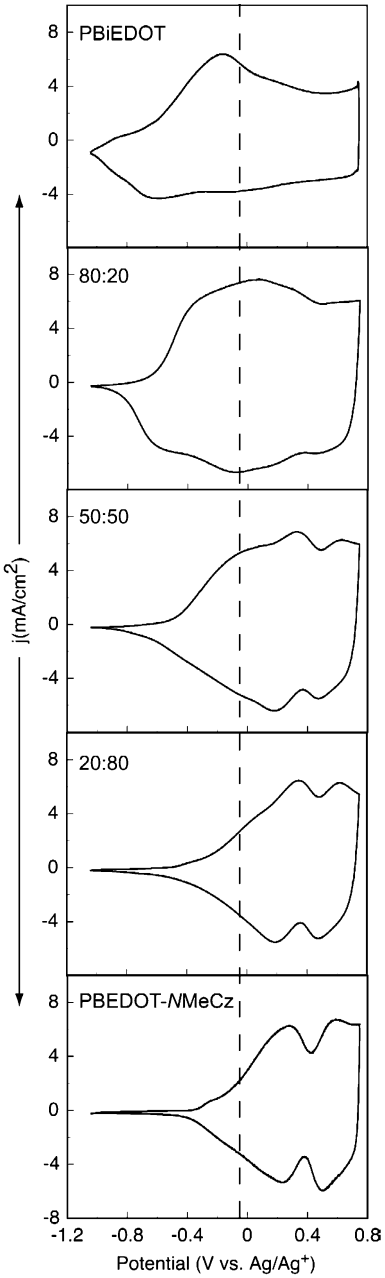


Figure 4. Copolymer electrochemistry for a series of varying monomer concentrations. The first number in the legend corresponds to BiEDOT concentration. The dashed line indicates the copolymer $E_{1/2}$ at −0.05 V.

Copolymers were electrosynthesized onto ITO-coated glass slides under constant potential conditions (at +0.5 V). To ensure consistent content of electroactive polymer on the electrode surface between polymerizations, the same amount of charge was passed during each copolymerization (∼20 mC/cm^2). After deposition, the blue, oxidized, ITO-adhered films were rinsed with monomer-free electrolyte solution, placed in cuvettes containing monomer-free electrolyte solution, and probed with UV−vis−NIR spectroscopy. Since all of the copolymer films are blue in their oxidized state, each was subsequently reduced to determine whether there was a direct correlation between comonomer composition and electrochromic response. Figure 5 displays the normalized neutral absorbances of each copolymer film and demonstrates a clear shift in the dominant wavelength as comonomer composition is varied from pure BiEDOT to

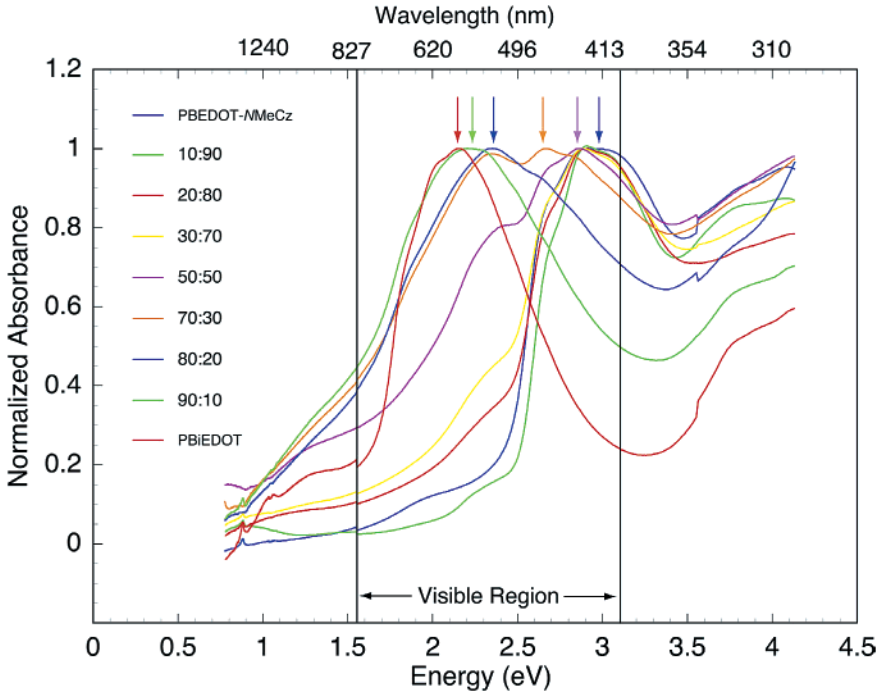


Figure 5. Neutral absorbance spectra for a series of electrochemical copolymers. The color-coded arrows indicate which copolymer is responsible for the dominate absorbance.

pure BEDOT−*N*MeCz. As the concentration of BEDOT−*N*MeCz is decreased in the copolymer chain, the dominate absorbance of the copolymer shifts from 424 to 580 nm, tracking across the visible region of the electromagnetic spectrum. Closer inspection reveals that it is not a single absorbance that is responsible for the neutral color but instead a combination of transitions associated with carbazole and EDOT units. As the concentration of BiEDOT is increased, longer segments of BiEDOT begin to be incorporated into the random copolymer chain. This would correspond to an evolution from zero BiEDOT linkages (pure PBEDOT−*N*MeCz) to one BiEDOT, to two or more BiEDOT's surrounded by the corresponding carbazole linkages as seen by the broad shoulders toward the lower energy side of the dominant absorbance. The carbazole units still absorb light, as do the EDOT units, resulting in two interdependent transitions. However, the general track across the visible region can be traced. Arrows placed at the top of Figure 5 indicate the absorbance shift of the neutral copolymer films and demonstrate how the colors of the neutral states traverse the visible spectrum. The observed red shift, indicates that a "tunable" electrochromic material can be synthesized by varying the concentration of each chromophore in the copolymer.

Table 1 summarizes the copolymer compositions and the dominant absorbances for each neutral film. In addition photographs of each neutral copolymer were taken which demonstrate the continuously variable electrochromic response possible. Each film was electrochemically reduced in 0.1 M TBAP/ACN electrolyte solution to −0.9 V, followed by immersion in a shallow crystallizing dish containing a dilute solution of hydrazine in propylene carbonate (PC). This ensured that the copolymers would remain in their unique neutral color states. As stated earlier, each copolymer passes through a green intermediate state upon oxidation before obtaining a blue oxidized state. This property may have significant implications for device applications where a single surface color is desired.

Table 1. Composition and Electrochromic Properties of Electrochemical Copolymers

Comonomer Solution Composition	Neutral Polymer λ_{max} (nm)	Neutral Electrochromic Response (Photograph)
100% BiEDOT	577	
90:10	559	
80:20	530	
70:30	464	
50:50	434	
30:70	431	
20:80	429	
10:90	420	
100% BEDOT-*N*MeCz	420	

Following inspection of the neutral states of each copolymer, the entire spectroelectrohemical series was obtained for each to further probe their electronic structures. As an example, Figure 6 displays the spectroelectrochemical series for a copolymer potentiostatically electrosynthesized from an 80:20 solution of BiEDOT:BEDOT−*N*MeCz in 0.1 M TBAP/ACN. The neutral form of the 80:20 copolymer shown in Figure 6 (−0.9 V) is reddish-purple in color, having a peak absorbance centered at 527 nm, which is blue shifted by about 60 nm compared to PBiEDOT ($\lambda_{max} = 587$ nm). This shift is a direct result of PBEDOT−*N*MeCz incorporation, which is yellow in the fully reduced state ($\lambda_{max} = 424$ nm).

Stepwise oxidation of the copolymer (up to +0.8 V) shows that the absorbance across the visible region is first depleted, as the color changes from red-purple to blue, while passing through a green intermediate state as shown in the inset of Figure 6. It should be noted that all of the copolymer films are blue in their oxidized state and pass through a green intermediate before achieving their unique neutral state colors. Upon oxida-

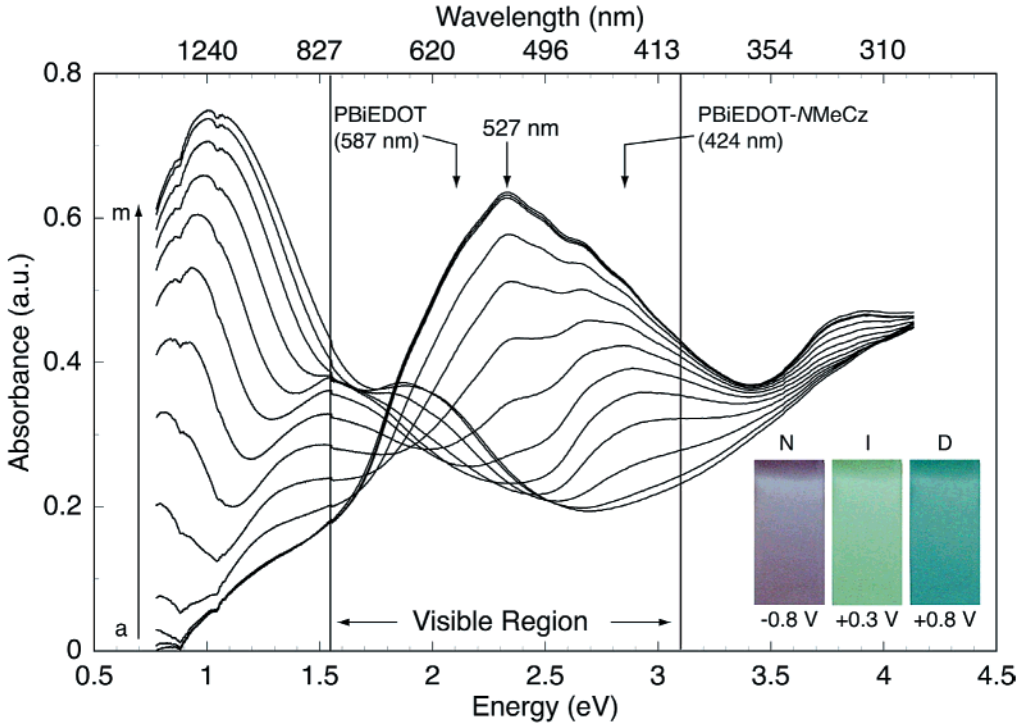


Figure 6. Spectroelectrochemical series for an 80:20 (BiEDOT:BEDOT−*N*MeCz) copolymer on ITO coated glass in 0.1 M TBAP/ACN at applied potentials between (a) −0.9 and (m) +0.8 V vs Ag/Ag^+. The λ_{max} values of the neutral states of PBiEDOT and PBEDOT−*N*MeCz are indicated. The inset shows the three color states of the copolymer in the neutral (N, −0.8 V), intermediate (I, +0.3 V), and the fully doped state (D, +0.8 V).

tion, lower energy transitions at 1.0 eV (E_{b1}) and 1.5 eV (E_{b2}) increase in intensity. These absorbances are typical of pure PBEDOT−NRCz homopolymers although E_{b2} is shifted to lower energies due presumably the increased BiEDOT content. Similarly, as the copolymer is oxidized further (+0.8 V), E_{b1} increases in intensity while shifting to higher energies while E_{b2} plateaus and shifts to higher energies. Elements from both PBiEDOT and PBEDOT−*N*MeCz are observed which are not independent of each other but are rather a hybrid of the two homopolymers. To exemplify this point, the normalized absorbances of the oxidized and reduced states of each homopolymer have been overlaid in Figure 7.

Unlike PBEDOT−*N*MeCz, which is a high band gap polymer (E_g = 2.5 eV and λ_{max} = 424 nm) that is yellow in its neutral state and blue in its oxidized state, the copolymer spectroelectrochemistry depicted in Figure 6 has a broad neutral absorbance at 527 nm. Note also that in the copolymer the absorbance at 592 nm is suppressed relative to pure PBEDOT−*N*MeCz. The broadening of the long wavelength absorbance can be attributed to longer run lengths of BiEDOT in the copolymer chain or to a mixture of chains. An increased concentration of BiEDOT within the comonomer solution would result in an increased number of BiEDOT repeat units inserted between carbazole units, allowing for the dication to be dispersed across several, more conjugated BiEDOT units, instead of being confined to the relatively short conjugation lengths of the carbazole unit. As the concentration of BiEDOT is decreased, this broadening is minimized, with the spectroelectrochemical series of the copolymer more closely resembling that of pure PBEDOT−*N*MeCz.

Soluble BEDOT—*N*RCz Polymerization. The electrochromic properties of BEDOT−*N*RCz materials are not limited to electrochemically prepared copolymers,

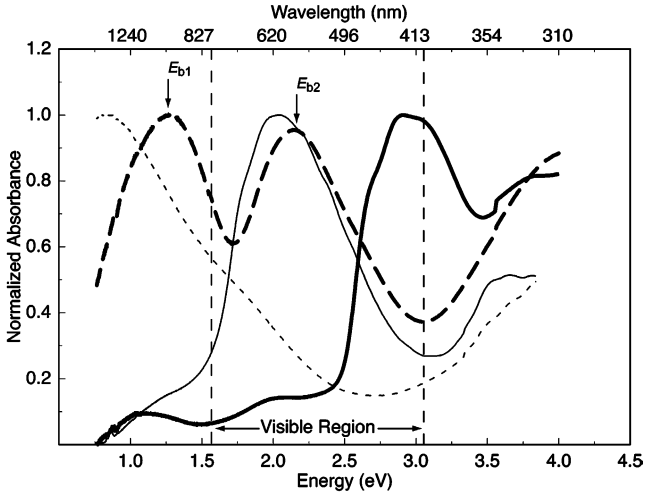
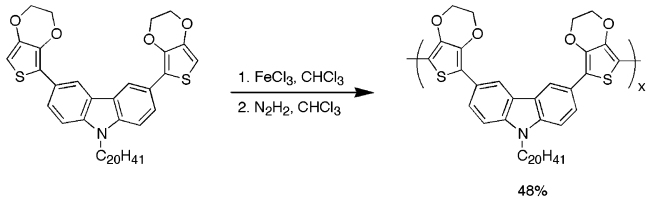


Figure 7. Extreme oxidized and reduced states of PBiEDOT and PBEDOT−*N*MeCz on ITO slides. Neutral PBiEDOT (thin solid line), oxidized PBiEDOT (thin dashed line), neutral PBEDOT−*N*MeCz (thick solid line), and oxidized PBEDOT−*N*MeCz (thick dashed line) are shown.

but rather their monomers can be synthetically modified to achieve the solubility required for the synthesis of bulk quantities of polymers. The solubility of EDOT-derivatized carbazole monomers can be significantly enhanced by substituting the carbazole nitrogen with either long or highly branched alkyl chains. BEDOT−NC_{20}Cz was chemically polymerized by reaction with anhydrous $FeCl_3$ in chloroform as shown in Scheme 2.

After being stirred at room temperature overnight, the black reaction mixture was treated with a solution of hydrazine in chloroform to reduce the oxidized copolymer. The neutral yellow polymer was obtained after removing the solvent under reduced pressure. The removal of low molecular weight oligomers and residual

Scheme 2. Oxidative Polymerization of BEDOT−NC_{20}Cz with $FeCl_3$.



iron salts was accomplished by utilizing a Soxhlet apparatus where the polymer was extracted with methanol, acetone, and tetrahydrofuran to yield the completely neutralized yellow/green copolymer in 48% yield.

Structural Characterization. ^{1}H and ^{13}C NMR spectra were obtained for the polymer and the peaks associated with the *N*-alkyl protons are present (0.82−1.13 ppm), as are those for both the terminal EDOT (6.25 ppm) and carbazole aromatic groups (7.57−8.35 ppm). The presence of the EDOT aromatic end group protons indicate that a relatively low molecular weight polymer was synthesized. The choice of NMR solvent was important for the analysis of this polymer in that deuterated chloroform possesses small amounts of HCl which tend to oxidize the polymer. In addition, the polymer is poorly soluble in this medium necessitating the use of deuterated THF. The polymer is freely soluble in this solvent and the THF peak resonances do not destructively interfere with structure elucidation.

The PBEDOT−NC_{20}Cz molecular weight was analyzed using both GPC and VPO. From GPC analysis the M_w and M_n values, relative to poly(styrene) standards, were measured as 5353 and 4556, respectively, which corresponds to a PDI of 1.17 and an X_n value of 6. This value corresponds to approximately 24 rings which include the two terminal EDOTs and the carbazole fused ring system. For comparison purposes, the monomer of PBEDOT−NC_{20}Cz was also analyzed and had an M_p of 771 vs the poly(styrene) standard, compared to the actual monomer molecular weight of 728. This indicates that the poly(styrene) is closely approximating the actual molecular weight of these short chain polymers.

VPO results were obtained based upon the calibration data recorded for hexadecane in toluene, and revealed an M_n of 5608. This is in close agreement with relative GPC results and confirms an X_n between 6 and 8, corresponding to between 24 and 32 rings. The X_n values calculated from both methods are within the theoretical limit for useful polymer optical and electrochemical properties. However, higher values of X_n may enhance these properties as well as film formation.

Soluble Copolymer Electrochemistry. The cyclic voltammogram for a toluene solution cast film of PBEDOT−NC_{20}Cz onto a Pt disk electrode (area = 0.02 cm^2) is shown in Figure 8. The two redox processes ($E_{1/2,p1}$ and $E_{1/2,p2}$) are centered at +0.35 and +0.72 V, respectively, and are indicative of radical cation and dication formation in carbazole polymers upon oxidation. These potentials are shifted to more positive values compared to electrochemically prepared PBEDOT−NC_{20}Cz (+0.23 and +0.46 V).[18] The positive shift may be a direct result of a more compact film morphology which would require higher potentials to oxidize and reduce the polymer. The redox processes of the polymer prepared via electrochemical and chemical methods are slightly different, but because of their close proximity polymers with similar electroactivity may be obtained.

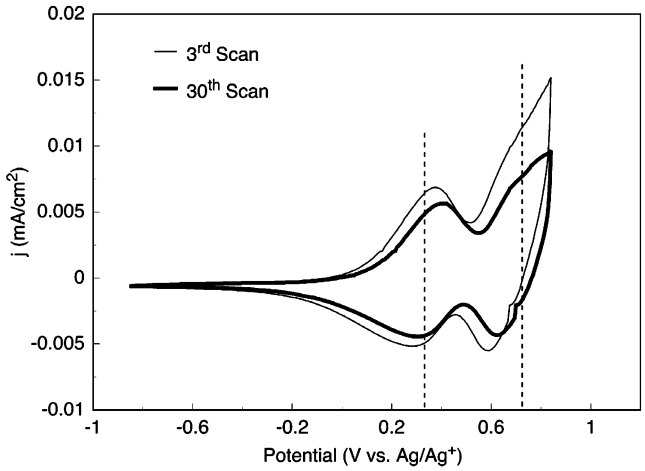


Figure 8. Cyclic voltammogram of PBEDOT−NC_{20}Cz film cast from toluene as a function of repeated scans at 20 mV/s in 0.1 M TBAP/ACN: after three scans (thin line) and 30 scans (thick line). The dashed lines indicate where each $E_{1/2}$ was measured.

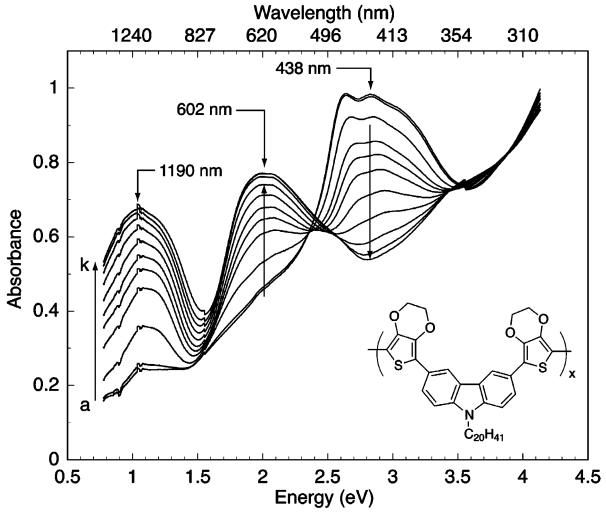


Figure 9. Spectroelectrochemical series of a cast film of PBEDOT−NC_{20}Cz in 0.1 M TBAP/ACN as a function of applied potential vs Ag/Ag$^+$: (a) −0.6, (b) −0.4, (c) −0.2, (d) −0.1, (e) −0.05, (f) 0.00, (g) +0.05, (h) +0.1, (i) +0.15, (j) +0.2, and (k) +0.25 V.

Repeated scanning results in a decreased current response (about 10% for $E_{1/2,p1}$ and about 25% for $E_{1/2,p2}$) after 30 scans. This is not surprising since most electroactive polymers exhibit a slight decrease in the current response as a function of initial repeated scanning.

Spectroelectrochemistry. The spectroelectrochemical series of a solution cast film of PBEDOT−NC_{20}Cz in 0.1 M TBAP/ACN, displayed in Figure 9, was obtained to determine whether electrochromism could be observed for chemically polymerized systems and how they compare to electrochemically prepared samples.[18] The neutral form of the polymer is achieved at −0.6 V vs Ag/Ag$^+$ and displays a broad electronic band gap of ∼2.25 eV.

PBEDOT−NC_{20}Cz is yellow in the neutral state and has maximum neutral absorbances at 438 and 477 nm. Stepwise oxidation of the polymer results in a decrease of the π to π^* transition and the increase of two lower energy transitions at 602 and 1190 nm, respectively. At intermediate potentials, the polymer film is green in

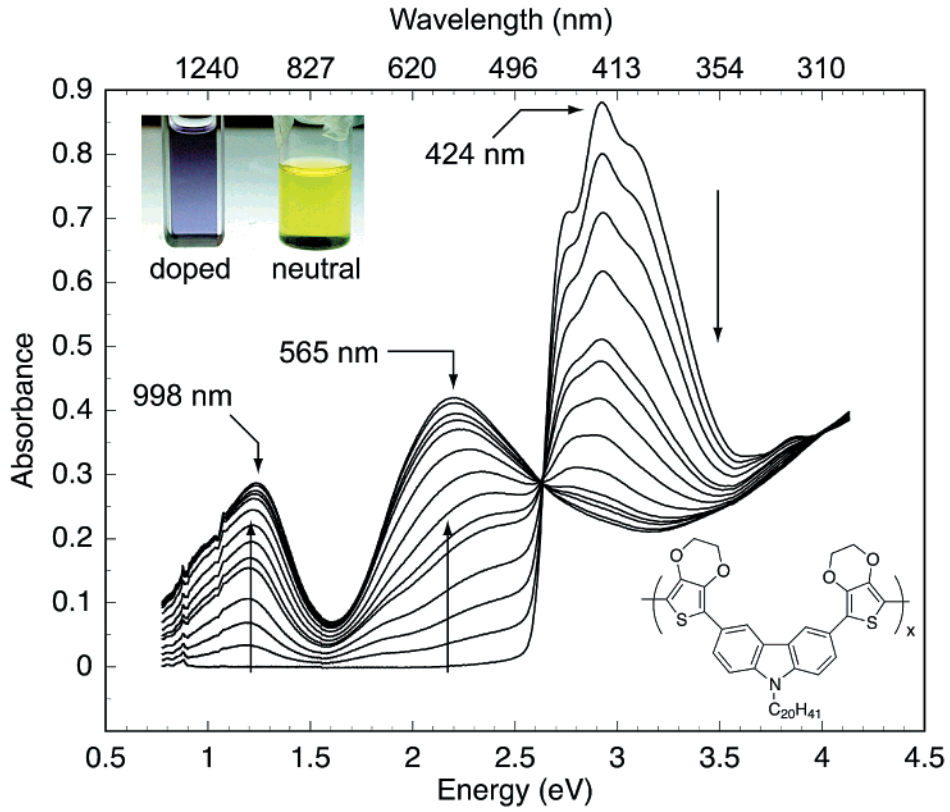


Figure 10. UV−vis−NIR spectra of a solution of PBEDOT−*N*C_{20}Cz in THF as a function of the addition of 2.0 μL aliquots of a 0.8 mM solution of $SbCl_5$ in CH_2Cl_2. The inset shows photographs of the neutral form and the doped form after oxidative doping.

color, and after complete oxidation, it is blue. The three color electrochromism observed for carbazole polymers is derived from the neutral state, followed by radical cation and dication formation. Unlike PEDOT or PPy, carbazole polymers have incomplete conjugation that is broken at the carbazole nitrogen, causing radical cation and dication charges to be trapped along the polymer chain.

The application of potentials negative of −0.6 V does not increase the π to π^* transition further, nor do they decrease the lower energy transition absorbances at 602 and 1190 nm, even after the addition of hydrazine. This is not surprising, since it has been found that BEDOT−*N*RCz polymers prepared electrochemically are also not completely neutralized even after the application of potentials of −1.2 V vs Ag/Ag^+.[18] This is especially true for solution cast films that are believed to be more compact, suppressing dopant ion migration through the polymer film. Therefore, the remaining absorbance is attributed to slight polymer oxidation by trapped dopant ions.

Solution Doping. A solution of PBEDOT−*N*C_{20}Cz in THF was oxidatively doped by the stepwise addition of 2 μL aliquots of a 0.8 mM solution of $SbCl_5$ in CH_2Cl_2, the results of which are shown in Figure 10. As can be seen from the initial spectrum, the polymer is completely neutralized with an onset of π to π^* at 2.5 eV and a maximum absorbance at 424 nm, which closely matches that of electrochemically prepared PBEDOT−*N*C_{20}Cz. Furthermore, the sharp onset of the π to π^* transition is noteworthy since the solution cast film of the polymer displayed a broad E_g due to trapped dopant ions and the more dense polymer morphology. Upon successive additions of $SbCl_5$, the π to π^* transition is depleted at the expense of two lower energy transitions at 565 and 998 nm, respectively. The dopant ion responsible for the observed changes is hexachloroantimonate ($SbCl_6^-$). It is expected that the dopant ion will not contribute any color to the polymer solution as tetramethylammoniumhexachloroantimonate is a colorless solid. Interestingly, there is a very distinct isosbestic point at 2.6 eV, a feature that was absent from cast film spectroelectrochemical series and is less defined in fully conjugated polymer films. Because of the trapping of charges along the polymer chain on the carbazole moieties, only two species can be present at any given time and their concentration is directly affected by the addition of oxidizing agents such as $SbCl_5$, resulting in their intersection in the absorbance spectrum at a single point. The oxidative doping also results in a striking color change in that the neutral solution is yellow in color and upon the addition of $SbCl_5$, the solution turns dark blue as is shown in the photograph inset of Figure 10.

Photoluminescence. Absorption and fluorescence spectra were obtained for PBEDOT−*N*C_{20}Cz and are displayed in Figure 11. When the solution of the polymer in THF is excited at 420 nm, a maximum emission wavelength of 470 nm is obtained accompanied by a weaker emission located at 506 nm. The inset of Figure 11 shows a photograph of the polymer solution emitting green light when placed under a standard laboratory UV lamp. PBEDOT−*N*C_{20}Cz has an efficiency (ϕ_f) of 0.12 when calibrated vs a coumarin 6 standard. Chemically prepared PXDOT-based polymers have been shown to exhibit modest photoluminescence efficiencies of 0.44. Low efficiencies have been attributed to close chain contact, leading to excimer formation, which leads to lower luminescence intensity.[36] Also, the discrete conjugation lengths of the carbazole copolymer could contribute to lower efficiencies. While a highly luminescent copolymer was not the goal of this work,

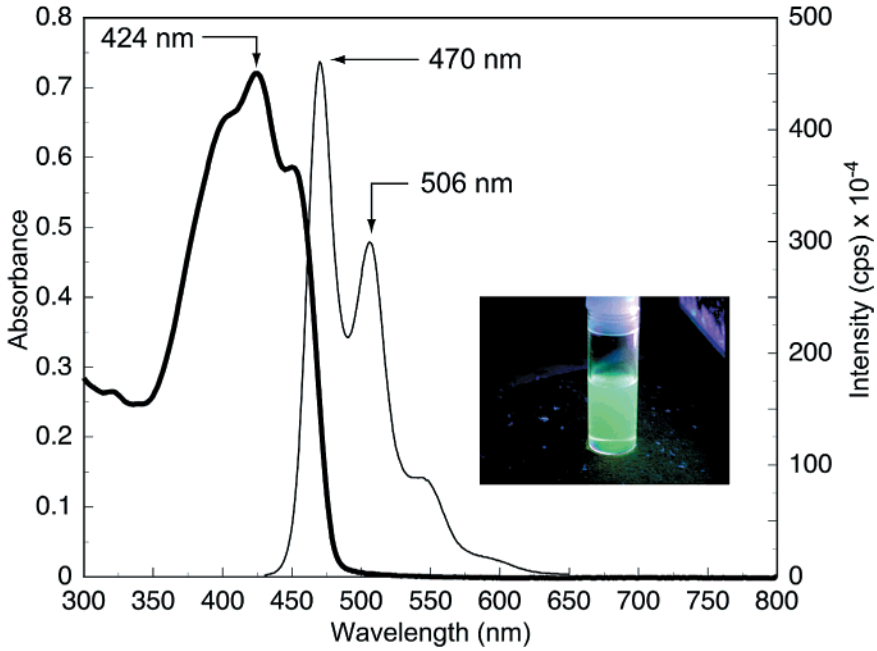


Figure 11. UV−vis absorption (thick line) and photoluminescence emission spectrum (thin line) excited at 420 nm of PBEDOT−*N*C_{20}Cz in THF. The inset shows a photograph of a solution of the polymer in THF emitting green light when illuminated with a UV lamp.

the finding does exemplify the myriad of interesting properties afforded by electroactive and conjugated polymers.

Conclusions and Perspective. BEDOT−*N*RCz-based copolymers provide a means to prepare multichromic and soluble systems for device applications under facile conditions due to the extreme electron rich character of the carbazole monomers and to the ease with which they can be synthetically modified. We have demonstrated that both electrochemical and chemical polymerization techniques can be applied to the preparation of tunable electrochromic copolymers. Through the judicious choice of comonomers and by varying the comonomer concentration, the neutral states of the electrochemical copolymers of BiEDOT and BEDOT−*N*MeCz range in color from blue, to red, to orange, and to yellow, spanning the entire visible spectrum. These copolymers can be switched easily between their unique neutral states to a common blue oxidized state. Furthermore, a soluble hybrid copolymer of BEDOT−*N*C_{20}Cz was prepared via $FeCl_3$ polymerization. Tetrahydrofuran solutions of the copolymer exhibit an intense yellow color that upon solution doping with $SbCl_5$ turn blue. These solutions also display modest photoluminescence, emitting green light. Solution cast films demonstrate redox switching comparable to electrochemically prepared carbazole polymers, switching from a yellow neutral state to a blue oxidized state while passing through a green intermediate state. The tunable multichromism exhibited by these copolymers can be further exploited by either careful choice of other suitable comonomers or by synthetic modification of starting monomers. With the large variety of electrochromic polymers available, there exists the possibility of many combinations of compatible monomers for electrochemical copolymerization. Furthermore, future synthetic modifications will allow for unique soluble hybrid copolymers to be prepared that display the same range of tunability. The application of these copolymer systems toward dynamic electrochromic devices, both large and small, is an important and compelling advancement in the field of electrochromic and conducting heterocyclic polymers.

Experimental Section

Chemicals. EDOT was purchased from Aldrich and was distilled under vacuum (0.2 mmHg) before use. Anhydrous *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), $FeCl_3$, sodium hydride, trimethyltin chloride, trimethylsilyl chloride, hexadecane, benzoyl chloride, 1-bromoeicosane, iodomethane, hydrazine, coumarin 6, and methylmagnesium bromide diethyl etherate ($MgBr_2$·Et_2O) were purchased from Aldrich and were used as received. *n*-Butyllithium was purchased from Acros and used as received. $PdCl_2(PPh_3)_2$ and $NiCl_2$(dppp) were purchased from Strem and used as received. Chloroform (Fisher) was dried over $MgSO_4$ prior to use. Toluene (HPLC grade) was used as received from Fisher. Acetonitrile (Fisher) was dried over calcium hydride and distilled under argon. Soluble polymer samples were solution doped with a 0.8 mM solution of antimony pentachloride (Aldrich) in anhydrous methylene chloride. BiEDOT, BEDOT−*N*MeCz, and BEDOT−*N*C_{20}Cz were synthesized according to previously reported procedures.[18,37]

Instrumentation. NMR spectra were recorded on a General Electric QE−300 FT-NMR. Mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. Elemental analyses were accomplished at Robertson Microlit Laboratories, Inc,. Madison, NJ.

GPC was performed on two 300 × 7.5 mm Polymer Laboratories PLGel 5 μm mixed-C columns with a Waters Associates liquid chromatography 757 UV absorbance detector at 450 nm. Molecular weights were referenced to poly(styrene) standards (Polymer Laboratories). Polymer samples were prepared in THF (1 mg/mL) and passed through a 0.2 μm filter prior to injection. A constant flow rate of 1 mL/min was used. VPO was performed on a Wescan Instruments model 233 molecular weight apparatus. Five polymer solutions in toluene ranging from 1 mg/mL to 10 mg/mL were prepared. Hexadecane (Aldrich) was used as the calibration standard.

Polymer electrochemistry was carried out on an EG&G Princeton Applied Research model 273 or 273A potentiostat/galvanostat employing a platinum disk working electrode (area = 0.02 cm^2), a platinum plate counter electrode, and a Ag/Ag^+

reference electrode. Spectroelectrochemistry experiments were carried out on a Cary 5E UV−vis−NIR spectrophotometer. Polymer films were deposited onto ITO-coated glass slides (7 × 50 × 0.5 mm, 20 Ω/square, Delta Technologies). Soluble polymers were cast onto ITO slides from dilute toluene solutions and were dried under an argon blanket prior to use.

Fluorescence data were collected with a Jobin Yvon Horiba FluoroMax photon counting fluorimeter, powered by Data Max 2.20 software, at room temperature. Emission quantum yields were measured relative to coumarin 6 in THF at 1.00×10^{-6} M where $\phi_f = 1.00$, and the optical density was kept below $A = 0.1$.

Synthesis. Poly(3,6-Bis(2-(3,4-ethylenedioxy)thienyl)-*N*-eicosylcarbazole). To a flame-dried three neck round-bottom flask was added BEDOT−NC_{20}Cz (0.5 g, 0.69 mmol). The monomer was exposed to vacuum for 15 min before being back-filled with argon. To the monomer was added anhydrous $CHCl_3$ (dried over $MgSO_4$) (20 mL). In another round-bottom flask was added anhydrous $FeCl_3$ (0.36 g, 2.2 mmol) which is black/red in color. [When $FeCl_3$ has been exposed to air/water, it becomes yellow in color.] Anhydrous $CHCl_3$ (30 mL) was added and the mixture was stirred. The $FeCl_3$ mixture was added in one portion to the monomer solution. The solution immediately turned black/blue in color. Dry argon was bubbled through the reaction vessel to remove HCl generated during the reaction. The polymerization was allowed to stir for 20 h at room temperature after which time the organic liquid was washed with water (to remove $FeCl_3$ and salts). After several washings, the $CHCl_3$ had a few drops of hydrazine hydrate added to reduce the polymer. The now yellow $CHCl_3$ layer was washed again with water, dried over $MgSO_4$, and evaporated under reduced pressure to give a dark green solid. The polymer was placed in a Soxhlet thimble and extracted for 24 h with methanol and 24 h with acetone to remove impurities. A final Soxhlet extraction with tetrahydrofuran (THF) was used to dissolve the polymer from the thimble, and the THF was removed to yield a dark yellow/green solid (0.24 g, 48%) of PBEDOT−NC_{20}Cz. GPC (vs poly(styrene standards): M_w = 5353, M_n = 4556. VPO (vs hexadecane standard): M_n = 5608. ^{1}H NMR (THF-d_8): δ 0.84 (−CH_3), 1.23 (−CH_2−), 1.82 (−CH_2−), 4.20 (−NCH_2), 4.30 (−OCH_2−), 4.42 (−OCH_2−), 6.25, 7.38, 7.79, 8.40. ^{13}C NMR (THF-d_8): δ 14.6, 23.6, 30.6, 32.9, 35.1, 65.4, 65.8, 108.3, 109.7, 116.9, 118.4, 124.1, 125.9, 129.4, 133.5, 138.0.

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