Soluble Variable Color Carbazole-Containing Electrochromic Polymers

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ABSTRACT: Three new carbazole-containing polymers were synthesized through Suzuki cross-coupling between *N*-octylcarbazole-3,6-bis(ethyleneboronate) (NOctCz($BO_2Et)_2$) and several arylene dibromides. 2,5-Dibromothiophene (DBT), 2,2′-dibromo-5,5′-bithiophene (DBBT), and 4,7-dibromo-2,1,3-benzothiadiazole (DBBTD) gave the three polymers PCzTh, PCzBi, and PCzBTD, respectively. Cyclic voltammetry showed two separate redox processes for each polymer, PCzTh ($E_{1/2}$ = 0.33 V and $E_{1/2}$ = 0.65 V vs Fc/Fc$^+$), PCzBi ($E_{1/2}$ = 0.32 V and $E_{1/2}$ = 0.60 V vs Fc/Fc$^+$), and PCzBTD ($E_{1/2}$ = 0.56 V and $E_{1/2}$ = 0.84 V vs Fc/Fc$^+$). The two redox couples signify the presence of stable radical cation and dication oxidation states. In addition, the three materials were observed to display electrochromic properties. UV/vis/NIR absorbance spectroscopy revealed that each of the polymers displayed a unique absorbance maximum (345 nm for PCzTh, 375 nm for PCzBi, and 460 nm for PCzBTD) in their neutral states. Spectroelectrochemical analyses demonstrated that the π to π^* transition was depleted upon application of increasingly positive potentials, giving rise to color changes. The different color states were quantified by colorimetry. PCzTh exhibits a yellow neutral state, a faint green radical cation state, and a pink dication state. PCzBi is yellow in its neutral state, light orange as a radical cation, and gray when fully oxidized. PCzBTD is orange when neutral, green-gray at intermediate potentials, and slate-gray as a dication.

Introduction

Electrochromic materials are those that exhibit different colors depending upon their oxidation state. A wide variety of electrochomic materials are presently known, ranging from metal oxides such as WO_3[1] and mixed-valence metal complexes like Prussian Blue[2] to organic molecules. In the realm of organic electrochromic systems, both small molecules like viologens[3] and conjugated polymers[4] have been shown to display electrochromic effects. Electrochromic materials exhibit at least two distinct color states and may give multiple colors, depending on the structure of the material.

The applications for electrochromic conjugated polymers are quite diverse due to several favorable properties of these materials. Since the various oxidation states of conjugated polymers are quite stable, the colors corresponding to these states are long-lasting. In addition, conjugated polymer electrochromics usually show fast switching times, allowing for rapid color changes from the materials upon application of appropriate potentials.[5] Finally, electrochromic polymers are known to have excellent switching reproducibility, meaning that they can be switched between their various color states many times without any noticeable decline in performance.[6] One of the more prominent uses for electrochromic polymers is in window applications, where a device can be cycled between transparent and tinted states through the use of a polymer with transmissive and absorptive color states. Also, as the palette of available colors in electrochromic polymers grows, these materials should become more useful for display technology.

There has been a considerable body of work reported concerning electrochromic polymers.[7] Through the use of a wide variety of conjugated structures, an impressive array of available colors has been attained in both two-color and multicolor electrochromic polymers. However, some difficulties exist with many of the known electrochromic polymer systems. Poly(3-alkyl thiophene)s[8] and the poly(2,2-dialkylpropylenedioxythiophene)[9] group of polymers are two of the few electrochromic conjugated polymer families that have been obtained through means other than electropolymerization or oxidative chemical polymerization. These techniques, while often useful and easily implemented, possess several inherent drawbacks. Anodic polymerization onto an ITO-coated substrate can give the thin films necessary for practical devices. However, obtaining large films of high quality and uniformity, such as those necessary for electrochromic windows, is often quite difficult due to nonuniform potentials across the electrode surface. In addition, this technique provides only a relatively small amount of material, making potential large-scale uses of this technique difficult. Chemical polymerization with an oxidant such as $FeCl_3$ can be used to produce large quantities of material rather easily, as demonstrated by Sugimoto et al.[10] However, this approach often leads to irregular linkages that dramatically diminish the desired properties of the material.[11] Ideally, electrochromic conjugated polymers would be produced through a nonoxidative chemical process in which the reactive sites on the monomers are clearly defined. This approach would give large quantities of materials with regular and consistent structures. In addition, solubility in common organic solvents is necessary in order to facilitate processing, such as spin- and spray-casting of films or printing onto the appropriate substrates.

One of the interesting multicolor systems is that based upon the 3,6-linked carbazole moiety.[12] This unit in conjugated polymer chains serves as a conjugation break, which in turn leads to some useful properties. Upon initial oxidation of a typical conjugated polymer, an electron is removed from the conjugated backbone, and a radical cation is formed as shown in Scheme 1 for a 1,4-phenylene linked bicarbazole. In most cases,

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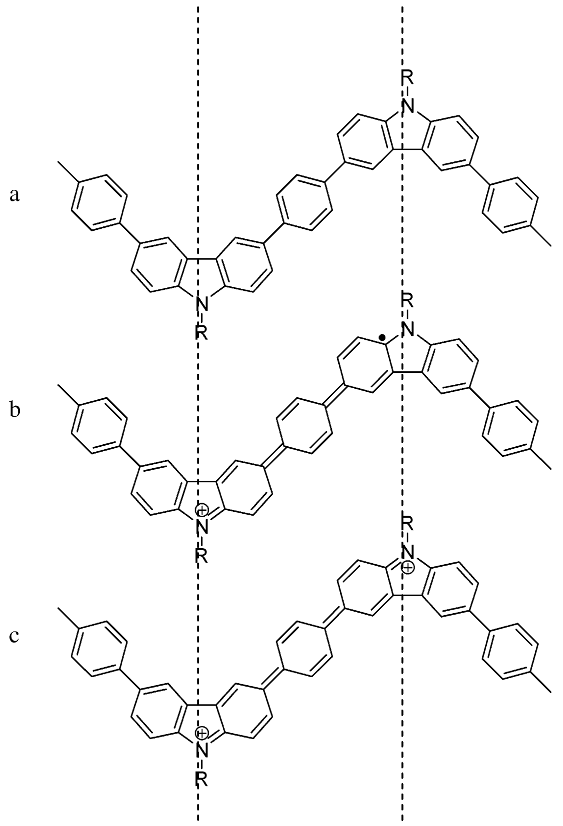
Scheme 1. A Segment of Poly(carbazole-*co*-phenylene) Depicting (a) Neutral State, (b) Radical Cation State, and (c) Dication State[a]

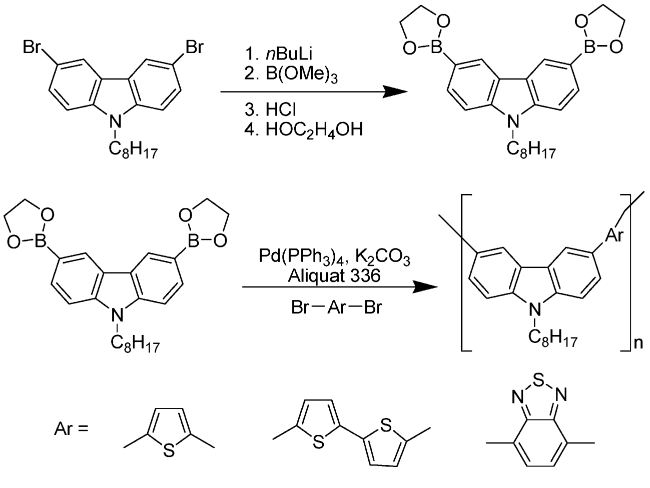


[a] Conjugation breaks are represented by dashed lines.

these radicals are unstable and combine to give dications. However, because of the conjugation breaks present due to the inclusion of 3,6-linked carbazole units, the radical cations are separated from one another and do not combine. Upon further oxidation at higher potentials, another electron is removed, giving dications. The ability of these materials to support two distinct oxidation states leads to a three-color electrochromic effect, with separate colors present for the neutral, radical cation, and dication states. It is important to note that while several examples of polymers containing 2,7-linked carbazole units[13] have been reported, these materials cannot support three stable oxidation states, as the 2,7-linked carbazole unit does not function as a conjugation break.

In addition to the presence of three colors, another advantage of electrochromic polymers containing 3,6-linked carbazole units is the elimination of color dependence on molecular weight. In typical conjugated polymers, electronic properties of oligomers change as the length of the chains increases. This effect continues until a maximum conjugation length is reached. Above this critical length, the physical properties of the material may change, but the conjugation length remains constant. However, with a material containing conjugation breaks in each repeat unit, the conjugation length of the polymer is set by the structure of the chromophore, meaning that both oligomers and high molecular weight materials will be the same color. Since shorter chains are often easier to synthesize and can show higher solubility, leading to easier processing, conjugated polymers whose electrochromic properties are independent of molecular weight can be quite useful.

Scheme 2. Synthetic Approach for NOctCz(BO$_2$Et)$_2$ and Suzuki Cross-Coupling Polymerization To Give PCzAr Family



In this work, we have synthesized three new carbazole-containing polymers through the use of Suzuki cross-coupling. This approach is well-suited for the task in that the reactive species, boronate esters and halides, can both be isolated and their purities verified, ensuring that the polymers produced have the desired structures with minimal defects.[14] The repeat units of these materials include *N*-octylcarbazole–thiophene (PCzTh), *N*-octylcarbazole–bithiophene (PCzBi), and *N*-octylcarbazole–benzothiadiazole (PCzBTD). By varying the comonomer used along with the carbazole unit, we have been able to control the electronic properties of the materials and therefore ultimately tune the colors exhibited by the polymers. Inclusion of appropriate substituents allows the polymers produced to be dissolved in a variety of organic solvents, such as chloroform, methylene chloride, toluene, and THF, thus facilitating processing. The new electrochromic carbazole-containing polymers reported here have been spray-cast onto ITO/glass slides, giving uniform films that exhibit electrochromism. This effort represents a foray into a new family of electrochromic polymers that can be easily synthesized and processed. In addition, the presence of conjugation-breaking 3,6-linked carbazole units allows for these materials to support three oxidation states, meaning that three distinct colors are available in each polymer.

Results and Discussion

Monomer Syntheses. *N*-Octylcarbazole–3,6-bis(ethyleneboronate) (NOctCz(BO$_2$Et)$_2$) was synthesized from 3,6-dibromo-*N*-octylcarbazole according to an established procedure as outlined in Scheme 2.[15] The crude material was recrystallized from hexanes and then from ethyl acetate immediately prior to use. After drying in vacuo at 100 °C, the ^{1}H NMR spectrum of the material displayed all the expected resonances with no discernible peaks corresponding to impurities. 2,5-Dibromothiophene and 2,2′-dibromo-5,5′-bithiophene were synthesized using NBS in DMF along with thiophene and 2,2′-bithiophene, respectively. 2,5-Dibromothiophene (DBT) was distilled, and 2,2′-dibromo-5,5′-bithiophene (DBBT) was recrystallized from acetone/water shortly before use. 4,7-Dibromobenzo-2,1,3-thiadiazole (DBBTD) was produced through the reaction of benzo-2,1,3-thiadiazole and bromine in aqueous HBr. This monomer was recrystallized from acetone/water immediately prior

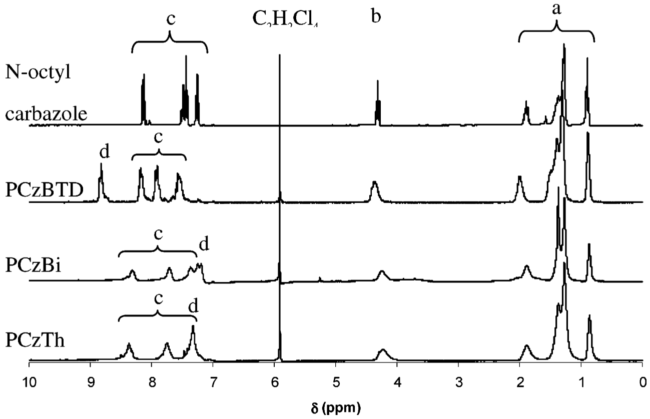


Figure 1. ^{1}H NMR spectra of (a) distal *N*-octyl protons, (b) α-methylene protons, (c) carbazole protons, and (d) comonomer protons.

to use. After distillation (DBT) and drying in vacuo at 100 °C (DBBT, DBBTD), the identities of these materials were verified by ^{1}H NMR. Tetrakis(triphenylphosphine)palladium was synthesized by addition of hydrazine to a solution of palladium(II) chloride and triphenylphosphine in DMSO at 120 °C. The solid was recrystallized from benzene/methanol, dried in vacuo, and used within a few hours after preparation.

Polymer Syntheses. The polymers described here were all produced using Suzuki cross-coupling techniques given in Scheme 2. A two-phase mixture of the monomers, $Pd(PPh_3)_4$, and Aliquat 336 in toluene and 2 M aqueous potassium carbonate served as the polymerization medium. The carbazole unit, ($NOctCz(BO_2Et)_2$), carries the boronate esters and is present to act as a conjugation break and also as a carrier of the solublizing octyl chain. The aryl dibromides serve as electronic tuning units, influencing the electronic properties of the polymers and ultimately allowing for some degree of control over the various color states of the materials. $NOctCz(BO_2Et)_2$ allows for a large number of carbazole-containing polymers to be synthesized by the procedure described here. This monomer can be combined with any of the numerous commercially available and easily synthesized aryl dihalides under the reaction conditions described here to give a wide variety of colors in soluble, easily processed electrochromic polymers.

Structural Characterization. Analysis of the polymers by ^{1}H NMR spectroscopy in 1,1,2,2-tetrachloroethane-d_2 at 120 °C is given in Figure 1. Each spectrum shows signals corresponding to the protons (a) bonded to carbons 2−8 of the aliphatic *N*-octyl group (2.0−0.8 ppm) as well as the methylene protons (b) adjacent to the carbazole nitrogen (4.2 ppm). While the chemical shifts of the more distal protons are not affected by the structure of the polymer backbone, in PCzBTD, the signal corresponding to the N-bonded methylene unit is shifted slightly downfield as compared to PCzTh and PCzBi. This change can be attributed to the strong electron-withdrawing character of the BTD units in the polymer backbone. In addition, peaks representing the aromatic protons (c) of the carbazole unit (8.5−7.0 ppm) were also observed. Finally, resonances (d) indicating the presence of the arylene groups (7.2 ppm for PCzTh, 7.2−7.0 ppm for PCzBi, and 8.8 ppm for PCzBTD) unique to each of the individual materials were also present. The differences in the aromatic region among the spectra indicate that the polymers synthesized contain both carbazole units and the appropriate arylene. Since each material is treated with 6 M HCl to remove any terminal boronates after completion of the polymerization, it is expected that the polymers obtained contain *N*-octylcarbazole or the appropriate bromoarylene as end groups. The ^{1}H NMR spectrum of *N*-octylcarbazole shows that the protons at the 3- and 6-positions overlap those at the 2- and 7-positions, giving a complex multiplet at 7.66 ppm. For each polymer sample, the corresponding peak integrates to roughly two hydrogens per repeat unit, indicating that very few protons in the 3- and 6-positions of the carbazole unit are present and that the material is indeed a polymer. However, since the crucial signals are not isolated from the peaks corresponding to the protons at the 2- and 7-positions of the carbazole unit, molecular weight estimation by ^{1}H NMR is not feasible.

Table 1. Summary of GPC Data (Polystyrene Standard) for PCzAr Polymers

polymer	M_n (g/mol)	M_w (g/mol)	PDI	X_n
PCzTh	2600	4100	1.57	7.2
PCzBi	3700	5800	1.57	8.4
PCzBTD	2800	3700	1.32	6.8

GPC analysis was used to estimate the molecular weight of each sample. The molecular weight data are summarized in Table 1. It was determined that the polymers were all of rather low molecular weights. All three polymers gave number-average molecular weights of about 3000 g/mol. This value corresponds to a degree of polymerization of seven to eight, meaning that the polymers synthesized here have an average of about 30 aromatic rings per chain. The identity of the arylene dibromide used in the polymerizations had no significant effect on the molecular weights of the materials. This result is unexpected in that electron-poor DBBTD would be expected to facilitate the coupling reaction by more readily participating in the oxidative addition step of the catalytic cycle. It is important to note that the molecular weights of these polymers do not affect their optical or redox properties, owing to the conjugation-breaking nature of the carbazole units. As noted below, the molecular weights obtained were adequate for processing and film formation, and thus, further optimization of the polymerization was not attempted.

UV/vis absorbance spectra of the neutral polymers in solution (methylene chloride for PCzTh and PCzBi, toluene for PCzBTD) are given in Figure 2a. These data show that the colors of the polymers produced through this method can be tuned by varying the identity of the aryl dibromide used as a comonomer. PCzTh absorbs at a fairly short wavelength, giving solutions of this material a bright yellow color with a λ_{max} of 345 nm. Addition of another thiophene ring to the repeat unit, as in PCzBi, shifts the absorbance to slightly longer wavelengths, giving a λ_{max} of 375 nm. Finally, as expected on account of the donor−acceptor interaction between the electron-poor benzothiadiazole unit and the relatively electron-rich carbazole, PCzBTD shows the greatest λ_{max} at 460 nm, leading to an orange color. As a point of comparison, Figure 2b shows UV/vis spectra and photography of neutral polymer films produced by spray-coating on ITO/glass. The spectra presented here are somewhat broadened and red-shifted as compared to their solution counterparts. This effect may be a result of some light scattering by the polymer films but is most likely due a wider range of environments for the chromophore in the solid state as opposed to solution

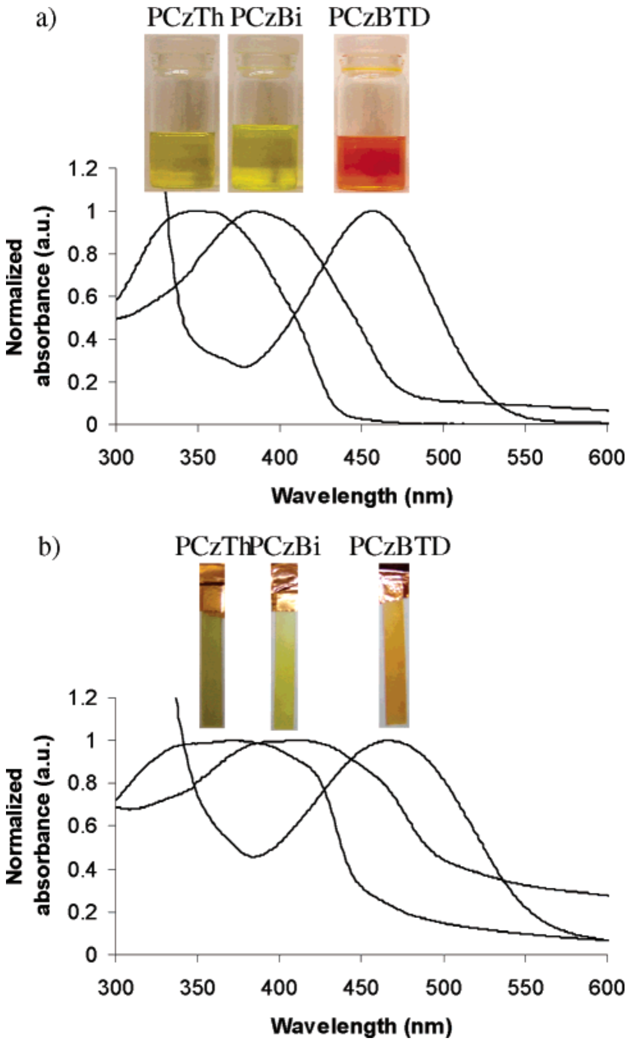


Figure 2. UV/vis spectra of PCzAr family (a) in solution and (b) as films. Photographs above each peak show solution and film colors.

and not a change in the optoelectronic nature of the chromophore.

Solution Doping. Solutions of the polymers in methylene chloride (2 mL, ~0.01 mg/mL) were treated with 20 μL portions of a 100 μM solution of antimony pentachloride in methylene chloride. The addition of $SbCl_5$ was continued until no further spectral changes were observed. For each polymer, the absorbance spectra were unaffected by additions of $SbCl_5$ above roughly 1 equiv $SbCl_5$ per 2 repeat units. Since $SbCl_5$ is a much stronger oxidant than the oxidized polymer and the hexachloroantimonate ion generated by the doping process does not contribute any color to the solutions, this doping method is effective for gauging the color changes of polymer solutions at varying degrees of oxidation as shown in Figure 3 for PCzBTD. In this instance, the distinct orange (neutral) to transmissive gray-blue (fully oxidized) states are evident as extremes, while the solution passes through less saturated intermediate colors upon oxidation. As the oxidant is added to the polymer solution, the π to π^* transition is gradually depleted, leading in each case to broad absorbances in the near-infrared region of the spectrum, as shown in Figure 4. Each spectrum shows isosbestic points between the π to π^* transition given by the neutral polymer and the absorbances that occur with addition of the oxidant. The well-defined isosbestic points are to be expected for oxidation of conjugated polymers having discrete chromophores in solution, as the chromophores are necessarily well-separated from

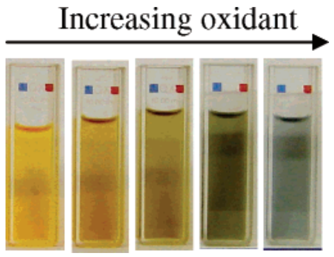


Figure 3. Photographs of a sample of PCzBTD in methylene chloride with gradual oxidation by $SbCl_5$.

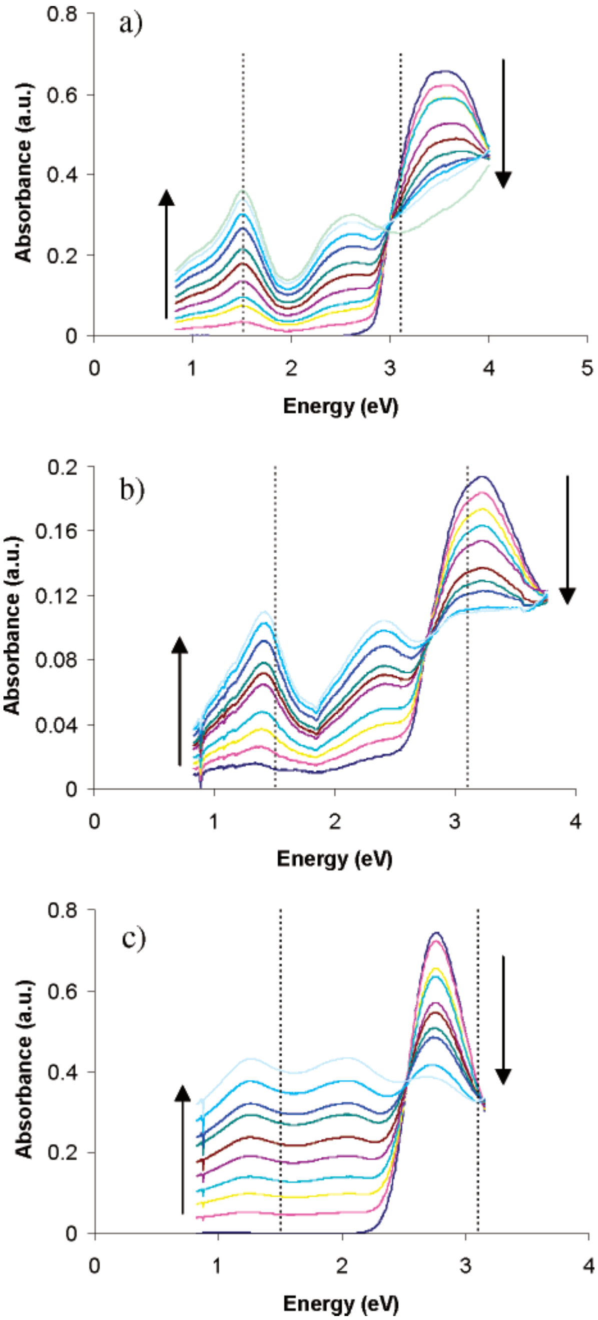


Figure 4. UV/vis/NIR spectra of (a) PCzTh, (b) PCzBi, and (c) PCzBTD as a function of added $SbCl_5$. Dashed lines indicate the visible region of the spectrum. Arrows signify the spectral changes with increasing oxidant. 20 μL aliquots of a 100 μM $SbCl_5$ solution were added to 2 mL of a ~0.01 mg/mL polymer solution until no further spectral changes could be observed.

one another under the relatively dilute conditions. This separation eliminates the range of chromophore oxidation potentials commonly observed in the solid state. The difference between solution and solid state spectra of the PCzAr materials upon oxidation will be presented in a following section. It is interesting to note that the polymers do show some deviance from the isosbestic points after the addition of a relatively large amount of $SbCl_5$. This effect may be due to some degree of overoxidation, meaning that the polymer is oxidized to such a great extent that structural changes may occur, making reneutralization impossible.

Film Formation. Films were produced by spraying solutions of the polymers (methylene chloride for PCzTh and PCzBi, toluene for PCzBTD) onto ITO-coated glass slides. As electroactive polymers become more common and find more uses in practical devices, it becomes necessary to easily process these materials. While electropolymerization of a desired monomer gives the films necessary for device construction, it is often difficult to obtain even films of any considerable size due to potential gradients across the electrode surface. On the other hand, spray-casting allows for films to be produced in which size is not a consideration. Simply by applying a uniform coating of a polymer solution, smooth, even films can be obtained. This attribute of the technique is especially important for applications such as electrochromic windows which are necessarily larger than a few square centimeters. In addition to the elimination of size considerations, spray-casting is more material-economic than the more traditional spin-casting technique, in that only a small fraction of the active material applied to the substrate is not incorporated into the film. The films produced by spray-casting with solutions of the PCzAr materials were insoluble in both acetonitrile and propylene carbonate, allowing for electrochemistry to proceed.

Polymer Film Electrochemistry. Cyclic voltammograms of the three polymers described here were obtained by casting films of the polymers onto a platinum button electrode (area = 0.02 cm^2). After the scans were completed, a small quantity of ferrocene was introduced to the cell, and a final scan was performed in order to calibrate the results. As depicted in Figure 5, two redox processes were observed for each polymer, indicative of the radical cation and dication states. As expected, the materials with more electron-rich comonomers, PCzTh ($E_{1/2}$ = 0.33 V vs Fc/Fc$^+$ for the radical cation, $E_{1/2}$ = 0.65 V vs Fc/Fc$^+$ for the dication) and PCzBi ($E_{1/2}$ = 0.32 V vs Fc/Fc$^+$ for the radical cation, $E_{1/2}$ = 0.60 V vs Fc/Fc$^+$ for the dication), showed less positive oxidation potentials than the more electron-deficient PCzBTD ($E_{1/2}$ = 0.56 V vs Fc/Fc$^+$ for the radical cation, $E_{1/2}$ = 0.84 V vs Fc/Fc$^+$ for the dication).

As expected, a slight decrease in the current recorded was observed after a few scans. The current density of the peaks corresponding to oxidation to the radical cation state decresased by about 5% and the that of the transition from radical cation to dication by about 15%. This effect is common among electroactive polymers. However, the current response stabilized after 5−6 scans, indicating that these materials possess good cycling stability and can be switched between color states many times without degradation.

Spectroelectrochemistry. The films obtained by spraying the polymer solutions onto ITO/glass slides were used to perform spectroelectrochemistry experiments in 0.1 M $TBAPF_6$/acetonitrile. Prior to recording absorption spectra, the films were conditioned by applying potentials between −500 and 1200 mV vs a silver wire through five cycles. This treatment produced a constant current response and allowed for reproducible cycling. The spectroelectrochemical series of each material is given in Figure 6. Initial scans of the films were recorded with the working electrode potential set at −500 mV vs Ag/Ag$^+$ in order to ensure that the films were completely neutral. The π to π^* transitions in the neutral films are somewhat red-shifted from those observed for the solution spectra as shown in Figure 2. Also, the absorption peaks are broader, and the onset of absorption is not as sharp with the solid samples as compared to the solution spectra. These effects are most likely due to dopant ions remaining in the solid from the initial conditioning treatment. In addition, as mentioned previously, the solid state gives rise to different environments for the individual chromophores, leading to a broader range of absorbances.

The differences among the three samples correspond quite well to the other data obtained here. The onset of

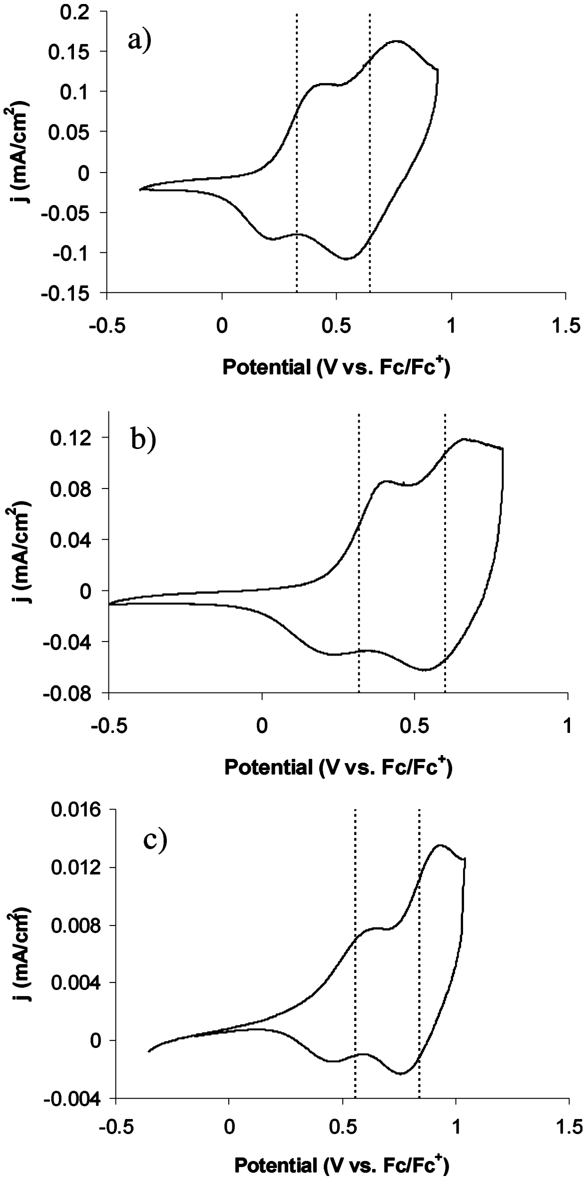


Figure 5. Cyclic voltammograms of (a) PCzTh, (b) PCzBi, and (c) PCzBTD at 20 mV/s in 0.1 M $TBAPF_6$/propylene carbonate. $E_{1/2}$ values are indicated by dashed lines.

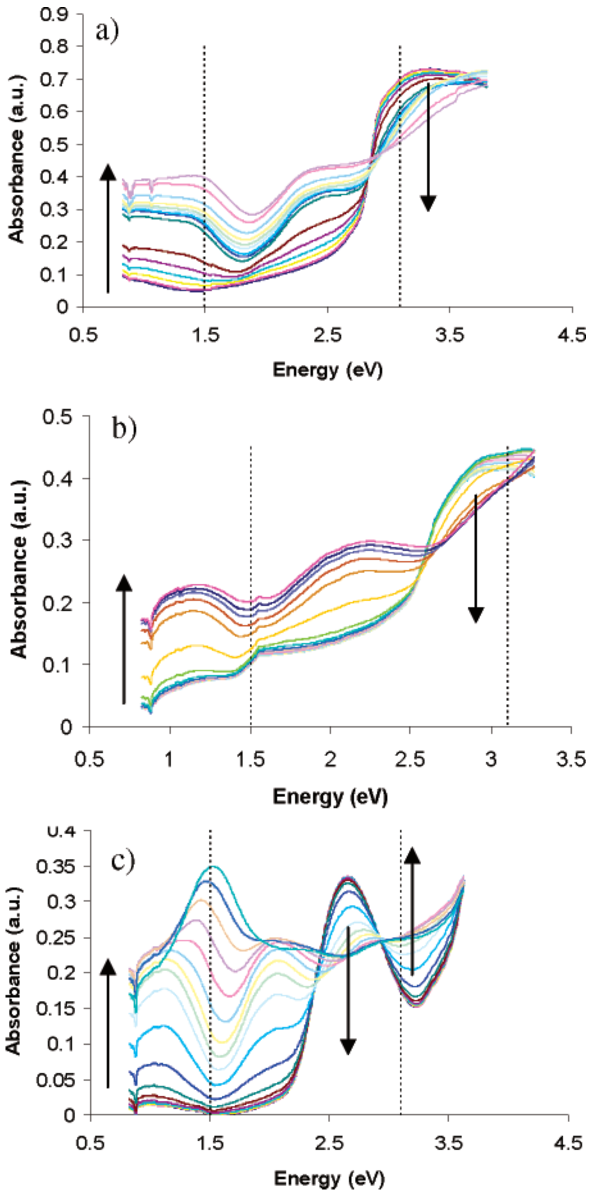


Figure 6. Spectroelectrochemical series of (a) PCzTh (400−1350 mV vs Ag/Ag$^+$), (b) PCzBi (300−1150 mV vs Ag/Ag+), and (c) PCzBTD (650−1500 mV vs Ag/Ag+). Potential steps are 50 mV. Dashed lines represent the visible region of the spectrum. Arrows represent the changes in the spectral profiles with increasing potential.

a color change was observed at 400, 500, and 900 mV for PCzBi, PCzTh, and PCzBTD, respectively. The color change continued as the applied potential was increased in a stepwise fashion until it reached 1100, 1350, and 1500 mV for for PCzBi, PCzTh, and PCzBTD, respectively. The various optical properties of each polymer in its various oxidation states were studied extensively by colorimetry and will be discussed below. At very positive potentials, all of the samples were observed to gradually become a transmissive yellow color with very little difference between the various polymers. After exposure to these high potentials, the films were observed to become detached from the substrates, and they could not be returned to their neutral states.

As compared to the solution doping results, an important difference can be observed. While isosbestic points are readily observed in the solution spectra, they are absent in the film spectra. As stated earlier, the absence of isosbestic points may be explained by differences between polymers in solution and those cast as films. The solid state gives rise to a wider range of oxidation potentials as well as a wider range of absorbances. The differing oxidation potentials are expressed in the absorption spectra of the polymers as an absence of isosbestic points since there are certainly more than two electrochemically different chromophores in the film during the oxidation process. Thus, it is important to note that the absence of isosbestic points is not necessarily proof of the presence of stable radical cations as it may be that this absence is simply an expression of the different chromophore environments.

Colorimetry. To accurately convey the color of a material, a more detailed description than that given by absorbance spectroscopy is necessary. A convenient way to approach this task is use colorimetric measurements.[16] In such experiments, three attributes of color can be determined: hue, or dominant wavelength, saturation, and luminance. These measurements are usually accomplished with electrochromic polymers by recording the Yxy color space coordinates of the material at different potential steps. The data obtained can then be plotted using CIE 1931 color coordinates to visually depict the path of the material's color change during potential switching.

Figure 7 depicts the CIE color space plots for the three polymers discussed here. The two materials with electron-rich comonomers, PCzTh and PCzBi, are both yellow in their neutral states, while the donor−acceptor polymer, PCzBTD, is orange. As the applied potential to each material is increased, the color of each material moves toward the white point in the center of the color space plot. It is interesting to note that each material changes color upon the application of relatively low potentials, but then the color stabilizes at intermediate potentials before changing again to a final color. This phenomenon can be attributed to the formation of the three oxidation states of each polymer, neutral, radical cation, and dication.

The three color states can be best compared and contrasted by plotting the linear distance between each point on the color space plot and the initial point, representing the completely neutral polymer. Since the color space plot represents different colors by their position on the plot, the distance from one point to another can be interpreted as a measure of the color difference between the two potentials represented by the points. To determine the magnitude of the vector between any two points on the color space plot, the differences between the x and y coordinates of the point in question and the initial point are squared and then summed with the square root of the resulting sum being representative of the linear distance between the two points. Figure 8 shows the relationship between the linear distance between each point on the CIE 1931 color space plot and the initial point as a function of the applied electrode potential. In each case, two steps are depicted, suggesting that three color states are indeed present for each material. In addition, colorimetrically determined color swatches for each color state are included. These results are of special note when studied in conjunction with the spectroelectrochemistry results. While the spectral series shown in Figure 6 nicely details the evolution of the spectra, the nonlinear change in color with potential is difficult to see. Close examination of Figure 6b, for example, shows a number of closely bunched points at relatively low potentials,

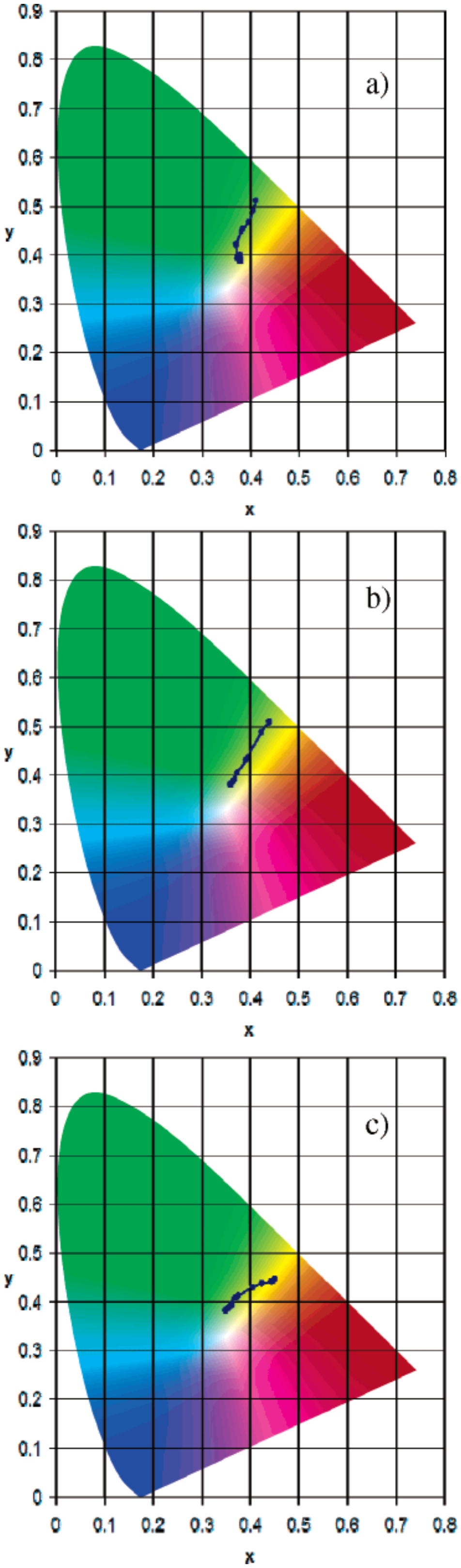


Figure 7. CIE color space plots for (a) PCzTh, (b) PCzBi, and (c) PCzBTD.

followed by a rapid absorption increase between 1.5 and 2.5 eV as the potential is stepped between 500 and 700 mV. These data correlate nicely with the results of Figure 8b, where a distinct color change is evident at ca. 600 mV.

The thiophene-containing polymers show very similar colors in their neutral states, as both are bright yellow.

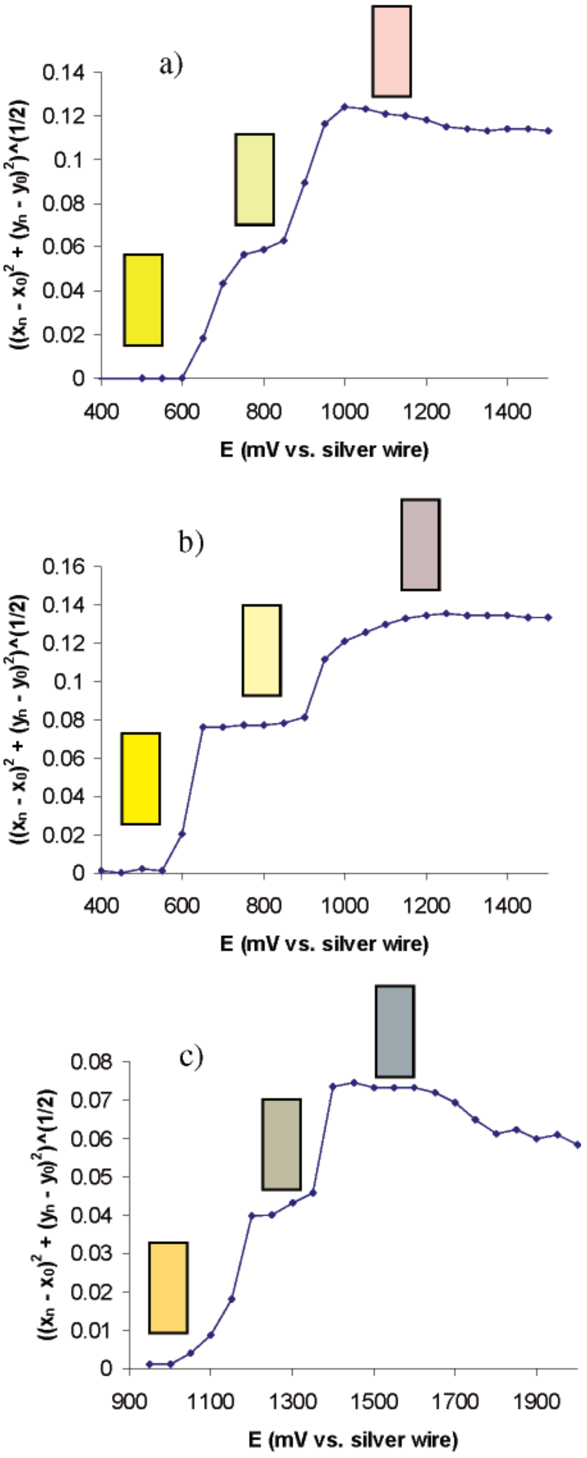


Figure 8. Plots of distance between points in CIE color space plots and the initial point for (a) PCzTh, (b) PCzBi, and (c) PCzBTD. Steps represent different color states.

A small change can be observed upon conversion to the radical cation state, with PCzTh taking on a faint green color and PCzBi showing a bleached orange hue. Finally, a greater difference can be seen in the dication states of the two polymers. PCzTh is a faint pink color, while PCzBi becomes a rather neutral gray. PCzBTD is orange in its neutral state, green-gray as a radical cation, and a neutral gray in its most oxidized state. The presence of neutral grays in these materials is promising, as one could imagine blending these materials with absorptive-to-transmissive electrochromic polymers such as the poly(ProDOT) family to give blends that would switch

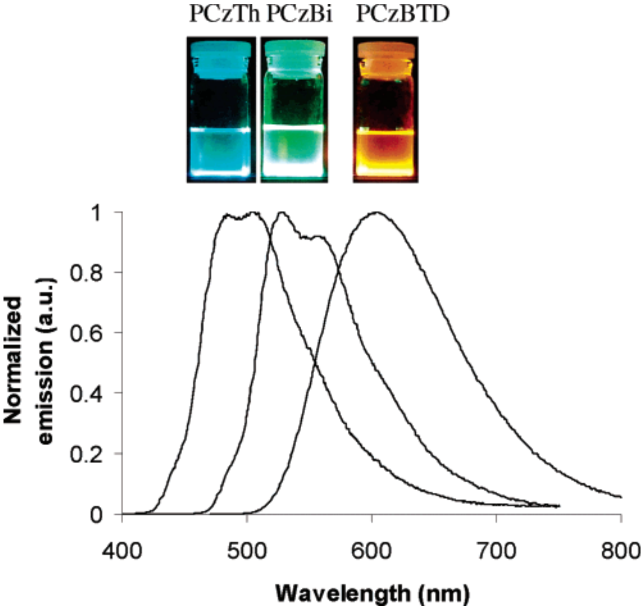


Figure 9. Emission spectra of PCzAr solutions. Photographs show emission of polymers when exposed to a standard laboratory UV lamp.

from a colored state to a gray state. In such situations, the specific color of the colored state and the intensity of the gray state could be controlled by the identity of the polymers used in the blend as well as the blending ratio.

Photoluminescence. Fluorescence spectra were obtained for each of the materials and are depicted in Figure 9. The excitation wavelengths were 345, 375, and 460 nm for PCzTh, PCzBi, and PCzBTD, respectively. The emission maxima recorded were 484 and 504 nm for PCzTh, 528 and 555 nm for PCzBi, and 604 nm for PCzBTD. The two thiophene-containing polymers, PCzTh and PCzBi, show two emissions, while PCzBTD gives only a relatively broad emission. Although the absorption, electrochemical, and colorimetric properties of PCzTh and PCzBi have been observed to be quite similar, the fluorescence spectra of these materials show quite a difference. PCzTh emits an aqua-blue colored light, while PCzBi emits a more intense green. Coupling these results with the orange emissions from PCzBTD gives a range of fluorescent colors that covers a great portion of the visible spectrum. Although the photoluminescence efficiencies of these polymers were not determined, a qualitative comparison suggests that they may have efficiencies (ca. 0.1) comparable to or greater than those of the carbazole-EDOT polymers reported earlier.[12a] While an array of photoluminescent materials was not a primary concern of this work, the preliminary results given here suggest that the polymers described may be useful for applications such as luminescent sensors. To use these materials for such applications, a more detailed study of their luminescent properties would be necessary.

Conclusions

Through the use of an easily synthesized carbazole diboronate and any number of readily available arylene dibromides, Suzuki polycondensation can be used to give electrochromic polymers which are soluble in common organic solvents and can be cast into uniform films. Although the molecular weight of the products is quite sensitive to experimental conditions, such as catalyst freshness and monomer purity, the conjugation-breaking nature of the 3,6-linked carbazole unit allows for the color of the polymers to be unaffected by molecular weight.

The three polymers described here show colors in their various oxidation states that include yellow, green, pink, and various grays as a result of the different arylene dibromides used. Simply by using different comonomers in the synthetic process, the colors of the electrochromic materials can be tuned while still giving an easily processed material. In addition to controlling the colors of the polymers, the oxidation potential of the polymers is strongly dependent on the electronic character of the arylene unit paired with carbazole in each material. Solution doping trials and their companion spectroelectrochemistry experiments demonstrated that upon oxidation, whether with a chemical oxidant or through electrochemical means, the absorbance corresponding to the π to π^* transition is depleted, and broad absorbances appear in the near-infrared region of the spectrum. As evidence of three stable color states corresponding to three separate oxidation states of each polymer, CV experiments show two distinct redox processes: one corresponding to oxidation from the neutral state to the radical cation and another representing further oxidation to the dication. In addition, colorimetric measurements show three distinct color states for each of the three polymers as various applied potentials.

On the basis of the results observed here, it becomes obvious that the next step for the polymers examined to be used as the active components in practical devices that call for electrochromic materials. The ability of these polymers to be sprayed to form uniform films means that there should be few, if any, limitations on the size of the devices constructed. Also, to fully utilize this family of materials, more members should be synthesized in order to expand the palette of available colors. The ease of synthesis should make such a task relatively easily accomplished and will ultimately provide a very useful new circle of functional polymers.

Experimental Section

Chemicals. Thiophene, 2,2′-bithiophene, 1,2-phenylenediamine, *N*-bromosuccinimide, carbazole, octyl bromide, Aliquat 336, antimony pentachloride, palladium(II) chloride, and trimethyl borate were purchased from Aldrich and used as received. Thionyl chloride, HBr, bromine, ethylene glycol, sodium hydride, toluene, DMF, methylene chloride, and THF were purchased from Fisher and used as received. Tetrakis(triphenylphosphine)palladium was purchased from Strem and used as received.

The syntheses of 2,5-dibromothiophene (DBT),[17] 2,2′-dibromo-5,5′-bithiophene (DBBT),[18] benzothiadiazole,[19] 4,7-dibromobenzo-2,1,3-benzothiadiazole (DBBTD),[20] and NOctCz($BO_2Et)_2$[15] were accomplished using methods reported elsewhere.

Instrumentation. Ambient temperature NMR spectra were obtained using a Varian Mercury 300 MHz apparatus. High-temperature NMR spectra were recorded with a Varian Mercury broadband 300 MHz spectrometer. UV/vis/NIR absorbance spectra were recorded with a Cary 5E spectrophotometer. GPC data were collected using two 300 by 7.5 mm Polymer Laboratories PL Gel 5μM mixed-C columns with a 2996 photodiode array detector. THF or chloroform was the eluting solvent at a flow rate of 1 mL/min. Molecular weights were referenced to a poly(styrene) standard. Colorimetric measurements were accomplished using a Minolta CS-100 Chroma Meter with the CIE recommended 0/0 (normal/normal) viewing geometry for transmittance measurements.

Electrochemical measurements were carried out using an EG&G Princeton Applied Research model 273 potentiostat. CV data were collected using a platinum button working electrode (area = 0.02 cm^2), a platinum flag counter electrode, and an Ag/Ag$^+$ reference. The electrolyte was 0.1 M TBAPF$_6$ in propylene carbonate. Spectroelectrochemistry was accomplished using films spray-cast from methylene chloride or toluene onto ITO-coated glass slides (7 × 50 × 0.5 mm, 20 Ω/square, Delta Technologies). The films were dried in vacuo prior to use. A platinum wire served as the counter electrode during the spectroelectrochemical measurements and a silver wire was the reference.

Representative Polymer Synthesis. *N*-Octylcarbazole-3,6-bis(ethyleneboronate) (1 g, 2.39 mmol, 1 equiv), 2,5-dibromothiophene (578 mg, 2.39 mmol, 1 equiv), and Aliquat 336 (300 mg, ~20% of the monomer weight) were combined in 10 mL of toluene. This solution was deoxygenated with bubbling argon for 60 min. In the meantime, 10 mL of 2 M aqueous potassium carbonate was refluxed while deoxygenating with bubbling argon. After 60 min had elapsed, the aqueous solution was cooled to room temperature and then transferred via cannula to the monomer solution. Immediately following the addition of the aqueous base, a solution of Pd(PPh$_3$)$_4$ (28 mg, 24 μmol, 0.01 equiv) in 2 mL of deoxygenated toluene was transferred via cannula to the two-phase reaction mixture. After addition of the catalyst, the reaction mixture was heated to 90 °C and stirred for 3 days.

After this time, the reaction mixture was cooled to room temperature and the organic phase was separated. This solution was added to 500 mL of methanol, giving a precipitate. The precipitate was collected by filtration and dissolved in 250 mL of methylene chloride. This solution was added to 250 mL of 6 M HCl, and the two-phase mixture was stirred vigorously for 60 min. Then, the organic phase was separated and washed with water. The volume of the solution was reduced to ~25 mL by rotary evaporation and added to 500 mL of methanol. The resulting precipitate was collected by filtration and washed with methanol, acetone, and hexanes in a Soxhlet extractor. The polymer was redissolved in a minimal amount of methylene chloride and added to 500 mL of methanol. The resulting solid was collected by filtration and dried overnight in vacuo.

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