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Article

Donor−Acceptor Polymer Electrochromes with Tunable Colors and Performance

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To demonstrate the effect of donor (D) and acceptor (A) units on the structure−property relationships of electrochromic polymers, design, synthesis, characterization and polymerization of a series of D−A type systems, **1**−**5**, based on thiophene, 3,4-ethylenedioxythiophene, and 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine as D units and 2,1,3-benzoselenadiazole, 2,1,3-benzothiadiazole and 2-decyl-2H-benzo[d][1,2,3]triazole as A units are highlighted. It is found that these units play key roles on the redox behavior, band gap, neutral state color, and the electrochromic performance (stability, optical contrast, coloration efficiency, and switching time) of the system. It is noted that electropolymerization of these D−A systems provides processable low band gap electrochromes, **P1**-**P5**, exhibiting high redox stability, coloration efficiency, transmittance and/or contrast ratio and low response time. Furthermore, **P1**-**P5** reflect various hues of blue and green pallets of the RGB color-space in the neutral state. In particular, it is noteworthy that **P5** is an excellent blue-to-colorless polymeric electrochrome, which, to our best knowledge, exhibits the highest optical contrast and coloration efficiency among the D−A type systems. The panoramic breadth of the neutral state colors and intriguing features of these polymeric materials further confirm that D−A approach allows engineering tunable electrochromes, which hold promise for commercialization of polymeric RGB electrochromics.

Introduction

Organic π-conjugated materials, especially polymers, have attracted considerable attention over the last three decades since they found a variety of advanced technological applications in the fields of light-emitting diodes,[1−4] photovoltaics,[5−9] transistors[10−13] and molecular electronics[14−16] owing to their low cost, compatibility and tunable intrinsic properties (electronic, optical, conductivity, and stability) offered by the structural design of the starting materials.[17−19] In particular, they have been envisioned as one of the most favored electrochromes in devices,[20,21] optical displays,[22] smart windows,[23,24] mirrors,[25,26] and camouflage materials[27,28] because of their promising advantages when compared to the earliest inorganic

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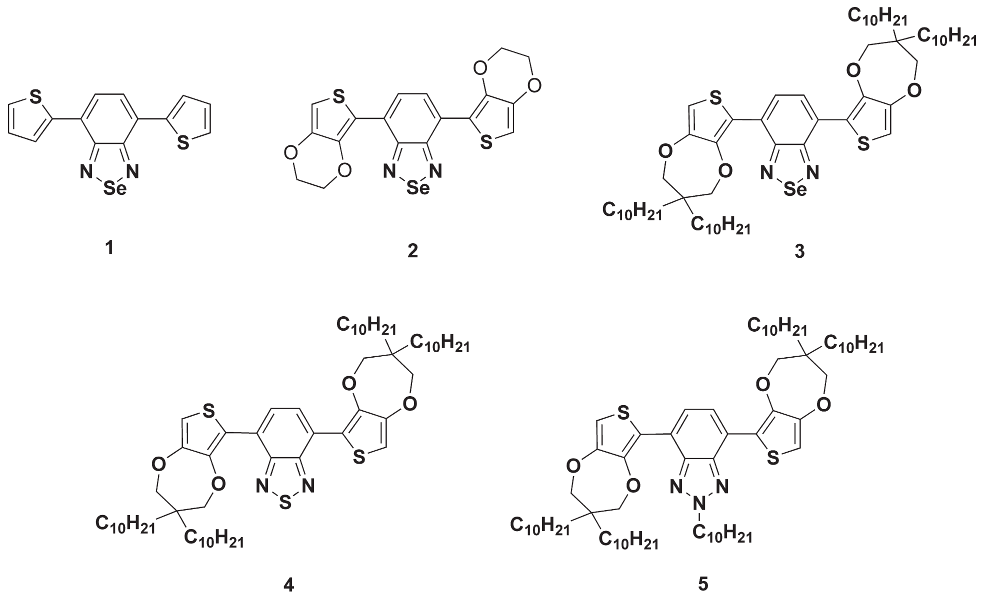
Chart 1. Engineering Tunable D−A Systems, 1−5



electrochromes:[29−34] e.g., ease of processing over the large surfaces via spin coating, spraying, and printing methods; high optical contrast ratio; multicolors with the same material; high redox stability; and long cycle life with low response time. For that reason, significant efforts have been devoted to the design and synthesis of polymeric electrochromics (PECs) based on organic π-conjugated materials. However, most of these PECs exhibit either red or blue colors in the neutral state, and the third leg (green) of the primary additive colors (red, green, and blue constitute the primary additive RGB color-space, whereas cyan, magenta, and yellow constitute the CMY primary subtractive color-space) has remained elusive for a long time. The construction of a neutral state truly green PEC possessed some major challenges due to the fact that the reflection of green color necessitated at least two absorption bands, which could deplete simultaneously during the redox processes, and it has been very difficult to control both of the absorption bands by the application of a voltage pulse. Fortunately, this puzzle has been solved by turning the spotlight on macromolecular conjugated systems based on alternating electron-rich (donor, D) and -poor (acceptor, A) units.[35] This D−A approach[36] not only allowed a fine-tuning of the band gap (E_g) of the as-prepared organic materials[37−40] but also provided access to a range of colors in the full visible spectrum, as exhaustively shown by both Reynolds'[41−44] and Toppare's[45−49] laboratories. However, it is still a challenging task to attain the two complementary color-spaces (RGB and CMY) in the context of innovative high-performance display technologies.

In this area, we recently reported the design and synthesis of novel D−A systems that could produce green color in the neutral state.[50,51] Considering the fact that a neutral-state PEC should not only produce the green color but should also be solution-processable[42,52] for polymeric RGB applications in an industrial platform, we turned our attention to processable variants of the D−A systems as a next step. To this purpose, we have undertaken an approach that emanates from various D- and A units with different electronic strength. This approach would give the opportunity to understand the effect of these units on both the neutral state color and the electrochromic performance of the corresponding D−A type polymers (Chart 1). It is important to note that only few reports

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have focused on systematic comparison of the structure–property relationship[17–19,44,53,54] in spite of the fact that much literature concerning the design of new systems for PECs exists. Furthermore, these newly designed D–A systems might hold promise for a processable blue to transparent PEC candidate which would also be highly valuable en route to the commercialization of PECs.[49] Although it is tempting to think that poly(3,4-ethylenedioxythiophene) (PEDOT), as an electrochrome, provides the color blue, it is unfortunate that this industrially important polymer is not solution processable. Very recently, a spray processable blue-to-highly transmissive switching polymer electrochrome was reported.[55] On the other hand, a systematic approach would also help us to surmount the barricade for accessing either to cyan color[44] which is one of the primary subtractive colors of CMY color-space or to a neutral state black PEC[43] by electrochemical means, which are highly difficult to attain because of the complexity of designing such materials.

In this article, we wish to report our research concerning the design, synthesis and properties of D–A type systems, **1**–**5**, based on thiophene, 3,4-ethylenedioxythiophene (EDOT), and 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b]-[1,4]dioxepine (ProDOT-decyl$_2$)[56] as D units and 2,1,3-benzoselenadiazole, 2,1,3-benzothiadiazole, and 2-decyl-2H-benzo[d][1,2,3]triazole as A units (Chart 1). It is noteworthy that electropolymerization of these systems provided processable and low band gap electrochromes, **P3**–**P5**, which reflect various hues of blue and green colors in the neutral state. Furthermore, these PEC candidates exhibit high redox stability, high coloration efficiency (CE), high transmittance (%T) and/or contrast ratio, and fast switching time in subsecond scale. The data presented herein indicate the D–A polymer electrochromes with tunable colors and performance.

Results and Discussion

Design and Synthesis. To demonstrate the effect of the D and A units on the structure–property relationships and the electrochromic performance, five different D–A systems, **1**–**5**, were taken into account. The synthesis and properties of two of these systems, **1**–**2**, have recently been accounted in a previous paper from our laboratories.[50] It was noted that 2,1,3-benzoselenadiazole scaffold as A part of electropolymerizable D–A type systems hold promise for producing blue-green and green colors in the neutral state when attached to thiophene and EDOT units, respectively. However, these combinations did not provide a solution-processable and truly green electrochrome in the neutral state. At this stage, we envisaged that replacement of the D parts with ProDOT-decyl$_2$ might provide the corresponding solution-processable electrochrome due to the presence of long alkyl chains. Furthermore, this combination would exhibit low oxidation potential, high contrast ratio, high transparency when oxidized, and low switching time between the redox states after polymerization (**P3**) because of its polyProDOT nature when compared to polythiophene and/or PEDOT.[57–59] On the other hand, it was further envisaged that the replacement of 2,1,3-benzoselenadiazole scaffold with 2-decyl-2H-benzo[d][1,2,3]triazole and 2,1,3-benzothiadiazole units would affect the neutral state color of the electrochrome, while keeping the solution-processability, if the D part is unaltered. This is not unexpected because of the fact that each acceptor unit has different electronic strength, thus providing different optical absorption in the visible region of the electromagnetic spectrum.

Being convinced by this strategy, our studies commenced with a comprehensive screen of substrates as potential precursors of the targeted D–A systems. Initial efforts that were directed toward the synthesis of the D part involved the preparation of ProDOT-decyl$_2$, which was stannylated with tributyltinchloride by using slightly modified literature methods to give **6**. The synthesis of the precursors of the A parts, **8**,[60] **10**,[60] and **14**, was carried out as outlined in Scheme 1. At this stage, it was noted that alkylation of **11** with 1-bromodecane resulted in the formation of a mixture of two isomeric products in a 1:1 ratio. Careful examination of ^{1}H and ^{13}C NMR data of the compounds after purification by flash column chromatography revealed the structures as **12** and **13**. The reaction of **12** with HBr/Br$_2$ provided **14** as the sole product.

Stille coupling reaction of **6** with **10** afforded D–A system **3** in 35% yield (Scheme 2). In a similar vein, compounds **4** and **5** were synthesized from the coupling reactions of **6** with **8** and **14** in 60 and 40% yields, respectively (Scheme 2). Initial characterization of **3**–**5** was based on ^{1}H, ^{13}C NMR and FTIR spectral (see the Supporting Information, Figures S1–S9) data along with the elemental analysis which firmly established the structures. Note that compounds **1**–**3** comprised 2,1,3-benzoselenadiazole scaffold as the A part that was linked with different D units, whereas **3**–**5** consisted of ProDOT-decyl$_2$ as the D parts that were linked with different A units in order to investigate the effect of the D and A groups, respectively, in a systematical manner.

Electrochemistry. The role of the D units on the redox behavior of 2,1,3-benzoselenadiazole based D–A systems, **1**–**3**, was investigated by cyclic voltammetry studies

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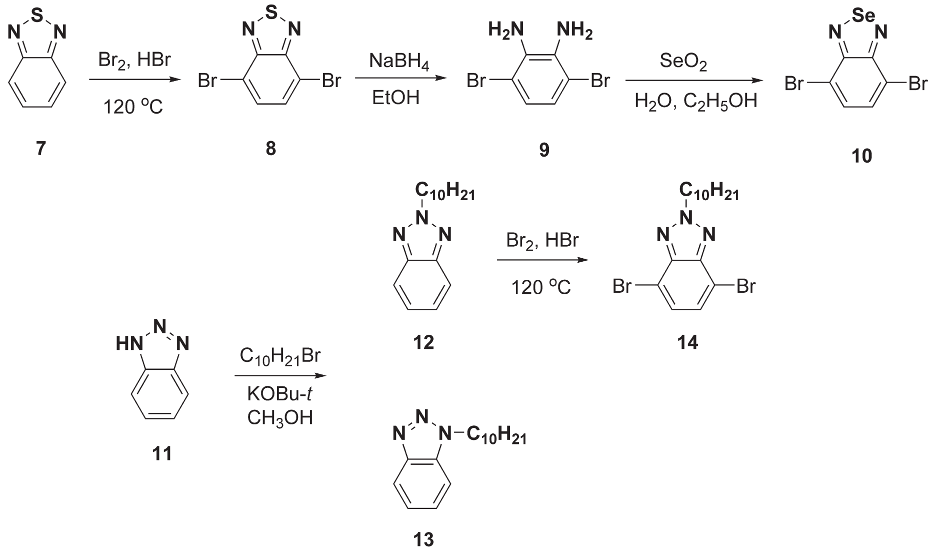
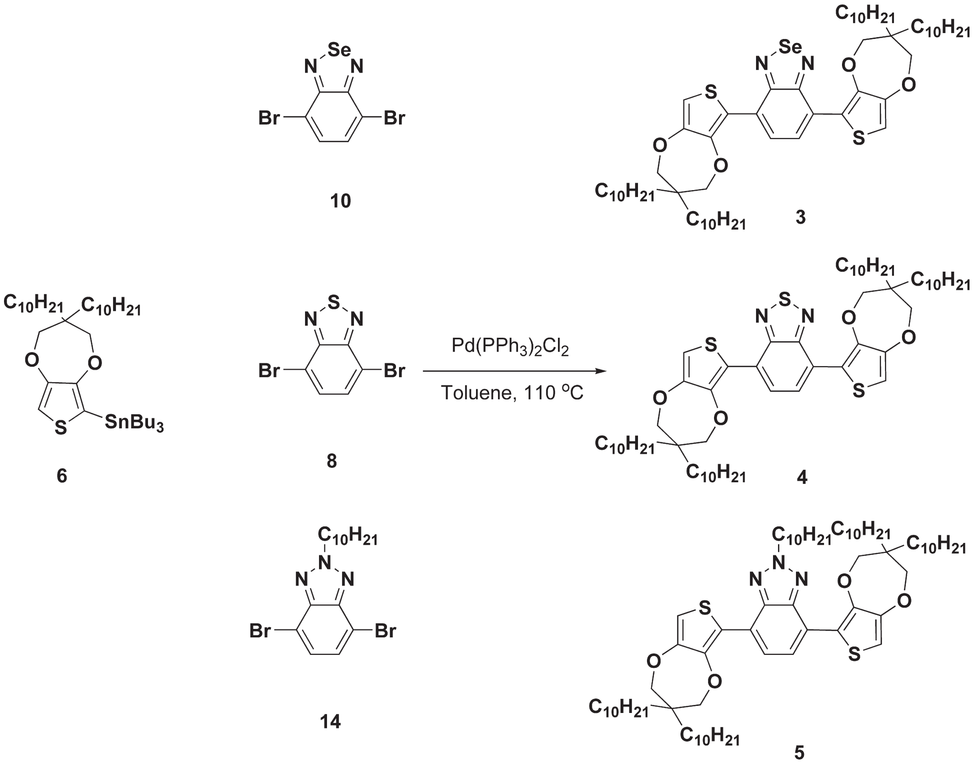
Scheme 1



Scheme 2

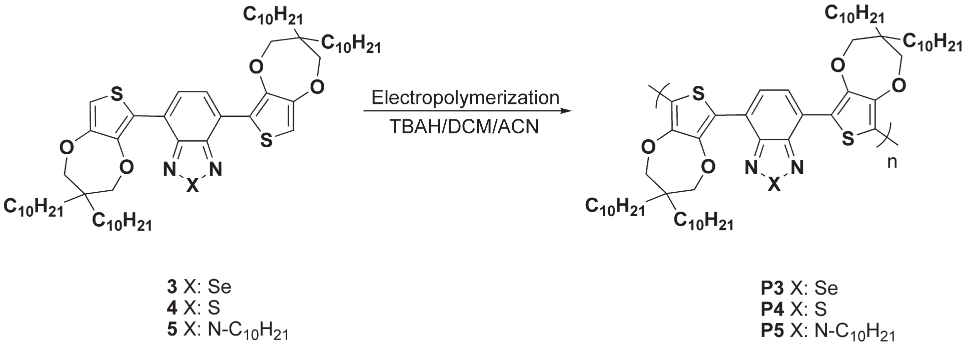


in 0.1 M TBAH (tetrabutylammonium hexafluorophosphate) dissolved in DCM (dichloromethane). It was found that these systems exhibited ambipolar redox behaviors. During anodic scans, irreversible oxidation peaks were observed at ($E_{\mathrm{m,a}}^{\mathrm{ox}}$) 1.21 V, 0.84 V and 0.98 V (vs Ag/AgCl) for **1**−**3**, respectively. As depicted in Figure 1, the voltammograms nicely reflected the electronic nature of the D units. **3** had an oxidation potential of 0.98 V, which is between those of **1** and **2**; this was attributed to higher electron density when compared to **1**, whereas increased bridge size from ethylene to propylene caused a higher oxidation potential when compared to **2**, respectively.[17]

On the other hand, during cathodic scans, **1**−**3** have shown reversible reduction peaks due to the A part with half peak potentials ($E_{1/2}^{\mathrm{red}}$) of −1.17 V, −1.22 V, and −1.23 V (vs Ag/AgCl), respectively. The observed somewhat higher negative peak potential for the formation of radicalic anions of **2** and **3** can be ascribed to higher electron density of the A part when compared to **1**. These results clearly suggested that the D units in **1**−**3** have a key role to tune the redox behavior and the interaction between HOMO and LUMO levels of the system.

However, no appreciable change was observed in the oxidation values of **3**−**5** which consisted of the same D, but different A units. All three monomers had similar

Scheme 3. Electropolymerization of 3−5 in 0.1 M TBAH-DCM/ACN (2/3 v/v) to give P3−P5



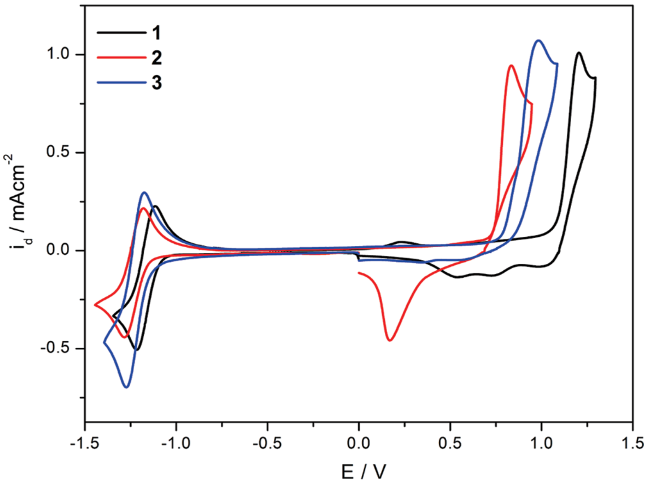


Figure 1. Cyclic voltammograms of compounds **1**−**3** in 0.1 M TBAH/DCM at 100 mV/s.

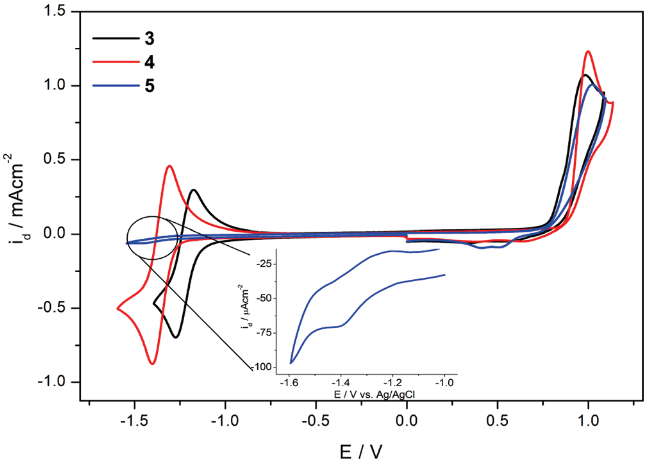


Figure 2. Cyclic voltammograms of compounds **3**−**5** in 0.1 M TBAH/DCM at 100 mV/s.

oxidation behavior which indicated that the oxidation value of the monomer can be fixed when the same D unit (ProDOT-decyl$_2$) was incorporated in the D−A system (Figure 2).

Interestingly, reductions peaks during cathodic scans of **3** and **4** did not follow the expected trend. For example, **4** exhibited a higher reversible reduction peak with a half peak potential ($E_{1/2}^{red}$) of −1.36 than **3** ($E_{1/2}^{red}$ = −1.23 V) (for a comparison of **1** and **2** with sulfur analogues, see ref 50). It is likely that the HOMO and LUMO energy levels, which determine the electrochemical behavior of the D−A systems, are affected in a different way in the case of an increasingly substituted donor unit such as ProDOT-decyl$_2$ when compared to thiophene or EDOT.[50] On the other hand, an indistinct reversible reduction peak was observed at −1.31 V for **5**, this was probably arising from the presence of long alkyl chains in both D- and A units of **5**, because it was evident that the reduction process clearly takes place, when the similar A (benzotriazole) unit was linked with EDOT,[49] thiophene,[61] or selenophene[62] as the D units, which had no alkyl chains.

Electropolymerization. Electropolymerization of **1** and **2** to give polymers **P1** and **P2** was previously reported.[50] After the determination of redox characteristics of **3-5**, the electropolymerization was carried out to get the corresponding polymers **P3**−**P5** in 0.1 M TBAH dissolved in a mixture of DCM and ACN (acetonitrile) solution (since the polymers were highly soluble in DCM) (Scheme 3). During the electropolymerization, new reversible redox couples appeared after repetitive anodic scans, which clearly indicated the formation of electroactive polymer films on the electrode surface (Figure 3). Also, thickness of the polymer films increased, which was confirmed by intensified current value of the redox couples after each successive cycle.

It was noteworthy that **P3**−**P5** were green, greenish-blue, and blue in the neutral state, respectively (see Table 1). Evidently, this panoramic breadth of the neutral state colors of **P1**−**P5**, ranging from various hues of green and blue legs of RGB color-space, further proves that the D−A approach allows engineering tunable electrochromes through a rational design where judicious selection of the D and A units were put forward. In other words, discrete selection of the A part of the D−A system (for example, compare **P1**−**P3** in Table 1), or even the replacement of one heteroatom in the A unit (compare **P3**−**P5** in Table 1) undoubtedly affected the color of the neutral state.

When **P3**−**P5** were scanned anodically in monomer-free electrolyte solution containing 0.1 M TBAH/ACN, they exhibited well-defined reversible redox couples ($E_{p,1/2}^{ox}$ = 0.66 V for **P3**, $E_{p,1/2}^{ox}$ = 0.48 V for **P4**, $E_{p,1/2}^{ox}$ = 0.56 V for **P5**),

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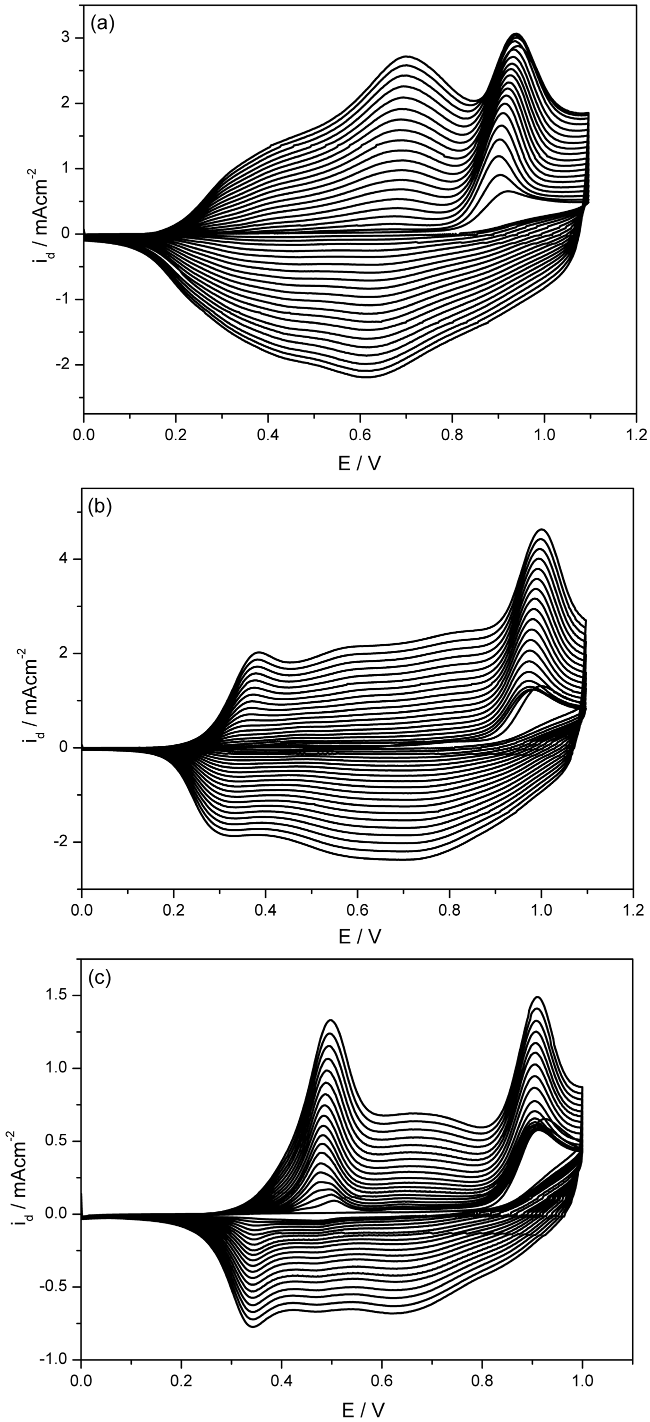


Figure 3. Electropolymerization of 1.5 × 10^{-3} M: (a) **3**, (b) **4**, and (c) **5** in 0.1 M TBAH-DCM/ACN (2/3 v/v) at 100 mV/s by potential scanning to give **P3**−**P5**, respectively.

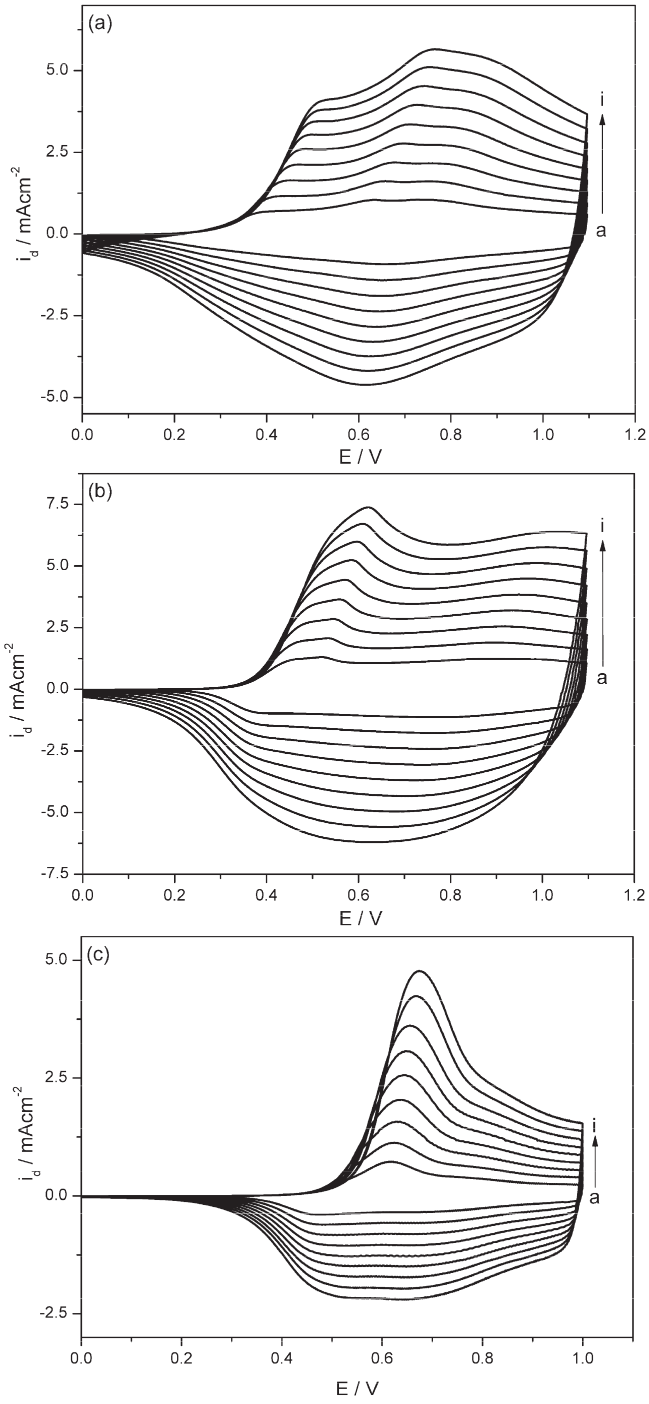


Figure 4. Cyclic voltammograms of p-doped (a) **P3**, (b) **P4**, and (c) **P5** in 0.1 TBAH/ACN at a scan rate of (a) 40, (b) 60, (c) 80, (d) 100, (e) 120, (f) 140, (g) 160, (h) 180, and (i) 200 mV/s.

which were consistent with the behaviors of the starting materials (see Figure 4). A linear increase in the peak currents as a function of the scan rates confirmed well-adhered electroactive polymer films on the electrode surface as well as nondiffusional redox process (see Figure S10 in the Supporting Information). The redox behaviors of **P3**−**P5** were also examined during n-doping. Although **P3** shows a slight activity indicating n-doping, **P4** and **P5** can not be n-doped.

The as-prepared polymers, **P3**−**P5**, were soluble in organic solvents such as DCM and $CHCl_3$, whereas slightly soluble in toluene, which clearly suggested that they all could easily be processed over surfaces via spin coating, spraying, and printing techniques.

To prove the solution processability, we have been able to show that **P3**−**P5**, which were obtained by chemical polymerization of **3**−**5**, could be dip- and/or spray-coated on ITO glass slide.

Oxidative polymerization of **4** with $FeCl_3$ provided **P4** which had a number average molecular weight (M_n) of 7652 with a low polydispersity index of 1.18. This indicates that its chain lengths vary over a narrow range of

Table 1. Electrochemical and Optical Data for 1−5, and Their Corresponding Polymers, P1−P5

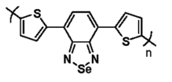
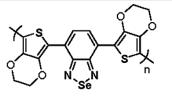
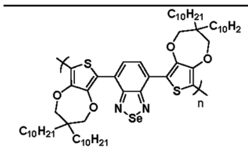
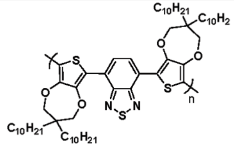
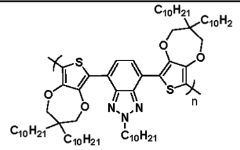
Polymer	$E^{ox}_{m,a}$	$E^{red}_{m,1/2}$	$E^{ox}_{p,1/2}$	$\lambda_{max,1}$	$\lambda_{max,2}$	$\lambda_{max,3}$	Neutral State	Oxidized State
 P1	1.21	-1.17	0.93	350	600	-		
 P2	0.84	-1.22	-0.09	343	448	796		
 P3	0.98	-1.23	0.66	343	419	700		
 P4	1.00	-1.36	0.48	408	685	-		
 P5	1.02	-1.31	0.56	585	-	-		

Table 2. Electrochemically Dtermined HOMO, LUMO, and E_g Values of Polymers P1−P5

polymer	E_{ox} onset (V)	HOMO (eV)	LUMO (eV)	E_g optical (V)
P1	0.42	5.22	3.76	1.46
P2	−0.12	4.68	3.55	1.13
P3	0.48	5.28	3.91	1.37
P4	0.33	5.13	3.65	1.48
P5	0.46	5.26	3.46	1.80

Table 3. Optical and Switching Time Data of Chemically (*) and Electrochemically Synthesized Polymers P1−P5, PEDOT, and Their Analogues[a]

polymer	wavelength (λ_{max}, nm)	contrast (%T)	CE (C/cm^2)	switching time t (s)
P1	600	12	89	2.4
P2	796	10.9	94	1.7
P3	715	40.3	208	0.6
P3*	732	42	220	1.0
P4	690	38.5	230	1.4
P4*	690	40	210	0.5
PESE[45]	755	23	130	0.4
P5	585	61.8	273	1.1
P5*	560	43	240	1.3
PENE[49]	618	53	211	1.1
PEDOT	615	44	183	2.2

[a] The given CE value is the best one at a given wavelength.

molecular masses (see Figure S11 in the Supporting Information). Also, **P4** polymer had a minimum average number of 7 repeating units including 21 heterocyclic units. The as-prepared **P3−P5**, which was dissolved in $CHCl_3$ (2 mg polymer/1 mL $CHCl_3$), was spray coated on ITO glass slide utilizing an Aztek airbrush at 10 psi Ar and it was found that **P3−P5** exhibited nearly the same characteristics (for CV, spectroelectrochemistry, and chronoabsorptometry, see Figures S12−14 in the Supporting Information) when compared to that of the electrochemically deposited **P3−P5**. Upon oxidation, chemically prepared **P3** can be switched from green to colorless (transparent), **P4** from greenish blue to colorless, and **P5** from blue to colorless. The optical contrasts and switching of **P3** were found to be 12% and 1.4 s for 340 nm, 44% and 1.3 s for 428 nm, 42% and 1.0 s for 732 nm, and 45% and 1.98 s for 1000 nm, respectively. Those of **P4** were found to be 34% and 0.85 s for 410 nm, 40% and 0.5 s for 690 nm, and 85% and 0.65 s for 1700, respectively. Those of **P5** were found to be 5.5% and 2 s at 330 nm, 43% and 1.3 s at 560 nm, and 36% and 7 s at 1000 nm (see Table 3). It was noted that the D units with decyl chains (e.g., ProDOT-decyl$_2$) provided the corresponding processable materials after polymerization. Note that Toppare et al.[49] tried to generate a processable polymer by the alkylation of benzotriazole A

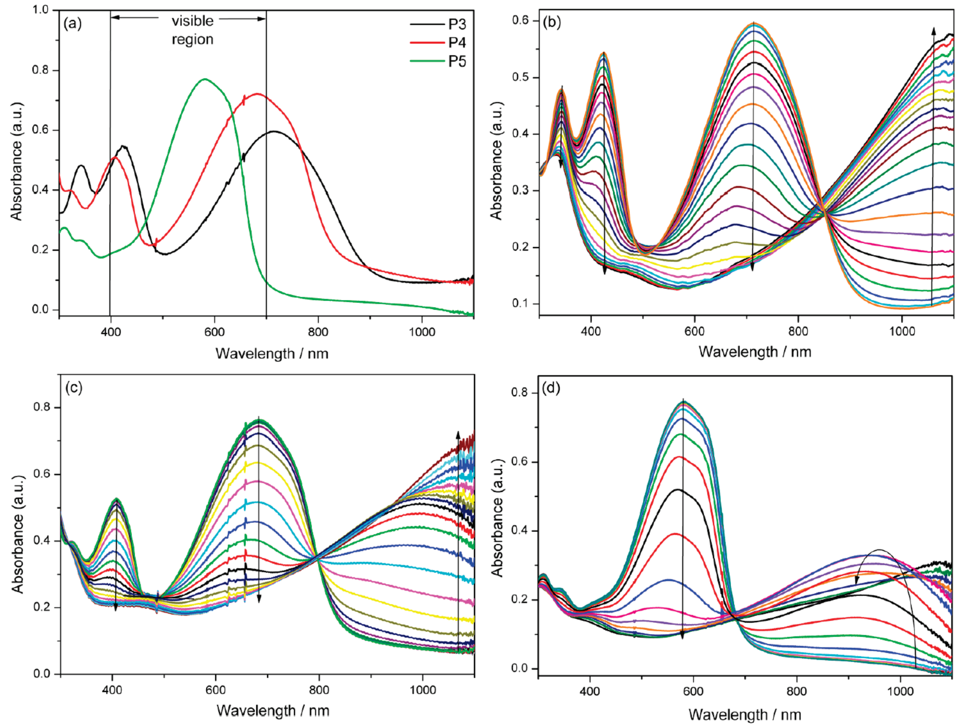


Figure 5. Optical spectra of (a) **P3**−**P5** in the neutral states, (b) **P3** (from −0.1 to 1.1 V), (c) **P4** (from −0.5 to 1.2 V), and (d) **P5** (from 0.0 to 1.0 V) on ITO in 0.1 M TBAH/ACN at various applied potentials.

unit with EDOT external units, but this approach was not sufficient to get a soluble polymer. On the other hand, this problem could easily be eliminated with **P5**.

Spectroelectrochemistry. From the viewpoint of device and high-performance display applications, spectroelectrochemical properties of the electrochromes should be manifested by using the changes in optical absorption spectra under voltage pulses. Therefore, UV−vis spectra of **P3-P5** films that were electrodeposited on ITO glass slides via potential cycling were recorded in situ after neutralization (Figure 5a).

It was observed that both A and D fragments of the D−A system influenced the absorption spectra of the polymers significantly. Upon oxidation, the intensity of the absorption bands started to decrease simultaneously with a concomitant increase in the near-IR region, indicating the formation of charge carriers. These changes in the absorption spectra were accompanied with color changes from green, greenish-blue, and blue to transparent (colorless) states for **P3**−**P5**, respectively, during p-doping process (Figure 5b−d and Table 1). The color change from one to a highly transmissive state, as in cases of **P3**−**P5**, is also a quite significant trait in RGB PECs and especially useful in display applications.

The band gaps (E_g) of **P1**−**P5** were calculated from the onset of the low energy end of the $\pi-\pi^*$ transitions to be 1.46, 1.13, 1.37, 1.48, and 1.80 eV, respectively, (Figures 5 and 6 and Table 2). It can be easily concluded that the smallest band gap can be obtained when EDOT units were attached as the D part to any A unit [45,49], probably because of the effective intramolecular charge transfer between the D and the A units (HOMO−LUMO interaction). On the other hand, the attachment of ProDOT-decyl$_2$ to different A-units results in similar HOMO energy levels, which is probably due to the fact that HOMO of the D−A system is mainly localized on D unit. On the other hand, LUMO energy levels of the systems are particularly different (compare **P3**−**P5** in Figure 6) because the LUMO of the D−A system probably lies on the A part of the system.

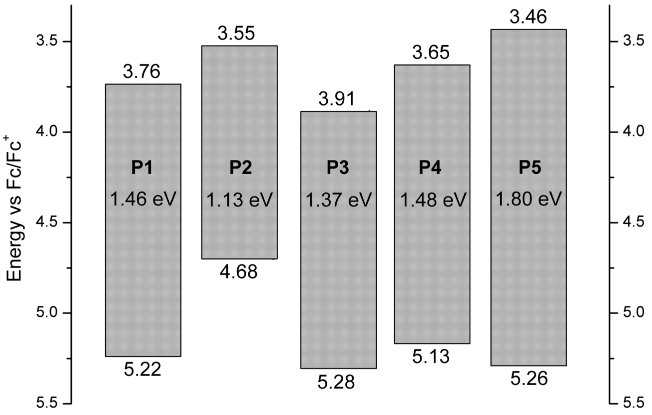


Figure 6. Energy band diagram of the polymers **P1-P5**.

Oxidation potentials are reported vs Fc/Fc$^+$. The energy level of Fc/Fc$^+$ was taken as 4.8 eV below vacuum.[63] The oxidation onset potential of Fc/Fc$^+$ was measured as 0.36 V vs Ag/AgCl. HOMO energy level was obtained from the onset potential of the oxidation at CV and LUMO energy level was calculated by the subtraction of the optical band gap from the HOMO level.

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[63] Shin, W. S.; Kim, S. C.; Lee, S.-J.; Jeon, H. S.; Kim, M.-K.; Naidu, B. V. K.; Jin, S.-H.; Lee, J.-K.; Lee, J. W.; Gal, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1394.

Switching and Stability. The long-term stability upon switching and/or cycling plays a key role on the electrochromic performance of the devices and smart windows. For that reason, the stability of **P1**−**P5**, which was deposited on Pt disk electrode, upon switching or cycling was elaborated by potential scanning between neutral and oxidized states. It was noted that the polymer films **P1**−**P5** exhibited excellent stability retaining at least 63, 84, 72, 72, and 76% of the electroactivity even after 2000 cycles, respectively (see Figure S15 in the Supporting Information). Note that the stability tests were carried out under an air atmosphere and the devices were not sealed (sealing would further increase the long-term stability of these materials upon switching and/or cycling). The electrochemical stability and robustness of the systems suggested that the polymers were promising candidates for electrochromic devices and optical displays. In special case of **P3**, for example, the response of the polymer film on ITO glass slide was almost that same as it was newly prepared, even after prolonged standing at ambient conditions (e.g., 2 months, and no further trial was done afterward).

Finally, the percent transmittance changes (the contrast ratio) as a function of time were monitored and the switching time of the polymers at a given absorption maxima (λ_{max}) was determined and summarized in Table 3. **P3**−**P5** displayed moderate to excellent transmittance ratios and higher CE values (see Table 3) when compared to PEDOT.[64,65] Moreover, they represented low switching times and the optical contrast remained nearly unaltered even at short switching times (Figure 7). For **P3**, estimated differences in percentage transmittance of the bands (at 343, 425, and 715 nm) with respect to the deep valleys were found to be 8.0, 12.3, and 15.5% for 343 nm and 32.4, 36.7, and 39.9% for 504 nm. These values were quite enough to get the green color with various hues as in cases of **P2**.[50] The percentage transmittance changes (Δ%T) between the neutral (at −0.1 V) and oxidized states (at 1.1 V) of **P3** were found to be 11.2% for 343 nm, 39.3% for 425 nm, 40.3% for 715 nm, and 53.8% for 1080 nm (see the Supporting Information, Figures S16−18. The CE (at 95% of the full contrast) of the **P3** film was found to be 45 cm^2/C for 343 nm (a response time of 1.2 s), 147 cm^2/C for 425 nm (a response time of 1.0 s), and 208 cm^2/C for 715 nm (a response time of 0.6 s) during p-doping. Apparently, these values are both higher than those of **P1** and **P2** and even than that of PEDOT (183 cm^2/C at 610 nm).[63,64]

CE = $\Delta\mathrm{OD}/Q_{\mathrm{d}}$, where Q_{d} is the injected/ejected charge per unit area (C/cm^2) during a redox step and the optical density $\Delta\mathrm{OD} = \log(T_{\mathrm{colored}}/\mathrm{T}_{\mathrm{bleached}})$, where T_{colored} and T_{bleached} are the transmittance in the oxidized and neutral processes, respectively.[58]

On the other hand, **P4** exhibited two well-defined absorption bands at 410 and 690 nm. Upon oxidation, while the color changed from greenish-blue to transparent state (colorless), the absorption bands started to decrease simultaneously and a new band at 1000 nm appeared due to the formation of charge carriers (Figure 5c). During this process, the optical contrasts and CE were found to be 32.7% and 147 C/cm^2 for 410 nm and 38.5% and 230 C/cm^2 for 690 nm, respectively. Obviously, the optical contrast and CE of **P4** were higher than that of its EDOT analogue (PESE) (see ref 45 and Table 3).

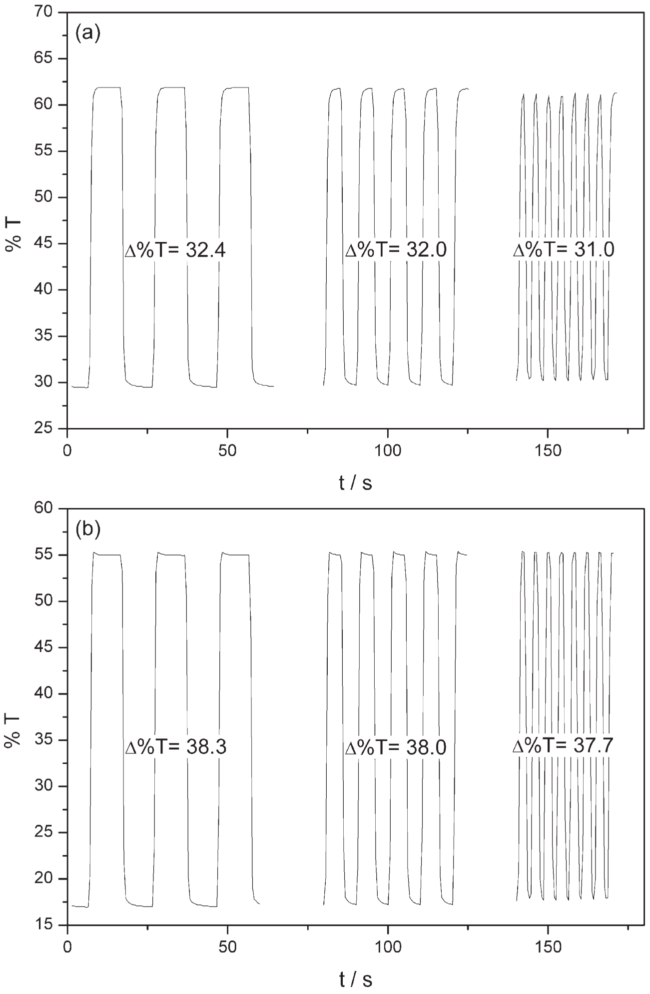

Figure 7. Chronoabsorptometry experiments for **P4** on ITO in 0.1 M TBAH/ACN while the polymer was switched between −0.5 and 1.2 V with a switch time of 10, 5, and 3 s at (a) 410 and (b) 690 nm.

The CE (at 95% of the full contrast) of **P5** was found to be 106 cm^2/C for 480 nm (a response time of 2.2 s) and 273 cm^2/C for 585 nm with a low response time of 1.1 s during the p-doping process. The data firmly established that **P5** is much better than PEDOT and even that of its EDOT analogue (PENE)[49] in terms of both optical contrast and CE (Table 3). Additionally, considering the fact that **P5** can easily be processed over surfaces, it is an excellent blue-to-colorless PEC candidate, which, to the best of our knowledge, exhibits the highest optical contrast and CE, when compared to PEDOT and/or PENE[49] (see Table 3).

Overall, these results clearly suggested that tailoring the absorption, CE, transmittance, optical contrast and the solubility of the polymers was possible by the introduction of proper D and A units into trimeric D−A systems.

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(64) Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* **2004**, *16*, 574.
(65) Gaup, G. L.; Walsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.

Conclusion

In summary, design, synthesis, and characterization of a series of D−A type systems, **1**−**5**, were described in order to demonstrate the effect of the D and A units on the structure−property relationships of electrochromic polymers. It was found that these units play key roles on the redox behavior, band gap, neutral state color, and the electrochromic performance (stability, optical contrast, CE, and switching time) of the system. It was noted that electropolymerization of these systems provided processable and low band gap electrochromes, **P1**−**P5**, exhibiting high redox stability, high CE, high transmittance (%T), and low response time. Furthermore, **P1**−**P5** reflects various hues of blue and green pallets of the RGB color-space in the neutral state. In particular, it is noteworthy that **P5** is an excellent blue-to-colorless PEC candidate, which to the best of our knowledge, exhibits the highest optical contrast and CE. The panoramic breadth of the neutral state colors and intriguing features of these PEC candidates further prove that the D−A approach allows engineering tunable electrochromes, which hold promise for commercialization of polymeric RGB electrochromics. Further work in this line is currently underway in our laboratories and the results will be reported in due time.

Experimental Section

Materials and Methods. All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) dissolved in dichloromethane (DCM) and acetonitrile (ACN) was used as electrolyte solution. A platinum disk (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a silver wire as a pseudoreference electrode (calibrated externally using 5 mM solution of ferrocene/ferrocenium couple) or Ag/AgCl in 1.0 M NaCl reference electrode. Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8−12 Ω, 0.7 cm ×5 cm) electrode as well as a platinum wire as counter electrode and a Ag wire as a pseudoreference electrode. In order to equilibrate the redox behavior of the polymer film and to obtain repeated results, the coated polymer films were switched between their neutral and oxidized states several times before electroanalytical and optical studies. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat. The electro-optical spectra were monitored on a Hewlett−Packard 8453A diode array spectrometer. FTIR spectra were recorded on Nicolet 510 FT-IR with attenuated total reflectance. Photographs of the polymer films were taken by using a Canon (PowerShot A75) digital camera. Mass spectra were acquired on a Voyager-DE PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-laser operating at 337 nm. Combustion analysis was performed using a LECO CHNS-932 analyzer. Spectra were recorded in linear modes with average of 100 shots. Compounds **1**,[50] **2**,[50] **8**,[60] and **10**[60] were prepared according to literature procedures.

*(3,3-Didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-(tributyl)stannane (**6**).* To an argon degassed solution of 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine[3] (420 mg, 0.96 mmol) in dry THF (10 mL) was added n-BuLi (2.5 M in n-hexane, 0.4 mL, 1.0 mmol) while stirring magnetically at −78 °C. After the addition was complete, stirring was continued for an additional 4 h, after which a solution of tributyltin chloride in THF (0.259 mL, 096 mmol) was added. The mixture was quenched with dropwise addition of water (1 mL) after it was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure. The residue was dissolved in DCM, washed with saturated NH_4Cl, and dried over $MgSO_4$. Removal of the solvent afforded **6**, which was used in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.66 (s, 1H, Ar−H), 3.65 (s, 4H, $-CH_2$), 1.85−1.06 (m, 69H; $-CH_2$ and $-CH_3$).

*2-Decyl-2H-benzo[d][1,2,3]triazole (**12**) and 1-decyl-1H-benzo-[d][1,2,3]triazole (**13**).* To a methanol solution of 1,2,3-benzotriazole (4.0 g, 33.6 mmol) and potassium *tert*-butoxide (5.6 g, 50.4 mmol), was added 1-bromodecane (8.88 g, 50.4 mmol), and the mixture was stirred under reflux for 12 h. After removal of the solvent by evaporation, the residue was diluted with water (200 mL) and extracted with $CHCl_3$ (3 × 100 mL). After evoparation of the solvent, the crude mixture was chromatographed on silica gel eluting with hexane-$CHCl_3$ (1:1, v/v) to give **12** (first fraction) and **13** (second fraction) as colorless oil in 1:1 ratio and a total yield of 90%.

2-Decyl-2H-benzo[d][1,2,3]triazole (**12**). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.90−7.86 (m, 2H), 7.42−7.38 (m, 2H), 4.74 (t, J = 7.2 Hz, 2H), 2.15−2.10 (m, 2H), 1.36−1.26 (m, 14H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz,$CDCl_3$, δ): 144.2, 126.1, 117.9, 56.6, 31.9, 31.8, 30.0, 29.6, 29.4, 26.5, 26.1, 22.6, 14.1. Calcd for $C_{16}H_{25}N_3$: C, 74.09; H, 9.71; N, 16.20. Found: C, 74.98; H, 9.86; N, 16.05.

1-Decyl-1H-benzo[d][1,2,3]triazole (**13**). ^1H NMR (400 MHz, $CDCl_3$,δ): 8.07 (d, J = 8.4 Hz, 1H), 7.55−7.47 (m, 2H), 7.39−7.35 (m, 1H), 4.64 (t, J = 7.2 Hz, 2H), 2.05−1.98 (m, 2H), 1.42−1.24 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz,$CDCl_3$, δ): 146.0, 132.9, 127.1, 123.7, 120.0, 109.3, 48.2, 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 26.7, 22.6, 14.0. Anal. Calcd for $C_{16}H_{25}N_3$: C, 74.09; H, 9.71; N, 16.20. Found: C, 74.98; H, 9.86; N, 16.05.

*4,7-Dibromo-2-decyl-2H-benzo[d][1,2,3]triazole (**14**).* **12** (1.29 g, 5 mmol) and an aqueous HBr solution (5.8 M, 10 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C. Bromine (2.0 g, 12.5 mmol) was added, and the mixture was stirred for 12 h at 135 °C. After the mixture was cooled to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The solvent was removed by evaporation, and the product was purified by column chromatography on a silica gel column by eluting with CH_2Cl_2 to afford **14** as yellow oil. Yield: 76%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.36 (s, 2H), 4.70 (t, J = 7.5 Hz, 2H), 2.11−2.03 (m, 2H), 134−1.17 (m, 14H), 0.85 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz,$CDCl_3$, δ): 147.4, 130.8, 110.8, 48.7, 32.1, 29.9, 29.7, 29.6, 29.4, 29.3, 26.9, 22.9, 14.3; FTIR (ATR, cm^{-1}): 2925, 2855, 1495, 1463, 1306, 1193, 1112, 949, 815, 720, 654. Anal. Calcd for $C_{16}H_{23}N_3Br_2$: C, 46.06; H, 5.56; N, 10.07. Found: C, 46.01; H, 5.59; N, 10.04.

Representative Procedure for the Synthesis of 3−5. To an argon-degassed solution of **6** (243 mg, 0.334 mmol) and **8**/**10** or 14 (45.6 mg, 0.134 mmol) in dry toluene (15 mL) was added $Pd(PPh_3)_2Cl_2$ (18.8 mg, 0.0268 mmol) and the mixture was heated under reflux overnight. After being cooled to room temperature, the solvent was removed under reduced pressure. The crude mixture was chromatographed on silica gel by eluting with methanol: chloroform (4:1, v/v) to give 3/4 or 5.

4,7-Bis(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2,1,3-benzoselenadiazole (**3**). 35% yield. ^1H NMR (400 MHz,

$CDCl_3$, δ): 8.11 (s, 2H,Ar H), 6.57 (s, 2H, Ar), 3.96 (s, 4H), 3.87 (s, 4H), 1.40−1.35 (m, 8H), 1.30−1.20 (m, 64H), 0.83−0.77 (m, 12H). ^{13}C NMR (100 MHz,$CDCl_3$, δ): 157.08, 148.45, 146.68, 127.01, 124.44, 116.50, 105.20, 78.08, 77.92, 42.48, 30.73, 30.60, 29.20, 28.34, 28.24, 28.03, 25.62, 21.57, 12.79. FTIR (ATR, cm^{-1}): 3115, 2920, 2853, 1478, 1377, 1259, 1168, 1028, 798; Anal. Calcd for $C_{60}H_{96}N_2O_4S_2Se$: C, 68.47; H, 9.19; N, 2.66; S, 6.09. Found: C, 68.45; H, 9.21; N, 2.58; S, 6.01.

4,7-Bis(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (**4**). 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.20 (s, 2H), 6.56 (s, 2H), 3.96 (s, 4H), 3.87 (s, 4H), 1.56 (t, J = 7.1 Hz, 2H), 1.41−1.33 (m, 8H), 1.29−1.21 (m, 62H), 0.90−0.86 (m, 12H). ^{13}C NMR (100 MHz,$CDCl_3$, δ): 151.6, 148.7, 146.8, 126.4, 123.2, 116.3, 105.1, 76.69, 76.54, 43.7, 30.9, 30.8, 29.4, 28.5, 28.4, 28.2, 21.7, 21.5, 13.0. FTIR (ATR, cm^{-1}): 2925, 2852, 1502, 1452, 1375, 1167, 1033, 855, 829, 804, 720, 633. Anal. Calcd for $C_{60}H_{96}N_2O_4S_3$: C, 71.66; H, 9.62; N, 2.79; S, 9.57. Found: C, 71.63; H, 9.65; N, 2.69; S, 9.56.

2-Decyl-4,7-bis(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepin-6-yl)-2H-benzo[d][1,2,3]triazole (**5**). 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.94 (s, 2H), 6.49 (s, 2H), 4.69 (t, J = 7.2 Hz, 2H), 3.95 (s, 4H), 3.86 (s, 4H), 2.09 (t, J = 7.2 Hz, 2H), 1.43−1.37 (m, 8H), 1.31−1.22 (m, 62H), 0.85−0.82 (m, 12H). ^{13}C NMR (100 MHz,$CDCl_3$, δ): 150.3, 147.5, 142.4, 124.7, 122.0, 118.3, 105.1, 78.05, 77.97, 44.1, 44.0, 32.3, 30.8, 30.2, 29.8, 29.6, 29.5, 29.3, 23.2, 23.1, 14.3. FTIR (ATR, cm^{-1}): 2917, 2851, 1516, 1480, 1451, 1407, 1378, 1255, 1164, 1029, 833, 797, 727, 647, 611. Anal. Calcd for $C_{70}H_{117}N_3O_4S_2$: C, 74.48; H, 10.45; N, 3.72; S, 5.68. Found: C, 74.44; H, 10.47; N, 3.69; S, 5.66.

Representative Procedure for Chemical Polymerization. Compound **4** (445 mg, 0.64 mmol) was dissolved in chloroform (45 mL). A solution of anhydrous $FeCl_3$ (444 mg, 2.74 mmol, 5 equiv) in nitromethane was added dropwise over a period of 45 min to the stirred monomer at room temperature (the bright orange monomer solution turned progressively dark blue with addition of oxidizing agent). The mixture was stirred 48 h at room temperature. It was then precipitated into methanol (300 mL). The precipitate was filtered, redissolved in chloroform (300 mL), and stirred for 6 h with hydrazine monohydrate (6 mL). After evaporation, the concentrate (dark blue) was precipitated into methanol (300 mL), the precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 48 h with methanol. The polymer was extracted with chloroform and concentrated by evaporation. Then, the polymer was precipitated in methanol (300 mL) and collected as a black solid (yield = 82% for **P3**, 84% for **P4**, and 86% for **P5**).

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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.