Color Control in π-Conjugated Organic Polymers for Use in Electrochromic Devices

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Contents

1. Introduction

In an emerging era of flexible, rollable, or foldable high-performance electronic displays, the perspective of manufacturing low-cost functional materials that can be easily processed over large areas along with being mechanically tolerant has become a sine qua non to commercial viability. In parallel, the idea of designing multifunctional semiconducting materials that can be integrated in various operating systems by inducing simple changes in device architectures has triggered new challenges for materials scientists who are now trying to answer the following: How can organic electronics reach or exceed the performance of their inorganic-based counterparts for a specific technology? Should they complement existing technologies in target applications, or should they seek to replace them in the most conventional areas of use? Can they remain cost-effective regardless of the number of manufacturing steps?

In portable applications where lightness, thickness, and low-power consumption are further desired, organic electronics that can be precisely printed, stamped, sprayed, drop-cast, or spin-coated into predefined patterns offer a competitive alternative to their conventional inorganic homologues. However, solution-processability, solid-state ordering, efficient electroluminescence, stable color-switching, and high charge-carrier mobility, for instance, are a variety of interconnected factors difficult to match up for the synthetic chemist, when not a priori exclusive.

In this context, π-conjugated organic polymers combining mechanical flexibility, and ease in band-gap/color-tuning via structural control, along with the potential for low-cost scalability and processing, are attractive in the fast-growing area of plastic electronics. For instance, in considering the most established applications, polymeric semiconductors are expected to find widespread application in thin film transistors (OTFTs),[1,2] photovoltaic cells,[3,4] radiofrequency identification (RFID) tags, sensors,[5] memories,[6,7] and light-emitting diodes (OLEDs).[8] Of all the possible applications, light-emitting and nonemissive electrochromic devices (ECDs) require precise control of the colors displayed in terms of their hue, saturation, intensity, and/or their brightness. Besides the requirements for aesthetically pleasing color

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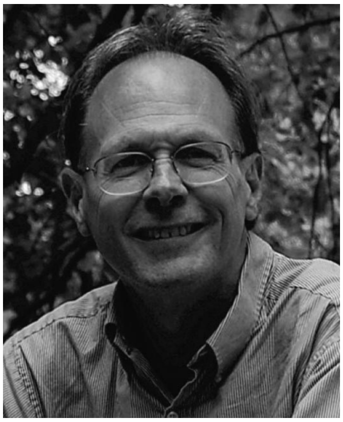


John R. Reynolds is a V.T. and Louise Jackson Professor of Chemistry at the University of Florida with expertise in polymer chemistry and serves as an Associate Director for the Center for Macromolecular Science and Engineering. His research interests have involved electrically conducting and electroactive conjugated polymers for over 30 years with work focused on the development of new polymers by manipulating their fundamental organic structure to control their optoelectronic and redox properties. His group has been heavily involved in the areas of visible and infrared electrochromism, light emission from polymer and composite LEDs (both visible and near-infrared), and light-emitting electrochemical cells (LECs). Further work is directed to using organic polymers and oligomers in photovoltaic cells. Reynolds obtained his M.S. (1982) and Ph.D. (1984) degrees from the University of Massachusetts in Polymer Science and Engineering. He has published over 225 peer-reviewed scientific papers, has 7 patents issued and 17 patents pending, and served as coeditor of the *Handbook of Conducting Polymers*, which was published in 2007. He serves on the editorial boards for the journals *ACS Applied Materials & Interfaces*, *Macromolecular Rapid Communications*, *Polymers for Advanced Technologies*, and *Journal of Macromolecular Science, Chemistry*.

patterns, displays, for instance, are expected to include emissive or nonemissive chromophores which can be brought together as pixels or superimposed to recreate several other desirable colors via the principles of color mixing theory.

In both light-emitting and electrochromic (EC) technologies, changing the composition of the polymers at the molecular level has been the most extensively investigated approach to color-tuning so far. Hence, a variety of synthetic strategies have been described over the years spanning varying the overall planarity of the backbones as a function of steric hindrance, changing the electron-rich and -poor character of the building blocks incorporated in the repeat unit, increasing the conjugation lengths via the use of fused heterocycles able to reduce the polymers' bond-length alternation, copolymerizing different monomers randomly and in different feed ratios, and so on. Alternatives have consisted in blending different electroactive components, or creating laminates and composites with other types of chromophores or insulating materials.

Combining high contrast ratios, fast response times, and narrow potential windows of application with the perspective for long-term optical stability, processable electrochromic polymers (ECPs) are now impacting the development of both transmissive and reflective EC technologies. With ubiquitous target applications encompassing smart window products, e-papers (see Figure 1, Note: prototype is not ECP-based here), optical shutters, transmissive and reflective displays (see Figure 2), self-darkening mirror devices, or optical memories, for example, ECPs have been subjected to significant synthetic effort during the past decade, and soluble systems with new colors, higher contrasts, and improved ambient stability have been successively developed. In parallel, some of the most effective strategies described in the construction of organic electronic-based devices have been applied to polymer ECDs, enhancing their lifetime and performance considerably. Given their relative ease of synthesis in general, ECPs are now only a step away from

Figure 1. Plastic Logic's e-paper, namely, "Take anywhere, read anywhere". Adapted with permission from Plastic Logic, http://www.plasticlogic.com/. Copyright 2009 Plastic Logic.

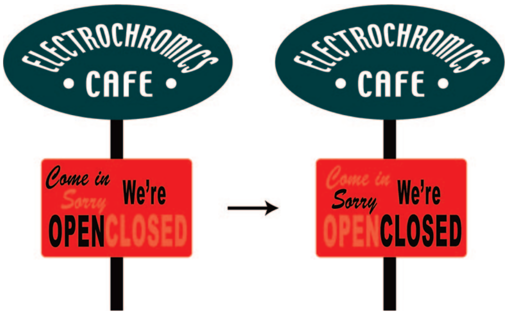


Figure 2. Electrochromic polymers that can change between a transparent colorless form and an opaque black form offer potential uses in nonemissive displays or signage. Adapted with permission from Krebs, F. C. *Nat. Mater.* **2008**, *7*, 766−767. Copyright 2008 Nature Publishing Group.

being accessible for technological development and transferred to everyday products.

In this review, we will first open the toolbox of polymer electrochromism and outline the basic concepts and well-established characterization techniques in this area. This first section will also refer to a few more recently proposed analytical tools and give constructive suggestions with respect to the study of polymer electrochromes or color-changing materials in general. Further, π-conjugated ECPs will be overviewed as a function of their color-changing properties and variations in molecular structure. The most influencing parameters in polymer band-gap/color-engineering will be discussed including repeat unit design, steric effects, electron density of the monomers, and functional substitutions. Finally, we will discuss the recent advances in polymer ECD (PECD) concepts, architectures, and fabrication techniques, and provide an outlook on the most promising applications for ECPs encompassing smart window devices, reflective-type information displays, and e-paper.

Importantly, for clarity, the scope of this review has been narrowed to all-organic and fully π-conjugated polymers, excluding polyaniline (PANI) and analogues which have been frequently reviewed.[9,10] Further, partially conjugated ECPs, π-conjugated oligomers, metal oxides, and small-molecule electrochromes (e.g., viologens, Prussian blue, etc.) are not included here. A major focus has been placed in systematically incorporating the studies addressing π-conjugated ECPs and PECDs that were published during the years 2006, 2007, and 2008. A large number of representative papers published prior to 2006 were selectively chosen for didactical purposes and are herein referenced. We have not aimed at completeness for years prior to 2006. In general, references do not appear chronologically.

2. Toolbox of Polymer Electrochromism

Beyond their different natures (e.g., organic vs inorganic, small molecules vs polymers), electrochromes can be differentiated on the basis of their redox-accessible optical states. A first class spans materials exhibiting at least one colored and one bleached state such as the metal oxide WO_3, most viologens, the metal coordination complex Prussian blue, and the conducting polymer poly(3,4-(ethylenedioxy)-thiophene) (PEDOT). Colored to transmissive electrochromes are finding applications in absorption/transmission devices (e.g., smart windows, information displays, optical shutters, and e-papers). A second class consists of electrochromes possessing two distinct colored states such as red to blue switching polythiophenes (PTs). If the absence of a transmissive state may preclude these materials from being employed in switchable glass applications, they remain potentially useful for display devices. A third class is represented by multicolored electrochromes comprising a bleached state or not. In this area, conjugated polymers and copolymers possessing multiple redox states have received the greatest deal of attention over the past few years. In this section, we briefly define and discuss some useful tools for the characterization of π-conjugated ECPs. Most of these parameters find utility in the study of various other EC technologies as well, such as metal oxides, and more details can be found in the literature.[9]

2.1. Electrochromic Contrast

Commonly reported as a percent transmittance change (ΔT, %) at a given wavelength, the electrochromic contrast is a primary tool in the overall characterization process of an electrochrome. While the control wavelength chosen is often the one at which the electrochrome exhibits its highest optical contrast, this EC contrast can practically be monitored and reported at any local absorption maximum, when desired. Transmittance values are generally recorded upon application of square-wave potential steps to the electroactive film placed in the beam of a spectrophotometer.

Alternatively, spectroelectrochemical experiments monitoring the formation of ionic states, namely, polarons (radical cations/anions) and bipolarons (dications/dianions), upon progressive application of an electrical bias, can be used to evaluate the transmittance changes undergone over a broad range of wavelengths. As the long-wavelength optical transitions associated with the charge-carrier formation arise, EC contrasts can generally be evaluated in the near-IR as well. In π-conjugated polymers, the extent of depletion of the neutral-state interband(s) transition(s) greatly depends on the degree of stability attained by the polymeric backbone in its quinoidal geometry, which relates to the formation of charge carriers.

Another practical approach to evaluate EC contrasts in the case of colored to transmissive switching electrochromes is provided by measuring the relative luminance change (ΔY, %) as a function of redox doping. Relative luminance values describe the overall contrast of a material across the visible region of the electromagnetic spectrum taking into account the sensitivity of the human eye in this range and rely on a calibrated light source. ΔY (%) values become particularly useful in the characterization of broadly absorbing materials where no distinct absorption maximum can be unambiguously chosen.

Padilla et al. have recently described EC materials in terms of photopic transmittance (T_{photopic}), which can be calculated using the spectra of the polymers in their colored and bleached states on the basis of the following equation:

$$T_{\text{photopic}} = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} T(\lambda)\, S(\lambda)\, P(\lambda)\, d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} S(\lambda)\, P(\lambda)\, d\lambda}$$

where $T(\lambda)$ is the spectral transmittance of the polymer film, $S(\lambda)$ the normalized spectral emittance of the light source, and $P(\lambda)$ the normalized spectral response of the eye. $\lambda_{\min}$ and $\lambda_{\max}$ define the considered range of wavelengths.[11]

The same group has recently presented a procedure to calculate the maximum contrast attainable by an ECP on the basis of the knowledge of its coloration efficiency (see the definition below).[12] Their methodology is applicable to ECDs and should facilitate further device optimizations.

2.2. Coloration Efficiency

The proportionality factor that relates the optical absorbance change of an electrochrome at a given wavelength (ΔA) to the density of injected/ejected electrochemical charge necessary to induce a full switch (Q_d) is called coloration efficiency (CE). CE values are inherent to the electrochromic material under characterization, some being intensely colored by nature in at least one redox state while others display fainter tones over their doping/dedoping cycles, regardless of the deposited film thickness. Derived from the Beer–Lambert law, the quantitative measure of the electrochromic contrast observed CE is estimated through the following equation:

$$\mathrm{CE} = \frac{\Delta A}{Q_\mathrm{d}} = \frac{\log\left(\dfrac{T_\mathrm{ox}}{T_\mathrm{neut}}\right)}{Q_\mathrm{d}}$$

where Q_d is in C cm^{-2}, CE is in cm^2 C^{-1}, and T_ox and T_neut are the doped- and dedoped-state transmittance values, respectively.

Given the above equation, a parameter affecting CE values substantially is the level of transmissivity attained in the one extreme state of the electrochrome, such that CEs become especially useful for the characterization of colored to transmissive switching materials. Upon doping, the charge-carrier transitions with significant overlap in the visible region tend to lower the CEs of the corresponding electrochromes. However, it is worth noting that low CE values do not always translate into modest optical changes as in the case of colored EC species switching to a different color state on doping.

In spite of their well-established utility in this field, the determination and further comparison of CE values between works suffer from the different methods available to measure them. In addition, most of the perceptible EC contrast is obtained within the first 90–95% of overall optical change such that smaller charge density windows could be used to calculate more representative CE values. One approach for the characterization of the extent of optical change undergone by an electrochrome at a given wavelength consists in estimating a composite coloration efficiency (CCE) measured at a representative percentage (e.g., 95%) of the total optical change. Quantitative comparisons between electrochromes can be achieved precisely and reliably by tandem chronocoulometry/chronoabsorptometry, during which variations of film transmittance and charge density are simultaneously monitored while the potential is repeatedly stepped from one redox state to the other.[13]

Fabretto et al. have recently proposed a new approach for measuring the CEs of polymers in ECDs by extracting the faradic charge from the total charge involved during a device switch.[14] The faradic-corrected CEs of several control polymers were found to be significantly larger than the CE values commonly described for the same materials. The same group has also commented on the importance of precisely identifying the conditions within which CE values are reported (e.g., full contrast vs portions of the full contrasts).[15]

2.3. Colorimetric Analysis

In 2000, Reynolds et al. introduced a methodology aimed at describing the different color states exhibited by an ECP on electrochemical switching on the basis of the CIE (Commission Internationale de l'Eclairage) standards for color matching.[16,17] As for a dye or pigment to be employed in commercial products, the potential of π-conjugated polymers for application in multichromic display devices relies on the ability to precisely define their color on the basis of the use of at least one of the several color spaces available.[18] Further, to avoid falling into a mode of trial and error when fabricating devices, it is essential to have rapid access to the color state of a deposited polymer film, which is to an extent controlled by its thickness. Finally, since ECPs are primarily desirable for their color changes, it is essential to map the color path followed by the polymer as well as its light transmission properties as a function of the doping level attained.

These aspects have encouraged the group to develop a protocol especially suitable for polymeric electrochromes and consisting in using a portable colorimeter calibrated to the sensitivity of the human eye, which not only accounts for the changes of color and light transmission observed but allows selecting and varying the illumination conditions as well. Further, the measurements can be subjected to practically any cell configuration, whereas obvious constraints and limitations arise from the use of a spectrophotometer as previously proposed.[19,20] In particular, the use of a colorimeter allows visual tracking of the sample color both in a reflectance and in a transmission mode depending on the considered application. The CIE-defined $L^*a^*b^*$ color space introduced in 1976 is employed as a means to define the color/light transmission changes undergone by the ECP as a function of the external bias applied. The $L^*a^*b^*$ values associated with a colored state are calculated from the Yxy tristimulus values determined by the colorimeter, where Y is the luminance and xy the two-dimensional set of coordinates defining the hue and saturation of the color state at the given Y value. Note that the relative lightness of a color Y is commonly described as a percentage of light transmitted with respect to that coming from a light source:[18]

$$Y\,(\%) = \frac{Y}{Y_0} \times 100$$

The proposed in situ colorimetric analysis has proven to be useful in the systematic study of electro-optical property relationships of π-conjugated polymers in general as well as in understanding the complex color changes in multilayer electrochromic devices. This method allows the construction of color databases from single-colored polymers and their resulting hues when in combination in devices, hence completing the "toolbox" for polymer ECD characterization.

Recently, Padilla and Otero have proposed an alternative approach to the optical characterization of ECPs in the visible range consisting in monitoring the polymer's redox charge density from which its optical properties derive.[21]

2.4. Reflectance Analysis

In a reflective ECD configuration, the reflectivity of a beam is controlled by the optical changes associated with the different redox states of an EC layer deposited onto a metallic substrate (e.g., gold, platinum). The variations in absorbance of the EC layer can be conveniently measured via the light reflected by the metallic surface. Reflectance analyses are especially useful for the characterization of optical attenuators, for instance, and can also provide information on the film topology by taking into account scattered and angular reflected lights.

2.5. Switching Rate

In the context of electrochromism, the switching rate can be defined as the time needed for an electrochrome to switch from one redox state to the other. It depends on several parameters, such as the ability of the electrolyte to conduct ions as well as the ease of diffusion of these counterbalancing ionic species across the EC active layer. In turn, the architecture of the device or the configuration of the cell and the extent of the external bias applied along with the thickness and morphology of the deposited EC layer affect the pace at which the optical change occurs. If rapid switching (in the subsecond magnitude order) is particularly desired for display applications and EC shutters for optical communications, other applications such as switchable window technologies, for instance, are less demanding. However, similarly to CE measurements, the switching rate determination suffers from the variety of methods commonly employed, making further data comparisons between different groups occasionally ambiguous.

2.6. Stability

An ECP must undergo stable redox processes for its electrochromic properties to be reproducible upon repeated switching. The degradation of one of the redox components in an ECD, for instance, will affect the overall performance of the couple, resulting in rapid loss of EC contrast. Typical degradation processes encompass irreversible redox behavior under high potentials, water and oxygen redox interferences with the EC components, degradation of electrode materials or evaporation of the electrolyte, and resistive heating on repeated switching. Improving the ease and effectiveness of the processing techniques employed will generally enhance the quality of the thin-film depositions (in homogeneity, smoothness, and thickness), hence setting the conditions for durable redox processes to occur. Long-term switching stability experiments are commonly carried out in a three-electrode electrochemical cell and via repeated potential cycling or by applying potential steps. The long-term switching performance of an ECP is evaluated on a button electrode or on a transparent conducting substrate such as indium tin oxide (ITO)-coated glass over 10^3-10^6 cycles. ECDs are generally sealed or encapsulated to reduce solvent evaporation and limit air-related side oxidations of the electroactive organic layers. Effective charge compensation across the device will considerably extend its lifetime.

2.7. Optical Memory

The optical or electrochromic memory of an ECP (also called open-circuit memory) can be defined as the propensity of the material to retain its redox/colored state upon removing the external bias. As opposed to emissive technologies such as LEDs and LECs, it is not always necessary for a polymer ECD or display to be powered to exhibit the desired color characteristics. On the other hand, solution-based ECDs (e.g., viologens) see their colored state bleach rapidly in the absence of applied voltage as the electrochromes can freely diffuse and exchange electrons (self-erasing mechanism). In contrast, π-conjugated polymers are well-adhered onto the device electrodes, hence minimizing this self-erasing effect. However, practically, it may be necessary to subject polymer ECDs to refreshing pulses to help maintain the desired redox/colored state. More details on the optical memory of π-conjugated polymers can be found elsewhere.[10,22]

3. Color Control in π-Conjugated Polymers

3.1. Multicolored EC Polymers

3.1.1. Homopolymers and Alternating Copolymers

3.1.1.1. Polythiophenes. To the best of our knowledge, the utility of PTs for EC applications was first suggested in 1983 by Garnier et al.[23,24] and Druy and Seymour[25,26] independently. The unsubstituted PT (**1**) was electrochemically polymerized, and its redox properties were investigated, revealing a red to blue switch on p-doping corresponding to the bleaching of its $\pi-\pi^*$ transition in the visible with simultaneous emergence of infrared charge-carrier optical transitions tailing into the red region. Shirakawa et al. later described the red to black-green color change undergone by **1** on electrochemical n-doping.[27] The energy gap of **1** depends on the molecular weight attained, but generally falls into the 2.0−2.2 eV range. With the idea that oligomers of thiophene can be polymerized at lower oxidation potentials, the electropolymerization of bithiophene has, for example, been achieved onto mesoporous TiO_2 (layered onto FTO-coated glass electrodes) and found to allow unusually large concentrations of polymer to be deposited when compared to using planar Pt or ITO, hence suggesting intimate ECP deposition at the scale of the TiO_2 nanocrystals.[28] The films were neutral-state red, light blue on oxidation (TiO_2 is clear and colorless when neutral), and dark blue on reduction mainly due to the metal oxide changing its valence state.

Given their ease in functionalization and structure-controlled optical properties, PTs have since then attracted a good deal of attention as electrochromes, and various strategies taking full advantage of the different substitution-induced backbone conformations have been proposed to fine-tune the colored neutral state. Table 1 combines useful electrochemical and electrochromic information related to a broad set of PT derivatives which have been investigated in the context of electrochromism.

While increasing the length of an alkyl side chain substituted at the 3-position of thiophene does not significantly change the electrochromic properties of the subsequent polymers (e.g., nonregioregular **2** and **3** are orange-red to blue switching on p-doping),[29,30] it greatly enhances their solution-processability, hence increasing their potential for commercial applications.[31−34] On the other hand, as described by McCullough et al., for example,[33] moving from a nonregioregular arrangement (containing head-to-head (HH) and tail-to-tail (TT) configurations) to a regioregular polymeric system (head-to-tail (HT)) changes the conjugation length and optical features in PTs dramatically. Hence, the electropolymerization of various methyl-substituted bithiophenes by Mastragostino et al. has revealed a coarse tuning of the neutral-state colors in PTs with the “regioregular” analogue of **2** (HT) being red to blue-purple, **4** (TT) being orange to blue-purple, and **5** (HH) being yellow to blue-purple switching on electrochemical oxidation.[29,35] The influence of regiochemistry and sterics in PTs was further emphasized when hexyl pendant groups were appended as illustrated by the pale-green hues exhibited by **6** (TT) and **7** (HH) in their neutral state.[29]

Electropolymerization of the octyl-substituted PT derivative (**3**) (nonregioregular) has been successfully achieved by Jin et al. in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), revealing an orange-yellow to dark blue switch on p-doping in [BMIM]PF_6/ACN and a band-gap of 2.1 eV.[36] Ionic liquids are desired for being environmentally friendly when compared to other common organic solvents. The electrochemical synthesis of nonregioregular **3** was also investigated in an aqueous medium in the presence of the surfactant sodium dodecyl sulfate.[37] This study revealed a dark red to blue-green switch on oxidation. The same polymer was further investigated in a polymer electrolyte-based ECD.[36,38] Other nonregioregular

Table 1. Representative Polythiophene Electrochromes

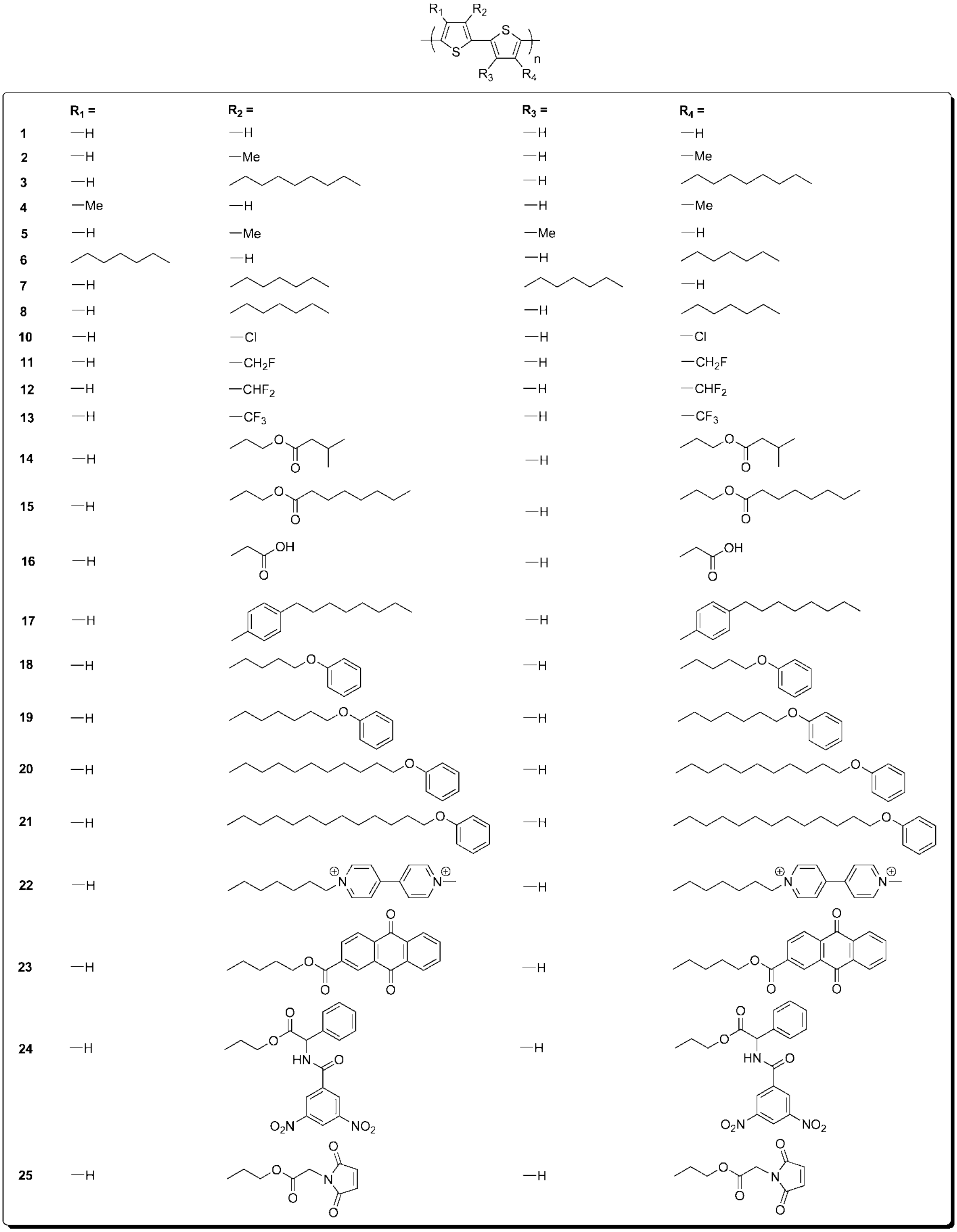
			polymer electrochromism[c]			
polymer	λ_{abs}[a] (nm)	E_{gap}[b] (eV)	n	i	d	ref
1	~480	2.0−2.2	red		blue	23−25, 35, 84
2[d]	500	1.97	orange-red		blue	29, 30, 36
2[e]	505	n/a	red		blue-purple	29, 35
3[d]	430−440	2.10	orange-red		blue	29, 30, 36, 44
4	445	n/a	orange		blue-purple	29, 35
5	414	n/a	yellow		blue-purple	29, 35
6	390	n/a	pale green		pale blue	29
7	390	n/a	pale green		pale blue	29
8[d]	460	2.00	orange-red		pale blue	36
8[e]	455	n/a	orange-red		pale blue	29
9	509	1.87	bright red		green-blue	39
10	520	1.74	deep red		deep blue	39
11	n/a	n/a	red-orange		slate-green	43
12	n/a	n/a	red		blue	43
13	n/a	n/a	red		blue	43
14	402	n/a	red		blue	44
15	434	1.96	yellow		blue	45
16	440	n/a	red		black	46
17	n/a	n/a	red-purple		blue-purple	47
24	425	2.92	yellow		light blue	53
25	417	2.34	yellow		blue	54
26	415	2.0	red-orange	brown	green	55
27	476	2.03	brown		blue	58
28	421	2.19	yellow		blue	59
29	456	2.12	orange	green	blue	59
30	427	2.2	brown		gray-blue	60
31	~775	~1	blue		transmissive green-yellow	63, 64
32	717	0.95	blue-black		transmissive light yellow	65
33−36	670−720	0.95−1.13	blue		transmissive yellow	66
37	804	0.85	deep blue		transmissive tan	67, 68
38	738	1.2	blue-green		pale blue-gray	72, 73
39	720	1.03	pale blue		transmissive light blue	74, 75
41	485−505	1	red		purple	77, 78
42	580	1.73	deep blue		transmissive	79
43−44	498 (533)	n/a	red		dark blue	82
45	n/a	n/a	yellow		dark blue	82
46−52	518−572	~1.7	dark red		dark blue	80
53	422	2.18	yellow		light gray	81

[a] Absorption maximum of the neutral-state thin-film polymer. [b] Optical band-gaps as calculated from the onset of the $\pi-\pi^*$ transition of the neutral-state polymer. [c] Key: (n) neutral state, (i) partially oxidized state, (d) fully oxidized state. [d] Nonregioregular. [e] "Regioregular" (electrochemical polymer of a head-to-tail dimer).

polymers such as **2** and **8** possessing bright red and orange-red neutral states have also been synthesized in [BMIM]PF_6.[36] Polymers **2**, **3**, and **8** exhibited switching times ranging from 1 to 2 s at the considered film thicknesses (nonindicated) which increased with lengthening alkyl substituent, coloration efficiencies on the order of 220−250 $cm^2\ C^{-1}$, and long-term switching stabilities in [BMIM]PF_6/ACN with only a few percent transmittance loss after 1000 cycles. Interestingly, the copolymer of a 3-chloro-substituted thiophene with a 3-methyl derivative yielded in [BMIM]PF_6 a polymer (**9**) with higher EC contrasts than the all chlorine-substituted nonregioregular homopolymer **10**.[39] While the homopolymer **10** showed a band-gap of 1.74 eV and switched from deep red to deep blue, the copolymer **9** showed a slightly higher band-gap of 1.87 eV and changed from bright red to green-blue on p-doping. The switching properties of the homopolymer **10** synthesized from [BMIM]PF_6 were also investigated on TiO_2 and incorporated into a TiO_2-based ECD which showed less than 2% contrast loss over 1000 cycles,[40] while the same polymer showed poor redox reversibility onto ITO and lost its switching ability after 580 cycles.[39]

Besides the conformational changes induced by incorporation of substituents along PT backbones, substitution at the 3- and 4-positions of thiophene inhibit the α,β- and β,β-cross-links which can be produced upon electropolymerization and typically lower the quality of the films obtained (e.g., conductivity, optical properties).[41] Substitutions have also been shown to increase the electron-rich character of thienyl monomers and lower their oxidation potential, hence preventing polymer overoxidation processes from occurring during the preparation of the films.[41] Alternatives have consisted in electropolymerizing blocks of several thienyl units (oligomers) which also have lower oxidation potential than a single thiophene unit[23,24,26] or in using strong Lewis acids[42] in replacement of the conventional organic solvents.

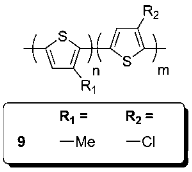
The effect of other pendant groups encompassing fluorinated substituents (as in nonregioregular **11−13**)[43] and various ester (as in nonregioregular **14−16**)[44−46] and aromatic groups (as in nonregioregular **17−21**)[47−50] on the redox and electrochromic properties of PTs has been investigated. For example, a simple variation in the nature of the ester substituent between **14** and **15** (branched vs linear, respectively) was sufficient to change the neutral-state color from red to yellow while retaining the same blue oxidized state. The acetic acid derivative **16** was found to switch from red to black on p-doping. From all the phenyl-substituted polymers **17**−**21**, the one with the aromatic ring directly appended to the thienyl core (**17**), switching from red-purple to blue-purple on p-doping, exhibited the most significant changes in color when compared to simple alkyl-substituted analogues. Other functionalities such as viologen[51] (**22**) and anthraquinone[52] (**23**) have been incorporated onto PT backbones to produce electrochromes with multiple color states attainable via reduction of the side chains. In particular, **22** switched to violet at the first viologen reduction and orange at the second, whereas **23** turned black on forming the radical anion on anthraquinone. The dinitrobenzoyl-derivatized PT **24** was electrochemically synthesized at relatively low potentials in the presence of a Lewis acid producing a neutral state yellow to light blue switching ECP on p-doping.[53] Similarly, with a band-gap of 2.34 eV, the maleimide-substituted PT **25** was found to change from yellow to blue on oxidation in good contrasts (41% as the considered film thickness, nonindicated) and switching time (1.7 s).[54]

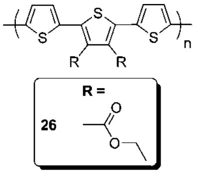


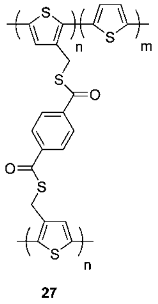
The electropolymerization of a terthiophene derivatized with ethyl ester groups has yielded a hybrid (**26**) with a band-gap of 2.0 eV notably lower than that of a conventional alkyl-substituted PT owing to the moderate electron-withdrawing character of the ester substituents.[55] The neutral-state red-orange polymer switched to brown and then green on electrochemical oxidation.

Sotzing et al. have reported on novel polynorbornylenes with terthiophene side chains which were thermally nanoimprinted by lithography onto ITO and the pendant groups electrochemically oxidized (into **1**) to demonstrate a nanopattern of π-conjugated ECP.[56] The deposited composite changed from colorless to blue upon oxidation of the terthiophenes and turned orange upon subsequent reduction of the oxidized PT backbone. In a different study, polynorbornylenes with terthiophene side chains were further imprinted onto ITO at the micrometer scale by photolithography.[57] The PTs were subsequently polymerized electrochemically from the pendant terthiophenes, hence without using high-energy UV radiations.

Toppare et al. have synthesized thienyl monomers bridged at their 3-position by a terephthalic linkage and have investigated their redox and EC properties in a copolymer with thiophene (**27**).[58] A band-gap of 2.03 eV was found, and the polymer could be switched from a brown neutral state to a blue oxidized state. Similarly, thienyl monomers bridged at their 3-position via a succinic linkage have been homo- and copolymerized with unsubstituted thiophene comonomers to yield **28** and **29** with band-gaps of ca. 2.2 eV.[59] While the homopolymer possessed only two color states on p-doping, a neutral-state yellow and a blue oxidized state, the copolymer was found to change from orange to green (intermediate state) to blue in the same conditions. A copolymer of unsubstituted thiophene and thienyl monomers bridged at their 3-position via a phenoxy linkage was also synthesized (**30**) which afforded a band-gap of 2.2 eV and a brown to gray-blue switch upon electrochemical oxidation.[60] Multichromic ECPs resulting from the random copolymerization of two significantly different monomers will be furthered discussed in section 3.1.2.







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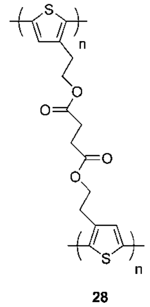

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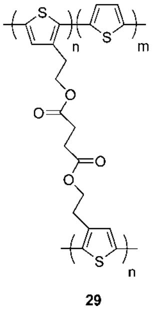

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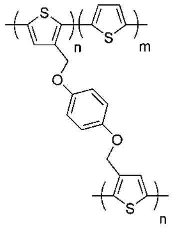

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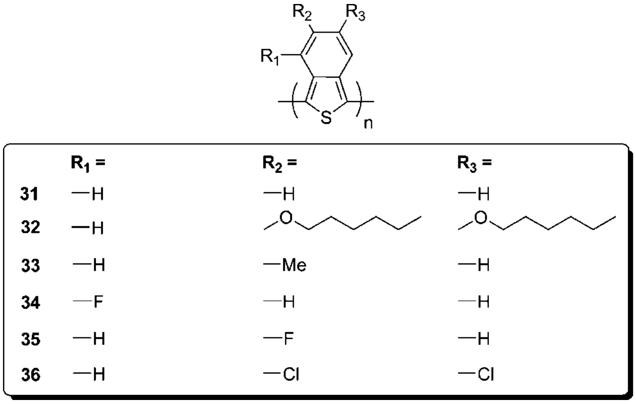
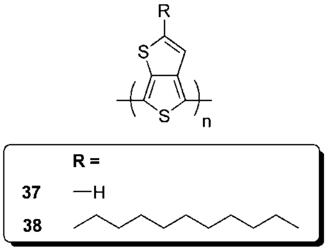
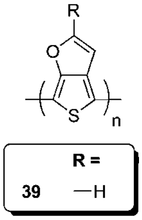
The original idea of Wudl for narrowing the energy gap in PTs via the polymerization of fused aromatic systems with high resonance energies, hence lowering the extent of bond-length alternation when in π-conjugation,[61] has led to the preparation of homopolymers of isothianaphthene.[62−64] Exhibiting a neutral-state blue to transmissive green-yellow switch on p-doping and a band-gap on the order of 1 eV, poly(isothianaphthene) (**31**) is one of the first reported examples of a cathodically coloring ECP.[64] The difficulties in film processing from **31** as well as its relatively low ambient stability or under p/n-doping conditions have motivated the synthesis of substituted derivatives susceptible to enhance at least one of these aspects. For instance, the introduction of electron-donating alkoxy substituents (as in **32**) has accounted for an increase in solvent-processability without significantly changing the energy gap (0.95 eV) when compared to **31**.[65] Polymer **32** was blue-black in its neutral state and transmissive light yellow on oxidation. In parallel, the presence of methyl (**33**), fluorine (**34**, **35**), or chlorine (**36**) groups on the adjacent benzene has resulted in polymers with lower reduction potentials (i.e., higher electron affinity), yet retaining similar band-gaps and electrochromicity.[66] Sotzing et al. have investigated the electrochromicity of homopolymers of thieno[3,4-*b*]thiophene-based precursors. The unsubstituted polymer **37** exhibited a band-gap of 0.85 eV and revealed a deep blue to transmissive tan switch on oxidation.[67,68] Poly(styrenesulfonate) (PSS)-dispersed water-soluble versions of **37** have been made by the same group.[69,70] From the unsubstituted thieno[3,4-*b*]thiophene monomer, a series of symmetrical dimers have been synthesized and electrochemically polymerized into polymeric networks with band-gaps of ~0.9 eV.[71] Their electrochromic behavior varied from a neutral-state sky blue switching to pale blue or brown or colorless on p-doping. Expectedly, the alkyl-substituted polymer **38** produced by Pomerantz et al. showed a higher band-gap value of 1.2 eV and was blue-green in the neutral state and pale blue-gray on full oxidation.[72,73] The unsubstituted thieno[3,4-*b*]furan polymer (**39**) was electrochemically synthesized, exhibited a higher band-gap of 1.03 eV when compared to **37** but lower than that of PEDOT (**210**) which will be further discussed in section 3.2.1.2, by about 0.6 eV. Polymer **39** revealed a pale blue to transmissive light blue switch on oxidation.[74,75] As in **37** and in the isothianaphthene-based polymer (**31**) the fused furan heterocycle stabilizes the quinoidal geometry of the polymer main chain and reduces the polymer's bond-length alternation.

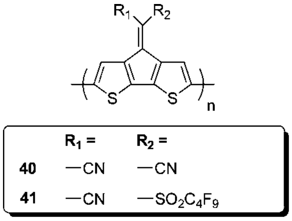
Increasing the planarity in π-conjugated polymers generally results in narrowing the energy gap of the material,[76] which in turn induces a bathochromic shift of its neutral-state spectral absorption and changes its color. Various homopolymers of cyclopentadithiophene (**40**−**42**) and naphthodithiophene (**43**−**45**) have been subjected to electrochemical and electrochromic characterization. While the electropolymerized analogue **41** exhibits a band-gap of about 1 eV and switches from red to purple on p/n-doping,[77,78] the chemically synthesized dialkyl-substituted polymer **42** possessing solubilizing groups out of the plane of the polyheterocyclic backbone was found to be deep blue in its neutral state and highly transmissive upon oxidation and revealed a notably larger optical band-gap of 1.73 eV.[79] For this latter analogue, CEs as high as 932 cm^2 C^{-1}, response times as short as 0.75 s, and less than 8% contrast loss over 1000

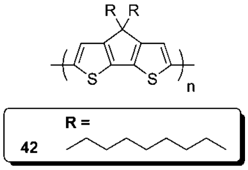


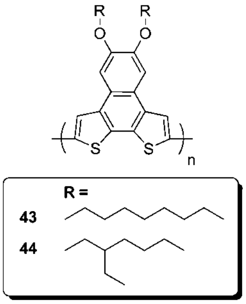


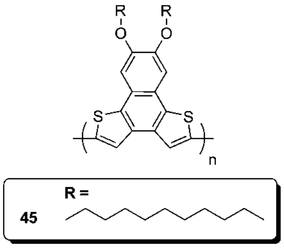


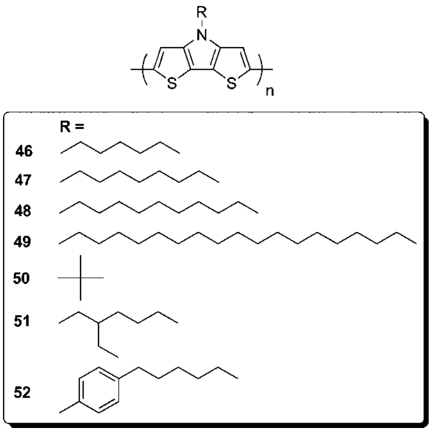
cycles were reported. Rasmussen et al. have synthesized a family of N-substituted dithienopyrroles (**46**−**52**) with band-gaps of ∼1.7 eV and switching from dark red to dark blue (colors were read from available photographs).[80] The electrochemically prepared polymer of a diphenyl-substituted dithienothiophene (**53**) showed a much wider band-gap of 2.18 eV, likely due to the steric hindrance associated with the bulky phenyl side groups.[81] This polymer switched from yellow to light gray on oxidation.

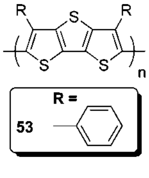












While the naphthodithiophene derivatives **43** and **44** are neutral-state red switching to dark blue on p-doping, the analogue **45** does not show the same conjugation path owing to the arrangement of its thienyl centers, thereby revealing a wider band-gap and a yellow neutral state.[82]

Deep blue to transmissive dialkyl-substituted cyclopentadithiophene homopolymer **42** was further investigated as a nanocomposite with TiO_2 nanorods.[83] A 50% increase of CE was monitored for the nanostructures when compared to that of the polymer alone with nearly no change in transmittance ratios.

3.1.1.2. Polypyrroles. Exhibiting lower oxidation potentials than PTs, hence better film-forming properties, along with superior compatibility in aqueous media and relatively high conductivities (>100 S cm^{-1} in early work), polypyrroles (PPs) have primarily been considered for their utility as synthetic metals as well as for biomedical applications.[10] PPs have occasionally been characterized in terms of their electrochromic properties, taking advantage of versatile functionalization methods operated either at the nitrogen or at the 3- and/or 4-positions of the pyrrole heterocycle.

Early work was focused on forming films of unsubstituted pyrrole to yield polymer **54**.[85−88] Interestingly, its band-gap value of 2.7 eV and yellow to brown-black switch[87] on p-doping were not significantly affected by the successive *N*-alkyl and *N*-phenyl functionalizations which yielded PPs **55**−**59**. This result demonstrated a small extent of substituent-induced steric hindrance along the backbone of the corresponding homopolymers.[89] On the other hand, the structural modifications achieved at the nitrogen position raised the monomer oxidation threshold and reduced the conductivity values of the doped PPs. This last result was later confirmed throughout a conductivity study of electrochemical copolymers of unsubstituted pyrrole with different *N*-substituted analogues and various monomer to comonomer compositions.[90,91] While the *N*-benzyl-PP (**60**) and *N*-tolyl-PP (**61**) showed only limited EC contrasts on oxidation in aqueous solution when compared to the *N*-methyl-derivatized PP (**55**), the *N*-phenyl-PP (**59**) and *N*-benzoyl analogue (**62**) did not show any EC activity at all.[92] In contrast, benzylideneamino groups *N*-substituted on pyrrole (such as in **63**−**67**) have shown notable bathochromic shifts in the visible as demonstrated by their red to blue electrochromism similar to that of PTs on p-doping.[93] The dinitrobenzoyl-derivatized PP (**68**) was electrochemically polymerized at various thicknesses, demonstrating a green-yellow to green-brown neutral state (depending on the considered thickness) and a blue-gray oxidized state.[94] The branched pyrrole-based system **69** obtained via electropolymerization of the pyrrole pendant groups revealed a band-gap of 2.97 eV and a red to turquoise switching behavior on oxidation.[95]

Besides the compatibility enhancement observed in aqueous solution, the use of a rfactant such as sodium dodecyl sulfate and sodium dodecyl benzenesulfonate has allowed a fine modulation of the electrochromicity of PP (**54**), switching from transmissive yellow to violet to brown on p-doping in the first instance and to dark blue in the second.[96,97] Electropolymerization of **54** in ionic liquids has been described to change the morphology of the films significantly (ordered nodular topologies) in comparison with those made in conventional organic solvents and to enhance the EC properties of the films.[98] Girotto et al. have reported on the effect of incorporating dyes on the EC behavior of a network of **54**. In this study, **54** was synthesized in the presence of Remazol Black and Dianix Red to yield composites with enhanced chain ordering (as demonstrated by XRD and Raman spectroscopy) and more efficient EC behavior.[99] Girotto and De Paoli have also demonstrated the EC enhancement by electropolymerizing PPs in the presence of both a dodecyl sulfate surfactant and a water-soluble dye as opposed to using the surfactant only.[100]

Song et al. have electrodeposited a polymer composite (**70**) resulting from the combination of doped **54** charge balanced with poly(3-methyl-2-{[3-(4-vinylbenzyl)-3*H*-benzothiazol-2-ylidene]hydrazono}-2,3-dihydrobenzothiazole-6-sulfonic acid) (PABTS) on ITO and have investigated its EC properties.[101] Three distinct color states have been identified encompassing a brown state (in the absence of an external bias), a yellow state (on reduction of PP), and a green-blue state (on oxidation of ABTS).

Films of **55** have been deposited onto carbon nanotubes in ionic liquids and the EC properties of the composite investigated, revealing a pale-yellow to brown switch on p-doping.[102]

In analogy with PTs, dimers of *N*-methylpyrrole possessed lower oxidation potentials than their monomer counterpart, thereby facilitating the film depositions and diminishing the risks of overoxidizing the growing polymer during the electropolymerization process. Surprisingly, a hypsochromic shift of the onset of optical absorption of the neutral polymer was monitored following this method, which enhanced the transmissivity of the subsequent polymer in its neutral state.[103−106] The corresponding electrochrome was transmissive pale yellow in its neutral state and gray-blue when fully oxidized.

In contrast with *N*-functionalizations, substitutions at the 3- and 4-positions of pyrrole are synthetically challenging owing to the low inherent stability of the monomer under atmospheric conditions, and the air sensitivity of the resulting polymers has seemingly hindered the development of this family of electroactive materials for EC applications. However, a few studies describing the redox properties of *C*-substituted PPs such as **71**−**73** and **74**−**77** (nonregioregular), for example, have been reported.[103,107,108]

Cihaner has investigated the electrochemical polymerization of pyrrole monomers bridged at the *N*- position by a polyether linkage as well as the EC properties of the resulting polymer **78**.[109,110] Polymers such as **78** are known to produce polyether pseudocages with metal ion complexing properties. In the case of **78**, a band-gap of 2.8 eV was found, and the polymer could be switched form a yellow-green neutral state to a dark green oxidized state. A copolymer with pyrrole (**79**) (1:1) exhibited a band-gap of 2.68 eV, which was intermediate to that of PPs **54** and **78**.[110]

Table 2. Representative Polypyrrole Electrochromes

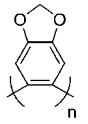
polymer	λ_{abs}[a] (nm)	E_{gap}[b] (eV)	polymer electrochromism[c] n	i	d	ref
54	~370	2.7	yellow		brown-black	87, 93
55−**58**	n/a	n/a	yellow		black	89
63−**67**	330−360	n/a	red		blue	93
68	350 (390)	n/a	green-yellow/ brown		blue-gray	94
69	346	2.97	red		turquoise	95
78	302	2.8	yellow-green		dark green	109, 110

[a] Absorption maximum of the neutral-state thin-film polymer. [b] Optical band-gaps as calculated from the onset of the $\pi-\pi^*$ transition of the neutral-state polymer. [c] Key: (n) neutral state, (i) partially oxidized state, (d) fully oxidized state.

Table 2 summarizes some of the key values and EC properties of the representative PPs that have been reported to date.

3.1.1.3. Poly((alkylenedioxy)benzene)s.

Xu et al. have electrosynthesized two poly((alkylenedioxy)benzene)s, namely, poly(1,2-(methylenedioxy)benzene) (**80**) and poly(1,2-(ethylenedioxy)benzene) (**81**), in the Lewis acid boron trifluoride diethyl etherate, and they have characterized the homopolymers' EC properties.[111] The proposed polymerization pathway through the 4- and 5-positions of the benzene rings suggested structures 1 and 2, which were supported by IR, NMR, and theoretical calculations. Polymer **80** exhibited a grass green to light nacarat (or light pink from the photographs available) switch upon p-doping, whereas polymer **81** showed a bottle green to nacarat color change under the same conditions. band-gaps of 2.12 and 2.45 eV were determined from the UV−vis spectra of **80** and **81**, respectively. **80** has also shown a good propensity to electropolymerize in the ionic liquid [BMIM]PF_6.[112]



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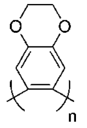

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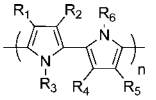
3.1.1.4. Poly(thienylenevinylene)s.

Thienylenevinylene copolymers illustrate well the effect of inserting an unsubstituted conjugated spacer between two heterocycles which would commonly interact in the parent homopolymer. For instance, as described by McCullough et al. and others, a polymer arising from the nonregioregular polycondensation of 3-alkythiophene shows a high extent of steric hindrance related to the in-plane substitution of the pendant groups and their forced proximity within the subsequent polymer backbone. In turn, the side-chain-induced steric hindrance causes the intrinsic band-gap of the polymer to increase in parallel with the degree of out-of-planarity twisting of the conjugated backbone. In contrast, the resulting increase in backbone planarity associated with the alternating insertion of an unsaturated linkage promotes the extension of conjugation and narrows the energy gap of the subsequent polymer, thereby providing a fine-color-tuning useful in the context of electrochromic applications. Experimentally, mono- and



	R_1 =	R_2 =	R_3 =	R_4 =	R_5 =	R_6 =
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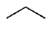
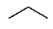
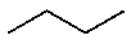
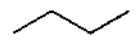
56	—H	—H		—H	—H	
57	—H	—H		—H	—H	
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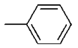
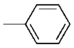
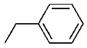
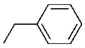
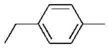
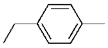
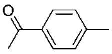
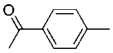
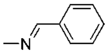
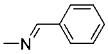
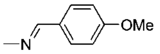
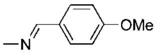
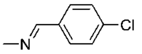
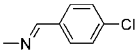
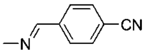
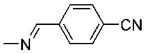
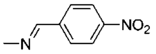
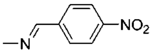
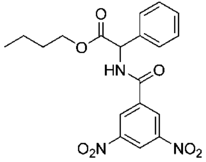
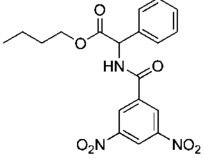
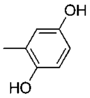
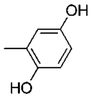
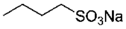
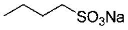
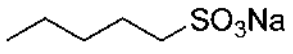
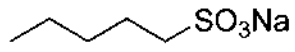
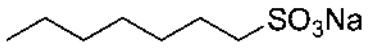
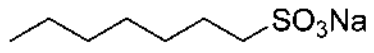
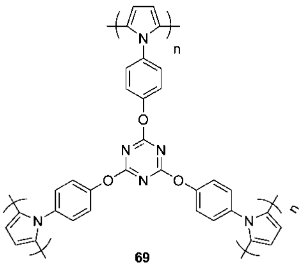
59	—H	—H		—H	—H	
60	—H	—H		—H	—H	
61	—H	—H		—H	—H	
62	—H	—H		—H	—H	
63	—H	—H		—H	—H	
64	—H	—H		—H	—H	
65	—H	—H		—H	—H	
66	—H	—H		—H	—H	
67	—H	—H		—H	—H	
68	—H	—H		—H	—H	
71	—Me	—H	—H	—H	—Me	—H
72	—H	—Me	—H	—Me	—H	—H
73	—H	—Me	—H	—H	—Me	—H
74	—H		—H	—H		—H
75	—H		—H	—H		—H
76	—H		—H	—H		—H
77	—H		—H	—H		—H



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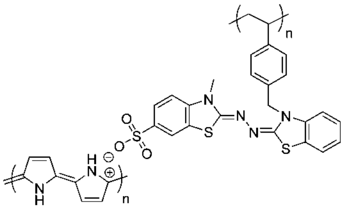

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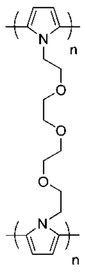

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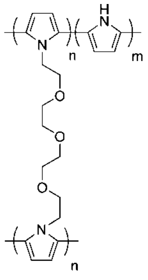


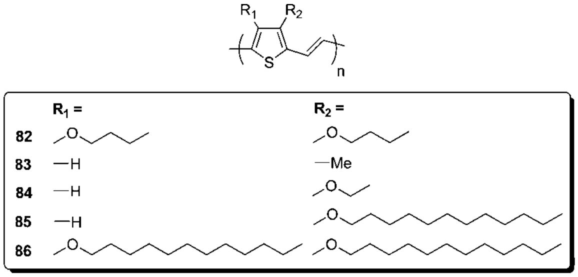
79

disubstituted poly(thienylenevinylene)s exhibited significant bathochromic shifts in comparison with their fully heterocyclic analogues and revealed band-gaps ranging from 1.5 to 1.7 eV while switching from a neutral-state deep blue to transmissive light gray on p-doping for the cited examples **82−86**.[113−115] A poly(bisthienylenevinylene) analogue has been described with emphasis on its thin-film conductivity and redox properties.[116] Its electrochromic properties were not reported.

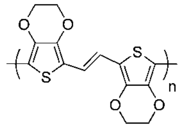
A thienylenevinylene copolymer with a repeat unit consisting of two 3,4-(ethylenedioxy)thiophene (EDOT) electron-rich units for only one vinylene spacer (**87**) has been investigated via the electropolymerization of its low oxidation potential macromonomer (*E*)-1,2-bis(3,4-(ethylenedioxy)-2-thienyl)vinylene.[117−119]

Polymer **87** exhibited a narrow band-gap of 1.4−1.5 eV[117−119] (i.e., a decrease on the order of 0.1−0.2 eV compared to that of **210**, which will be discussed further in section 3.2.1.2), and thin films made thereof could be redox cycled reversibly between a deep purple neutral state and a transmissive sky blue upon full oxidation in less than 2 s. After 600 cycles (applying square-wave potential steps), the polymer retained 47% of its optical contrast. The strictly alternating homologue **88** showed a band-gap as low as 1 eV,[118,120] although its electrochromic properties were not explored.

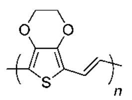
Yongfang Li et al. have developed various thienylenevinylene polymeric hybrids with π-conjugated side chains and/or tethered π-conjugated building blocks (the tether being π-conjugated as well) with the goal of producing polymers absorbing over a broad bandwidth of the UV−vis spectrum.[121] If their mainstay has been to apply their systems in photovoltaic devices and compare the performance of their polymers as a function of the structural changes operated, they have nonetheless mentioned the potential of their materials such as **89** switching from black to yellow on p-doping for EC applications.[122]

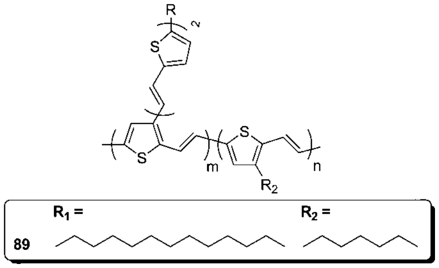


87



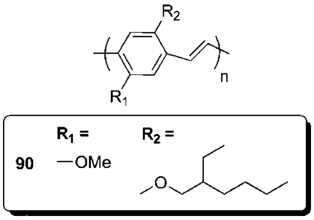
88





3.1.1.5. Poly(phenylenevinylene)s.

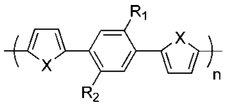
Besides the considerable research effort placed on characterizing its charge-transport and light-harvesting performance, poly(1-methoxy-4-((2-ethylhexyl)oxy)-*p*-phenylenevinylene) (MEH-PPV, **90**) has been investigated in terms of its EC properties.[123,124] **90** shows a band-gap of 2.18 eV and a relatively stable red-orange to brown-green[123] or blue[124] switch on p-doping. The polymer did not appear particularly stable on repeated n-doping.[123]

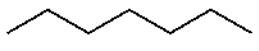
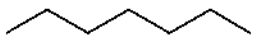
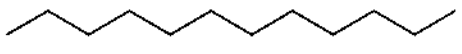
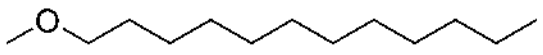
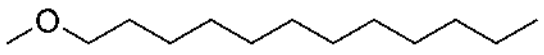
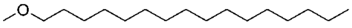
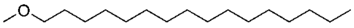
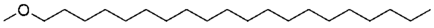
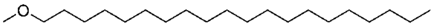
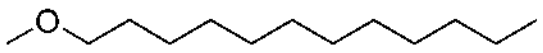
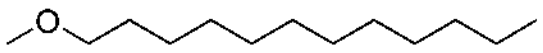
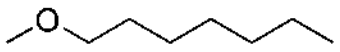
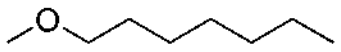


3.1.1.6. Poly(thienylenephenylene)s and Analogues.

Taking advantage of the ease in functionalizing phenylene heterocycles (symmetrically or not) and the effect of the substitution on the torsion of the subsequent backbone, polymeric hybrids with band-gaps varying from 2.1 to 2.7 eV have been chemically or electrochemically synthesized and their redox properties described. For instance, while the unsubstituted bis(thienyl)phenylene (**91**) shows a gap of 2.3 eV,[125−127] the functionalization of the phenyl heterocycle with methyl groups as in **92** raises the gap to 2.7 eV.[128] In contrast, substituting the phenyl with alkoxy groups as in **93** increased the electron density of the ring considerably while adding a favorable oxygen−sulfur interaction, hence overcoming the effect of the sterics and narrowing the gap to values as low as 2.1 eV. Although further substitutions with longer solubilizing groups were achieved,[127−129] opening perspectives in solution-processed device fabrication, the electrochromic properties of the corresponding polymers **94**−**100** were not provided. In general, pyrrolyl- and furanylphenylene analogues **101**−**108** showed similar trends,[130−133] with the pyrrolylphenylene derivatives exhibiting energy gaps (2.3−2.4 eV) lower than those of the pyrrole and *p*-phenylene parent homopolymers, but again the EC properties were not described. Toppare et al. have synthesized the poly(selenophene-ylbenzene) hybrid **109** switching from a neutral-state orange to green oxidized state on p-doping (as seen from the photographs available).[134] This polymer exhibited a relatively low band-gap of 1.85 eV when compared to that of the unsubstituted **91** (2.3 eV). On the other hand, the alternating oligoether-substituted polymers **110**−**113**, soluble in most polar organic solvents, possessed enhanced film-forming properties which allowed the polymers to be switched reversibly from their neutral-state red to their blue oxidized state more than 10 000 times in water and ACN without significant loss of redox performance.[135,136]

When the thiophenes were replaced by the more electron-dense EDOT, polymers with especially low oxidation potentials (**114**−**119**) were produced with energy gaps ranging from 1.8 to 2.2 eV as a function of the nature of the pendant groups substituted on the phenyl ring. Switching from their neutral-state pale red to green when partially oxidized and deep blue when fully oxidized, the synthesized EDOT−dialkoxybenzene derivatives **114**−**118** appeared as excellent candidates for multicolor display applications.[137−139] In a separate study, the fluorinated derivative **119** was produced which exhibited a neutral red to blue-black hue on oxidation.[140] As demonstrated by



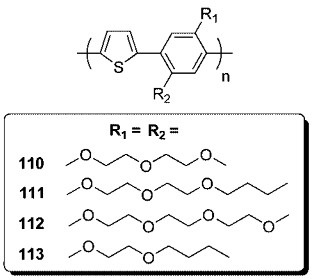
	X =	R_1 =	R_2 =
91	S	—H	—H
92	S	—Me	—Me
93	S	—OMe	—OMe
94	S		
95	S		—OMe
96	S	—OMe	
97	S		
98	S		
99	S		
100	S		
101	NH	—H	—H
102	NH	—OMe	—OMe
103	NH		
104	O	—H	—H
105	O	—Me	—Me
106	O	—OMe	—OMe
107	O		
108	O	—OMe	
109	se	—H	—H

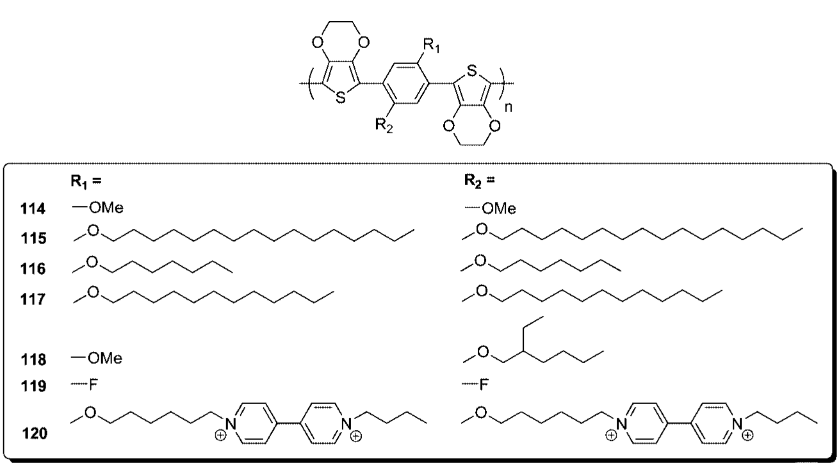
Moon et al. in incorporating viologen moieties onto a BisEDOT−phenylene main chain,[141] EC pendant groups can also be appended along an EC backbone and controlled separately when their changes in redox state occur at different thresholds. Thereby, novel color states become available which are not readily accessible from the nonfunctionalized analogues. In the case of **120**, a crimson hue was observed in the neutral state (main-chain neutral, pendant-chromophore neutral) that changed to purple on partial oxidation of the pendant viologen (radical cation), magenta on further oxidation (dication), pale tan-cream on partial oxidation of the polymer backbone, and transmissive light blue when both chromophores are fully oxidized. Following this, the optical and redox properties of the (3,4-(propylenedioxy)thiophene-yl)phenylene analogues **121** and **122** were reported along with their EC behavior.[142] In particular, homogeneous films of **122** could be prepared by spin-coating or spray-casting which were then progressively oxidized to yield a neutral-state orange-red and a light gray oxidized state. Both polymers showed an optical band-gap of 2.1 eV, which is 0.2 eV lower than that of the unsubstituted thiophenic parent **91**. The out-of-plane conformation adopted by the ProDOT substituents (which will be further described in section 3.2.1.3) in the polymeric hybrids **121** and **122** thus proved useful in affording materials with band-gaps practically independent of the substitution pattern.

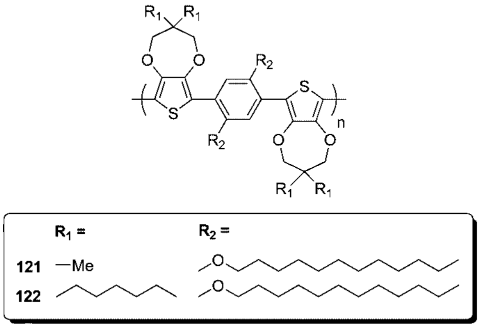
The incorporation of either an extra phenylene moiety or a fused phenylene-derivatized building block shows only limited effect on the band-gap and electrochromic features of the subsequent poly(thienylenephenylene) copolymers. For instance, while **123** changes from yellow to green on oxidation, **124**−**128** all show a comparable transmissive yellow to blue-green switch and band-gaps ranging from 2.4 to 2.9 eV.[125,143]

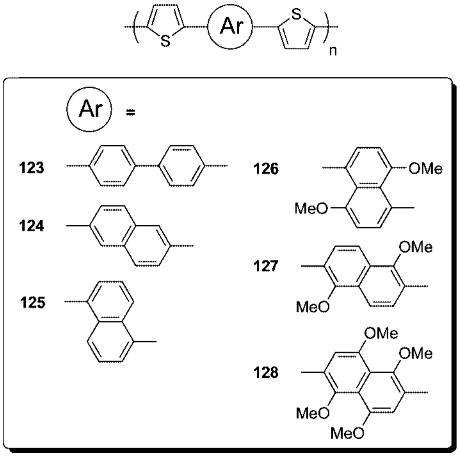
The BisEDOT−anthracene polymer hybrid **129** revealed a remarkably lower band-gap of 1.57 eV as estimated from the ITO-electropolymerized films.[144] Surprisingly for a polymer with such a low reported band-gap, its neutral state was found to be yellow and switched to blue on p-doping.

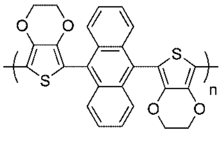
3.1.1.7. Poly(thienylenepyrrole)s and Analogues. Following the work of Ferraris et al.,[145,146] Toppare et al. and Cihaner et al. have investigated the redox behavior of a series of ECPs achieved by the electropolymerization of various *N*-functionalized dithienopyrrole macromonomers, reporting band-gaps and the sometimes surprising color shades described below. While the nonfunctionalized dithienopyrrole derivative **130** possesses a relatively high band-gap of 2.61 eV and switches from yellow-orange to dark blue on p-doping,[147] the phenyl-substituted analogue **131** shows a yellow to green switch and a much lower band-gap of 2.2 eV.[148] In contrast, the benzyl-substituted derivative **132** revealed a light gray to dark gray switch on p-doping and an even smaller band-gap of 1.9 eV.[149] The naphthyl (**133** and **134**), fluorene (**135**), and benzo-crown (**136**) derivatized hybrids were found to switch from a neutral-state yellow to green and blue on partial oxidation and to violet when fully oxidized.[150−153] Interestingly, the benzo-crown showed the smallest energy gap (2.14 eV) of this series (2.14−2.4 eV). In contrast, the alkylamine-functionalized polymer **137** showed a claret red to blue switch upon p-doping and a band-gap of 2.27 eV.[154] The benzamine-substituted analogue **138** changed from yellow to blue on oxidation with a smaller band-gap of 2.12 eV.[155] The (fluorophenyl)- and (nitrophenyl)dithienopyrrole polymers **139**, **140**, **141** and **142** have shown band-gaps of 1.94, 2.11, 2.18, and 2.15 eV, respectively.[156−160] **139** changed from yellow to blue, **140** changed from yellow to green to light purple, and **141** changed from yellow to green to gray to blue on p-doping. A dithienopyrrole system based on the substitution of the dye 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene at the *N*-center was polymerized (**143**) with a band-gap of 2.9 eV and a purple to violet to gray-green switching pattern on p-doping and purple to pink on n-doping.[147]











129

Toppare et al. have investigated the electrochemical polymerization of dithienopyrrole monomers bridged at the *N*-position by a polyalkyl linkage as well as the EC properties of the resulting polymer **144**.[161] A band-gap of 2.16 eV was found, and the polymer switched from a yellow neutral state to a green intermediate state to dark green when fully oxidized. A copolymer with EDOT (1:1) exhibited a smaller band-gap of 1.89 eV which was intermediate to that of **210** and **144**, as well as five different color states on oxidation: purple, brown, green, teal, and blue.

Pozo-Gonzalo et al. have investigated the EC properties of the thienopyrrole hybrid **145** resulting from the electropolymerization of the unsymmetrical precursor 2-(2-thienyl)-1*H*-pyrrole.[162] Surprisingly, the energy gap of **145** (1.6−1.7 eV claimed) was lower than that of both **54** (2.7 eV) and **1** (2.3 eV), which was attributed to an effect of enhanced delocalization. The regiorandom hybrid **145** was found to switch from its neutral-state orange to a black colored state on p-doping. On further investigations, the *N*-substituted derivatives **146** and **147** revealed a multicolored EC behavior changing from light brown (neutral) to light blue (partially oxidized) to blue-gray (fully oxidized) to brown (partially reduced) on oxidation, while changing to dark orange (partially reduced) and light orange (fully reduced) on reduction.[163] Optical contrasts as high as ~30% were monitored for **146** and **147**, whereas only ~20% was attainable with **145** (at the considered film thicknesses, nonindicated).

3.1.1.8. Poly(thienylenefuran)s and Analogues. Several groups have described the polymerization of furan[164−169] (**148**), with the earliest study dating back to 1982 and reported by Garnier et al.[170] More recently, Önal et al. have successfully electropolymerized the high oxidation potential furan heterocycle in a mixture of ACN, BF_3, and Et_2O/$TBABF_4$ solution electrolyte.[171] Spectroelectrochemical characterization of the polymer thin films deposited on ITO-coated glass revealed a band-gap of 2.1 eV, along with a yellow-green to gray switch on p-doping.

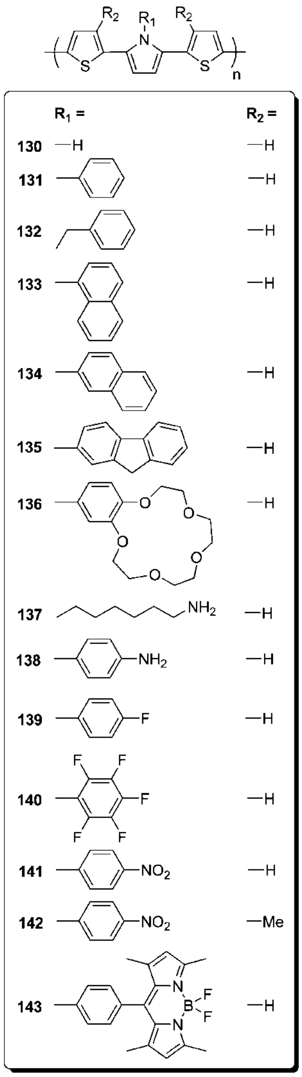
Electropolymerization of a 2,5-bis(2-thienyl)furan in an EtOH/$LiClO_4$ solution electrolyte has yielded an ECP (**149**) with a moderate band-gap of 2.2 eV, switching from a neutral-state orange to a black oxidized state.[172] However, the maximum transmittance change observed was relatively modest (~21%) at the considered film thickness (nonindicated) and the polymer's response time rather long: 4.5 s to attain 90% of the total transmittance from the neutral to oxidized state and 8.5 s from the oxidized state back to the neutral state. With a significantly lower optical band-gap of 1.7 eV, the BisEDOT−furan electrochemical polymer analogue **150** was found to switch from deep blue to blue on oxidation.[117,173]

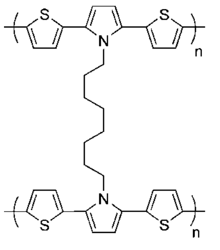
A series of 1,4-bis(2-furanyl)benzene derivatives (**151**−**155**) with band-gaps ranging from 2.3 to 2.6 eV was electrochemically polymerized, and the thin-film conductivities were investigated when electrochemically oxidized with perchlorate dopants.[131] As previously mentioned in section 3.1.1.6, their EC properties were not described.

3.1.1.9. Poly(thienylenepyridine)s and Analogues. When questions relative to the nature of the charge carriers that could possibly be created as a function of the supporting π-conjugated polymer backbone emerged, the donor−acceptor approach came rapidly into sight[76,174,175] as a means to narrowing the polymer's oxidation and reduction onsets to a stable potential window of application.[76,176] In particular, while p-type doping of organic polymers was subjected to steady research effort, polymers exhibiting electron-dominated charge-transport properties or ambipolar redox chemistry were much less accessible. Besides the difficulties encountered in lowering the polymer's reduction threshold to values positive enough that the subsequent carbanions would be unreactive to both water and oxygen, the misconception that n-type-doped states could be systematically accessed by inducing a reduced state was pointed out early.[177,178] In fact, the electrochemically observed reduction must be accompanied by the observation of significant changes in conductivity and/or spectral features occurring during the doping process to confirm the n-type character.[179] In fact, for many cases where a reduction can be monitored, the corresponding redox process is irreversible, cannot be maintained, triggers polymer degradation, or leads to pinned anions and does not yield true n-doping.[178]

With the synthesis of the dual p- and n-type electropolymerized donor−acceptor poly[2,5-bis(3,4-(ethylenedioxy)-2-thienyl)pyridine] (**156**)[180] came the perspectives of generating new color states on protonation and deprotonation or by application of oppositely charged external biases. For instance, **156** revealed a band-gap of 1.9 eV[180,181] along with a red colored neutral state changing to blue-purple upon oxidation and pale-blue upon reduction, although the redox state could only be obtained under inert conditions considering the reduction wave centered at −1.9 V vs Fc/Fc$^+$.[181] As illustrated in Figure 3, the nitrogen-containing polyheterocyclic hybrid was also responsive to the pH of the electrolyte solution as desired for sensing applications exhibiting a blue-indigo in its protonated state. Later on, in situ conductance studies performed on thin films deposited on an interdigitated electrode network confirmed the nature of the charge carriers upon reduction, thereby supporting the true n-type character of this multichromic ECP.[179]

In fact, it is now well established that the incorporation of a "pyridine-like" (sp^2) nitrogen-containing heterocycle into a more electron-rich system induces the reduction of the polymer energy gap as further described in several other studies and review works.[10,76,182] More precisely, a low-lying LUMO arises from their pronounced electron-deficient character which, on hybridization, impacts the





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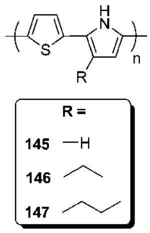

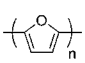

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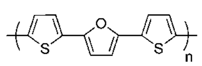

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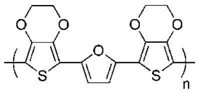

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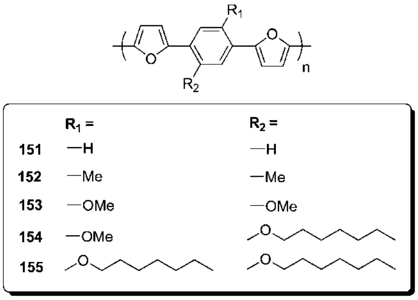

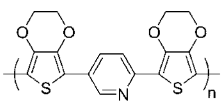

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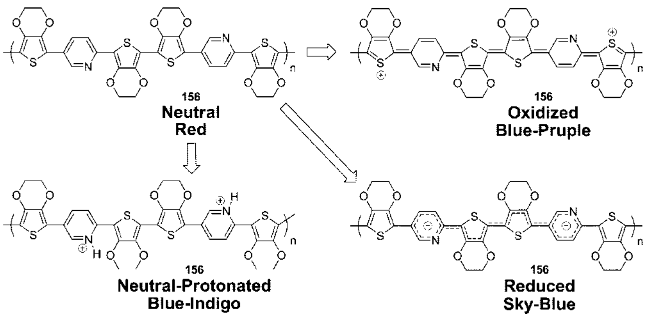
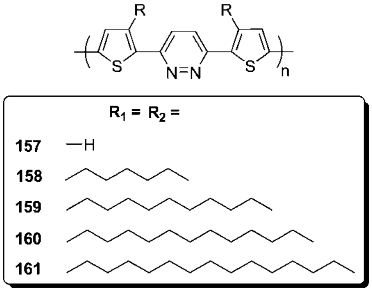
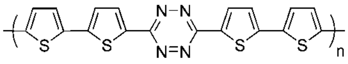


Figure 3. Dual p- and n-type-dopable **156**.

bottom of the conduction band of the resulting DA π-conjugated polymer. As a result, the polymer optical absorption undergoes a bathochromic shift that increases with increasing concentration of nitrogen atoms present in the phenylene-type moiety. This last point is well illustrated by the work of Yamamoto et al. on thienylenepyridazine[183] (**157**−**161**) and Audebert et al. on thienylenetetrazine[184] (**162**) systems with the soluble pyridazine derivatives **157**−**161** switching from orange (neutral) to dark gray on n-doping and black on p-doping.





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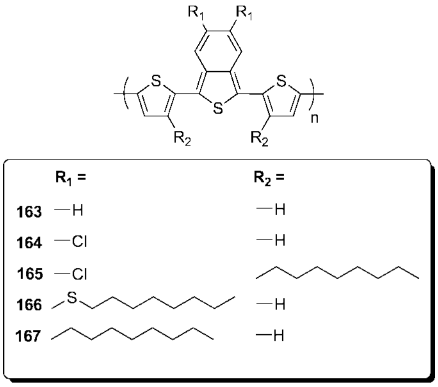
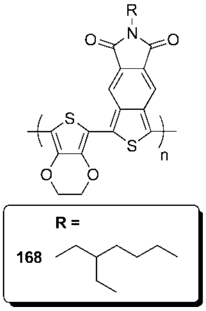
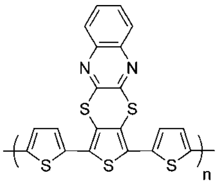
Replacing a single pyridine-like phenylene ring by a fused heterocycle possessing high nitrogen content such as a pyridopyrazine or a 2,1,3-benzothiadiazole, for example, can lower the band-gap of the thienylene-based polymeric hybrids even further, inducing the polaronic states to arise essentially in the near-IR such as desired for colored to transmissive EC applications. The ensuing ECPs will be discussed later in section 3.2.2.

3.1.1.10. Thienylene-Based Isothianaphthene-Type Hybrids. In an alternative effort to lower the energy gap of π-conjugated polymers without taking advantage of the donor−acceptor theory, building blocks with high resonance energies able to favorably alter the bond-length alternation in π-conjugated polymers and stabilize their quinoidal resonance geometries[61] have been employed in combination with more conventional thienylene substituents (**163**−**167**).[185,186] By activating an electron-withdrawing propensity on isothianaphthene through an appended *N*-alkyl-functionalized dicarboxylic imide moiety, the hybrid polymer **168** was produced, which revealed a band-gap of 1.1 eV and a blue to transmissive switch on electrochemical oxidation.[187,188]

3.1.1.11. Other Thienylene-Based Fused Hybrids. Skabara et al. have synthesized an orange to green-blue switching ECP (**169**) based on a dithienylthienodithiinoquinoxaline precursor.[189] The hybrid exhibited a band-gap of 1.9 eV and a CE as high as 381 cm^2 C^{-1} (at it absorption maximum). The fast switching performance of this material (∼1 s) when compared to **210**, for instance (∼2.2 s),[190] was attributed to the nonplanarity of the thienodithiinoquinoxaline building unit, which presumably inhibits the strong π-stacking interactions between chains and facilitates the diffusion of the counterbalancing ions during the doping−dedoping process.







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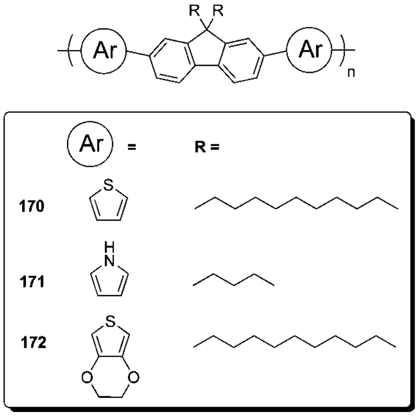
3.1.1.12. Thienylenefluorenes and Analogues. The incorporation of fluorene building units has produced ECPs with moderate band-gaps due to the contribution of the lower energy HOMO (higher ionization potential) of the fused phenylene system when compared to that of EDOT, for example.[191,192] While the thienyl- and pyrrole-based polymers **170** and **171** showed similar band-gaps in the range 2.3−2.4 eV, swapping the electron-rich substituents by EDOT as in polymer **172** reduced this range to 2.15−2.20 eV. In comparison, polymer **170** was neutral-state olive green, switching to dark green on p-doping, whereas polymer **172** switched between red-tan and a dark blue oxidized state, demonstrating the large effect of a small band-gap reduction (∼0.1−0.2 eV) on the electrochromicity of the corresponding polymers.

3.1.1.13. Thienylenecarbazoles and Analogues. *N*-Alkyl-substituted 3,6-carbazole derivatives have been probed in terms of their EC behavior in all-donor (**173**−**179**) and donor−acceptor (**180**) backbones.[193,194] In these systems with band-gaps ranging from 2.2 (**180**) to 2.5 (**173**) eV, conjugation through the nitrogen atom governs the electrochromicity by inducing isolated radical cations on p-doping and retarding the formation of dications, hence adding a third accessible and stable redox state. This is demonstrated in **174**, which switches from yellow (neutral) to faint green (radical cation) to faint pink on full oxidation (dication), or by **175**, which changes from yellow (neutral) to light orange (radical cation) to gray on full oxidation (dication).[193] The donor−acceptor analogue **176** revealed

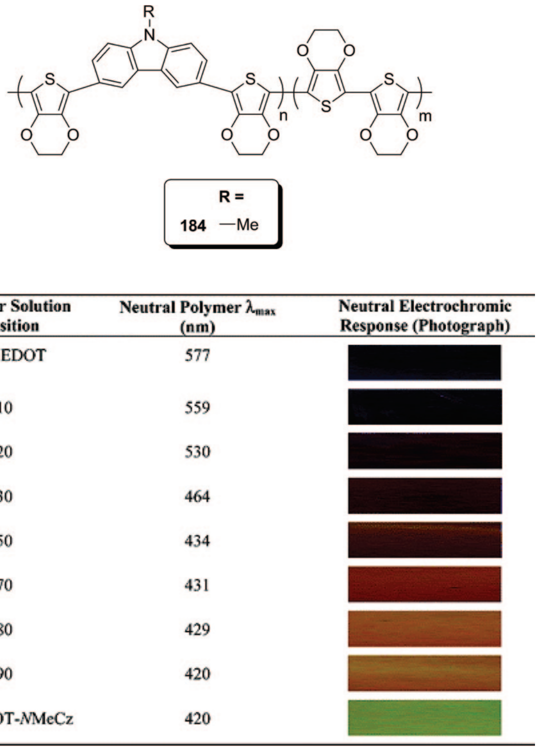


an orange (neutral) to green-gray (radical cation) to slate-gray on full oxidation (dication).[193]

More recently, Leclerc et al. have incorporated *N*-alkyl-substituted 2,7-carbazole moieties in all-donor (**181** and **182**) and donor−acceptor (**183**) backbones and have probed the solution-processable polymer analogues for their electrical and thermoelectric properties.[195] Optical band-gaps of 2.34, 2.41, and 1.88 eV were respectively estimated for **181**, **182**, and **183**. The spectroelectrochemical data were reported for the polymers, though the color states attained in the neutral form and upon oxidation were not indicated.

3.1.2. Random Copolymers

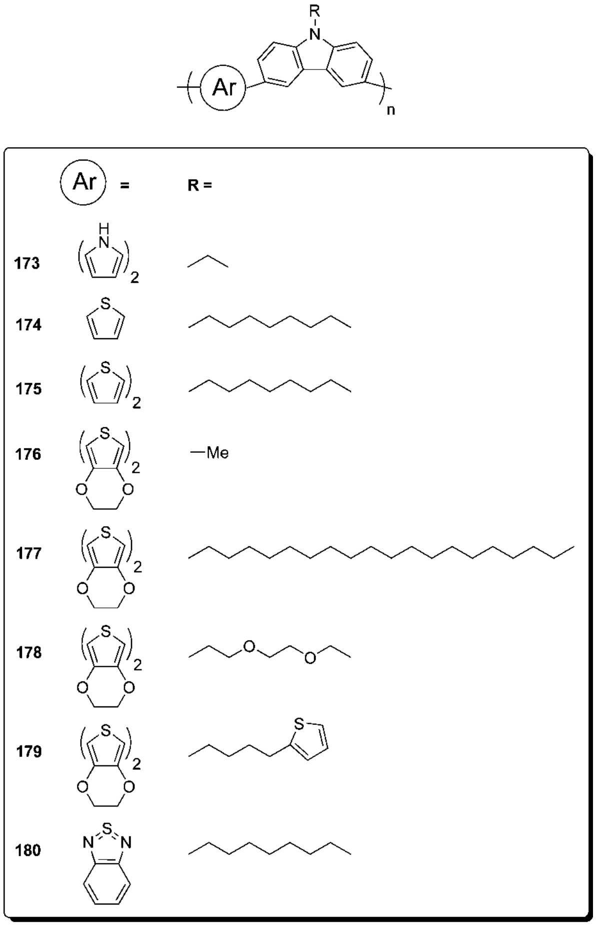
The random electrochemical copolymerization of monomers possessing similarly low oxidation potentials has been proposed by Reynolds et al. as a way to fine-tune the neutral-state hue of several previously described polymers, along with introducing new color palettes without further synthetic effort at the monomer level.[196] For instance, the *N*-methyl-substituted carbazole monomeric precursor to **184** (BisEDOT-*N*MeCz) was copolymerized with BisEDOT in different feed ratios to produce ECPs with neutral-state colors ranging from blue to red to orange to yellow with increasing concentration of BisEDOT-*N*MeCz (see Figure 4). Given the close peak oxidation thresholds of the monomer used (BisEDOT, +0.56 V vs Ag/Ag$^+$; BisEDOT-*N*MeCz, +0.41 V vs Ag/Ag$^+$), the resulting polymer hybrids showed “true” random copolymer character as demonstrated by their solution optical absorption features significantly different from that of their parent homopolymers. Interestingly, the subsequent polymers (including a soluble analogue made chemically for comparison) all revealed a green colored intermediate state and a blue colored oxidized state, regardless of the polymer composition.

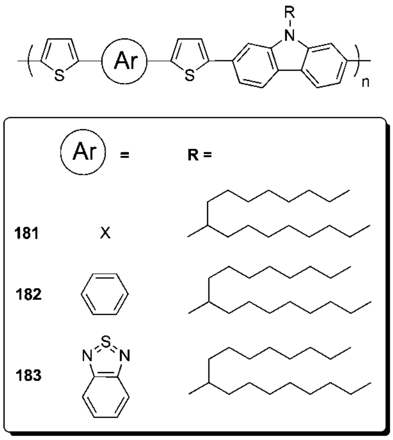


Comonomer Solution Composition	Neutral Polymer λ_{max} (nm)	Neutral Electrochromic Response (Photograph)
100% BiEDOT	577	
90:10	559	
80:20	530	
70:30	464	
50:50	434	
30:70	431	
20:80	429	
10:90	420	
100% BEDOT-*N*MeCz	420	

Figure 4. The *N*-methyl-substituted carbazole monomeric precursor to **184** (BisEDOT-*N*MeCz) was copolymerized with BisEDOT in different feed ratios to produce ECPs with neutral-state colors ranging from blue to red to orange to yellow with increasing concentration of BisEDOT-*N*MeCz. Adapted with permission from ref 196. Copyright 2003 American Chemical Society.

Toppare et al. have electrochemically copolymerized a series of dithienopyrrole macromonomers with EDOT (**185**−**193**), demonstrating a palette a novel multichromic ECPs exhibiting distinct energy gaps and EC behaviors. For example, the copolymerization of a *p*-tolyl-substituted dithienopyrrole with EDOT (1:2) led to polymer **185**, switching from chestnut to khaki to green to blue upon oxidation and showing a band-gap of 1.65 eV,[197] while the phenyl-substituted dithienopyrrole copolymer with EDOT (1:1) analogue (**186**) had a higher band-gap of 1.9 eV and showed only two colors on switching (neutral-state claret red and blue).[198] The alkylamine-functionalized copolymer with EDOT (**187**) (1:1) also showed a claret red to blue switch upon p-doping along with a band-gap of 1.73 eV.[154] In contrast, the aniline-substituted copolymer **188** changed from purple to brown to green to teal to blue on oxidation with a similar band-gap of 1.7 eV.[155] The benzyl-substituted copolymer **189** revealed a claret red to yellow to green to blue switch on p-doping and a band-gap of 2.0 eV.[199] The copolymerization of an *N*-fluorophenyl-substituted dithienopyrrole building block with EDOT produced an ECP (**190**) possessing five different color states: purple, red, light gray, green, and blue on progressive oxidation, whereas the homopolymer (see polymer **139** in section 3.1.1.7) could only switch from yellow to blue.[156] The band-gap of the copolymer **190** was found identical to that of **210** (∼1.6 eV) and much lower than that of the homopolymer **139** (1.94 eV).[200] Similarly, electrochemical copolymerizations of *N*-nitrophenyl-substituted dithienopyrrole building blocks with EDOT (1:1) produced ECPs **8** and **9** possessing color states nearly identical to those of **190** (light red or dark purple, red, light gray, green, and blue on progressive oxidation) and a band-gap ranging from 1.6 to 2.1 eV depending on the feed ratio used between monomers.[157,201] With an intermediate band-gap of 1.7 eV, the perfluorophenyl-substituted copolymer analogue with EDOT (**193**) achieved maroon, red-violet, dark purple, green, blue, and indigo depending on the potential applied.[202] In general, as the feed ratio of EDOT was increased, the band-gap of the copolymers was decreased, the contrasts were enhanced, and the switching times were reduced. A quinoxaline-substituted dithiothienyl monomer was copolymerized with bithiophene (1:1) to yield a hybrid (**194**) possessing a band-gap of 1.81 eV and a red to blue switch upon p-doping. In a different study, a copolymer made with a quinoxaline-substituted dioxythienyl monomer and bithiophene (**195**) (1:4) showed a slightly smaller band-gap

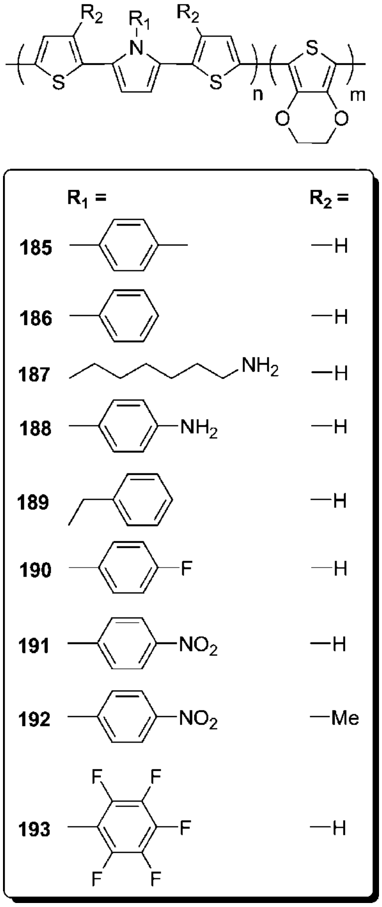




of 1.76 eV and a red to blue switch as well.[157] The copolymerization of a quinoxaline-substituted dioxypyrrole monomer with the same comonomer led to an orange to blue switching ECP (**196**) with a band-gap slightly larger than 1.89 eV.[203]

Reau et al. have electrochemically copolymerized a dithienothioxophosphole building block with EDOT and achieved a DA hybrid (**197**) possessing a narrow band-gap of 1.13 eV, which was smaller by ~0.6 eV than that of the two corresponding homopolymers.[204] This hybrid exhibited a blue to black electrochromism with a maximum of optical contrast of 13% in the visible and 15% in the NIR.

The DA copolymer **198**, synthesized in a 1:1 monomer to comonomer ratio, provided a low band-gap of 0.88 eV and switched from purple to light blue on p-doping.[205] DA polymers will be further described in section 3.2.2.

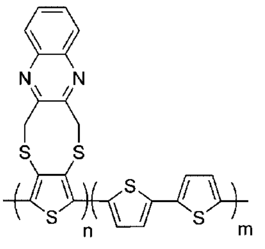


Random copolymers of EDOT and 5-cyanoindole (**199**) were electropolymerized and their electrochemical properties investigated.[206] While the homopolymer of 5-cyanoindole switched from yellow to green on oxidation, the copolymer revealed a purple to blue color change in the same conditions.

The BisEDOT−anthracene building block constitutive of a homopolymer previously described (see polymer **129** in section 3.1.1.6) was copolymerized with EDOT using different feed ratios to reveal polymer hybrids **200** with band-gaps of ~1.6 eV.[144] These copolymers were multichromic, changing from claret red (neutral state) to gray to red to blue on p-doping.

Organic−inorganic EC hybrids consisting of regiorandom poly[3-hexylthiophene-*co*-*N*-(3-(trimethoxysilyl)propyl)pyrrole)] (**201**) anchored onto silica particles via the trimethoxysilyl functionalities have been achieved and subsequently characterized.[207] The resulting composites exhibited a neutral-state orange-yellow to dark blue switch on p-doping along with an improved adhesion and EC durability upon repeated cycling when compared to P3HT (**8**) alone.

Electrochemical copolymerization of an octathienyl-substituted silsesquioxane with pyrrole (**202**) has been achieved with the idea of improving the EC properties of PPs by incorporating bulky substituents facilitating the ion diffusion during redox switching. The copolymer exhibited a band-gap of 2.25 eV and a multicolored EC behavior, switching from yellow to red to green-gray to blue on p-doping.



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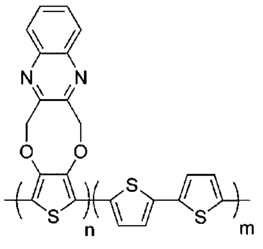

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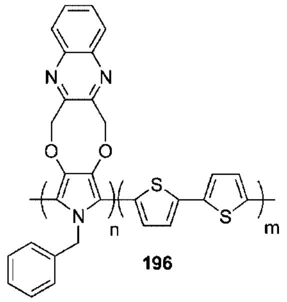

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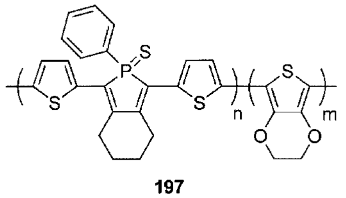

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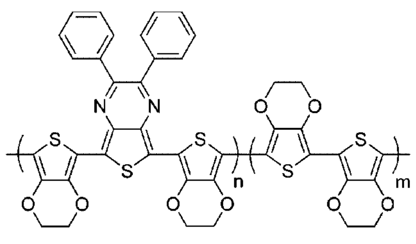

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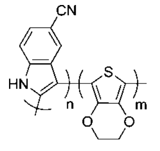

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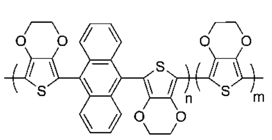

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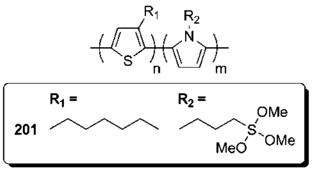

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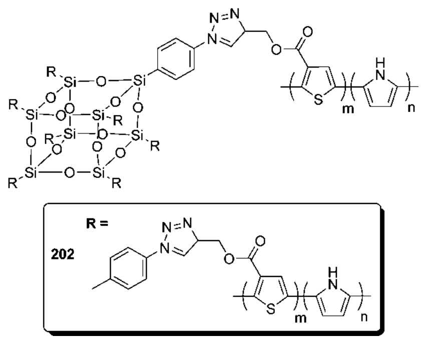

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3.2. Cathodically Coloring Polymers

3.2.1. Poly(dioxythiophene)s and Analogues

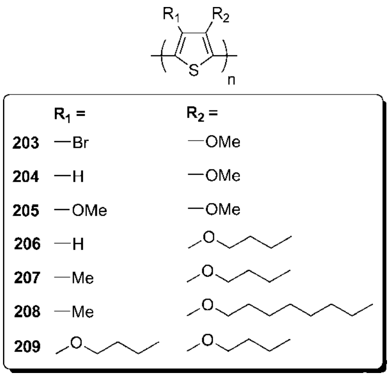
3.2.1.1. Poly(alkoxythiophene)s. Whether they are monofunctionalized (alkOTs) or difunctionalized (DalkOTs), only a few reports have described the EC properties of alkoxy-substituted PTs. It is especially surprising when considering the extensive effort that has been placed on developing their poly((alkylenedioxy)thiophene) derivatives with various bandgaps and functionalities (see section 3.2.1.2 and section 3.2.1.4) for application in ECDs, PSCs, or supercapacitors.

For example, Cihaner et al. have recently reported on the EC performance of the electrochemical polymer of 3-bromo-4-methoxythiophene (**203**), which switches from red-pink to transmissive blue on p-doping and exhibits a moderate bandgap of 1.97 eV.[208] In particular, an excellent maximum transmittance change of ca. 39% was monitored (at the considered film thickness, not indicated), as well as a response time of 1.2 s to reach 90% of the full switch.

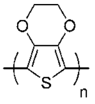
In addition, the work from Miller et al. describing the redox properties of the electrochemical polymer of 3-methoxythiophene (**204**) is worth mentioning.[209−211] The electrochemical polymer of 3,4-dimethoxythiophene (**205**) has been carefully investigated by Aaron et al. in organic and aqueous micellar media without further information on its color-switching behavior.[212] Leclerc et al. have reported the chemical polymerization of 3-butoxythiophene (**206**), 3-butoxy-4-methylthiophene (**207**), 3-(octyloxy)-4-methylthiophene (**208**), and 3,4-dibutoxythiophene (**209**) using ferric chloride.[213] Solution-processable polymers were produced which exhibited moderately low oxidation potentials (0.60−0.64 eV vs SCE) and thus more stable conducting states when compared to PTs in general. Thin films of **207** and **208** were found to be red-violet when the polymers were in their neutral state. Upon chemical or electrochemical doping, these polymers showed blue-black color states.

A number of alkoxythiophene-based analogues have been reported under their thienylenevinylene copolymer form (**82**, **84−86**) as previously described in section 3.1.1.4.

3.2.1.2. Poly(3,4-(ethylenedioxy)thiophene)s. Engineered during the late 1980s at the Bayer AG research laboratories in Germany,[214−217] an innovative electron-rich polymeric backbone possessing high oxygen content and a molecular structure inhibiting α,β- and β,β-cross-links on polymeri-



zation was proposed to address the lack of processability exhibited by the more conventional unsubstituted aromatic-based polymeric systems, namely, PP, PT, polyphenylene and poly(phenylenevinylene) (PPV). With a highly conducting, nearly transparent, and especially stable doped state as desired for numerous applications spanning antistatic coatings for plastics, see-through electrodes, and organic transistors, the new PT analogue, namely, **210**, was initially insoluble when prepared using traditional chemical and electrochemical polymerization conditions. It was nonetheless rapidly brought to the forefront of the growing field of conducting polymers as its PSS-combined water-soluble form PEDOT:PSS (**211**). PEDOT:PSS, subsequently known under its trade name BAYTRON P and now Clevios, finds extensive use in the development of novel organic electronics-based advanced technologies such as light-emitting devices, sensors, memories, polymer photovoltaic cells, and field effect transistors (see further details in section 4).



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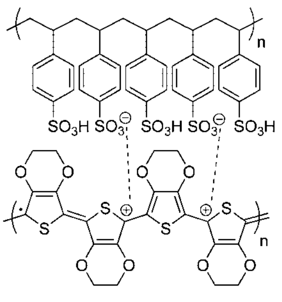

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In the context of electrochromism, it is **210** and not **211** that prevails. Combining a narrow optical band-gap of about 1.6 eV and an especially low oxidation potential when compared to its unsubstituted PT parent (**1**), neutral deep blue PEDOT shows a relatively stable and highly transmissive sky blue oxidized state as demonstrated in the pioneering work of Inganäs et al., who have described the first electrochemically prepared PEDOT-based ECDs.[47] Considering the onset of optical absorption of neutral PEDOT lying in the near-IR region of the electromagnetic spectrum, along with minimal tailing in the visible of its charged carrier transitions produced on electrochemical oxidation (see Figure 5), the excellent transmissivity of **210** attracted significant attention as illustrated by the reports of Jonas,[215] Heinze,[218] and Inganäs et al.[219] and has been the focus of a considerable number of publications since then.

By appending solubilizing side chains to the alkylenedioxy bridge of PEDOT (**212**−**215**), Havinga[114] and Reynolds et al.[190,220−223] have produced the first neutral-state solution-processable PEDOT derivatives **213**−**215** and investigated their electrochemical performance relative to that of the unsubstituted PEDOT counterpart (**210**). Besides the direct effect of this structural modification on the energy gap of the subsequent analogues, which depends on the length and bulkiness of the substituted pendant group (1.75−1.8 eV), the substitution was found to enhance the switching properties of PEDOT. For instance, when about 10 s was necessary to fully oxidize PEDOT (in 0.1 M TBAP/ACN), films of the tetradecyl-substituted PEDOT (**215**) could be switched within 5 s in the same electrolyte solution and within 1−2 s when a smaller counteranion such as Li^+ was used.[221] Additionally, a more effective depletion of the neutral-state optical absorption was observed on full oxidation. This has been attributed to the reduced overlap of the charge carriers' near-IR optical transitions with the visible region presumably due to facilitated diffusion of the dopant ions into the electroactive layer.[224] Similarly, the nearly orthogonal pendant phenyl of **216** afforded higher doping densities and superior transmissivities.[190] In long-term stability experiments (in 0.1 M $LiClO_4$/ACN), the same tetradecyl-substituted **215** deposited on ITO stood out with less than 30% electrochromic loss after 1100 cycles versus more than 50% for the parent **210** after only 140 switches. Under inert conditions (glovebox) and using a Li counter electrode to avoid the side redox processes occurring between platinum and the Li-based electrolyte under atmospheric conditions, PEDOT (**210**) retained about 65% of its electroactivity after 6000 cycles, PEDOT-C_8 (**214**) about 50% after 9000 switches, and PEDOT-C_{14} (**215**) more than 60% of its electroactivity after 16 000 cycles.[221]

With a narrow band-gap of 1.65 eV, the perfluoroalkyl ester-functionalized derivative PEDOT-F (**217**) has been reported as a hydrophobic analogue exhibiting particularly high contrast ratios (ΔT (%) and ΔY (%) of ca. 63%) and rapid switching times (ca. 1.2 s at the considered film thickness (nonindicated) and at 95% of the full switch), along

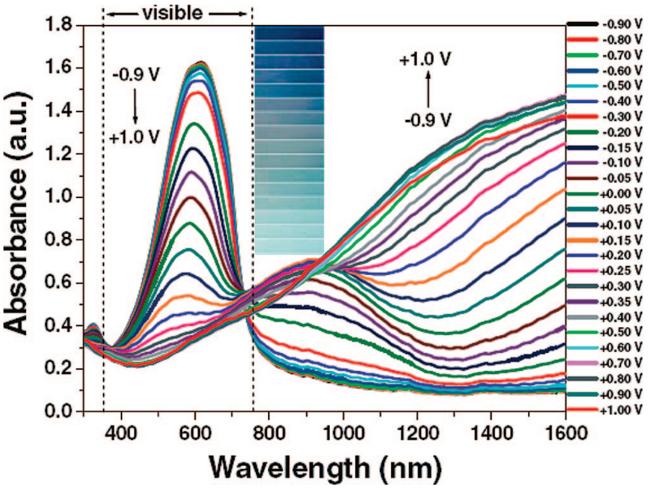


Figure 5. Spectroelectrochemistry of a thin film of **210**. The inset shows the variety of hues produced on application of various biases as reported by Sonmez et al. Adapted with permission from ref 286. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

with the same dark blue to transmissive sky blue switch on electrochemical oxidation.[224] Perfluorinated materials exhibit low surface energies, are commonly chemically and thermally stable, and are useful for applications encompassing nonadhesive surfaces and membranes.

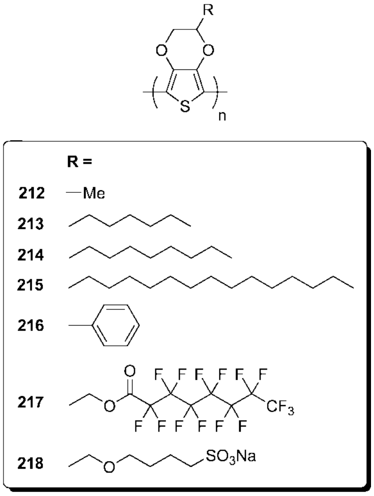
The perspective of combining the EC properties of PEDOT with the ability of processing the polymer from aqueous solutions, for example, has driven the synthesis of the self-doped sulfonate-derivatized homopolymer PEDOT **218**.[225,226] As expected, chemically polymerized **218** exhibited an especially low oxidation potential (~0.0 V vs Ag/Ag$^+$) when compared to sulfonated PT analogues (~0.75 V vs Ag/Ag$^+$).[227−229] Films prepared from the layer-by-layer deposition of **218** and poly(allylamine hydrochloride) (PAH) onto ITO-coated glass and redox cycled in aqueous media showed a pink-purple to light blue switch on oxidation and EC contrasts as high as 45% (40 bilayers).[225] Sulfonate-derivatized PEDOT analogues have also been investigated by Chevrot et al. with an emphasis on their cation-exchange properties.[230,231]

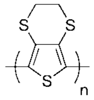
One considerable advantage of chemically synthesized and solution-processable PEDOT derivatives lies in the possibility of separating the shorter and less electroactive macromolecules (oligomers) from their longer counterparts by various purification techniques such as multiple precipitations or Soxhlet extractions. For example, work from Lopez-Palacios et al. shows that oligomers (four to six monomer units) are trapped during the electrosynthesis of **210** in aqueous media.[232] The presence of oligomers commonly reduces the optical contrast observed in ECDs by altering the transmissivity of the doped state of a cathodically coloring ECP.

It is worth noting that replacing the strongly electron-donating oxygen atoms of EDOT by the less electronegative sulfur counterparts lowers the HOMO level of the subsequent polymer PEDTT (**219**) relative to **210** such that the band-gap of the corresponding chemically and electrochemically polymerized homopolymers falls into the 2.1−2.2 eV range.[233] In addition, the resulting EC properties of PEDTT differ significantly from those of **210**, with **219** being brown-yellow in the neutral state and dark green in the oxidized state instead of the transmissive sky blue invaluable for display applications. Similarly, poly(dithienodithiine) (**220**) exhibited a multicolor electrochromism ranging from brick-red in the neutral state to green on partial oxidation to light gray in the fully oxidized state to transmissive and brown on n-doping.[234] Its band-gap (1.85 eV) was lower by 0.25−0.35 eV than that of **219** presumably due to the more electron rich character of the dithienodithiine repeat unit. Although electrochromic, the sulfur-derivatized polymer analogues **219** and **220** do not meet the requirements for cathodically coloring electrochromes.

On the other hand, removing one oxygen atom from the ethylenedioxy bridge of EDOT as in polymer **221** has also proved to induce a drastic change in EC behavior, changing the neutral state from blue to red and the oxidized state from transmissive light blue to a darker blue-black tone as the charge-carrier transitions overlap significantly in the red region of the visible spectrum.[235]

The electrochemical copolymerization of EDOT and its methanol-substituted counterpart EDOT-MeOH onto ITO has been investigated by Saavedra et al. as a function of the monomer/comonomer feed ratio (**222**).[236,237] The electrochromic contrast was found to increase with increasing insertion of EDOT-MeOH into the PEDOT backbone, although EDOT polymerized more rapidly (at equimolar feed), which translated into a preferential deposition of EDOT onto ITO.[236] The charge-transfer kinetics and EC response of the films were analyzed by potential-modulated attenuated total reflectance spectroscopy, which revealed an increase of the response time of the copolymer with increasing proportion of EDOT-MeOH in the backbone, suggesting conformational changes slow as the number of methanol-substituted units in interaction with ITO increases.[237]





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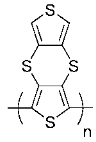

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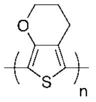

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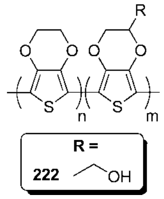
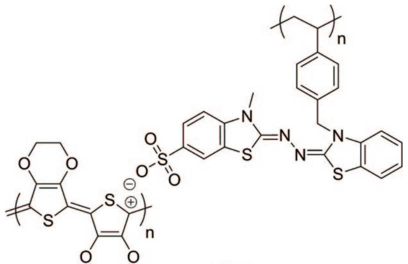


Palmore et al. have electrodeposited a polymer composite (**223**) resulting from the combination of doped **210** charge balanced with PABTS on ITO and have investigated its EC properties.[238] As illustrated in Figure 6, three distinct color states (instead of two for PEDOT:PSS) have been identified encompassing a clear state (in the absence of external bias), a blue state (on reduction of PEDOT), and a green state (on oxidation of ABTS).

It is worth noting that the quality of **210** films electropolymerized onto ITO can be greatly enhanced (in homogeneity) by the presence of a predeposited layer of **211** (or base coating).[239] Devices based on this approach exhibited higher contrasts than devices constructed on bare ITO, which was attributed to the difference in film morphology. Adhesion and uniformity are two determining parameters that greatly depend on the sheet resistance and cleanliness of the substrate used.[240]

Deepa et al. have grown **210** nanostructures in the presence of the micellar surfactant camphorsulfonic acid (CSA) and lithium triflate. As demonstrated by AFM, this strategy led to a porous morphology (with long polymer shapes of 25−30



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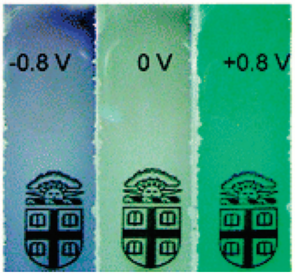


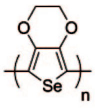
Figure 6. Electrodeposited polymer composite **223** resulting from the combination of doped **210** charge balanced with PABTS onto ITO as developed by Palmore et al. Three distinct color states (instead of two for PEDOT:PSS) have been identified: a clear state (in the absence of an external bias), a blue state (on reduction of PEDOT), and a green state (on oxidation of ABTS). Adapted with permission from ref 238. Copyright 2008 American Chemical Society.

nm) facilitating the ionic diffusion across the film upon redox cycling.[241] Their EC properties were investigated, revealing up to 50% contrast in the visible. Further, using dodecyl sulfate (SDS) and lithium triflate, a nanostructured network of nearly spherical grains of **210** (50−150 nm in size) and pores was achieved, which yielded up to 62% contrast and high stability upon repeated cycling in aqueous solution.[242] Surfactants have been used by other groups for the polymerization of **210**.[243] Lee et al. have achieved **210** nanotubes[244] that can be synthesized and deposited onto thin porous anodic aluminum oxide-coated ITO using low monomer concentrations and high potentials to yield subsecond color-changing window-type devices.[245]

When hydrous ruthenium oxide-embedded **211** composite EC particles were fabricated, enhanced capacitance and optical contrasts were observed when compared to the combination of PEDOT:PSS and RuO_2 simple films. This result was attributed to the large surface area of the small-size RuO_2 particles.[246]

Akagi et al. have reported on the electrochemical synthesis of an optically active EC composite based on**210** and the lyotropic liquid crystal polymer hydroxypropyl cellulose (HPC). The blue to transmissive switching EC hybrid revealed an electrochiroptical effect as demonstrated by the changes in circular dichroism observed during the EC variations induced.[247]

Gleason et al. have achieved **210** films on ITO-coated plastic by a solventless oxidative chemical vapor deposition approach (oCVD).[248,249] The deposited films (~100 nm) were electrochromic with 45% EC contrast at their maximum wavelength of absorption and switching times of ~10 s.



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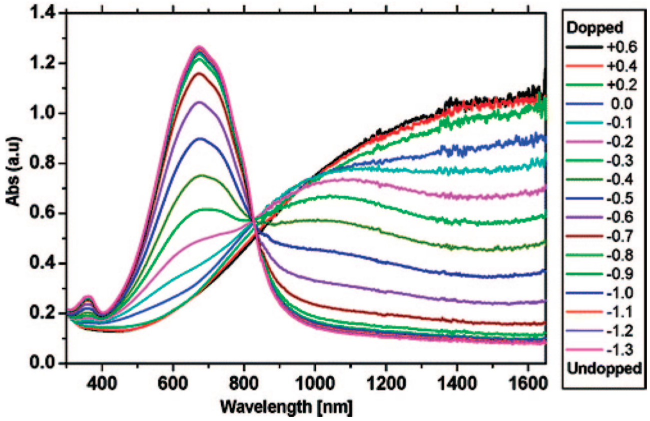


Figure 7. Spectroelectrochemistry of a thin film of **224** as a function of the applied potential (between +0.6 and −1.3 V vs Fc/Fc$^+$) in propylene carbonate as reported by Bendikov et al. Adapted with permission from ref 251. Copyright 2008 American Chemical Society.

3.2.1.3. Poly(3,4-(ethylenedioxy)selenophene)s. The selenium analogue of EDOT, namely, 3,4-(ethylenedioxy)selenophene (EDOS), was first achieved and electrochemically and chemically polymerized by Cava et al.[250] to afford the neutral-state deep blue to transmissive switching polymeric derivative PEDOS (**224**). More electron-rich than the parent sulfur-based heterocycle, EDOS was shown to possess a lower oxidation potential (1.22 V relative to Fc/Fc$^+$ vs 1.4 V relative to Fc/Fc$^+$ for EDOT) and its subsequent polymer a narrower energy gap (1.4 eV, optically determined) than that of **210**. As a result, both the polymer electrochemical activity and its optical properties were expected to differ substantially from those of the poly(dioxythienyl) analogue, thereby offering the potential for fine-tuning of colors in the context of electrochromic device applications.

While **210** and its poly(dioxythiophene) derivatives have commonly shown good to excellent conductivities in their doped states (up to 500 S cm^{-1}), highly reversible redox activities, and long-term EC performance, only recently have the same properties been more carefully assessed in the case of **224**. Thus, Bendikov et al. have last reported on the high conductivity of doped PEDOS (up to 30 S cm^{-1} in pressed pellets) and reinvestigated its thin-film electrochemical behavior.[251] With a polaron peaking at around 1050 nm which tails moderately into the visible (Figure 7), revealing a transmissive gray doped state on electrochemical oxidation and a redox stability comparable to that of **210** over time, **224** stands as an excellent candidate in the fabrication of transparent conducting electrodes as well as in the context of electrochromism.

3.2.1.4. Poly(3,4-(propylenedioxy)thiophene)s and Analogues. Of all documented PXDOT syntheses (where X is an alkylene bridge) and electrochemical characterizations, the ones relying on poly(3,4-(propylenedioxy)thiophene) (PProDOT) derivatives prevail today in the context of electrochromism. It is in fact now well-established that the nature of the alkylene bridge plays a determining role in the many redox and optical specificities of PXDOTs.

Dietrich et al. first reported on the differences between PEDOT (**210**) and PProDOT (**225**) with respect to their electrochemical and optical properties in 1994.[218] This was followed by a systematic study of the structure−electrochromic property relationships in PXDOTs by Reynolds et al.[190] In the combined in situ conductivity and comparative electrochromic analysis of a series of electropolymerized alkyl-substituted and unsubstituted poly(3,4-(alkylenedioxy)thiophene)s differing by the size of the alkylenedioxy ring or the nature of the substituent(s), derivatized PProDOT analogues stood out from their ethylenedioxy-substituted parent PEDOT analogues. For example, **225** exhibited sharper and better resolved redox features on cyclic voltammetry in 0.1 M TBAP/ACN solution electrolyte. The EC contrasts (ΔT) measured at the absorption maximum for electropolymerized films of constant film thickness (ca. 300 nm, as determined by profilometry), increased with the alkylenedioxy ring size from 44% for PEDOT (**210**) to 54% for PProDOT (**225**) to 63% for PBuDOT (**226**). Further, if the switching times allowing full color change on oxidation of the polymers were found identical in the case of **210** and **225** (2.2 s), **226** was found to switch nearly 2 times as fast (1.3 s) upon the square wave potential steps applied. Because this primary set of results constituted a strong indication of a more efficient redox process occurring for the larger alkylenedioxy rings (or for the more substituted ones as shown when the ethylenedioxy bridge of PEDOT was increasingly substituted),[190,223] a second report came to support the favorable consequences of facilitating the diffusion of the electrolyte-supplied counterions through a more open morphology.[252] When the switching performance of the first symmetrically dialkyl-substituted ProDOT-based π-conjugated polymer, a dimethyl-substituted derivative, namely, PProDOT-Me_2 (**227**), was investigated and compared to that of PEDOT (**210**) and PProDOT (**225**), a remarkably high EC contrast (ΔT) of 78% was monitored at the absorption maximum of the electropolymerized film deposited at optimum film thickness. The transmittance ratio found for the monomethyl-substituted derivative PProDOT-Me (**228**) ($\Delta T = 77\%$) confirmed the determining role of the substitution on the central carbon of the propylene bridge. As the doped state of **227** was also found to be more transmissive by spectroelectrochemical comparison with **225**, it was then tentatively proposed that the alkyl substitution hindered the interchain charge transport, hence possibly attenuating the near-IR optical transitions tailing in the visible and responsible for the residual hue observed. It is worth noting here that, alternatively, by facilitating the diffusion of the counterions across the entire film as previously described in this section, the bipolaronic transition arises more effectively, which represses both the visible and adjacent polaronic transitions, hence resulting in a transmissivity enhancement on full oxidation. **227** switched from its neutral to oxidized state at a rate ranging from 0.3 to 0.8 s when considering 95% of full contrast and the different film thicknesses investigated. The CCE measured at the absorption maximum for electropolymerized films of constant film thickness (ca. 150 nm, as determined by profilometry) also increased with the alkylenedioxy ring size from 183 $cm^2\ C^{-1}$ for **210** to 285 $cm^2\ C^{-1}$ for **225** to 375 $cm^2\ C^{-1}$ for **227** due to a combination of higher optical contrasts at the absorption maximum and higher doping levels.[13] Their CE values ranged from 100 to 300 $cm^2\ C^{-1}$ when EC metal oxide values commonly ranged from 10 to 100 $cm^2\ C^{-1}$.

PProDOTs of increasingly long and bulky substitution patterns were further investigated by Reynolds et al. with the intention of matching optimum EC properties and polymer structure.[253−255] Solution-processable polymers can be achieved starting with linear butyl groups as demonstrated when using Grignard metathesis (GriM) polymerization conditions.[254] Interestingly, the solution drop-cast films of the dibutyl-substituted PProDOT-Bu_2 (**229**) did not exhibit as high an EC contrast on electrochemical switching ($\Delta T = 45\%$ at ca. 400 nm) as the electrochemically synthesized version of this polymer ($\Delta T = 75\%$ at the same thickness) likely due to the more compact nature of the cast films, which appeared to not allow the same level of doping to be attained, hindering full bleaching of the polymer visible absorption. In a separate study,[255] the transmittance change (ΔT (%), measured at the λ_{max}) and relative luminance ratio (ΔY, %) for films of the chemical polymers homogenously spray-cast onto ITO (ca. 150−250 nm, as determined by profilometry) increased with the length and the branching of the solubilizing side chains anchored on ProDOT from $\Delta T = 51\%$ and $\Delta Y = 51\%$ for PProDOT-Bu_2 (**229**) to $\Delta T = 70\%$ and $\Delta Y = 58\%$ for the dihexyl-substituted PProDOT-Hx_2 (**230**) to $\Delta T = 79\%$ and $\Delta Y = 70\%$ for the bis(2-ethylhexyl)-substituted PProDOT-$EtHx_2$ (**231**). While drop-cast films are typically inhomogeneous and compact and tend to crack and peel on redox cycling, the use of an airbrush in spray-casting the polymers allowed the deposition of highly homogeneous films (see Figure 8) of consistent thickness and low surface roughness. The ECPs were switched from dark red-purple to transmissive sky blue upon p-doping and showed subsecond switching times (as low as 0.2 s for spray-cast **229**) and remarkably high CCE values in the 1000 $cm^2\ C^{-1}$ range. On the other hand, the moderate contrast ratios ($\Delta T = 51\%$ and $\Delta Y = 42\%$), slow switching time (2.2 s), and low CCE (472 $cm^2\ C^{-1}$ as cast) observed in the case of PProDOT-MeOC18_2 (**232**) indicated the existence of a threshold by which the nonelectroactive character of the solubilizing side chains alters the electrochromic properties of the soluble polymers. In spite of the apparent trade-off found in **230** and a bis(2-ethylhexyloxy)-substituted analogue, PProDOT-MeOEtHx_2 (**233**), between processability and performance, an unarguable optimal side chain length has not been reported to date in this respect.

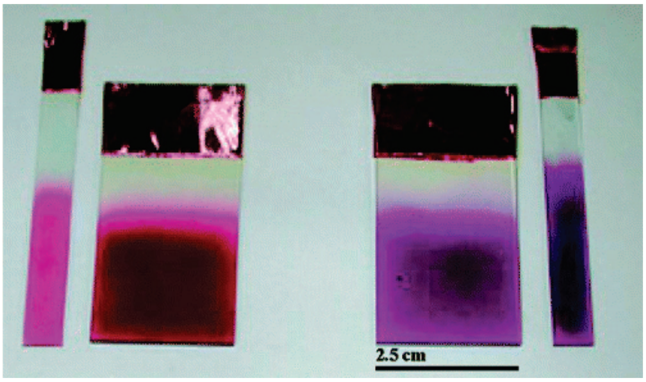


Figure 8. Photographs of spray-cast films of **233** (left) and **232** (right) from 5 mg mL^{-1} toluene solutions using an airbrush as reported by Reynolds et al. Adapted with permission from ref 255. Copyright 2004 American Chemical Society.

By linking two ProDOT molecules together at the position of the central carbon of the propylene bridge, a new monomeric entity was synthesized which could be electropolymerized, resulting in a cross-linked polymer film, hence insoluble in any solvent.[256] The polymer in question, namely, P(SpiroBiProDOT) (**234**), was found to switch from a dark

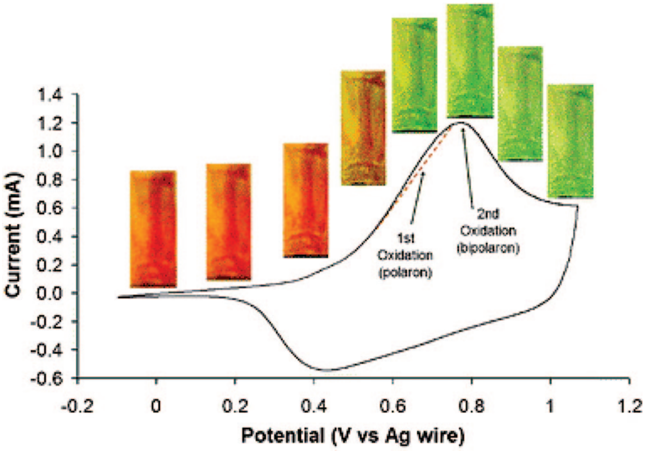


Figure 9. Cyclic voltammogram of conformationally restricted PProDOT **247**, electrodeposited onto an ITO/glass electrode, and its pictures at different potentials. The conformational lock affects the π-conjugation and increases the polymer band-gap such that unconventional switches for PXDOTs arise on p-doping, here a neutral-state orange to transmissive switch. Adapted with permission from ref 258. Copyright 2007 The Royal Society of Chemistry.

red-purple neutral state to a transmissive blue-gray on partial oxidation and to dark blue in its fully oxidized state with a relatively moderate luminance change (ΔY) of 30% (at the considered film thickness, nonindicated).

On the basis of a synthetic design of monomers incorporating alkylene tethers of varying lengths, a series of conformationally restricted PProDOTs (see polymer series **235**−**247**) were electropolymerized and their redox and EC properties investigated.[257,258] While maintaining low polymer redox potentials, the conformational locks affected the degree of intramolecular π-overlap and changed the polymer's conjugation length and band-gap (from 1.94 to 2.26 eV) such that unconventional switches for PXDOTs were demonstrated spanning a neutral-state orange to transmissive color change (on p-doping) as illustrated in Figure 9.[258]

Motivated by the process of thermal defunctionalization of ester-substituted conducting polymers and oligomers successfully employed by Fréchet et al. in the fabrication of photovoltaic devices and transistors,[259−262] Reynolds et al. have developed and reported a base-mediated defunctionalization method suitable for EC applications.[263] In particular, the perspective of being able to incorporate several ECPs into multilayer-stacked devices without altering the last deposited film when casting the next one triggered the design of ester-substituted PProDOTs which can eliminate their solubilizing side chains under solid-state saponification conditions to form films with limited solubility in most common organic solvents (see polymer series **248**−**253**). As the spray-cast polymers were submersed into 0.1 M KOH in hot methanol for 1 h, the pendant groups were removed, leaving an insoluble electroactive layer possessing EC properties similar to those of the pristine polymer film (see Table 3). Further, the ability to render cast polymers insoluble may prove useful in the construction of display devices where the presence of solvent or gel electrolyte affects the long-term adhesion of conventional solvent-processable electroactive materials onto electrically conducting surfaces. Interestingly, the all ester-substituted

Table 3. Representative PXDOT Electrochromes and Analogues

polymer	λ_{abs}[a] (nm)	E_{gap}[b] (eV)	polymer electrochromism[c] n	i	d	ref
203	550 (597)	1.97	red-pink		transmissive blue	208
207, **208**	545 (590)	n/a	red-violet		blue-black	213
210	610−625	1.6−1.7	deep blue		sky blue	190, 215, 218, 219
212−**215**	~625	1.7−1.8	dark blue		transmissive light green	114, 190, 220−223
216	~625	~1.7	dark blue		transmissive light green	190
217	608	1.65	blue		sky blue	224
218	n/a	524	pink-purple		light blue	225, 226
219	434	2.1−2.2	brown-yellow		dark green	233
220	n/a	1.85	brick red	green	light gray	234
221	460	n/a	red		blue-black	235
223	~340	n/a	clear	blue	green	238
224	673	1.4	deep blue		transmissive gray	250, 251
225	625 (567)	~1.7	dark blue		transmissive light green	190, 218
226	n/a	~1.7	dark blue		transmissive light green	190, 223
229	544	1.80	dark red-purple		transmissive sky blue	254, 255
230	595 (553)	1.84	dark red-purple		transmissive sky blue	255
231	611 (559)	1.92	dark red-purple		transmissive sky blue	255
232	594 (553)	1.89	dark red-purple		transmissive sky blue	255
233	581 (543)	1.97	dark red-purple		transmissive sky blue	255
234	606	1.75	deep purple	transmissive blue-gray	dark blue	256
235	580 (627)	1.75	blue-purple		transmissive green-blue	257, 258
236−**247**	445−535	1.9−2.3	red-orange		transmissive green-blue	257, 258
248	n/a	1.8	blue-purple		transmissive sky blue	263
249	n/a	1.8	blue-purple		transmissive sky blue	263
250	n/a	1.8	blue-purple		n/a[d]	263
251	n/a	1.8	blue-purple		n/a[d]	263
252	541	2.0	burgundy		n/a[d]	263
253	556 (595)	1.95	blue-purple		n/a[d]	263
254	580	1.75	dark blue		sky blue	253
263	556	1.73	plum		blue	266

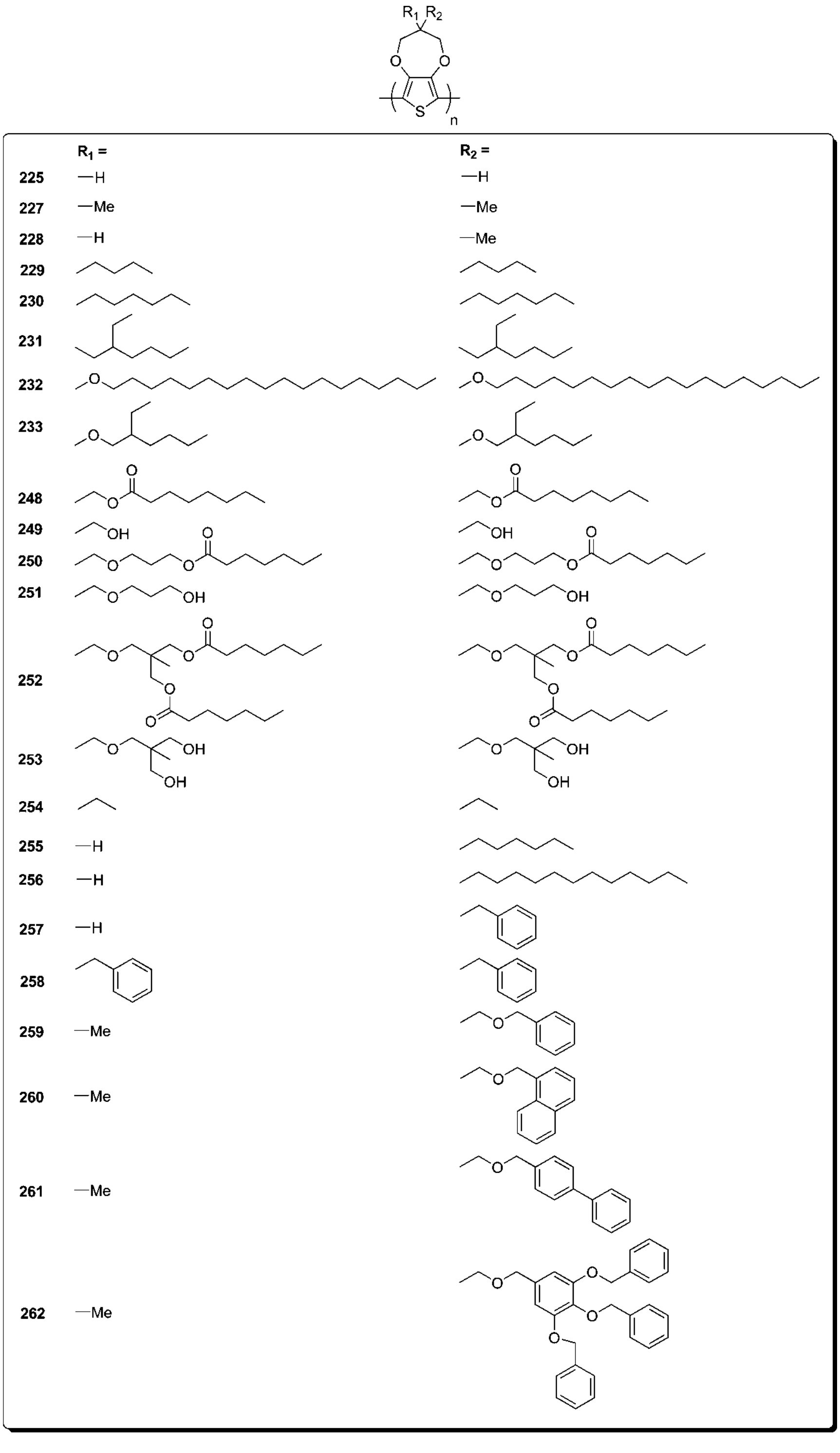
[a] Absorption extremum of the neutral-state thin-film polymer. [b] Optical band-gaps as calculated from the onset of the $\pi-\pi^*$ transition of the neutral-state polymer. [c] Key: (n) neutral state, (i) partially oxidized state, (d) fully oxidized state. [d] The polymer film exhibited excess solubility in solution electrolyte and was not investigated.

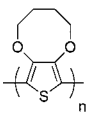
polymers were soluble in ethyl acetate, a processing solvent of choice in contrast with the more conventional chlorinated and aromatic alternatives when considering environmental aspects.

A few other interesting PProDOT analogues (**254**−**262**) have been synthesized and electrochemically characterized by Kumar et al. and others.[253,255,264,265] Some of them have been investigated in EC devices (see section 4).

Analogous to **226** in terms of the number of carbons constitutive of the dioxy bridge, the quinoxaline-substituted dioxythienyl-based homopolymer **263** exhibited a band-gap of 1.73 eV, along with a plum to blue switch on p-doping.[266]

In summary, substituting the ethylene bridge of EDOT by a propylene moiety increases the degree of optical transparency of the oxidized polymer film by opening the morphology of the corresponding polymer network, thereby favoring the diffusion of the charge-balancing counterions on electrochemical switching. Importantly, a fine-tuning of the electron-rich character of the dioxythienyl building units results from this simple structural modification. More precisely, the insertion of an extra methylene disrupts the coplanarity of the bridge with the adjacent aromatic center, alters its electron-donating effect, which lowers the polymer HOMO level (~0.1−0.3 eV) relative to the air oxidation threshold (5.2−5.3 eV vs vacuum), and enhances the





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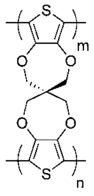

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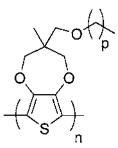
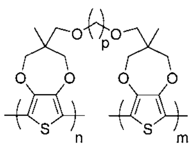
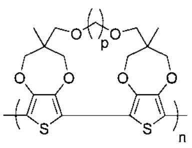


	p =
235	3



	p =
236	4
237	5
238	6
239	7
240	8
241	9
242	10
243	12



	p =
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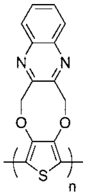
245	6
246	7
247	8



263

switching stability of the subsequent polymers under atmospheric conditions. In addition to the various inexpensive propylene dihalide or propylenediol substituents commercially available for the formation of the ProDOT ring, the subsequent polymers can be easily oxidized and reversibly switched to their neutral state as desired for EC applications.

Table 3 summarizes some of the key values and EC properties of the representative PXDOTs and analogues that have been reported to date.

3.2.2. Donor–Acceptor Systems

3.2.2.1. Narrow Band-Gap Cyanovinylene-Based DA CPs. To the best of our knowledge, the use of the donor–acceptor approach was first illustrated in the context of electrochromism by Reynolds et al. via the electropolymerization of low oxidation potential bis(thienyl)cyanovinylene donor–acceptor–donor (DAD) precursors.[177] It is worth noting that Roncali et al. had earlier described the electropolymerization of thienyl- and cyanovinylene-based oligomers with low oxidation potentials, along with the cathodic properties of their subsequent polymers.[267] In the report from Reynolds and co-workers, the electron-withdrawing cyanovinylene moiety was incorporated in a Knoevenagel condensation as a means to further lower the band-gaps of the formerly described deep purple to transmissive switching poly(*trans*-1,2-bis(thienyl)vinylene)s (see section 3.1.1.4), with the intention to achieve polymers exhibiting reversible n-doping processes. For example, careful electrochemical oxidation of EDOT-derivatized DAD macromonomers EDOT-CNV-Th and BisEDOT-CNV afforded p/n-dopable polymers **264** and **265** with low optical band-gap estimated values of 1.3 and 1.1 eV, respectively. Keeping the electron-deficient cyanovinylene moiety unchanged, the effect of the electron-rich character of the thienyl substituents on the band-gap of the subsequent polymers was later reported in a more extensive investigation involving a series of six DAD macromonomers (**264**–**269**).[268] The donors were chosen from thiophene, EDOT, or 3,4-(ethylenedioxy)pyrrole (EDOP), hence by electron-donating ability, and the redox and optoelectronic properties of the corresponding polymers were systematically compared to highlight the fine-band-gap-tuning described in Figure 10. In spite of the relatively wide range of energy gaps exhibited (0.4–0.5 eV), both spectroelectrochemical and colorimetry studies revealed similar color palettes on redox switching due to the spectral changes occurring essentially in the near-IR. Polymers **264**–**269** were found to switch reversibly from a moderately absorbing neutral-state blue to a transparent light blue oxidized state with relative luminance change values on the order of 50% (e.g., **264**).

The donor–acceptor approach relying on the electron-deficient cyanovinylene moiety previously employed in

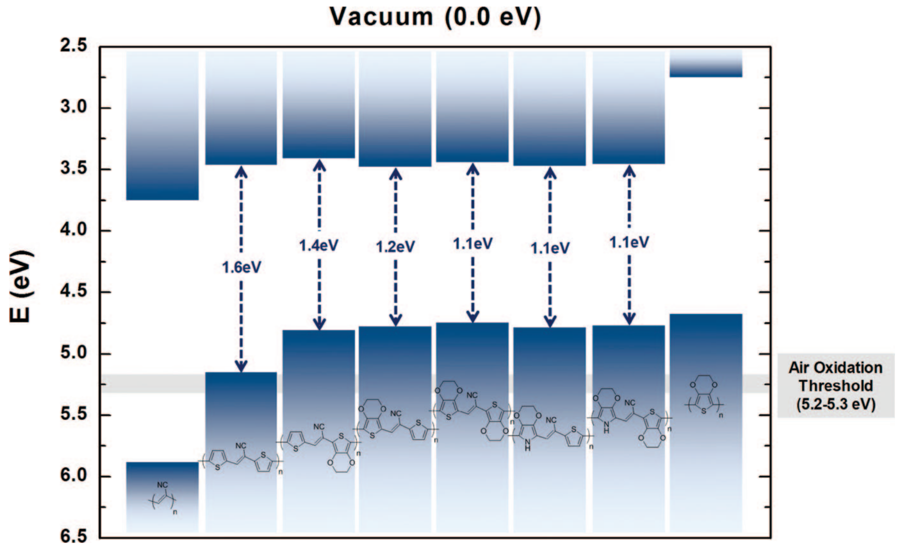
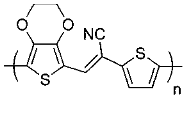


Figure 10. Energy band diagram highlighting the fine-band-gap-tuning obtained throughout a series of narrow band-gap cyanovinylene-based DA copolymers with various donor substituents and possessing cathodically coloring electrochromic properties. Adapted with permission from ref 268. Copyright 2004 American Chemical Society.



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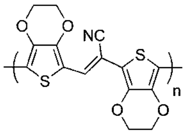

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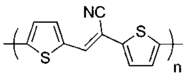

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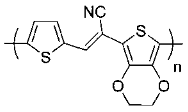

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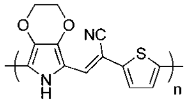

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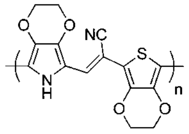

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making electropolymerized, yet insoluble, low band-gap materials was later on extended to a family of solution-processable homologues comprising a dialkyl-substituted ProDOT donor.[269] The soluble ProDOT-based analogues **270**, **271**, and **272** (PProDOT-CNVs) exhibited significantly wider energy gaps ranging from 1.5 to 1.8 eV as illustrated in Figure 11 and were compared to the cyanovinylene-based model copolymers **273**, **274**, and **275** to highlight the benefits of the specific electron-rich substituents incorporated in the DA backbones. The polymers showed an absorptive blue to purple neutral state along with a transmissive sky blue to gray colored state upon p/n-doping. In general, the color changes observed for this series of soluble DA polymers (see the corresponding spectroelectrochemical data in Figure 12) were found similar to that of **210**. However, the external biases required to initiate the depletion of the neutral-state visible absorption (0 to +0.5 V vs Fc/Fc$^+$) was higher than that for **210**, which has been shown to undergo spectral changes at potentials as low as −0.4 V vs Fc/Fc$^+$.[190] Further, while **210** can maintain its transmissive oxidized state effectively under atmospheric conditions owing to the location of its HOMO level (5.0−5.1 eV) relative to the air oxidation threshold (5.2−5.3 eV), the incorporation of ProDOT resulted in DA polymeric hybrids possessing deeper HOMOs and thus exhibiting stable neutral colored states instead.

In an effort to further the utility of PProDOT-CNV DA polymers in electrochromic and light-emitting device applications by improving the polymers' processability and film-forming propensity, four additional analogues (**276**−**279**) containing linear and branched alkoxy substituents were synthesized and characterized.[270] Exhibiting band-gaps in the range 1.70−1.75 eV, the polymers were successfully spray-cast (via an airbrush) to thin electrochromic films. The films switched from a blue (**276, 277**, and **279**) or purple (**278**) neutral state to transmissive gray on both electrochemical oxidation and reduction with relative luminance ratios up to 50% (at the considered film thickness, not indicated), hence showing potentially useful for large-area ECD applications.

Sotzing et al. have reported on the redox and EC properties of two DA polymers (**280** and **281**) resulting from the electrochemical polycondensation of unsymmetrical isomeric thieno[3,4-*b*]thiophene−cyanovinylene-based building blocks.[271] The corresponding hybrids exhibited a low band-

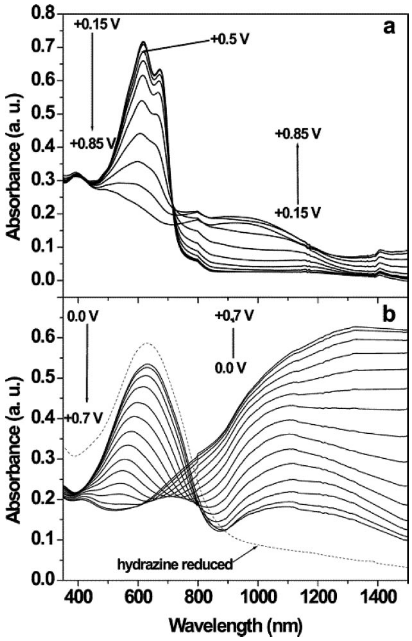


Figure 12. Spectroelectrochemistry of (a) **270** and (b) **272** cast from dichloromethane solution (1%, w/w) onto ITO-coated glass. The potentials are reported vs Fc/Fc$^+$ in 0.1 M TBAP/ACN electrolyte solution (50 mV steps). Adapted with permission from ref 269. Copyright 2006 American Chemical Society.

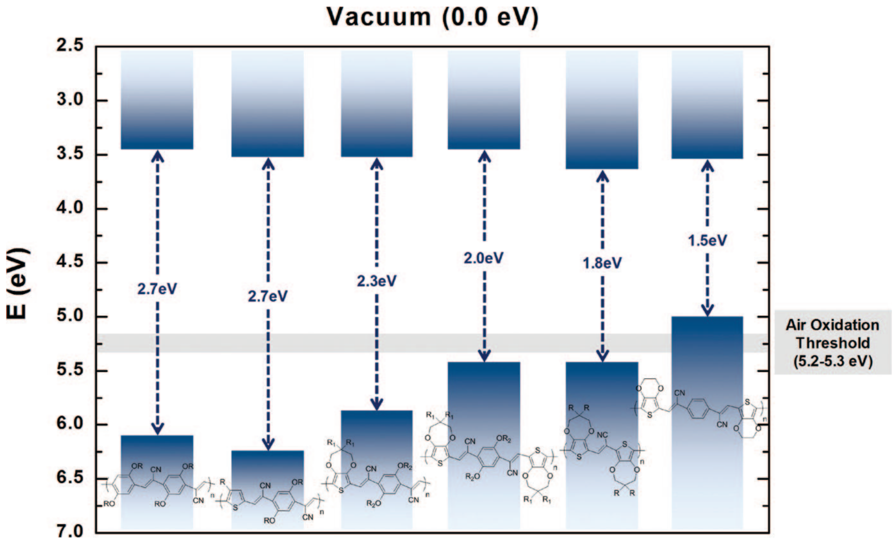
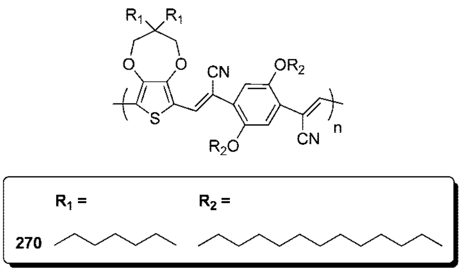
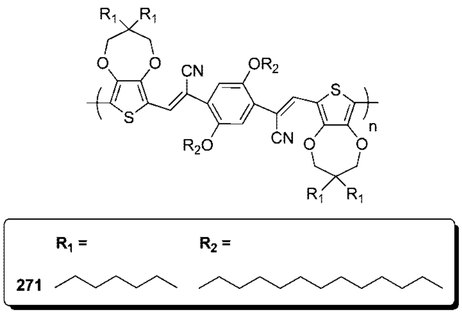
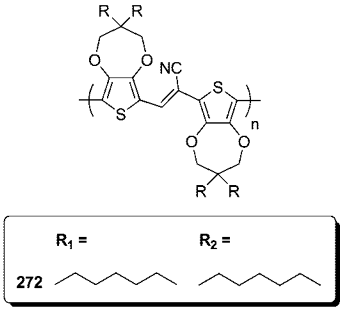
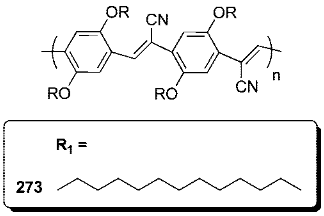


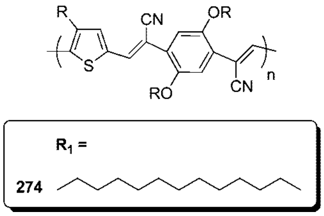
Figure 11. Band structures for a homologous series of cyanovinylene-based DA copolymers incorporating ProDOT moieties. With their appended solubilizing groups, the ProDOT-containing hybrids are solution processable and exhibit improved cathodically coloring electrochromic properties. Adapted with permission from ref 269. Copyright 2006 American Chemical Society.

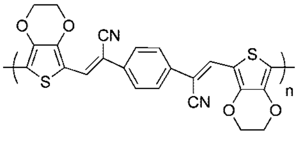












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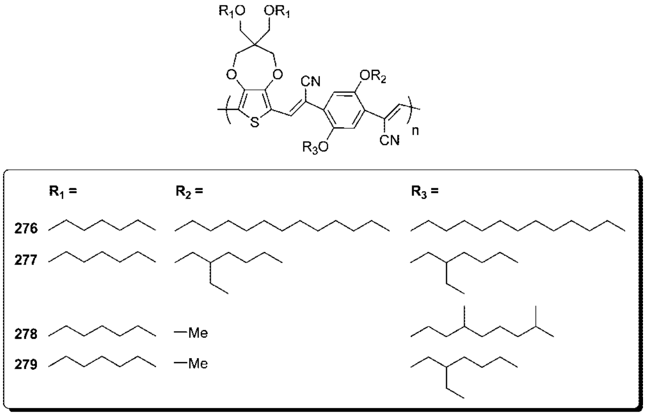
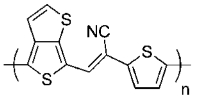


gap of ~1.2 eV along with a deep blue to transmissive sky blue switch on p-doping. Neither polymer showed stable n-doping.



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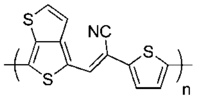
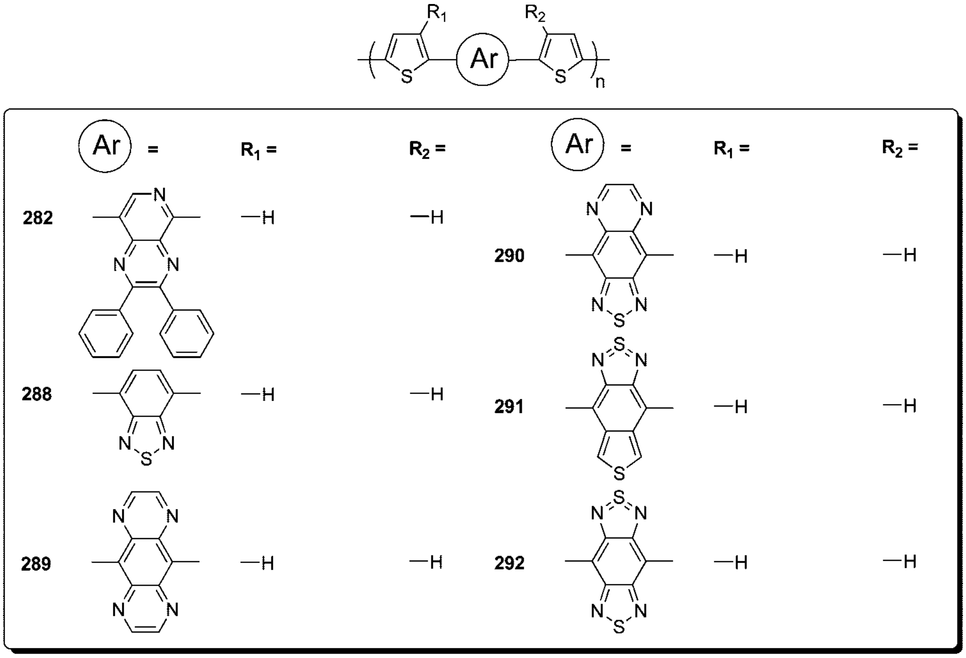
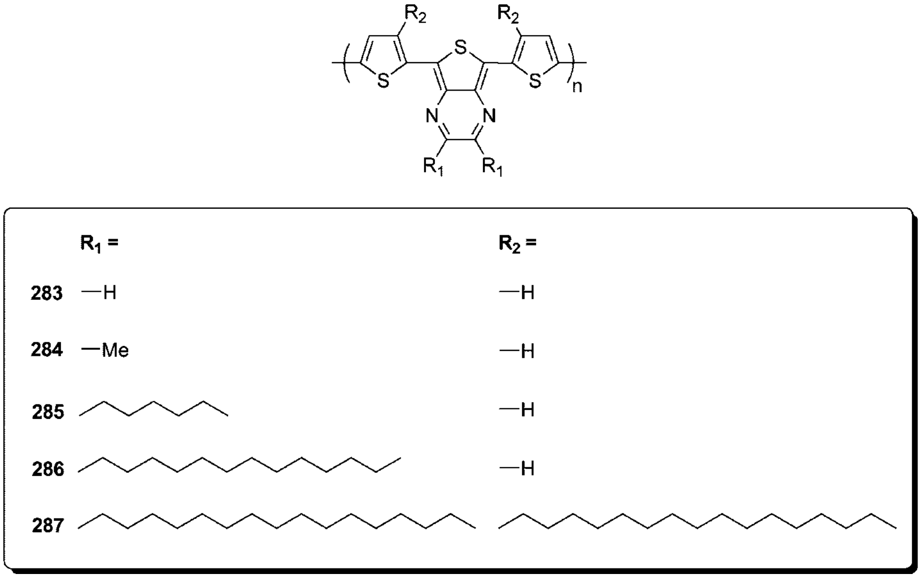


281

3.2.2.2. All Heterocyclic DA CPs. As previously mentioned (see section 3.1.1.9), swapping a pyridine-like electron-withdrawing heterocycle by a fused heterocyclic unit possessing high nitrogen content such as a pyridopyrazine or 2,1,3-benzothiadiazole can lower the energy gap of a thienylene-based polymeric hybrid remarkably. When the electron-accepting moiety is sufficiently strong and/or the resulting DA polymer backbones are sufficiently planar (i.e., reduced steric repulsions between donor and acceptor or among appended side chains), the polaronic states arise essentially in the near-IR, yielding colored to transmissive ECPs.

The presence of pyridopyrazine in polymer **282** sets a band-gap of 1.6 eV, resulting in a neutral-state dark purple to pale blue oxidized state on electrochemical switching.[272] DA hybrids combining unsubstituted or alkyl-substituted thienylene units with thienopyrazine (**283**−**287**) have been shown by Yamashita et al. to exhibit lower band-gaps (~1 eV) and dark blue to dark blue-black hues in their neutral state.[273,274] Sonmez et al. have revisited the dithienobenzothiadiazole DA polymer (**288**) (1.5 eV energy gap), placing a good deal of attention on its EC properties.[275] The use of stronger acceptors, such as in **289**−**292**, afforded band-gaps believed to be as low as 0.3 eV and neutral-state colors ranging from dark blue to dark blue-green.[273,276] For example, the BisEDOT−benzobis(thiadiazole) DA hybrid (**293**) was found to exhibit a band-gap of ~0.5−0.8 eV (depending on the method employed in gap measurement) and an olive green to dark blue switch on p-doping.[277] The thienyl units of **283**−**287** were also replaced by the more electron-donating EDOT moiety to produce polymer **294** with a band-gap of 0.77 eV, a red-purple to colorless gray switch on p-doping and a blue color on n-doping.[205] The alternating EDOT−thienopyrazine homologue **295** exhibited an even lower claimed band-gap of 0.36 eV.[278] The acenaphthylquinoxaline-based DA polymer **296** was electrochemically produced to reveal a band-gap of 1.2 eV, a blue-green to transmissive green switch on p-doping, and a red-purple color on n-doping.[279] In comparison, the diphenyl-substituted quinoxaline-based DA polymer **297** revealed a larger band-gap of 1.75 eV and changed from its red-purple neutral state to green on partial oxidation and to dark gray when fully oxidized.[280] With an identical band-gap of 1.75 eV, the electrochemically prepared bithiazole DA hybrid **298** revealed a blue to transmissive switch on p-doping (as read from the photographs available).[281] The low band-gap perylenediimide-containing DA hybrid **299** (1.5 eV) was recently shown to exhibit excellent reversibility upon both p- and n-doping processes. This polymer was yellow-green in the neutral state and pale cyan and blue in its first and second reduced states, respectively.[282] With a band-gap identical to that of PEDOT (1.6 eV) and a deep blue to transmissive switch on p-doping, the BisEDOT−benzotriazole-based DA hybrid **300** has been proposed as an alternative to the all-EDOT parent polymer in EC applications.[283] An increase of optical contrast at the absorption maximum (53% vs 44% for PEDOT) and a reduction of the polymer's response time (1.1 vs 2.2 s for PEDOT) were suggested (although it was not specified whether the deposited films had the same thickness). Polymer **300** was found pale blue-gray upon n-doping.

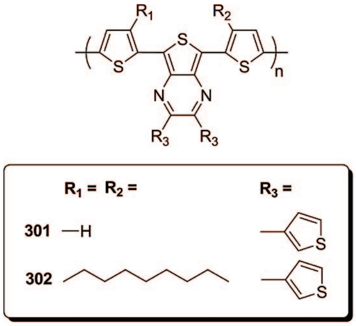


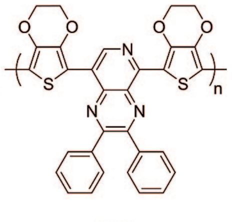


3.2.2.3. Green ECPs and the Color Mixing Theory.

As described throughout section 3.1, section 3.2.1, section 3.2.2.1, and section 3.2.2.2 in particular as well as in other review works on EC technologies,[9,10] a number of neutral-state red and blue π-conjugated ECPs were synthesized and their properties investigated over the past two decades. However, attempts in making saturated green ECPs, chemically or electrochemically synthesized, had not initially been reported likely due to the complexity of the required polymer neutral-state absorption spectrum that must contain two discrete optical transitions in the visible.

By reporting on the first neutral green π-conjugated polymer potentially useful for EC applications, Wudl et al. reinforced in 2004 the idea that the donor−acceptor approach was a well-chosen avenue toward accessing hues and saturations commonly difficult to achieve.[284] Beyond broadening the range of red and blue ECPs available to the color green, hence completing the additive primary color space, red, green, and blue (RGB), their suggestion of using careful synthetic design to literally create two bands of visible absorption centered around the transmissive spectral range of interest provided a unique path to tackling a long-term challenge. To this end, the first reported neutral green ECP was designed to combine an alternating DA molecular structure with two distinct chromophores: the red-absorbing DA macromolecular main chain and a short blue-absorbing conjugated entity present on each repeat unit, yet in broken conjugation with the main chain.[284] The corresponding 2,3-dithien-3-yl-5,7-dithien-2-ylthieno[3,4-*b*]pyrazine (DDTP) macromonomer was synthesized and electropolymerized to afford polymer **301** absorbing concomitantly at wavelengths longer than 600 nm (with a maximum at 725 nm) and shorter than 500 nm (with a maximum at 370 nm) (see Figure 13). Films of **301** deposited on a platinum button electrode exhibited a high degree of stability upon electrochemical switching between neutral and fully oxidized states in 0.1 M $LiClO_4$/propylene carbonate with no significant current density variation or charge density loss (calculated from





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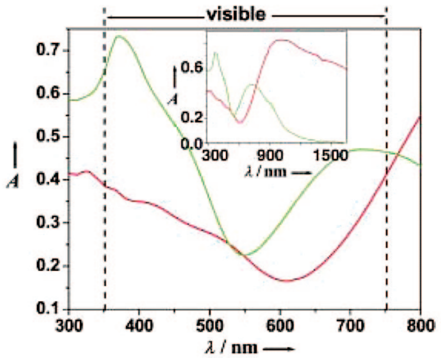
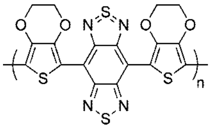


Figure 13. Spectroelectrochemistry of a film of **301** as described by Wudl et al. The film was deposited on an ITO-coated glass slide and characterized in 0.1 M TBAPF$_6$/ACN electrolyte solution. The figure shows two different oxidation states: neutral (green curve) and oxidized (red curve). Adapted with permission from ref 284. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.



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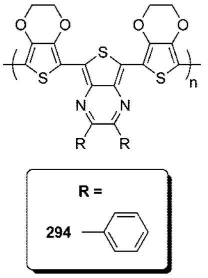
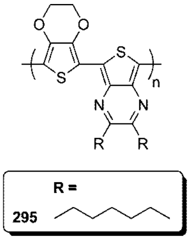
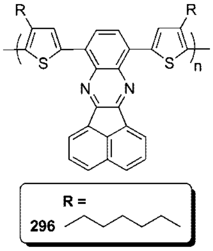
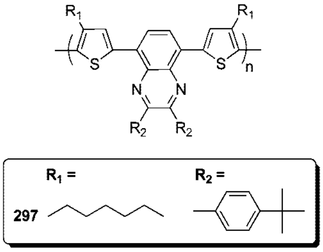








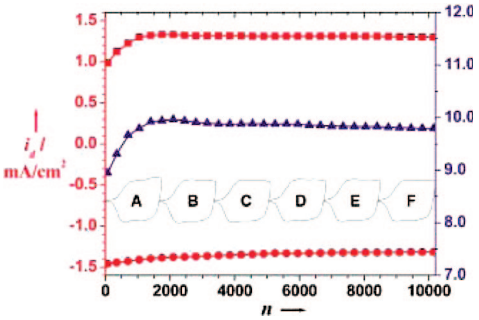
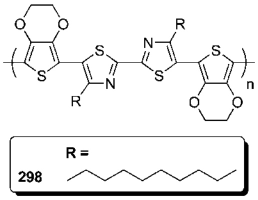
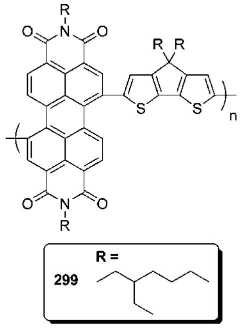
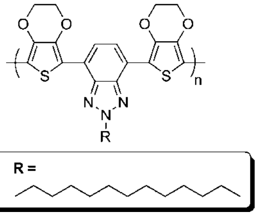


Figure 14. Long-term switching of a thin film of **301** deposited onto a Pt button electrode. Variation of anodic (i_{pa}; red squares) and cathodic (i_{pc}; red circles) peak currents, along with that of the charge stored (Q_{stored}; blue triangles) for the polymer film as a function of the number of cycles (n). The film was cycled 10 000 times at a scan rate of 200 mV s^{-1} between −0.80 and +0.58 V vs Ag/Ag$^+$ in 0.1 M LiClO$_4$/PC. Adapted with permission from ref 284. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.







integration of the current during the redox process) after 10 000 cycles as described in Figure 14. However, this material revealed low contrast ratios in the visible (23% at 370 nm and 12% at 725 nm) in agreement with the yellow-brown hue of relatively moderate transmissivity characteristic of its oxidized state. As illustrated in Figure 13, the optical transition associated with the smaller chromophore (the one in broken conjugation with the main chain) does not bleach effectively on progressive electrochemical oxidation and a polaronic transition arises in the near-IR with significant overlap in the visible region, hence interfering with the depleting longer wavelength absorption band. The resulting persistent hue of the doped state remained an obstacle that could not be overcome even after a soluble version of this first promising neutral-state green ECP was achieved (**302**).[285,286]

In fact, as previously mentioned, ECPs exhibiting a high degree of transparency in at least one of their redox states are of particular interest for display technologies where multiple chromophores can be incorporated and overlaid to obtain new color states. For example, by being able to fully bleach the visible absorption of one of a given pair of chromophores, a new saturated hue appears which nearly corresponds to the chromophore left in its colored state. If the pair of chosen chromophores corresponds to a pair of primary colors in the sense of the color-mixing theory, a wide range of useful colors can be obtained. In the case of a polymeric material transmitting/reflecting green light, attaining a highly transmissive state upon application of an external bias is an additional challenge owing to the necessity for simultaneous and effective bleaching of the two absorption bands present in the blue and red portions of the visible region.

At the same time, Reynolds et al. reported on electrolyte-controlled redox conductivity and n-type doping in BisEDOT−pyridine polymer analogues[287] and pointed out the ability to

Figure 15. Use of red (**2** or **8**), blue (**210**), and green (**301** or **302**) ECPs in work from Sonmez et al. The different colors are obtained using mixtures of the polymers and by switching them between their two redox states. Adapted with permission from ref 286. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

generate the color green via the donor−acceptor approach without being able to reach a satisfyingly transmissive state on p-doping. For example, spectroelectrochemical analysis of a BisEDOT−pyridopyrazine-based analogue (**303**) revealed a lime green to gray-green switch upon stepwise oxidation in all investigated electrolyte systems. The lack of transmissivity of the p-doped state was attributed to the near-IR-absorbing charge carriers, the corresponding transition of which tailed strongly in the visible region. Using conditions favoring true n-doping (i.e., via an adequate electrolyte cation−anion pair), the same polymer changed from its lime green neutral state to burgundy red and dark gray once fully reduced.

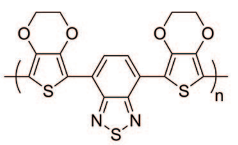
On the basis of color-mixing theory principles, with three primary colors on hand, all other color states can virtually be attained by simply combining those states in different proportions. Following the additive color-mixing model (as in overlapping lights, in opposition to combining pigments), when only two color states are mixed, the resulting hue can be predicted from drawing a straight line between the two initial states on a chromaticity diagram with the location of the new state depending on the ratio of colors mixed. In the context of light emission, the full spectrum can practically be generated (except the color black) by mixing three primary colors (e.g., red, green, and blue), including white. In analogy, by mixing dyes of three primary colors associated with the subtractive model (e.g., magenta, cyan, and yellow), it is possible to obtain all other colors (except white) including red, green, blue, and black.

With the intention of taking advantage of the color-mixing theory, Sonmez et al. rapidly introduced the idea of overlaying red, green, and blue colored ECPs two by two.[286] The electroactive polymers were chosen from the methyl-substituted PT (**2**) for the red, **210** as the blue, and the DA hybrid **301** as the green. Homogeneous films of the electropolymerized materials were placed face-to-face in a quartz cuvette containing the electrolyte and switched separately to generate the hues illustrated in Figure 15, including a variety of brown, gray, and sky blue colorations. Then again, the same Figure 15 highlights the impracticality to generate, with the chosen polymers, a set of primary colors corresponding to the subtractive model (such as magenta, cyan, and yellow), thereby emphasizing the need for a different strategy to attain the expected full range of colors. To this end, it is believed that careful selection of a new set of electroactive polymers with hues corresponding to a triad of primaries in the sense of the subtractive model instead could lead to the expected result.

The first series of green to transmissive switching ECPs was reported along with the observation that donor−acceptor alternating copolymers can exhibit two inherent and distinct optical transitions[288,289] without the need to incorporate two separate chromophores with different conjugation lengths as previously described.[284,286,290,291] In theoretical work from Salzner et al. on evaluating the potential of the donor−acceptor approach in the design of organic metals,[288,289] donor−acceptor systems involving two distinct absorption bands are tentatively rationalized by considering the presence of low-lying unoccupied and localized energy levels forming a discrete energy “band” within the band-gap of the conjugated system in its ground state. In this case, the discrete energy band (expectedly governed by the most electron poor heterocycles) lying beneath the conduction band in the orbital correlation diagram of the conjugated polymer is easily accessed from the valence band.[289] On the basis of these assumptions, the optical spectrum corresponding to the undoped donor−acceptor system described features (1) low-energy transitions from the valence band to the low-lying unoccupied and localized energy levels resulting in a long-wavelength absorption band and (2) higher energy transitions from the valence band to the true conduction band which are responsible for the presence of a distinct absorption band at shorter wavelengths in the visible spectrum.

These considerations have been well supported since then by separate work from Toppare et al. and the Reynolds group. For instance, in 2007, the BisEDOT−benzothiadiazole-based analogue **304**, the synthesis and electrochemical properties of which had been previously reported,[292−294] was electropolymerized and reinvestigated by Toppare and co-workers as a candidate for electrochromic applications. Throughout their study, electrochemically deposited insoluble films of **304** were found to switch rapidly and reversibly from a neutral-state saturated green to a transmissive light blue oxidized state as illustrated in Figure 16.[295] Films of **304** coated on a platinum wire exhibited excellent stability upon electrochemical switching between neutral and fully oxidized states in 0.1 M $LiClO_4$/propylene carbonate with less than 2% charge density loss (calculated from integration of the current during the redox process) after 5000 cycles. While high EC contrasts were monitored in the visible (38% and 51% calculated with respect to the local minimum of absorption at around 500 nm), the polaronic transition arising in the near-IR on progressive increase of the potential applied tailed significantly in the red region of the visible (see Figure 16) and accounted for the relatively blue tone of the fully doped state.

Following the results obtained with the polymer electrochrome **304**, a series of reports appeared to support the use of EDOT in the design of two-band-absorbing donor−acceptor ECPs.[296−298] First, two BisEDOT−quinoxaline macromonomers were electropolymerized onto ITO in 0.1 M $TBAPF_6$/dichloromethane solution electrolyte to afford their corresponding polymers **305** and **306**.[296] Spectroelectrochemical analysis of the thin films highlighted the spectral variations existing between the two polymeric analogues differing only by the nature of the functionalities present on the quinoxa-



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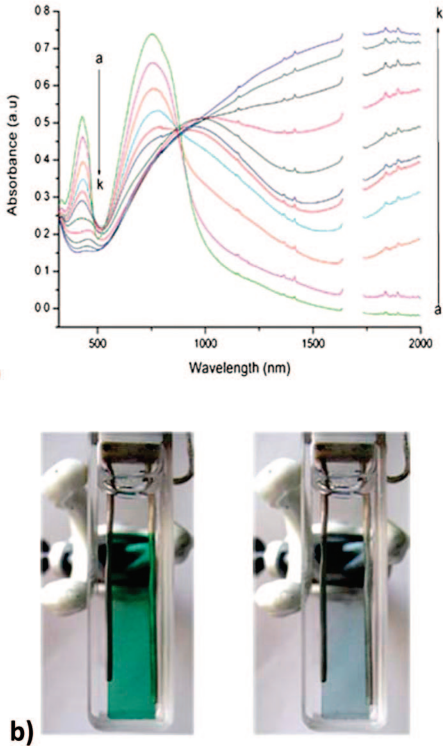
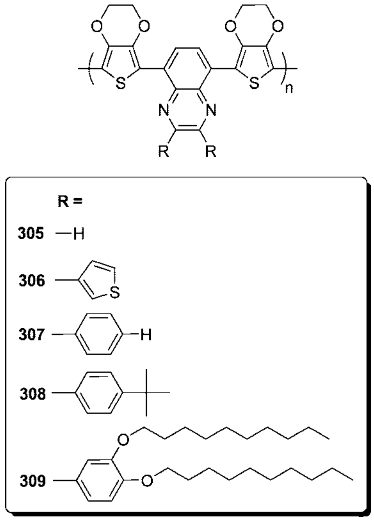


Figure 16. (a) Spectroelectrochemistry of a film of **304** as described by Toppare et al. The film was cast on an ITO-coated glass slide and characterized in 0.1 M $TBAPF_6$/ACN electrolyte solution. (b) Color state for **304** in the neutral (green) and oxidized (light blue) states. Adapted with permission from ref 295. Copyright 2007 The Royal Society of Chemistry.

line-type electron-accepting substituent. For instance, the neutral-state blue-green tone of **305**, when compared to the saturated green color of **306**, was attributed to the stronger accepting propensity of the 2,3-dithiophene-2-ylquinoxaline versus that of simple quinoxaline, resulting in an overall red shift of the two-band absorption in the visible. Further, the longer wavelength absorption band appeared significantly broader in the case of **306**, and the presence of the thienyl-based chromophore in broken conjugation with the polymer main chain absorbed the blue portion of the visible more effectively, such that the interband window of transmission shifted into the 500−550 nm region, which could explain the difference in hue of the neutral-state polymers **305** and **306**. On stepwise oxidation, **305** bleached to a transmissive blue, whereas **306** exhibited a pale brown doped state similar to that previously described in the case of polymers **301** and **302**. The EC contrasts monitored in the visible on electrochemical oxidation were significantly larger for **305** (36% at 410 nm and 30% at 660 nm) than they were for **306** (20% at 370 nm and 30% at 725 nm) with respect to the shorter wavelength absorption band, and the films switched in subsecond switching times (at the considered film thickness, nonindicated). As for **304**, the polaronic transition arising in the near-IR on progressive increase of the potential applied tailed in the red portion of the visible in the case of **305**, accounting for the blue tone of the fully doped state. Films of **305** and **306** deposited on a platinum electrode via repeated scanning exhibited less than 5% charge density loss after 5000 cycles upon electrochemical switching between neutral and fully oxidized states in 0.1 M $LiClO_4$/propylene carbonate. Interestingly, only **306** was found n-dopable, producing a purple color contrast on electrochemical reduction in 0.1 M $TBAPF_6$/ACN. In two separate studies,[297,298] three phenyl-substituted BisEDOT−quinoxaline analogues were reported by the same group and electropolymerized onto ITO to yield their corresponding polymer hybrids **307**−**309**. Films of **307** and **308** deposited on a platinum wire via repeated scanning exhibited less than 8% charge loss after 5000 cycles in 0.1 M $LiClO_4$/propylene carbonate. Interestingly, a film of **309** deposited on ITO exhibited only about 10% charge loss after 5000 cycles using the same electrolyte/solvent system. On stepwise oxidation, **307**−**309** bleached from their saturated green neutral state to a light green, "colorless" and "transparent" doped state, respectively. It is worth noting that as opposed to **301**, **302**, and **306**, which exhibited a relatively absorptive oxidized state (yellow-brown or pale brown) likely due to the thienyl-based short chromophore substituted on each acceptor unit as described above, their phenyl-based polymer analogues **307**−**309** showed some notably more transmissive doped states. The contrast ratios monitored in the visible on electrochemical oxidation (applying potential steps) were larger for **308** (33% at 452 nm and 43% at 711 nm) than they were for **307** (35% at 448 nm and 29% at 732 nm) with respect to the longer wavelength absorption band, yet the films were found to switch in about 1 s in both cases (at the considered film thickness, nonindicated). It is possible that the presence of the *tert*-butyl solubilizing group in **308** facilitates the diffusion of the charge-balancing ions across the polymer network, the formation of charge carriers, and the depletion of the visible absorption of the polymer. The visible EC contrasts estimated in the case of **309** (29% at 415 nm and 42% at 690 nm) on electrochemical oxidation were similar to those of **308**. **309** was also chemically polymerized via the oxidizing agent $FeCl_3$, and its electrochemical/electrochromic properties were successfully matched with the electropolymerized parent polymer. **307** and **308** were found to follow an effective and reversible n-doping process, producing a red color contrast on electrochemical reduction in 0.1 M $TBAPF_6$/ACN (**309** was not investigated).



In parallel, Reynolds and co-workers emphasized the idea that a two-band optical absorption in the visible reflecting

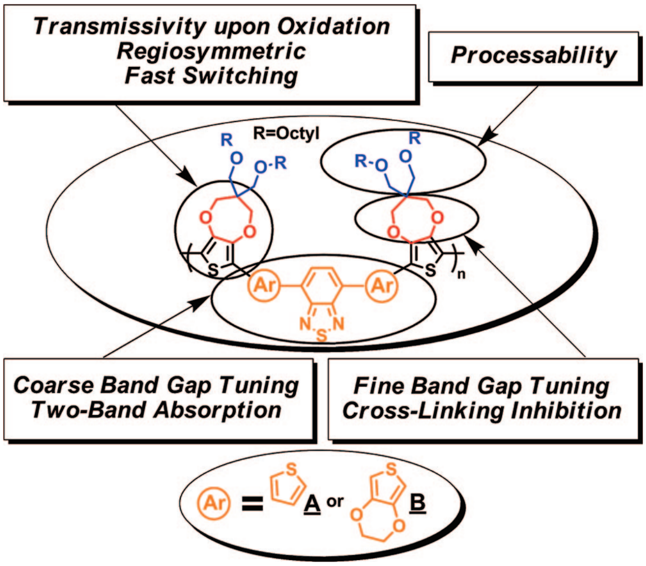


Figure 17. Schematic describing the rationale for the synthetic design employed by Reynolds et al. to access solution-processable neutral-state green to transmissive switching polymer electrochromes **310** and **311** with tunable hue, fast switching properties, and highly transmissive oxidized states. Adapted with permission from ref 301. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

the color green can be obtained on the sole basis of a linear combination of well-chosen electron-rich and -poor building units.[299] Using a synthetic design relying on the symmetrical functionalization of the acceptor 2,1,3-benzothiadiazole with several alkoxy-substituted and unsubstituted thienyl donor substituents (see Figure 17), pentameric oligomers exhibiting especially low oxidation potentials were synthesized and chemically polymerized using mild oxidative conditions (**310** and **311**). In particular, alkoxy-derivatized ProDOT moieties were incorporated to provide the desired solution-processability, fine-band-gap-tuning, switching performance, and high color contrasts observed (up to 44% EC contrast at the higher wavelength absorption maximum of **311**). By varying the nature of the intermediate heterocycle (the one connected to benzothiadiazole), two distinct green hues demonstrating the versatility of the synthetic approach employed were obtained, which could be bleached to the highly transmissive color states illustrated in Figure 18 on p-doping. Besides the possibility of adjusting the polymer band-gap, and to control the green color state by fine-tuning the repeat unit, the proposed synthetic approach did not involve the presence of a second chromophore in broken conjugation with the main chain. As a result, the polymers' higher energy transitions depleted effectively on full oxidation as described in Figure 19 such that only the near-IR-absorbing charge carriers were found responsible for the residual light blue of the p-doped state.

Cihaner et al. have substituted 2,1,3-benzothiadiazole with 2,1,3-benzoselenadiazole in **288** and **304** to yield the DA derivatives **312** and **313**,[300] which exhibited essentially the same electrochromic contrasts as their benzothiadiazole parent polymers[275,295] (switching from blue-green to purple and from green to sky blue, respectively). Both polymers showed good propensity to n-type doping with **313** switching from green to dark purple upon reduction.

Table 4 summarizes some of the key values and EC properties of the green ECPs that have been reported to date.

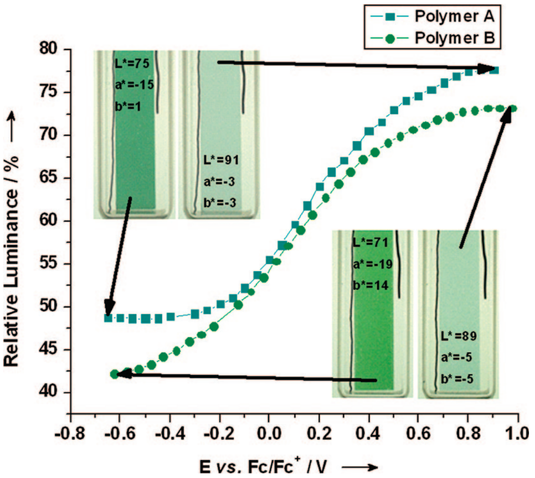
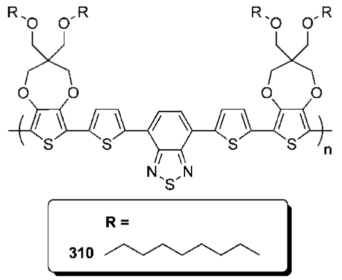
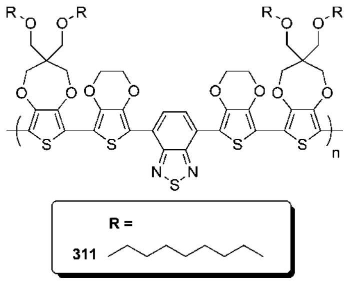
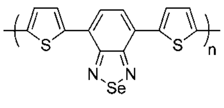


Figure 18. Relative luminance vs applied potential for spray-coated **310** and **311**. Pictures show the different hues of green perceived and indicate the degree of transmissivity attained by the polymers when fully doped. For color matching, $L^*a^*b^*$ values (in the sense of the CIE 1976 $L^*a^*b^*$ color model) of fully neutral and oxidized states appear on the films. Adapted with permission from ref 301. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.







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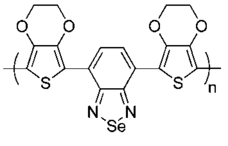


313

3.2.2.4. Black ECPs. The complexity of designing materials absorbing effectively across the visible region of the electromagnetic spectrum and into the near-IR is well established in the field of polymer-based solar cells where the challenge remains a matter of steady research effort.[302−309] It is thus not surprising that the same difficulty be encountered in developing saturated black ECPs (i.e., absorbing homogeneously over the visible spectrum) as specifically desired for "smart" window technologies and e-paper applications, for example. As for the green ECPs discussed above and suitable for display applications, the requirement for transparency (i.e., for coincident bleaching of the full visible absorption in this case) in one of the accessible redox

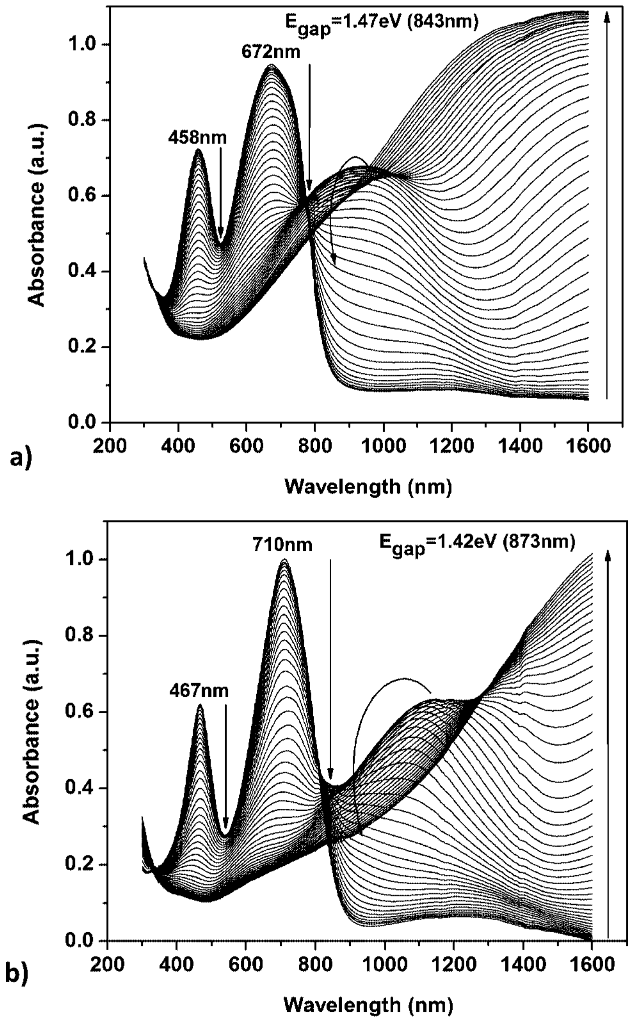


Figure 19. Spectroelectrochemistry of (a) **310** and (b) **311** spray-cast onto ITO-coated glass from solution (2 mg mL^{-1}) in toluene (**310**) or from a hot mixture of toluene and chloroform (**311**). The potentials are reported vs Fc/Fc$^+$ in 0.1 M LiBF$_4$/ACN electrolyte solution (25 mV steps). Adapted with permission from ref 301. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

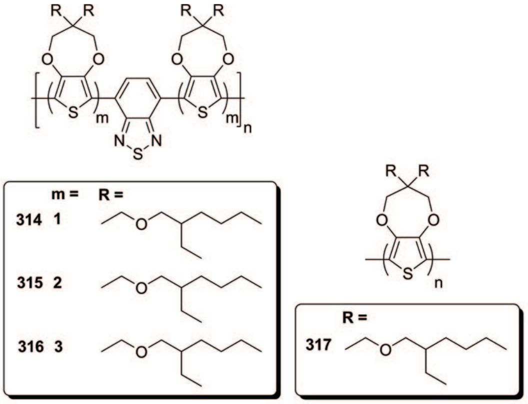
states is an additional constraint that adds to the difficulty in designing strongly absorbing ECPs.

Reporting on the utility of the donor−acceptor approach in designing two-band-absorbing polymer electrochromes reflecting and/or transmitting colors commonly difficult to achieve such as saturated greens, Reynolds et al. have recently described how low- and high-energy transitions could be adjusted in terms of their relative intensity and overlap by varying the relative contribution of electron-rich and -poor moieties incorporated in the polymer repeat unit (see Figure 20, **314**−**317**).[299] More precisely, as the electron-withdrawing substituent was first increasingly substituted with donor substituents and subsequently polymerized, the "merging" optical transitions were found to yield gradually darker color states with the most homogenously absorbing material **316** appearing dark green in solution (and essentially black as a deposited thin film). In an effort to overcome the relative lack of coverage in the blue and green regions of the visible (see Figure 20), a copolymer (**318**) possessing the same number of electron-rich and -poor units as **316** was chemically polymerized using the monomers constitutive of **314** and **317** (in a random fashion) to yield a disordered material exhibiting an absorption spectrum extended over the entire visible region (400−700 nm) (see Figure 21). Copolymer **318** was spray-cast on ITO and subjected to spectroelectrochemical analysis to reveal an EC contrast of ca. 50% at its maximum of absorption upon p-doping. Further colorimetric study showed relative luminance changes as high as 52% and L^* values up to 85 at the same film thickness, hence demonstrating the ability of this ECP to nearly reach the "white point" of color space in its clear state. The polymer completed its full and reversible black to transmissive switch (see Figure 21) in a narrow potential window of less than 1 V as desired for low-voltage-driven ECDs. Less than 28% variation in charge density was monitored upon 10 000 cycles in a test experiment performed in a simple three-electrode electrochemical cell placed under atmospheric conditions. Solution-processable black to transmissive ECPs have the potential to impact the development of electronic-ink technologies suitable for "e-paper" applications and EC window-type devices by providing lower synthetic, device fabrication, and processing costs when compared to other existing technologies (see section 4.4.6).

Table 4. Reported Green ECPs

					polymer electrochromism[e]					
polymer	λ_{max1}[a] (nm)	λ_{min}[b] (nm)	λ_{max2}[c] (nm)	E_{gap}[d] (eV)	n	d	ΔT_1[f] (%)	ΔT_2[g] (%)	CE[h]	ref
301	370	550	725	1.10	green (7, −47, 30)[i]	yellow-brown (53, −5, 11)[i]	23	12	n/a	284
302	410 (485)	n/a	670 (790)	1.30	green	pale brown	n/a	n/a	n/a	290
303	424	n/a	750	1.20	lime green	gray-green	n/a	n/a	n/a	179
304	428	500	755	1.19	green	light blue	37	23	130	295
305	410	n/a	660	1.40	green-blue (433, 0.254, 0.321)[j]	transmissive blue (683, 0.283, 0.326)[j]	36	30	n/a	296
306	405	n/a	780	1.20	green (236, 0.319, 0.481)[j]	pale brown (361, 0.330, 0.380)[j]	20	30	n/a	296
307	448	530	732	1.01	green (311, 0.299, 0.439)[j]	light green (571, 0.298, 0.344)[j]	35	29	n/a	297
308	452	530	711	1.18	green (444, 0.293, 0.431)[j]	"colorless" (655, 0.308, 0.355)[j]	33	43	n/a	297
309	415	500	690	1.45	green (443, 0.270, 0.400)[j]	"transparent" (626, 0.314, 0.348)[j]	29	42	n/a	298
310	458	n/a	672	1.47	green (71, −19, 14)[i]	light blue (89, −5, −5)[i]	27	36−39	121−126	301
311	467	n/a	710	1.42	green-yellow (75, −15, 1)[i]	light blue (91, −3, −3)[i]	45	40−44	n/a	301
312	350	n/a	600	1.46	blue-green	purple	8	12	89	300
313	448	542	796	1.05	green	sky blue	27.3	10.9	94	300

[a] Short-wavelength absorption maximum of the neutral-state thin-film polymer. [b] Absorption minimum. [c] Long-wavelength absorption maximum. [d] Optical band-gaps as calculated from the onset of the $\pi-\pi^*$ transition of the neutral-state polymer. [e] Key: (n) neutral state, (d) fully oxidized state. [f] Representative EC contrast at the shorter wavelength absorption maximum. [g] Representative EC contrast at the longer wavelength absorption maximum. [h] Coloration efficiency measured at the longer wavelength absorption maximum. [i] Color coordinates expressed in the CIE-defined $L^*a^*b^*$ color space. [j] Color coordinates expressed in the Yxy color space.



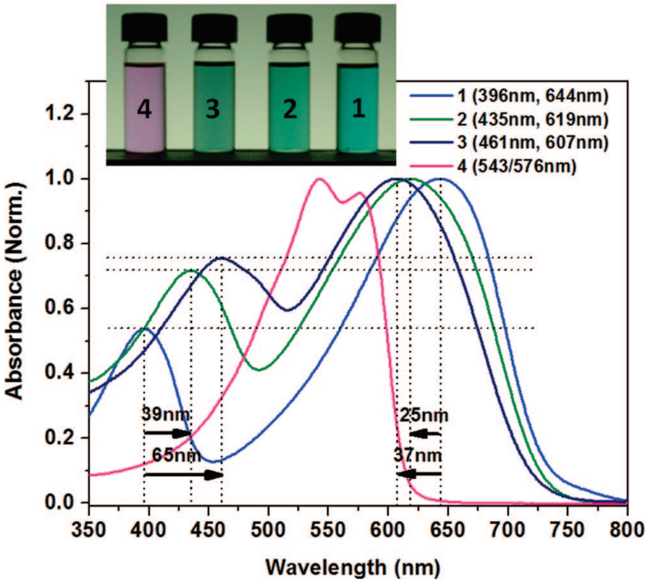
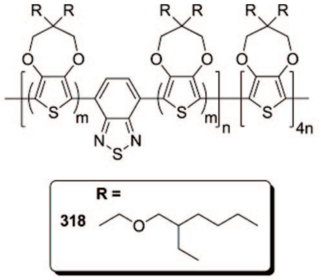


Figure 20. Solution optical absorption spectra (in toluene) of donor−acceptor polymers **314** (1), **315** (2), and **316** (3) compared to that of their all-donor parent polymer **317** (4) (the spectrum of each system is normalized at the longer wavelength absorption maximum). The legend specifies the values of the respective absorption maxima for both high- and low-energy transitions. Adapted with permission from ref 299. Copyright 2008 Nature Publishing Group.



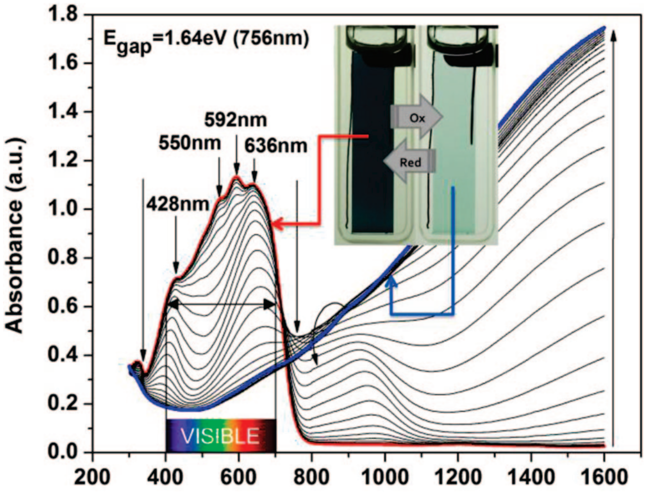


Figure 21. Spectroelectrochemistry of polymer **318** with its respective band-gap as estimated from the onset of absorption. The applied potential was increased in 25 mV steps from +0.04 to +0.74 V. The inset shows the color states of **318** reversibly obtained on electrochemical switching (left, neutral state; right, oxidized state). Adapted with permission from ref 299. Copyright 2008 Nature Publishing Group.

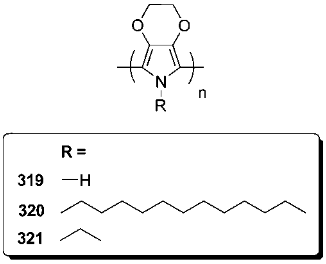
3.3. Anodically Coloring Polymers

3.3.1. Poly(3,4-dioxypyrrole)s: From Cathodically to Anodically Coloring ECPs

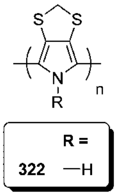
Of all established pyrrole-based electroactive π-conjugated polymer electrochromes, poly(3,4-dioxypyrrole)s (PXDOPs) and analogues have received the greatest deal of attention over the past decade[310] owing to their low oxidation potential, along with highly tunable optical and electrochemical behaviors. To demonstrate the myriad of colors accessible from PXDOPs' various redox states, dioxypyrrole (DOP) monomeric precursors have been synthesized in various ways including *N*-functionalizations, structural modifications of the alkoxy substituents or alkylene bridge (in the way of cathodically coloring PXDOTs), and new alternative pathways to the *N*-hydro parent monomer.[310] As for the PXDOTs, the substitution in the 3- and 4-positions of a pyrrole induces more than a sole band-gap-tuning, but it also prevents the formation of α,β- and β,β-cross-links on polymerization, hence limiting the concentration of structural defects occurring in the growing backbones. Similarly, the low oxidation potential in the PXDOPs, resulting from the increase of ring electron density when compared with polypyrroles, provides the subsequent polymers with improved ambient stability in their doped state.[311−313]

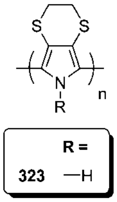
In comparison with PEDOT (**210**), PEDOP (**319**) exhibits both higher HOMO and higher LUMO energy levels. Its corresponding band-gap is wider (~2.0 eV) than that of PEDOT (~1.6 eV) by about 0.4 eV owing to the more significant energy difference between their respective LUMOs (which is analogous to pyrroles in general having higher LUMOs than thiophenes) and lower by 0.7 eV than that of **54** (~2.7 eV).[311−315] On electrochemical p-doping the polymer switches from a bright red neutral state to a highly transmissive blue-gray in its fully oxidized state with optical contrasts as high as 59% and switching rates on the order of 1 s.[312] The chemically polymerized *N*-dodecyl-substituted derivative **320** was synthesized and revealed a band-gap of 3.26 eV, impressively higher than that of its unsubstituted parent **319** owing to the solubilizing group induced steric hindrance effectively twisting the polymer main chain.[304] The *N*-ethyl-substituted PEDOP (**321**) exhibited a green to violet to gray switch on progressive oxidation as demonstrated by spectroelectrochemical analysis.[316]

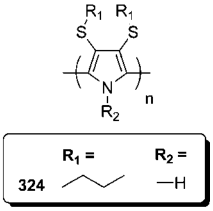
Achieved by Lambert et al., two alkylsulfanyl analogues of **319**,[317,318] namely, 3,4-(methylenedithio)pyrrole **322** and 3,4-(ethylenedithio)pyrrole **323**, as well as the 3,4-(dialkylthio)pyrrole **324** were electrochemically prepared and characterized. Expectedly, the corresponding polymers showed higher oxidation potentials than their dioxypyrrole parent **319** likely due to the reduced electron-rich character of the sulfur atoms and possibly higher level of associated steric hindrance. While only limited electrochromicity was observed



for polymer **322** in the visible as demonstrated by spectroelectrochemical analysis, **323** and **324** exhibited a more pronounced charge-carrier formation on p-doping. The band-gaps increased in the order **322**, **323**, and **324** and were estimated to be 1.8, 2.1, and 2.3 eV, respectively. **322** exhibited a yellow to black switch on electrochemical oxidation.[317]

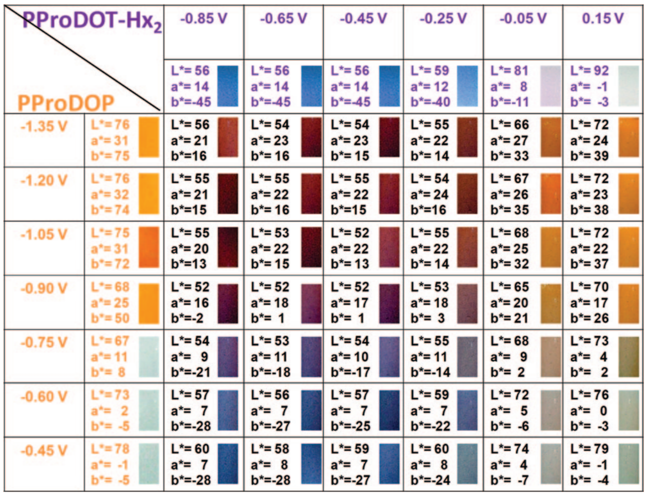






With a band-gap of about 2.2 eV, the propylenedioxy-substituted analogue PProDOP (**325**) shows enhanced electrochromic properties to an extent similar to that of **225** relative to **210**. In particular, both the optical contrast (up to 70%) and the transmissivity of the oxidized state could be improved by increasing the size of the alkylenedioxy bridge leading to a bathochromic shift of the charge-carrier-related spectral transitions in the near-IR which commonly tail in the visible region.[312,313,319] Switching in subseconds (∼0.25 s) from a neutral-state orange to brown on partial oxidation to light gray-blue on p-doping with remarkable redox switching stability values (only about 10% loss of electroactivity after 40 000 cycles onto a Pt electrode), **325** rapidly appeared as an excellent platform toward the synthesis and characterization of a novel family of π-conjugated ECPs holding promises for commercial applications. Further substitution at the central carbon of the propylene bridge such as in **326** and **327** produced insoluble materials on electrodeposition exhibiting contrast ratios as high as 76%. Interestingly, **326**, **327**, and the butylenedioxy-substituted derivative **328** exhibited the same band-gap value of 2.2 eV and switched from neutral-state orange to red-brown or orange-brown on partial oxidation to light blue when fully oxidized.[312] **325** was shown useful in electrochromic cells where a pair of ECPs placed under separate potentiostatic control are used to generate additive color states not accessible in a cell composed of a single ECP.[320] In the presented case, **325** was used in combination with **210** or PProDOT **230** as illustrated in Figure 22 to demonstrate how desirable colors can be attained by precisely controlling the oxidation state of each polymer without having to synthesize a single polymer that would possess the exact targeted hue in one of its redox states.

As briefly mentioned above, *N*-substitutions have a greater impact on the electronics of the subsequent PXDOPs than the structural modifications described above.[313,321] Hence, by effectively altering the steric hindrance, planarity, and overall conjugation length of the polymer main chains, pendant groups directly anchored onto the XDOP pyrrole-like nitrogen have been employed to produce polymers with band-gaps as wide as 3.4 eV and neutral-state absorptions entirely shifted into the UV region of the electromagnetic spectrum.[322] While retaining the low oxidation potential inherent to their other PXDOP analogues, the resulting polymers then often either are anodically coloring (with charge-carrier transitions arising in the visible on p-doping) or exhibit spectral changes restricted to the UV and the near-IR regions, remaining essentially transmissive regardless of their doped state.[322,323]



PProDOT-Hx$_2$ / PProDOP		-0.85 V	-0.65 V	-0.45 V	-0.25 V	-0.05 V	0.15 V
		L*= 56 a*= 14 b*=-45	L*= 56 a*= 14 b*=-45	L*= 56 a*= 14 b*=-45	L*= 59 a*= 12 b*=-40	L*= 81 a*= 8 b*=-11	L*= 92 a*= -1 b*= -3
-1.35 V	L*= 76 a*= 31 b*= 75	L*= 56 a*= 21 b*=16	L*= 54 a*= 23 b*= 16	L*= 54 a*= 23 b*= 15	L*= 55 a*= 22 b*= 14	L*= 66 a*= 27 b*= 33	L*= 72 a*= 24 b*= 39
-1.20 V	L*= 76 a*= 32 b*= 74	L*= 55 a*= 21 b*=15	L*= 55 a*= 22 b*= 16	L*= 55 a*= 22 b*=15	L*= 54 a*= 24 b*=16	L*= 67 a*= 26 b*= 35	L*= 72 a*= 23 b*= 38
-1.05 V	L*= 75 a*= 31 b*= 72	L*= 55 a*= 20 b*=13	L*= 53 a*= 22 b*= 15	L*= 52 a*= 22 b*= 13	L*= 55 a*= 22 b*= 14	L*= 68 a*= 25 b*= 32	L*= 72 a*= 22 b*= 37
-0.90 V	L*= 68 a*= 25 b*= 50	L*= 52 a*= 16 b*=-2	L*= 52 a*= 18 b*= 1	L*= 52 a*= 17 b*= 1	L*= 53 a*= 18 b*= 3	L*= 65 a*= 20 b*= 21	L*= 70 a*= 17 b*= 26
-0.75 V	L*= 67 a*= 11 b*= 8	L*= 54 a*= 9 b*=-21	L*= 53 a*= 11 b*=-18	L*= 54 a*= 10 b*=-17	L*= 55 a*= 11 b*=-14	L*= 68 a*= 9 b*= 2	L*= 73 a*= 4 b*= 2
-0.60 V	L*= 73 a*= 2 b*= -5	L*= 57 a*= 7 b*=-28	L*= 56 a*= 7 b*=-27	L*= 57 a*= 7 b*=-25	L*= 59 a*= 7 b*=-22	L*= 72 a*= 5 b*= -6	L*= 76 a*= 0 b*= -3
-0.45 V	L*= 78 a*= -1 b*= -5	L*= 60 a*= 7 b*=-28	L*= 58 a*= 8 b*=-28	L*= 59 a*= 7 b*=-27	L*= 60 a*= 8 b*=-24	L*= 74 a*= 4 b*= -7	L*= 79 a*= -1 b*= -4

Figure 22. Table summarizing the *L*a*b** color coordinates and photographs of a dual electrochemical cell employing **325** in combination with PProDOT **230** and using 0.1 M $LiClO_4$/PC as the solution electrolyte (all potentials are reported vs Fc/Fc^+). These data demonstrate how desirable colors can be attained by precisely controlling the oxidation state of each polymer without having to synthesize a single polymer that would possess the exact targeted hue in one of its redox states. Adapted with permission from ref 320. Copyright 2008 American Chemical Society.

Consecutive to an extensive synthetic report communicated in 2001,[319] the first consequent systematic study of *N*-substituted PProDOPs was reported in 2003.[321] The series constituted by *N*-methyl-PProDOP (**329**), *N*-propyl-PProDOP (**330**), *N*-octyl-PProDOP (**331**), *N*-glycol-PProDOP (**332**), and the self-dopable and water-soluble *N*-propanesulfonate-PProDOP (**333**) was characterized with perspectives in electrochromic applications. As seen in Table 5, the band-gaps ranged from ca. 3.0 eV for the sulfonated derivative **333** and for the shorter *N*-alkyl-substituted PProDOP **329** to 3.4 eV for the longer *N*-substituted ones **330**−**332**. All polymers revealed a π−π* transition located in the UV depleting as the polaronic and bipolaronic transitions arose in the visible and near-IR, respectively, on electrochemical oxidation. The color states exhibited by **329, 330, 332**, and **333** on p-doping were less saturated when compared to those of the cathodically coloring **325** and PXDOTs in their neutral state and resulted from the combined polaronic absorption in the visible and the near-IR tail of the dicationic states as shown in Figure 23. While **329** exhibited a transmissive purple to blue switch, **332** and **333** were highly transmissive in their neutral state and blue-gray once fully oxidized. **332** and **333** can thus be considered more strongly anodically coloring polymers.[324] Interestingly, the use of the sulfonated derivative **333** induced an optical contrast enhancement when combined with cathodically coloring **227** in a dual switchable window device.[325]

Employing the key synthon 3,4-(propylenedioxy)pyrrole-*N*-acetic acid (ProDOP-*N*-AcOH, **334**), having a synthetic

Table 5. Representative PXDOP Electrochromes and Analogues

			polymer electrochromism[c]			
polymer	λ_{abs}[a] (nm)	E_{gap}[b] (eV)	n	i	d	ref
319	537	~2.0	bright red		transmissive blue-gray	312
320	n/a	3.26	n/a	n/a	n/a	304
321	n/a	2.1	green	violet	gray	316
322	481	1.8	yellow		black	317, 318
323	482	2.1	yellow		n/a	318
324	413	2.3	yellow		n/a	318
325	522	2.2	orange	brown	light gray-blue	312, 313, 319
326−328	530 (**8**), 534 (**9**), 533 (**10**)	2.2	orange	red/orange-brown	light blue	312
330	330	~3.0	transmissive purple		blue	321
331	306	3.4	transmissive		n/a	321
332	n/a	3.4	transmissive		n/a	321
333	306	3.4	transmissive		blue-gray	321
334	340	~3.0	transmissive		blue-gray	321
335[d]	n/a	n/a	n/a	n/a	n/a	322
336−338	n/a	n/a	transmissive	transmissive	transmissive	322
339−341[d]	n/a	n/a	n/a	n/a	n/a	322
342	n/a	3.4	transmissive		bright red	322
343	n/a	3.1[e]	transmissive	red[f]	gray-green[f]	323
344	n/a	3.0[e]	transmissive	red[f]	gray-green[f]	323
345	n/a	3.2[e]	transmissive	red[f]	gray-green[f]	323
346	n/a	3.3[e]	transmissive	red[f]	gray-green[f]	323
347	460 (500)	2.7	n/a		blue-gray	315
348	n/a	3.0	n/a		dark brown	314, 326

[a] Absorption extremum of the neutral-state thin-film polymer. [b] Optical band-gaps as calculated from the onset of the $\pi-\pi^*$ transition of the neutral-state polymer. [c] Key: (n) neutral state, (i) partially oxidized state, (d) fully oxidized state. [d] Poor film-forming properties. EC properties were not reported. [e] Value was obtained via correspondence with the author. [f] Solution oxidation.

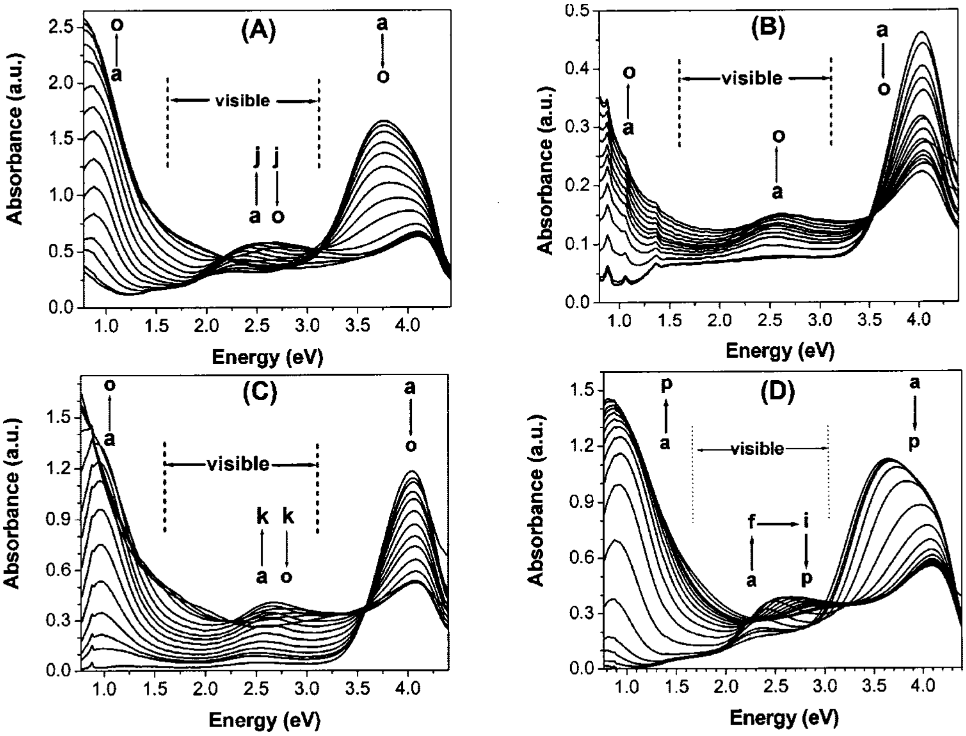
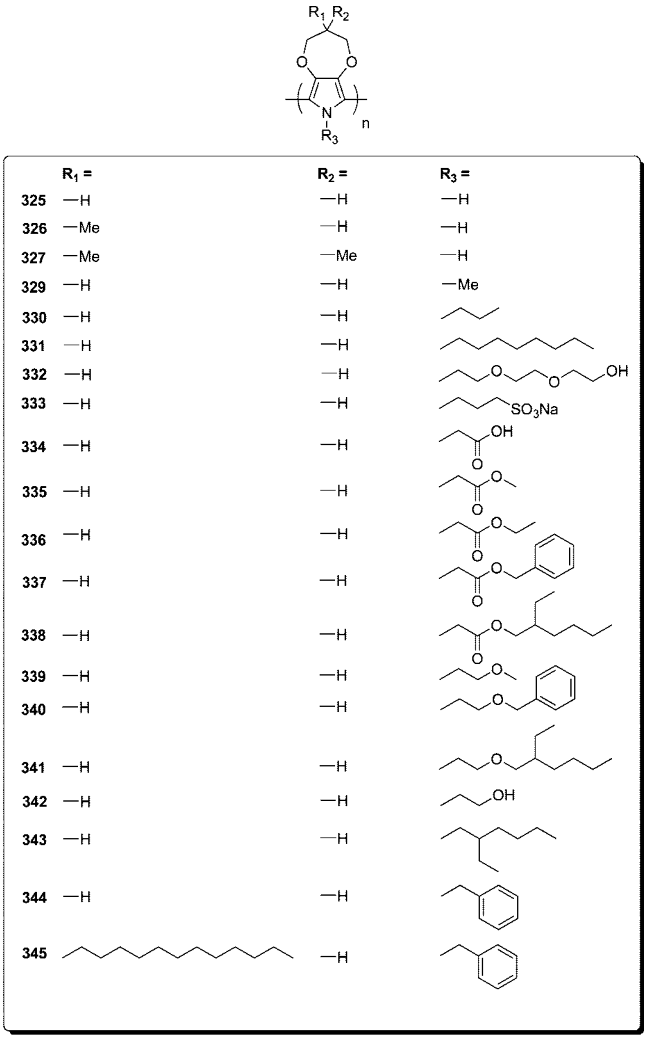


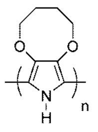
Figure 23. Spectroelectrochemistry of (a) **329**, (b) **330**, (c) **332**, and (d) **333**. The color states exhibited by **329**, **330**, **332**, and **333** on p-doping were moderately saturated when compared to those of the cathodically coloring **325** and PXDOTs in their neutral state and resulted from the combined polaronic absorption in the visible and near-IR tail of the dicationic states. Adapted with permission from ref 321. Copyright 2003 American Chemical Society.

pathway optimized to use commercially available starting materials and high-yielding steps, a variety of monomer derivatives differing by the nature of the transformation subjected to the *N*-pendant group and spanning ester (**335−338**), ether (**339−341**), and hydroxyl (**342**) analogues were designed.[322] Investigation of the electrochemical and electrochromic properties of electrochemically formed films revealed distinct polymer redox activities highly dependent on the *N*-functional group. For instance, the steric interactions resulting from the *N*-substitution of ester pendant groups on ProDOP (as in **335−338**) induced a hypsochromic shift of the $\pi-\pi^*$ transition such that the neutral absorption of the subsequent polymers arose in the UV. Interestingly, most of the bias-triggered spectral changes were monitored in the near-IR and UV regions of the electromagnetic spectrum. In particular, on electrochemical oxidation of **335−338**, the polymers' UV optical transition depleted with simultaneous formation of a near-IR bipolaronic transition and minimal polaronic features in the visible, suggesting an especially planar backbone in its quinoidal geometry. As a result, only faint visible electrochromic contrasts were observed encompassing blue-gray, red or magenta, and pale yellow, and these materials were consequently proposed for applications outside the visible spectrum or as counter electrodes in dual ECDs employing more strongly electrochromic cathodically coloring ECPs. In contrast, with a surprisingly wide band-gap of 3.4 eV, the hydroxyl-substituted PProDOP **342** is anodically coloring, revealing a brilliant red color state on p-doping while being transmissive in its neutral state. This divergence when compared to the ester-derivatized analogues was attributed to the strong hydrogen-bonding interactions practically cross-linking the hydroxyl-substituted polymer **342** and trapping radical cations in the visible.[322] On the other hand, the ether derivatives **339**−**341** showed relatively poor film-forming properties on ITO, and their electrochromicity was thus not reported.

The synthesis of solution-processable PXDOP derivatives involving a temperature-controlled deiodination polycondensation[323] was developed to produce a novel series of PXDOPs (**343**−**346**) possessing band-gaps higher than 3.0 eV and a UV to near-IR electrochromism analogous to that reported for polymers **335**−**338** (with minimal changes in the visible range) in the case of spray-cast **344** and **345**. While **343** exhibited an excess of solubility as a film in the most common solution electrolytes (ACN-, PC-, and DCM-based), it revealed a transmissive neutral state which changes to red and then gray-green on progressive solution doping with $NOPF_6$. Amphiphilic polymer **346** showed enhanced electrochromic performance in aqueous solution when compared to the other analogues of the series, which was tentatively attributed to the presence of hydrophilic oligoethoxy substituents favoring the ion diffusion at the polymer−solution electrolyte interface and also chelating the counterbalancing ions into the polymer network.

Although a few 3,4-dialkoxy-substituted pyrroles (such as **346**, **347**, and **348**) have been synthesized and succinctly characterized in terms of their redox and/or optical properties,[315,323,326,327] it is worth noting that this branch of dioxypyrrole-based polymers has not yet received the same level of attention. In particular, in spite of its lower band-gap (2.7 eV) when compared to PEDOP (**319**) (∼2.0 eV), PDMOP (**347**) is relatively transmissive in its fully oxidized state with a residual blue-gray hue due to the near-IR charge-carrier absorption tailing in the visible region as demonstrated by spectroelectrochemical analysis.[315] Further, the oligoethoxy-substituted polymer **346** showed excellent redox electrochemistry and enhanced electrochromic response in aqueous solution, which was attributed to the hydrophilicity of the pendant groups inducing better film swelling and ionic diffusion through the participation of the chelating side chains.





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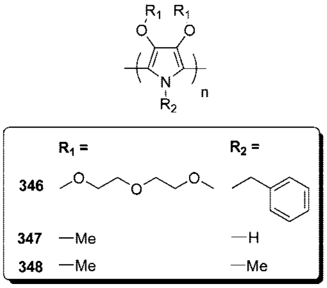


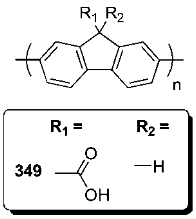
Overall, the PXDOPs offer the potential for producing polymers that can be either cathodically or anodically coloring depending on the structural modifications including *C*- or *N*-pendant group functionalization and nature of the 3,4-substitution pattern. In general, PXDOP derivatives have been found to exhibit high long-term switching stabilities, low polymer oxidation potentials combined with air-stable oxidized states, high optical contrasts, and a broad range of band-gaps ideal in the context of electrochromism. Competing with a relatively tedious access to and ambient stability of the key monomers in comparison to the parent XDOT precursors, these remarkable properties clearly justify the research effort initiated.

Table 5 summarizes some of the key values and EC properties of the representative PXDOPs that have been reported to date.

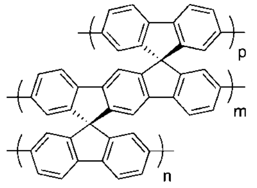
3.3.2. Polyfluorenes and Analogues

3.3.2.1. Polyfluorenes. The electrochemically prepared poly(9-fluorenecarboxylic acid) (**349**) was achieved by electropolymerization in the presence of the Lewis acid boron trifluoride diethyl etherate (BFEE), yielding a clear to brown-orange switching ECP with reversible behavior on p-doping and a wide band-gap of 3.1 eV.[328]

3.3.2.2. Poly(dispirofluorene−indenofluorene)s. Poriel et al. have reported on the synthesis of a novel dispirofluorene−



indenofluorene precursor (**350**) which could be electropolymerized into an electroactive three-dimensional network through the fluorene chain ends.[329] The corresponding polymer showed a band-gap of 3.51 eV which was 0.40 eV lower than that of conventional poly(dispirofluorene) and ~0.45 eV lower than that of poly(fluorene) but only 0.1 eV lower than that of poly(indenofluorene). Its EC properties were investigated, demonstrating a clear to purple color change on oxidation and good long-term switching stability with only about 5% current density loss over more than 1000 cycles.



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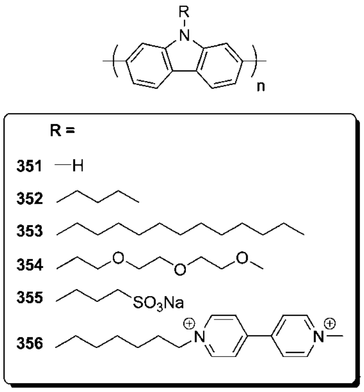
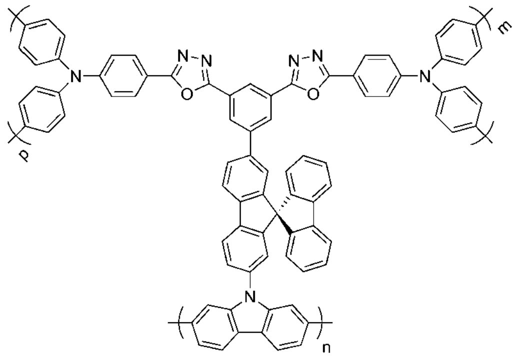
3.3.2.3. Polycarbazoles. Oxidatively prepared polymers of unsubstituted carbazole (**351**) possess a yellow to green switch upon p-doping and can be oxidized at relatively low potentials.[330,331] Further functionalizations at the *N*-position have been shown to induce a slight hypsochromic shift such that nearly clear neutral states can be obtained as demonstrated by work form Chevrot et al. on the *N*-butyl- and *N*-dodecyl-substituted polymers **352** and **353** switching from colorless (neutral) to green (partially oxidized) to blue (fully oxidized).[332,333] With the intention of enhancing the solubility of polycarbazoles in aqueous media, an oligoether substituent was appended to the *N*-position and the subsequent polymer (**354**) was produced chemically and electrochemically in aqueous solution.[334] The corresponding polymer films were found to switch from a highly transmissive neutral state to dark green on p-doping, as did the water-soluble sulfonated analogue **355** introduced over a decade earlier.[335]

Although carbazoles have not generally been employed alone for EC polymer applications, several instances are available in the literature where the carbazole moieties were functionalized at the *N*-position with EC pendant groups. For example, the viologen-substituted polycarbazole **356** was used in the fabrication of a device switching from clear to green on p-doping and to violet on n-doping.[336]

Wong et al. have synthesized the bichromophore-containing polymeric system **357** in which the triphenylamine and carbazole moieties serve as polymerization sites.[337] The hybrid was electropolymerized through the triphenylamine groups at low oxidation potentials and cross-linked through the 3- and 6-positions of the carbazole groups at higher potentials. Films of **357** were found to switch from clear to orange to blue-green on oxidation (as seen from the photographs available) with a switching time of 1.4 s at 90% of the maximum transmittance change, which was ~72%, taken from the neutral-state polymer's absorption maximum (at the considered film thickness, nonindicated).





357

4. Polymer Electrochromic Devices

An electrochromic device consists of an electrochemical cell where one or several electroactive components undergo an optical change (occurring in the visible or not) on application of an external bias. While an ionic conducting interface allows the various electroactive constituents of the device to communicate, the performance of an ECD is commonly diffusion-limited and depends on the nature of this interface, as well as that of each electroactive constituent employed. For instance, liquid-crystal displays (LCDs), where the molecules react quasi-instantaneously to the electrical bias applied, exhibit much shorter switching times than metal oxide-based ECDs, which commonly require multiple seconds to fully switch between colored states. On the other hand, unlike their LCD and LED counterparts, nonemissive electrochromic technologies present the advantage of being viewable from practically any angle or lighting conditions including direct sunlight. Considering the potential of π-conjugated polymers for cost-effective processing of multicolored patterns which can be obtained without further addition of dyes (required in LCD technologies, for example), the escalating research effort observed in device architecture over the past decade, enhancing response times and lifetimes, is impressive, yet not surprising.

Herein, some of the most important concepts and recent advances in the field of π-conjugated organic polymer ECDs are reviewed with a stress on color control. The specifics of ECDs relying on metal oxides and other inorganic electrochromes, metal coordination complexes, viologens, and other small molecules as well as combinations of organic and inorganic components have been described elsewhere.[9]

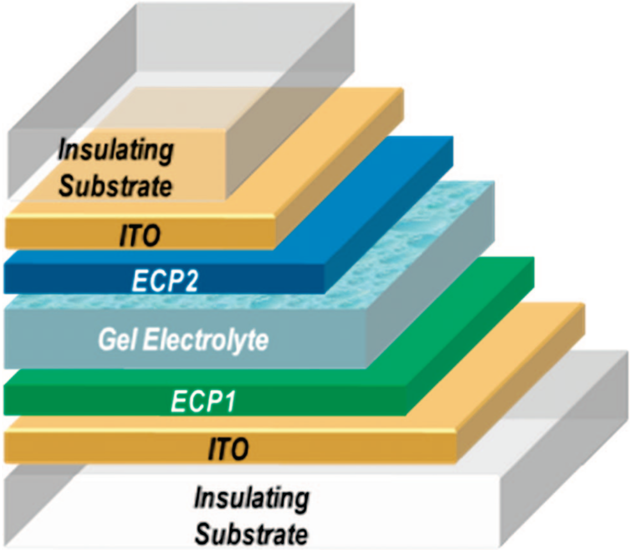


Figure 24. Schematic illustration of a conventional dual polymer transmission ECD (not to scale).

4.1. Absorption/Transmission ECDs

4.1.1. Dual EC Material Approach

An absorption/transmission ECD switches reversibly between a state of high optical density (colored) and a more transmissive state (ideally transparent) on application of an electrical bias. To take advantage of the full contrast in an EC cell, the color-changing materials are sandwiched between two transparent substrates as illustrated in Figure 24. For the same reason, the electrode materials must be transmissive to the wavelength range of interest. Smart windows, optical shutters, and window-type displays are the main target applications.[9]

For reasons relating to chemical compatibility and redox stability issues, ECDs with good switching performances can only be obtained when using a counter electrode stable in the potential window of application of both the EC material deposited at the working electrode and the supporting electrolyte.[338−340] Hence, pairs of complementary EC materials must be found to not only address the color requirements according to the device made but also balance the redox processes occurring in the cell to enhance its lifetime on repeated cycling. In most cases, the constraint for contrast maximization prevails and one EC constituent has to be cathodically coloring while the second is anodically coloring, thereby exhibiting simultaneous colored to transmissive switches (under opposite redox processes). Alternatively, the charge storage layer can be noncoloring, yet electroactive (see PProDOPs **335−338** in section 3.3.1). The performances of **210** in absorption/transmission ECDs possessing an electroactive counter electrode material, relative to those without, have been compared and found dramatically distinct.[341,342]

A number of strategies have been proposed to achieve dual ECDs encompassing the use of PANI (in its doped form) at the counter electrode,[30,343] the use of the same ECP at both the counter and the working electrodes (but in opposite redox states),[78,344] and the use of a different cathodically coloring ECP (in opposite redox states) at each electrode,[345,346] for example. However, the combination of narrow and wide energy gap ECPs allows the best results to be attained in terms of contrast ratios and long-term stability, as illustrated by a prototype made from cathodically coloring **210** and anodically coloring PBisEDOT-CZ (**176**), which revealed a dark opaque violet to pale transparent green switch of 34% contrast (ΔT) at the absorption maximum in 1 s (and 22% in 0.1 s).[340] Long-term switching stability was successfully achieved over 10 000 cycles. In this device, replacing **176** by PANI caused a rapid drop in device performance attributed to the strong acid−base character of the replacement electrode inducing environmental incompatibility issues. This undesired phenomenon was also described early by Zotti et al. in a device based on **54** and PANI.[338] Contrast enhancements have been obtained by carefully selecting the two ECPs incorporated.[325,347] In one example, **227** (ΔT = 78% at its absorption maximum)[252] was used as the cathodically coloring ECP and **333** (ΔT = 50% at its absorption maximum)[324] served as the anodically coloring counterbalancing polymer.[325] The contrasts (ΔT) obtained in the dual device architecture investigated were as high as 68% at the device absorption maximum wavelength. The same device showed only 9% contrast (ΔT) loss after 20 000 cycles. Sotzing et al. have recently demonstrated large area window devices (30 cm^2) of **210** and **176** with up to 30% photopic contrast and switching speeds as low as 0.6 s.[348]

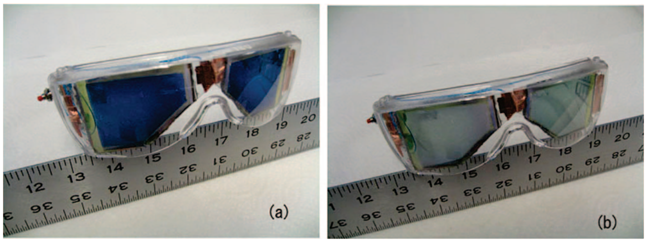


Figure 25. Prototype of smart sunglasses as constructed by Xu et al. A cell battery powers the switching process from (a) a deeply colored state to (b) a fully transparent state. Adapted with permission from ref 355. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

Other ECP components integrated in similar device architectures have come to support the efficiency of this approach based on the use of π-conjugated polymers possessing complementary redox and electrochromic activities (i.e., at least electrochemically compatible).[11,55,60,81,95,105,144,148,149,154−160,197,199−203,208,222,266,328,349−353]

Composite devices with a polymer EC layer and an inorganic ion storage layer at the counter electrode have also been described with excellent switching performance.[354] This device configuration has been applied by Xu et al. in the fabrication of smart sunglasses (see Figure 25).[355] Metal complexes such as Prussian blue at the counter electrode have been described as well.[341,342,356]

Pozo-Gonzalo et al. have investigated formulations of **210** in ACN or DMF and ionic liquid-based electrolytes in symmetrical flexible devices for near-IR applications.[344] Optical contrasts as high as 50% in the visible and 44% in the near-IR were achieved in only a few seconds. Other symmetrical devices using **210** have been reported.[357]

With the intention of simplifying the processing of electroactive materials at the device electrodes, Hammond et al. have proposed to assemble the EC layers electrostatically (in a layer-by-layer fashion) using dilute solutions of doped ECPs and polyionic species.[358] As a proof of concept, devices made of **210** and PANI were produced that switched reversibly between a deep blue-green colored state to a pale yellow transmissive state over 35 000 cycles without significant change in electroactivity. The layer-by-layer assembly approach for π-conjugated polymers has generally been explored in the context of more fundamental electrochemical and morphological characterization studies[359−364] with only occasional looks at the EC perspectives.[225,226] For example, Heflin et al. have demonstrated millisecond switching times (31 ms in coloration and 6 ms in decoloration for a device area of 0.6 cm^2), albeit with a low EC contrast (ΔT) of 20% in the visible range, in solid-state devices based on the self-assembly of multilayers of **211** and PAH (40 bilayers).[365] These rates are compatible with those required for flat-panel display applications. Kim et al. have investigated the spin self-assembly of **211** and PAH and the EC behavior of the resulting multilayer composite.[366]

4.1.2. Color Control in Dual EC Cells and Devices

As discussed in section 2 relative to the fundamentals of electrochromism, the tailorability of colors during the device fabrication process is a sine qua non for companies willing to proceed further with commercial applications. While pairs of ECPs can be employed to generate colors otherwise difficult to access, this strategy adds extra degrees of complexity to the device assembly associated with the effect of film thickness and absorption coefficients of the respective polymers incorporated. In this respect, in situ colorimetric analysis[16,17] has shown a high level of reliability in the prediction of colors produced by dual ECDs.[16,325] Hence, the use of a portable colorimeter calibrated to the sensitivity of the human eye to monitor the changes of color and light transmission undergone during the device preparation and redox switching allows convenient characterization of absorption/transmission ECDs in particular. In situ colorimetric analysis has alternatively been used to probe the stability of dual ECDs.[325]

Recently, a traditional dual electrochromic cell (ECPs under the same potentiostatic control) was “decoupled” to allow separate control of the two ECP components with simultaneous characterization of the mixed color states generated.[320] The two stacked cathodically coloring polymers (**325** and **210** or **325** and **230**) were sequentially oxidized, revealing new palettes of colors (see Figure 22 in section 3.3.1) typically not accessible via the traditional dual cell. In this case as well, in situ colorimetric analysis allowed precise determination of the most subtle color changes occurring under the external bias progressively applied. The proposed approach to generating colors is expected to prove useful as it is transferred to actual ECDs.

Similarly, Padilla et al. have introduced a two-step methodology for the characterization of dual polymer systems consisting in (1) studying the redox properties of each polymer separately and (2) tracking the same redox parameters in the dual system.[367] The proposed dual setup allows following the evolution of each EC component individually controlled with only one potentiostat, while a conventional three-electrode cell can only monitor the redox behavior at the working electrode. This is possible via introducing a reference electrode connected to a multimeter alternatively monitoring either the working or the counter electrode of a two-electrode cell configuration. EC cells made of **176** and **210** or PProDOT **262** were assembled to demonstrate the concept. This method proved especially useful to prevent the degradation of side processes associated with the application of potentials harming the EC constituents.

If the deposition of an ECP at the counter electrode can prevent potentially harmful side reactions from occurring at the working electrode (which commonly bears the functional ECP), thereby enhancing the lifetime of an ECD,[340] Padilla and Otero have recently pointed out that it may not always result in an increase of contrast as may be expected when considering the utility of the “dual” approach. More precisely, the maximum contrast attainable by a dual ECD has been shown to be systematically lower than that of one of its electroactive components alone (i.e., when incorporated in a single polymer-only device).[368] While dual ECDs remain an attractive alternative for addressing the challenge of finely controlling colors in the field of π-conjugated organic polymer electrochromes, this optical limitation should become a motivation for the development of novel electroactive polymers either with enhanced transmissivities in their doped state or undergoing spectral changes essentially out of the visible portion of the electromagnetic spectrum.

4.1.3. Interpenetrating Polymer Network-Based ECDs

Chevrot et al. have described the preparation of ECDs made of semi-interpenetrating networks of **210** and cross-linked polyethylene oxide (PEO).[369] Polymer interpenetrating networks generally possess improved morphological stability in comparison with blends. Their processing method toward all-plastic ECDs resulted in a self-supported and symmetrical PEDOT/polymer electrolyte/PEDOT configuration where the PEDOT/PEO-depleted inner region acts as the polymer electrolyte (in the presence of lithium salt or ionic liquid) and the PEDOT-rich outer regions act as electrodes for the device. EC contrasts (ΔT) as high as 33% without noticeable loss of optical density over 1500 cycles and a CE of 110 cm^2 C^{-1} were monitored. While 60 s was necessary to attain the colored state (dark blue), the transmissive state (light blue) could be reached in about 30 s. The device thermal stability was described elsewhere.[370] The same group has also fabricated conducting networks of polybutadiene, PEO, and **210** with potential utility as actuators operating in atmospheric conditions.[371,372]

4.2. Reflective ECDs

4.2.1. Extending Electrochromism into the IR

With most π-conjugated ECPs possessing high contrast ratios in the near-IR owing to the charge-carrier-associated low-energy transitions arising and depleting on doping and dedoping, electrochromism is not limited to the visible region of the electromagnetic spectrum. In fact, various reports have proposed to take advantage of these important optical changes occurring in the near-IR, mid-IR, and microwave regions. For example, Reynolds et al. have incorporated the high contrast polymeric electrochrome **227**[16,252] in a reflective device architecture consisting of an outward facing active electrode bearing the ECP of interest[373] and originally reported by Bennett et al.[374] and Chandrasekhar et al.[375] in the patent literature (see Figure 26). In the presented device, the electrodes were made of gold-coated Mylar, the working electrode was slitted to account for ion diffusion, and a highly viscous polymeric electrolyte consisting of LiClO$_4$, ACN, PC, and PMMA was employed that further induced self-sealing of the structure (by evaporation of ACN). In analogy with absorption/transmission devices, a complementary ECP was deposited onto the counter electrode to account for the redox balance and faradic reversibility of the structure. Reflectance contrasts (ΔR) as high as 55% at 0.6 μm in the visible, greater than 80% in the near-IR 1.3−2.2 μm range,

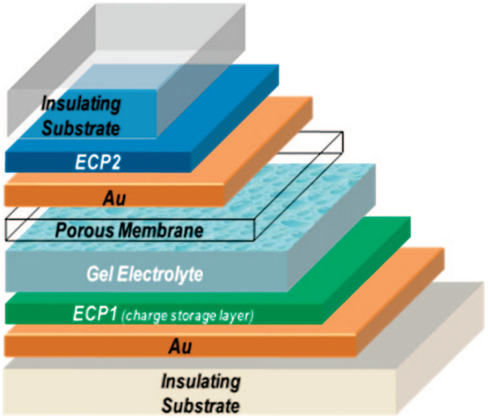


Figure 26. Schematic illustration of a reflective-type PECD using a porous membrane electrode (not to scale).

and greater than 50% between 3.5 and 5.0 μm were monitored, demonstrating a redox-switchable reflectivity extending into the IR as desired for thermal control applications (though reflective devices are also suitable for displays). By changing the lithium salt, the device exhibited less than 20% loss in contrast upon 10 000 cycles.

In this area, a notable focus has also been placed on PANI.[376−379] For example, ground-breaking work from Chandrasekhar et al. describes the use of PANI in flexible solid-state devices for spacecraft applications, with the polymer exhibiting broad-band IR electrochromism (from 2.5 to 45 μm).[380] Considerable research effort is placed on investigating the potential of metal oxides for IR-modulating applications as well.[381−384]

4.2.2. Spectral Modulation and Device Optimizations

Various patents and studies have described the use of a gold-coated porous substrate (such as nylon, polyester, or polycarbonate, for example) to enhance ion diffusion properties and switching uniformity[347,385−389] in reflective ECDs when compared to devices relying on slitted electrodes.[373]

Interestingly, the integration of the spray-processable branched alkoxy-substituted **233** in a reflective device configuration has revealed an unusual EC behavior consisting in large variations of electrochromic contrast in the IR with no significant changes occurring in the visible region over a specific potential window of operation (negative biases in the work described).[347] While reflectance contrasts (ΔR) greater than 70% could be observed at 2 μm, for example, they were smaller than 3% in the visible, hence resulting in an IR-active-only device in the corresponding potential range (see Figure 27a). In contrast, a modulation of the visible spectrum with essentially no change at wavelengths longer than 1.6 μm was attained when a different potential window (positive biases in the work described) was employed (see Figure 27b). This asymmetric switching was further reported in the context of an electrochromic variable optical attenuator (EC-VOA)[390] modulating fiber-optic signals for application in optical telecommunications.[391] In this work, the unconventional switching process was found occurring in the reflective device architecture only (where the working electrode is outward facing) and was shown to be especially film thickness dependent. The action of a conductive front composed of redox-doped centers initiated at the metal electrode and propagating progressively across the neutral (i.e., insulating) polymer before reaching the active-layer surface was proposed. This phenomenon was also described in previous work from Lacaze et al.[392] and Tezuka et al.[393] Considering that longer wavelengths induce greater penetration depths than shorter ones, the near-IR light is prone to see the changes undergone at the electrode−polymer interface while the visible light still sees the neutral surface of the polymer film, as illustrated by Figure 27a. The device exhibited 12 dB of optical attenuation at 1.31 and 1.55 μm (the two wavelengths of interest for silica-based optical fibers) with minimal optical loss (<0.2 dB) and a subsecond switching time.

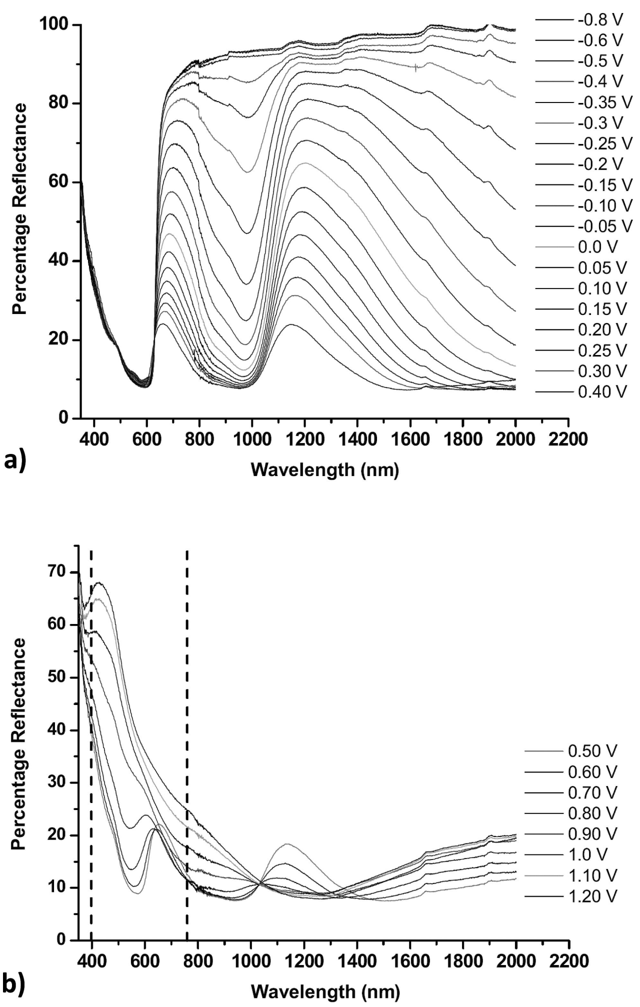


Figure 27. Total (diffuse and specular) reflectance spectroelectrochemistry of a reflective ECD made with **233**: (a) device switched between negative and low positive biases, (b) device switched between positive biases. Adapted with permission from ref 391. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

4.3. Patterning Electrodes for PECDs

To meet the demand in device architectures minimizing the size of the different active components while enhancing the definition and contrast of the display, various ways to produce contact electrodes have been developed. Hence, as new device concepts have emerged, a variety of patterning methods addressing the metallization of organic or inorganic and rigid or flexible surfaces have been proposed. If the metallization by vapor deposition on porous membranes allowing rapid ion diffusion across the ECD has become popular over the years, other methods encompassing screen printing and line patterning have also been demonstrated in the context of ECD construction. The following subsections

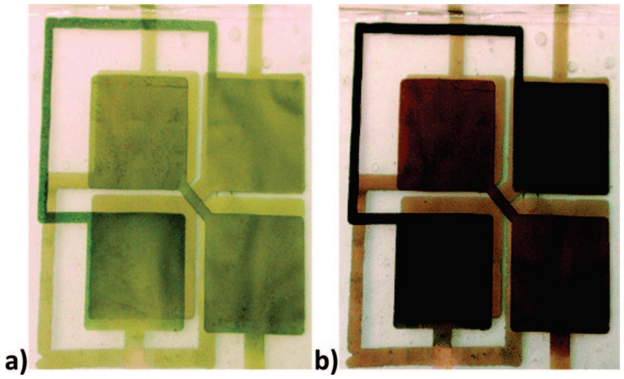


Figure 28. Pixelated (2 × 2) device including two cathodically coloring electrochromic polymers (**210** and PBisEDOT-B(OR)$_2$ **117**) and providing color-matched EC contrasts: (a) both polymers oxidized (bleached state), (b) both polymers reduced. (colored state). Adapted with permission from ref 386. Copyright 2004 American Chemical Society.

draw an overview of the patterning tools which have proved the most useful in PECDs so far. It is expected that future work in this area will implement the toolbox.

4.3.1. Microporous Electrodes via Metal-Vapor Deposition

Highly porous metallized membranes have been incorporated into polymeric ECDs[386] (see Figure 26) with the goal of demonstrating fast-switching and highly contrasted reflective surfaces suitable for color-matched EC applications, for instance. On the basis of this modified device architecture, a 2 × 2 pixelated display device was assembled as illustrated in Figure 28. The metal electrodes were patterned via a shadow mask to address the two electrodes independently and coated with two cathodically coloring ECPs of different hues (red and blue) that bleached simultaneously to reveal the golden reflective membrane: **210** and PBisEDOT-B(OR)$_2$ **117**. Devices with less than 10% contrast loss over 180 000 cycles and switching times on the order of 200 ms were achieved. The later improvement was attributed to the microporous nature of the metallized membrane increasing the ion diffusion lengths when compared to the slitted electrodes, which generally induce color changes starting at the slits and then moving laterally across the working electrode. Conjugated polymers have been electropolymerized directly onto the gold patterns or spray-cast from solutions as described by work employing porous polycarbonate membranes and **233**.[347]

Pages et al. have also used porous gold reflective electrodes with optimized thickness and pore size to characterize the IR electrochromism of **210**.[394]

In an effort to bring pixels closer together, thereby improving both resolution and aesthetics in EC display devices, a method to prepare patterned electrodes onto microporous track-etched substrates with backside contacts addressing the electrodes has been reported (see Figure 29).[395] As a proof of concept, cathodically coloring **227** was used as the electroactive layer controlling the reflectance of the outward-facing gold-coated porous membrane (see Figure 30). It was noted that this concept extends beyond ECDs and could be applied to a variety of electronic devices based on vertically integrated architectures such as light-emitting devices, thin-film transistors, or solar cells in particular.

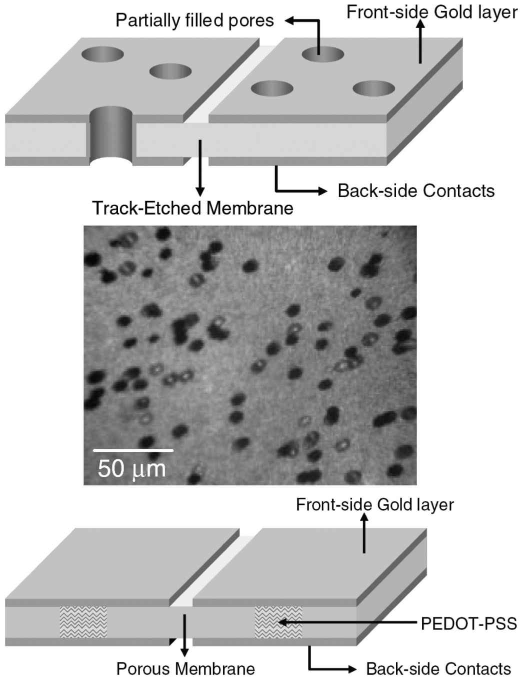


Figure 29. Schematic representation of electrodes patterned onto microporous track-etched substrates whereby the backside of the substrate becomes conducting and can serve as the device electrode. Adapted with permission from ref 395. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

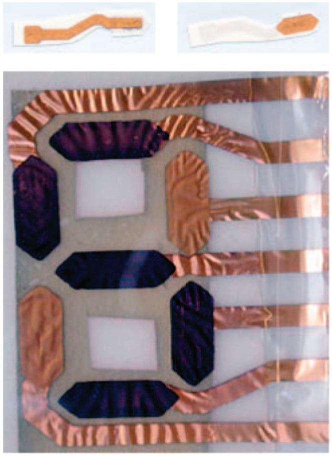


Figure 30. Reflective display device incorporating microporous backside-contacted, outward-facing electrodes coated with cathodically coloring **227**. Adapted with permission from ref 395. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

4.3.2. Screen Printing

Consisting in selective depositions of active material through a mask placed on the substrate to pattern, the screen printing approach in electroactive polymers was first introduced by Garnier et al. for the elaboration of logic circuitry in polymer FETs.[396] This additive patterning technique was successfully employed with resolutions as high as 10 μm. However, only a limited number of illustrations of this approach adapted to polymer ECDs can be found in the literature. For example, Coleman et al. have demonstrated printed electrical contacts,[397] and Brotherston et al. have described checkerboard- and strip-patterned composite ECDs made of **210** and V$_2$O$_5$.[398] Recently, a substantial focus has been placed by Andersson, Berggren, and co-workers on screen printing organic electronic components onto paper, and an active matrix display including EC pixels and electrochemical transistors was achieved.[399] Malliaras et al. have demonstrated negative masks of Parylene that can be deposited onto plastic substrates, coated with an electrode material (**211** in the described case) and subsequently etched by oxygen plasma to reveal the desired conducting pattern.[400]

4.3.3. Line Patterning

First reported by Hohnholz and MacDiarmid[130,401] in the context of conducting polymers, the line patterning approach can be advantageously utilized over conventional lithographic deposition techniques to build finely structured electrodes on plastic or paperlike substrates.[402,403] The method includes printing ink-type patterns on a plastic substrate via a commercial laser printer and removing the pattern selectively after a polymeric electrode material has been deposited in the nonprinted areas. The selective removal process is based on the difference in surface adhesion of the resulting conducting network and the printed ink, hence allowing cost-effective atmospheric depositions of solution-processable polymeric electronics on flexible surfaces.

For example, **210** and **176** have been used (see Figure 31) on deformable and laterally configured ECDs[402] using polymer (**211**) or metal (Au) line-patterned electrodes, attaining subsecond switching times. As the EC switching kinetics of two-lane, four-lane, and six-lane ECDs were investigated (see Figure 31a), it was found that the extent of interdigitation of the electrodes played a key role in the EC performance of the devices as both the ionic diffusion distances and the resistance of the electrolyte vary as a function of spacing. Using a commercial laser printer, resolution values as low as 30 μm were attained as demonstrated by reflective optical micrography.

By eliminating the need for expensive mask preparation steps, difficult etching, and dry-clean processing conditions to generate complex conducting networks, the nonlithographic line patterning technique is suitable in the design of high-definition flexible display arrays of fast-switching and multicolored ECPs. Further, on the basis of the close proximity of the ECP supporting electrodes, line-patterning could become a useful way of obtaining new color states via color mixing (when the pixels become sufficiently fine to be averaged by the human visual perception). It is expected to see this convenient processing tool compete with the most direct and cost-effective printing methods encompassing microcontact printing,[404] screen printing,[396] or inkjet printing (see section 4.4.7) without hindering device performance.

4.4. Advances and Perspectives in PECDs

4.4.1. Use of Ionic Liquids in PECDs

In 2002, Mattes et al. reported on the use of room temperature ionic liquids in different types of π-conjugated polymer ECDs encompassing electrochemical mechanical actuators, EC windows, and numeric displays made from PANI, **54**, and **1**.[405] In long-term stability experiments (10^6 cycles at 1 Hz), transmission ECDs made with PANI and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] showed no significant loss in current density. PEDOT and regioregular **3** were employed as the cathodically coloring polymers in [BMIM][BF_4]-based window devices with PANI at the counter electrode. EC contrasts as high as 63% were monitored from a 7 pixel numeric display along with ~1 s switching times. Owing to their environmental stability as electrolytes, ionic liquids have since then attracted a good deal of attention for the electrochemical synthesis of π-conjugated ECPs as well as in the fabrication of ECDs in general.[36,38-40,98,102,405,406]

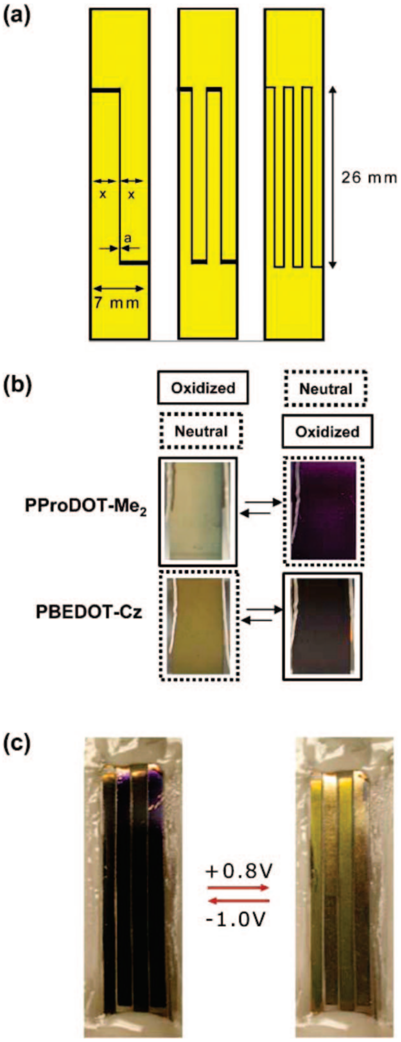


Figure 31. (a) Negative computer images of interdigitated electrodes with varying finger widths. (b) Arrangement of optically and redox complementary polymers (**210** and **176**) for lateral-type ECDs (photographs on gold slides). (c) EC switching between a strongly absorptive colored state (left) and the reflective state (right). Adapted with permission from ref 402. Copyright 2005 The Royal Society of Chemistry.

4.4.2. EC Blends, Laminates, and Composites

A different approach to color control in π-conjugated polymers consists in blending different EC systems. In addition, as mentioned in the previous device sections of this paper (e.g., section 4.1), laminates and composites have been specifically developed for EC applications. ECPs have been combined with metal oxide and small molecule electrochromes as well as with various insulating polymers, for instance. Besides modifying the inherent EC behavior of polymer electrochromes, the fabrication of laminates and composites induces changes in physical properties and structure. Considering the variety of approaches that have been described in this area, we direct the reader toward comprehensive papers and available review works on this topic.[10,398,407−409]

4.4.3. EC Nanotubes

The use of conducting polymer nanotubes for EC applications is relatively new as explained by Lee et al. in their recent review work on the “fast electrochemistry of conducting polymer nanotubes”.[244] Polymer nanotubes have been investigated for applications requiring fast color-switching such as animated displays (<40 ms is desirable). While conventional ECPs such as **210** usually switch within 1−2 s depending on the film thickness, for instance, PEDOT nanotubes have been found to attain subsecond switching times (<10 ms) without significant loss of contrast.[410] In particular, their long and tubular shape accounts for rapid diffusion of the counterbalancing ions in and out of the nanostructures. Flexible transmission- and reflective-type devices were constructed on the basis of this technology.[410] In a reflective architecture using a gold-sputtered electrode, PEDOT nanotubes switched from deep blue to a transmissive pale blue with response times of 20 and 30 ms upon oxidation and reduction, respectively. In window-type devices, porous alumina templates sputter-deposited onto ITO were used to grow the PEDOT nanostructures, which exhibited 50 and 70 ms switching times upon oxidation and reduction, respectively.[245]

4.4.4. EC Nanofibers

Sotzing et al. have described the fabrication of polymer EC nanofibers by electrostatic spinning.[411] The ∼120 nm average diameter nanofibers were subsequently welded into a loose interconnected network via oxidative cross-linking without changing the overall morphology of the initial network. When incorporated in devices (31 cm^2), the fibers exhibited switching times on the order of a few seconds only. E-spinning is attractive as it offers easy access to the production of high quantities of nanofibrous materials in continuous fabrication processes. However, only a few other conjugated polymers have been successfully employed for electrostatic spinning due to their inherent intractability in general.[412−414]

4.4.5. Strictly All-Polymer ECDs

The substitution of ITO by **211** in an otherwise all-plastic designed device architecture has resulted in a strictly “all-polymer” electrochromic device.[415] ITO being an inorganic electrode component, polymer ECDs made thereof should be considered as hybrid devices unlike sometimes claimed.[105,344,349,385,416−418] In particular, this electrode material is highly brittle and scratch-intolerant when deposited on plastic substrates. In the prototypes made,[415] as *N*-methylpyrrolidone (NMP) or diethylene glycol (DEG) was incorporated into the aqueous **211** casting solutions, the conductivities of the subsequent conducting films were increased more than 2 orders of magnitude (from 0.6 to 120 S cm^{-1}). Two ECPs (either the complementary pair **227** and **176** or the cathodically coloring pair **227** and PBisEDOT-B(OR)$_2$ **117**) were next electrochemically deposited onto separate **211**-coated plastic substrates and placed front-to-front in window-type devices. The all-polymer devices made exhibited excellent relative luminance change up values, as high as 51% for the one based on the complementary polymers, the contrast of which was nearly as high as that obtained when using ITO-coated glass electrodes (56%).[325] However, the switching time increased considerably in the same device (about 8 s to reach 80% of the full switch) when compared to the subsecond switching possible to attain the same contrast with the ITO-based architecture. This undesired effect was attributed to the higher surface resistivity of the polymer electrode **211**. In the meantime, high stabilities were demonstrated with only a few percent contrast loss over more than 30 000 switches corresponding to 3.5 days of work as shown in Figure 32.

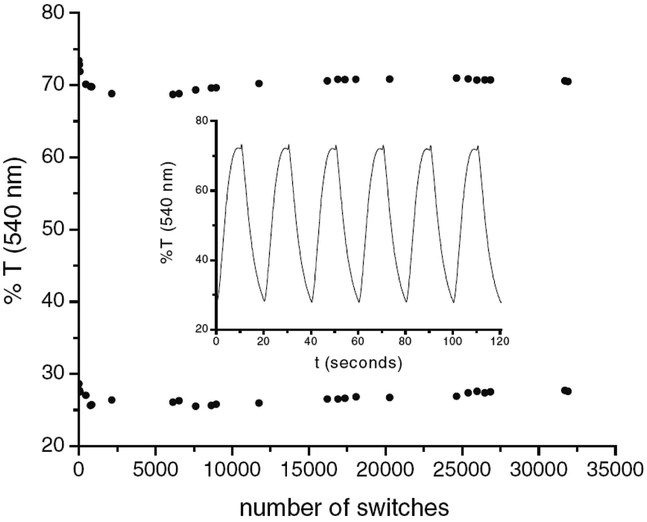


Figure 32. Long-term stability experiment of the strictly all-polymer electrochromic device described by Reynolds et al. Only a few percent contrast loss was observed over more than 30 000 switches corresponding to 3.5 days of work. Adapted with permission from ref 415. Copyright 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

4.4.6. Advances and Perspectives in e-Paper Devices

Various technologies are presently being considered for e-paper application encompassing the use of electrowetting techniques,[419] liquid crystals,[420,421] and electric-field-reactive microsized beads (or electrophoretic microcapsules)[422] (e.g., E-Ink and Gyricon beads). However, the number of reports exploring π-conjugated polymers as candidates for e-paper applications remains limited. In ground-breaking work from Berggren et al., **211** was printed onto a polyethylene-coated paper substrate and served for the different components of an active matrix display including EC pixels and electrochemical transistors (addressing each pixel independently).[399] In additional effort to address the demand for polymer-based circuitry suitable for flexible backplanes, a number of other works employing **211** in the fabrication of organic electrochemical transistors and logic have been reported.[423,424] For example, the system-on-a-sheet demonstrator illustrated in Figure 33 combines PEDOT:PSS-based electrochemical transistors, displays, logic, and batteries.[425] In this device, the display was controlled via the logic circuits including the transistors which processed the signal triggered by the operator pressing one of the push buttons. It was suggested that such devices could be used as single-use sensors or security features on packages, for example. In parallel, it is worth noting that Wrighton et al., for instance, have pioneered the area of microelectrochemical transistors.[426−431]

In recent times, Berggren et al. proposed to enhance the electrochromic contrast of PEDOT:PSS-based paper displays by superimposing an extra EC layer on top of the PEDOT

Figure 33. System-on-a-sheet demonstrator developed by Linköping University and the Acreo Institute (Sweden). PEDOT/PSS-based electrochemical transistors, displays, logic, and batteries are combined into a stand-alone label demonstrator. Adapted with permission from ref 425. Copyright 2007 Nature Publishing Group.

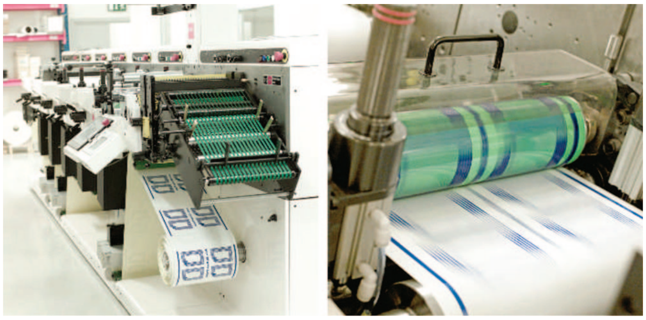


Figure 34. Nilpeter rotolabel FA3300/5 printing press at the Acreo Institute where flexoprinting, rotary printing, screen printing, and offset printing can be combined. Flexoprinting (where the ink is transferred from a cylinder) is commonly used in packaging technology and patterning with speeds exceeding 100 m min^{-1}. Paper and plastic-based active-matrix displays could ultimately be manufactured in a roll-to-roll process via this type of high-speed printer. Adapted with permission from ref 425. Copyright 2007 Nature Publishing Group.

pixel electrodes.[432] Interestingly, the deposition of **211** onto paper does not induce complete reduction of the doped polymer to its neutral state, and the residual charge can be utilized to transport electrons into the stacked neutral-state ECP (e.g., **230**). In this case, the added ECP was complementary in the absorption spectrum so that a 2-fold contrast enhancement resulted from the superimposition. To demonstrate the extent of the promises held by their technology with respect to its potential for cost-effective processing conditions, a roll-to-roll printing press was used to pattern the pixel arrays (see Figure 34).

Other competitive technologies have also been proposed in this emerging area such as the use of EC terephthalate derivatives by Kobayashi et al.[433] In this work, an 8 × 8 passive matrix was presented displaying black, magenta, cyan, yellow, red, blue, and green pixels in which the red, green, and blue colors were generated by mixing magenta and yellow, cyan and yellow, and magenta and cyan, respectively. Corr et al. have described the colored EC behavior of viologen-modified mesoporous films of TiO_2 incorporated in a paperlike reflective display.[434] Monk et al. have dispersed inorganic electrochromes such as WO_3 and MoO_3 as well as small molecules such as Prussian blue and viologens into paper.[435] However, while Prussian blue was found insufficiently electroactive in paper, the viologen derivative employed could not retain its colored state, and only the metal oxides showed promise throughout this approach.

4.4.7. First Inkjet-Printed ECD

Inkjet printing of conducting polymers stands among the most recent and promising processing techniques employed in the field of organic electronics.[436,437] It is a direct noncontact patterning approach yielding high resolution in a short period of time. Foulger et al. have recently transferred this cost-effective technology to the fabrication of ECDs, employing PANI− and **210**−silica colloidal composite particles (200−300 nm diameter) in their depositions.[438] The inks were transferred onto ITO-coated PET substrates using a commercial printer, and patterns as small as 500 μm in size were achieved. It is worth noting that the concept of printing ECPs via inkjet methods had been introduced earlier by Ferraris et al. in the patent literature.[439]

4.4.8. Photoelectrochromic Devices (PhotoECDs)

Photoelectrochromic devices combine electrochromism and light-harvesting ability for power generation. PhotoECDs can be self-powered switchable devices only or can be used as power sources for different applications. In a favorable situation, the photogenerated current triggers the coloring of the EC layer, resulting in an optical attenuation of the transmitted light.[440−442] PhotoECDs using the dye-sensitized solar cell (DSSC) approach have been fabricated based on metal complexes (e.g., Prussian blue)[440,443] or based on a two-electrode configuration where a metal oxide (e.g., WO_3) acts as the electrochrome on one electrode while the second electrode consists of the dye-sensitized TiO_2.[444,445] Other interesting device configurations have been described based on metal oxides and dye-sensitized TiO_2.[446,447] PANI and viologens have been described in PhotoECDs as well.[448,449] However, PANI, viologens, and Prussian blue are anodically coloring such that the corresponding PhotoECDs bleach upon illumination, hence limiting the utility of these conventional electrochromes for self-switchable sunglasses, for instance.

Ho et al. have demonstrated the first ECP-based PhotoECD consisting of a dual ECD/DSSC all-in-one device (as opposed to a tandem configuration[450]) replacing the conventional metal oxide electrochromes by a film of **210** (see Figure 35).[451] Possessing much larger CE values than those of WO_3, **210** is expected to require lower photocurrents to induce the desired optical changes. The same group has recently reported on a PProDOT-Et_2 (**254**)-based PhotoECD with enhanced contrasts (~34% transmittance attenuation) and higher power conversion efficiencies (up to 0.65%).[452]

4.4.9. Light-Pen Input Device

Malliaras et al. have developed a light-pen input device consisting of a photosensor array (made of the photosensitive bacteriorhodopsin blended with **211**) including an integrated electrochromic display made of **211** as well.[400] The device was fabricated from a plastic substrate without the presence of metal oxide electrodes, hence was mechanically flexible, and responded to light-pen input by changing the color of the EC pixels corresponding to the stimulated sensing cells (see Figure 36).

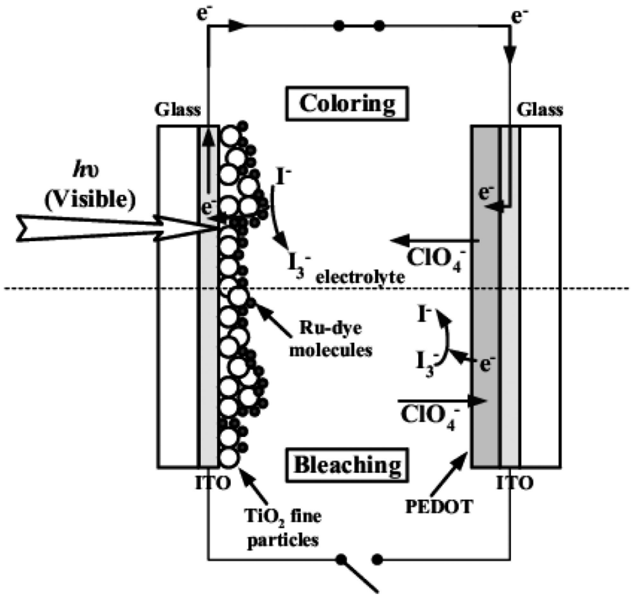


Figure 35. Schematic PhotoECD cell configuration including cathodically coloring **210** as described by Ho et al. Adapted with permission from ref 451. Copyright 2005 New Materials for Electrochemical Systems).

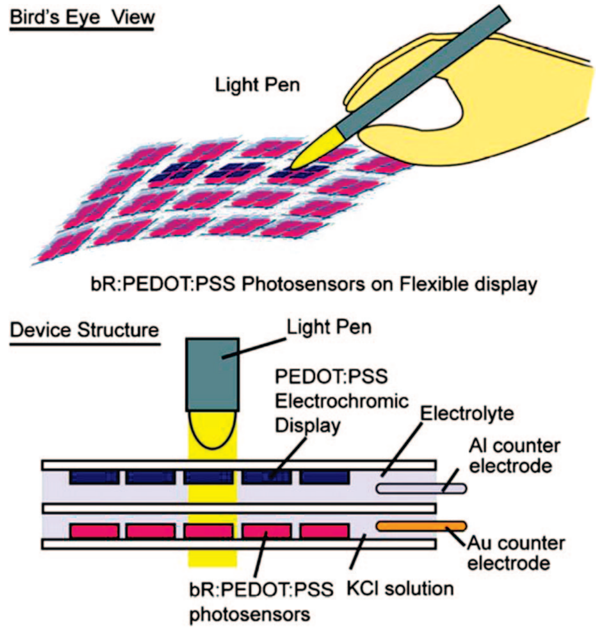


Figure 36. Schematic illustration of the light-pen input device concept as proposed by Malliaras et al. A photosensor array recognizes input from the light pen and activates the integrated EC display. Adapted with permission from ref 400. Copyright 2008 Elsevier B.V.

5. Conclusions and Outlook

Given the breadth of recent progress in the design of π-conjugated polymer electrochromes with particularly desirable color states, along with the fast-growing demand for innovative display technologies, it is not surprising to see the current interest for electrochromics in general expand and trigger the development of new device concepts. With the ability to manipulate the polymer energy band structure by varying the molecular structure of its repeat unit, and the opportunity to fine-tune colors simultaneously, comes the perspective to synthesize ambient-stable materials operating over tens to hundreds of thousands of switching cycles. As a result of their synthetic scalability, unique film-forming properties, and applicability in solution-processed device manufacturing conditions, electrochromic polymers are on the path for commercialization.

It is evident from the number of electroactive materials described in the literature, and briefly highlighted in this overview work, that adding one more ECP candidate to the available library may not represent a substantial contribution aimed at moving the field ahead. If electrochemical polymerizations can be employed to demonstrate a concept, the same approach suffers from important limitations spanning large-scale applicability, tedious purifications, or the introduction of molecular defects, and importantly, the subsequent polymers do not always reach their optical saturation threshold due to the lack of solubility of the growing backbone. In contrast, further research effort should now be directed toward designing solution-processable ECPs with improved optical contrasts, switching ability, and optimized performance in devices, hence facilitating technology transfer and promoting the perspectives for mass-produced displays.

In particular, the next generation of electrochromic polymers should intend to address a number of essential aspects including (1) the compromise between solution-processability and film-to-substrate adhesion upon repeated switching, (2) the presence of at least one accessible highly transmissive state allowing the combination and separate redox control of several ECPs to generate multiple colors and shades otherwise difficult to achieve, (3) the polymer response time at various desirable film thicknesses, and (4) the long-term environmental stability. These goals are not exclusive and will be attained by understanding the structure−property relationships governed by the careful structural modifications operated at the molecular level and by proposing new methodologies for the study of systems with more complex energy band patterns/optical features. The correlation among optical density, switching performance, and film thickness−quality has been widely ignored so far in spite of the obvious interplay. Similarly, coloration efficiencies and color coordinates for the polymer electrochromes are not systematically reported, which complicates further comparison between works.

Correct use and implementation of the existing characterization toolbox for polymer electrochromism will be a key variable in the overall equation leading to widespread applications of this fascinating technology.

6. Glossary

ACN	acetonitrile
CE	coloration efficiency
CCE	composite coloration efficiency
CP	conjugated polymer
DA	donor−acceptor
DAD	donor−acceptor−donor
DCM	dichloromethane
E_g	HOMO−LUMO gap or band-gap
EC	electrochromic
ECP	electrochromic polymer
ECD	electrochromic device
EDOT	(ethylenedioxy)thiophene
HOMO	highest occupied molecular orbital
ITO	indium tin oxide
LED	light-emitting diode
LEC	light-emitting electrochemical cell
LUMO	lowest unoccupied molecular orbital
PANI	polyaniline

PC	propylene carbonate
PECD	polymer electrochromic device
PhotoECD	photoelectrochromic device
PP	polypyrrole
ProDOT	(propylenedioxy)thiophene
ProDOP	(propylenedioxy)pyrrole
PMMA	poly(methyl methacrylate)
PSC	polymer solar cell
PT	polythiophene
SCE	saturated calomel electrode

7. Acknowledgments

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8. References

(1) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296.
(2) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070.
(3) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.
(4) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
(5) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.
(6) Moller, S.; Perlov, C.; Jackson, W.; Taussig, C.; Forrest, S. R. *Nature* **2003**, *426*, 166.
(7) Ling, Q.-D.; Song, Y.; Lim, S.-L.; Teo, E. Y.-H.; Tan, Y.-P.; Zhu, C.; Chan, D. S. H.; Kwong, D.-L.; Kang, E.-T.; Neoh, K.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2947.
(8) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.
(9) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: Cambridge, U.K., 2007.
(10) Dyer, A. L.; Reynolds, J. R. in *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A.; Reynolds, J. R. (eds.) CRC Press: Boca Raton, FL, 2007.
(11) Padilla, J.; Seshadri, V.; Filloramo, J.; Mino, W. K.; Mishra, S. P.; Radmard, B.; Kumar, A.; Sotzing, G. A.; Otero, T. F. *Synth. Met.* **2007**, *157*, 261.
(12) Padilla, J.; Seshadri, V.; Sotzing, G. A.; Otero, T. F. *Electrochem. Commun.* **2007**, *9*, 1931.
(13) Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.
(14) Fabretto, M.; Vaithianathan, T.; Hall, C.; Mazurkiewicz, J.; Innis, P. C.; Wallace, G. G.; Murphy, P. *Electrochim. Acta* **2008**, *53*, 2250.
(15) Fabretto, M.; Vaithianathan, T.; Hall, C.; Murphy, P.; Innis, P. C.; Mazurkiewicz, J.; Wallace, G. G. *Electrochem. Commun.* **2007**, *9*, 2032.
(16) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563.
(17) Thompson, B. C.; Schottland, P.; Sonmez, G.; Reynolds, J. R. *Synth. Met.* **2001**, *119*, 333.
(18) Overheim, R. D.; Wagner, D. L. *Light and Color*; Wiley: New York, 1982.
(19) Meeker, D. L.; Mudigonda, D. S. K.; Osborn, J. M.; Loveday, D. C.; Ferraris, J. P. *Macromolecules* **1998**, *31*, 2943.
(20) Hyodo, K. *Electrochim. Acta* **1994**, *39*, 265.
(21) Padilla, J.; Otero, T. F. *Bioinspiration Biomimetics* **2008**, *3*, 035006.
(22) Sonmez, G.; Sonmez, H. B. *J. Mater. Chem.* **2006**, *16*, 2473.
(23) Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J. C. *J. Electroanal. Chem.* **1983**, *148*, 299.
(24) Gazard, M.; Dubois, J. C.; Champagne, M.; Garnier, F.; Tourillon, G. *J. Phys., Colloq.* **1983**, *44*, 537.
(25) Druy, M. A.; Seymour, R. J. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 561.
(26) Druy, M.; Seymour, R. *J. Phys., Colloq.* **1983**, *44*, 595.
(27) Aizawa, M.; Watanable, S.; Shinohara, H.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1985**, *5*, 264.
(28) Cecchet, F.; Bignozzi, C. A.; Paolucci, F.; Marcaccio, M. *Synth. Met.* **2006**, *156*, 27.
(29) Arbizzani, C.; Bongini, A.; Mastragostino, M.; Zanelli, A.; Barbarella, G.; Zambianchi, M. *Adv. Mater.* **1995**, *7*, 571.
(30) Collomb-Dunand-Sauthier, M. N.; Langlois, S.; Genies, E. *J. Appl. Electrochem.* **1994**, *24*, 72.
(31) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.
(32) Elsenbaumer, R. L.; Jen, K. Y.; Miller, G. G.; Shacklette, L. W. *Synth. Met.* **1987**, *18*, 277.
(33) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202.
(34) Lère-Porte, J.-P.; Moreau, J. J. E.; Torreilles, C. *Eur. J. Org. Chem.* **2001**, *2001*, 1249.
(35) Mastragostino, M.; Arbizzani, C.; Bongini, A.; Barbarella, G.; Zambianchi, M. *Electrochim. Acta* **1993**, *38*, 135.
(36) Pang, Y.; Li, X.; Ding, H.; Shi, G.; Jin, L. *Electrochim. Acta* **2007**, *52*, 6172.
(37) Sheng, C.; Wenting, B.; Shijian, T.; Yuechuan, W. *J. Appl. Polym. Sci.* **2008**, *109*, 120.
(38) Pang, Y.; Li, X.; Shi, G.; Jin, L. *Int. J. Electrochem. Sci.* **2007**, *9*, 681.
(39) Pang, Y.; Xu, H.; Li, X.; Ding, H.; Cheng, Y.; Shi, G.; Jin, L. *Electrochem. Commun.* **2006**, *8*, 1757.
(40) Pang, Y.; Li, X.; Shi, G.; Wang, F.; Jin, L. *Thin Solid Films* **2008**, *516*, 6512.
(41) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(42) Alkan, S.; Cutler, C. A.; Reynolds, J. R. *Adv. Funct. Mater.* **2003**, *13*, 331.
(43) Ritter, S. K.; Noftle, R. E.; Ward, A. E. *Chem. Mater.* **1993**, *5*, 752.
(44) Lee, C.; Kim, K. J.; Rhee, S. B. *Synth. Met.* **1995**, *69*, 295.
(45) Camurlu, P.; Cirpan, A.; Toppare, L. *Mater. Chem. Phys.* **2005**, *92*, 413.
(46) Giglioti, M.; Trivinho-Strixino, F.; Matsushima, J. T.; Bulhões, L. O. S.; Pereira, E. C. *Sol. Energy Mater. Sol. Cells* **2004**, *82*, 413.
(47) Gustafsson-Carlberg, J. C.; Inganäs, O.; Andersson, M. R.; Booth, C.; Azens, A.; Granqvist, C. G. *Electrochim. Acta* **1995**, *40*, 2233.
(48) Iraqi, A.; Crayston, J. A.; Walton, J. C. *J. Mater. Chem.* **1995**, *5*, 1831.
(49) Ribeiro, A. S.; Gazotti, W. A.; dos Santos Filho, P. F.; De Paoli, M.-A. *Synth. Met.* **2004**, *145*, 43.
(50) Ribeiro, A. S.; Nogueira, V. C.; Faria dos Santos Filho, P.; De Paoli, M. A. *Electrochim. Acta* **2004**, *49*, 2237.
(51) Ko, H. C.; Park, S.-a.; Paik, W.-k.; Lee, H. *Synth. Met.* **2002**, *132*, 15.
(52) Iraqi, A.; Crayston, J. A.; Walton, J. C. *J. Mater. Chem.* **1998**, *8*, 31.
(53) Ribeiro, A. S.; Ribeiro, L. M. O.; Leite, S. M. M.; da Silva, J. G., Jr; Ramos, J. C.; Navarro, M.; Tonholo, J. *Polymer* **2006**, *47*, 8430.
(54) Ak, M.; Durmus, A.; Toppare, L. *J. Appl. Electrochem.* **2007**, *37*, 729.
(55) Asil, D.; Cihaner, A.; AlgI, F.; önal, A. M. *J. Electroanal. Chem.* **2008**, *618*, 87.
(56) Choi, J.; Kumar, A.; Sotzing, G. A. *J. Macromol. Sci., Part A* **2007**, *44*, 1305.
(57) Kumar, A.; Jang, S.-Y.; Padilla, J.; Otero, T. F.; Sotzing, G. A. *Polymer* **2008**, *49*, 3686.
(58) Turkarslan, O.; Erden, A.; Sahin, E.; Toppare, L. *J. Macromol. Sci., Pure Appl. Chem.* **2006**, *43*, 115.
(59) Sacan, L.; Cirpan, A.; Camurlu, P.; Toppare, L. *Synth. Met.* **2006**, *156*, 190.
(60) Erden, A.; Sahin, E.; Güllü, M.; Toppare, L. *Eur. Polym. J.* **2006**, *42*, 1866.
(61) Bredas, J. L.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1986**, *85*, 4673.
(62) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382.
(63) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.
(64) Yashima, H.; Kobayashi, M.; Lee, K. B.; Chung, D.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1987**, *134*, 46.
(65) Hung, T.-T.; Chen, S.-A. *Polymer* **1999**, *40*, 3881.
(66) King, G.; Higgins, S. J. *J. Mater. Chem.* **1995**, 5.
(67) Lee, K.; Sotzing, G. A. *Macromolecules* **2001**, *34*, 5746.
(68) Sotzing, G. A.; Lee, K. *Macromolecules* **2002**, *35*, 7281.
(69) Lee, B.; Seshadri, V.; Sotzing, G. A. *Langmuir* **2005**, *21*, 10797.
(70) Lee, B.; Seshadri, V.; Sotzing, G. A. *Synth. Met.* **2005**, *152*, 177.
(71) Lee, B.; Yavuz, M. S.; Sotzing, G. A. *Macromolecules* **2006**, *39*, 3118.
(72) Pomerantz, M.; Gu, X.; Zhang, S. X. *Macromolecules* **2001**, *34*, 1817.
(73) Pomerantz, M.; Gu, X. *Synth. Met.* **1997**, *84*, 243.
(74) Kumar, A.; Buyukmumcu, Z.; Sotzing, G. A. *Macromolecules* **2006**, *39*, 2723.

(75) Kumar, A.; Bokria, J. G.; Buyukmumcu, Z.; Dey, T.; Sotzing, G. A. *Macromolecules* **2008**, *41*, 7098.

(76) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(77) Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc., Chem. Commun.* **1991**, *18*, 1268.

(78) Ferraris, J. P.; Henderson, C.; Torres, D.; Meeker, D. *Synth. Met.* **1995**, *72*, 147.

(79) Wu, C.-G.; Lu, M. I.; Chang, S. J.; Wei, C. S. *Adv. Funct. Mater.* **2007**, *17*, 1063.

(80) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771.

(81) Mert, O.; Sahin, E.; Ertas, E.; Ozturk, T.; Aydin, E. A.; Toppare, L. *J. Electroanal. Chem.* **2006**, *591*, 53.

(82) Tovar, J. D.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 1775.

(83) Wu, C.-G.; Lu, M.-I.; Jhong, M.-F. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 1121.

(84) Druy, M. A.; Seymour, R. J. *J. Phys., Colloq.* **1983**, 595.

(85) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, *19*, 854.

(86) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, *14*, 635.

(87) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115.

(88) Wynne, K. J.; Street, G. B. *Macromolecules* **1985**, *18*, 2361.

(89) Diaz, A. F.; Castillo, J.; Kanazawa, K. K.; Logan, J. A.; Salmon, M.; Fajardo, O. *J. Electroanal. Chem.* **1982**, *133*, 233.

(90) Reynolds, J. R.; Poropatic, P. A.; Toyooka, R. L. *Synth. Met.* **1987**, *18*, 95.

(91) Reynolds, J. R.; Poropatic, P. A.; Toyooka, R. L. *Macromolecules* **1987**, *20*, 958.

(92) Bjorklund, R.; Andersson, S.; Allenmark, S.; Lundstrwm, I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 263.

(93) Murakami, Y.; Yamamoto, T. *Polym. J.* **1999**, *31*, 476.

(94) Ribeiro, A. S.; Silva, A. U. d.; Navarro, M.; Tonholo, J. *Electrochim. Acta* **2006**, *51*, 4892.

(95) Ak, M.; Ak, M. S.; Toppare, L. *Macromol. Chem. Phys.* **2006**, *207*, 1351.

(96) De Paoli, M. A.; Panero, S.; Prosperi, P.; Scrosati, B. *Electrochim. Acta* **1990**, *35*, 1145.

(97) Peres, R. C. D.; Juliano, V. F.; De Paoli, M.-A.; Panero, S.; Scrosati, B. *Electrochim. Acta* **1993**, *38*, 869.

(98) Deepa, M.; Ahmad, S. *Eur. Polym. J.* **2008**, *44*, 3288.

(99) Ferreira, J.; Santos, M. J. L.; Matos, R.; Ferreira, O. P.; Rubira, A. F.; Girotto, E. M. *J. Electroanal. Chem.* **2006**, *591*, 27.

(100) Girotto, E. M.; De Paoli, M.-A. *Adv. Mater.* **1998**, *10*, 790.

(101) Song, H.-K.; Lee, E. J.; Oh, S. M. *Chem. Mater.* **2005**, *17*, 2232.

(102) Ahmad, S.; Singh, S. *Electrochem. Commun.* **2008**, *10*, 895.

(103) Benincori, T.; Brenna, E.; Sannicolo, F.; Zotti, G.; Zecchin, S.; Schiavon, G.; Gatti, C.; Frigerio, G. *Chem. Mater.* **2000**, *12*, 1480.

(104) Gatti, C.; Frigerio, G.; Benincori, T.; Brenna, E.; Sannicolo, F.; Zotti, G.; Zecchin, S.; Schiavon, G. *Chem. Mater.* **2000**, *12*, 1490.

(105) De Paoli, M. A.; Casalbore-Miceli, G.; Girotto, E. M.; Gazotti, W. A. *Electrochim. Acta* **1999**, *44*, 2983.

(106) Gazotti, W. A.; De Paoli, M. A.; Casalbore-Miceli, G.; Geri, A.; Zotti, G. *J. Appl. Electrochem.* **1999**, *29*, 757.

(107) Havinga, E. E.; Ten Hoeve, W.; Meijer, E. W.; Wynberg, H. *Chem. Mater.* **1989**, *1*, 650.

(108) Kon, A. B.; Foos, J. S.; Rose, T. L. *Chem. Mater.* **1992**, *4*, 416.

(109) Cihaner, A. *J. Macromol. Sci., Pure Appl. Chem.* **2006**, *43*, 1379.

(110) Cihaner, A. *J. Electroanal. Chem.* **2007**, *605*, 8.

(111) Liu, H.; Li, Y.; Xu, J.; Le, Z.; Luo, M.; Wang, B.; Pu, S.; Shen, L. *Eur. Polym. J.* **2008**, *44*, 171.

(112) Dong, B.; Zheng, L.; Xu, J.; Liu, H.; Pu, S. *Polymer* **2007**, *48*, 5548.

(113) Blohm, M. L.; Pickett, J. E.; Van Dort, P. C. *Macromolecules* **1993**, *26*, 2704.

(114) Havinga, E. E.; Mutsaers, C. M. J.; Jenneskens, L. W. *Chem. Mater.* **1996**, *8*, 769.

(115) Kwan-Yue Jen, H. E.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, *3*, 215.

(116) Martinez, M.; Reynolds, J. R.; Basak, S.; Black, D. A.; Marynick, D. S.; Pomerantz, M. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 911.

(117) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

(118) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720.

(119) Fu, Y.; Elsenbaumer, R. L. *Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng., Proc.* **1995**, *72*, 315.

(120) Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1451.

(121) Li, Y.; Zou, Y. *Adv. Mater.* **2008**, *20*, 2952.

(122) Hou, J.; Tan, Z. a.; He, Y.; Yang, C.; Li, Y. *Macromolecules* **2006**, *39*, 4657.

(123) Santos, L. F.; Faria, R. C.; Gaffo, L.; Carvalho, L. M.; Faria, R. M.; Gonçalves, D. *Electrochim. Acta* **2007**, *52*, 4299.

(124) Nah, Y.-C.; Kim, S.-S.; Park, J.-H.; Kim, D.-Y. *Electrochem. Solid-State Lett.* **2007**, *10*, J12.

(125) Mitsuhara, T.; Kaeriyama, K.; Tanaka, S. *J. Chem. Soc., Chem. Commun.* **1987**, *10*, 764.

(126) Danieli, R.; Ostoja, P.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, *19*, 1473.

(127) Child, A. D.; Sankaran, B.; Larmat, F.; Reynolds, J. R. *Macromolecules* **1995**, *28*, 6571.

(128) Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S. *Macromolecules* **1991**, *24*, 678.

(129) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849.

(130) Larmat, F.; Soloducho, J.; Katritzky, A. R.; Reynolds, J. R. *Synth. Met.* **2001**, *124*, 329.

(131) Reynolds, J. R.; Child, A. D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S. *Macromolecules* **1993**, *26*, 2095.

(132) Reynolds, J. R.; Katritzky, A. R.; Soloducho, J.; Belyakov, S.; Sotzing, G. A.; Pyo, M. *Macromolecules* **1994**, *27*, 7225.

(133) Sotzing, G. A.; Reynolds, J. R.; Katritzky, A. R.; Soloducho, J.; Belyakov, S.; Musgrave, R. *Macromolecules* **1996**, *29*, 1679.

(134) Aydemir, K.; Tarkuc, S.; Durmus, A.; Gunbas, G. E.; Toppare, L. *Polymer* **2008**, *49*, 2029.

(135) Lere-Porte, J.-P.; Moreau, J. J. E.; Serein-Spirau, F.; Torreilles, C.; Righi, A.; Sauvajol, J.-L.; Brunet, M. *J. Mater. Chem.* **2000**, *10*, 927.

(136) Silva, R. A.; Serein-Spirau, F.; Bouachrine, M.; Lere-Porte, J.-P.; Moreau, J. J. E. *J. Mater. Chem.* **2004**, *14*, 3043.

(137) Irvin, J. A.; Reynolds, J. R. *Polymer* **1998**, *39*, 2339.

(138) Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochim. Acta* **2001**, *46*, 2023.

(139) Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* **2004**, *16*, 574.

(140) Irvin, D. J.; Reynolds, J. R. *Polym. Adv. Technol.* **1998**, *9*, 260.

(141) Ko, H. C.; Kim, S.; Lee, H.; Moon, B. *Adv. Funct. Mater.* **2005**, *15*, 905.

(142) Galand, E. M.; Mwaura, J. K.; Argun, A. A.; Abboud, K. A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2006**, *39*, 7286.

(143) Sankaran, B.; Alexander, M. D.; Tan, L.-S. *Synth. Met.* **2001**, *123*, 425.

(144) Yildirim, A.; Tarkuc, S.; Ak, M.; Toppare, L. *Electrochim. Acta* **2008**, *53*, 4875.

(145) Ferraris, J. P.; Andrus, R. G.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, *18*, 1318.

(146) Ferraris, J. P.; Newton, M. D. *Polymer* **1992**, *33*, 391.

(147) Cihaner, A.; AlgI, F. *Electrochim. Acta* **2008**, *54*, 786.

(148) Tarkuc, S.; Sahmetlioglu, E.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Electrochim. Acta* **2006**, *51*, 5412.

(149) Tarkuc, S.; Sahmetlioglu, E.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Sens. Actuators, B* **2007**, *121*, 622.

(150) Cihaner, A.; AlgI, F. *Electrochim. Acta* **2008**, *54*, 665.

(151) Cihaner, A.; AlgI, F. *Electrochim. Acta* **2008**, *53*, 2574.

(152) AlgI, F.; Cihaner, A. *Tetrahedron Lett.* **2008**, *49*, 3530.

(153) Cihaner, A.; AlgI, F. *J. Electroanal. Chem.* **2008**, *614*, 101.

(154) Tarkuc, S.; Ak, M.; Onurhan, E.; Toppare, L. *J. Macromol. Sci., Part A* **2008**, *45*, 164.

(155) Yildiz, E.; Camurlu, P.; Tanyeli, C.; Akhmedov, I.; Toppare, L. *J. Electroanal. Chem.* **2008**, *612*, 247.

(156) Turkarslan, O.; Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4496.

(157) Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Thin Solid Films* **2008**, *516*, 4334.

(158) Sahin, E.; Sahmetlioglu, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Org. Electron.* **2006**, *7*, 351.

(159) Varis, S.; Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Solid State Sci.* **2006**, *8*, 1477.

(160) Varis, S.; Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Eur. Polym. J.* **2006**, *42*, 2352.

(161) Ak, M.; Sahmetlioglu, E.; Toppare, L. *J. Electroanal. Chem.* **2008**, *621*, 55.

(162) Pozo-Gonzalo, C.; Pomposo, J. A.; Alduncin, J. A.; Salsamendi, M.; Mikhaleva, A. b. I.; Krivdin, L. B.; Trofimov, B. A. *Electrochim. Acta* **2007**, *52*, 4784.

(163) Pozo-Gonzalo, C.; Salsamendi, M.; Pomposo, J. A.; Grande, H.-J.; Schmidt, E. Y.; Rusakov, Y. Y.; Trofimov, B. A. *Macromolecules* **2008**, *41*, 6886.

(164) Pons, S.; Hinman, A. S. *Electrochim. Acta* **1984**, *29*, 1251.

(165) Glenis, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12519.

(166) Carrillo, I.; de la Bianca, E. S.; González-Tejera, M. J.; Hernández-Fuentes, I. *Chem. Phys. Lett.* **1994**, *229*, 633.

(167) Zotti, G.; Schiavon, G.; Comisso, N.; Berlin, A.; Pagani, G. *Synth. Met.* **1990**, *36*, 337.

(168) Wan, X.; Yan, F.; Jin, S.; Liu, X.; Xue, G. *Chem. Mater.* **1999**, *11*, 2400.
(169) Del Valle, M. A.; Ugalde, L.; Díaz, F. R.; Bodini, M. E.; Bernède, J. C. *J. Appl. Polym. Sci.* **2004**, *92*, 1346.
(170) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(171) Seha, T.; önal, A. M. *J. Appl. Polym. Sci.* **2007**, *103*, 871.
(172) Içli, M.; Cihaner, A.; önal, A. M. *Electrochim. Acta* **2007**, *52*, 8039.
(173) Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R.; Steel, P. J. *Synth. Met.* **1997**, *84*, 199.
(174) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875.
(175) Van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *32*, 1.
(176) De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.
(177) Sotzing, G. A.; Thomas, C. A.; Reynolds, J. R.; Steel, P. J. *Macromolecules* **1998**, *31*, 3750.
(178) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275.
(179) DuBois, C. J.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 1844.
(180) Irvin, D. J.; DuBois, C. J., Jr.; Reynolds, J. R. *Chem. Commun.* **1999**, *20*, 2121.
(181) Du Bois, C. J.; Larmat, F.; Irvin, D. J.; Reynolds, J. R. *Synth. Met.* **2001**, *119*, 321.
(182) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761.
(183) Yasuda, T.; Sakai, Y.; Aramaki, S.; Yamamoto, T. *Chem. Mater.* **2005**, *17*, 6060.
(184) Audebert, P.; Sadki, S.; Miomandre, F.; Clavier, G. *Electrochem. Commun.* **2004**, *6*, 144.
(185) Musmanni, S.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1993**, *2*, 172.
(186) Vangeneugden, D. L.; Kiebooms, R. H. L.; Vanderzande, D. J. M.; Gelan, J. M. J. V. *Synth. Met.* **1999**, *101*, 120.
(187) Cravino, A.; Loi, M. A.; Scharber, M. C.; Winder, C.; Neugebauer, H.; Denk, P.; Meng, H.; Chen, Y.; Wudl, F.; Sariciftci, N. S. *Synth. Met.* **2003**, *137*, 1435.
(188) Meng, H.; Tucker, D.; Chaffins, S.; Chen, Y.; Helgeson, R.; Dunn, B.; Wudl, F. *Adv. Mater.* **2003**, *15*, 146.
(189) Berridge, R.; Wright, S. P.; Skabara, P. J.; Dyer, A.; Steckler, T.; Argun, A. A.; Reynolds, J. R.; Harrington, R. W.; Clegg, W. *J. Mater. Chem.* **2007**, *17*, 225.
(190) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 896.
(191) Larmat, F.; Reynolds, J. R.; Reinhardt, B. A.; Brott, L. L.; Clarson, S. I. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3627.
(192) Tsuie, B.; Reddinger, J. L.; Sotzing, G. A.; Soloducho, J.; Katritzky, A. R.; Reynolds, J. R. *J. Mater. Chem.* **1999**, *9*, 2189.
(193) Witker, D.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 7636.
(194) Sotzing, G. A.; Reddinger, J. L.; Katritzky, A. R.; Soloducho, J.; Musgrave, R.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1997**, *9*, 1578.
(195) Aïch, R. B.; Blouin, N.; Bouchard, A.; Leclerc, M. *Chem. Mater.* **2009**, *21*, 751.
(196) Gaupp, C. L.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 6305.
(197) Yigitsoy, B.; Varis, S.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Electrochim. Acta* **2007**, *52*, 6561.
(198) Tarkuc, S.; Sahmetlioglu, E.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Opt. Mater.* **2008**, *30*, 1489.
(199) Camurlu, P.; Tarkuç, S.; Sahmetlioglu, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 154.
(200) Arslan, A.; Türkarslan, ö.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Mater. Chem. Phys.* **2007**, *104*, 410.
(201) Varis, S.; Ak, M.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *J. Electroanal. Chem.* **2007**, *603*, 8.
(202) Camurlu, P.; Sahmetlioglu, E.; Sahin, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Thin Solid Films* **2008**, *516*, 4139.
(203) Beyazyildirim, S.; Camurlu, P.; Yilmaz, D.; Gullu, M.; Toppare, L. *J. Electroanal. Chem.* **2006**, *587*, 235.
(204) Carrasco, P.-M.; Pozo-Gonzalo, C.; Grande, H.; Pomposo, J. A.; Cortázar, M.; Deborde, V.; Hissler, M.; Reau, R. *Polym. Bull.* **2008**, *61*, 713.
(205) Gunbas, G. E.; Camurlu, P.; Akhmedov, I. M.; Tanyeli, C.; önal, A. M.; Toppare, L. *J. Electroanal. Chem.* **2008**, *615*, 75.
(206) Nie, G.; Qu, L.; Xu, J.; Zhang, S. *Electrochim. Acta* **2008**, *53*, 8351.
(207) Yu, Y.-H.; Lai, C.-Y.; Chen, C.-L.; Yeh, J.-M. *J. Electron. Mater.* **2006**, *35*, 1571.
(208) Cihaner, A.; önal, A. M. *J. Electroanal. Chem.* **2007**, *601*, 68.
(209) Blankespoor, R. L.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1985**, *2*, 90.
(210) Chang, A.-C.; Blankespoor, R. L.; Miller, L. L. *J. Electroanal. Chem.* **1987**, *236*, 239.
(211) Chang, A.-C.; Miller, L. L. *Synth. Met.* **1987**, *22*, 71.
(212) Fall, M.; Assogba, L.; Aaron, J. J.; Dieng, M. M. *Synth. Met.* **2001**, *123*, 365.
(213) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.
(214) Bayer-AG. Eur. Patent 339 340, 1988.
(215) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(216) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41*, 831.
(217) Winter, I.; Reese, C.; Hormes, J.; Heywang, G.; Jonas, F. *Chem. Phys.* **1995**, *194*, 207.
(218) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.
(219) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.
(220) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 7629.
(221) Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 2582.
(222) Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101.
(223) Welsh, D. M.; Kumar, A.; Morvant, M. C.; Reynolds, J. R. *Synth. Met.* **1999**, *102*, 967.
(224) Schwendeman, I.; Gaupp, C. L.; Hancock, J. M.; Groenendaal, L.; Reynolds, J. R. *Adv. Funct. Mater.* **2003**, *13*, 541.
(225) Cutler, C. A.; Bouguettaya, M.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 684.
(226) Cutler, C. A.; Bouguettaya, M.; Kang, T. S.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 3068.
(227) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
(228) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.
(229) Ikenoue, Y.; Outani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1989**, *30*, 305.
(230) Stéphan, O.; Schottland, P.; Le Gall, P.-Y.; Chevrot, C.; Mariet, C.; Carrier, M. *J. Electroanal. Chem.* **1998**, *443*, 217.
(231) Stéphan, O.; Schottland, P.; Le Gall, P.-Y.; Chevrot, C. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1168.
(232) Ventosa, E.; Colina, A.; Heras, A.; Martínez, A.; Orcajo, O.; Ruiz, V.; López-Palacios, J. *Electrochim. Acta* **2008**, *53*, 4219.
(233) Wang, C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 58.
(234) Sahin, E.; Camurlu, P.; Toppare, L. *Synth. Met.* **2006**, *156*, 124.
(235) Inagi, S.; Fuchigami, T. *Synth. Met.* **2008**, *158*, 782.
(236) Doherty, W. J.; Wysocki, R. J.; Armstrong, N. R.; Saavedra, S. S. *Macromolecules* **2006**, *39*, 4418.
(237) Doherty, W. J.; Wysocki, R. J.; Armstrong, N. R.; Saavedra, S. S. *J. Phys. Chem. B* **2006**, *110*, 4900.
(238) Fei, J.; Lim, K. G.; Palmore, G. T. R. *Chem. Mater.* **2008**, *20*, 3832.
(239) Wang, X. J.; Wong, K. Y. *Thin Solid Films* **2006**, *515*, 1573.
(240) Sindhu, S.; Narasimha Rao, K.; Ahuja, S.; Kumar, A.; Gopal, E. S. R. *Mater. Sci. Eng., B* **2006**, *132*, 39.
(241) Bhandari, S.; Deepa, M.; Singh, S.; Gupta, G.; Kant, R. *Electrochim. Acta* **2008**, *53*, 3189.
(242) Deepa, M.; Bhandari, S.; Arora, M.; Kant, R. *Macromol. Chem. Phys.* **2008**, *209*, 137.
(243) Manisankar, P.; Vedhi, C.; Selvanathan, G.; Gurumallesh Prabu, H. *J. Appl. Polym. Sci.* **2007**, *104*, 3285.
(244) Cho, S. I.; Lee, S. B. *Acc. Chem. Res.* **2008**, *41*, 699.
(245) Cho, S. I.; Xiao, R.; Lee, S. B. *Nanotechnology* **2007**, *18*, 405705.
(246) Huang, L.-M.; Wen, T.-C.; Gopalan, A. *Electrochim. Acta* **2006**, *51*, 3469.
(247) Goto, H.; Akagi, K. *Chem. Mater.* **2006**, *18*, 255.
(248) Lock, J. P.; Lutkenhaus, J. L.; Zacharia, N. S.; Im, S. G.; Hammond, P. T.; Gleason, K. K. *Synth. Met.* **2007**, *157*, 894.
(249) Lock, J. P.; Im, S. G.; Gleason, K. K. *Macromolecules* **2006**, *39*, 5326.
(250) Aqad, E.; Lakshmikantham, M. V.; Cava, M. P. *Org. Lett.* **2001**, *3*, 4283.
(251) Bendikov, M.; Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G. *J. Am. Chem. Soc.* **2008**, *130*, 6734.
(252) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379.
(253) Gaupp, C. L.; Welsh, D. M.; Reynolds, J. R. *Macromol. Rapid Commun.* **2002**, *23*, 885.
(254) Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517.
(255) Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559.
(256) Reeves, B. D.; Thompson, B. C.; Abboud, K. A.; Smart, B. E.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 717.
(257) Walczak, R. M.; Cowart, J. S. J.; Abboud, K. A.; Reynolds, J. R. *Chem. Commun.* **2006**, 1604.
(258) Walczak, R. M.; Cowart, J. S. J.; Reynolds, J. R. *J. Mater. Chem.* **2007**, *17*, 254.
(259) Liu, J.; Kadnikova, E. N.; Liu, Y.; McGehee, M. D.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9486.
(260) Murphy, A. R.; Frechet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596.

(261) Chang, P. C.; Lee, J.; Huang, D.; Subramanian, V.; Murphy, A. R.; Frechet, J. M. J. *Chem. Mater.* **2004**, *16*, 4783.

(262) Murphy, A. R.; Chang, P. C.; VanDyke, P.; Liu, J.; Frechet, J. M. J.; Subramanian, V.; DeLongchamp, D. M.; Sambasivan, S.; Fischer, D. A.; Lin, E. K. *Chem. Mater.* **2005**, *17*, 6033.

(263) Reeves, B. D.; Unur, E.; Ananthakrishnan, N.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 5344.

(264) Mishra, S. P.; Sahoo, R.; Ambade, A. V.; Contractor, A. Q.; Kumar, A. *J. Mater. Chem.* **2004**, *14*, 1896.

(265) Mishra, S. P.; Krishnamoorthy, K.; Sahoo, R.; Kumar, A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 419.

(266) Ak, M. S.; Ak, M.; Güllü, M.; Toppare, L. *Eur. Polym. J.* **2007**, *43*, 3452.

(267) Ho, H. A.; Brisset, H.; Elandaloussi, E. H.; Frère, P.; Roncali, J. *Adv. Mater.* **1996**, *8*, 990.

(268) Thomas, C. A.; Zong, K.; Abboud, K. A.; Steel, P. J.; Reynolds, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 16440.

(269) Thompson, B. C.; Kim, Y. G.; McCarley, T. D.; Reynolds, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 12714.

(270) Galand, E. M.; Kim, Y. G.; Mwaura, J. K.; Jones, A. G.; McCarley, T. D.; Shrotriya, V.; Yang, Y.; Reynolds, J. R. *Macromolecules* **2006**, *39*, 9132.

(271) Seshadri, V.; Sotzing, G. A. *Chem. Mater.* **2004**, *16*, 5644.

(272) Lee, B.-L.; Yamamoto, T. *Macromolecules* **1999**, *32*, 1375.

(273) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.

(274) Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1994**, *13*, 1585.

(275) Atwani, O.; Baristiran, C.; Erden, A.; Sonmez, G. *Synth. Met.* **2008**, *158*, 83.

(276) Tanaka, S.; Yamashita, Y. *Synth. Met.* **1995**, *69*, 599.

(277) Steckler, T. T.; Abboud, K. A.; Craps, M.; Rinzler, A. G.; Reynolds, J. R. *Chem. Commun.* **2007**, 4904.

(278) Akoudad, S.; Roncali, J. *Chem. Commun.* **1998**, *19*, 2081.

(279) Udum, Y. A.; Durmus, A.; Gunbas, G. E.; Toppare, L. *Org. Electron.* **2008**, *9*, 501.

(280) Ozyurt, F.; Gunbas, E. G.; Durmus, A.; Toppare, L. *Org. Electron.* **2008**, *9*, 296.

(281) Cebeci, F. Ç.; Sezer, E.; Sarac, A. S. *Electrochim. Acta* **2007**, *52*, 2158.

(282) Hou, J.; Zhang, S.; Chen, T. L.; Yang, Y. *Chem. Commun.* **2008**, 6034.

(283) Balan, A.; Gunbas, G.; Durmus, A.; Toppare, L. *Chem. Mater.* **2008**, 0.

(284) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498.

(285) Sonmez, G. *Chem. Commun.* **2005**, 5251.

(286) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Wudl, F. *Adv. Mater.* **2004**, *16*, 1905.

(287) DuBois, C. J.; Abboud, K. A.; Reynolds, J. R. *J. Phys. Chem. B* **2004**, *108*, 8550.

(288) Salzner, U. *J. Phys. Chem. B* **2002**, *106*, 9214.

(289) Salzner, U.; Kose, M. E. *J. Phys. Chem. B* **2002**, *106*, 9221.

(290) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. *Macromolecules* **2005**, *38*, 669.

(291) Sonmez, G.; Wudl, F. *J. Mater. Chem.* **2005**, *15*, 20.

(292) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, *11*, 939.

(293) Blanchard, P.; Raimundo, J. M.; Roncali, J. *Synth. Met.* **2001**, *119*, 527.

(294) Aldakov, D.; Palacios, M. A.; Anzenbacher, P. *Chem. Mater.* **2005**, *17*, 5238.

(295) Durmus, A.; Gunbas, G. E.; Camurlu, P.; Toppare, L. *Chem. Commun.* **2007**, 3246.

(296) Durmus, A.; Gunbas, G. E.; Toppare, L. *Chem. Mater.* **2007**, *19*, 6247.

(297) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Mater.* **2008**, *20*, 691.

(298) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Funct. Mater.* **2008**, *18*, 2026.

(299) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795.

(300) Cihaner, A.; Algi, F. *Adv. Funct. Mater.* **2008**, *18*, 3583.

(301) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Adv. Mater.* **2008**, *20*, 2772.

(302) Holmes, A. B.; Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C. *Nature* **1995**, *376*, 498.

(303) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.

(304) Kim, I. T.; Lee, J. Y.; Lee, S. W. *Chem. Lett.* **2004**, *33*, 46.

(305) Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4647.

(306) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988.

(307) Kietzke, T.; Egbe, D. A. M.; Horhold, H. H.; Neher, D. *Macromolecules* **2006**, *39*, 4018.

(308) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222.

(309) Marder, S. R.; Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B. *J. Am. Chem. Soc.* **2007**, *129*, 7246.

(310) Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121.

(311) Gaupp, C. L.; Zong, K.; Schottland, P.; Thompson, B. C.; Thomas, C. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 1132.

(312) Schottland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 7051.

(313) Thomas, C. A.; Zong, K.; Schottland, P.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 222.

(314) Merz, A.; Schropp, R.; Dötterl, E. *Synthesis* **1995**, 795.

(315) Zotti, G.; Zecchin, S.; Schiavon, G.; Groenendaal, L. *Chem. Mater.* **2000**, *12*, 2996.

(316) Kraft, A.; Rottmann, M.; Gilsing, H.-D.; Faltz, H. *Electrochim. Acta* **2007**, *52*, 5856.

(317) Li, H.; Lambert, C. *J. Mater. Chem.* **2005**, *15*, 1235.

(318) Li, H.; Lambert, C.; Stahl, R. *Macromolecules* **2006**, *39*, 2049.

(319) Zong, K.; Reynolds, J. R. *J. Org. Chem.* **2001**, *66*, 6873.

(320) Unur, E.; Jung, J.-H.; Mortimer, R. J.; Reynolds, J. R. *Chem. Mater.* **2008**, *20*, 2328.

(321) Sonmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639.

(322) Walczak, R. M.; Jung, J. H.; Cowart, J. S. J.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 7777.

(323) Walczak, R. M.; Leonard, J. K.; Reynolds, J. R. *Macromolecules* **2008**, *41*, 691.

(324) Sonmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639.

(325) Schwendeman, I.; Hickman, R.; Sonmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118.

(326) Merz, A.; Scnwarz, R.; Schropp, R. *Adv. Mater.* **1992**, *4*, 409.

(327) Merz, A.; Graf, S. *J. Electroanal. Chem.* **1996**, *412*, 11.

(328) Bezgin, B.; Cihaner, A.; önal, A. M. *Thin Solid Films* **2008**, *516*, 7329.

(329) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. *Chem.—Eur. J.* **2007**, *13*, 10055.

(330) Verghese, M. M.; Ram, M. K.; Vardhan, H.; Ashraf, S. M.; Malhotra, B. D. *Adv. Mater. Opt. Electron.* **1996**, *6*, 399.

(331) Verghese, M. M.; Ram, M. K.; Vardhan, H.; Malhotra, B. D.; Ashraf, S. M. *Polymer* **1997**, *38*, 1625.

(332) Siove, A.; Ades, D.; N'Gbilo, E.; Chevrot, C. *Synth. Met.* **1990**, *38*, 331.

(333) Chevrot, C.; Ngbilo, E.; Kham, K.; Sadki, S. *Synth. Met.* **1996**, *81*, 201.

(334) Tran-Van, F.; Henri, T.; Chevrot, C. *Electrochim. Acta* **2002**, *47*, 2927.

(335) Yong-Jian, Q.; John, R. R. *J. Electrochem. Soc.* **1990**, *137*, 900.

(336) Lim, J. Y.; Ko, H. C.; Lee, H. *Synth. Met.* **2006**, *156*, 695.

(337) Natera, J.; Otero, L.; Sereno, L.; Fungo, F.; Wang, N.-S.; Tsai, Y.-M.; Hwu, T.-Y.; Wong, K.-T. *Macromolecules* **2007**, *40*, 4456.

(338) Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *30*, 151.

(339) Jelle, B. P.; Hagen, G.; Sunde, S.; Ødegård, R. *Synth. Met.* **1993**, *54*, 315.

(340) Sapp, S. A.; Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R. *Adv. Mater.* **1996**, *8*, 808.

(341) Sindhu, S.; Narasimha Rao, K.; Gopal, E. *Bull. Mater. Sci.* **2008**, *31*, 15.

(342) Deepa, M.; Awadhia, A.; Bhandari, S.; Agrawal, S. L. *Electrochim. Acta* **2008**, *53*, 7266.

(343) Lin, T.-H.; Ho, K.-C. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 506.

(344) Pozo-Gonzalo, C.; Mecerreyes, D.; Pomposo, J. A.; Salsamendi, M.; Marcilla, R.; Grande, H.; Vergaz, R.; Barrios, D.; Sánchez-Pena, J. M. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 101.

(345) Arbizzani, C.; Mastragostino, M.; Meneghello, L.; Morselli, M.; Zanelli, A. *J. Appl. Electrochem.* **1996**, *26*, 121.

(346) Huang, S.-W.; Ho, K.-C. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 491.

(347) Cirpan, A.; Argun, A. A.; Grenier, C. R. G.; Reeves, B. D.; Reynolds, J. R. *J. Mater. Chem.* **2003**, *13*, 2422.

(348) Seshadri, V.; Padilla, J.; Bircan, H.; Radmard, B.; Draper, R.; Wood, M.; Otero, T. F.; Sotzing, G. A. *Org. Electron.* **2007**, *8*, 367.

(349) De Paoli, M.-A.; Nogueira, A. F.; Machado, D. A.; Longo, C. *Electrochim. Acta* **2001**, *46*, 4243.

(350) Sahin, E.; Camurlu, P.; Toppare, L. *Synth. Met.* **2006**, *156*, 1073.
(351) Coskun, Y.; Cirpan, A.; Toppare, L. *J. Mater. Sci.* **2007**, *42*, 368.
(352) León-Silva, U.; Nicho, M.; Hu, H. *J. Solid State Electrochem.* **2008**, *12*, 71.
(353) Gazotti Jr, W. A.; Casalbore-Miceli, G.; Geri, A.; De Paoli, M.-A. *Adv. Mater.* **1998**, *10*, 60.
(354) Ma, C.; Taya, M.; Xu, C. *Electrochim. Acta* **2008**, *54*, 598.
(355) Ma, C.; Taya, M.; Xu, C. *Polym. Eng. Sci.* **2008**, *48*, 2224.
(356) Tung, T.-S.; Ho, K.-C. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 521.
(357) Vergaz, R.; Barrios, D.; Pena, J. M. S.; Marcos, C.; Pozo, C.; Pomposo, J. A. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 107.
(358) DeLongchamp, D.; Hammond, P. T. *Adv. Mater.* **2001**, *13*, 1455.
(359) Zotti, G.; Zecchin, S.; Berlin, A.; Schiavon, G.; Giro, G. *Chem. Mater.* **2001**, *13*, 43.
(360) Ferreira, M.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107.
(361) Fou, A. C.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7115.
(362) Ferreira, M.; Cheung, J. H.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 806.
(363) Lukkari, J.; Salomaki, M.; Viinikanoja, A.; Aaritalo, T.; Paukkunen, J.; Kocharova, N.; Kankare, J. *J. Am. Chem. Soc.* **2001**, *123*, 6083.
(364) Lukkari, J.; Salomaki, M.; Aaritalo, T.; Loikas, K.; Laiho, T.; Kankare, J. *Langmuir* **2002**, *18*, 8496.
(365) Vaibhav, J.; Hank, M. Y.; Reza, M.; Heflin, J. R. *Appl. Phys. Lett.* **2008**, *92*, 033304.
(366) Nah, Y.-C.; Choi, W. S.; Kim, D.-Y. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1547.
(367) Padilla, J.; Seshadri, V.; Otero, T. F.; Sotzing, G. A. *J. Electroanal. Chem.* **2007**, *609*, 75.
(368) Padilla, J.; Otero, T. F. *Electrochem. Commun.* **2008**, *10*, 1.
(369) Tran-Van, F.; Beouch, L.; Vidal, F.; Yammine, P.; Teyssié, D.; Chevrot, C. *Electrochim. Acta* **2008**, *53*, 4336.
(370) Verge, P.; Vidal, F.; Aubert, P.-H.; Beouch, L.; Tran-Van, F.; Goubard, F.; Teyssié, D.; Chevrot, C. *Eur. Polym. J.* **2008**, *44*, 3864.
(371) Vidal, F.; Plesse, C.; Teyssié, D.; Chevrot, C. *Synth. Met.* **2004**, *142*, 287.
(372) Plesse, C.; Vidal, F.; Randriamahazaka, H.; Teyssié, D.; Chevrot, C. *Polymer* **2005**, *46*, 7771.
(373) Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, *13*, 634.
(374) Bennett, R. B.; Kokonasky, W. E.; Hannan, M. J.; Boxall, L. G. U.S. Patent 5 446 577, 1995.
(375) Chandrasekhar, P. U.S. Patent 5 995 273, 1999.
(376) Topart, P.; Hourquebie, P. *Thin Solid Films* **1999**, *352*, 243.
(377) Rose, T. L.; D'Antonio, S.; Jillson, M. H.; Kon, A. B.; Suresh, R.; Wang, F. *Synth. Met.* **1997**, *85*, 1439.
(378) Gervais, F.; Petit, N.; Popon, C.; Buvat, P. *Eur. Phys. J. B* **2003**, *31*, 47.
(379) Petit, N.; Gervais, F.; Buvat, P.; Hourquebie, P.; Topart, P. *Eur. Phys. J. B* **1971**, *12*, 367.
(380) Chandrasekhar, P.; Zay, B. J.; Birur, G. C.; Rawal, S.; Pierson, E. A.; Kauder, L.; Swanson, T. *Adv. Funct. Mater.* **2002**, *12*, 95.
(381) Bessiere, A.; Beluze, L.; Morcrette, M.; Lucas, V.; Viana, B.; Badot, J. C. *Chem. Mater.* **2003**, *15*, 2577.
(382) Bessiere, A.; Marcel, C.; Morcrette, M.; Tarascon, J. M.; Lucas, V.; Viana, B.; Baffier, N. *J. Appl. Phys.* **2002**, *91*, 1589.
(383) Franke, E. B.; Trimble, C. L.; Hale, J. S.; Schubert, M.; Woollam, J. A. *J. Appl. Phys.* **2000**, *88*, 5777.
(384) Hale, J. S.; Woollam, J. A. *Thin Solid Films* **1999**, *339*, 174.
(385) Gazotti, W. A.; Casalbore-Miceli, G.; Geri, A.; Berlin, A.; De Paoli, M. A. *Adv. Mater.* **1998**, *10*, 1522.
(386) Aubert, P. H.; Argun, A. A.; Cirpan, A.; Tanner, D. B.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 2386.
(387) Reynolds, J. R.; Zong, K.; Schwendemann, I.; Sonmez, G.; Schottland, P.; Argun, A. A.; Aubert, P. H. PCT Int. Appl. WO03046106, 2004.
(388) Bennett, R. N.; Kokonaski, W. E.; Hannan, M. J.; Boxall, L. G. PCT/U.S. WO/1994/016356, 1994.
(389) Chandrasekhar, P. PCT/U.S. WO/1999/044093, 1999.
(390) Zhang, J. D.; Yu, H. A.; Wu, X. G.; Wang, Z. Y. *Opt. Mater.* **2004**, *27*, 265.
(391) Dyer, A. L.; Grenier, C. R. G.; Reynolds, J. R. *Adv. Funct. Mater.* **2007**, *17*, 1480.
(392) Lacroix, J. C.; Fraoua, K.; Lacaze, P. C. *J. Electroanal. Chem.* **1998**, *444*, 83.
(393) Tezuka, Y.; Aoki, K.; Yajima, H.; Ishii, T. *J. Electroanal. Chem.* **1997**, *425*, 167.
(394) Pagès, H.; Topart, P.; Lemordant, D. *Electrochim. Acta* **2001**, *46*, 2137.
(395) Argun, A. A.; Berard, M.; Aubert, P. H.; Reynolds, J. R. *Adv. Mater.* **2005**, *17*, 422.
(396) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
(397) Coleman, J. P.; Lynch, A. T.; Madhukar, P.; Wagenknecht, J. H. *Sol. Energy Mater. Sol. Cells* **1999**, *56*, 395.
(398) Brotherston, I. D.; Mudigonda, D. S. K.; Osborn, J. M.; Belk, J.; Chen, J.; Loveday, D. C.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993.
(399) Andersson, P.; Nilsson, D.; Svensson, P. O.; Chen, M.; Malmström, A.; Remonen, T.; Kugler, T.; Berggren, M. *Adv. Mater.* **2002**, *14*, 1460.
(400) Takamatsu, S.; Nikolou, M.; Bernards, D. A.; DeFranco, J.; Malliaras, G. G.; Matsumoto, K.; Shimoyama, I. *Sens. Actuators, B* **2008**, *135*, 122.
(401) Hohnholz, D.; MacDiarmid, A. G. *Synth. Met.* **2001**, *121*, 1327.
(402) Argun, A. A.; Reynolds, J. R. *J. Mater. Chem.* **2005**, *15*, 1793.
(403) Hohnholz, D.; Okuzaki, H.; MacDiarmid, A. G. *Adv. Funct. Mater.* **2005**, *15*, 51.
(404) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.
(405) Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace, G. G.; MacFarlane, D. R.; Forsyth, S. A.; Forsyth, M. *Science* **2002**, *297*, 983.
(406) Ma, L.; Li, Y.; Yu, X.; Yang, Q.; Noh, C.-H. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1253.
(407) Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Prog. Polym. Sci.* **1998**, *23*, 993.
(408) Gomez-Romero, P. *Adv. Mater.* **2001**, *13*, 163.
(409) Gangopadhyay, R.; De, A. *Chem. Mater.* **2000**, *12*, 608.
(410) Cho, S. I.; Kwon, W. J.; Choi, S. J.; Kim, P.; Park, S. A.; Kim, J.; Son, S. J.; Xiao, R.; Kim, S. H.; Lee, S. B. *Adv. Mater.* **2005**, *17*, 171.
(411) Jang, S.-Y.; Seshadri, V.; Khil, M. S.; Kumar, A.; Marquez, M.; Mather, P. T.; Sotzing, G. A. *Adv. Mater.* **2005**, *17*, 2177.
(412) Li, D.; Babel, A.; Jenekhe, S. A.; Xia, Y. *Adv. Mater.* **2004**, *16*, 2062.
(413) Norris, I. D.; Shaker, M. M.; Ko, F. K.; MacDiarmid, A. G. *Synth. Met.* **2000**, *114*, 109.
(414) Pinto, N. J.; Johnson, J. A. T.; MacDiarmid, A. G.; Mueller, C. H.; Theofylaktos, N.; Robinson, D. C.; Miranda, F. A. *Appl. Phys. Lett.* **2003**, *83*, 4244.
(415) Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338.
(416) Fungo, F.; Jenekhe, S. A.; Bard, A. J. *Chem. Mater.* **2003**, *15*, 1264.
(417) Panero, S.; Scrosati, B.; Baret, M.; Cecchini, B.; Masetti, E. *Sol. Energy Mater. Sol. Cells* **1995**, *39*, 239.
(418) Antinucci, M.; Chevalier, B.; Ferriolo, A. *Sol. Energy Mater. Sol. Cells* **1995**, *39*, 271.
(419) Hayes, R. A.; Feenstra, B. J. *Nature* **2003**, *425*, 383.
(420) Huitema, H. E. A.; Gelinck, G. H.; Van der Putten, J. B. P. H.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; De Leeuw, D. M. *Adv. Mater.* **2002**, *14*, 1201.
(421) Huitema, H. E. A.; Gelinck, G. H.; Van der Putten, J. B. P. H.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; Herwig, P. T.; Van Breemen, A. J. J. M.; De Leeuw, D. M. *Nature* **2001**, *414*, 599.
(422) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. *Nature* **1998**, *394*, 253.
(423) Nilsson, D.; Robinson, N.; Berggren, M.; Forchheimer, R. *Adv. Mater.* **2005**, *17*, 353.
(424) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.
(425) Berggren, M.; Nilsson, D.; Robinson, N. D. *Nat. Mater.* **2007**, *6*, 3.
(426) McCoy, C. H.; Wrighton, M. S. *Chem. Mater.* **1993**, *5*, 914.
(427) White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.
(428) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.
(429) Ofer, D.; Park, L. Y.; Schrock, R. R.; Wrighton, M. S. *Chem. Mater.* **1991**, *3*, 573.
(430) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.
(431) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133.
(432) Tehrani, P.; Hennerdal, L.-O.; Dyer, A. L.; Reynolds, J. R.; Berggren, M. *J. Mater. Chem.* **2009**, *19*, 1799.
(433) Kobayashi, N.; Miura, S.; Nishimura, M.; Urano, H. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 136.
(434) Corr, D.; Stobie, N.; Bach, U.; Fay, D.; Kinsella, M.; McAtamney, C.; O'Reilly, F.; Rao, S. N. *Solid State Ionics* **2003**, *165*, 315.
(435) Monk, P. M. S.; Delage, F.; Costa Vieira, S. M. *Electrochim. Acta* **2001**, *46*, 2195.
(436) De Gans, B.-J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203.
(437) Calvert, P. *Chem. Mater.* **2001**, *13*, 3299.
(438) Shim, G. H.; Han, M. G.; Sharp-Norton, J. C.; Creager, S. E.; Foulger, S. H. *J. Mater. Chem.* **2008**, *18*, 594.

(439) Ferraris, J. P.; Dam, T. H.; Meeker, D. U.S. Patent 6 598 966, 2002.
(440) Nishizawa, M.; Kuwabata, S.; Yoneyama, H. *J. Electrochem. Soc.* **1996**, *143*, 3462.
(441) Kuwabata, S.; Takahashi, N.; Hirao, S.; Yoneyama, H. *Chem. Mater.* **1993**, *5*, 437.
(442) Yoneyama, H.; Takahashi, N.; Kuwabata, S. *J. Chem. Soc., Chem. Commun.* **1992**, *9*, 716.
(443) DeBerry, D. W.; Viehbeck, A. *J. Electrochem. Soc.* **1983**, *130*, 249.
(444) Bechinger, C.; Ferrere, S.; Zaban, A.; Sprague, J.; Gregg, B. A. *Nature* **1996**, *383*, 608.
(445) Gregg, B. A. *Endeavour* **1997**, *21*, 52.
(446) Hauch, A.; Georg, A.; Baumgärtner, S.; Opara Krasovec, U.; Orel, B. *Electrochim. Acta* **2001**, *46*, 2131.
(447) Hauch, A.; Georg, A.; Krasovec, U. O.; Orel, B. *J. Electrochem. Soc.* **2002**, *149*, H159.
(448) Li, Y.; Hagen, J.; Haarer, D. *Synth. Met.* **1998**, *94*, 273.
(449) Santa-Nokki, H.; Kallioinen, J.; Korppi-Tommola, J. *Photochem. Photobiol. Sci.* **2007**, *6*, 63.
(450) Ahn, K.-S.; Yoo, S. J.; Kang, M.-S.; Lee, J.-W.; Sung, Y.-E. *J. Power Sources* **2007**, *168*, 533.
(451) Liao, J.-Y.; Ho, K.-C. *J. New Mater. Electrochem. Syst.* **2005**, *8*, 37.
(452) Hsu, C.-Y.; Lee, K.-M.; Huang, J.-H.; Justin Thomas, K. R.; Lin, J. T.; Ho, K.-C. *J. Power Sources* **2008**, *185*, 1505.

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