

Matched-Dual-Polymer Electrochromic Lenses, Using New Cathodically Coloring Conducting Polymers, with Exceptional Performance and Incorporated Into Automated Sunglasses

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ABSTRACT: Reported are syntheses of several new monomer precursors of cathodically coloring conducting polymers (CPs), based on a propylene dioxythiophene skeleton. These are shown to yield CPs—both as homopolymers and as copolymers—that are nearly “perfectly” matched electrochemically and electrochromically with a set of anodically coloring poly(aromatic amines), for use in dual-polymer electrochromic lenses. Resulting dual-polymer electrochromic lenses display very high light/dark contrast (typically up to 70/7% or 50/0.5% Transmission (integrated over visible spectrum, vs. *air* reference), Haze < 2%, very high cyclability (> 10 K cycles), multiyear shelf life, appealing transparent to dark-blue-black transition, and excellent optical memory. Dramatic lowering of switching time, from 8 to < 1 s, is demonstrated using unique applied-potential algorithm resident on inexpensive Microcontroller chip. Working, practical dual-polymer electrochromic spectacles are demonstrated with electrochromic lenses retrofitted to spectacles meeting ANSI Z87.1, GL-PD 10–12 (U.S. military) specifications. These incorporate photosensor, rechargeable Li battery, Microcontroller, allow for automated operation. *Ab-initio*-design spectacles, also conforming to above specifications, are also demonstrated, with components seamlessly hidden within frame. To the best of our knowledge, the electrochromic lenses and sunglasses reported herein represent the best visible-region electrochromic performance for dual-polymer CP electrochromic systems to date and the first practical implementation in working sunglasses. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41043.

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INTRODUCTION

Transmission-mode (i.e., window-like), visible-spectral-region electrochromic systems based on Conducting polymers (CPs) have seen several decades of development.^{1–30} In spite of this, however, and in spite of attempts to adapt new or esoteric technologies such as ionic liquid electrolytes, carbon nanotubes and nonlinear optical properties of the polymers,^{31–36} successful, practical commercial implementation has thus far eluded these materials. This is in marked contrast to inorganic metal-oxide-based electrochromics,^{37–40} which have seen some application, for example, in building windows.³⁹ (Reflectance-mode, i.e., mirror-like, visible-region electrochromics based on CPs have been in commercial use for some time now, for example, as implemented in automobile rearview mirrors by Gentex, among other very limited uses.^{41–43} In further contrast, reflectance-mode, IR-region electrochromics based on CPs, for military camouflage,

spacecraft thermal control, and related applications, have been marketed for some years now.^{44–52})

A subset of CP electrochromic systems, those based on “complimentarily coloring” or “dual-polymer” CPs, have seen more recent development and have been extensively described.^{53–71} In these systems, a “cathodically coloring” CP on one electrode is paired with an “anodically coloring” CP on the other, so that they reinforce each other in lightening and darkening. Some improvements in cyclability [i.e., number of light/dark (L/D) cycles before degradation] and switching time is also observed in these systems. In this respect however, nearly all complimentarily coloring CP electrochromics reported thus far^{53–71} have used CPs that are relatively poorly matched electrochemically and electrochromically. An exemplary manifestation of poor matching is that when a potential is applied, in a 2-electrode device, at which one CP is in its fully oxidized form, its complimentary CP is not in its fully reduced form.

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This yields less than optimal L/D contrast as well as poorer cyclability.

In this communication, we report:

1. Syntheses of new monomer precursors of cathodically coloring CPs, designed to be nearly “perfectly” matched electrochemically and electrochromically with a set of anodically coloring poly(aromatic amines), for use in dual-polymer devices. These new monomers are based on a propylene dioxythiophene (ProDOT) skeleton. They include, specifically: (i) 2,2-(bis-4-chlorobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-chlorobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; Cl-Bz-ProDOT). (ii) 2,2-(bis-4-bromobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-bromobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; Br-Bz-ProDOT). (iii) 2,2-(bis-4-nitrobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-nitrobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; Nitro-Bz-ProDOT). (iv) 2,2-(bis-4-aminobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-aminobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; Amino-Bz-ProDOT).
2. Complimentarily coloring, dual-polymer electrochromic devices (“lenses”) made with these new monomers constituting the cathodically coloring polymer (used singly as well as in the form of copolymers), paired with several anodically coloring poly(aromatic amines), which we had reported on earlier,^{23,44,45,48} again used singly as well as in the form of copolymers. The cathodically and anodically coloring polymer pairs in these devices are shown to be nearly “perfectly” matched electrochemically and electrochromically, in contrast to nearly all prior art^{53–71} where the cathodically and anodically coloring polymers are poorly matched. The resulting electrochromic lenses display very high L/D contrast (typically up to 70/7% or 50/0.5% Transmission, integrated over the visible spectrum (“real-life,” against *air* reference, not substrate reference, see below), very high cyclability (>10 K cycles) and very long (multiple-years) shelf life. Furthermore, the color transition in nearly all our devices is an appealing transparent to dark-blue-black. They also have an excellent optical memory (i.e., they retain the color state they are in when disconnected). Haze is shown to be <2% in D and L states, important for sunglasses use.
3. Dramatic lowering of the switching time, from about 8 to < 1 s, using a unique applied-potential algorithm resident on an inexpensive Microcontroller chip, which employs unique, timed overvoltages.
4. Working⁷² electrochromic safety spectacles (“sunglasses”), conforming to ANSI Z87.1-2010 and U.S. military specifications such as GL-PD 10–12.^{73,74} The spectacles are retrofitted with our electrochromic lenses. They incorporate a photosensor, rechargeable Li battery and a Microcontroller chip, and allow for automated sunglasses operation based on a user-selected light level.
5. Nonretrofitted, wearable, extremely inexpensive, electrochromic spectacles. These employ a frame designed *ab initio*, in which the Li battery, Microcontroller, photosensor, recharge port, and wiring are all seamlessly hidden within the frame. They also conform to ANSI Z87.1–2010/GL-PD 10–12, and have a prescription-insert for users with prescriptions.

To the best of our knowledge and based on an extensive search of the literature,^{1–71,75–99} the electrochromic lenses and sunglasses we report herein represent the best visible-region electrochromic performance for dual-polymer CP electrochromic systems to date. They also are, to our knowledge, the first practical implementation in working sunglasses, that is, they represent practical, functional, and applied polymers.

EXPERIMENTAL

Materials and Methods

All chemicals, solvents, and materials were procured from Sigma-Aldrich, Alfa-Aesar, or Thermo Fisher (Fisher Scientific) and were ACS Reagent Grade or better. NMR analyses were carried out using a Varian (now Agilent) Unity INOVA 400 MHz NMR with 5 mm broadband solution probe and Oxford magnet; and a Bruker DRX-500 (both 500 MHz) instruments, with appropriate external standards. UV–vis–NIR spectra, which included electrochromic characterization, were carried out on a Perkin-Elmer (P-E) Model Lambda 12. Haze measurements were performed on a BYK-Gardner Haze-Gard Plus instrument. FTIR spectra, again where relevant, were carried out using a P-E Spectrum One, and, later, a Spectrum Two instrument. GC analyses were carried out using a Shimadzu Model GC-2014-CAP FID NO D/S (split/splitless injection port, auto-ranging FID, all-digital Advanced Flow Control, temperature programmable). The different instrument parameters and columns used are available on request. All instruments were interfaced to PCs, controlled by vendor-supplied software. Elemental analyses, again where appropriate, were done at Galbraith Labs (Knoxville, TN).

Syntheses of New Monomer Precursors of Cathodically Coloring CPs

Our syntheses, as described below, can be taken in the context of and compared with the extensive prior work in the syntheses of monomer precursors and, eventually, CPs, having ethylene dioxythiophene (EDOT) and ProDOT skeletons,^{75–91} especially the recent work of Krishnamoorthy et al.⁷⁵ Since the resulting electrochromic CPs are mostly cathodically coloring, our work may also be taken in the context of early work with cathodically coloring CPs such as poly(isothianaphthene) (PITN).^{92–94}

Typical syntheses are depicted in the schemes in Figures 1–4 below and briefly described stepwise here for each monomer in turn. More detailed descriptions are available in the patent publication.⁴⁶ (Detailed yield and other data are available on request from the authors.)

Synthesis of the Monomer 2,2-(bis-4-chlorobenzyl)-3,4-propylenedioxythiophene (3,3-bis(4-chlorobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Cl-Bz-ProDOT”). *Synthesis of initial intermediate, diethyl bis(4-chloro-benzyl) malonate (cf. Figure 1).* The synthesis was carried out under inert atmosphere with dry Ar gas using a balloon apparatus. To a 250 mL round bottom flask added 11.2 g (0.0545 mol) of 4-chlorobenzyl bromide, 17.0 g (0.123 mol) of potassium carbonate, and 100 mL of anhydrous DMF. The neck of the flask was closed with a rubber septum and the flask was purged with Ar. A rubber balloon/needle apparatus was filled with Ar and inserted into the

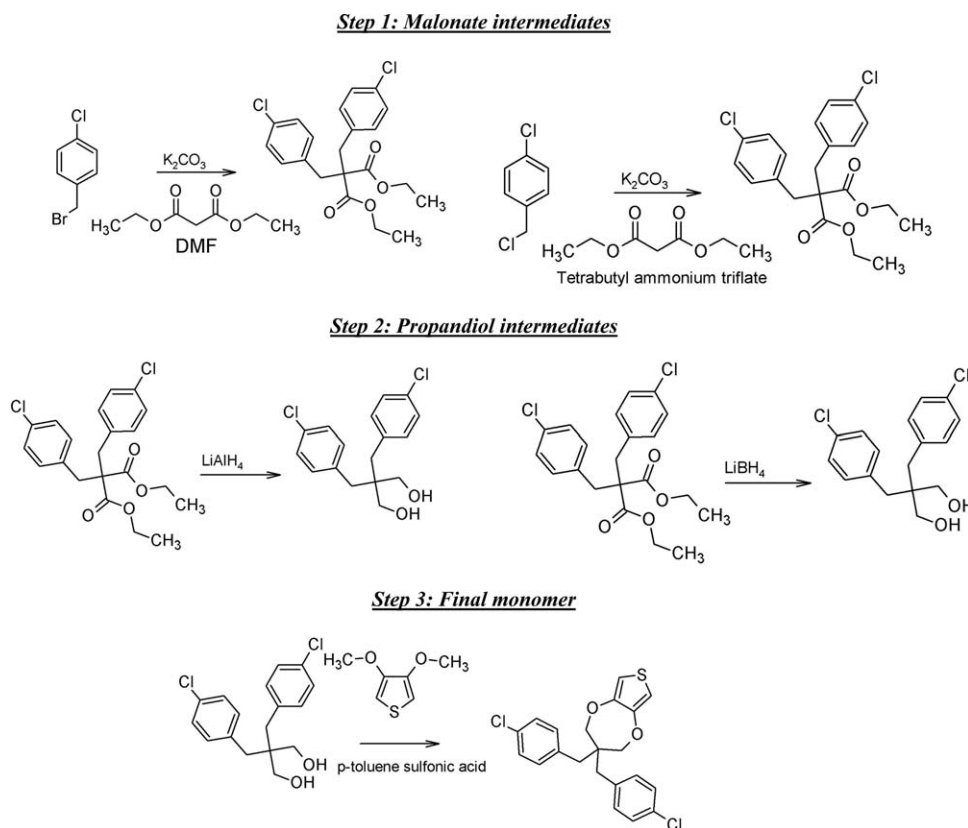


Figure 1. Scheme summarizing typical synthesis of the monomer 2,2-(bis-4-chlorobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-chlorobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Cl-Bz-ProDOT”).

septum. After the balloon was attached, 3.3 mL (0.022 mol) of diethyl malonate was inserted via a syringe and the flask was heated to 100°C for 16 h. The flask was cooled to room temperature and the reaction mixture was poured into 200 mL of water. The product was extracted with diethyl ether. The ether layer was washed three times with 100 mL of water and once with 100 mL of brine. The ether layer was dried with MgSO_4 and filtered. Solvent was removed *in vacuo*. The residue was recrystallized from hexanes to give 2.87 g (32%). Identity of intermediates and products were confirmed via TLC and NMR (^1H). An alternate synthesis of this intermediate, again with dry Argon gas using a balloon apparatus, was carried out as follows (cf. Figure 1): To a 250 mL round bottom flask was added 8.8 mL (0.0746 mol) of 4-chlorobenzyl chloride, 17.0 g (0.123 mol) of potassium carbonate, 0.59 g tetrabutylammonium triflate (0.00150 mol), and 80 mL of anhydrous toluene. The mixture was heated to reflux for 16 h. The solution was cooled to room temperature. The insoluble salts were filtered and washed thoroughly with dichloromethane. The solvents were removed *in vacuo*. Column chromatography was performed on the residue with a silica gel column (25 × 2.5 cm²) using a gradient of pure hexanes to 20% (v/v) dichloromethane in hexanes as the eluent. 3.3 g (11%) of the desired material was obtained. Again, identity of intermediates and products were confirmed via TLC and NMR (^1H). It is to be noted that when the proportionate molarities of triethyl amine, or di-isopropyl ethyl amine, or 0.9M solution of Na ethoxide in ethanol, were substi-

tuted for the K_2CO_3 in the procedure above, the reaction was observed to be extremely slow and no product was obtained over a period of 72 h.

Reduction of diethyl bis-(4-chlorobenzyl) malonate to 2,2-bis(4-chloro-benzyl)-1,3-propandiol (cf. Figure 1). To a 250 mL three neck round bottom flask added 1.92 g (50.5 mmol) of lithium aluminum hydride. The flask was purged with Ar and cooled to 0°C; 20 mL of anhydrous THF was added to the flask. To this flask was added 3.3 g (8.06 mmol) of diethyl bis(4-chlorobenzyl) malonate dissolved in 15 mL THF. The addition was done slowly via a syringe at approximately a dropwise addition pace. The mixture was stirred overnight. After stirring, the mixture was cooled to 0°C and 1.92 mL of deionized water was added very slowly. After this addition, 1.92 mL of 15% sodium hydroxide was added then 5.76 mL of de-ionized water. The mixture was stirred for 1 h. The solid was filtered off and thoroughly washed with diethyl ether. The solvent was removed *in vacuo*. Column chromatography was performed on the residue with a silica gel column (25 × 2.5 cm²) using a gradient of pure hexanes to 60% (v/v) ethyl acetate in hexanes as the eluent; 2.58 g (98%) of the desired material was obtained. IR, and ^1H NMR, in addition to TLC were used to confirm identity of the product. An alternate procedure for this reduction was as follows: To a 50 mL round bottom flask added 2.87 g (7.01 mmol) of diethyl bis(4-chlorobenzyl) malonate. The neck of the flask was closed with a rubber septum and the flask was purged with Ar. A rubber balloon/needle apparatus was filled with Ar

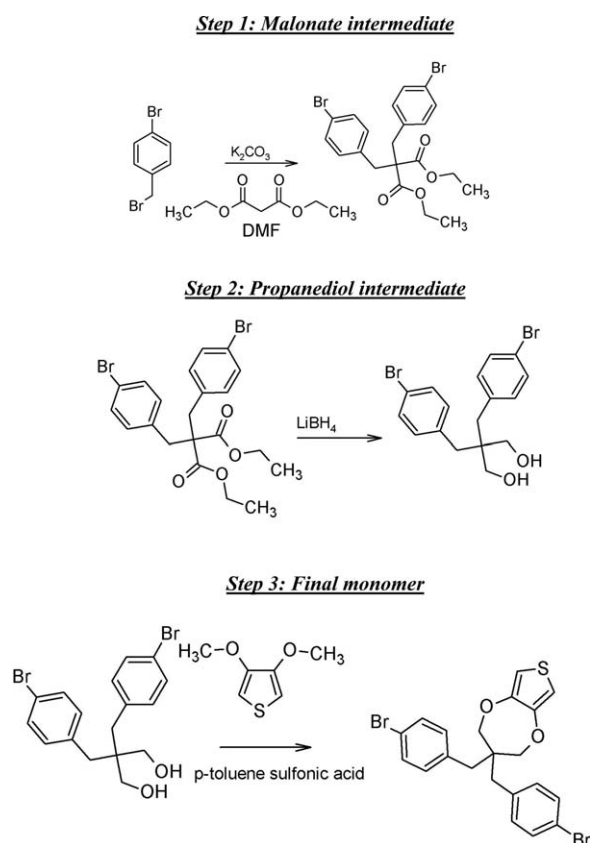


Figure 2. Scheme summarizing typical synthesis of the monomer 2,2-(bis-4-bromobenzyl)-3,4-propylenedioxythiophene ((3,3-Bis(4-bromobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Br-Bz-ProDOT”).

and inserted into the septum. To the flask was added 15 mL (30 mmol) of 2.0M LiBH₄. The flask was heated to 50°C overnight. It was then cooled to 0°C and 12 mL of a saturated solution of (NH₄)₂SO₄ was slowly added to the flask. The solution was then poured into a 250 mL separatory funnel and the product was extracted with ethyl acetate. The organic layer was washed twice with 100 mL of water and once with brine. The solution was dried with MgSO₄. Solvent was removed *in vacuo* to give 1.65 g (72%) of the alcohol. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product. This material was used without purification in next step.

Reaction of 2,2-bis(4-chloro-benzyl)-1,3-propanediol with 3,4-dimethoxythiophene, to produce the final monomer, 2,2-(bis-4-chlorobenzyl)-3,4-propylenedioxythiophene ((3,3-bis(4-chlorobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Cl-Bz-ProDOT”; **Figure 1).** To a 500 mL round bottom flask was added 1.65 g (5.07 mmol) 2,2 bis(4-chlorobenzyl)-1,3 propanediol, 0.200 g (1.05 mmol) *p*-toluenesulfonic acid monohydrate and 100 mL of toluene. The neck of the flask was closed with a rubber septum and the flask was purged with N₂. A rubber balloon/needle apparatus was filled with N₂ and inserted into the septum. To the mixture was added 0.49 mL (4.11 mmol) of 3,4 dimethoxythiophene and the flask was heated to 80°C for 1 d (~17 h). The flask was cooled to room temperature and the solvent was removed *in vacuo*. Column chromatography was performed on the residue with a silica gel column (25 × 2.5 cm²)

using a gradient of pure hexanes to 30% (v/v) dichloromethane in hexanes as the eluent; 1.03 g (50%) of the desired material was obtained. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product. NMR data [cited in ACS (American Chemical Society) format]: ¹H NMR (400 MHz, CDCl₃) δ 2.79 (4H, s), 3.80 (4H, s), 6.50 (2H, s), 7.10 (4H, d, *J* = 8.3 Hz), and 7.26 (4H, d, *J* = 8.3 Hz).

Synthesis of the Monomer 2,2-(bis-4-bromobenzyl)-3,4-propylenedioxythiophene ((3,3-bis(4-bromobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Br-Bz-ProDOT”). **Synthesis of initial intermediate, diethyl bis(4-bromo-benzyl) malonate** (cf. **Figure 2**). To a 250 mL round bottom flask was added 8.63 g (0.0345 mol) of 4-bromobenzyl bromide, 17.0 g (0.123 mol) of potassium carbonate and 100 mL of anhydrous DMF. The neck of the flask was closed with a rubber septum and the flask was purged with Ar. A rubber balloon/needle apparatus was filled with Ar and inserted into the septum. After the balloon was attached, 2.2 mL (0.014 mol) of diethyl malonate was inserted via a syringe and the flask was heated to 100°C for 16 h. The flask was cooled to room temperature and the reaction mixture was poured into 200 mL of water. The product was extracted with diethyl ether. The ether layer was washed three times with 100 mL of half brine and once with 100 mL of brine. The ether layer was dried with MgSO₄ and filtered. Solvent was removed *in vacuo*. The residue was recrystallized from hexanes to give 1.42 g (20%). IR and ¹H NMR, in addition to TLC were used to confirm identity of the product

Synthesis of intermediate, 2,2 bis(4-bromobenzyl)-1,3 propanediol (cf. **Figure 2**). To a 50 mL round bottom flask was added 1.42 g (2.85 mmol) of diethyl bis(4-bromobenzyl) malonate. The neck of the flask was closed with a rubber septum and the flask was purged with Ar. A rubber balloon/needle apparatus was filled with Ar and inserted into the septum. To the flask was added 15 mL (30 mmol) of 2.0M LiBH₄. The flask was heated to 50°C overnight. It was then cooled to 0°C and 12 mL of a saturated solution of (NH₄)₂SO₄ was slowly added to the flask. An additional 50 mL of water was added to the mixture and the solution was then poured into a 250 mL separatory funnel. The product was extracted with ethyl acetate and the organic layer was washed twice with 100 mL of water and once with brine. The solution was dried with MgSO₄. Solvent was removed *in vacuo* to give 1.00 g (85%) of the alcohol. This material was used without purification in next step. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product.

Reaction of 2,2-bis(4-bromo-benzyl)-1,3-propanediol with 3,4-dimethoxythiophene to produce the final monomer, 2,2-(bis-4-bromobenzyl)-3,4-propylenedioxythiophene ((3,3-bis(4-bromobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; Br-Bz-ProDOT; cf. **Figure 2**). To a 200 mL round bottom flask was added 1.00 g (2.41 mmol) 2,2 bis(4-bromobenzyl)-1,3 propanediol, 0.1 g (0.5 mmol) *p*-toluenesulfonic acid monohydrate and 30 mL of toluene. The neck of the flask was closed with a rubber septum and the flask was purged with N₂. A rubber balloon/needle apparatus was filled with N₂ and inserted into the septum. To the mixture was added 0.34 mL (2.85 mmol) of 3,4

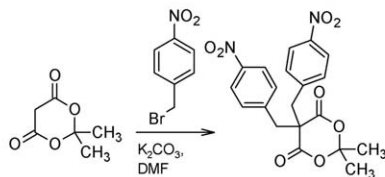
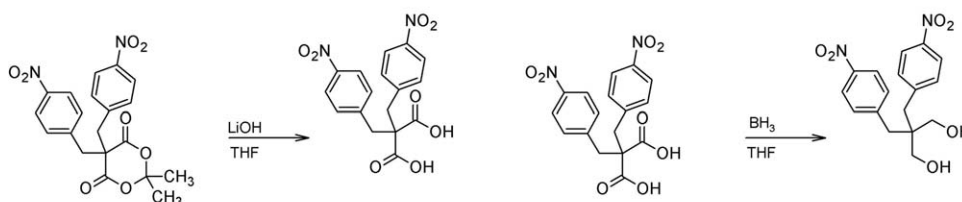
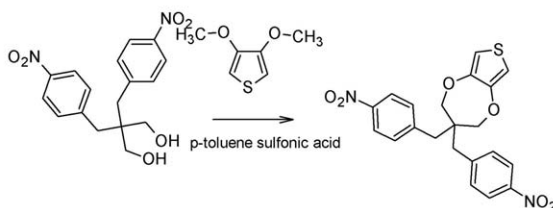
Step 1: Malonate intermediates**Step 2: Propandiol intermediate****Step 3: Final monomer**

Figure 3. Scheme summarizing typical synthesis of the monomer 2,2-(bis-4-nitrobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-nitrobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Nitro-Bz-ProDOT”).

dimethoxythiophene and the flask was heated to 80°C for 1 d (17 h). The flask was cooled to room temperature and the solvent was removed *in vacuo*. Column chromatography was performed on the residue with a silica gel column (25 × 2.5 cm²) using a gradient of pure hexanes to 30% (v/v) dichloromethane in hexanes as the eluent. 0.153 g (13%) of the desired material was obtained. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product. NMR data (cited in ACS format): ¹H NMR (400 MHz, CDCl₃) δ 2.78 (4H, s), 3.79 (4H, s), 6.51 (2H, s), 7.04 (4H, dd, *J* = 8.5, 2.0 Hz), and 7.42 (4H, dd, *J* = 8.3, 1.9 Hz).

Synthesis of the Monomer 2,2-(bis-4-nitrobenzyl)-3,4-propylenedioxythiophene (3,3-bis(4-nitrobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Nitro-Bz-ProDOT”). *Synthesis of the intermediate 2,2-dimethyl-5,5-di(4-nitrobenzyl)-1,3-dioxane-4,6-dione* (cf. Figure 3). An adaptation of the procedure of Fillion et al.⁹⁵ was followed. To a 1 L round bottom flask was added 11.23 g (0.0520 mol) of 4-nitrobenzyl bromide, 3.0 g (0.0208 mol) of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid), 9.5 g (0.0687 mol) of potassium carbonate, and 150 mL of DMF. This mixture was stirred for 12 h then 700 mL of water was added to the round bottom flask. The resulting precipitate was collected and washed with water. This precipitate give was recrystallized from a methanol/ dichloromethane mixture to give 7.39 g (86%). IR and ¹H NMR, in addition to TLC were used to confirm identity of the product.

Synthesis of the intermediate 2,2-bis(4-nitrobenzyl)malonic acid (cf. Figure 3). An adaptation of the procedure described by Tiefenbacher and Rebek⁹⁵ was followed. To a suspension of 5.33 g (12.9 mmol) of 2,2-dimethyl-5,5-di(4-nitrobenzyl)-1,3-dioxane-4,6-dione in 60 mL of a 9 : 1 mixture of THF to water was added 1.11 g (46.3 mmol) LiOH. This suspension was stirred for ~17 h. After stirring, 100 mL of water was added to the suspension. The aqueous solution was washed twice with 50 mL of diethyl ether. The aqueous solution was then acidified to pH = 1. The product was extracted with ethyl acetate. The ethyl acetate solution was washed once with 100 mL of water and once with 100 mL of brine. The ethyl acetate solution was dried with MgSO₄ and the solvent was removed *in vacuo* to yield 4.21 g (87%) of the desired material. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product.

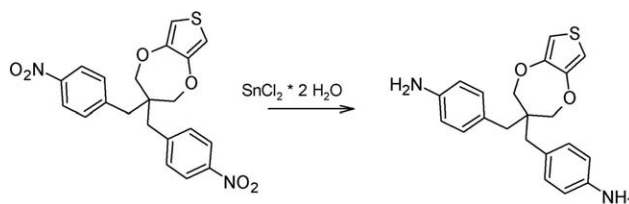


Figure 4. Scheme summarizing typical synthesis of the monomer 2,2-(bis-4-aminobenzyl)-3,4-propylenedioxythiophene (3,3-Bis(4-aminobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; “Amino-Bz-ProDOT”), from the corresponding nitro monomer.

Synthesis of the intermediate 2-bis(4-nitrobenzyl)propane-1,3-diol (cf. Figure 3). An adaptation of the procedure described by Tiefenbacher and Rebek⁹⁶ was followed. A 500 mL round bottom flask was purged with Ar and the neck of the flask was closed with a rubber septum. A rubber balloon/needle apparatus was filled with Ar and inserted into the septum. To the 500 mL round bottom flask was added 67 mL (67 mmol) of a 1.0M solution of BH₃ in THF. The septum on the round bottom flask was replaced with a 125 mL addition funnel and a septum was inserted into the top of addition funnel. The whole setup was purged again with Ar and a rubber balloon/needle apparatus was filled with Ar and inserted into the septum. To the addition funnel was added 4.21 g (11.2 mmol) of 2,2-bis(4-nitrobenzyl)malonic acid in 60 mL of THF. The malonic acid solution was added to BH₃ solution dropwise over a period of 2 h. After the addition, the entire solution was stirred for 17 h. After the stirring, 20 mL of water was added dropwise to the solution. 20 mL of a 1M HCl was added to the solution and this mixture was stirred for 1.5 h. The product was then extracted with ethyl acetate (three times, 50 mL) and dried with MgSO₄. The solvent was removed *in vacuo*. To the resulting residue was added 50 mL of THF and 20 mL of a 1M HCl solution. This mixture was stirred for 1.5 h. The THF was removed *in vacuo* and 100 mL of water was added to the residue. The product was extracted with ethyl acetate (three times, 50 mL) and dried with MgSO₄. Solvent was removed *in vacuo* to give 2.73 g (70%) of material. IR, and ¹H NMR, in addition to TLC were used to confirm identity of the product.

Synthesis of the final monomer, 2,2-(bis-4-nitrobenzyl)-3,4-propylenedioxythiophene (3,3-bis(4-nitrobenzyl)-3,4-dihydro-2H-thieno [3,4-b][1,4]-dioxepine; "Nitro-Bz-ProDOT"; cf. Figure 3). To a 200 mL round bottom flask was added 2.15 g (6.21 mmol) 2,2 bis(4-nitrobenzyl)-1,3 propanediol, 0.2 g (1 mmol) *p*-toluenesulfonic acid monohydrate, and 150 mL of toluene. The neck of the flask was closed with a rubber septum and the flask was purged with N₂. A rubber balloon/needle apparatus was filled with N₂ and inserted into the septum. To the mixture was added 0.90 mL (7.55 mmol) of 3,4 dimethoxythiophene and the flask was heated to 80°C for 1 d (17 h). The flask was cooled to room temperature and the solvent was removed *in vacuo*. Column chromatography was performed on the residue with a silica gel column (15 × 2.5 cm²) using a gradient of pure hexanes to 60% (v/v) dichloromethane in hexanes as the eluent. A second column (25 × 2.5 cm²) was carried out using a gradient of pure hexanes to 35% (v/v) ethyl acetate in hexanes as the eluent. 0.388 g (15%) of the desired material was obtained. IR and ¹H NMR, in addition to TLC were used to confirm identity of the product. NMR data (cited in ACS format): ¹H NMR (400 MHz, CDCl₃) δ 2.77 (4H, s), 3.79 (4H, s), 6.51 (2H, s), 7.04 (4H, dd, *J* = 8.4 Hz, 2.0 Hz), and 7.42 (4H, dd, *J* = 8.0 Hz, 2.0 Hz).

Synthesis of the Monomer 2,2-(bis-4-aminobenzyl)-3,4-propylenedioxythiophene (3,3-bis(4-aminobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine; "Amino-Bz-ProDOT"), from the Corresponding Nitromonomer. Synthesis of the final monomer (cf. Figure 4). To a 200 mL round bottom flask was added 0.307 g (0.722 mmol) of 3,3-Bis(4-nitrobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine, 2.1 g (9.3 mmol) of tin(II) chlo-

ride dihydrate and 50 mL of ethyl acetate. The solution was heated to reflux for overnight. After heating, the mixture was allowed to cool to room temperature. After cooling, 20 mL of a 0.25M solution of sodium carbonate and 100 mL of dichloromethane were added. This mixture was vigorously stirred for 30 min. The mixture was then filtered through a celite pad and poured into a 500 mL separatory funnel. The organic layer was removed and washed twice with 50 mL of water and once with 50 mL of brine. The solution was dried with MgSO₄ and the solvent was removed *in vacuo* to give the product, 3,3-bis(4-aminobenzyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine, in quantitative yield. IR, and ¹H NMR, in addition to TLC were used to confirm identity of the product. NMR data (cited in ACS format): ¹H NMR (400 MHz, CDCl₃) 2.71 (4H, s), 3.81 (4H, s), 6.48 (2H, s), 6.61(4H, dd, *J* = 8.4, 2.1 Hz), and 6.96 (4H, dd, *J* = 7.6, 2.0 Hz).

Electrochemical Deposition of CP Films onto ITO/Mylar® Substrates

ITO/Mylar® [Mylar® = poly(ethylene terephthalate), PET] substrates, preferred surface resistivity < 60 Ohms/square, on 7 mil (ca. 175 μm) thick Mylar®, were procured COTS (commercial-off-the-shelf), from Solutia-CP Films (Canoga Park, CA); these were cleaned as described elsewhere^{23,46} before use. A custom-built potentiostat capable of handling high currents (up to 5 A) was used, although a research grade potentiostat (Princeton Applied Research Corp Model 363) was also occasionally used. Acetonitrile and Li triflate salt used in the depositions were dried, respectively, using activated molecular sieves and overnight at 50–55°C overnight before use.

Cathodically Coloring Polymers. Poly(2,2-(bis-4-chlorobenzyl)-3,4-propylenedioxythiophene; poly(Cl-Bz-ProDOT). A stock solution of 250 mL of 0.4M Li triflate in acetonitrile was prepared. A 4 mM solution of the Cl-BzProDOT monomer was prepared in 250 mL stock solution, yielding a yellow deposition solution. The polymer, poly(Cl-Bz-ProDOT) was deposited on ITO/Mylar using a 3 electrode configuration, with graphite counter electrode and Pt wire quasi-reference electrode. A multiple potential sweep method was used to deposit polymer as described in more detail elsewhere,⁴⁶ with the number of sweeps dependent on the thickness of polymer desired, which was monitored by measuring the total charge deposited using standard electrochemical methods. The optimal CP films had a typical %*T*, at 575 nm, of <50%. A potential sweep method was found to be superior to a potentiostatic method. After deposition, the polymer film was held at an applied potential of 0.0 V for 1 min, then emersed from the deposition solution while at this potential. Films were rinsed with acetonitrile, soaked in an electrolyte solution for 1 min, rinsed again with acetonitrile, and dried at 50–75°C. Highly uniform, homogeneous polymer films with a blue/violet coloration were obtained.

Poly(2,2-(bis-4-bromo-benzyl)-3,4-propylenedioxythiophene) poly(Br-Bz-ProDOT). The procedure used to deposit Poly(Br-Bz-ProDOT) was substantially the same as described in the previous paragraph, except for differences in the potential sweep parameters and total charge deposited, as described in detail

elsewhere.⁴⁶ Highly uniform, homogeneous polymer films with a greenish-blue coloration were obtained.

Copolymer of 2,2-(bis-4-chloro-benzyl)-3,4-propylenedioxythiophene, 2,2-(bis-4-bromo-benzyl)-3,4-propylenedioxythiophene, and 2,2-dibenzyl-3,4-propylenedioxythiophene (“Full Copolymer”). The monomers, 2,2-(bis-4-chloro-benzyl)-3,4-propylenedioxythiophene, 2,2-(bis-4-bromo-benzyl)-3,4-propylenedioxythiophene, and 2,2-dibenzyl-3,4-propylenedioxythiophene, were used to prepare a deposition solution and then to electrochemically deposit films of the corresponding copolymer on ITO/Mylar substrates, in a manner substantially identical to that described above for the single monomers, except with the following changes: (1) The individual monomer concentrations in the deposition solution were: 2,2-(bis-4-chloro-benzyl)-3,4-propylenedioxythiophene, 0.5 mM; 2,2-(bis-4-bromo-benzyl)-3,4-propylenedioxythiophene, 0.5 mM; 2,2-dibenzyl-3,4-propylenedioxythiophene, 5 mM. (2) The optimal total charge during deposition differed from that used for the monomers, with the %*T* of optimally performing films at 575 nm being 41–55%. (3) A potential sweep method was used, but with slightly different potential limits and scan rate highly uniform, homogeneous polymer films with a dark blue/violet coloration were obtained.

PITN (Used as a reference cathodically coloring polymer). A PITN film was electrochemically polymerized on ITO/Mylar as described by Chandrasekhar et al.⁹⁴

Anodically Coloring Polymers. Copolymer of *N,N'*-diphenyl benzidine, diphenyl amine, and 4-amino-biphenyl. A volume of 7.5 g of the monomer *N,N'*-diphenyl benzidine were added to 700 mL of dry acetonitrile. The mixture was refluxed over about 4 h in a N₂ atmosphere in an appropriately sized 3-neck round bottom flask (reflux temperature ~83°C). At the end of this period of reflux, 120 mL of dry *N,N'*-dimethyl formamide (DMF; i.e., 5.83:1 v/v% ratio, acetonitrile : DMF) were added slowly to this mixture. The temperature at first dropped slightly and then increased to about 87°C. Reflux was continued for about 2 h, the temperature remaining about 87°C. The entire solution was then sealed under N₂ and allowed to cool overnight. To this solution was added with stirring previously dried Li triflate salt in a proportion of about 6.24 g per 100 mL of solution. This solution could be used as is for electrochemical polymerization, if it was desired to produce the single polymer, poly(*N,N'*-diphenyl benzidine). If however, it was desired to produce copolymers then to this solution were added, with stirring, quantities of the monomers diphenyl amine and 4-amino-biphenyl so as to obtain final concentrations of each monomer in the ratios *N,N'*-diphenyl benzidine : diphenyl amine:4-amino-biphenyl of about 5 : 1 : 1. Previously dried Li triflate salt was added to the solution with stirring in a proportion of about 6.2 g per 100 mL of solution. The end result in either case was “stock solution,” which was then used for all depositions (electrochemical polymerizations), onto ITO/Mylar substrates, using a potentiostatic (i.e., constant potential) mode of deposition. A 3-electrode setup, with graphite counter and Pt wire quasi-reference electrodes was used, with potentiostatic deposition at +0.5 V (vs. Pt quasi-reference). Charge during deposition

was monitored coulometrically, and set to specific values (in mC/cm²) selected for very light or very dark films, with transmission at 575 nm of about 69% *T* yielding the best-performing electrochromic devices. Films were emersed at an applied voltage of 0.0 V, rinsed with acetonitrile, soaked in Li triflate/acetonitrile solution for 1 min, rerinsed, and dried at about 60°C for 1 h. Highly homogeneous, uniform, and green-blue films were obtained.

Thicknesses of CP Films. These were calculated using several measured parameters, including charge deposited during electropolymerization and measured density of the CP films; they correlated well with those reported in the literature for electrochromic CPs.^{60–90} In devices for which electrochromic data are reported in this article, the thicknesses were as follows: For the poly(aromatic amine), the anodically coloring CP, the thicknesses were 4.1 and 10.1 μm for typical light- and dark-lens films, respectively; for the poly(subst-Bz-ProDOTs), the cathodically coloring CP, the thicknesses were 1.7 and 2.5 μm for typical light- and dark-lens films, respectively.

Automation of Electrochemical Deposition. It is to be noted that the entire electrochemical deposition and assembly procedure described above is being fully automated in our laboratories in ongoing work as of this writing, complete with specially designed, custom-built “dep tanks” (for electrochemical deposition).

Synthesis of Gel Electrolyte

A 125 mL wide-mouth conical flask was used. Three gram of Li triflate, previously dried (overnight, 60°C, vacuum oven) were added to 70 g of dry acetonitrile (ACS reagent grade, dried over molecular sieves) therein with stirring until dissolved. Seven gram of poly(methyl methacrylate) were added very slowly (to prevent clumping) to the stirring mixture with mild heat, over 0.5 h. Now 20 g of dry propylene carbonate (ACS reagent grade, dried over molecular sieves) were added to the mixture, now a solution, which was then allowed to sit without stirring for 1 h. Next, a pipette for N₂ bubbling was introduced into the flask and slow bubbling with dry N₂ commenced. Slow stirring was then commenced and mild heat was applied to the flask to bring the temperature of the solution to 40°C, taking care to never exceed 50°C. This N₂ bubbling under stirring at about 40°C was continued over a period of several hours until the volume reduced to 25 mL, yielding the final gel electrolyte as to be used in the electrochromic devices. In addition to the above described electrolyte, a large number of nonaqueous-based, prior art electrolytes, for example, those described by Welsh et al. and coworkers,^{78–80} Sapp et al.,⁷¹ Gazotti et al.,⁷⁰ and Groenendaal et al. and coworkers,^{76,77} could be used, after suitable (and in some cases, significant) modification to accommodate the particular CP combinations used in this work.

Fabrication (Assembly) of Dual-Polymer Electrochromic Devices (“Lenses”)

Electrochromic devices (“lenses”) were assembled per the schematic of Figure 7, using the above components. The gasket used was typically of polyethylene, of thickness 0.5 to 2.0 mil (ca. 13–50 microns). Gel electrolyte was rewarmed to about 30°C

for the procedure. Gaskets were set into place using the gel electrolyte as a setting glue. Electrolyte was first applied individually to the bulk of both polymer/ITO/Mylar films using a doctor blade method. Devices were then fully assembled, according to the schematic of Figure 7. They were then clamped together using spring-loaded clamps. The clamped devices were allowed to sit overnight. Excess gel electrolyte from outer surfaces and edges was then cleaned with a Kimwipe wetted with acetonitrile. Optionally, the edges of the device could be sealed with inert, 2-component, polyurethane adhesives. For testing, electrical contact was simply made with alligator clips to the two electrodes of the devices. For a more permanent attaching of electrical lead wires, a special, commercial, space-qualified (low-outgassing) Ag epoxy was used.

Characterization of Electrochromic Devices (“Lenses”)

Electrochromic devices (“lenses”) as assembled above were characterized via cyclic voltammetry (in 2-electrode mode) and spectroscopically. The latter was carried out using a PC-controlled Perkin-Elmer Lambda 12 double-beam spectrometer, with nothing (i.e., air) in the reference compartment. We note, again, that this may be contrasted with most of the published academic and patent literature,^{1–71,75–96} which use a “blank” substrate or device, i.e. one of identical construction to the electrochromic device except that it does not have any active electrochromic material, as reference; this of course considerably enhances the *L/D* contrast observed, in many cases yielding light-state %*T* of >90%, whereas even the %*T* of clear glass is about 89%. UV–vis–NIR spectra were taken while the device was held potentiostatically at appropriate potentials corresponding to its extreme light and dark, or intermediate states, as desired. For monitoring the switching time, the spectrometer was brought to the wavelength of maximum absorption of the devices (575 nm for most) and the device then rapidly switched between its extreme light and dark state with appropriate applied voltage. This voltage was applied using a standard laboratory potentiostat as well as using the Microcontroller chip with the specially designed overvoltage algorithms, as described below, and powered by rechargeable Li batteries. In addition to the %*T* at a specific wavelength (usually 575 nm), we also used an industry-standard algorithm^{73,74,97} that weights wavelengths in the 380–780 nm region to conform to human vision and then integrates the result, providing a “broadband” %*T* across the visible-region spectrum. As an example, this algorithm gives the lowest weight (0.005) to 390 nm and the highest (9.79) to 550 nm. (This algorithm is available, as an Excel spreadsheet, from the authors, on request.) For long-term lifetime testing (up to 10,000 cycles), a special Microcontroller chip (see below) interfaced to a PC was programmed for continuous operation with a counter displaying the number of cycles effected.

Coloration efficiency (CE) and CIE ($L^*a^*b^*$, color profile) parameter measurements were carried out, the latter using digital versions of standard, published¹⁰⁰ experimental procedures. CE, in cm^2C^{-1} , is defined as the ratio of the change in Absorbance, at a specific wavelength, to the injected/ejected charge per unit electrode area. The ideal electrochromic material or device should exhibit a large absorbance change with a small amount of charge, giving rise to a high CE.¹⁰¹ In the 3-d CIE color profile, the L^* represents intensity/luminescence along the vertical

axis; a^* represents green and red on the (–) and (+) of one of the horizontal axes respectively; and b^* represents blue and yellow on the (–) and (+) of the other horizontal axis.

“Smart” Microchip Controller, Overvoltage Algorithms, and Photosensor Input and Calibration

To dramatically reduce the Light (L) \leftrightarrow Dark (D) switching time, a unique overvoltage algorithm was developed and used, as described at some length in the “Results and Discussion” section. This algorithm resided as an EPROM (erasable programmable memory or flash memory) on a specially designed Microcontroller, based on a PIC chip design, which used input from a photosensor. The photosensor was positioned inside the lens. Prior to use, the photosensor was calibrated to the light level desired by the user at the eye. Thereafter, the Microcontroller would adjust the %*T* of the electrochromic lens such that the light level at the user’s eye was constant, at the level set during the calibration. The Microcontroller power source was two rechargeable Li batteries, Tenenergy Model No. PL38203 (150 mAh). The circuit diagram for the Microcontroller is available elsewhere.⁴⁷ The Microcontroller was fabricated, based on our design, at one of several outside vendors, e.g. ExpressPCB (<http://www.expresspcb.com/>). As noted above, for long-term lifetime testing (up to 10,000 cycles), this Microcontroller chip was modified to program it for continuous operation with a counter displaying the number of cycles effected.

Assembly of Sunglasses as Retrofit of Safety Glasses

As a first step in the fabrication and testing of working, automated-operation (i.e., with photosensor control) sunglasses, Smith Optics Elite Model # AEGABK12-2R (Aegis arc eyeshield) safety spectacles, which conform to APEL (US military), ANSI Z87.1 and GL-PD 10–12 (US military) specifications, were retrofitted, as shown in Figure 20 (in “Results and Discussion” section). The retrofit involved inserting the electrochromic lenses on the inside (i.e., on the side closer to the user’s eyes) of the polycarbonate eyepieces, adding the Microcontroller, Li Battery, recharge-port, ON/OFF switch and wiring, somewhat crudely attaching all these with adhesive tape (cf. Figure 20).

Assembly of Sunglasses with Original (Nonretrofit) Frames Design

As a further step from the retrofit sunglasses as described above, an ANSI Z87.1-2000-compatible design was arrived at *ab initio* for a seamless frame directly incorporating all parts such as the Microcontroller, battery, recharge port and wiring (as a flex circuit) hidden directly into the frame, as depicted in Figure 21 (in “Results and Discussion” section), with the electrochromic lenses snapped-in. A prescription-insert was also provided (cf. Figure 21), for users with a prescription. The outer piece remained polycarbonate, with the snap-in electrochromic lens just beneath this. At this writing, the design (cf. Figure 21) is being used to fabricate proto-molds, from which production of the sunglasses may be started.

RESULTS AND DISCUSSION

Syntheses of New Monomers, Precursors to the Cathodically Coloring CPs

Among cathodically coloring CPs, it has been observed for some time that derivatives of poly(3,4-propylenedioxythiophene) (P(ProDOT)) show improved electrochromic

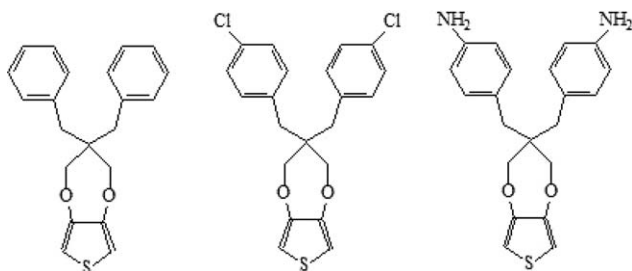


Figure 5. Illustrative structures of two of the four new monomers synthesized in this work and another base monomer, the monomer precursors of the cathodically coloring CPs. From left to right: 2,2-(dibenzyl)-3,4-propylenedioxythiophene (Bz-ProDOT); 2,2-(bis(4-chloro-benzyl))-3,4-propylenedioxythiophene (Cl-Bz-ProDOT); and 2,2-(bis(4-amino-benzyl))-3,4-propylenedioxythiophene (NH₂-Bz-ProDOT).

performance over those of poly(3,4-ethylenedioxythiophene) (PEDOT).^{75–91} The latter (PEDOTs) were among the first practical cathodically coloring polymers.^{76,77,84–86,91} Welsh et al. and Amb et al.^{78–80} were one of the first to demonstrate significant improvement of electrochromic properties upon 2,2' di-Me substitution on the propylene moiety of the ProDOT. Most recently, Krishnamoorthy et al.⁷⁵ reported the synthesis and electrochromic performance of dibenzyl-substituted derivatives of P(ProDOT); their electrochromic performance was shown to be the best among all ProDOT derivatives reported thus far.

In this work, we report the syntheses of the following new monomers: (i) 2,2-(bis(4-chloro-benzyl))-3,4-propylenedioxythiophene (Cl-Bz-ProDOT); (ii) 2,2-(bis(4-bromo-benzyl))-3,4-propylenedioxythiophene (Br-Bz-ProDOT); (iii) 2,2-(bis(4-nitro-benzyl))-3,4-propylenedioxythiophene (NO₂-Bz-ProDOT); and (iv) 2,2-(bis(4-amino-benzyl))-3,4-propylenedioxythiophene (NH₂-Bz-ProDOT). Structures of some of these are depicted in Figure 5, whilst their syntheses are given in detail in the Experimental section.

Krishnamoorthy et al.⁷⁵ synthesized the dibenzyl derivative of ProDOT, Bz-ProDOT, using a transesterification reaction between 3,4-dimethoxy-thiophene and 2,2-dibenzyl-propane-1,3-diol. The latter in turn was synthesized starting with diethyl malonate and reacting it with benzyl chloride to yield 2,2-dibenzyl-diethyl malonate using a strong base (sodium ethoxide in ethanol medium). The 2,2-dibenzyl-diethyl malonate was in turn reduced to yield the 2,2-dibenzyl-propane-1,3-diol using a standard lithium-aluminum-hydride reduction. We attempted to adapt these procedures to the synthesis of the *p*-substituted-benzyl-ProDOT derivatives that we had targeted. However, this task was not straightforward. While diethyl malonate may react in a straightforward manner with benzyl chloride, facilitated by

the strong base sodium ethoxide, the same cannot be said for the *p*-substituted benzyl chlorides, for example, the *p*-chloro-substituted benzyl chloride. In fact, we observed in our work that the reaction in sodium ethoxide medium failed, as did the reaction with other commonly used bases, for example, triethyl amine and di-isopropylethyl amine. It appeared that the availability of the *para* position on the benzyl rings is required for the success of this reaction with common organic bases, and when it is blocked, the reaction fails. Thus, in our successful synthesis of our first target monomer, Cl-Bz-ProDOT, a different base and reaction conditions were used. These involved steps through the intermediates diethyl-bis(4-Cl-benzyl) malonate and 2,2-bis(4-chlorobenzyl)-propanediol; see scheme in “Experimental” section, Figure 1). In our successful synthesis of the nitrosubstituted analog of the chloro-substituted monomer, NO₂-Bz-ProDOT, which is a precursor to the corresponding amino-substituted monomer, we started with 4-nitrobenzyl bromide and included a series of steps which involve use of protective groups, as described at length in the “Experimental” Section (cf. Figures 1–4). It may be noted, coincidentally, that the bromo-substituted derivative monomer provides a very facile route to monomers substituted with alkyl- and other substituents.

Monomer Precursors to the Anodically Coloring CPs

Turning now to the monomer precursors for the anodically coloring CPs, it is noted that electrochromic performance of a number of poly(aromatic amines), for example, poly(diphenyl amine), poly(4-amino-biphenyl), poly(aniline), and poly(*N,N'*-diphenyl benzidine) has been reported earlier.^{23–30} We found however that some of this work was not reproducible. For example, in the preparation of the monomer solution of the *N,N'*-diphenyl benzidine, as described in the work of Suzuki et al.,²⁴ it was found that their procedures for electrochemical polymerization from solutions of the monomer (*N,N'*-diphenyl benzidine) in DMF and acetonitrile solvents were not reproducible. We subsequently developed a modified procedure with DMF and acetonitrile solvents which produced excellent electrochemically deposited films (see “Experimental” This applied to *N,N'*-diphenyl benzidine alone as well as its copolymers with other aromatic amines. Chemical structures of the anodically coloring polymer precursors (monomers) are shown in Figure 6.

Fabrication of Matched-Dual-Polymer Electrochromic Devices (“Lenses”)

Dual-polymer electrochromic devices were assembled according to the schematic of Figure 7, (see detail in “Experimental” section). As the anodically coloring CP, a copolymer of *N,N'*-diphenyl benzidine (as the majority component), diphenyl

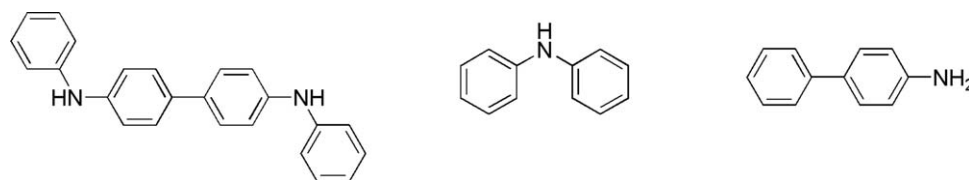


Figure 6. Chemical structures of the anodically coloring polymer precursors (monomers). From left to right: *N,N'*-diphenyl benzidine; diphenyl amine; 4-amino-biphenyl.

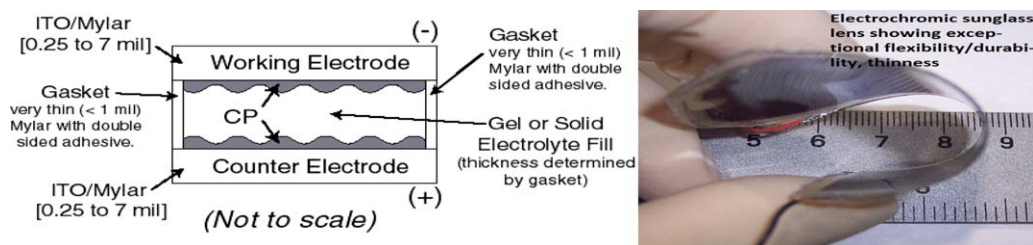


Figure 7. Left: Schematic of the electrochromic lenses (devices) fabricated in this work. Right: Edge-on photograph of a flexed electrochromic lens, demonstrating exceptional flexibility, thinness, and durability. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amine and 4-amino-biphenyl (both as minority components) was eventually found to have the best performance in our work.

With respect to the cathodically coloring polymer, lenses were fabricated with: (i) the single-monomer polymers, poly(Cl-Bz-ProDOT), poly(Br-Bz-ProDOT), and poly(NH₂-Bz-ProDOT) and poly(Bz-ProDOT); (ii) copolymers of these. Of the copolymers, that with Cl-Bz-ProDOT, Br-Bz-ProDOT, and Bz-ProDOT as comonomers was found to yield the best electrochromic performance, superior to that of the individual-monomer CPs. Additionally, to serve as a reference (control) cathodically coloring CP, to demonstrate the poor electrochemical and electrochromic matching with the anodically coloring CP used), PITN was also prepared according to literature procedures.^{92–94}

Electrochemical and Electrochromic Properties of the Dual-Polymer Lenses and Comparison of Well-Matched and Poorly Matched CP Pairs

As briefly noted above, nearly all complementarily coloring (dual-polymer) CP electrochromics reported thus far in the literature.^{53–71} have used CPs that are relatively poorly matched electrochemically and electrochromically. One, exemplary manifestation of poor matching is that, in a 2-electrode device, at an applied potential at which one CP is in its fully oxidized form, its complimentary CP is not in its fully reduced form. This then yields less than optimal L/D contrast as well as poorer cyclability.

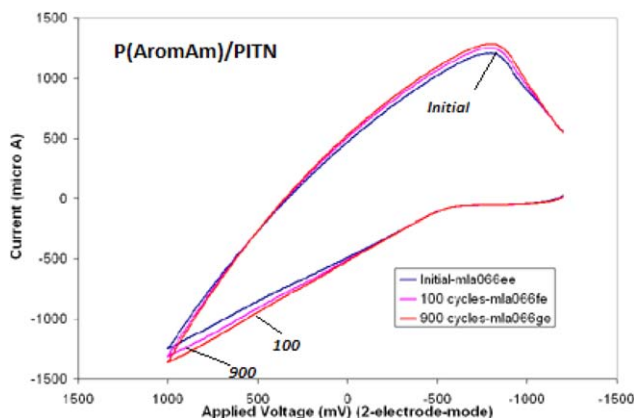


Figure 8. CV of a poly(aromatic amine)/PITN dual-polymer electrochromic device, used as a reference or benchmark, to compare with our dual-polymer systems. It shows very poor definition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A clear indicator of whether or not a dual-polymer system is well matched is seen in the properties of the cyclic voltammogram (CV) of a 2-electrode dual-polymer electrochromic device. To illustrate this, we fabricated a dual-polymer lens having our “standard” CP (copolymer of *N,N*-diphenyl benzidine, diphenyl amine, and 4-amino biphenyl) as the anodically coloring CP and PITN, one of the first cathodically coloring CPs discovered,^{92–94} and useful comparative benchmark, as the cathodically coloring polymer. The CV of the PITN/Poly(aromatic amine) system is shown in Figure 8. The potential limits therein are those corresponding to the extreme light and dark states of this dual-polymer device. While the reduction peak (at ca. -800 mV) is well defined, and the cyclability to 900 cycles as shown respectable (as to be expected of a dual-polymer device), the voltammogram is seen to have poorly defined oxidation peaks. More telling is the poor electrochromic performance embodied in Figure 9, which shows the UV–vis–NIR spectra of this device in its extreme light and dark states; the poor contrast (ΔT) is clearly seen.

The CV for the poly(aromatic amine)/PITN system shown in Figure 8 above may be compared with the CVs shown in Figure 10, for dual-polymer electrochromic devices comprising poly(Cl-Bz-ProDOT)/poly(aromatic amine) and [poly((Cl-Bz-ProDOT)-*co*-(Br-Bz-ProDOT)-*co*-(Bz-ProDOT))]/poly(aromatic amine). Here, it is seen that, for polymer films having nearly identical equivalent charge during deposition, the voltammogram for the copolymer device is more well defined and has

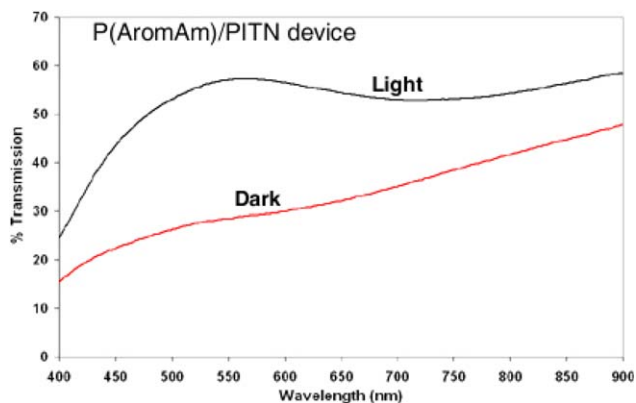


Figure 9. Extreme-light/extreme-dark electrochromic data for the poly(aromatic amine)/PITN dual-polymer electrochromic device of the previous Figure, showing very poor contrast. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

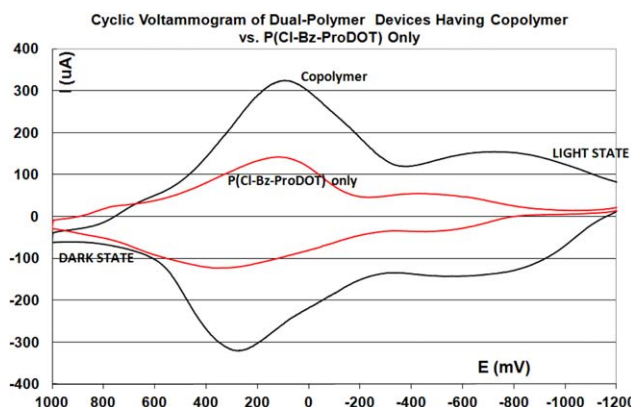


Figure 10. CVs for dual-polymer electrochromic devices comprising poly(Cl-Bz-ProDOT)/poly(aromatic amine) and [poly((Cl-Bz-ProDOT)-co-(Br-Bz-ProDOT)-co-(Bz-ProDOT))]/poly(aromatic amine), deposited with identical equivalent charge. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significantly higher currents than that for the P(Cl-Bz-ProDOT)-only device. This implies^{23,44,46,52} that more of the polymer in the former case is electroactive and switching. These CVs show that the copolymer is a better match for the aromatic amine than poly(Cl-Bz-ProDOT) alone. (It is also of course seen from the CV that the voltages required for electrochromic switching of these derivatized-ProDOT-based dual polymer systems between extreme light and dark states are comparatively small and symmetric: In essence, nearly all our systems could be switched thus with application of ± 1.0 V.)

The reasons for our targeting of the Cl-, Br- and NH₂-substituted dibenzyl propylene dioxythiophenes (Bz-ProDOTs) as good monomer precursor candidates for cathodically coloring CPs, with the potential to “perfectly” match with the specific anodically coloring poly(aromatic amines) of our prior work may now be briefly elaborated upon: first, it is noted again that one of the reasons for selection of derivatives of ProDOT as the cathodically coloring CPs was the significantly improved electrochromic properties reported for Poly(ProDOT) and Poly(dibenzyl ProDOT) CPs in recent studies,^{75,78–80,83,89} as compared with prior cathodically coloring CPs.^{76,77,81,82,84–87,90,91} Second, the electrochemical potential window of P(Bz-ProDOT), as reported in Krishnamoorthy et al. work,⁷⁵ calculated out, in 2-electrode-mode, to very close to that of our poly(aromatic amine), both being about ± 1.1 V between extreme light and dark states (in 2-electrode mode).

This thus provided a basis for an electrochemical and electrochromic match. Third, and most importantly, it was reasoned, based on the prior electrochemical and electrochromic data, that substituting with electron-withdrawing groups such as Cl- and Br- would move the bandgap of these semiconducting CPs just sufficiently that they would better match that of the poly(aromatic amine). (The Bz-ProDOT monomer substituted with the electron-donating NH₂-group, which was not used in the final copolymer employed in our dual-polymer devices, was targeted for synthesis simply as a reference or “control,” to provide comparison of the electron-withdrawing Cl- and Br- substitu-

ents.) Our predictions of near-“perfect” matching were confirmed with electrochemical data, as discussed above, and electrochromic data, as discussed below.

This near “perfect” matching can be seen in the two CVs shown in Figure 11, for the cathodically coloring P(Bz-ProDOT) alone and for the anodically coloring poly(aromatic amine) alone. As clearly seen therein, the redox potential limits of the two nearly overlap.

Figure 12 shows typical L/D contrast of a rectangular-shaped dual-polymer electrochromic device having the poly(aromatic amine) copolymer (see Experimental Section) as the anodically coloring CP and the copolymer [poly((Cl-Bz-ProDOT)-co-(Br-Bz-ProDOT)-co-(Bz-ProDOT))] as the cathodically coloring polymer. The device is hooked up to the Microcontroller chip (see Description and Discussion further below) for fast switching and automated control. The high contrast is clearly seen.

The exceptionally good electrochromic behavior, in terms of large L/D contrast and broad-band absorptions, is seen clearly in the electrochromic (spectral) data shown in Figure 13(a–d). Among several features illustrated by these data, the following are noteworthy: (1) With the same anodically coloring CP, the best-performing cathodically coloring CP is the copolymer [poly((Cl-Bz-ProDOT)-co-(Br-Bz-ProDOT)-co-(Bz-ProDOT))]. (2) The L/D spectra “window” can be shifted up or down with ease. For example, if the D and L state %T of a device are 8 and 60%, respectively, (at 575 nm), then with appropriate adjustment of the total charge during deposition of the polymers, the D and L %T can be shifted, for example, to 2 and 54%, in an approximately linear fashion. This is seen in the L/D data in Figure 13(a–c). (3) With optimization of the copolymer composition, the absorption characteristics can also be optimized such that there is more broad-band absorption; this is seen in Figure 13(d). (4) It is to be noted that a 0%T seen at some wavelengths, as seen in Figure 13(c), is somewhat deceptive in terms of the visibility through such a lens. Such a

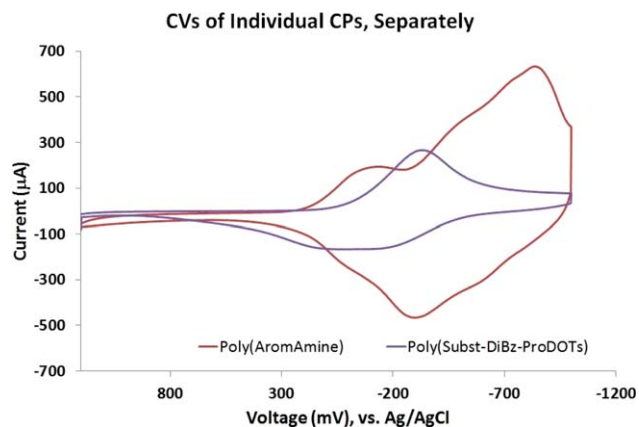


Figure 11. CVs for the cathodically coloring P(Substituted-BZ-ProDOT) alone and for the anodically coloring poly(aromatic amine) alone. As clearly seen therein, the redox potential limits of the two nearly overlap. (The light state is at about -1200 mV, the dark state at about $+1000$ mV; Scan rate: 10 mV/s.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

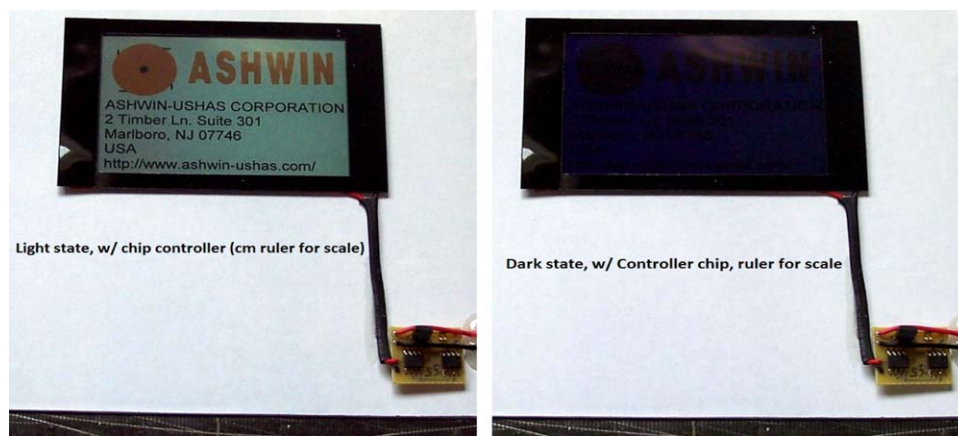


Figure 12. Typical L/D contrast of a rectangular dual-polymer electrochromic device having the poly(aromatic amine) copolymer as the anodically coloring CP and the copolymer [poly((Cl-Bz-ProDOT)-co-(Br-Bz-ProDOT)-co-(Bz-ProDOT))] as the cathodically coloring polymer. The device is hooked up to the Microcontroller chip (see description further below) for fast switching and automated control. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lens just appears darkly tinted, and is still easily seen through; there is no impediment to visibility whatsoever, due to the fact that there is significant transmission at the other visible wave-

lengths. (5) Also shown in Figure 13(d) are the values for the L and D state integrated over the entire visible spectrum using an industry standard algorithm^{73,74}; this algorithm, weighted

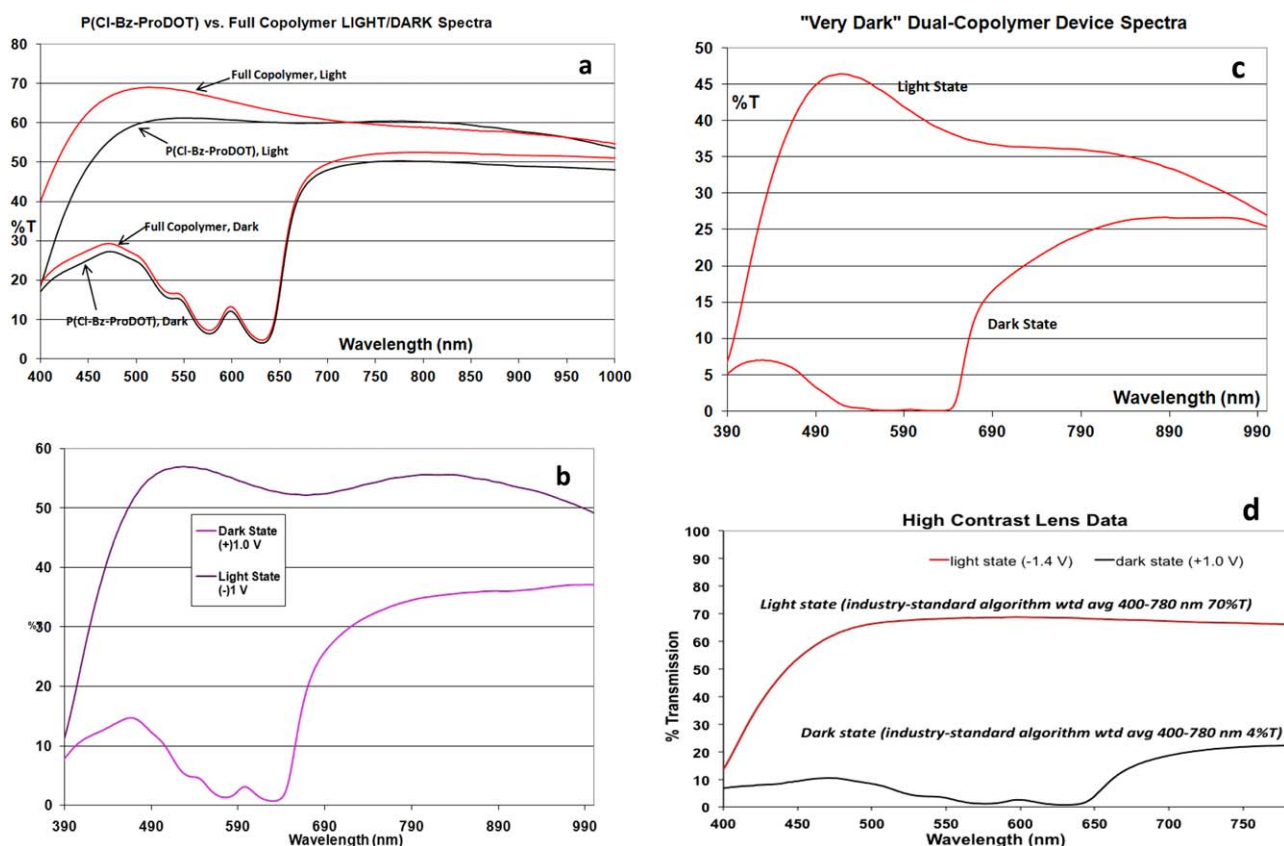


Figure 13. (a–d) Spectral data showing exceptional electrochromic performance of the dual-polymer electrochromic devices of this work. It is again noted that these “real-life” data are taken with air in the reference compartment of the spectrometer, in contrast to most of the data reported in the literature,^{1–22,24–35,53–71,75–93} which reports data with device substrates in the reference compartment, thus significantly enhancing L/D contrast and other performance parameters. For all spectra, the anodically coloring CP is the poly(aromatic amine) described in the Experimental Section. Cathodically coloring CPs are (see Experimental Section): (a) Poly(Cl-Bz-ProDOT) and copolymer [poly((Cl-Bz-ProDOT)-co-(Br-Bz-ProDOT)-co-(Bz-ProDOT))]. (b) Poly(Cl-Bz-ProDOT). (c) Same copolymer as in (a). (d) Optimized copolymer composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

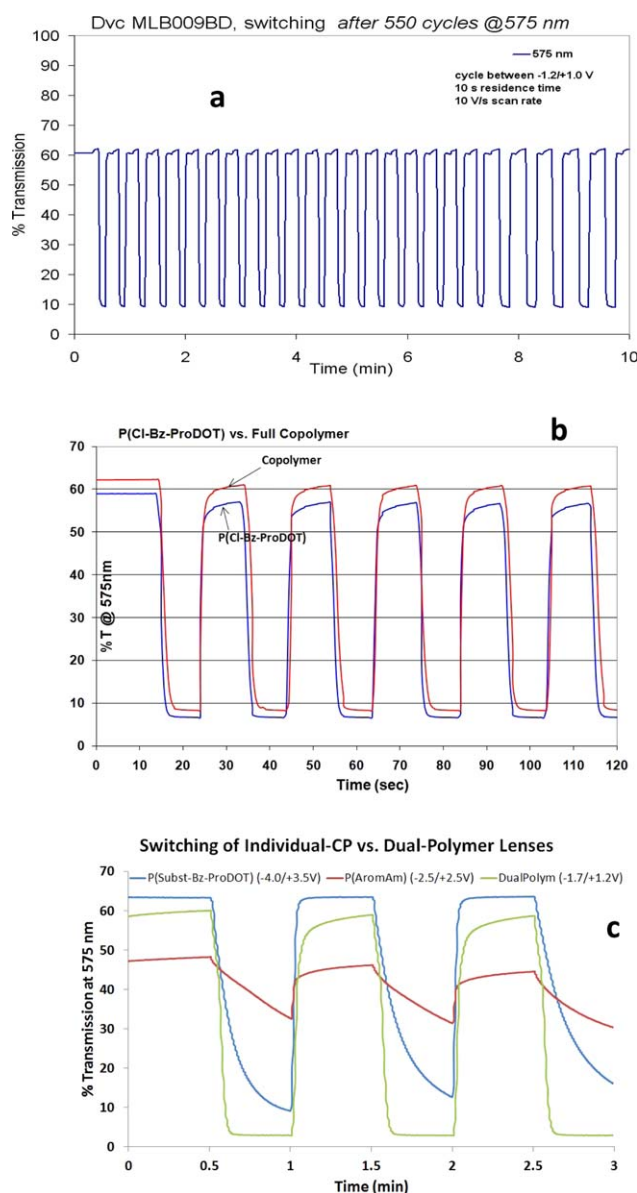


Figure 14. (a–c) Electrochromic switching data (again vs. air reference) for our dual-polymer lenses, and for single-CP lenses (for comparison), demonstrating exceptional stability, durability, and reproducibility for the dual-polymer lenses. (a) Cathodically coloring polymer is single polymer, as in previous Figure. (b) Comparison of single polymer versus copolymer as the cathodically coloring polymer. Provided in (c) is a comparison of switching of individual CP components of the lenses with the full dual-polymer device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for human vision across the Visible spectral region (cf. Experimental), is used extensively in the industry. This weighted L/D contrast for our best dual-polymer system, as shown in Figure 13(d), is 70/4%. To the best of published knowledge,^{1–71,75–94} this is the best observed thus far in a dual-polymer electrochromic device based on CPs. (Again, it is emphasized, further that our data are “real-life,” taken with air in the reference compartment of the spectrometer, in contrast to nearly all of the data reported in the

literature,^{1–22,24–30,31–35,53–71,75–93} which are with device substrates in the reference compartment.)

Figure 14(a–c) show typical electrochromic switching data, between extreme L and D states, for our dual-polymer lenses, and for single-CP lenses. They demonstrate exceptional stability, durability, and reproducibility. They also show, again, that the performance of the copolymer (as the cathodically coloring polymer) is superior to that of single-polymer devices, when identical total equivalent charges are used during electro-deposition of the polymers. The dramatically reduced switching time of the combined, dual-polymer electrochromic system, over that of its individual CP components, can also be seen in this figure: the individual CPs do not even switch completely within the switching time interval used in the data.

Typical switching times for the fully assembled, single-CP and dual-polymer lenses (per the standard definition, that is, 10–90% of full transition, measured at 575 nm, the point of highest transmission), measured without the smart control algorithm of our Microcontroller (see below), were as follows: P(Subst-Bz-ProDOT) Lens: L → D 12.9 s; D → L 9.4 s. P(AromAmine) Lens: L → D 15.1 s; D → L 13.2 s. Dual-Polymer Lens: L → D 9.1 s; D → L 5.2 s. (As noted further below, with the use of the smart Microcontroller, the Dual-Polymer Lens figures were approximately as follows: L → D 1.7 s; D → L ~ instantaneous.)

As a minor note relevant for practical use in sunglasses, it is noted that the ITO/Mylar® (Mylar = PET) substrates that we purchased possessed a UV-filter coating that cut off UV light below about 390 nm. Thus, all electrochromic lenses and devices described in this communication possessed inherent UV filters and were impervious to damage by UV light.

With respect to shelf life and long-term durability, three electrochromic lenses were randomly selected for long-term/lifetime testing. After fabrication and initial characterization, they were left on the shelf and re-tested after a period of 23 months. Their electrochromic performance, measured in terms of the L and D state UV–vis–NIR spectra and switching time, was found to have changed <3.5%. In particular, the L/D contrast, measured in units of Delta-%T at any particular wavelength, was found to have degraded <3% for two of the devices and to actually have increased by 1.5% for the third device. L/D switching times, measured at 575 nm, were found to have increased less than 2.5%. Peaks of the CVs of the devices before and after this 23 month period were very similar, with mA-scale peaks in all cases. (These data are available as Supporting Information, on request from the authors.)

Haze measurements on two typical “light” electrochromic lenses are given in Table I. They show that the Haze was <2%, even for the dark electrochromic state. A required <4% Haze, and a preferred <2% Haze, is a necessary requirement for practical sunglasses, according to extensive discussions we had with personnel from Oakley, a large manufacturer of designer sunglasses (see Acknowledgements). We also note in this respect that, to our knowledge, prior studies on Visible-region electrochromic polymers^{1–71} have not reported Haze measurements.

Table I. Haze Measurements on Two Typical “Light” Electrochromic Lenses

Lens#	Light state %T	Light state Haze	Dark state %T	Dark state Haze	$\Delta\%T$
S1D109ED	58.3%	0.98%	12.0%	1.5%	46.3%
S1D109FD	57.0	1.06%	9.0%	1.41%	48.0%

The %T values given are integrated over the visible spectral region using the industry-standard algorithm (see experimental section) and of course against air reference.

Coloration efficiencies, calculated using standard methods (see Experimental section), were as follows (D = dark, L = light, AromAm = aromatic amine): P(subst-BzProDOT), -4.0 V/+3.5 V: D→L $692\text{ cm}^2\text{C}^{-1}$. L→D $467\text{ cm}^2\text{C}^{-1}$. P(AromAm), $+/-2.5$ V, D→L $209\text{ cm}^2\text{C}^{-1}$. L→D $168\text{ cm}^2\text{C}^{-1}$. Dual-polymer device, -1.7 V/+1.2 V: D→L $288\text{ cm}^2\text{C}^{-1}$. L→D $264\text{ cm}^2\text{C}^{-1}$. These are generally higher than most published values, for example, the 135 to 192 cm^2C^{-1} reported by Mortimer and Reynolds.¹⁰¹ L^* , a^* , b^* values (CIE coordinates, i.e., color profile, see Experimental section), and actual colors, for the individual CPs and for dual-polymer and single-CP lenses are summarized in Figure 15.

Drastic Reduction of Switching Times through Use of Unique Applied-Potential Algorithm, and Automated, Photosensor-Based Operation of Electrochromic Lenses

In the dual-polymer devices and lenses reported in this communication, switching times between L and D electrochromic states

were about 7 to 9 s for L to D and 3 to 6 s for D to L when voltage was applied using a standard lab potentiostat or DC power source. These times were drastically lowered, using a unique, patented⁴⁷ overvoltage algorithm resident on a very inexpensive Microcontroller chip, to about 2 to 3 s for the L to D transition and <0.5 s (instantaneous to the naked eye) for the D to L transition. This Microcontroller used input from a photosensor that measured the ambient light level and made a decision on what electrochromic state to drive the lens or device to, based on the photosensor input and the desired light level at the user's eyes, pre-set by the user. Furthermore, the algorithm and Microcontroller circuit allowed for voltage application only to achieve the desired the desired light level, after which the voltage application ceased and the Controller went into a dormant, monitoring-only mode, monitoring the ambient light level via the photosensor. This greatly conserved battery power. The Microcontroller as fabricated in lots of 10 for the present work cost about US\$20 each. Its ultimate cost for lots of 1,000

Dual-Polymer Lens, Lightest State

$L^* = 72$ $a^* = -6$, $b^* = 3$



Dual Polymer Lens, Darkest State

$L^* = 14$ $a^* = 12$, $b^* = -30$



Single-CP Lens, P(Subst-BzProDOT) Lightest State

$L^* = 77$ $a^* = -3$, $b^* = 2$



Single-CP Lens, P(Subst-BzProDOT), Darkest State

$L^* = 29$ $a^* = 24$, $b^* = -62$



Single-CP Lens, P(AromAmine) Lightest State

$L^* = 69$ $a^* = 2$, $b^* = 17$



Single-CP Lens, P(AromAmine), Darkest State

$L^* = 41$ $a^* = -1$, $b^* = 10$



Figure 15. Representative results for L^* , a^* , and b^* values (CIE coordinates, i.e., color profile), and actual colors, for the individual CPs and for dual-polymer and single-CP lenses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

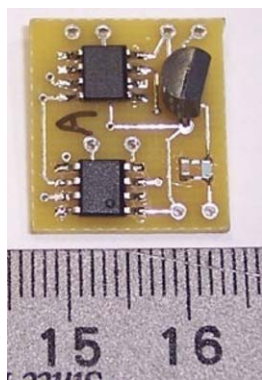


Figure 16. Microcontroller, ultimately costing < US\$8, as used in the work reported here. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

or more was estimated to be < US\$8, including amortized NRE (non-recurring engineering) costs. Figure 16 is a photograph of the tiny Microcontroller.

The unique algorithm and method used by the Microcontroller is now briefly described (more detail is available elsewhere⁴⁷). A brief background on how electrochromics function with applied voltage is in order first. In the case of electrochromics based on CPs and metal oxides, a critical requirement is that the voltage applied not exceed the redox stability limits of the system.^{1,23,38,44,46–48} If these limits, generally determined from the CV of the system, are exceeded, irreversible oxidative or reductive degradation of the active electrochromic occurs. An additional issue is that of the “conductivity drop” of the underlying substrate [e.g., indium-tin-oxide (ITO) on glass or plastic]: the switching speed of the device from one extreme electrochromic state to another can be slow, and the transition can also be uneven, with the electrochromic material closer to the point of electrical contact switching fastest and that furthest from the point of electrical contact switching slowest.

One simple means of increasing the switching speed (and the evenness of the switching) is to apply an overvoltage to the system. For example, in the poly(aniline) IR electrochromics described by Chandrasekhar et al.^{44,48} where the recommended applied voltage for stable switching within the redox stability limits is ± 1.1 V, the applied voltage may be increased to, for example, ± 2.0 V or ± 3.0 V or even ± 4.0 V. However, one would invariably risk irreversible damage to the electrochromic system, with perhaps only a marginal increase in the switching speed (reduction in switching time). Then, after a few such switches, the electrochromic device would essentially stop functioning.

This behavior is visualized clearly in the CVs of the best dual-polymer electrochromic system described in the present communication, as embodied in Fig17(a,b). Fig17(a) shows the CV of an actual dual-polymer lens, taken at a very slow scan rate (10 mV/s). It shows the highly reversible nature of the redox behavior for this system: The primary and secondary voltammetric peaks responsible for the electrochromism nearly overlap each other, a sign of a highly reversible system. [Primary at ca. +250 mV (oxidation, negative current) and about

+200 mV (reduction); secondary at about -850 mV (oxidation) and $+850$ mV (reduction).] This voltammogram further shows that the potential limits for application of a voltage for achieving an acceptable electrochromic transition between the light and dark states lie between about $(-)$ 1.0 V and $(+)$ 1.0 V. Fig17(b) shows the CV of the same system, identical except that it is for an expanded window, between $(-)$ 3.0 V and $(+)$ 3.0 V. Several irreversible peaks are seen, the most prominent one being at about +2.55 V, which may be ascribed to an irreversible oxidative degradation of one of the polymers; it may be noted that there is no corresponding reductive peak for this oxidative peak. This expanded CV indicates that if one were to apply an overvoltage to make it switch faster, the system may undergo irreversible oxidative damage.

In practice, when one applies such overvoltages, as little as ± 1.0 V above the recommended redox limits to our dual-polymer electrochromic systems using a lab potentiostat or DC power source, one observes both significantly faster switching as well as irreversible degradation and eventual non-function of the lens. This in fact happens within about 5 to 10 L/D switching

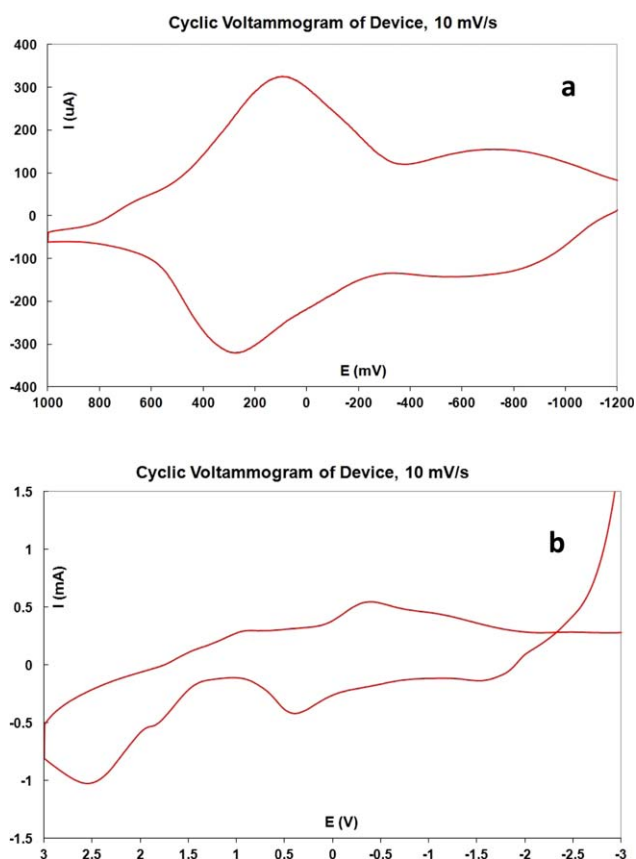


Figure 17. (a) CV of a dual-polymer electrochromic lens for the best system reported in the present communication [poly(aromatic amine)/poly(cosubstituted-Bz-ProDOT)], between its stable electrochromic limits (ca. -1.2 V/ $+1.0$ V, 2-electrode mode). The CV demonstrates the highly reversible nature of this redox process. (b) CV of the same dual-polymer electrochromic lens, but now with an expanded electrochemical window, showing irreversible degradation behavior. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Algorithms (Programs) Found to be the Best for Drastic Reduction in Switching Time of the Best Dual-Polymer Electrochromic System Combined with indefinite Stability and Long-Term (to 10^5 Cycles) Cyclability

Algorithm A	
0.25V/0.1s	(± 3.0 , ± 2.75 , ± 2.5 , ± 2.25 , ± 2.0)
0.25V/0.2s	(± 2.0 , ± 1.75 , ± 1.5 , ± 1.25 , ± 1.0)
Algorithm B	
0.25V/0.1s	(± 3.25 , ± 3.0 , ± 2.75 , ± 2.5 , ± 2.25)
0.25V/0.2s	(± 2.25 , ± 2.0 , ± 1.75 , ± 1.5 , ± 1.25 , ± 1.0)
Algorithm C	
0.25V/0.15s	(± 3.0 , ± 2.75 , ± 2.5 , ± 2.25 , ± 2.0)
0.25V/0.2s	(± 2.0 , ± 1.75 , ± 1.5 , ± 1.25 , ± 1.0)
Algorithm D	
0.25V/0.2s	(± 2.75 , ± 2.5 , ± 2.25 , ± 2.0)
0.25V/0.2s	(± 2.0 , ± 1.75 , ± 1.5 , ± 1.25 , ± 1.0)

See text for interpretation of the shorthand notation used.

cycles. It is also however observed that if the overvoltage is applied for very short periods of time, generally < 1.0 s (500 ms), then redox damage to the CPs is observed only over hundreds of L/cycles. This observation then provides a clear direction for a method for faster switching of the lenses together with avoidance of degradation of the CPs, as a tradeoff between the magnitude and duration of the overvoltage applied and the resulting reduction in switching time of the electrochromic system: One must clearly select applied voltage programs or algorithms that combine very short voltage pulses of appropriate overvoltage with carefully selected times of their application. Quite evidently, such algorithms would be specific to a particular dual-polymer electrochromic system. Exactly such algorithms were devised in our work after painstaking, time-consuming experiments, as now described.

The four best algorithms (programs) found in our studies are summarized in Table II. These four yielded the most drastic reduction in switching time of our best dual-polymer electrochromic system, combined with indefinite stability and long-term cyclability (up to 10^5 cycles). Of these in turn, Algorithm C was found to be the best; results reported in this communication are thus for Algorithm C.

The shorthand notation used in Table II may be explained illustratively for Algorithm A as follows: Microcontroller applies ($-$)3.0 V for 0.1 s, then steps to ($-$)2.75 V and applies this for 0.1 s, then steps to ($-$)2.5 again for 0.1 s, then to ($-$)2.25 V again for 0.1 s, then to ($-$)2.0 V also held for 0.1 s. For the next 1.0 V program the step voltage remains the same, that is, 0.25 V; however, the duration of the hold at each voltage is now increased to 0.2 s from 0.1 s. This is done until ($-$)1.0 V is reached. It is also important to note that, during all this time, the device never goes to open circuit (OC), that is, the Open Circuit Potential is never used or in effect. Only when the desired darkness or lightness is achieved, as determined by the light incident on the photosensor, is the voltage switched off. More detail on these Algorithms and the Microcontroller is available elsewhere.⁴⁷

The results of application of these overvoltage algorithms is dramatic, as seen in Figure 18, which shows a comparison of the switching

time using a steady DC voltage, as applied from a potentiostat (or a DC power source), with that obtained using Algorithms A and C (used as examples). It is clearly observable that the switching time is dramatically reduced, from about 8 s for the DC voltage to < 1 s for Algorithm C. (The switching time is defined customarily as the time for transition between 10 and 90% of the maximum and minimum %T, and the above values are measured using this definition.) Although this more than 8-fold reduction of switching time, from about 8 to < 1 s, as above, may not seem extraordinarily large, it is in fact most consequential, for it determines the difference between a commercially viable electrochromic lens (< 2 s switching time) and a nonviable one (8 s switching time, a bit less than 1/2 that of photochromic lenses).

Figure 19 shows the long term cyclability, at 0 and 10,000 cycles, between light and dark states, using Algorithm C. It is clearly seen that there is no effect whatsoever on the electrochromic switching characteristics and stability of the system, even though an overvoltage of ± 3.0 V has been applied to the system 10,000 times for very short periods of time.

The very rapid electrochromic switching and automated photosensor-based operation is seen in sunglasses retrofitted with our dual-polymer electrochromic lenses in a video available for viewing elsewhere⁷² (<http://www.youtube.com/watch?v=yDA-Z0YauM0>).

Comparison with Other ProDOT-Based CP Electrochromics

The performance of our electrochromic lenses may firstly be compared with the work of Krishnamoorthy et al.⁷⁵ with poly(unsubstituted-DiBz-ProDOT), which we have also discussed at some length above. In their data demonstrating L/D switching at 632 nm, Krishnamoorthy et al.⁷⁵ show L and dark states with about 93% and about 3% Transmission. Once again, their measurements are clearly with substrate in the reference compartment of the spectrometer (whereas our measurements are against air only), since even clear glass (a microscope slide) and ITO/Mylar (50 Ohms/square substrate used in our work) have %T at this

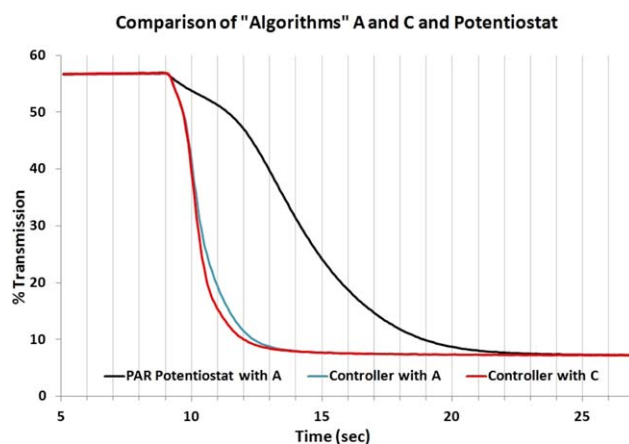


Figure 18. Comparison of switching time using a steady DC voltage (potentiostat or DC power source) versus that obtained using Algorithms A and C. The dramatic reduction in switching time, from about 8 s for the DC voltage to < 1 s for Algorithm C, is clearly observable. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

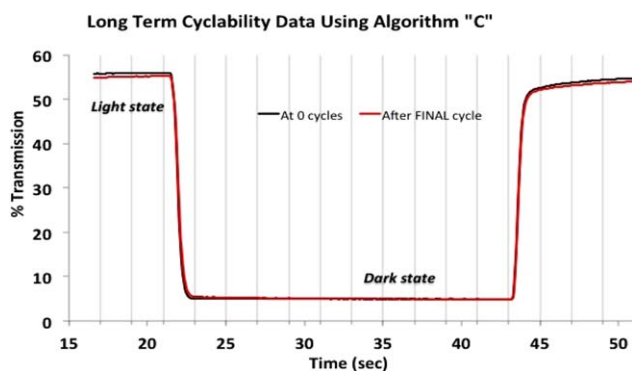


Figure 19. Long term cyclability, at 0 and 10,000 cycles, between light and dark states, using Algorithm C. It is clearly seen that there is no effect whatsoever on the electrochromic switching characteristics and stability of the system, even though an overvoltage of ± 3.0 V has been applied to the system 10,000 times for very short periods of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wavelength of about 91 and 80% Transmission respectively, and their 93% value exceeds the value for clear glass. Thus, it is difficult to gauge the true L/D contrast of their CP system. In the L/D absorption spectra presented by them, the two absorption maxima occur at about 560 and 625 nm, with %*T* values of about 2.5 and 1.1% Transmission respectively (and a ratio thus of 2.27), to be compared with the two absorption maxima in our system occurring at about 575 and 640 nm, with a ratio of typically 1.4–1.6. More significantly, in their system, there is an absorption crossover (though not a clearly seen isosbestic point) at about 720 nm, and

at > 720 nm, their system behaves like an anodically coloring polymer; in contrast, our dual-polymer system has no such crossover, and continues the same electrochromic behavior well into the NIR (to 990 nm). Our systems may next be compared with the work of Welsh et al.,^{78–80} who studied poly(2,2'-(CH₃)₂-ProDOT), showing electrochromic contrast very slightly improved over that of the unsubstituted poly(ProDOT). In their CP system, maximum L state Transmission was about 80% (at ca. 450 nm) and minimum D state Transmission was about 3% (at ca. 550 nm). Here again, however, their data were collected with substrate in the reference compartment of the spectrometer; hence it is difficult to determine the “real-life” L/D contrast of their CP system. In a similar vein, Groenendaal et al.⁹¹ describe poly(substituted-ProDOT) CPs with claimed improved electrochromic properties. Their best CP system shows an absorption maximum at about 590 nm, maximum L/D contrast of about 75/25% at about 520 nm, and, remarkably, continued cathodically coloring behavior in the NIR to about 900 nm. Amb et al.^{78–80} describe poly(phenylene-*co*-ProDOT) copolymer systems with reasonable L/D contrast and switching time. However, again, their data are collected with substrate in the spectrometer reference compartment, so it is hard to gauge their systems’ “real-life” performance. More importantly, their best systems show an undesirable dark yellow-to-very-light-yellow color transition.

The performance of our electrochromic lenses may also be compared with the recent work of Ma et al.,^{98,99} who reported an electrochromic device based on the CP poly((CH₃)₂-Bz-ProDOT) as the cathodically coloring material (synthesized earlier by Welsh et al.^{78–80}) and the metal oxide V₂O₅ as the anodically coloring material. They subsequently produced lens-shaped devices and,

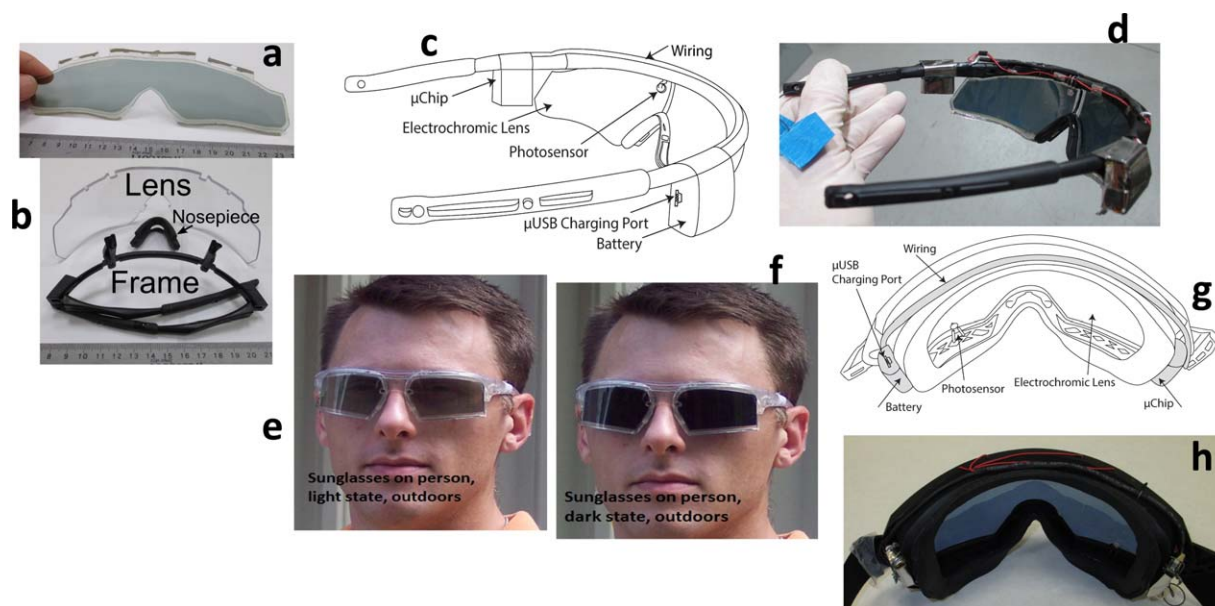


Figure 20. Elements of the retrofit of the Smith Optics Elite Model # AEGABK12-2R (“Aegis arc eyeshield”) safety spectacles, and Smith Optics Elite Model # OTW01BK12-2R (“Outside-the-wire goggle”) goggles, both of which conform to ANSI Z87.1 and GL-PD 10–12 (US military) specifications,^{73,74} with our dual-polymer electrochromic lenses. (a) Photograph of electrochromic lens. (b) Elements of the spectacles frame, disassembled. (c) Schematic of the retrofit of spectacles. (d) Photo of actual, retrofitted spectacles. (e) Photographs of a user wearing retrofitted spectacles, in light state. (f) Same, in dark state. [A video of their automated, photosensor-based operation is available elsewhere⁷² (<http://www.youtube.com/watch?v=yDA-Z0YauM0>)]. (g) Schematic of retrofitted goggles. (h) Photograph of actual, retrofitted goggles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

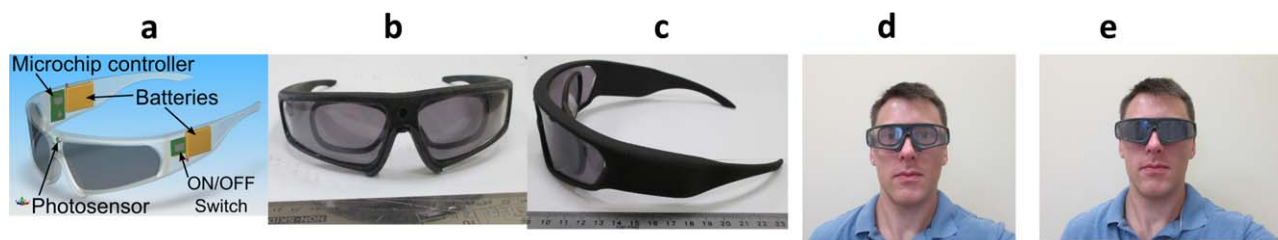


Figure 21. Summary of work in arriving, *ab initio*, at a spectacles frame and sunglasses, which seamlessly and invisibly incorporated all components, such as the Li battery, photosensor, microcontroller, wiring, and recharge port. A snap-in prescription insert was also included for users wearing prescriptions. Left to Right: (a) Schematic of the design. (b) Actual spectacles, including prescription insert, front view. (c) Same, side view. (d) Same, worn by user, in light state. (e) Same, in dark state. The prescription insert is seen in (b–e) inside the outer eyepiece. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

eventually, retrofitted them into a pair of sunglasses. The comparison with our electrochromics can be briefly summarized as follows: (1) Due to the use of a metal oxide electrochromic as the anodically coloring material, the stability, environmental durability and shelf-life of their devices is significantly compromised due to the known issues in this regard with metal oxide electrochromics.^{37–40} (2) Their “transparent” state still has a bluish tinge (as compared to close to total transparency in our devices) and their dark state is not nearly as dark as ours, as a comparison of photos in their publications with Figure 12 above clearly shows. (3) The L/D %T spectra of their devices have a large element in the near-IR region (>700 nm), and very little contrast through 500 nm, indicating they are not optimized for human vision (400–700 nm). (4) Their switching times are significantly slower than those for our devices (due of course to the use of the patented applied-potential algorithm in our devices, as described above, in our devices).

Fabrication of Working, Automated (Photosensor-Based) Sunglasses via Retrofit of Existing Safety Glasses Qualified for ANSI Z87.1 and GL-PD 10–12 Specifications

As a proof-of-concept, existing safety spectacles conforming to ANSI Z87.1 and GL-PD 10–12 (US military) specifications^{73,74} were retrofitted with the dual-polymer electrochromic lenses, to arrive at sunglasses capable of automated, photosensor-based operation. Several existing spectacles and goggles were used. The ones reported in this communication are the Smith Optics Elite Model # AEGABK12-2R (“Aegis arc eyeshield”) safety spectacles, and the Smith Optics Elite Model # OTW01BK12-2R (“Outside-the-wire goggle”) goggles. Figure 20 shows elements of the retrofit. While the retrofitted spectacles may appear somewhat crude (Microcontroller/battery fastened to spectacles frame duct tape), they served as a useful proof-of-concept for further, *ab initio* design of spectacles frames, as described in the next section. As noted above, a video of their automated, photosensor-based operation is available elsewhere (<http://www.youtube.com/watch?v=yDA-Z0YauM0>).⁷²

Fabrication of Working, Automated (Photosensor-Based) Sunglasses Based on *Ab Initio*-Designed Frames, with Seamless, Invisible Incorporation of Battery, Photosensor, Microcontroller, Wiring, and Other Components

The experience gained from the retrofit proof-of-concept work above was used to design, *ab initio*, a spectacles frame which

seamlessly and invisibly incorporated all components, such as the Li battery, photosensor, Microcontroller and recharge port, and which has a snap-in prescription insert. Wiring was incorporated using a snap-in flex circuit. Iterations of the design were 3-D printed for iterative improvement, to arrive at a final design. Results of this work are summarized in Figure 21.

Testing of Retrofitted Spectacles with Older Veterans (Human Subjects) with Age-Related Macular Degeneration (ARMD) and Other Ocular Diseases

As part of a project funded by the (U.S.) National Institutes of Health,¹ our retrofitted spectacles were extensively tested on 11 low-vision subjects having ARMD at Atlanta Veterans Administration Rehabilitation R&D Center for Vision Loss (Decatur, GA). ARMD is an eye disease affecting older persons, with the characteristic that the afflicted persons find going rapidly indoors and outdoors, especially in bright sunlight, extremely problematic; photochromic sunglasses are too slow to accommodate their requirements, and multiple sunglasses are too cumbersome.) In this work, a vast majority of subjects showed >2X (and in some cases >3X) reduction in time required to complete specific tasks, using our electrochromics vs. their current glasses or multiple sunglasses. They overwhelmingly preferred our electrochromics to their current remedies. All subjects observed a “significant”¹ (at least 40%) improvement in their daily activities wearing our electrochromic sunglasses. These results, which are somewhat voluminous, will be published in detail separately elsewhere; they are mentioned here only since they have relevance to some of the final end-uses of our dual-polymer electrochromics.

CONCLUSIONS

In this communication, we have reported syntheses of several new monomer precursors of cathodically coloring CP systems based on a ProDOT skeleton. These are designed to yield CPs that are nearly “perfectly” matched electrochemically and electrochromically with a set of anodically coloring poly(aromatic amines), for use in dual-polymer (complementarily coloring)

¹Fast-Switching, High-Contrast, Electrochromic Sunwear for Persons with Age-Related Macular Degeneration (ARMD) and Other Age-Related Ocular Diseases”, (U.S.) National Institutes of Health (NIH) Grant No. 1R43AG039897-01 to Ashwin-Ushas Corporation, 2012.

devices (“lenses”). The monomers include Cl-, Br-, and NH₂-derivatives of dibenzyl propylene dioxythiophene (Bz-ProDOT). Complementary coloring, dual-polymer electrochromic devices (“lenses”) were made with these new monomers constituting the cathodically coloring polymer (used both as a single polymer as well as in the form of copolymers), paired with several anodically coloring poly(aromatic amines). The cathodically and anodically coloring polymer pairs in these devices were shown to be nearly “perfectly” matched electrochemically and electrochromically, in contrast to poor matching in nearly all prior art. The resulting electrochromic lenses displayed very high L/D contrast (typically up to 70/7% or 50/0.5% Transmission, integrated over the visible spectrum (and measured against air reference), very high cyclability (> 10 K cycles) and very long (multiple-years) shelf life. The color transition in the devices is an appealing nearly transparent to dark-blue-black, and they have excellent optical memory. Dramatic lowering of the switching time of these dual-polymer electrochromic devices, from about 8 to < 1 s, was demonstrated using a unique applied-potential algorithm resident on an inexpensive Microcontroller chip. Working electrochromic safety spectacles (“sunglasses”) were fabricated with the electrochromic lenses retrofitted to existing (Smith Optics and other) spectacles meeting ANSI Z87.1 and GL-PD 10–12 (U.S. military) specifications. These incorporated a photosensor, rechargeable Li battery and a Microcontroller chip, and allowed for automated sunglasses operation (lightening/darkening) based on a user-preselected light level at the user’s eyes that is automatically maintained. *Ab initio* design of non-retrofitted, electrochromic spectacles, also conforming to ANSI Z87.1/GL-PD 10–12 specifications, was also completed to the proto-mold stage; these incorporated Li battery, Microcontroller, photosensor, recharge port and wiring all seamlessly hidden within the frame. To the best of our knowledge and based on an extensive search of the literature,^{1–71,75–96} the electrochromic lenses and sunglasses we report herein represent the best visible-region electrochromic performance for dual-polymer CP electrochromic systems to date and also the first practical implementation in working sunglasses, that is, practical, applied functional polymers.

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REFERENCES

1. Mortimer, R. J. *Ann. Rev. Mat. Res.* **2011**, *41*, 241.
2. Žmija, J.; Małachowski, M. J. *J. Achiev. Mat. Manuf. Eng.* **2011**, *48*, 14.

3. Yigit, D.; Udum, Y. A.; Gullu, M.; Toppare, L. *J. Electroanal. Chem.* **2014**, *712*, 215.
4. Beaupre, S.; Dumas, J.; Leclerc, M. *Chem. Mater.* **2006**, *18*, 4011.
5. Liu, L.; Xu, C.; Legenski, S. E.; Taya, M. U.S. Pat. 7,547,658 B2 (**2009**).
6. Ram, M. K.; Maccioni, E.; Nicolini, C. *Thin Solid Films* **1997**, *303*, 27.
7. Beyazyildirim, S.; Camurlu, P.; Yilmaz, D.; Gullu, M.; Toppare, L. *J. Electroanal. Chem.* **2006**, *587*, 235.
8. Sahin, E.; Camurlu, P.; Toppare, L.; Mercore, V. M.; Cianga, I.; Yagci, Y. *J. Electroanal. Chem.* **2005**, *579*, 189.
9. Camurlu, P.; Eren, E.; Gueltekin, C. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4847.
10. Ak, M.; Ak, M. S.; Kurtay, G.; Guellue, M.; Toppare, L. *Solid State Sci.* **2010**, *12*, 1199.
11. Ak, M.; Gancheva, V.; Terlemezyan, L.; Tanyeli, C.; Toppare, L. *Eur. Polym. J.* **2008**, *44*, 2567.
12. Ak, M.; Ak, M. S.; Gullu, M.; Toppare, L. *Smart Mater. Struct.* **2007**, *16*, 2621.
13. Tarkuc, S.; Ak, M.; Onurhan, E.; Toppare, L. *J. Macromol. Sci. Pure Appl. Chem.* **2008**, *45*, 164.
14. Ak, M.; Durmus, A.; Toppare, L. *Solid State Sci.* **2007**, *9*, 843.
15. Ak, M.; Ak, M. S.; Guellue, M.; Toppare, L. *Eur. Polym. J.* **2007**, *43*, 3452.
16. Coskun, Y.; Cirpan, A.; Toppare, L. *J. Mater. Sci.* **2007**, *42*, 368.
17. Ak, M.; Camurlu, P.; Yilmaz, F.; Cianga, L.; Yagci, Y.; Toppare, L. *J. Appl. Polym. Sci.* **2006**, *102*, 4500.
18. Varis, S.; Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Eur. Polym. J.* **2006**, *42*, 2352.
19. Sahin, E.; Sahmetlioglu, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Org. Electron.* **2006**, *7*, 351.
20. Tarkuc, S.; Sahmetlioglu, E.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Electrochim. Acta* **2006**, *51*, 5412.
21. Yildiz, U. H.; Sahin, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2215.
22. Bingol, B.; Camurlu, P.; Toppare, L. *J. Appl. Polym. Sci.* **2006**, *100*, 1988.
23. Chandrasekhar, P.; Gumbs, R.W. *J. Electrochem. Soc.* **1991**, *138*, 1337.
24. Suzuki, T.; Yoshikawa, M.; Kojima, A. U.S. Pat. 4,874,481 (**1989**).
25. Guay, J.; Dao, L. H. *J. Electroanal. Chem.* **1989**, *274*, 135.
26. Nguyen, M. T.; Dao, L. H. *J. Electroanal. Chem. Interface Electrochem.* **1990**, *289*, 37.
27. Guay, J.; Leclerc, M.; Dao, L. H. *J. Electroanal. Chem. Interface Electrochem.* **1988**, *251*, 31.
28. Leclerc, M.; Guay, J.; Dao, L. H. *J. Electroanal. Chem. Interface Electrochem.* **1988**, *251*, 21.
29. Nguyen, M. T.; Dao, L. H. *J. Chem. Soc. Chem. Commun.* **1990**, 1221.

30. Yano, J.; Higuchi, Y. *Kobunshi Ronbunshu* **1990**, *47*, 817.
31. Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mzurkiewicz, J.; Zhou, D.; Wallace, G. G.; MacFarlane, D. R.; Forsyth, S. A.; Forsyth, M. *Science (Online edition, ScienceExpress)*, 10.1126/science.1072651 (4 July **2002**).
32. Lu, W.; Fadeev, A. G.; Qi, B.; Mattes, B. R. *J. Electrochem. Soc.* **2004**, *151*, H33.
33. Lu, W.; Mattes, B. R.; Fadeev, A. G. U.S. Pat. 6,828,062 (**2004**).
34. Lu, W.; Fadeev, A.G.; Qi, B.; Mattes, B.R. *Synth. Met.* **2003**, *135-136*, 139.
35. Vasilyeva, S. V.; Unur, E.; Walczak, R. M.; Donoghue, E. P.; Rinzler, A. G.; Reynolds, J. R. *Appl. Mater. Inter.* **2009**, *1*, 2288.
36. Chandrasekhar, P.; Thorne, J. R. G.; Hochstrasser, R. M. *Appl. Phys. Lett.* **1991**, *59*, 1661.
37. Hamelmann, F.; Gesheva, K.; Ivanova, T.; Szekeres, A.; Abrashev, M.; Heinzmann, U. *J. Optoelectron. Adv. Mater.* **2005**, *7*, 393.
38. Granqvist, C., Ed. *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, The Netherlands, **2002**.
39. The Sage Glass site. Available at: <http://sageglass.com>. Accessed on February **2014**.
40. Dautremont-Smith, W. C. *Displays* **1982**, *3*, 3.
41. Epstein, A.; Yue, J. U.S. Pat. 5,137,991 A (**1992**).
42. Loo, Y.-L.; Yoo, J. E.; Tarver, J. U.S. Pat. 8,248,681 B2 (**2012**).
43. Gentex Corporation. Available at: <http://www.gentex.com/automotive/products/driver-safety>. Accessed on February **2014**.
44. Chandrasekhar, P.; Zay, B. J.; Birur, G. C.; Rawal, S.; Pierson, E. A.; Kauder, L.; Swanson, T. *Adv. Funct. Mater.* **2002**, *12*, 95.
45. Chandrasekhar, P.; Zay, B. J.; McQueeney, T. M.; Birur, G.; Sitaram, V.; Menon, R.; Elsenbaumer, R. L. *Synth. Met.* **2005**, *155*, 623.
46. Chandrasekhar, P. U.S. Pat. Application (No. 61/560,243) (**2011**).
47. Chandrasekhar, P. U.S. Pat. Application No. 14/084,684 (**2013**).
48. Chandrasekhar, P. U.S. Pat. 5,995,273 (**1999**).
49. Chandrasekhar, P. U.S. Pat. 6,033,592 (**2000**).
50. Chandrasekhar, P. Can. Pat. 2,321,894 (**2007**).
51. Chandrasekhar, P. Eur. Pat. 99908208.4 (**2009**).
52. Chandrasekhar, P. In *Basic Electrochromics of CPs*; Kluwer Academic Publishers: Dordrecht, The Netherlands and Norwell, MA, **1999**; Chapter 3.
53. 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.
54. Bhandari, S.; Deepa, M.; Pahal, S.; Joshi, A. G.; Srivastava, A. Kumar; Kant, R. *ChemSusChem* **2010**, *3*, 97.
55. Lee, S.-H.; Tracy, E.; Pitts, R.; Jorgensen, G. J. U.S. Pat. 6,859,297 (**2005**).
56. Hsu, C.-Y.; Lee, K.-M.; Huang, J.-H.; Thomas, K. R. J.; Lin, J. T.; Ho, K.-C. *J. Power Sources* **2008**, *185*, 1505.
57. Invernale, M. A.; Seshadri, V.; Mamangun, D. M. D.; Ding, Y.; Filloramo, J.; Sotzing, G. A. *Chem. Mater.* **2009**, *21*, 3332.
58. Unur, E.; Jung, J.-H.; Mortimer, R. J.; Reynolds, J. R. *Chem. Mater.* **2008**, *20*, 2328.
59. da Silva, A. J. C.; Nogueira, F. A. R.; Tonholo, J.; Ribeiro, A. S. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2255.
60. Seshadri, V.; Padilla, J.; Bircan, H.; Radmard, B.; Draper, R.; Wood, M.; Otero, T. F.; Sotzing, G. A. *Org. Electron.* **2007**, *8*, 367.
61. Yildiz, H. B.; Sahin, E.; Cirpan, A.; Toppare, L.; Yagci, Y. *Polym. Int.* **2007**, *56*, 674.
62. Camurlu, P.; Toppare, L. *J. Macromol. Sci. Pure Appl. Chem.* **2006**, *43*, 449.
63. Ak, M.; Cirpan, A.; Yilmaz, F.; Yagci, Y.; Toppare, L. *Eur. Polym. J.* **2005**, *41*, 967.
64. Bulut, U.; Cirpan, A. *Synth. Met.* **2005**, *148*, 65.
65. Camurlu, P.; Cirpan, A.; Toppare, L. *J. Electroanal. Chem.* **2004**, *572*, 61.
66. Kang, J.-H.; Xu, Z.-C.; Paek, S.-M.; Wang, F.; Hwang, S.-J.; Yoon, J.-Y.; Choy, J.-H. *Chem. Asian J.* **2011**, *6*, 2123.
67. Nikolou, M.; Dyer, A. L.; Steckler, T. T.; Donoghue, E. P.; Wu, Z.; Heston, N. C.; Rinzler, A. G.; Tanner, D. B.; Reynolds, J. R. *Chem. Mater.* **2009**, *21*, 5539.
68. Reynolds, J. R.; Dyer, A. L.; Unur, E. U.S. Pat. 8,284,473 B2 (**2012**).
69. Schwendeman, I.; Hickman, R.; Soenmez, G.; Schottland, P.; Zong, K.; Welsh, Dean M.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118.
70. Gazotti, W. A.; Casalbore-Miceli, G.; Geri, A.; De Paoli, M.-A. *Adv. Mater.* **1998**, *10*, 60.
71. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101.
72. Ashwin-Ushas Corporation. Available at: <http://www.youtube.com/watch?v=yDA-Z0YauM0>. Accessed on February 2014 and Available at: http://www.ashwin-ushas.com/Ele-Home/Electrochromic_Sunglasses_-Vid/index.html. Accessed on February **2014**.
73. ANSI Z87.1-2003. American National Standard Practice for Occupational and Educational Eye and Face Protection. Available at: https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9778. Accessed on February **2014**.
74. GL-PD 10-12. Military Combat Eye Protection (MCEP) Program; US Army Natick Soldier Center: Natick, MA. Available at: http://nsrdec.natick.army.mil/APBI/Eyewear/Army_2011_Apr_22_APBI_Military%20Combat%20Eye%20Protection.pdf. Accessed on February **2014**.
75. Krishnamoorthy, K.; Ambade, A. V.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *J. Mater. Chem.* **2001**, *11*, 2909.

76. Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
77. Kim, J.; You, J.; Kim, B.; Park, T.; Kim, E. *Adv. Mater.* **2011**, *23*, 4168.
78. Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379.
79. Amb, C. M.; Kerszulis, J. A.; Thompson, E. J.; Dyer, A. L.; Reynolds, J. R. *Polym. Chem.* **2011**, *2*, 812.
80. Shen, D. E.; Abboud, K. A.; Reynolds, J. R. *J. Macromol. Sci. Pure Appl. Chem.* **2010**, *47*, 6.
81. Invernale, M. A.; Seshadri, V.; Mamangun, D. M. D.; Ding, Y.; Filloramo, J.; Sotzing, G. A. *Chem. Mater.* **2009**, *21*, 3332.
82. Xu, C.; Taya, M. U.S. Pat. 7,038,828 B2 (2006).
83. Reeves, B. D.; Thompson, B. C.; Abboud, K. A.; Smart, B. E.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 717.
84. Turac, E.; Sahmetlioglu, E.; Demircan, A.; Toppare, L. *J. Appl. Polym. Sci.* **2012**, *126*, 808.
85. Camurlu, P.; Durak, T.; Balan, A.; Toppare, L. *Synth. Met.* **2011**, *161*, 1898.
86. Li, Z.; Zhang, Y.; Holt, A.; Kolasa, B. P.; Wehner, J. G.; Hampp, A.; Bazan, G. C.; Nguyen, T.-Q.; Morse, D. E. *New J. Chem.* **2011**, *35*, 1327. DOI: 10.1039/c0nj00837k.
87. Reeves, B. D.; Grenier, C. R. G.; Reynolds, J. R. In Abstracts of Papers, 228th ACS National Meeting; American Chemical Society: Philadelphia, PA, **2004**.
88. Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; Cunningham, G. B.; McCarley, T. D.; Reynolds, J. R. *Polym. Prepr.* **2004**, *45*, 284.
89. Sotzing, G. A. U.S. Pat. 7,951,902 B2 (2011).
90. Ho, K.-C.; Tung, T.-S.; Chen, B.-Y. U.S. Pat. 7,342,708 B2 (2008).
91. Groenendaal, B.; Reynolds, J. R.; Gaupp, C. L.; Schwendeman, I. U.S. Pat. 7,022,811 B2 (2006).
92. Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules*, **1987**, *20*, 212.
93. Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
94. Chandrasekhar, P.; Masulaitis, A. M.; Gumbs, R. W. *Synth. Met.* **1990**, *36*, 303.
95. Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J. M. *J. Org. Chem.* **2005**, *70*, 1316.
96. Tiefenbacher, K.; Rebek, Jr. *J. Am. Chem. Soc.* **2012**, *134*, 2914.
97. European Standard EN 169 and German Standard DIN EN 169 for Eye & Face Protection. Available at: <http://www.hootsmart.co.uk/upload/supplyppehivis/News/EN166-Euro-Standards-Eye-and-Face-Protection.pdf>, <http://www.techstreet.com/products/1062414>, and <http://engineers.ihs.com/document/abstract/ZXWXJBAAAAAAAAAAAA>. Accessed on February **2014**.
98. Ma, C.; Taya, M.; Xu, C. *Electrochim. Acta* **2008**, *54*, 598.
99. Ma, C.; Taya, M.; Xu, C.; Ma, C.; Taya, M.; Xu, C. *Polym. Eng. Sci.* **2008**, *48*, 2224.
100. Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.
101. Mortimer, R. J.; Reynolds, J. R. *J. Mater. Chem.* **2005**, *15*, 2226.