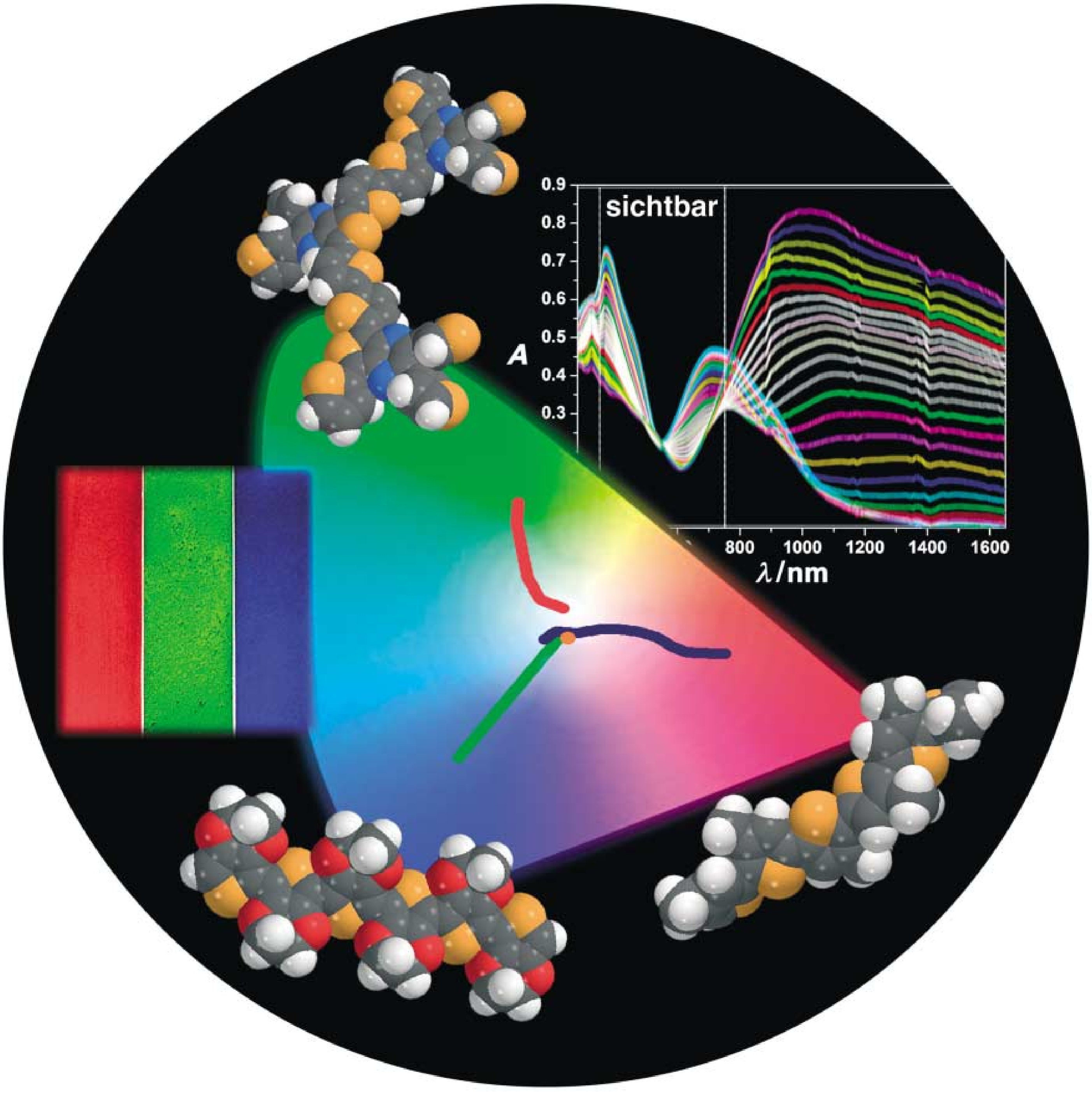
Zuschriften



Das erste in seiner Neutralform grüne leitfähige Polymer wurde hergestellt. Hohe Farbsättigung, schnelles Schalten und außerordentlich hohe Stabilität machen dieses Polymer hoch interessant für Anwendungen auf dem Gebiet elektrochromer Polymere. Mehr hierzu erfahren Sie in der Zuschrift von F. Wudl et al. auf den folgenden Seiten.

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Conducting Polymers

A Red, Green, and Blue (RGB) Polymeric Electrochromic Device (PECD): The Dawning of the PECD Era**

*Gursel Sonmez, Clifton K. F. Shen, Yves Rubin, and Fred Wudl**

The ability to have three complementary colors, red, green, and blue (RGB) constitutes an important step forward to the use of conducting polymers in polymeric electrochromic devices (PECDs). Although many red and blue colored polymers in their neutral form have been reported, no green colored conducting polymer has been reported to date because of the difficulty to obtain the absorptions required in the visible region to reflect the color green. Herein we report the electrochemical and optical properties of the first electrochemically prepared, neutral, green-colored conjugated polymer. The extreme stability of this polymer after 10000 double potential steps makes it the best, and only, candidate for completing the third leg of color space for polymeric electrochromics.

In the last few decades, conducting polymers (CPs) have been very actively pursued.[1] Several discoveries brought the CPs to full commercialization with applications in electrochromic rearview mirrors,[2,3] windows,[4,5] thin-film transistors,[6] displays,[7,8] sensors,[9,10] polymer light-emitting diodes,[11,12] photovoltaics,[13] and electrochromic devices.[14–17] More recently, research on CPs has mostly focused on their optical properties in the visible[17–20] and near infra-red (NIR)[21–25] spectral regions. Poly(thiophene) derivatives have been the most studied materials because they exhibit fast switching times, outstanding stability and high contrast ratios in the visible and NIR regions.

The earliest electrochromic materials in the visible region were the inorganic tungsten trioxide (WO_3) and iridium dioxide (IrO_2).[26] Because of the increased versatility of organic materials (viologens, metallophtalocyanines, and conducting polymers),[27,28] these compounds have recently received the brunt of attention for potential electrochromic applications.[29] Among organic materials, conjugated polymers have several advantages over small molecules and inorganic solids; these are, outstanding coloration efficiency, fast switching times,[30,31] multiple colorations with the same material,[17,20] fine-tunability of the band gap (and the color),[32,33] high stability,[14,16] thin film flexibility and cost effectiveness.

The three primary colors, red, blue, and green, are required for commercial electrochromic application. When three legs of color space are completed, all other colors can be obtained according to color mixing theory[34] which states that if two color stimuli are mixed, the resulting color stimulus will lie somewhere along a straight line connecting two points on the chromaticity diagram. The position of the point depends on the ratio of the amounts of the two mixed colors. A “fine tuning” of color is possible by adjusting film thickness. Owing to its effect on the brightness of transmitted light, sample thickness has a large influence on the perceived color. Unfortunately, the polymers studied so far mainly absorb/reflect blue and red light in their neutral states. Since absorption at only one dominant wavelength is required to give blue or red, these can be obtained relatively easily by tuning the CP's band gap. At least two absorption bands (red and blue) are required to observe a green color. While these chromophores absorb red and blue in the neutral form of the polymer, they should also deplete together when the polymer is oxidized. However, control of both chromophores at the same time with the same applied potential is very difficult. This difficulty to create and deplete two absorption bands in the visible from the same polymer, make a green neutral polymer almost impossible to realize. It is important to note that green can be obtained by color mixing theory but in this case at least three polymers will be required to obtain another color, which would be green. Therefore, it is crucial to obtain a real green color from an individual polymer to complete the three main legs of color space.

Recently, our group has initiated a study to obtain a conjugated polymer which reflects green light in the neutral state and is transparent in the oxidized state. We believed that the goal could be achieved with the synthesis of a polymer backbone containing two well-defined, isolated, conjugated systems which absorb blue and red light. Thus, a 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*]pyrazine (DDTP) monomer that would afford two conjugated chains was designed and synthesized (Supporting Information; Figure S1). One chain has electron donor and acceptor groups to decrease the band gap, which results in absorption of the blue light at wavelengths longer than 600 nm, and the other chain absorbs in the red at wavelengths below 500 nm.

PolyDDTP (PDDTP) films[35] were synthesized on platinum or indium tin oxide (ITO) coated glass slides by oxidative electropolymerization from a mixture in dichloromethane and acetonitrile (20/80, v/v) solution containing 10^{-2} M monomer and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6; Figure 1). The electrochemistry of polymerization and the polymer showed similar behavior to that of other CPs. An irreversible oxidation of the monomer appeared in the first cycle at +0.50 V versus Ag/Ag^+, followed by very fast deposition on subsequent cycles,

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Supporting information (synthesis schemes, cyclic voltammograms) for this article is available on the WWW under http://www.angewandte.org or from the author.

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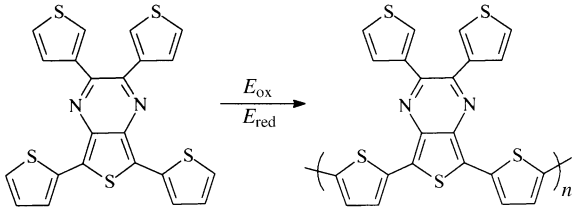

Figure 1. Electrochemical polymerization of DDTP.

owing to the redox system that grows rapidly at potentials lower than that of the monomer oxidation (Supporting Information; Figure S3). Note that the electrochemical oxidation of DDTP gives two oxidation peaks at 0.50 and 1.17 V (vs. Ag/Ag^+, Supporting Information; Figure S4). The first potential (0.50 V) corresponds to the oxidation of terthiophene and the second potential (1.17 V) may stem from the oxidation of 3-substituted thiophenes or follow-up reactions. As the monomer was polymerized at 0.50 V, the desired green material was obtained. A half-wave oxidation potential ($E^{ox}_{1/2}$) of the polymer, in monomer-free electrolyte solution, was observed at about 0.0 V (vs. Ag/Ag^+, Supporting Information; Figure S5). The linear dependence of the anodic and cathodic currents on the scan-rate demonstrates that the electrochemical processes are not diffusion limited. Since the main polymer backbone has both electron acceptor and donor groups, the polymer film can be both n- and p-doped. The half-wave reduction potential ($E^{red}_{1/2}$) of the polymer is at −1.42 V (vs. Ag/Ag^+, Supporting Information; Figure S6). From the difference between onset of oxidation and reduction potentials the band gap was determined to be approximately 1.15 eV.

The stability and the optical properties of the polymer for long-term switching between the oxidized and neutral states are the most important factors for the commercial application of CPs as PECDs. PDDTP films on a Pt button electrode were cycled 10000 times between their fully oxidized state at 0.58 V and the neutral state at −0.80 V in $LiClO_4$/propylene carbonate (PC; Figure 2). The charge involved during the electrochemical process was calculated for each voltammogram from the integration of the current during the redox process. The stability test of the polymer over a period of 10000 double potential cycles showed remarkable robustness without any significant charge or current loss. The cyclic voltammetry of the polymer was almost identical at the beginning and end of the stability test (Figure 2, insets). The small changes in the currents (ca. 4.5% increase in anodic and 1.5% decrease in cathodic peak current) and charge (ca. 10% increase) at the beginning of the stability test stem from the process of polymer electrochemical equilibrations. After reaching equilibrium at the 1500th cycle, the changes in anodic peak currents (i_{pa}), cathodic peak currents (i_{pc}) and the charge stored (Q_{stored}) are 0.26, 1.0, and 1.5%, respectively. This result indicates that PDDTP films can be cycled many times between oxidized and neutral states without any considerable change in electroactivity.

Figure 3 depicts the spectroelectrochemistry of PDDTP films. The π–π* transition of the neutral polymer (at −0.8 V vs. Ag/Ag^+) is split into two well-separated broad bands, as expected for green. One of these bands is located at wavelengths shorter than 500 nm with a maximum at 370 nm and covers the visible range, where red is absorbed. The other band is located at wavelengths longer than 600 nm, with a maximum at 725 nm; covering the visible range where blue is absorbed. The deep valley between these two absorption bands with a minimum at 550 nm controls the fine-tuning of the green color. The differences in transmittance (%Δ*T*) of the peaks at 370 and 725 nm and the lowest part of the valley at 550 nm are 42% and 27%, respectively. These values are sufficient to produce a highly saturated green color. Since the polymer has two absorption bands, the electronic band gaps are calculated from the onset of two π–π* transitions, which are 2.05 and 1.10 eV for the transitions at 377 and 725 nm, respectively. Noted that the band-gap value determined from electrochemistry is in agreement with the second value determined from spectroelectrochemistry. Upon electrochemical oxidation of the film, the π–π* transitions of both bands are depleted at the expense of an intense absorption band centered in the NIR, which corresponds to low-energy

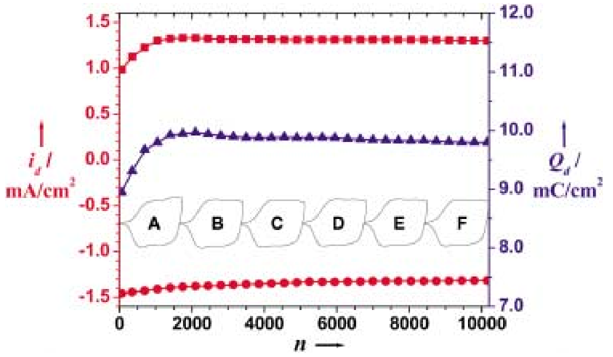

Figure 2. Stability test for long term switching: Variation of anodic (i_{pa}; ■) and cathodic (i_{pc}; ●) peak currents and the charge stored (Q_{stored}; ▲) by the polymer film as a function of number of cycles (*n*). The film was cycled more than 10000 times at a scan rate of 200 mVs^{-1} between −0.80 and +0.58 V versus Ag/Ag^+ in 0.1 M $LiClO_4$/PC. The cyclic voltammograms inserted between the i_{pc} (●) and Q_{stored} (▲) curves show the essential invariability with cycle number; A = 500, B = 2000, C = 4000, D = 6000, E = 8000, F = 10000th cycle.

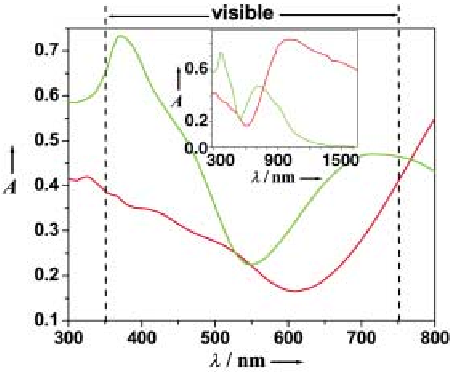

Figure 3. Spectroelectrochemistry of PDDTP film on an ITO-coated glass slide in 0.1 M Bu_4NPF_6/MeCN solution in two different oxidation states: neutral (——) and oxidized (——).

charge carriers. This depletion upon oxidation makes the polymer film more transparent but, unfortunately, residual absorptions remain in the visible region giving, a transmissive brown color. The detailed spectroelectrochemistry of PDDTP films as a function of applied potential is given in the Supporting Information (Figure S7).

The stability and response time upon electrochromic switching of the polymer film between its neutral and oxidized forms in the visible (370 and 725 nm) and NIR region (1600 nm) was monitored (Figure 4). The film was switched between its neutral (reduced) and oxidized form. The contrast ratios (Δ% T) of the polymer at 370, 725, and 1600 nm are 23, 12 and 85 %, respectively. These transmittance changes in the visible are sufficient to change the color from green to transmissive yellowish-brown. The extreme stability of the Δ% T in time and the fast switching property (about 0.5 s) at all three wavelengths makes this polymer a promising material for completion of the RGB colors.

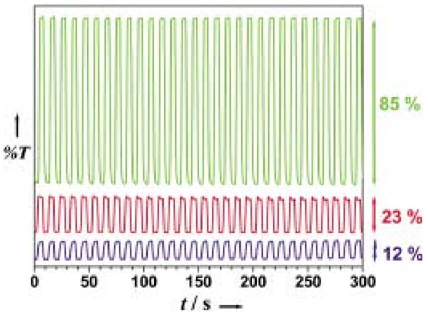

Figure 4. Double potential switching of PDDTP film on an ITO-coated glass slide at 370 (——), 725 (——), and 1600 (——) nm between its reduced state at −0.80 V and oxidized state at +0.58 V (vs. Ag/Ag$^+$) in 0.1 M Bu_4NPF_6/MeCN.

After having demonstrated the electrochemistry, stability, and optical properties of our new polymer, we selected two well-known CPs, poly(3-methylthiophene) (P3MT) as the red and poly(3,4-ethylenedioxythiophene) (PEDOT) as the blue, to complete three legs of the color space. Representation of the hue and saturation for these two polymers with PDDTP is given in Figure 5. The colors of the polymers in their neutral states are located in the color space where the three main colors, RGB, are located. As the polymers are exposed to oxidation, they move towards the white point located at the center of the x–y color track and they become transparent. Lab and Yxy coordinates of P3MT, PEDOT, and PDDTP in their neutral and oxidized states are given in the Supporting Information (Table S1). Figure 6 shows the actual colors of these three polymers in a PECD. The polymer films present highly saturated RGB colors in their neutral state at the applied potential.[36]

In conclusion, the first neutral, green conducting polymer was synthesized. High green color saturation, fast switching, and extreme stability, make this material promising for completion of the deficient third leg of color space and also brings polymer electrochromics closer to RGB realization. Now that RGB is established, it will be only a matter of clever engineering to take full advantage of PECDs.

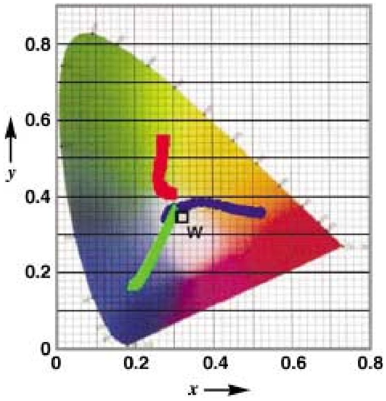

Figure 5. Representation of the hue and saturation x–y track for P3MT (●), PDDTP (■), and PEDOT (▲) film as the applied potential changes from −0.8 to +0.8 V (vs. Ag/Ag$^+$; W = white point).

Figure 6. RGB colors obtained from polymeric electrochromic device (PECD): P3MT, PDDTP, and PEDOT were used as red, green, and blue polymers, respectively. The polymer films were held at the same potential of −0.80 V (vs. Ag/Ag$^+$) to keep them in their neutral form.

Experimental Section

All chemicals were purchased from Aldrich Chemical. Propylene carbonate (PC; 99.7 %, anhydrous), dichloromethane (DCM) and acetonitrile (MeCN) were distilled over calcium hydride before use.

All reactions were performed under argon or glove box unless stated. The products were put under high vacuum overnight after flash chromatography. NMR spectroscopy studies were carried out on Bruker Avance-500 or Avance-600 spectrometers. Tetramethylsilane (TMS) was used as the internal standard for ^{1}H NMR and the deuterated solvent ($CDCl_3$) was used as a standard for ^{13}C NMR spectroscopy. FT-IR spectra were recorded on a Mattson Infinity IIa spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit. High-resolution mass spectra (HRMS) were obtained with a VG ZAB-SE mass spectrometer with EI source. Column chromatography was performed on silica gel 230–400 mesh (flash) from E. Merck or from Scientific Absorbents; thin layer chromatography (TLC) was performed on glass plates coated with silica gel $^{60}F_{254}$ from E. Merck.

Electropolymerization was carried out with a BAS 100B/W potentiostat, employing a platinum button (diameter: 1.6 mm; area 0.02 cm^2) or ITO coated glass slides as working electrode, a platinum flag or wire as counter electrode, and a silver wire or 0.01 M Ag/$AgNO_3$ (Ag/Ag$^+$) as reference. The electrolytes used were 0.1 M of $LiClO_4$ or tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in PC, CH_2Cl_2, MeCN or mixture of MeCN and CH_2Cl_2. The electrodeposition was performed from a 0.01 M solution of the monomer in the electrolyte potentiodynamically at a scan rate of 20 mV s^{-1} or potentiostatically at 0.52 V vs. Ag/Ag^+. Cyclic voltammetry was carried out using the same electrode setup using monomer-free electrolyte solution.

Spectroelectrochemical data were recorded on a Shimadzu UV 3101PC UV/Vis-NIR spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was an ITO-coated glass slides ($7 \times 50 \times 0.6$ mm, $R_s \leq 10\ \Omega/\square$, Delta Technologies Inc.), the counter electrode was a platinum wire, and a Ag wire was used as pseudo reference electrode. The pseudo reference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(Fc/Fc^+) = +0.140$ V vs. Ag wire and $+0.075$ V vs. Ag/Ag^+ in 0.1 M $LiClO_4$/PC). The potentials are reported versus Ag/Ag^+. Polymer films for spectroelectrochemistry were prepared by potentiodynamic deposition on ITO-coated glass slides.

Colorimetry measurements were obtained using a Minolta Chroma Meter CS-100A and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements.[37] As for spectroelectrochemistry, a three-electrode cell was employed. The potential was controlled by the same BAS 100B/W potentiostat. The sample was illuminated from behind by a D50 (5000 K) light source in a light booth (Minolta GTI ColorMatcher) specially designed to exclude external light and to illuminate from behind. The color coordinates are expressed in the CIE 1931 *Yxy* color space where the *Y* value is a measure of the luminance in Cd/m^2. The relative luminance, expressed in %, was calculated by dividing the *Y* value measured on the sample by the Y_0 value corresponding to the background. Note that the relative luminance is frequently reported instead of the luminance because it gives a more meaningful value.

A Fujifilm (FinePix 4500) digital camera was used to take photographs and movie of the polymer electrochromic device at high resolution.

DDTP: 1,2-di(thien-3-yl)ethane-1,2-dione (363 mg, 1.63 mmol)[39] and catalytic amount of *p*-toluene sulfonic acid (15 mg) were added to a solution of 3′,4′-diamino-2,2′:5′,2′′-terthiophene (350 mg, 1.26 mmol)[38] in chloroform (50 mL), under argon atmosphere. The reaction mixture was heated under reflux for 12 h before cooling down. After removing all volatiles, the residue was redissolved in dichloromethane and absorbed onto silica gel. The crude product was purified by column chromatography on silica gel using a solvent mixture (hexanes:CH_2Cl_2 1:1) to give the pure product after removal of solvent as a dark purple powder in 94.2 % yield (550 mg, 1.18 mmol). M.p. > 230 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.12$ (dd, $J = 5.0$ Hz, $J = 3.7$ Hz, 2H), 7.33 (dd, $J = 5.0$ Hz, $J = 3.0$ Hz, 2H), 7.39 (dd, $J = 5.0$ Hz, $J = 1.0$ Hz, 2H), 7.42 (dd, $J = 5.0$ Hz, $J = 1.2$ Hz, 2H), 7.60 (dd, $J = 3.0$ Hz, $J = 1.2$ Hz, 2H), 7.65 ppm (dd, $J = 3.7$ Hz, $J = 1.0$ Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 124.51$, 124.60, 125.21, 126.64, 127.26, 127.78, 129.00, 134.58, 137.12, 140.29, 148.09 ppm; HRMS calcd for $C_{22}H_{12}N_2S_5$ [M^+] 463.9604, found 463.9603.

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[35] Since PDDTP was insoluble in any solvent, an alkyl-substituted counterpart of the monomer (Supporting Information; Figure S2) was synthesized and electrochemically polymerized under the same conditions. Then polymer films were reduced electrochemically in monomer-free electrolyte solution and dissolved in [D_2]tetrachloroethane. ^{13}C NMR spectroscopy of the resulting polymer demonstrated that hydrogen atoms on the α and α' positions of the thiophene rings labeled with the letters c and d (Supporting Information) remained after electrochemical polymerization confirming the proposed structure for PDDTP.

The related work for alkyl-substituted PDDTP will be published separately.

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