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SAND2018-10177J

A single molecular template-based full-colour electrochromic polymer

Hui Zhang[1], Yuzhang Liang[1], A. Alec Talin[2,*], Ting Xu[1,*]

1. National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences and Collaborative Innovation Centre of Advanced Microstructures, Nanjing University, Nanjing 210093, China

2. Sandia National Laboratories, Livermore, CA 94551, USA

*Email: xuting@nju.edu.cn, aatalin@sandia.gov

With low-cost and simple room-temperature processing, organic electrochromic polymers have attracted considerable attention as a promising material platform for flexible, low-power-consuming optoelectronic devices. However, the complexity of having to combine several distinct polymers to achieve a full-color gamut have limited polymer electrochromic devices to niche applications. Here we report an electrochromic conjugated polymer based on the molecular template, [4,7-di((3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-yl)-3,4-ethylenedioxythiophene)] (PEP)which exhibits fast full-color reversible tuning capability, good electrochemical stability and high optical memory effect. As a proof-of-concept demonstration, we fabricate a poly(PEP)-based, single-layer solid-state electrochromic device exhibiting full-color response. This single molecular template-based electrochromic polymer offers an effective approach to dynamically manipulate color and enables a variety of optoelectronic applications in the visible spectrum.

Keywords: full-color tuning, single molecular template, conjugated polymer, electrochromic material, electrochromic device.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Electrochromic materials show a reversible colour change when reduced or oxidized electrochemically by application of a small voltage. Both organic and inorganic EC materials have generated much interest in academia and industry for their fascinating spectroelectrochemical properties and practical applications[1-3]. Compared with the complexity and high-cost of thin film deposition typically required in fabrication of inorganic EC materials such as WO3, organic conjugated polymers can be prepared using ambient pressure, room temperature solution-based processing[4,5]. Other important advantages for polymer ECs is their synthetic flexibility to tune their optoelectronic properties as well as their mechanical flexibilitys[6-11]. Flexible, low cost EC devices are particularly attractive for retrofitting onto existing windows for energy savings or window based displays, as well as for a variety of wearable medical and fashion related applications. Unfortunately, most of the conjugated polymers, such as Poly(3,4-ethylenedioxythiophene) (PEDOT) and Poly(3,4-propyylenedioxythiophene) (PProDOT), can only be switched from natural-colored to oxidized-transparent states[5, 12-13]. The monotony of the generated colors significantly limits their application in colorful electrochromic displays[14-15].

As an important factor to evaluate the performance of electrochromic materials, color gamut directly links to the human visual perception and determines electrochromic materials' application scenarios[16-17]. Most EC polymers displaying several different colors reported to date are obtained by copolymerizing two (or more) kinds of EC monomers together to increase the color gamut[18-22]. However, the complicated copolymerization process as well as concerns about chemical compatibility between different conjugated polymers restrict their practical applications. As an alternative method, recently, single polymer-based full-colour ECs have been achieved by employing plasmonic nanostructured electrodes[23]. The working principle of this approach is to use surface plasmon polaritons (SPPs) in a nanostructured electrode to filter the spectrum of white light and generate individual colours. Although the EC polymer may have a narrow absorption spectrum, the confinement of the electromagnetic field characteristic of SPPs near the nanostructured electrode allow effective modulation across the visible spectrum, so long as the extinction coefficient is non-zero. Nevertheless, the high-cost associated with fabrication of large-scale nanostructured electrodes represents a significant challenge for mass production.

Herein we report the synthesis of a conjugated polymer, {poly(4,7-di((3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-yl)-3,4-ethylenedioxythiophene)), poly(PEP) and demonstrate its applicability for full-color reversible EC tuning. To our knowledge, this is the first report on the synthesis of a single molecular template-based conjugated polymer with full-color tunability and where the EC derived colors form a closed loop in the CIE chromaticity diagram. In addition to full-color tunability, poly(PEP) exhibits excellent electrochemical stability, , sub-second switching time and good optical memory effect. This single molecular template-based EC polymer offers an effective way to dynamically manipulate its absorption spectrum in the visible range colors and we potentially enabling a myriad ofoptoelectronic applications.

Figure 1a shows schematically the poly(PEP) synthesis route, where the detailed experimental procedures are given in the Methods Section. First, ProDOT(Me)$_2$ is obtained from the reaction between 3,4-dimethoxythiophene and 2,2-dimethyl-1,3-propanediol (route i)[5]. Then, 2-(tributylstannly)-3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (2-(tributylstannly)-ProDOT(Me)$_2$, yield: 89%) is synthesized by combining ProDOT(Me)$_2$ with n-butyllithium (n-BuLi), tributylstannyl chloride (Bu_3SnCl) in dry tetrahydrofuran (THF) (route ii), of which could be further used for the Stille coupling reaction[24]. On the other side, 2,5-dibromo-3,4-ethylenedioxythiophene (2,5-dibromo-EDOT) is synthesized according to bromine substitution reaction (route iii)[25]. Next, the 4,7-di((3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-yl)-3,4-ethylenedioxythiophene) (ProDOT(Me)$_2$-EDOT-ProDOT(Me)$_2$, PEP), a yellow green solid (yield: 20%), is obtained via Stille coupling reaction between 2-(tributylstannly)-ProDOT(Me)$_2$ and 2,5-dibromo-EDOT (route iv). Here, proton nuclear magnetic resonance (^{1}H NMR) spectra of 2-(tributylstannly)-ProDOT(Me), 2,5-dibromo-EDOT and PEP are provided as shown in Figure 1b. All alkyl peaks of corresponding monomers are well presented, indicated that the experimental results are consistent with expectations. Herein, all preliminary preparations for poly(PEP) synthesis have been completed. Then, the single molecular template-based poly(PEP) is obtained via electrochemical polymerization[26,27] of its corresponding monomer (PEP) in acetonitrile (ACN) and tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6, 0.1mol L^{-1}) system (route v).

During the electropolymerization process, the monomers are oxidized to form a radical

cation. According to molecular orbital theory, the reaction between radical cations mainly occurs on the frontier molecular orbital. Considering the structure of PEP molecule, the atoms at α-sites of the thiophene rings have a negative Mulliken charge and will donate electrons during electrochemical polymerization[25]. Therefore, quantum chemical calculation is applied to elucidate the polymerization mechanism and structure of the newly-obtained compound, PEP. Figure 2 shows the quantum chemical calculation results of PEP, including highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and electron spin density (ESD). The calculated molecular orbitals of PEP show that the both HOMO and LOMO proportions of α-sites are higher than those of other atoms (Figure 2a and 2b), which implies that atoms of α-sites are more easily be excited to the lowest energy orbital. Therefore, it can be concluded that the polymerization site of PEP is mainly located at the α-sites[25,28]. In addition, the ESD is regarded as an important factor in controlling polymerization. It is generally believed that cationic radicals interacting with each other is most likely to occur at the highest position of the ESD. For poly(PEP), the highest unpaired ESDs are all obviously located at α-sites of thiophene ring as shown in Figure 2c. Hence, the calculation of ESD further proves the conclusion that the polymerization of PEP only happened at α-sites of thiophene ring.

Figure 3a displays the recorded cyclic voltammograms (CVs) during the potentiodynamic electrochemical polymerization of PEP. There is a pair of reversible reduction peak (0.17 V) and oxidation peak (0.66 V) in the potential range of -1.0 to 1.5 V, which can be respectively assigned to the oxidation and the reduction process of PEP radical anions. This representative electrochemical growth reveals electroactivities of monomers and formation of corresponding polymers. The broad redox peaks of the polymer can be ascribed to the wide distribution of polymer chain length with increasing π-π* conjugation on the polymer backbone and the conversion of conductive species on the polymer main chain from a neutral to a metallic state[25,28-30].

To investigate the electrochemical behaviors of poly(PEP), a polymer-coated Pt electrode is studied by cyclic voltammetry in monomer-free electrolyte to test its electroactivity. Figure 3b shows the CVs of poly(PEP) under different potential scanning rates which exhibit broad anodic and cathodic peaks. Since the current densities of anodic peaks ($j_{p,a}$) and cathodic peaks

($j_{p,c}$) are linearly proportional to the scan rate we conclude that the redox processes is non-diffusion controlled[31-33] and the electroactive materials are well-adhered to the working electrode surface (Figure 3c). The linear behavior further implies that poly(PEP) does not diffuse into electrolyte solution even with the scan rates up to 300 mV s^{-1}.

In general, the electrochemical stability of conducting polymers is critical to device lifetime, an essential requirement for practical applications. The long-term stability upon cycling of poly(PEP) film deposited on the Pt electrode is investigated with a fixed potential scan rate (100 mV s^{-1}) in monomer-free electrolyte solution system. Figure 3d shows the corresponding recorded CVs of poly(PEP) film. By comparing the integral area from 0 V to 0.6 V with the initial cycle, we observe that the electrochemical activity retained up to 85.73% of its original valued after 5000 cycles. (Table S1). Even with the potential range extended from 0 V to 1.0 V, the electrochemical activity of poly(PEP) film maintains ~82 % (Figure S1 and Table S2). These results imply that poly(PEP) is an excellent conducting polymer with long-term electrochemical cycling stability.

Color gamut is an important factor in the performance evaluation of an electrochromic polymer intended for full-color display applications. Figure 4a shows the visible to near-infrared absorption spectra of the poly(PEP) film measured under different applied voltages ranging from -0.7 V to 0.6 V in monomer-free electrolyte solution. Due to π-π* transitions of thiophene rings[12,33], Poly(PEP) film has a dominant absorption band in the wavelength range from 500 nm to 600 nm with negative potentials. When the applied potential gradually increases from -0.7 V to 0.6 V, the intensity of the valence of π-π* transition decreases, which results reduced absorption in this wavelength range. At the same time, a new absorption band appears at ~850 nm, due to the formation of polaronic and biopolaronic carriers on the polymer backbone[16,25]. Figure 4b shows the unaltered color of poly(PEP) film under several potentials. Depending on the applied voltage, the film yields different colors ranging from purple, red, orange, yellow, yellowish green, green, cyan to blue. For better quantification the colors of poly(PEP) films, we map these colors into CIE 1931 chromaticity diagram, as show in Figure 4c. It can be seen that the color coordinates form a closed loop, indicating that the poly(PEP) is a truly full-color tunable electrochromic material. The detailed data of coordinate and applied voltage for each color are given in Table S3.

To characterize the optical switching properties of poly(PEP), film a square wave potential step is applied to a sample in monomer-free ACN-Bu_4NPF_6 (0.1 mol L^{-1}) system. The electrochromic parameters including optical contrast ratio (ΔT%) and response time are determined by measuring the change in transmittance with respect to time at a specific absorption wavelength. Figure 5a shows the measured transmittance of the poly(PEP) film at 550 nm when it is switched between green and purple states. After sweeping 6100 cycles over a period of 17 hours, the value of Δ%T between these two states held at 39.75%, without any significant change as compared with its initial state (Δ%T=40.88%). Meanwhile, the poly(PEP) film only needs 0.8 s to change from green to purple color. Together, these results indicate that poly(PEP) film has promising long-term optical stability and fast switching speed.

In addition to stability and switching speed, we investigate the optical memory of poly(PEP) films using optical spectroscopy combined with double step chronoamperometry. The polymer film is polarized by application of 0.25 V for green state (-0.55 V for purple state) for 2 s, and then the circuit is held disconnected for 100 s while the optical transmittance is recorded. Figure 5b illustrates the measured transmittance spectra at the wavelength of 550 nm as a function of time. Both green and purple states are highly stable and the device maintains its color without significant variations in optical contrast after a 4 000s continuous testing. Only 0.6% (4.5%) of the Δ%T value decreases for the green (purple) state, which indicates the poly(PEP) has excellent optical memory.

Finally, as a proof-of-concept demonstration, we design and fabricate a poly(PEP)-based, solid-state electrochromic device. The schematic diagram of the device is shown in Figure 6a. Here we use the mixture of tetrabutylammonium tetrafluoroborate (TBATFBA), ACN, poly(methyl metacrylate) (PMMA) and propylene carbonate (PC) (mass ratio of 3:70:7:20) as the gel electrolyte. The electropolymerized poly(PEP) film and gel electrolyte are sandwiched between two indium tin oxide (ITO) coated glass slides, one of which has a pattern of mass-energy equation ($E=mc^2$) prepared by laser etching (Figure S2). As expected, the device exhibits vivid colors and the color of each characters can be individually controlled under different potentials, including purple, red, yellow, green, and blue with the applied voltage from -2.0 V to 2.5 V (Figure 6b-d). This applied voltage range is a little bit higher than the previous test because the ionic conductivity of gel electrolyte is less than that of the liquid electrolyte

(leading to higher resistive losses) and detailed voltage value for each color is given in Table S4.

In conclusion, we have synthesized a single molecular template-based organic electrochromic material poly(PEP). It displays full-color reversible tunability, long-term cyclability and stability. As a proof-of-concept demonstration, we fabricated a poly(PEP)-based, solid-state electrochromic device exhibiting full-color response. As an effective approach to dynamically manipulate colors, this single molecular template-based electrochromic polymer is promising for a variety of low-cost optoelectronic applications in the visible range.

Methods

Chemicals and Equipment.

3,4-dimethoxythiophesssne (98%, J&K Scientific Ltd.), 2,2-dimethyl-1,3-propanediol (98%, J&K Scientific Ltd.), p-toluenesulfonic acid monohydrate (pTSA, 99%, J&K Scientific Ltd.), 3,4-ethylenedioxythiophene (EDOT, 98%, Sigma-Adrich), N-bromosuccinimide (NBS, 99%,), n-butyllithium (n-BuLi, 2.5 mol L^{-1} in hexanes, J&K Scientific Ltd.), tributylstannyl chloride ($SnBu_3Cl$, 98%, Sigma-Adrich), N,N-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Adrich), dichloromethane (CH_2Cl_2, 99.8%, J&K Scientific Ltd.), chloroform ($CHCl_3$, >99%, J&K Scientific Ltd.), toluene (anhydrous, 99.8%, Sigma-Adrich). Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 99%, Energy Chemical) are stored at 4ºC and used without further purification. Acetonitrile (ACN, >99%) is purified by distillation with calcium hydride under a nitrogen atmosphere before use. Tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6, for electrochemical analysis, ≥99.0%, Sigma-Aldrich) is dried under vacuum at 100ºC for 24 h before use. Tetrabutylammonium tetrafluoroborate (TBATFBA, Acros Organics, 95 %) is dried in vacuum at 80 ºC for 24 h before use. Tetrahydrofuran (THF, 99.5%, J&K Scientific Ltd.) is distilled over Na/benzophenone prior to use. Propylene carbonate (PC, 99.5%, SuperDry) and poly(methyl metacrylate) (PMMA), and other reagents (analytical grade, >98%) are purchased commercially from J&K Scientific Ltd. and are used without any further treatment.

Electrochemical experiments are performed on a Gamry REF3000-31122 (Gamry Instruments, USA) electrochemical workstation. Spectroelectrochemical studies and colorimeter measurements are carried out on an Ocean View USB 2000+ H15520 ultraviolet–visible (UV-vis) spectrophotometer (Ocean Optics Inc.). The Bruker AV 400 NMR spectrometer is employed for ^{1}H NMR spectra, and $CDCl_3$ is selected as the solvent. Infrared spectra are determined with a Bruker Vertex 70 Fourier-transform infrared (FT-IR) spectrometer with samples in KBr pellets. Film thicknesses are determined using a DEKTAK 3030, Surface Profile Measuring System.

Synthesis

3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (ProDOT(Me_2)).

4.5 g (31.2 mmol) of 3,4-dimethoxythiophene, 21.6 g (208 mmol) of 2,2-dimethyl-1,3-propanediol, 0.4 g (3.1 mmol) of p-toluenesulfonic acid monohydrate, and 30 mL of toluene. The solution is heated at 80°C, stirred for 12h. Then filtered and washed with water, and the toluene is removed under vacuum by rotary evaporation to yield a green viscous oil. Purified the oil by silica column chromatography (2:3 methylene chloride/heptane as eluent) to afford 2.1 g (Yield: 56%) of white product. ^{1}H NMR (400 MHz, $CDCl_3$, Figure S3): δ 1.02 (s, 6H), 3.73 (s, 4H), 6.47 (s, 2H).

2,5-dibromo-3,4-ethylenedioxythiophene (2,5-dibromo-EDOT).

EDOT (2.0 g, 14.07 mmol) and N-bromosuccinimide (5.5 g, 30.9 mmol) are dissolved in 50 mL DMF. Stirred for 2.5 h at room temperature then poured into 200 mL of distilled water. The organic layer is separated, neutralized with sodium bicarbonate, and filtered. The solvent is removed under vacuum. The crude product is purified by silica column chromatography ($CHCl_3$ as eluent) to yield 3.63 g (85%) of white crystals. ^{1}H NMR (400 MHz, $CDCl_3$, Figure S4): δ 4.27 (s, 4H).

2-(tributylstannly)-3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (2-(tributylstannly)-ProDOT($Me)_2$).

A solution of ProDOT$(Me)_2$ (4.0 g, 21.7 mmol) in 100 mL dry THF is cooled to -78°C and blanketed three times by argon atmosphere. 12.8 mL (16.0 mmol) of n-BuLi (2.5 M in hexane)

is slowly added dropwise to the solution within 30 min under argon. The mixture is stirred for 1.5 h under -78°C, and then warmed to -40°C. Tributyltin chloride (11.7 g, 18.0 mmol) is added slowly to the solution, stirred and then the temperature is slowly warmed to room temperature. Moreover, the mixture was stirred at room temperature for 12 h under argon atmosphere. The residue is filtered, and then the solvent is evaporated under vacuum by rotary evaporation. The new production (9.92 g, yield: 89%) is used directly for the Stille coupling reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, Figure S5): δ 6.72 (s, 1H), 3.70 (s, 2H), 3.63 (s, 2H), 1.01 (s, 6H), 1.56 (t, 6H), 1.32 (t, 6H), 1.08 (t, 6H), 0.89 (t, 9H).

4,7-di((3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-yl)-3,4-ethylenedioxythiophene (ProDOT(Me)$_2$-EDOT-ProDOT(Me)$_2$).

Under nitrogen atmosphere, a solution of 1.8 g (6 mmol) of 2,5-Dibromo-EDOT and 6.1 g (13 mmol) of 2-(tributylstannly)-ProDOT(Me)$_2$ are formed in dry THF, $Pd(PPh_3)_4$ is also added as the catalyst. Following the mixture is magnetically stirred at room temperature for 30 min under nitrogen atmosphere. The mixture is heated to reflux with vigorous stirring for another 24 h, and then, concentrated under vacuum. The desired compound PEP is finally separated as yellow green solid (0.62 g, yield: 20%) by silica column chromatography ($CHCl_3$ as the eluent). ^{1}H NMR (400 MHz, $CDCl_3$, Figure S6): δ 6.43 (s, 2H), 4.35 (s, 4H), 3.84 (s, 4H), 3.73 (s, 4H), 1.08 (s, 12H).

Electrochemistry

The potentiodynamic and potentiostativ electrochemical polymerization of PEP is carried out in ACN-Bu_4NPF_6 (0.1 mol L^{-1}) system in a three electrodes sealed cell with a platinum working electrode. In electrochemical syntheses, the working and counter electrode are platinum wires with a diameter of 1.0 mm. Ag/AgCl electrode is used as the reference. To obtain a sufficient amount of polymer for characterizations, Pt sheets with surface area of 12 and 10 cm^2 platinum sheet are used as working and counter electrodes, respectively. Polymer film is washed repeatedly with diethyl ether to remove the electrolyte and monomer after the polymerization. The electrochemical polymerized poly(PEP) give a number-average molecular weight 3486.8 g mol^{-1} with polydispersity of 1.2. FT-IR and UV-vis spectra of the PEP and poly(PEP) are also recorded for the structural characterization as shown in Figure S7 and Figure S8, respectively.

For spectroelectrochemistry, poly(PEP) film is obtained by direct anodic oxidation of corresponding monomer PEP (0.05 mol L^{-1}) on ITO-glass (10 × 50 × 1.1 mm, <10 ohm/sq) slides at a constant potential of 0.70 V for 50 s in ACN-Bu_4NPF_6 (0.1 mol L^{-1}) system. For electrochromic device, the poly(PEP) film that on the mass-energy equation shaped ITO-glass (50 × 100 × 1.1 mm, <10 ohm/sq) is synthesized by electrochemical polymerization in ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution at the potential of 0.70 V for 70 s with a monomer concentration of 0.05 mol L^{-1}. The thickness of poly(PEP) film is 300~350 nm.

Quantum chemical calculations

Quantum chemical calculations are implemented with the Gaussian 09 program package. The geometry optimization of the PEP is performed using density functional theory (DFT) method at B3LYP/6-31 G(d,p) level of theory. Vibrational frequencies are assessed at the same level to identify the real minimum energy structures. Electronic transition energies and oscillator strengths are obtained by time-dependent density functional theory (TD-DFT) using B3LYP functional and the 6-31 G(d,p) basis set.

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Acknowledgements

The authors acknowledge support from the Thousand Talents Program for Young Professionals,

Collaborative Innovations Center of Advanced Microstructures and Key Research and Development Program from Ministry of Science and Technology of China under Grant No. 2016YFA0202100 and 2017YFA0303700. AAT was funded by Sandia's Laboratory-Directed Research and Development program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Author Contributions

H. Z. and Y. L synthesized the material and performed the experiment. T. X. directed the project. All authors contributed to the interpretation of results and participated in manuscript preparation.

Competing Interests

The authors declare no competing financial interests.

Figure and caption

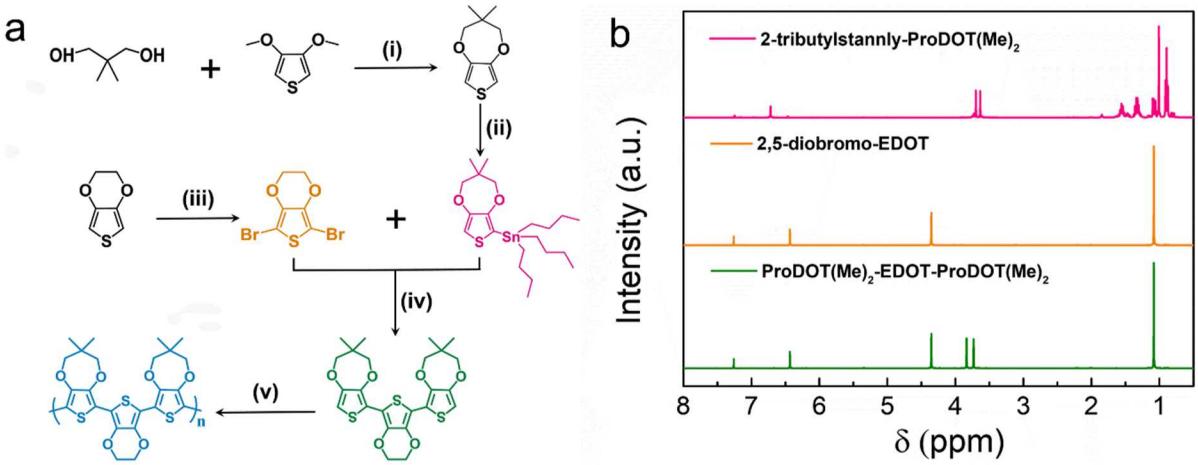

Figure 1. Materials synthesis and characterization. (a) Synthetic route of poly(PEP), conditions: (i) pTSA, toluene, 80 ^{0}C; (ii) *n*-BuLi, dry THF, -78 ^{0}C, chlorotributyltin, -40 ^{0}C, RT; (iii) NBS (2.2 eq.), $CH_3COOH/CHCl_3$, RT; (iv) $Pd(PPh_3)_4$, dry THF, refluxing, (v) ACN-Bu_4NPF_6, electrochemical polymerization; (b) ^{1}H NMR spectra of 2-(tributylstannyl)-ProDOT(Me)$_2$, 2,5-dibromo-EDOT and ProDOT(Me)$_2$-EDOT- ProDOT(Me)$_2$.

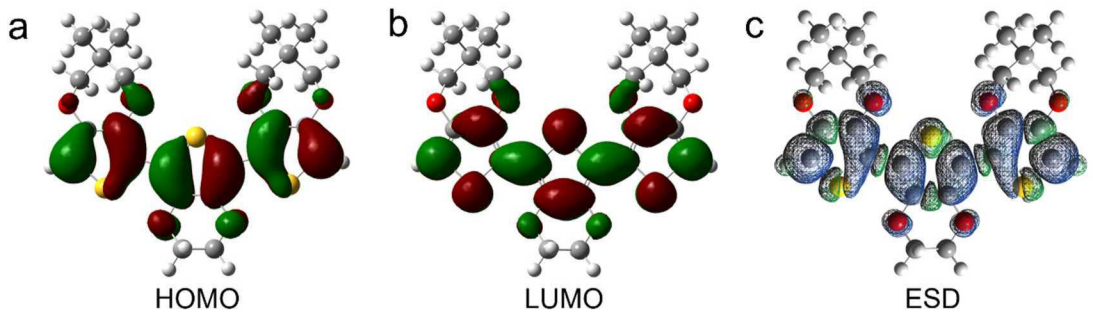

Figure 2. Quantum chemical calculations. (a) HOMO, (b) LUMO orbitals of PEP monomers and (c) ESD for its radical cations.

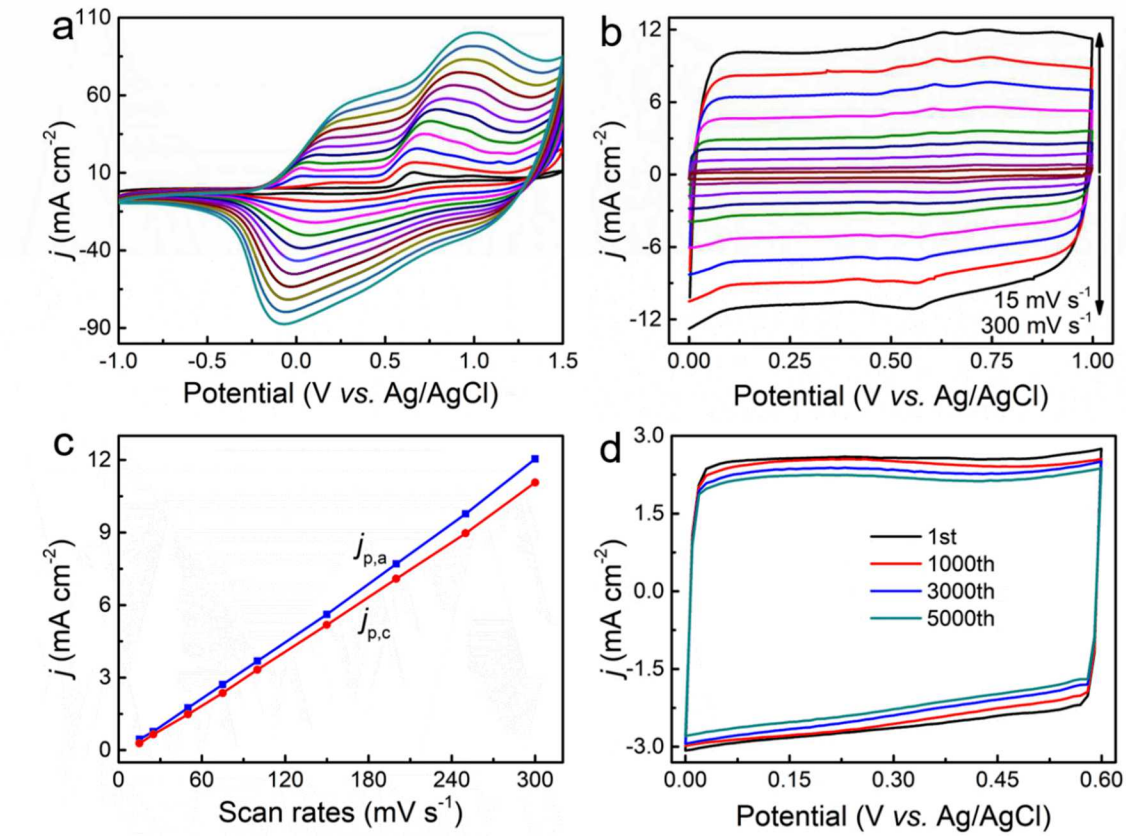

Figure 3. Electrochemical properties. (a) CVs of PEP (0.05 mol L^{-1}) in ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution at the potential scan rate of 100 mV s^{-1}; (b) CVs of poly(PEP) in monomer-free ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution, potential scan rates: 15 ~ 300 mV s^{-1}; (c) plots of redox peak current densities as a function of potential scan rates. (d) Long-term CVs of poly(PEP) in monomer-free ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution, the potential range is 0 ~ 0.6 V, potential scan rate: 100 mV s^{-1}.

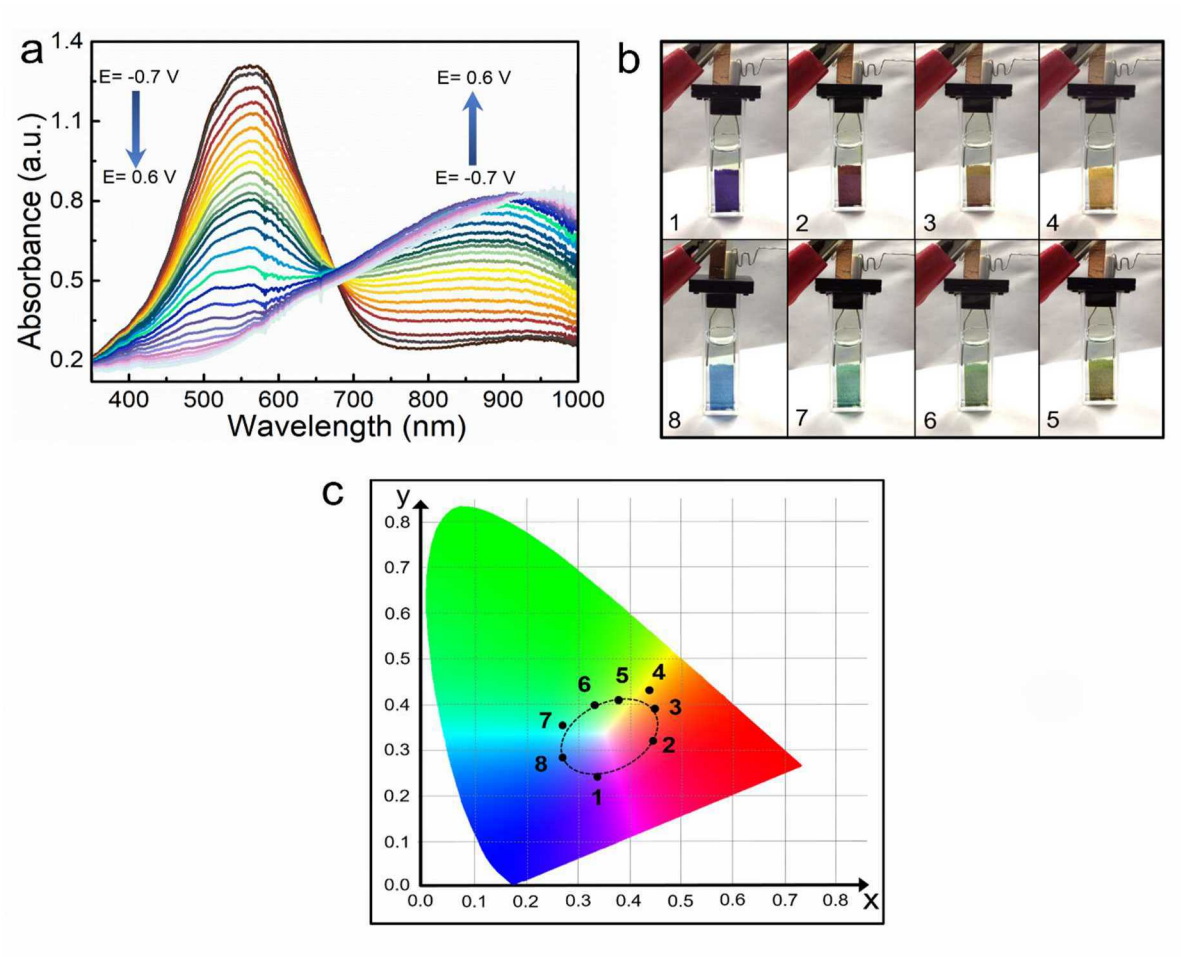

Figure 4. Spectroelectrochemistry and the color change of poly(PEP) film under different potentials. (a) Measured absorption spectra of poly(PEP) in the potential range (-0.7 V to 0.6 V, with a 0.05 V step); (b) color changes and (c) color coordinates of poly(PEP) film with different applied potentials: (1) -0.55 V, (2) -0.45 V, (3) -0.25 V, (4) -0.20 V, (5) 0.10 V, (6) 0.25 V, (7) 0.35 V, (8) 0.45 V.

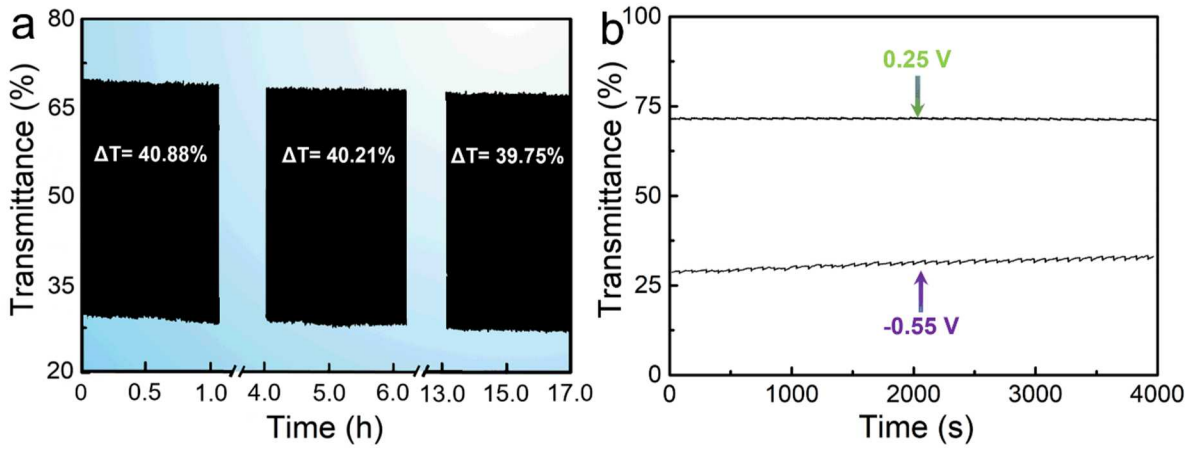

Figure 5. Optical stability of poly(PEP) film. (a) Transmittance-time profile of poly(PEP) film at the wavelength of 550 nm under an applied square voltage signal with a time step of 5 s. (b) Open circuit memory of poly(PEP) film monitored at the wavelength of 550 nm. Applied voltages: -0.55 V and 0.25 V.

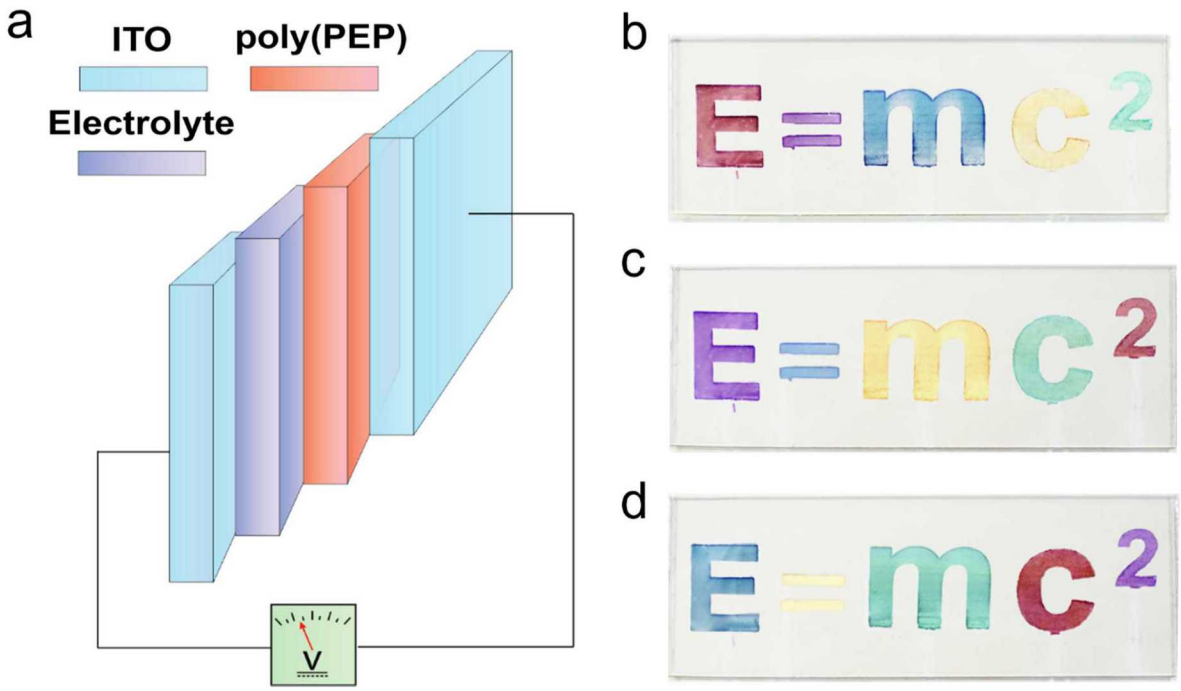

Figure 6. A full-color electrochromic device. (a) Schematic diagram of the fabricated poly(PEP)-based, solid-state electrochromic device. (b)-(d) Color changes of the electrochromic device with different applied potentials.