

Supporting Information

**Self-bleaching Behaviors in Black-to-Transmissive
Electrochromic Polymer Thin films**

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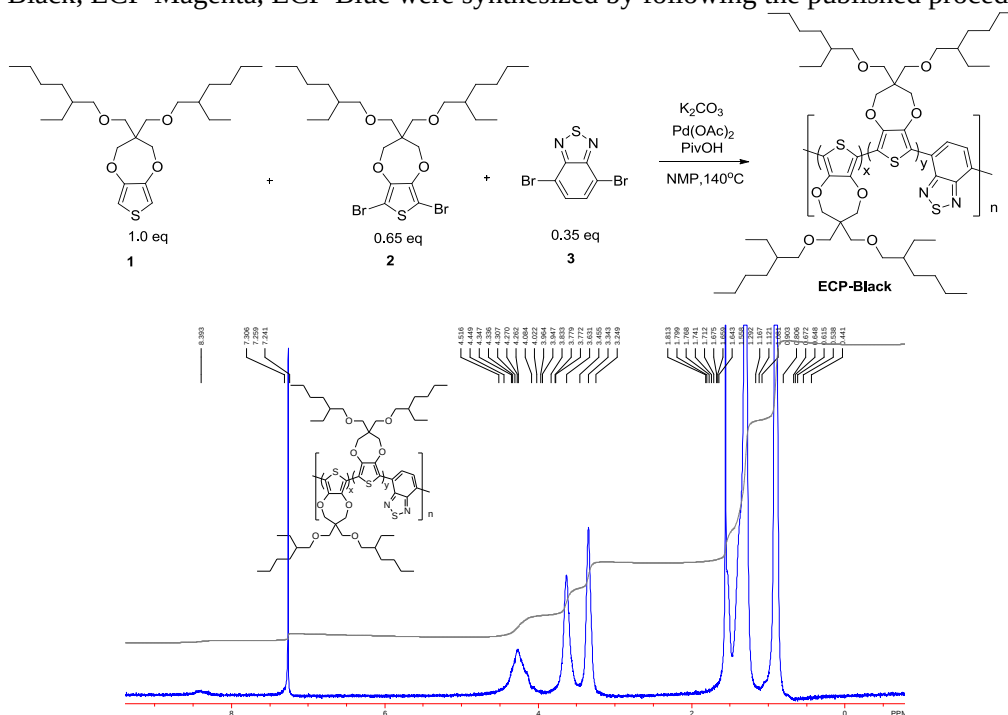
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Experiment Section

Materials

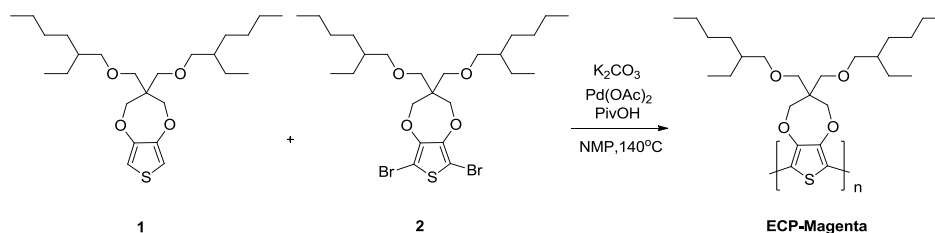
ITO slides (CG-501N-CUV) were purchased from delta technologies, LTD. Anhydrous propylene carbonate (PC), Tetrabutylammonium hexafluorophosphate (TBAPF₆) ($\geq 99.0\%$, for electrochemical analysis), silver wire ($\geq 99.0\%$) with 1.5 mm diameter, platinum wire (99.0%) with 0.5 mm in diameter were purchased from Sigma-Aldrich.

The ECP-Black, ECP-Magenta, ECP-Blue were synthesized by following the published procedures.^{1,2}



¹H NMR (300 MHz, CDCl₃) δ 8.44-8.20 (m, 1H), 4.52-4.26 (m, 10H), 3.63 (bs, 10H), 3.34 (bs, 10H), 1.55-1.29 (m, 45H), 0.90 (bs, 30H).

Figure S1. Synthesis and ¹H NMR spectrum of ECP-Black.



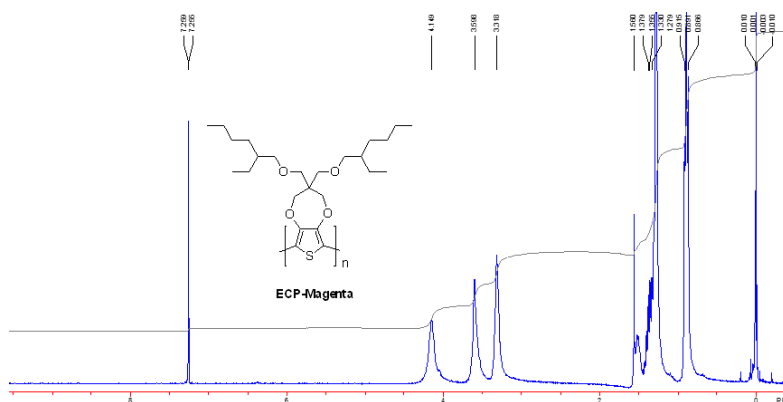


Figure S2. Synthesis and ¹H NMR spectrum of ECP-Magenta.

¹H NMR (300 MHz, CDCl₃) δ 4.15 (br, 4H), 3.60 (br, 4H), 3.32 (br, 4H), 1.56-1.33 (m, 18H), 0.92-0.87 (bs, 12H).

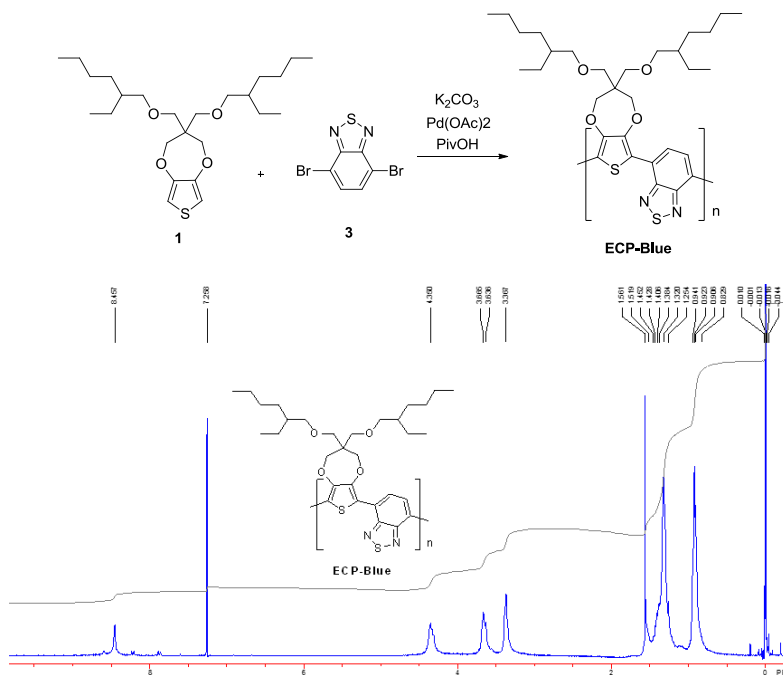


Figure S3. Synthesis and ¹H NMR spectrum of ECP-Blue.

¹H NMR (300 MHz, CDCl₃) δ 8.46 (br, 2H), 4.35 (br, 4H), 3.64-3.67 (m, 4H), 3.37 (br, 4H), 1.56-1.25 (m, 18H), 0.94-0.83 (bs, 12H).

Instrumentation

All the electrochemistry related experiments were performed using BioLogic SP-150. The UV/Vis spectrum and the optical memory measurement were obtained from Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The AFM images were taken by using the Veeco dimension 3100. Contact Angle measurements were carried out by using Ramé-Hart Model 790.

Cyclic Voltammetry (CV)

CV experiments were carried out by using a conventional three-electrode system. The working electrode is ITO coated by the polymer thin film; the pseudoreference electrode is an Ag wire coated by AgCl;³ the counter electrode is the platinum wire; the electrolyte is 0.2 M TBAPF₆ in PC. The thin film of polymer was made by spin-coating ~ 0.1 ml of 40 mg/ml solution on top of the ITO with a 1500 rpm/s spin rate to form a film with ~ 375 nm thick which shows the highest optical contrast.⁴⁻⁶ (Figure S5) The voltage is scanned from -0.2 V to 1.0 V at a 40 mV/s scan rate for ECP-Black and ECP-Magenta, and from -0.2V to 1.3V at a 40 mV/s scan rate for ECP-Blue. Same set-up and parameters were also used for the CV cycling stability test. The anodic peak current density in the voltammogram was used to indicate the cycling stability of the polymer thin film. Moreover, 15 cycles of break-in were applied before the characterizations of the polymer thin films unless otherwise mentioned. The CVs of a typical break-in process were shown in Figure S7.

Differential Pulse Voltammetry (DPV)

DPV measurements were done by using a platinum bottom as a working electrode. A thin polymer layer was coated on top of the platinum bottom by drop casting the 3 - 5 mg/ml solution. All other set-ups were same as CV experiments unless otherwise mentioned. 20 mV pulse height, 50 ms pulse width, 1.0 mV step height, and 100 ms step time were used. The potential range for the experiment was set between -0.2 V and 1.0 V.

The degree of Self-bleaching

The degree of self-bleaching was quantified as the percentage change of optical density of the thin films under open circuit conditions. The broken in thin films were oxidized by applying 1.0 V for 30 s for ECP-Black and ECP-Magenta, and 1.3 V for 30s for ECP-Blue. Then, the percentage change of optical density at bleached state was recorded for 2 mins. Right after 2 mins, a - 0.2 V cathodic potential was applied for certain time (5 s, 10 s, 20 s, 30 s, 60 s, 300 s). Finally, the potential was switched to voltage off and the percentage change of optical density at colored state was recorded for 120 s for short-term measurement, and 900 s for long-term measurement. The detailed processes of the experiments were shown in the Scheme S1. For the measurement under the N₂ protection, N₂ was pre-purged into the chamber of the Cary 5000 for 30 mins at 10 L/mins before the experiments, and was continuous supplying in the rest of the experiments.

Partial OTS Surface Modification

ITO substrates were washed by ultrasonic bath in the order of ethanol, acetone, ethanol for 10 mins each. The washed ITO substrates were dried by nitrogen blowing. Then, the conducting sides of the ITO slides

were treated for 20 mins in a UV-ozone chamber. ITO were partially covered by OTS (POTS) monolayer after immersing in a 1 vol% OTS hexane solution for 80 mins.

Ferrocene/ferrocenium redox couple was used as electrochemical probe to exam the formation of POTS monolayer. The CV experiments were done in a propylene carbonate solution with 0.1 M of ferrocene and 0.1 M of TBAPF₆. The potential was scan from -0.4 V to 1.0 V vs. Ag/AgCl at 40 mV/s.

Electrochemical Impedance Spectroscopy & AFM

The EIS experiments were obtained using a 20 mV perturbation amplitude ($V_{\text{rms}} = 14.4 \text{ mV}$) in a frequency ranging from 1.0 Hz to 1.0 MHz. AFM images were obtained in a tapping mode at a 0.5 Hz scan rate. The average R_q was calculated based on three different images.

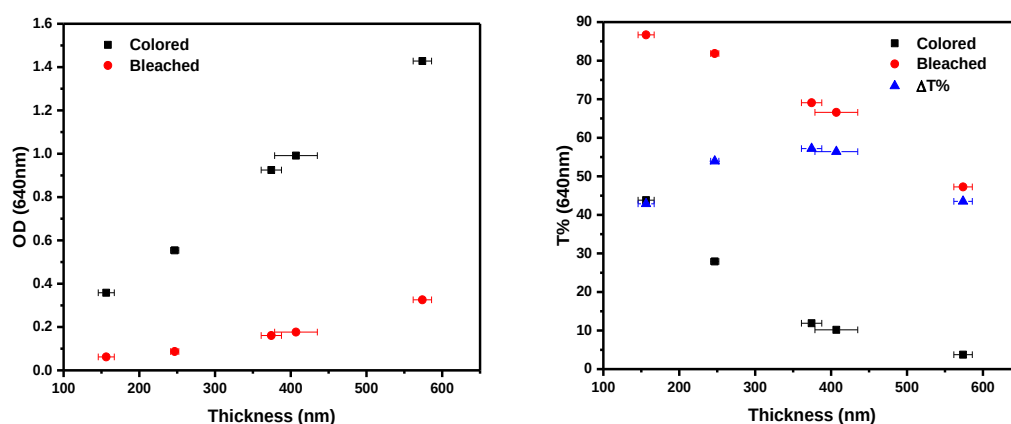


Figure S4. Optical density and transmittance of ECP-Black thin films with different thicknesses

The ECP-Black thin films with different thicknesses were obtained by spin coating ECP-Black solution with different concentrations including 20 mg/ml, 30 mg/ml, 40mg/ml, 50 mg/ml, 60 mg/ml at 1500 rpm. The results showed that the highest contrast can be achieved by the ECP-Black thin film with ~ 375 nm obtained from the 40 mg/ml solution. Thus, the 40 mg/ml ECP-Black solution was used in our studies for fabricating thin films unless otherwise mentioned.

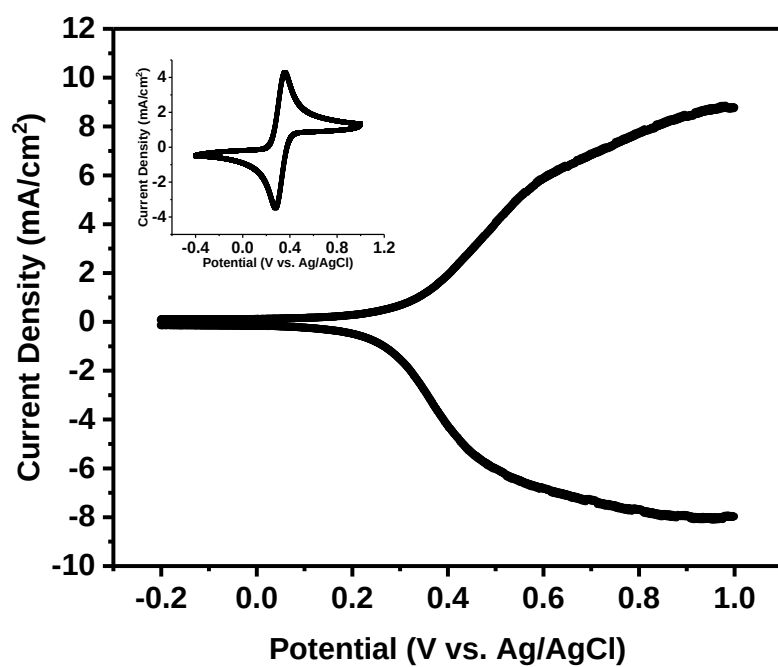


Figure S5. DPV of ECP-Black on platinum (inset: the CV of ferrocene in 0.1 M TBAPF₆ PC)

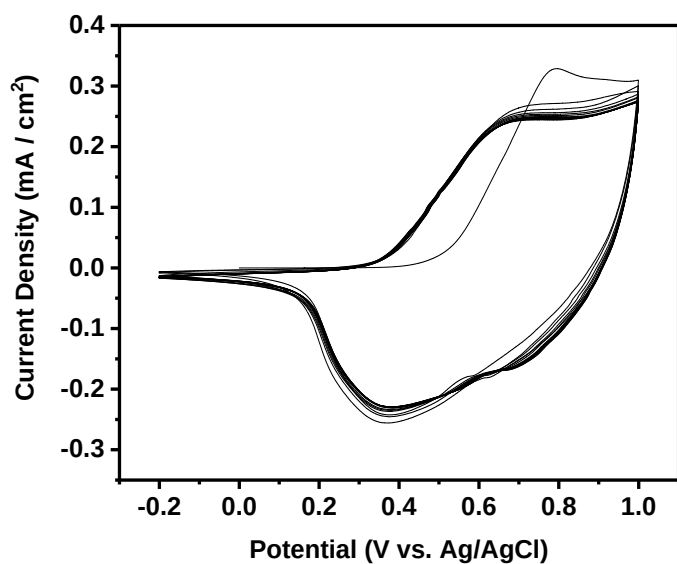


Figure S6. Typical CVs (15 cycles) of the break-in process

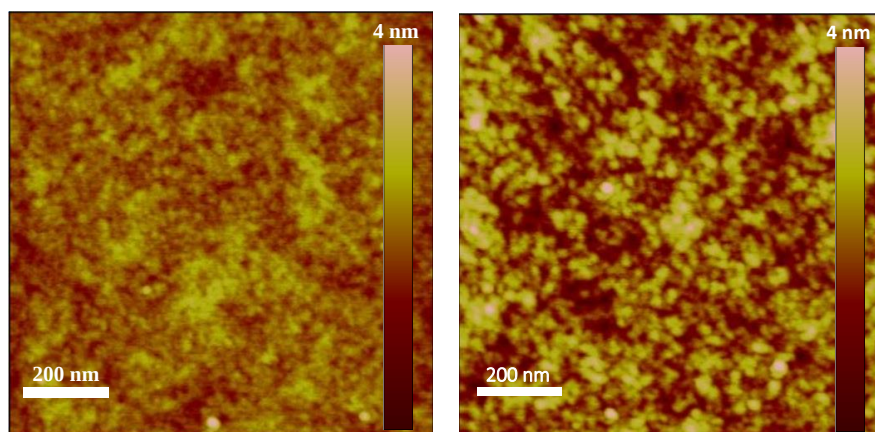


Figure S7. AFM images of a ECP-Black thin film before (left) and after break-in (right).

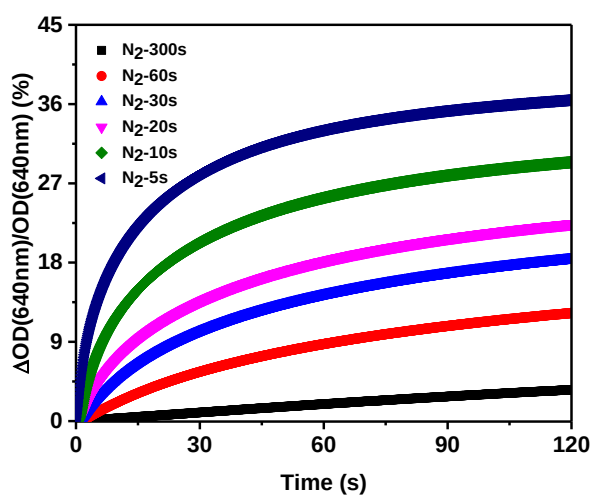
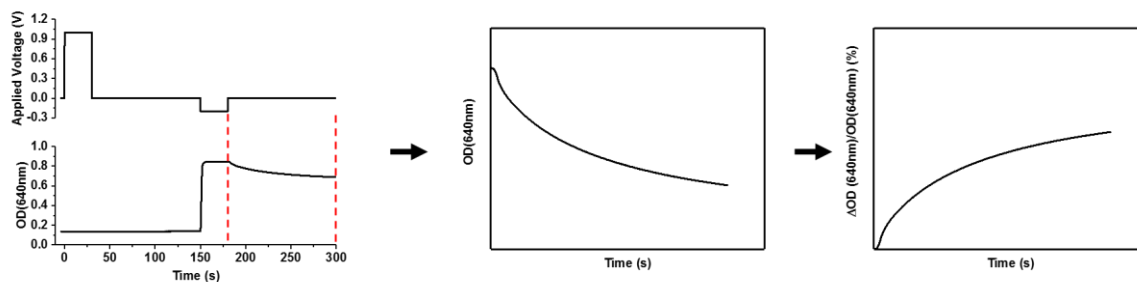
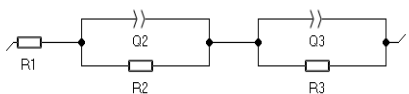


Figure S8. Short-term percentage change of optical density after different durations of reverse bias (-0.2 V) under nitrogen flow with 10 L/min flow rate.



Scheme S1. The procedure for obtaining the degree of self-bleaching from UV/Vis optical density measurement



Scheme S2. R(QR)(QR) Equivalent circuit

Table S1. The R(QR)(QR) fitting results of EIS spectrums of the pristine film and the thin film after break-in followed by 300 s polarization

	Pristine Film	Thin film (after break-in + 300s polarization)
R_s / Ω	52.72	59.93
$Q_{\text{film}} / F \cdot s^{(a-1)}$	0.5713×10^{-6}	2.04×10^{-6}
a_{film}	0.959	0.8896
R_{film} / Ω	45.97×10^6	1.97×10^5
$Q_{\text{dl}} / F \cdot s^{(a-1)}$	4.313×10^{-6}	2.461×10^{-6}
a_{dl}	0.5649	0.6049
R_{ct} / Ω	6693	111.4

Table S2. Average contact angles of bare-ITO, ITO treated by UV-ozone, POTS-ITO

Bare ITO		UV-Ozone-ITO		POTS-ITO	
79.87 ± 5.91	80.02 ± 6.30	49.12 ± 2.43	49.04 ± 3.27	115.95 ± 2.09	115.46 ± 1.63

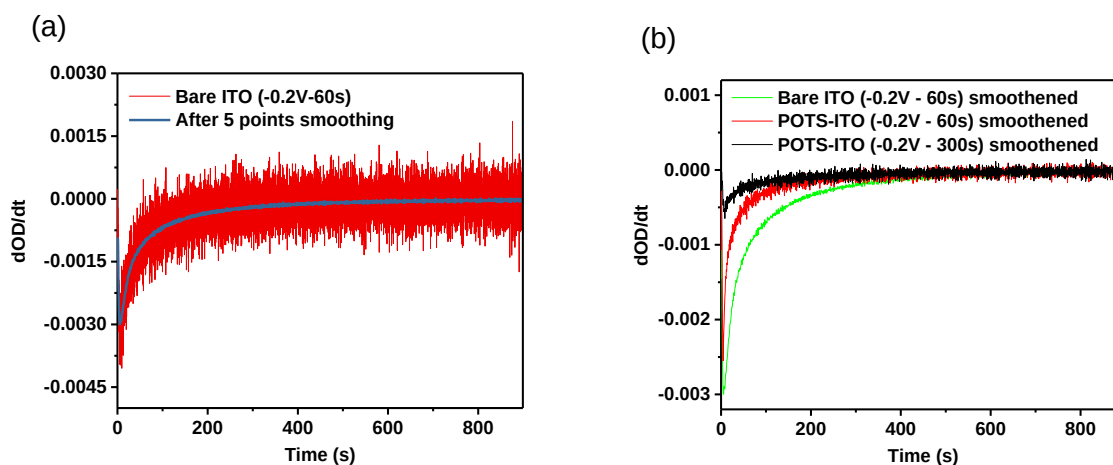


Figure S9. (a) An example of the first derivative of OD(640nm) of ECP-Black with respect to time during self-bleaching processes before and after 5 points FFT smoothing. (b). The smoothed first derivative curve of OD(640nm) of ECP-Black on bare ITO with 60 s cathodic polarization, and POTS-ITO with 60 s cathodic polarization and 300 s cathodic polarization.

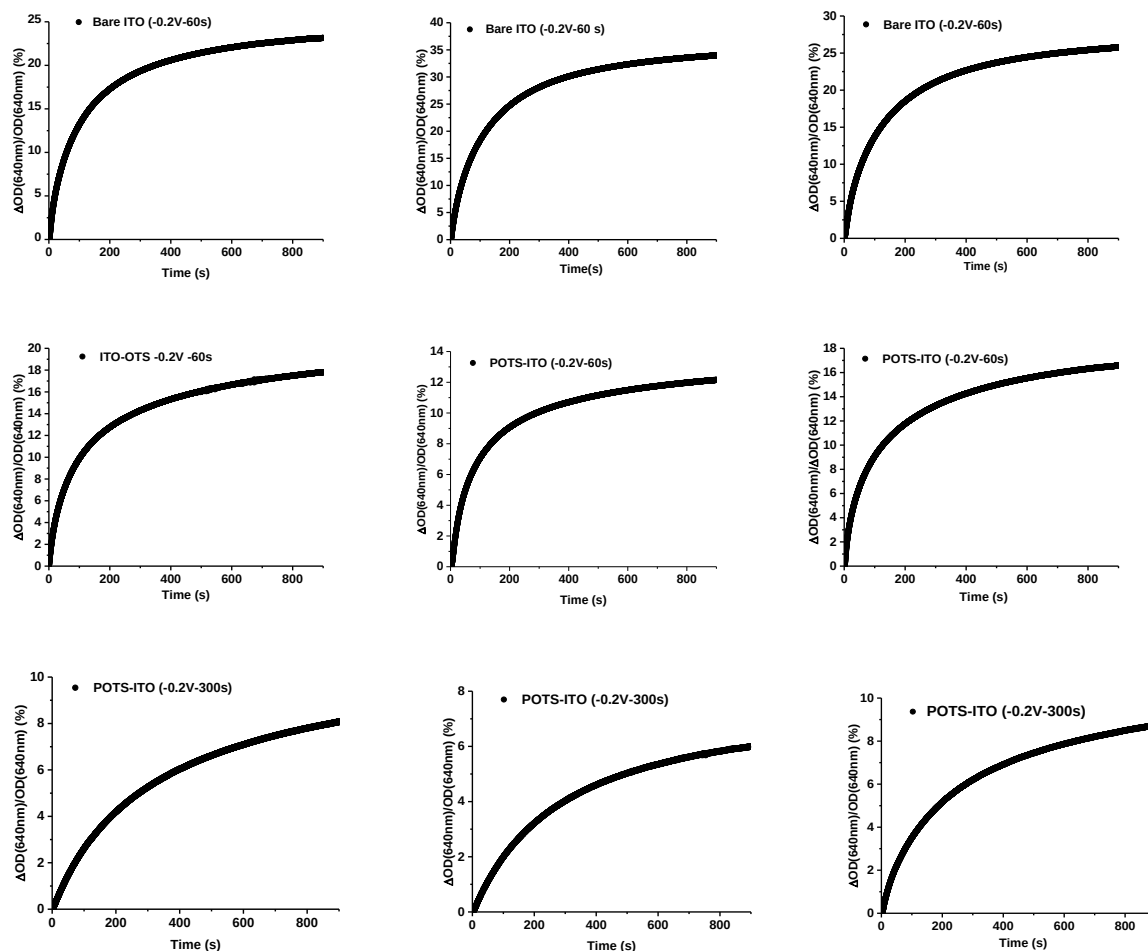


Figure S10. Three individual long-term (900 s) percentage change of optical density measurements of ECP-Black on bare-ITO (top: with 60 s cathodic polarization) and POTS-ITO (middle: with 60 s cathodic polarization; bottom: with 300 s cathodic polarization)

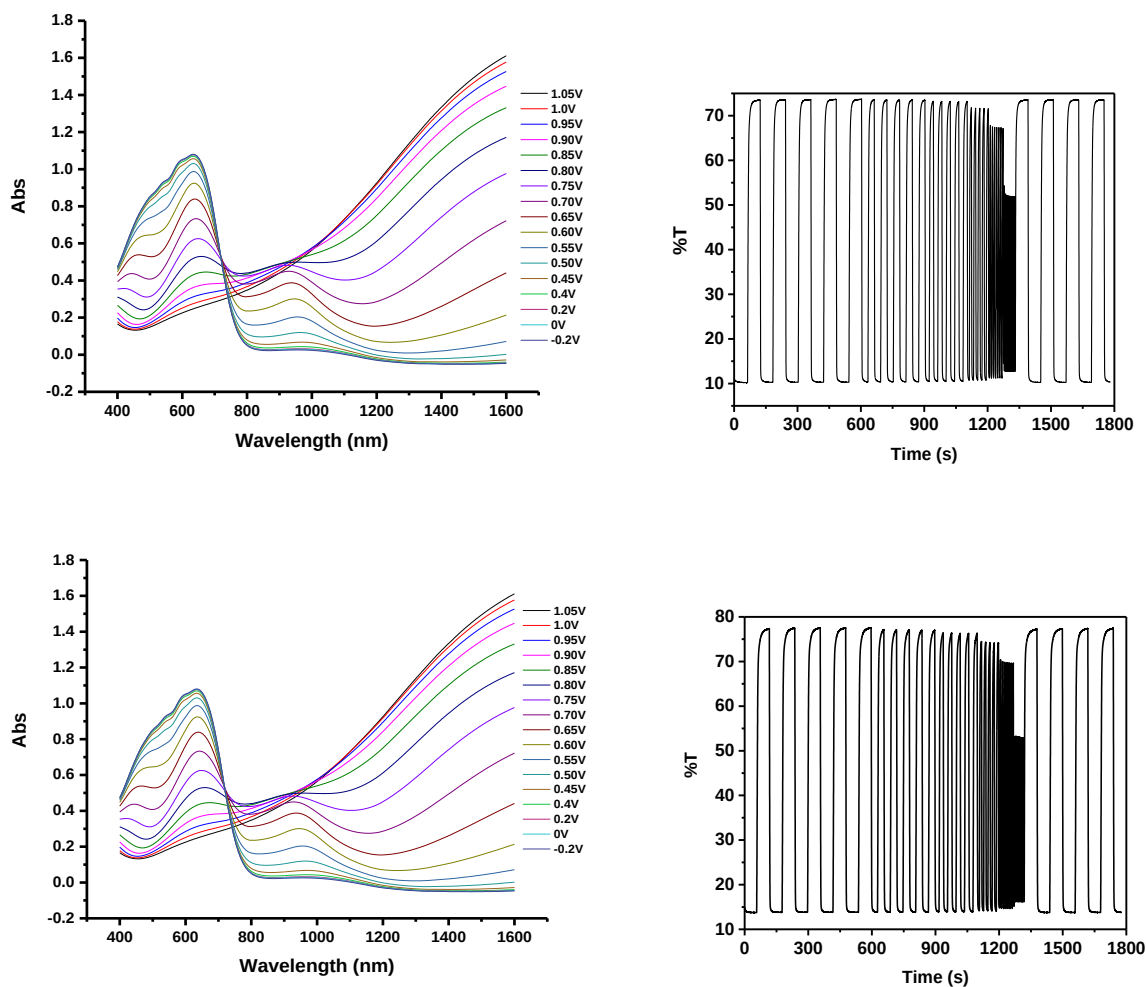


Figure S11. Spectro-electrochromic behaviors and double potential step chronoamperometric experiments (T% at 640nm) of ECP-Black on the POTS-ITO (top) and bare ITO (bottom).

Table S3. Comparison of ECP-Black thin films on bare ITO and POTS-ITO

Substrate	$\Delta T/\%$	$t_b(95\%)/s$	$t_c(95\%)/s$	CE/ cm^2/C
Bare ITO	63	11.5	3.3	203.23 ^a
POTS-ITO	63	9.5	5.6	473.4 ^a

a) Coloration efficiency is calculated based on the initial slope highlighted in Figure 6a.

Reference

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