

Supporting Information

Improving Electrochemical Cycling Stability of Conjugated Yellow-to-Transmissive Electrochromic Polymers by Regulating Effective Overpotentials

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1. Methods

1.1 Chemicals and Materials

Zinc oxide nanoparticles (ZnO, average $d \approx 25$ nm), lithium chloride (LiCl, 99%), vanadyl sulfate hydrate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, $3 < x < 5$, 99.99%), vanadium oxytriisopropoxide, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%), lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), poly(ethylene glycol) methyl ether acrylate (PEGMEA, average $M_n \approx 480$), propylene carbonate (PC, anhydrous, 99.7%), 2-hydroxy-2-methylpropiophenone (97%) and 3,5-dimethylphenyl terminated poly(9,9-dioctyl-9H-fluorene-2,7-diyl) were purchased from Sigma Aldrich. Isopropanol (IPA) and chloroform (CHCl_3) were purchased from Fisher Scientific. ECP-Magenta, ECP-Yellow, ECP-Orange, and ECP-Black were synthesized using the methods published in previous work.¹⁻³ All chemicals were used as received except propylene carbonate, which was dried using at least three freeze-pump-thaw cycles. All electrolytes were made in an N_2 -filled glovebox with H_2O and O_2 levels both below 0.1 ppm.

1.2 Synthesis of modified VO_x nanostructures

The synthesis of ion storage VO_x nanostructures is modified from our previously published method.⁴ 100mg of ZnO nanoparticles were dispersed in 10mL of deionized water under sonication. 60mg of LiCl salt was dissolved in 10mL of deionized water and mixed with the ZnO suspension. 500mg of $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ salt was dissolved in 10mL of DI water. Under sonication, the VOSO_4 solution was swiftly injected into the ZnO nanoparticle and LiCl suspension. The mixture was then centrifuged at 9000 rpm for 3 minutes. The sediment was dispersed in deionized water and centrifuged one more time. The final sediment, amorphous VO_x nanoparticles, was dispersed in 6 mL of deionized water.⁴

The sediment was then subject to a hydrothermal reaction as we previously reported.⁴ In a 20 mL vial, 50 μL of vanadyl oxytriisopropoxide was mixed with 3 mL of IPA. The amorphous VO_x nanoparticles in deionized water was then mixed with the vanadyl oxytriisopropoxide solution. After sonication, the mixture was transferred to a 50 mL Teflon-lined autoclave. The autoclave was heated up in an oven, where the temperature was increased to 140 $^\circ\text{C}$ within 30 minutes and kept at 140 $^\circ\text{C}$ for 90 minutes. After cooling down, the product was centrifuged again at 9000 rpm and washed with IPA. The final product was dispersed in IPA with a concentration of about 2 mg/mL.⁴

1.3 Construction of solid-state devices

The construction of ECP-Yellow and ECP-Magenta solid-state electrochromic devices is modified from our previous report.⁴ The construction of each device consists of the coating of working electrode (ECP on ITO/glass), the preparation of counter electrode (VO_x on ITO/glass), and the curation of the device by in-situ polymerization of the electrolyte.

To prepare the working electrode, the ECP in CHCl_3 solution was first stirred overnight under ambient conditions. For ECP-Yellow, the concentration was 18 mg/mL. For ECP-Magenta, the concentration was 20 mg/mL. For each working electrode, 0.2 mL of ECP in CHCl_3 solution was drop-cast onto a $30 \times 25 \times 0.7 \text{ mm}^3$ ITO/glass substrate, following a spin-coating process at a speed of 1500 rpm and kept for 30 s.

To prepare the counter electrode, 0.2 mL of the VO_x nanoparticle solution was spin-cast onto a $30 \times 25 \times 0.7 \text{ mm}^3$ ITO/glass substrate at a speed of 1500 rpm and kept for 30 s. The process was then repeated for 8 more times for the counter electrode in ECP-Yellow solid-state device and 3 more times for the counter electrode in ECP-Magenta device. The VO_x on ITO/glass was then transferred onto a hotplate and kept heating at 150°C for 90 minutes.

To assemble the solid-state device, an in-situ polymerized electrolyte composed of an Li salt and a PEGMEA polymer is prepared by mixing the lithium salt in the PEGMEA with a concentration of 1 M ($\sim 287 \text{ mg}$ of LiTFSI in 1 mL of PEGMEA, or $\sim 152 \text{ mg}$ of LiPF_6 in 1 mL of PEGMEA) and stirring overnight. Prior to the device construction, 0.1 mL of the photoinitiator, 2-hydroxy-2-methylpropiophenone was added into the Li salt in PEGMEA and mixed thoroughly. 0.1 mL of the LiPF_6 /PEGMEA electrolyte with photoinitiator was drop-cast onto the counter electrode substrate, with the VO_x side facing up. The working electrode, with the ECP side facing down, was placed on top of the electrolyte and the electrolyte drop spreads within 30 s. The device was then transferred under a UV lamp and kept for 10 minutes for the in-situ polymerization of the PEGMEA to complete. After the in-situ polymerization process, the working electrode and counter electrode was each connected to copper tape for further testing.

1.4 Electrochemical and spectroelectrochemical measurements

All electrochemical and spectroelectrochemical characterizations in three-electrode liquid cells are performed on a Biologic SP150 Potentiostat under ambient conditions, except the impedance data, which was collected by a CHI 660E Potentiostat in an N_2 filled glovebox with H_2O and O_2 level both below 0.1ppm. All spectroelectrochemical and optical measurements, either for three-

electrode liquid cell or for solid-state devices, were performed on a Cary 5000 UV-Vis spectrometer with a blank cuvette (ITO and identical electrolyte in the cuvette) or blank device (ITO|electrolyte|ITO) on the reference holder.

All ECPs, including ECP-Yellow ($M_n = 20.0$ kDa, PDI = 1.8, thickness = 146.6 ± 2.9 nm), ECP-Magenta ($M_n = 11.1$ kDa, PDI = 1.3, thickness = 152.4 ± 7.9 nm), ECP-Orange (thickness = 123.0 ± 10.7 nm), ECP-Black (thickness = 228.0 ± 36.3 nm), and polyfluorene (thickness = 46.4 ± 3.3 nm), were dissolved in CHCl_3 by stirring overnight. The ECP on ITO/glass working electrodes for three-electrode tests were prepared by spin-coating 0.1 mL of polymer solution onto a $50 \times 7 \times 0.7$ mm³ ITO/glass substrate at a speed of 1500 rpm and held for 30 s. The thicknesses of the ECP were selected based on trial-and-error based optimization of optical contrast at λ_{max} (445 nm for ECP-Yellow, 490 nm for ECP-Orange, 550 nm for ECP-Magenta, 550 nm for ECP-Black, and 390 nm for polyfluorene).

1.5 Electrochemical cycling

each switching cycle contains 10s of bleaching (voltage step at 1.0 V vs. Ag/AgCl) and 10s of coloration (voltage step at -0.2 V vs. Ag/AgCl). For ECP-Black, each switching cycle contains 10s of bleaching (voltage step at 0.8V vs. Ag/AgCl) and 10s of coloration (voltage step at -0.2 V vs. Ag/AgCl).

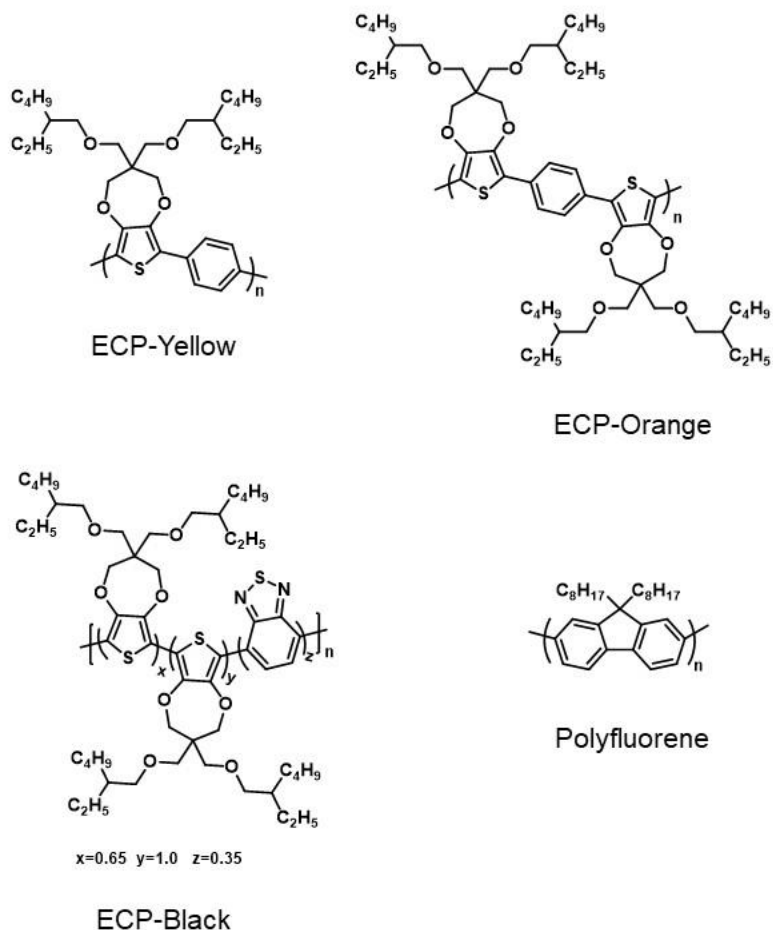
Electrochemical cycling of ECP-Yellow solid-state device and ECP-Magenta device were performed using two-electrode setup (reference electrode electrically connected to the counter electrode). For solid-state ECP-Yellow device, each switching cycle contains 10s of bleaching (voltage step at 1.4 V) and 10s of coloration (voltage step at -0.2 V). For solid-state ECP-Magenta device, each switching cycle contains 5s of bleaching (voltage step at 1.0 V) and 5 s of coloration (voltage step at -0.2 V).

Electrochemical cycling of the polyfluorene in three-electrode liquid cell was performed in two sets of experiments. CV cycles were performed at 40 mV/s within the range of 1.6 V to 0.8 V vs. Ag/AgCl. Step voltage cycles together with in-situ monitoring of transmittance at λ_{max} were performed where switching cycle contains 10 s of bleaching (voltage step at 1.6 V vs. Ag/AgCl) and 10s of coloration (voltage step at 0.8 V vs. Ag/AgCl).

1.6 In-situ mass and thickness measurements

EQCM-D measurements were performed using a QSense Explorer with the electrochemical module. 9 mg/mL of ECP-Yellow in CHCl_3 solution were spin-coated onto the sensor at the speed of 2000 rpm and hold for 30s. The thickness of ECP-Yellow film on EQCM sensor is around 59.5 ± 7.8 nm, determined by profilometer. In-situ nanoindentation measurements were performed on a G200 Nanoindenter coupled with a VersaSTAT 3 potentiationstat following the published method. In-situ observation of ion front movement was obtained using the same setup.^{5,6}

2. Chemical Formula



Scheme S1. Chemical formula of ECP-Yellow, ECP-Orange, ECP-Black and Polyfluorene.

3. Electrochemical and spectro-electrochemical characterizations

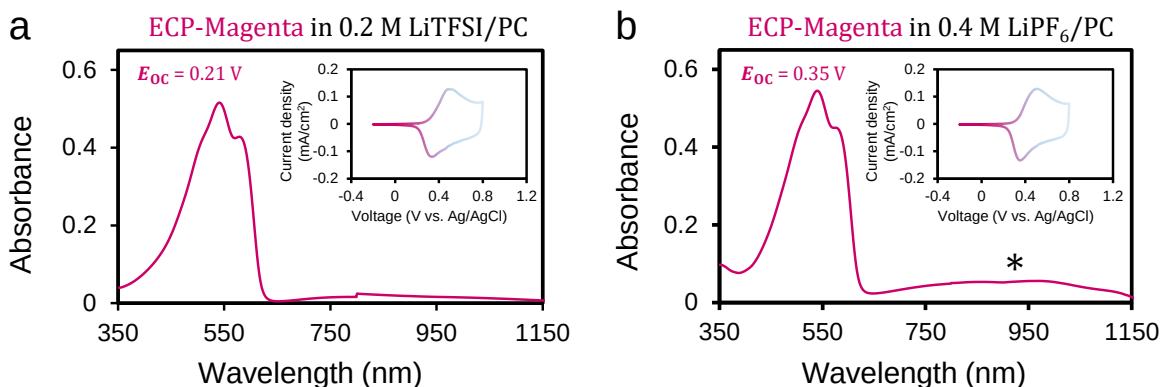


Figure S1. Absorbance spectra and cyclic voltammograms (inset) for ECP-Magenta at different open circuit potential E_{OC} , in (a) 0.2M LiTFSI/PC and (b) 0.4M LiPF₆/PC. The * indicates the enhancement of

polaronic absorbance when E_{OC} is numerically closer to the oxidation onset potential, $E_{OX, onset}$. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

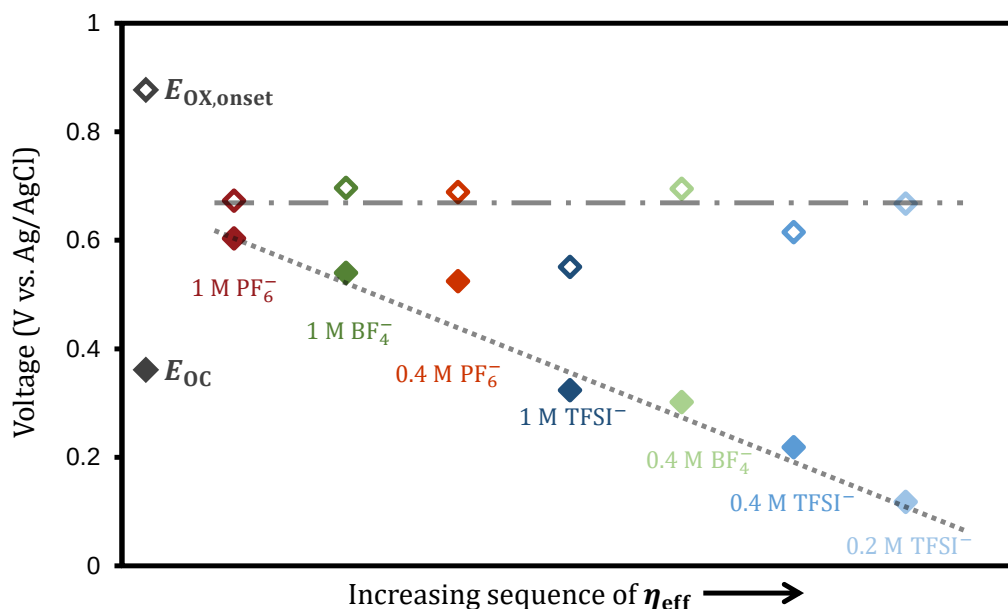


Figure S2. The open circuit potential, E_{OC} , and oxidation onset potential, $E_{OX, onset}$, of ECP-Yellow in a series of electrolyte conditions. All electrolytes are dissolved in PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode

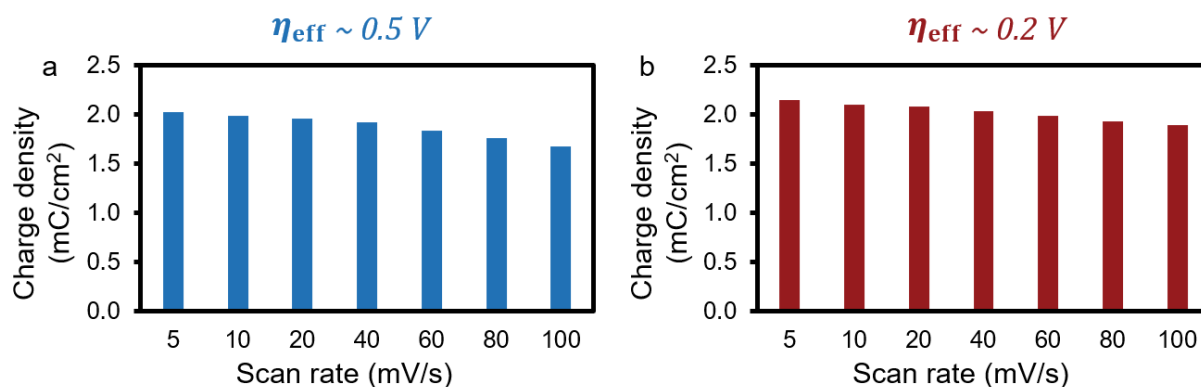


Figure S3. Charge density as a function of scan rate for ECP-yellow tested at (a) higher $\eta_{eff} \sim 0.5$ V in 0.2 M LiTFSI/PC and (b) lower $\eta_{eff} \sim 0.2$ V in 0.4 M LiPF₆/PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

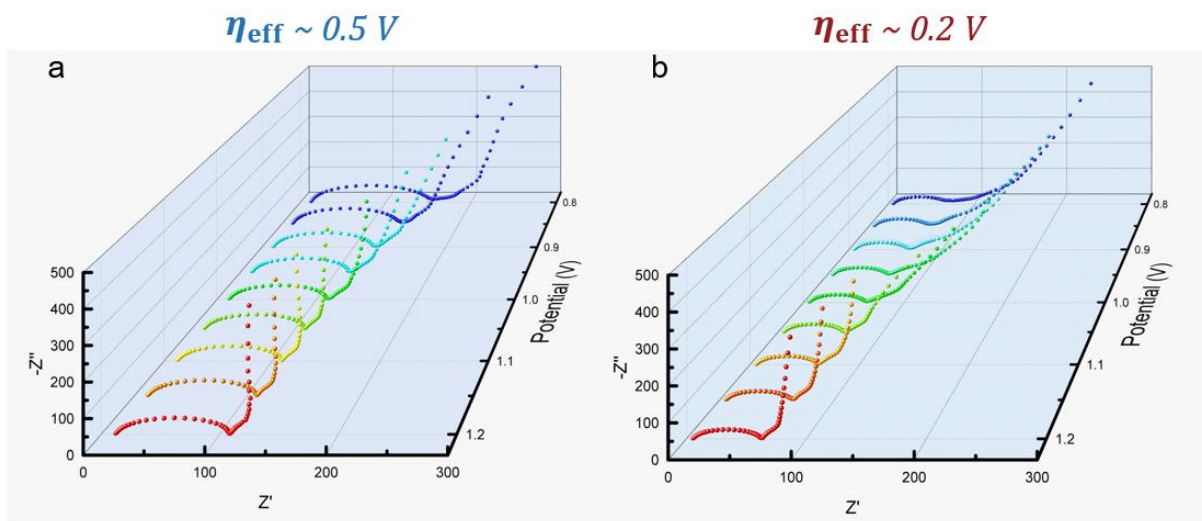


Figure S4. Voltage-dependent impedance tested at (a) higher $\eta_{\text{eff}} \sim 0.5$ V in 0.2 M LiTFSI/PC and (b) lower $\eta_{\text{eff}} \sim 0.2$ V in 0.4 M LiPF₆/PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

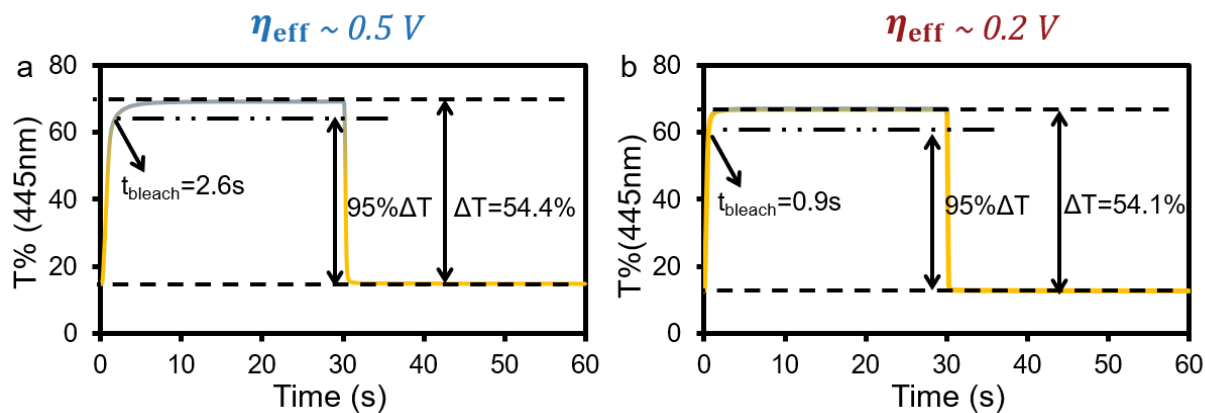


Figure S5. 95% switching time tested at (a) higher $\eta_{\text{eff}} \sim 0.5$ V in 0.2 M LiTFSI/PC and (b) lower $\eta_{\text{eff}} \sim 0.2$ V in 0.4 M LiPF₆/PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

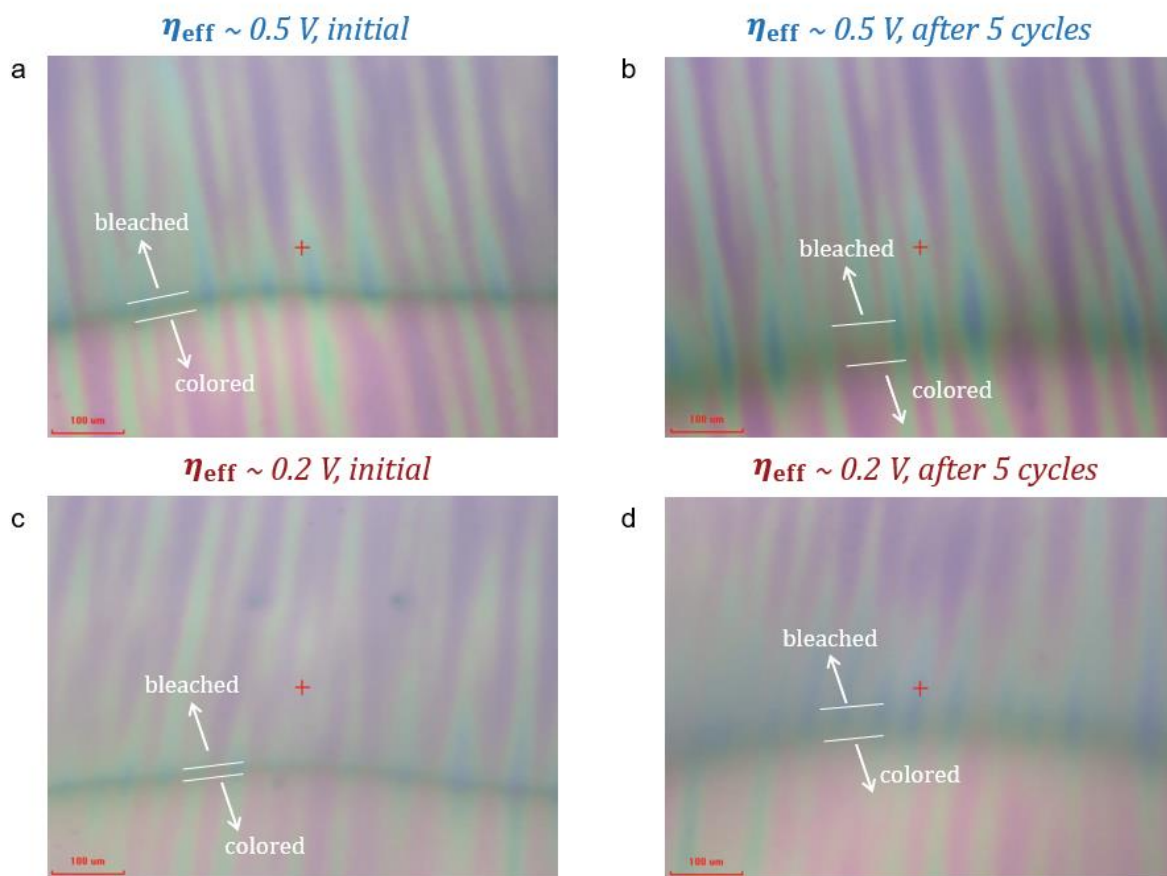


Figure S6. Snapshots of identical ECP-Yellow ion front tested at (a,b) higher $\eta_{\text{eff}} \sim 0.5 \text{ V}$ in 0.2 M LiTFSI/PC and (c,d) lower $\eta_{\text{eff}} \sim 0.2 \text{ V}$ in 0.4 M LiPF₆/PC, in the initial state and after 5 cycles. The measurements were performed in Nanoindentation setup, with Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

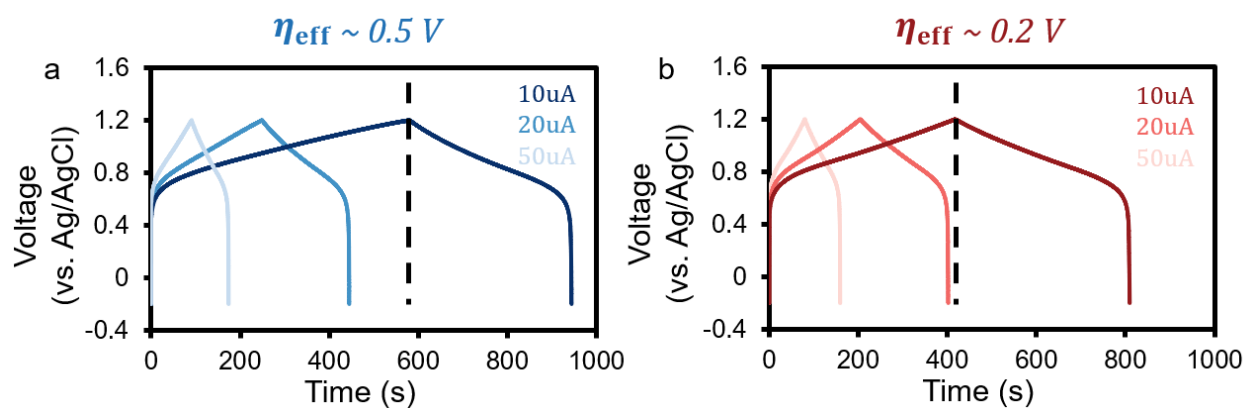


Figure S7. Charge-discharge curve for ECP-Yellow tested in three-electrolyte liquid cell at (a) higher $\eta_{\text{eff}} \sim 0.5 \text{ V}$ in 0.2 M LiTFSI/PC and (b) lower $\eta_{\text{eff}} \sim 0.2 \text{ V}$ in 0.4 M LiPF₆/PC.

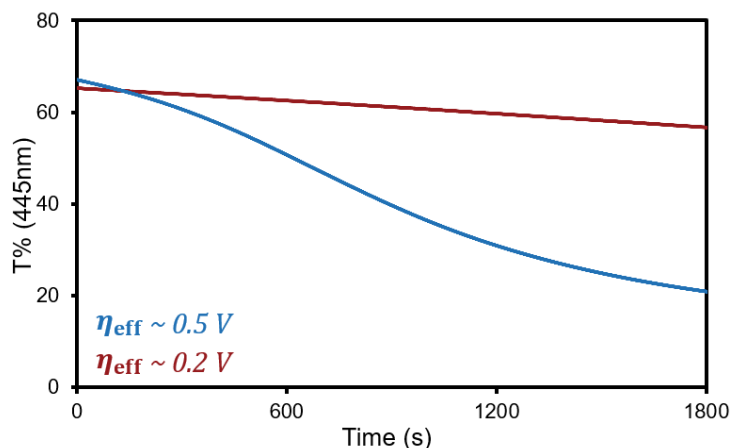


Figure S8. Change in transmittance of ECP-Yellow tested in three-electrode liquid cell, during self-coloration from bleached state at open circuit, tested at higher $\eta_{\text{eff}} \sim 0.5 \text{ V}$ in 0.2 M LiTFSI/PC (blue) and lower $\eta_{\text{eff}} \sim 0.2 \text{ V}$ in 0.4 M LiPF₆/PC (red).

4. Control experiments

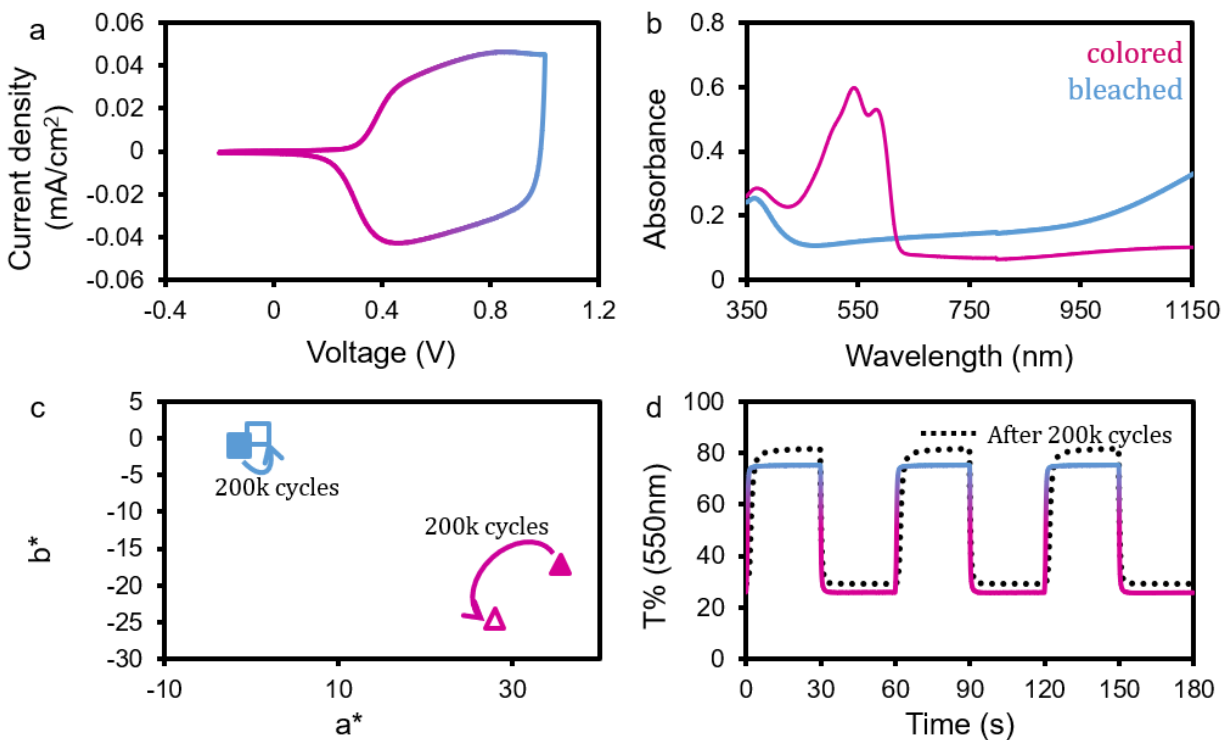


Figure S9. Electrochemical and spectroelectrochemical properties of a solid-state ECP-Magenta device. (a) cyclic voltammogram of the device, in the voltage range of 1.0 V (bleaching) and -0.2 V (coloration). (b) absorbance spectra of the device at bleached (1.0 V) and colored (-0.2 V) state. (c) a^* and b^* coordinate values showing the coloration of the device at bleached (1.0 V, $L^* = 89.6$) and colored (-0.2 V , $L^* = 67.0$) states, in the initial state (solid) and after 200k cycles (hollow). (d) switching kinetics taken at 550 nm, in the initial state (solid) and after 200k cycles (dashed).

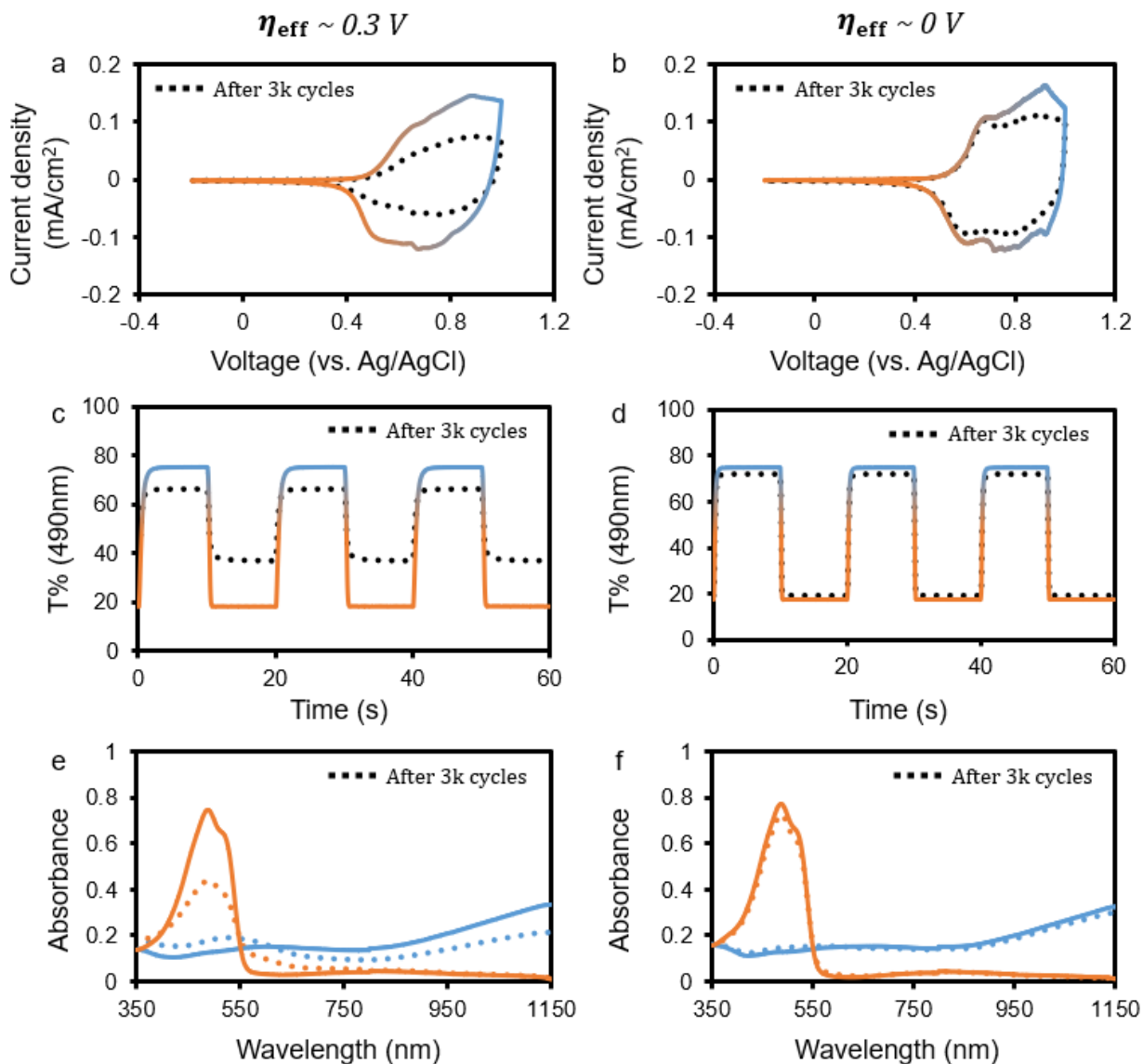


Figure S10. Optical and electrochemical properties of ECP-Orange in the initial state (solid) and after 3000 SPFC cycles (dash), in the voltage range of 1.0 V to -0.2 V, tested at higher $\eta_{\text{eff}} \sim 0.3$ V in 0.4 M LiTFSI/PC, and lower $\eta_{\text{eff}} \sim 0$ V in 0.4 M LiPF₆/PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode

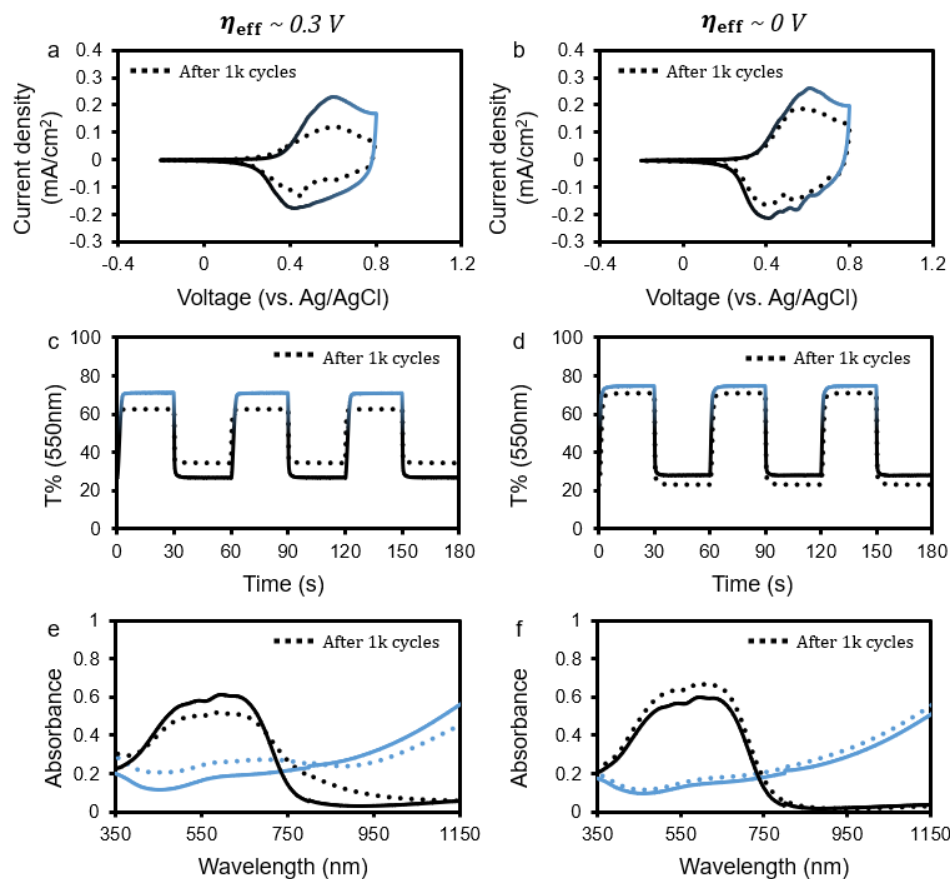


Figure S11. Optical and electrochemical properties of ECP-Black in the initial state (solid) and after 1000 SPFC cycles (dash), in the voltage range of 0.8V to -0.2V , tested at higher $\eta_{\text{eff}} \sim 0.3 \text{ V}$ in 0.2 M LiTFSI/PC, and lower $\eta_{\text{eff}} \sim 0 \text{ V}$ in 0.4 M LiPF₆/PC. The measurements were performed in standard three-electrode liquid cells with Ag/AgCl as the reference electrode and Pt wire as the counter electrode

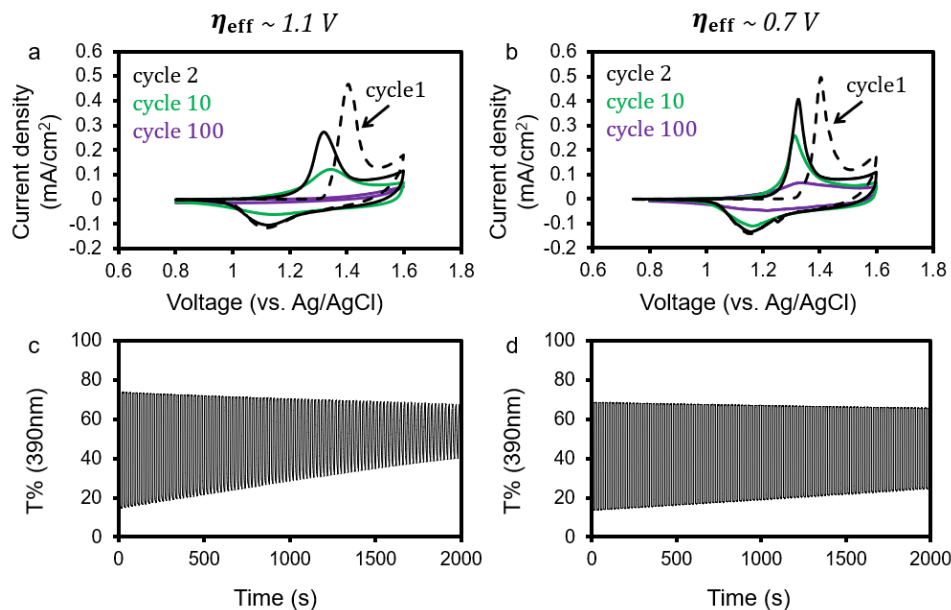


Figure S12. (a,b) CV cycles and (c,d) in-situ optical contrast under SPFC cycles for polyfluorene at higher $\eta_{\text{eff}} \sim 1.1 \text{ V}$ in 0.2 M LiTFSI/PC, and lower $\eta_{\text{eff}} \sim 0.7 \text{ V}$ in 1 M LiPF₆/PC, tested in the voltage range of 1.6 V to 0.8V in three-electrode liquid cell.

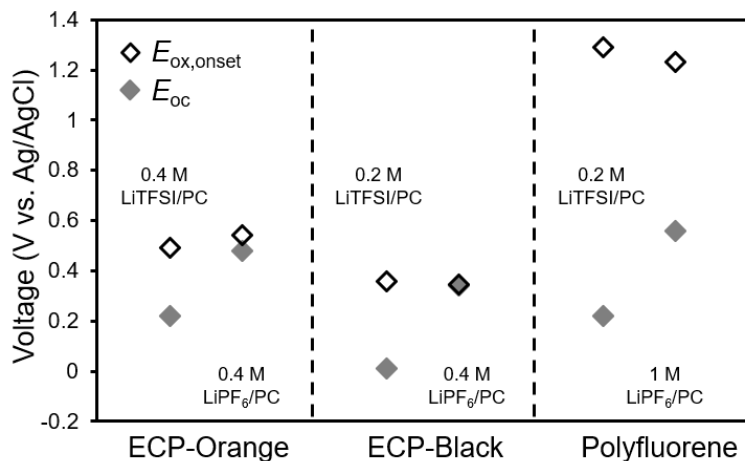


Figure S13. E_{OC} and $E_{\text{OX,onset}}$ values for ECP-Orange, ECP-Black, and polyfluorene, measured in three-electrode liquid cells with Ag/AgCl reference electrode and Pt wire counter electrode.

5. References

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