

Supporting Information

Water-soluble CMY primary color electrochromic polymers: Design, Synthesis and Full Color Control

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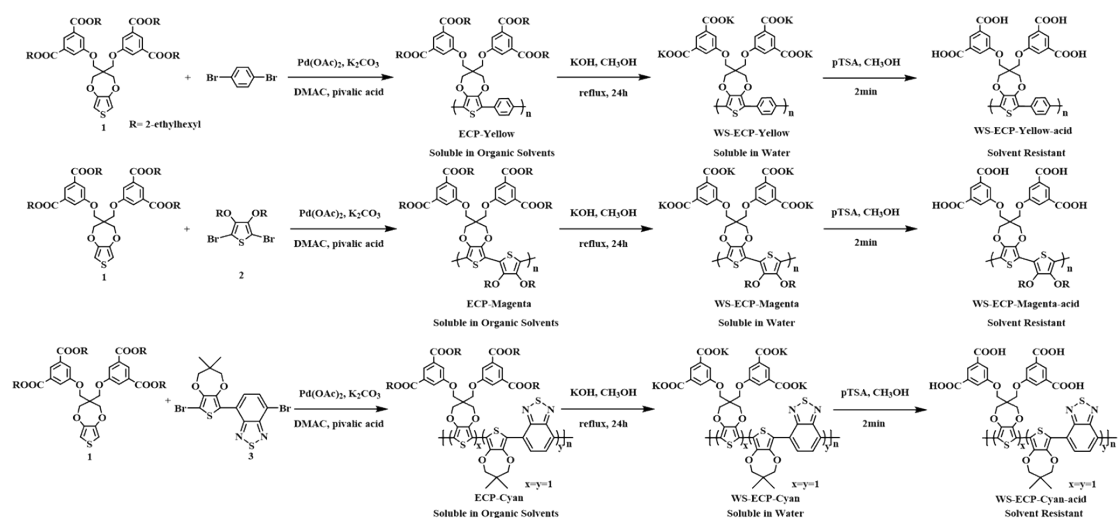
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Figure S1. The diagram of the subtractive primary colors. The color of the outer square can be adjusted by the internal CMY three primary colors.



Scheme S1. Synthetic route from monomers to the final insoluble polymers.

Detailed steps as follow:

Synthesis of ECP-Yellow

A solution of compound 1 (1 g, 1.01 mmol), 1,4-dibromobenzene (0.24 g, 1.01 mmol), Palladium (II) Acetate (20 mg, 0.089 mmol), pivalic acid (30.82 mg, 0.302 mmol) and K_2CO_3 (0.28 g, 2.01 mmol) in DMAC (20 mL) were charged in a 100 mL flask, then heated at 135°C for 24 h in an oil bath. After the reaction, the solution was precipitated into methanol (300 mL). The precipitate was filtered through a cellulose thimble, then the precipitate was soxhlet extracted with methanol, hexane, acetone, and chloroform solvents for 48h in turn, and the chloroform portion of the wash was collected. The solvent was evaporated and the collected polymer was a yellow solid (0.93 g, 86%). 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 7.79 (s, 8H), 4.47 (d, $J = 28.7$ Hz, 8H), 4.26 (s, 8H), 1.79-1.32 (m, 36H), 0.95-0.86 (m, 24H). GPC analysis: $M_n = 22.85$ kDa, M_w

= 53.74 kDa, PDI = 2.35.

Synthesis of ECP-Magenta

Compound 1 (1 g, 1.01 mmol), compound 2 (0.50 g, 1.01 mmol), Palladium (II) Acetate (20 mg, 0.089 mmol), pivalic acid (30.82 mg, 0.302 mmol) and K_2CO_3 (0.28 g, 2.01 mmol) in DMAC (20 mL) were charged in a 100 mL flask and the above procedure was followed. The collected polymer was a magenta solid (1.19 g, 89%). 1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 7.76 (s, 4H), 4.49 (s, 8H), 4.19 (s, 8H), 3.94 (s, 4H), 1.77-1.37 (m, 36H), 0.95-0.73 (m, 54H). GPC analysis: M_n = 21.14 kDa, M_w = 41.29 kDa, PDI = 1.95.

Synthesis of ECP-Cyan

Compound 1 (1 g, 1.01 mmol), compound 3 (0.48 g, 1.01 mmol), Palladium (II) Acetate (20 mg, 0.089 mmol), pivalic acid (30.82 mg, 0.302 mmol) and K_2CO_3 (0.28 g, 2.01 mmol) in DMAC (20 mL) were charged in a 100 mL flask and the above procedure was followed. The collected polymer was a black solid (1.09 g, 83%). 1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 8.24 (s, 2H), 7.82 (s, 4H), 4.50 (s, 8H), 4.26 (s, 12H), 4.08 (s, 6H), 1.77-1.37 (m, 36H), 0.88-0.78 (m, 24H). GPC analysis: M_n = 9.3 kDa, M_w = 26.71 kDa, PDI = 2.87.

Synthesis of WS-ECP-Yellow

ECP-Yellow (500 mg) and a solution of 1 M KOH in methanol (45 mL) were added to a 100 mL flask. This suspension was refluxed for 24 h, during which the polymer dispersed into fine particles. The suspension was filtered on a nylon filter membrane, washed with 100 mL of methanol. Then the resulting powder was dried under a vacuum to yield 333 mg of a dark yellow solid (92%).

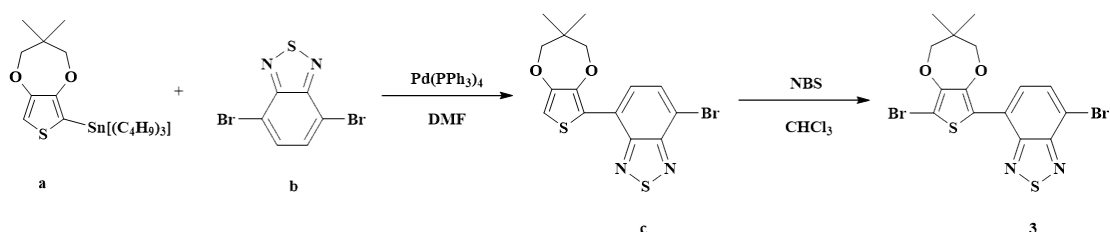
Synthesis of WS-ECP-Magenta

The same reaction and purification procedure as described for WS-ECP-Yellow was followed, except for replacing ECP-Yellow (500 mg) with ECP-Magenta (450mg). Polymer WS-ECP-Magenta was obtained as a dark red powder (308 mg, 88%).

Synthesis of WS-ECP-Cyan

The same reaction and purification procedure as described for WS-ECP-Yellow was followed, except for replacing ECP-Yellow (500 mg) with ECP-Cyan (400mg).

Polymer WS-ECP-Cyan was obtained as a black powder (279 mg, 90%).



Scheme S2. The synthesis route for compound **c** and **3**.

Detailed steps as follow:

Synthesis of 4-bromo-7-(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole

Under the protection of nitrogen, ProDOT-Me₂ (1g, 5.43 mmol) was dissolved in 20 mL of anhydrous and oxygen-free tetrahydrofuran, and then hexane solution of n-butyllithium (2.5 M, 2.17 mL) was added dropwise at -78°C with holding and stirring for 1 h. After that, tributyltin chloride (2.30 g, 7.07 mmol) was added and holding and stirring were continued for 1 h, followed bring to room temperature and stirring for 12 h. After the reaction, using aluminum trioxide as stationary phase and dichloromethane as mobile phase, the eluent containing the target compound was collected and the solvent was evaporated to afford the crude product which was used for the next step without further purification. Next, DMF (20 mL) was added to a 100 ml flask containing 4,7-dibromo-2,1,3-benzothiadiazole (3.19g, 10.86 mmol) and Pd(PPh₃)₄ (20 mg, 0.02 mmol) and the mixture was stirred at 135°C for 15 h. After the reaction completed, the solvent added to water and extracted multiple times with DCM. The organic phase was washed with brine, water, dried over magnesium sulfate and the solvent was evaporated, then the product was purified by column chromatography on silica with hexane/dichloromethane (1:2) as eluent. Compound **c** was obtained as a white solid (0.67 g, 76 %). The collected filtrate was then concentrated via rotary evaporation to obtain as a rosy solid (1.68g, 78 %). ¹H NMR (600 MHz, CDCl₃) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.87-7.80 (m, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 3.91 (s, 2H), 3.84 (s, 2H), 1.09 (s, 6H).

Synthesis of 4-bromo-7-(8-bromo-3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole

NBS (0.49 g, 2.78 mmol) was added to a 50 mL flask containing compound c (1g, 2.53 mmol) and chloroform (20ml), and the mixture was stirred in the dark at room temperature for 4 h. The solvent was evaporated and the product was purified by column chromatography on silica with DCM as eluent. Compound 3 was obtained as a rosy solid (1.08 g, 90%). ^1H NMR (600 MHz, CDCl_3) δ 8.13 (t, $J = 6.6$ Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 1H), 3.93 (d, $J = 12.1$ Hz, 4H), 1.11 (s, 6H).

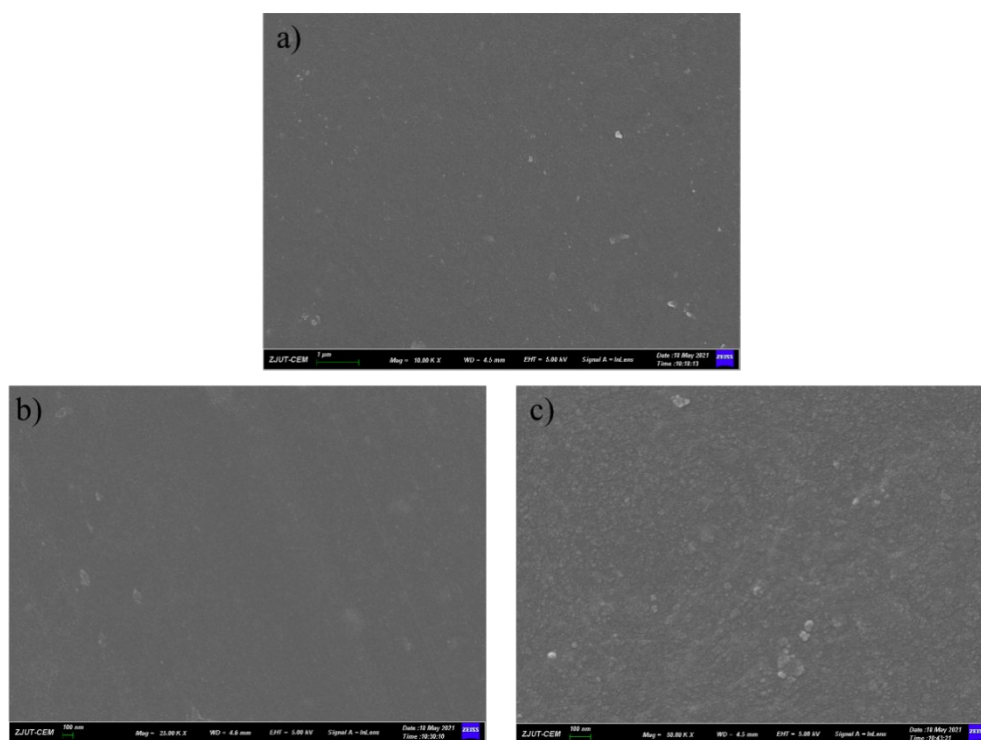


Figure S2. a) The SEM top-view of WS-ECP-Cyan-acid film; b) The SEM top-view of WS-ECP-Magenta-acid film; c) The SEM top-view of WS-ECP-Yellow-acid film;

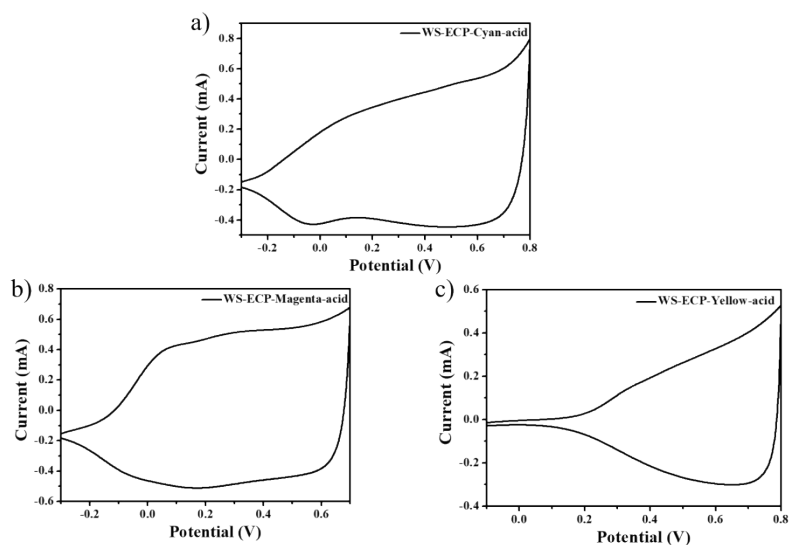


Figure S3. The cyclic voltammety curves of a) WS-ECP-Cyan-acid film; b) WS-ECP-Magenta-acid film; c) WS-ECP-Yellow-acid film. Measurements were performed in 0.2 M KNO_3 /water with a Pt foil counter electrode and an Ag/Ag^+ reference electrode (scanning speed: 100 mV/s).

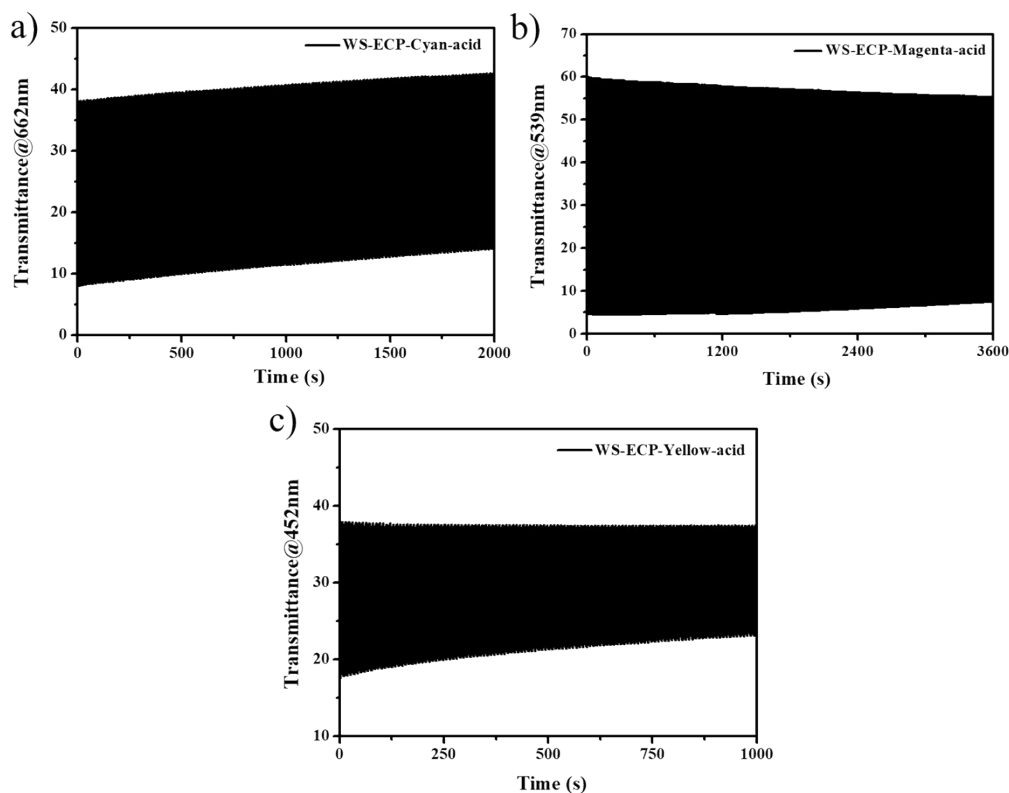


Figure S4. (a) long-term optical transmittance data (0-2000 s) with intervals of 10 s of the WS-ECP-Cyan-acid film at 659 nm between -0.2 V and 0.8 V. (b) long-term optical transmittance data (0-3600 s) with intervals of 3 s of the WS-ECP-Magenta-acid film

at 539 nm between -0.2 V and 0.7 V. (c) long-term optical transmittance data (0-1000 s) with intervals of 5 s of the WS-ECP-Yellow-acid film at 452 nm between 0 V and 0.8 V.

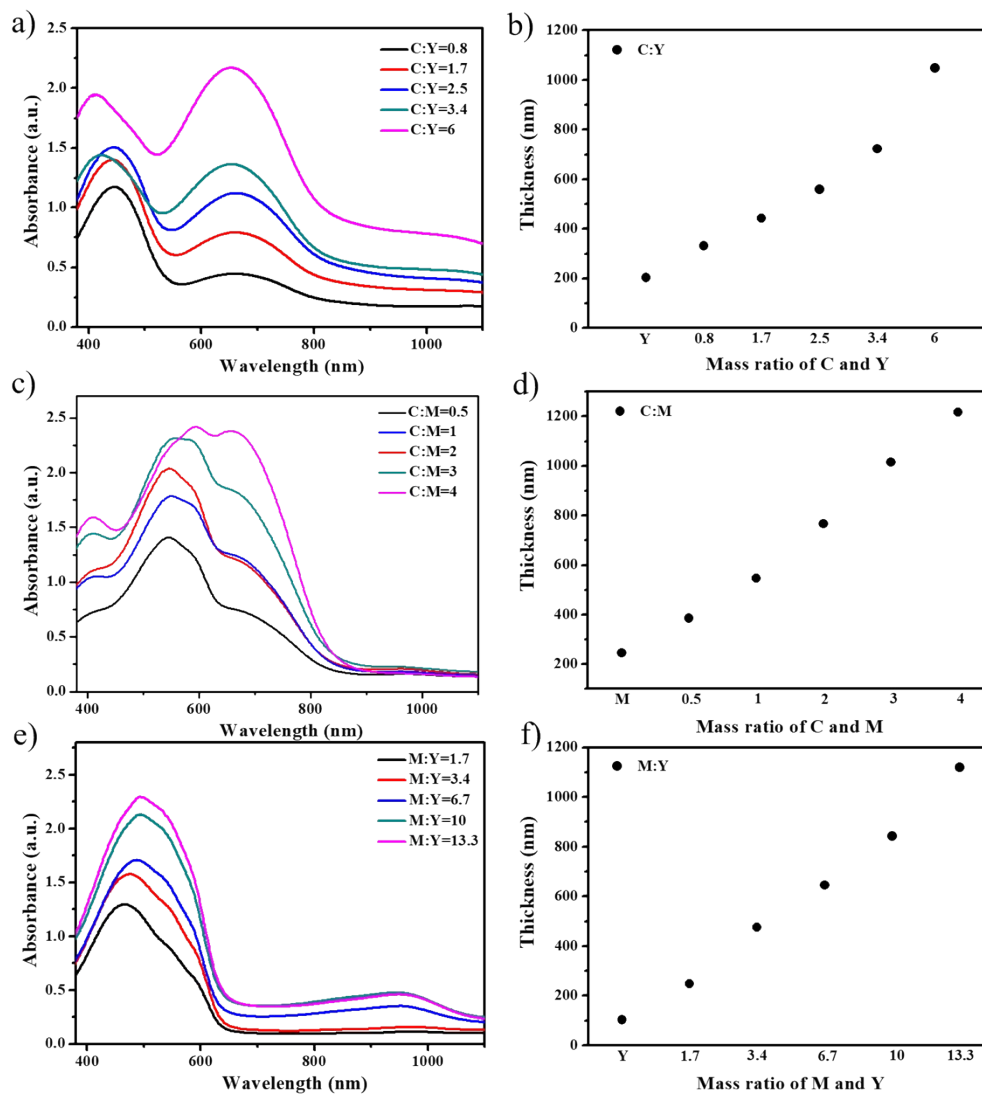


Figure S5. The bilayer films absorbance spectra of a) C:Y, c) C:M, and e) M:Y versus their mass ratio. The corresponding film thickness of b) C:Y, constant Y film thickness, d) C:M, constant M film thickness, e) M:Y, constant Y film thickness.

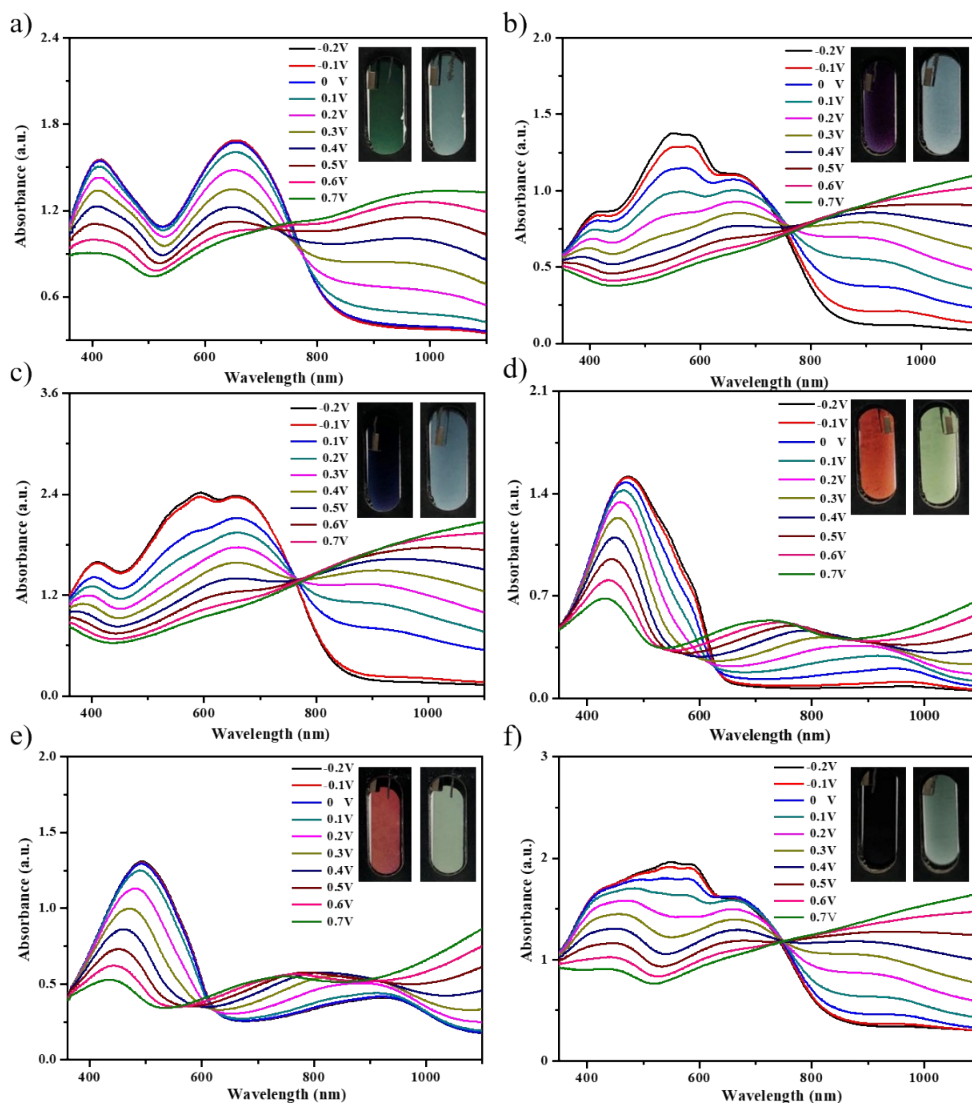


Figure S6. Spectroelectrochemistry and photographs of (a) WS-ECP-Green-acid (-0.2 V to 0.6 V), (b) WS-ECP-Purple-acid (-0.2 V to 0.7 V), (c) WS-ECP-Blue-acid (-0.2 V to 0.7 V). (d) WS-ECP-Orange-acid (-0.2 V to 0.7 V), (e) WS-ECP-Red-acid (-0.2 V to 0.7 V), (f) WS-ECP-Black-acid (-0.2 V to 0.7 V). The composite films were spray-cast onto ITO-coated glass via SLbL to form double-layer or multilayer film. The mass ratio of each layer in the composite film is (a) C:Y=6:1, (b) C:M=1:1, (c) C:M=4:1, (d) M:Y=5:1, (e) M:Y=12:1, (f) C:M:Y=8:3:1. Electrochemical oxidation of the composite films were carried out in 0.2 M KNO_3 /water supporting electrolyte using an Ag/AgCl reference electrode. A platinum wire was used as the counter electrode. The applied potential was increased in step of 100 mV.

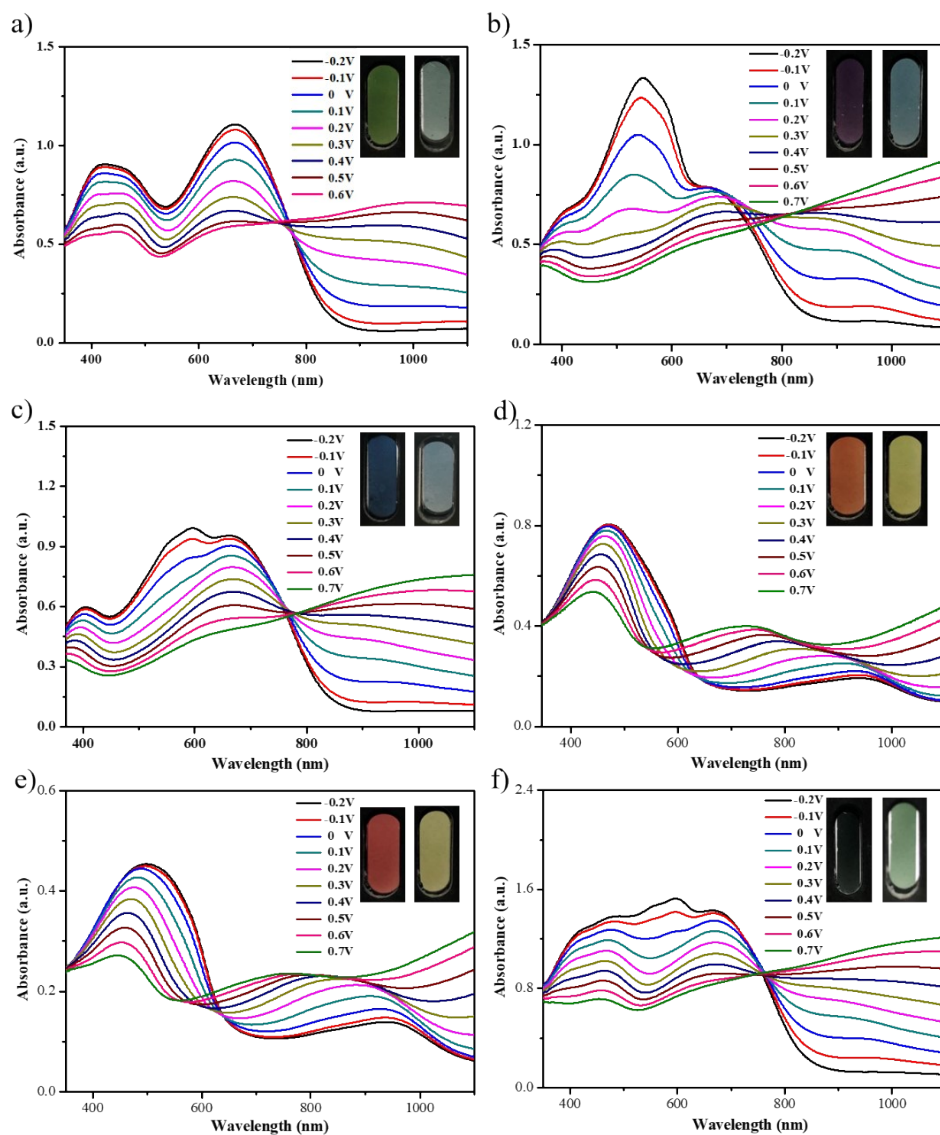


Figure S7. Spectroelectrochemistry and photographs of (a) WS-ECP-Green-acid (-0.2 V to 0.6 V), (b) WS-ECP-Purple-acid (-0.2 V to 0.7 V), (c) WS-ECP-Blue-acid (-0.2 V to 0.7 V), (d) WS-ECP-Orange-acid (-0.2 V to 0.7 V), (e) WS-ECP-Red-acid (-0.2 V to 0.7 V), (f) WS-ECP-Black-acid (-0.2 V to 0.7 V). The films were spray-cast onto ITO-coated glass from aqueous solution via co-processing. The mass ratio of mixture of (a) C:Y=6:1, (b) C:M=1:1, (c) C:M=4:1, (d) M:Y=5:1, (e) M:Y=12:1, (f) C:M:Y=8:3:1. Electrochemical oxidation of the films was carried out in 0.2 M KNO_3 /water supporting electrolyte using an Ag/AgCl reference electrode. A platinum wire was used as the counter electrode. The applied potential was increased in step of 100 mV.

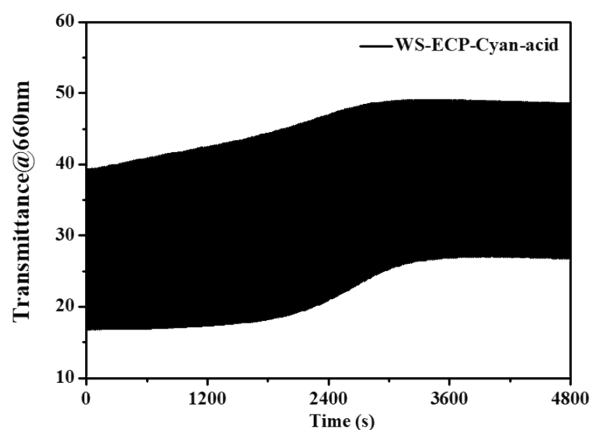


Figure S8. Long-term optical transmittance data (0-4800 s) with intervals of 3 s of the WS-ECP-Cyan-acid film at 660 nm between -0.2 V and 0.6 V.

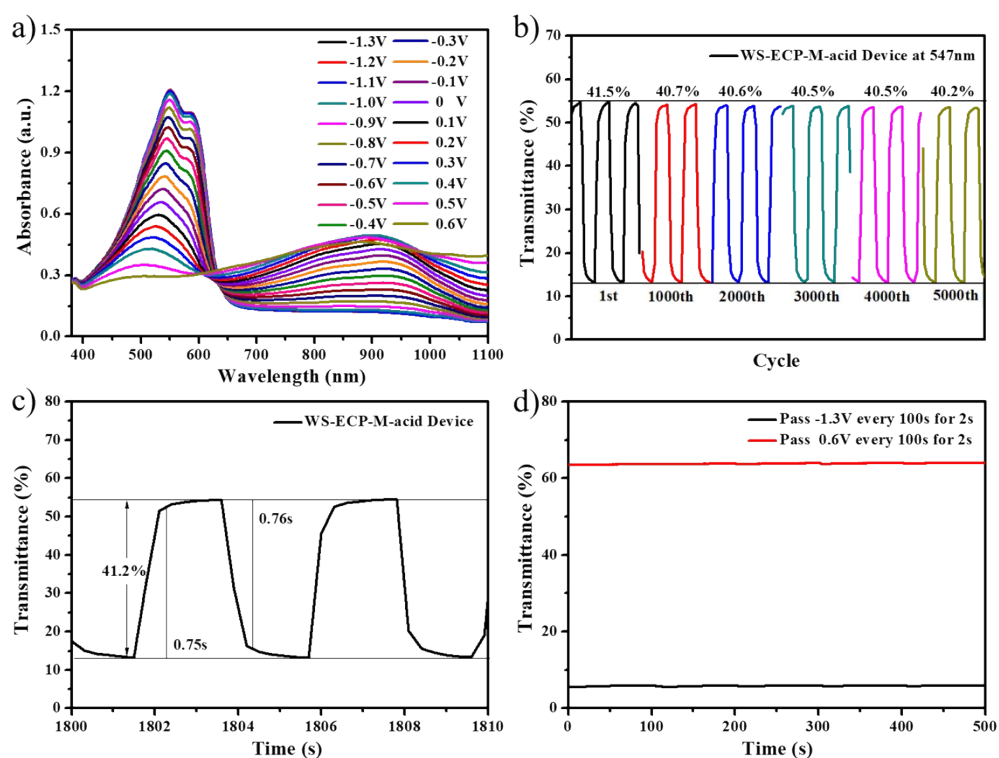


Figure S9. The monochromatic devices. (a) Spectroelectrochemistry. (b) Long-term optical transmittance data (0-5000th cycle) with intervals of 3 s at 547 nm between -1.3V and 0.6 V. (c) Optical contrast and switching time. (d) Memory effect.