

Supporting Information

**Printing Dynamic Color Palettes and Layered Textures through  
Modeling-Guided Stacking of Electrochromic Polymers**

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## **Materials and methods**

### ***Materials***

Chloroform, ethanol (99.5%), and acetone (99.5%) were purchased from Fisher Scientific. The propylene carbonate (PC), lithium bis(trifluoromethane) sulfonamide (LiTFSI), and platinum wire (99%, 0.5 mm) were purchased from Sigma-Aldrich. All chemicals were used as received unless otherwise specified.

### ***Preparation of electrochromic polymer stackings***

Electrochromic polymers (ECP-M, ECP-Y, ECP-C, ECP-blue, ECP-orange) and crosslinker (bisFA) were synthesized following the reported works.<sup>1-8</sup> The three ECPs were dissolved in chloroform solvent with certain concentrations and stirred for 12 hours, forming homogenous ECP/chloroform solutions for later use. On the other hand, the crosslinker was dissolved in chloroform solvent with a concentration of 10 mg/mL and stirred for 12 hours before use. Glass/ITO substrates were cleaned by sonicating in acetone and ethanol for 10 mins respectively and dried out in an oven at 100 °C. For a certain volume of ECP chloroform solution, 5 w% of crosslinker was added and mixed with it. The mixture was spin-coated on glass/TIO substrates at a spin speed of 1500 rpm for 1 min. The obtained ECP/crosslinker thin film was exposed to a UV lamp, which emitted at both 365 nm and 405 nm, for 5 minutes to complete the cross-linking. In photolithography printing, the photomask was covered tightly on top of the ECP/crosslinker thin film before it was exposed to the UV lamp. After the cross-linking, the ECP film was washed using chloroform. The areas exposed to UV light were crosslinked and solvent resistant while the remaining un-crosslinked film was washed away. On top of the cross-linked ECP film or ECP pattern, another layer of ECP can be spin-coated or patterned following the same protocol.

### ***Electrochemical and optical measurements***

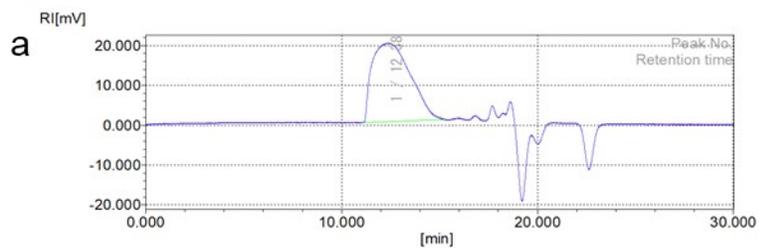
All the cyclic voltammetry (CV) experiments were carried out in a three-electrode cell at a scan rate of 40 mV/s. 0.2 M LiTFSI in propylene carbonate was used as the supportive electrolyte, a platinum wire was used as the counter electrode and a leakless Ag/AgCl electrode was used as reference electrode. All

spectroelectrochemistries of the ECPs were measured using a Biologic SP-150 potentiostat in combination with the Agilent Carry 5000 UV-Vis spectrometer. The absorbance/transmittance spectra of as-coated ECPs were measured first. Then the films were preconditioned using CV until a steady current was observed. The spectroelectrochemical experiments were carried out by recording the absorbance/transmittance spectra between 350 nm to 800 nm after a constant voltage was applied. The colorimetric values (x, y, z) of the spectra were extracted using Agilent color application software under D65 standard illumination.

### ***Instrumentations***

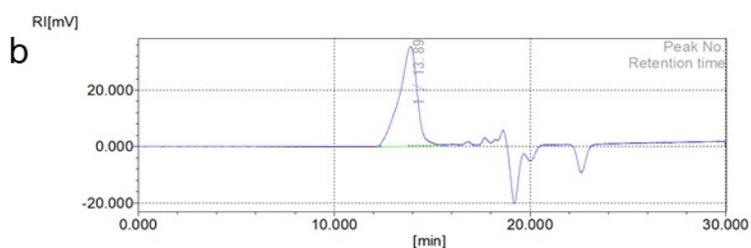
All the spectra were measured using an Agilent Cary 5000 UV/vis-NIR spectrophotometer. A Laurel spin-coater (WS-650Mz-23NPPB) was used to coat electrochromic thin films. All electrochemical measurements were studied using a Biologic SP-150 potentiostat. Profilometer-Stylus (Bruker Dektak XT) was used to measure the ECP films with thicknesses higher than 100 nm and AFM (Veeco Dimension 3100) was used to measure the films with thicknesses lower than 100 nm. Olympus BX-51 Optical Microscope was used to monitor the color switching of ECPs. Hitachi S-4800 Field Emission SEM was used to characterize the double-layer ECP. F10-RT UVX Filmetrics was used to measure the optical constant values. Tosoh EcoSEC 8320 GPC was used to measure the molecular weights and dispersity of ECPs. Non-contact 3D optical profiler (Bruker ContourX-200) was used to measure the ECP textures. NMR spectra were taken by Bruke AV-III-400-HD spectrometer.





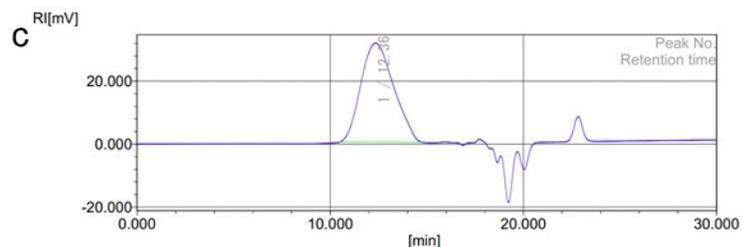
Result of molecular weight calculation (RI)

Peak 1 Base Peak					
	[min]	[mV]	[mol]	Mn	Mw
Peak start	11.012	0.630	207.288	Mw	51,269
Peak top	12.380	20.640	49.976	Mz	78,742
Peak end	15.293	1.444	2.417	Mz+1	99,068
				Mv	51,269
Height [mV]		19.750		Mp	49,976
Area [mV*sec]		2676.500		Mz/Mw	1.536
Height% [%]		100.000		Mw/Mn	1.987
[eta]		51268.91079		Mz+1/Mw	1.932



Result of molecular weight calculation (RI)

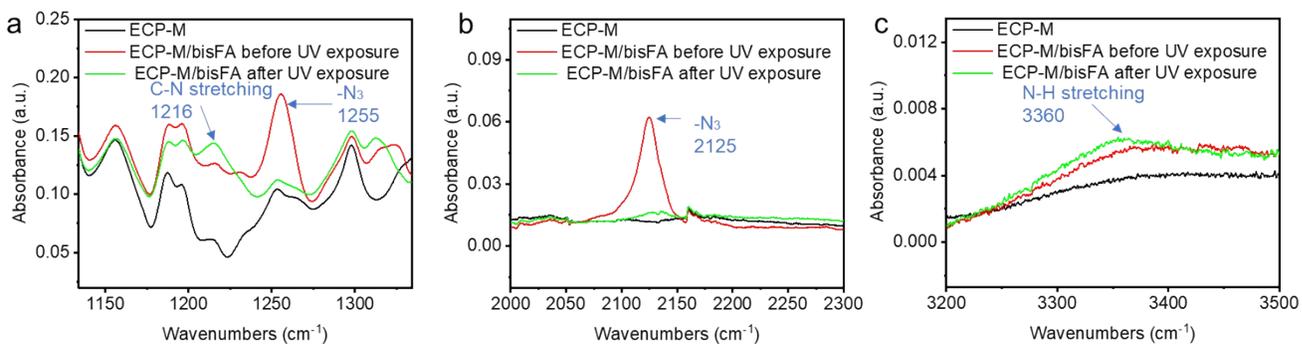
Peak 1 Base Peak					
	[min]	[mV]	[mol]	Mn	Mw
Peak start	12.110	-0.072	66.171	Mz	14,299
Peak top	13.892	35.541	10.380	Mz+1	18,810
Peak end	15.512	0.475	1.926	Mv	24,475
				Mp	14,299
Height [mV]		35.327		Mz/Mw	10,381
Area [mV*sec]		2264.340		Mw/Mn	1.316
Height% [%]		100.000		Mz+1/Mw	1.288
[eta]		14299.03392			1.712



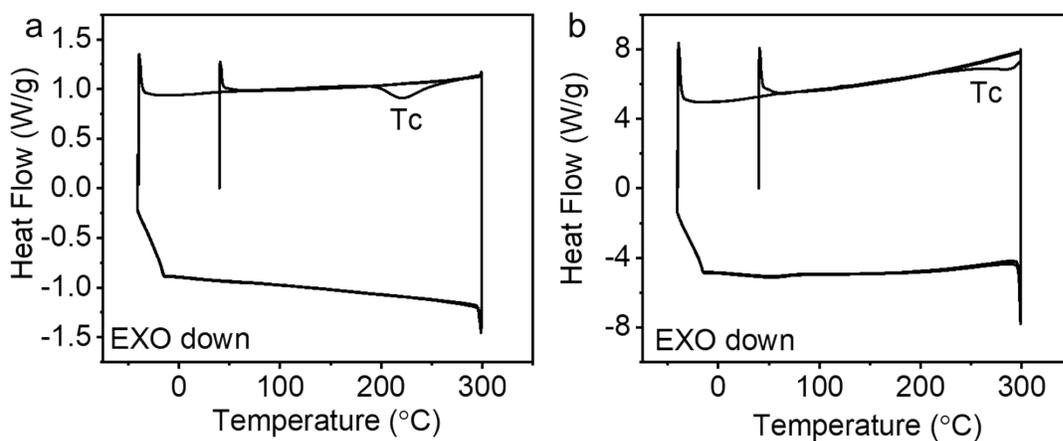
Result of molecular weight calculation (RI)

Peak 1 Base Peak					
	[min]	[mV]	[mol]	Mn	Mw
Peak start	10.463	0.694	366.565	Mz	32,175
Peak top	12.362	32.203	50.937	Mz+1	58,480
Peak end	14.817	0.598	3.968	Mv	93,339
				Mp	129,646
Height [mV]		31.551		Mz/Mw	58,480
Area [mV*sec]		3713.034		Mw/Mn	50,938
Height% [%]		100.000		Mz+1/Mw	1.596
[eta]		58479.64258			1,818
					2,217

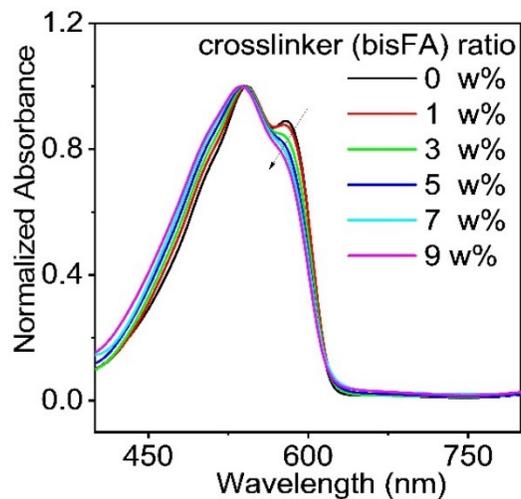
**Figure S3.** Raw GPC chromatograms for (a) ECP-C, (b) ECP-M, and (c) ECP-Y.



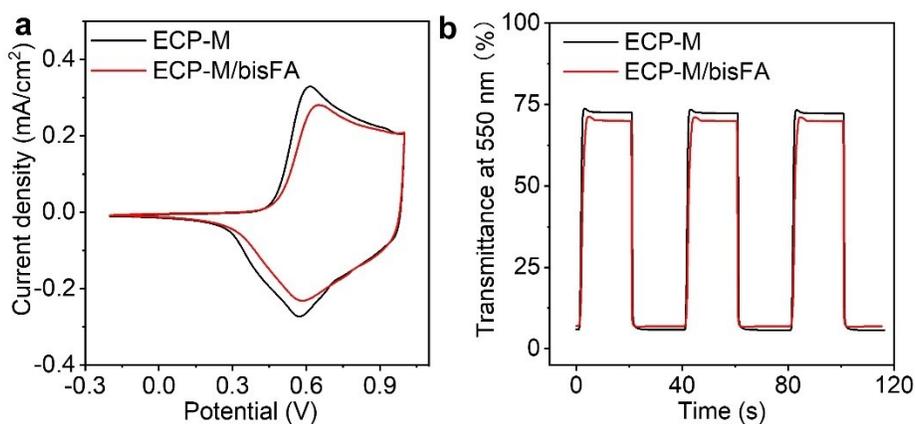
**Figure S4.** Fourier-transform infrared spectrum of pure ECP-M (black curve), ECP-M/bisFA before (red curve) and after UV exposure (green curve). (a)-(c) show different spectrum ranges.



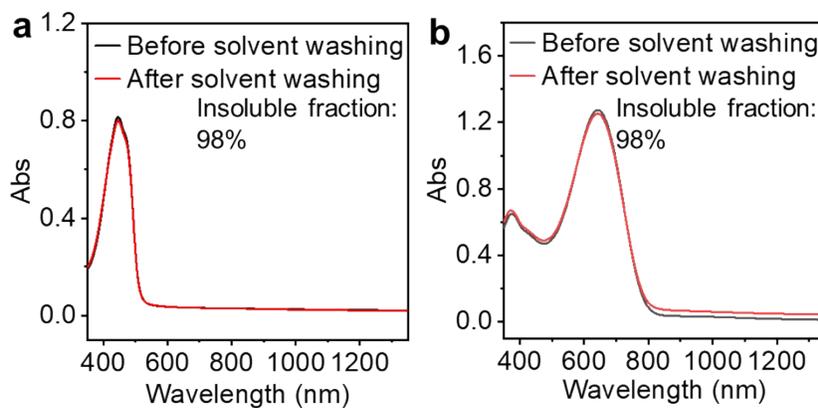
**Figure S5.** DSC thermogram for (a) pure ECP-M and (b) crosslinked ECP-M. Polymers are recorded at 10°C/min



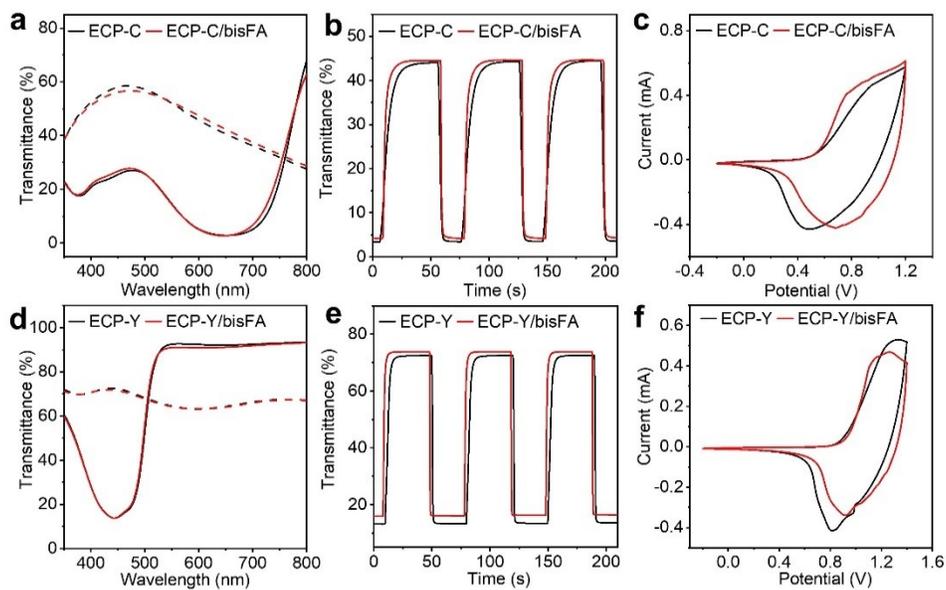
**Figure S6.** Absorbance spectra of ECP-M with different crosslinker/ECP-M weight ratios.



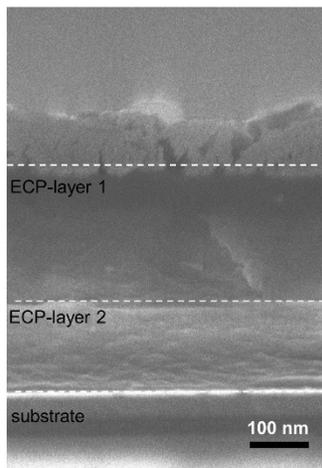
**Figure S7.** (a) Cyclic voltammograms and (b) double potential step chronoabsorptometry of pure ECP-M and cross-linked ECP-M.



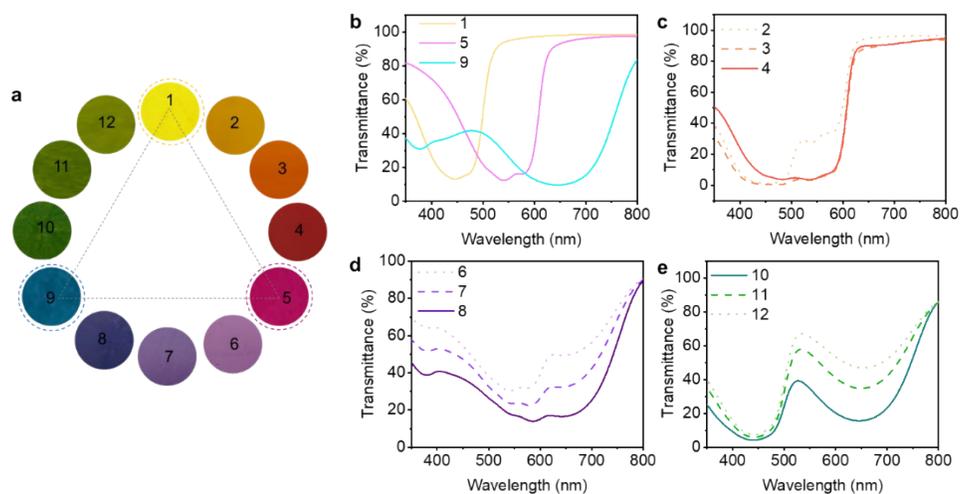
**Figure S8.** Absorbance spectra of cross-linked (a) ECP-Y and (b) ECP-C before and after chloroform washing.



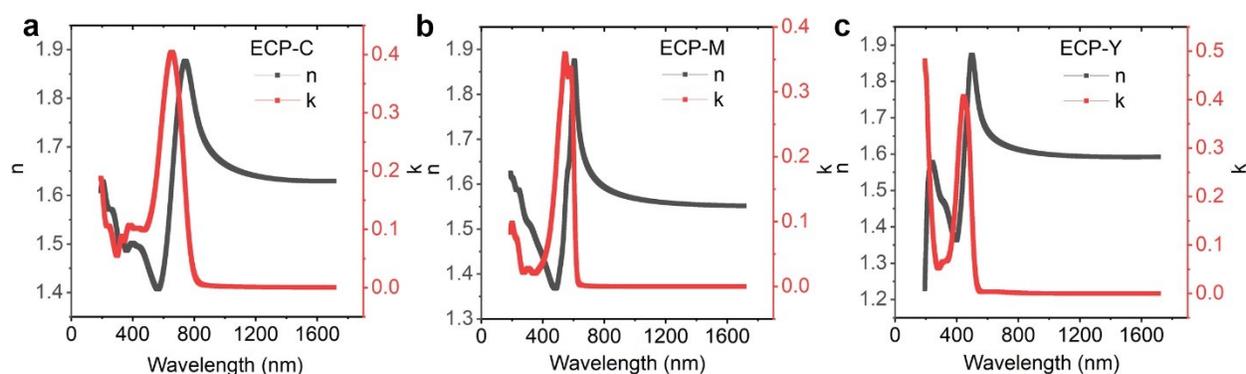
**Figure S9.** (a) Spectroelectrochemistry, (b) double potential step chronoabsorptometry, and (c) cyclic voltammogram of pure ECP-C and cross-linked ECP-C. (d) Specielectrochemistry, (e) double potential step chronoabsorptometry, and (f) cyclic voltammogram of pure ECP-Y and cross-linked ECP-Y.



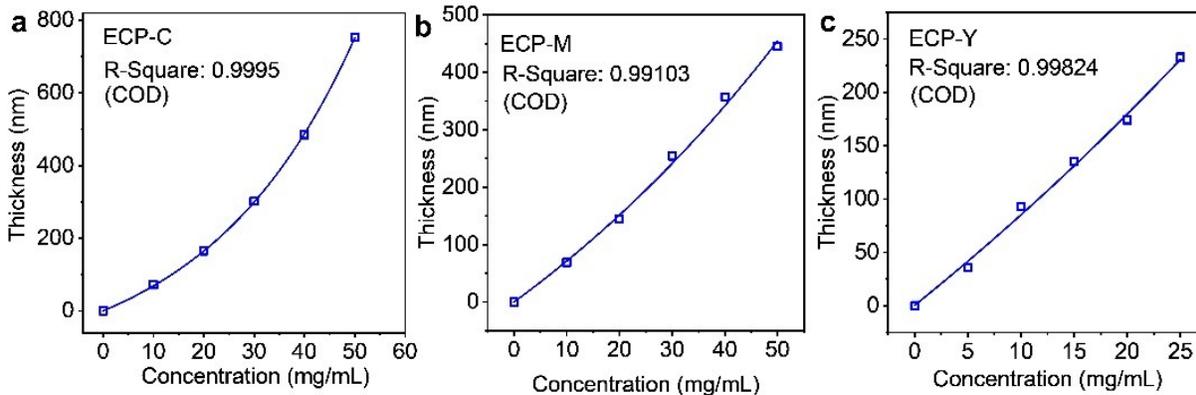
**Figure S10.** Scanning electron microscopic image of a double-layer ECP.



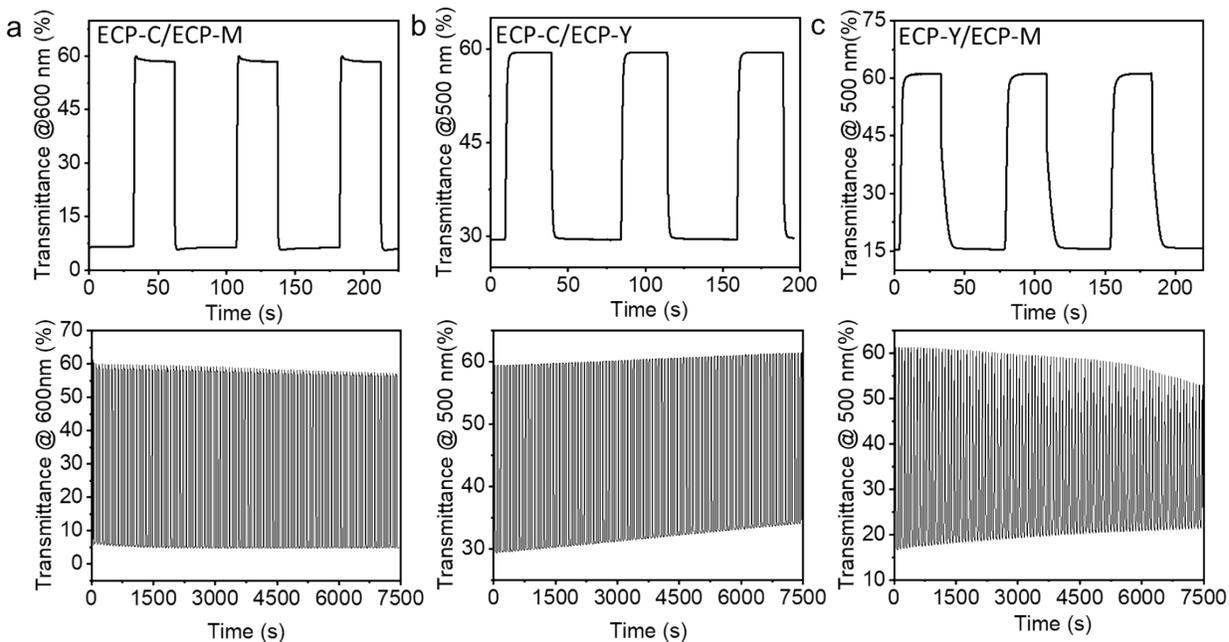
**Figure S11.** (a) A color palette with 12 colors and (b-d) the transmittance spectra for each color in the palette.



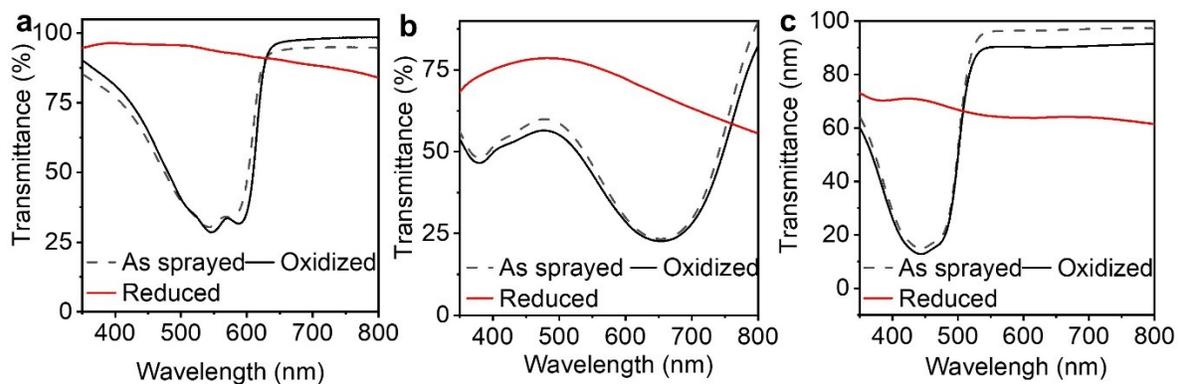
**Figure S12.** Optical constant values of (a) ECP-C, (b) ECP-M, and (c) ECP-Y



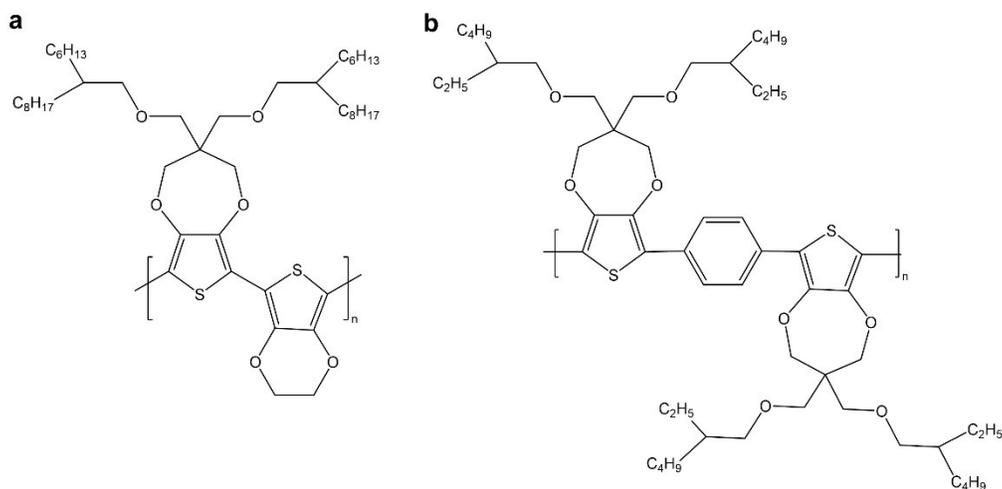
**Figure S13.** Thickness-concentration correlations of (a) ECP-C, (b) ECP-M, and (c) ECP-Y. The data are fitted to exponential functions with R-squares shown in the figure.



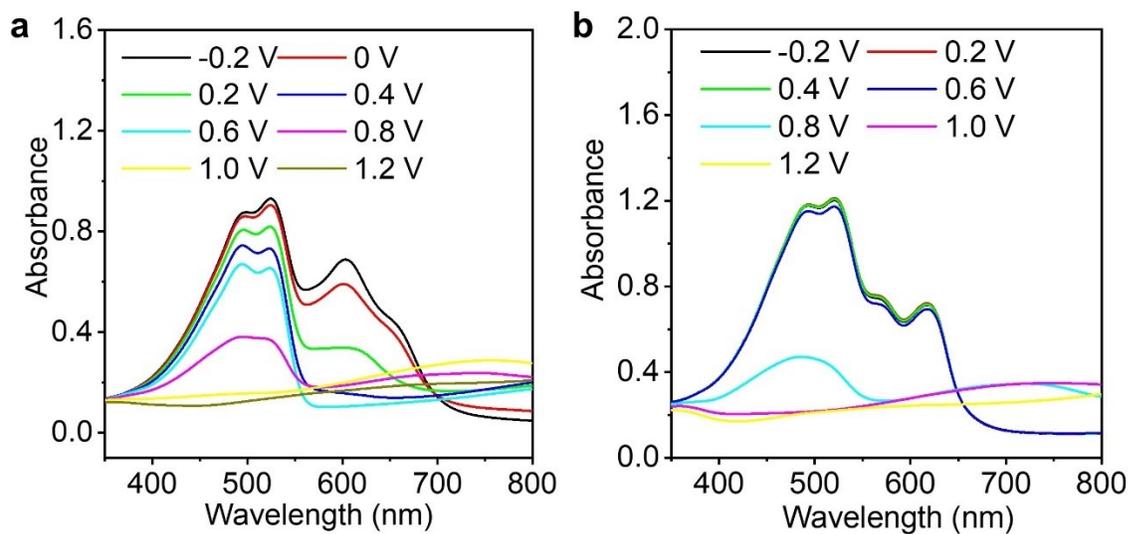
**Figure S14.** Double potential step chronoabsorptometries and long cycling optical contrast tests of (a) ECP-C/ECP-M, (b) ECP-C/ECP-Y and (c) ECP-Y/ECP-M stackings.



**Figure S15.** Spectroelectrochemistries of single-layer (a) ECP-M, (b) ECP-C, and (c) ECP-Y.



**Figure S16.** Molecular structures of (a) ECP-blue and (b) ECP-orange



**Figure S17.** Spectroelectrochemistries of (a) ECP-blue/orange blending and (b) ECP-blue/orange stacking.

**Table S1.** Molecular weights and dispersities of electrochromic polymers

Polymer	Mn [g.mol <sup>-1</sup> ]	Polydispersity [PDI]
ECP-C	25.8k	2.0
ECP-M	11.1k	1.3
ECP-Y	32.2k	1.8

**Table S2.** Thickness information of the color pallet in Figure S11 and Figure 1

Sample #	Stacking information
1	ECP-Y (174)
2	ECP-Y (335 nm)/ECP-M (155 nm)
3	ECP-Y (333 nm)/ECP-M (380 nm)
4	ECP-Y (136 nm)/ECP-M (352 nm)
5	ECP-M (254 nm)
6	ECP-M (89 nm)/ECP-C (102 nm)
7	ECP-M (88 nm)/ECP-C (150 nm)
8	ECP-M (90 nm)/ECP-C (253 nm)
9	ECP-C (302 nm)
10	ECP-C (256 nm)/ECP-Y (225 nm)
11	ECP-C (143 nm)/ECP-Y (215 nm)
12	ECP-C (98 nm)/ECP-Y (222 nm)

**Table S3. Modeling and experimental xyz chromaticity values of double-layer ECP stackings**

sample	x	y	z
ECP-C/M experimental	0.26	0.20	0.54
ECP-C/M modeling	0.25	0.20	0.55
ECP-C/Y experimental	0.34	0.47	0.19
ECP-C/Y modeling	0.34	0.47	0.19
ECP-Y/M experimental	0.48	0.38	0.14
ECP-Y/M modeling	0.48	0.37	0.15

**Table S4.** Electrochromic parameters for the double-layer electrochromic stackings

ECP stacking	$\Delta\% T$	Response time <sup>a</sup>		CE <sup>b</sup> ( $\text{cm}^2 \text{c}^{-1}$ )	Optical activity after 100 cycles (%)
		Tc (s)	Tb (s)		
ECP-Y/ECP-M	46.4 @ 500 nm	6.9	3.4	104.5	70.7%
ECP-C/ECP-M	53.8 @ 600 nm	1.3	0.7	198.1	98.5%
ECP-C/ECP-Y	30.7 @ 500 nm	2.1	1.5	118.4	91.7%

<sup>a</sup> Time for completing 95% of full transmittance change

<sup>b</sup> Coloration efficiency (CE)= $\log(\%T_{0.95\Delta\%T}/\%T_{\text{colored}})/Q$ , Q is charge density

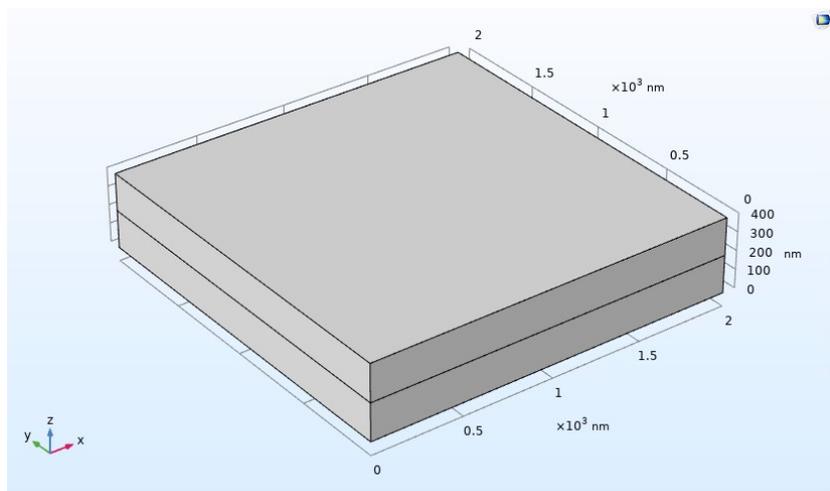
## Supplementary notes

### Step1: Set up model environment.

3-dimensional space was selected for study. Wave electromagnetics problems was solved with Wave Optics modules. Wavelength domain was included to compute the electromagnetic transmittance and reflectance versus wavelength in our system.

### Step2: Create double-layer geometry.

To simulate the electrochromic polymer thin films, block geometries with large width-thickness ratios were created. The number of blocks were determined by stacked polymer layers. Here, we use a double-layer stacking as an example, as shown in Figure S12. The widths, depths and heights of the blocks were set to 2000 nm, 2000 nm and 200 nm, respectively. The positions of the two block geometries were adjusted to make them stacked seamlessly.



**Figure S18.** A stacking geometry used to simulate a double-layer electrochromic thin film.

### **Step3: Specify material property.**

The block 1 and block 2 were assigned two blank materials, named as ECP-1 and ECP-2, respectively. To describe the optical properties of the blank materials, refractive index properties were added from electromagnetic models. We imported the refractive index and extinction coefficient data, which were obtained by Filmetric measurements with interpolation setting. We denoted the refractive index function and extinction coefficient function as  $n$  and  $k$ , respectively. These two variables were defined as  $n(c\_const/freq)$  and  $k(c\_const/freq)$  in the material contents. In interpolation settings, linear model was selected for interpolation and constant model was selected for extrapolation.  $nm$  was input as the units.

### **Step 4: Define physics and boundary conditions.**

#### (1) Ports

Two ports were added for the double-layer stackings to simulate electromagnetic waves that propagate into materials. One port was allocated to the top surface and had wave excitation turned on, while the other was assigned to the bottom surface and had wave excitation turned off. Both ports were configured as periodic with a power of 1 W. The amplitudes of the electric field at  $x$ ,  $y$ ,  $z$  were all set to 1 V/m. The incident angle of elevation and the incident angle of azimuth were both set to 0.

#### (2) Periodic boundary condition

Periodic conditions were applied to the opposing surfaces of the stacking geometry. The Floquet periodicity was chosen, and the  $k$  vector for the Floquet periodicity was established from the periodic port.

### **Step 5: Create mesh.**

Normal predefined mesh was used for solving the solution.

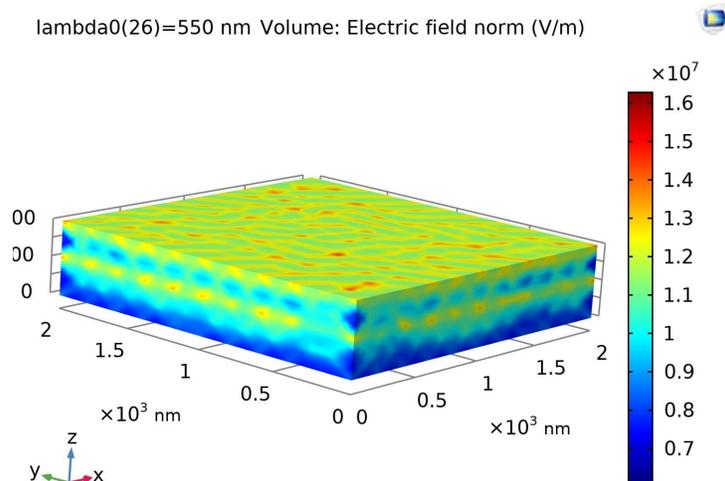
### **Step 6: Run simulation.**

We utilized the step study technique in the wavelength domain. As an example, we set the study range from 350 nm to 800 nm with a 10 nm increment. We obtained comparable simulation outcomes with larger ranges and fewer steps, which are computationally more expensive.

### **Step 7: Postprocess results**

#### (1) Electromagnetic field distributions

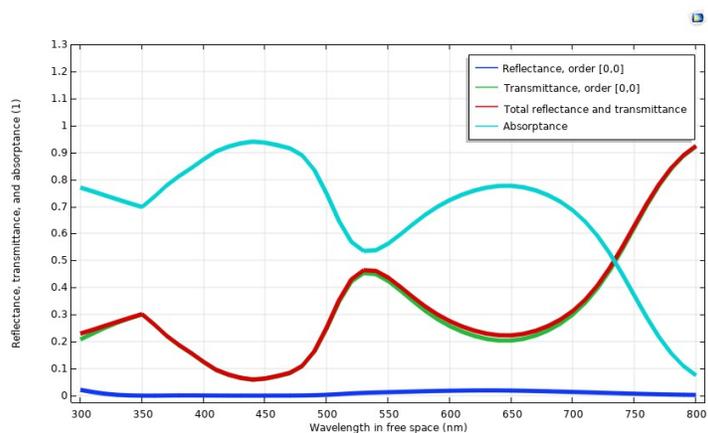
The simulation results of electromagnetic field-ECP interactions were visualized as a three-dimensional heatmap (Figure S13). The color codes represent the light intensity at a specific wavelength (550 nm) in the geometry.



**Figure S19.** A 3D heatmap showing interactions between electromagnetic wave and electrochromic polymer stacking.

(2) Reflectance, transmittance and absorbance plot

We plotted reflectance, transmittance and absorbance spectra of the stacking electrochromic polymer as shown below.



**Figure S20.** Transmittance, reflectance and absorbance of the electrochromic polymer stacking.

(3) Derived values

In the derived value column, a variety of values, such as transmittance, reflectance or total reflectance and transmittance can be derived and exported for postprocessing.

## References

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