Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Three primary colors (cyan/magenta/yellow) electrochromic devices based on PEDOT:PSS and ‘electrobase/electroacid’ theory

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5. Supplementary figure for devices

Figure S8. (a) Changes in absorption at 575 nm when added -1.5 V with various time. (b) The cycle stability of device at 575 nm (1.24 V-5 s, -0.36 V-15 s).

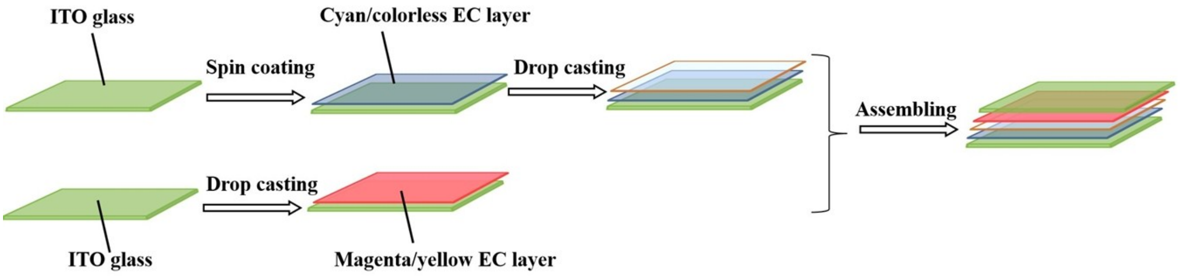
1. Experimental details

Materials.

Polymethyl methacrylate (PMMA, Mw~100,000), Propylene carbonate (PC), p-benzoquinone (p-BQ), potassium tert-butoxide (t-BuOK), trifluoroacetic acid (CF_3COOH) and 4-OH-TEMPO were purchased from Energy Chemicals, China. Phenol Red (PR) and Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were purchased from Aladdin Chemicals, China. Poly(3,4-ethylenedioxythiophene)-poly(sodium-p-styrenesulfonate) (PEDOT:PSS) (PH 1000) was purchased from Heraeus, Germany. Acetone (AR) was purchased from Beijing Chemical Works，China. The ITO glasses were purchased from South China Xiang Science & Technology company (Sheet Resistance =8.27 Ω; Transmittance >84%; the thickness of ITO is 185 nm).

Fabrication of multicolor (cyan/magenta/yellow) electrochromic device

The preparation process is as follows : The solutions of the layers for device were prepared firstly. Magenta/yellow-electrochromic layer: PMMA 0.72 g, PC 0.15 mL, $TBAPF_6$ 0.3 g, p-BQ 3.024 mg, PR 1.5 mg, 4-OH-TEMPO 5 mg, CH_3COCH_3 6 mL; Cyan/colorless-electrochromic layer: PEDOT:PSS (PH 1000) 100 μL; Ion conductive layer: PMMA 2.16 g, PC 0.45 mL, $TBAPF_6$ 0.9 g, CH_3COCH_3 15 mL. The above solutions were heated at 50 ^oC and stirred until transparent solutions were formed. As shown in **Scheme S1**, the Magenta/yellow-electrochromic layer was coated to an ITO glass by drop casting as counter electrode. The Cyan/colorless-electrochromic layer was formed by 100 μL PEDOT:PSS which deposited on another ITO glass by spin coating with the spin speed of 4500 r/s for 60 seconds as working electrode. Then, the conductive layer was coated between Cyan/colorless-electrochromic layer and Magenta/yellow-electrochromic layer by drop casting. Finally, two electrodes with functional layers were connected tightly and the device was assembled successfully. The initial state of the device was yellow.



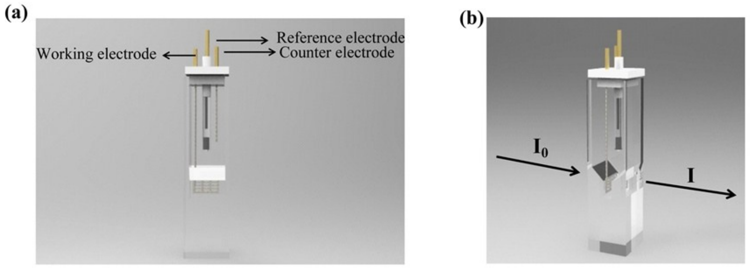
Scheme S1. The preparation process of multicolor (cyan/magenta/yellow) electrochromic device.

Instruments and Characterization.

The electrochemical data were recorded with a Bio-logic electrochemical work station. UV-Vis absorption spectra were measured with a Shimadzu UV-2550 PC double-beam spectrophotometer. Color density was measured with x-rite eXact Scan spectrophotometer. The sheet resistances were measured with ST-2258C multifunction digital four-probe tester. The ITO glasses were etched by Xi-Ai FB30-Z -Z HPWU0300-SKS Laser marking machine. ^{1}H NMR spectra were recorded by a Bruker 500M NMR spectrometer. Chemical shift values are given relative to TMS.

The measurement methods of spectroelectrochemistry

As shown in **Scheme S2**, a thin-layer (1 mm) quartz glass electrochemical cell (ida, China) was used to measure spectroelectrochemical spectra. The three electrodes are consisted of a Pt network working electrode, a Pt wire counter electrode and a Ag reference electrode.

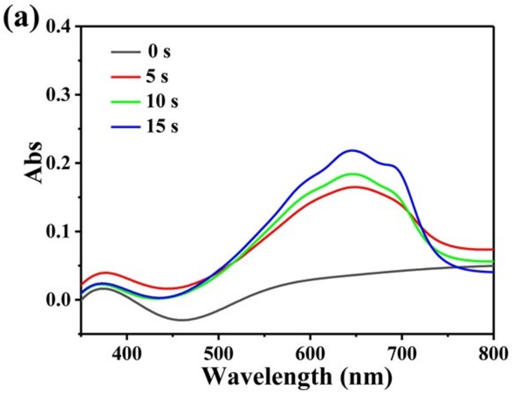


Scheme S2. (a) The structure of a thin-layer quartz electrochemical cell which is used to measure in-situ the UV-Vis spectra of redox state in solution. (b) The route of ultraviolet and visible lights.

The patterning methods of device

ITO glass electrodes in both sides are photo-etched to various patterns by layer mask machine FB30-Z HPWU0300-SKS. Then the devices with photo-etched ITO electrodes were fabricated according to the procedure of the preparation of multicolor (cyan/magenta/yellow) electrochromic devices.

2. Spectroelectrochemical measurements for cyan/colorless layer



(b)

Time (s)	L*	a*	b*
0	78.10	2.49	-9.77
5	61.67	-4.77	-16.25
10	61.97	-6.54	-17.86
15	50.14	-7.88	-18.78

Figure S1. (a) UV-vis absorption spectra of PEDOT:PSS deposited on ITO glass when added -1.0 V with various time and (b) its corresponding values of CIE coordinates.

3. pH-sensitive properties of phenol red (PR-Y)

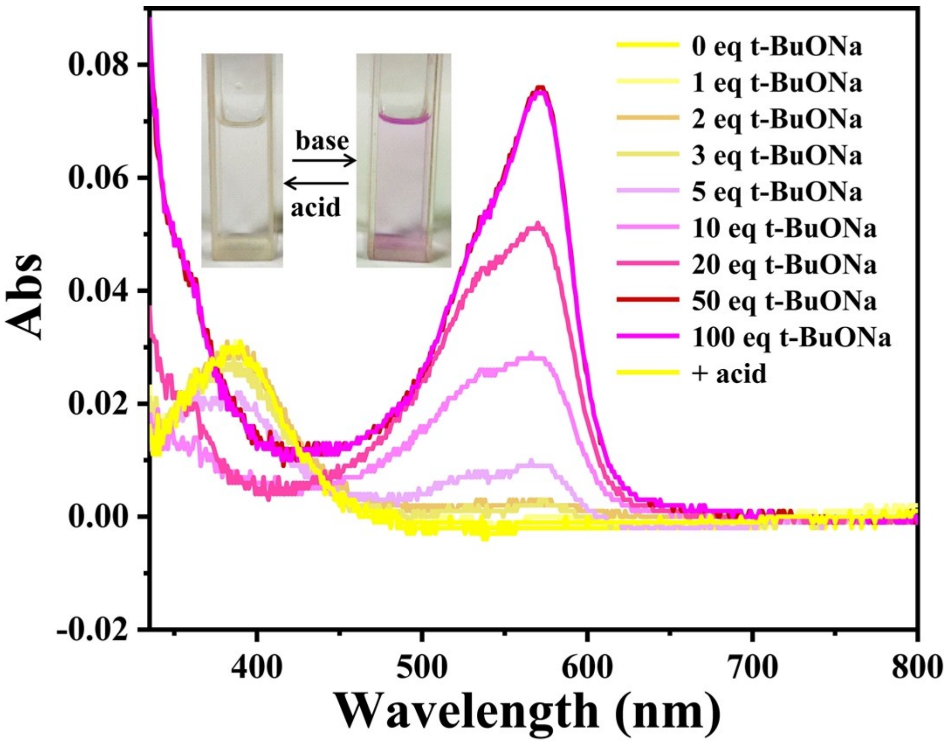


Figure S2. UV-vis absorption spectra of 1.0*10^{-5} M phenol red (PR-Y) in acetone when added various equivalent chemical base (t-BuONa) and chemical acid (CF_3COOH).

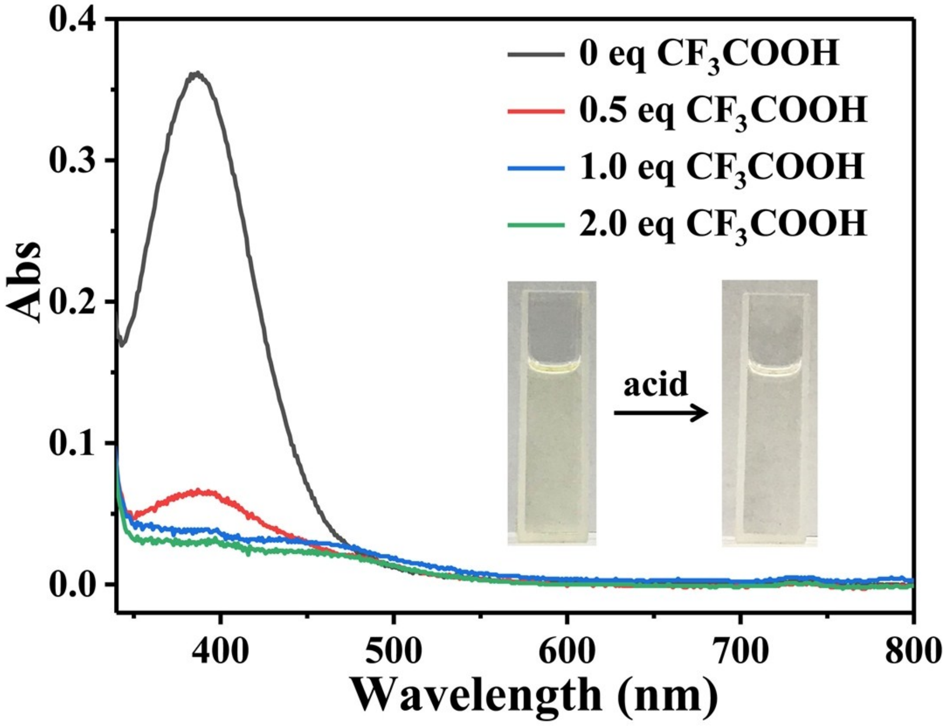


Figure S3. UV-vis absorption spectra of 1.0*10^{-4} M phenol red (PR-Y) in acetone when added various equivalent chemical acid (CF_3COOH).

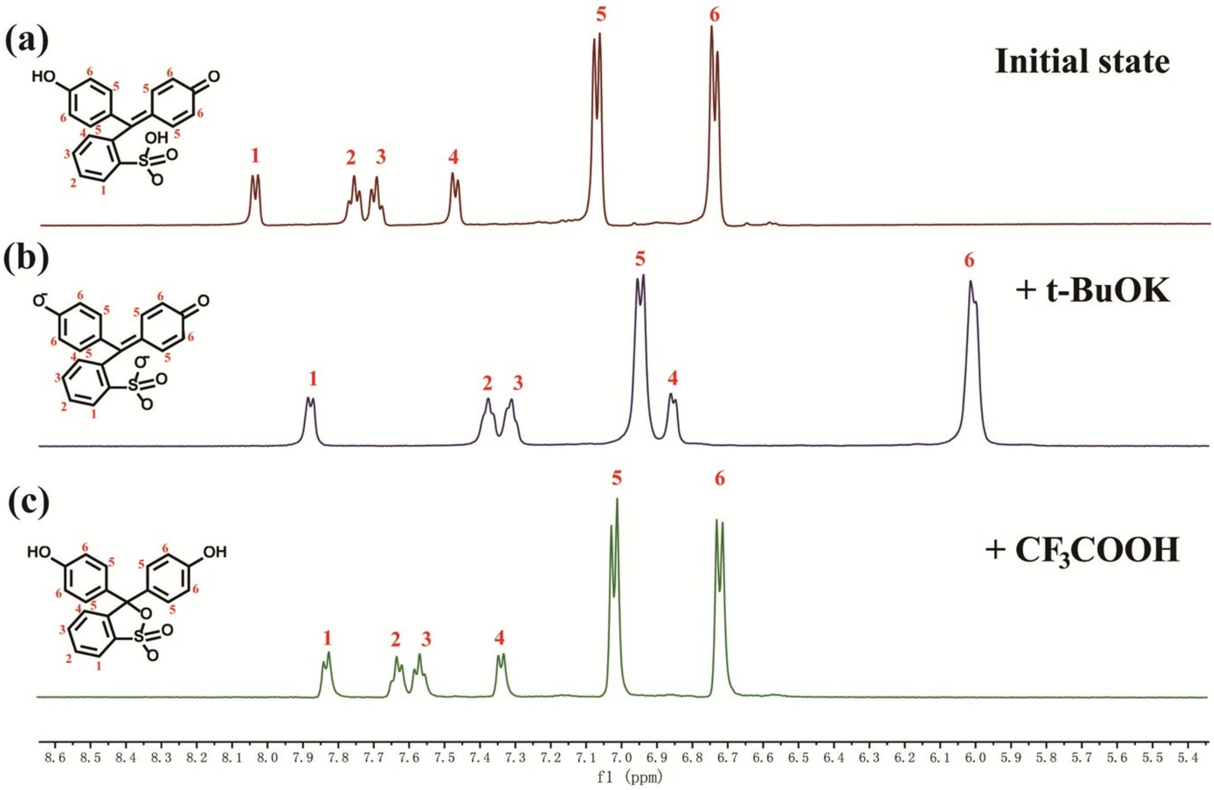


Figure S4. ^{1}H NMR ~~spectrum~~ of phenol red (PR-Y) in DMSO (a), PR-Y +100 eq CF$_3$COOH (~~b~~), ~~PR-Y +10 eq t-BuOK (c~~) recorded at 500 M Hz at room temperature.

4. Spectroelectrochemical measurements in situ

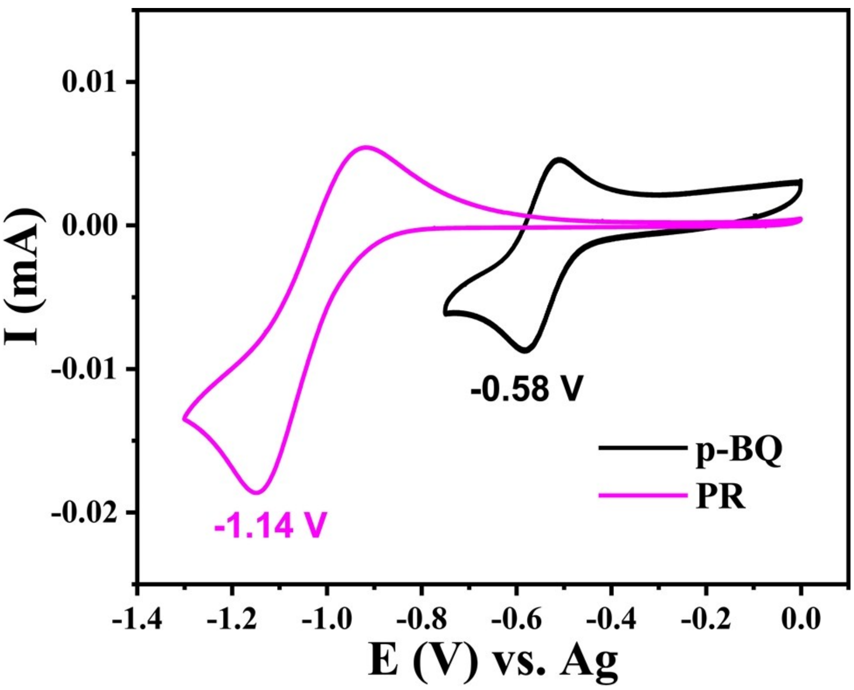


Figure S5. Cyclic voltammetry (CV) curves of 1.0 mM p-BQ and 1.0 mM PR-Y in 0.1 M $TBAPF_6$/acetone.

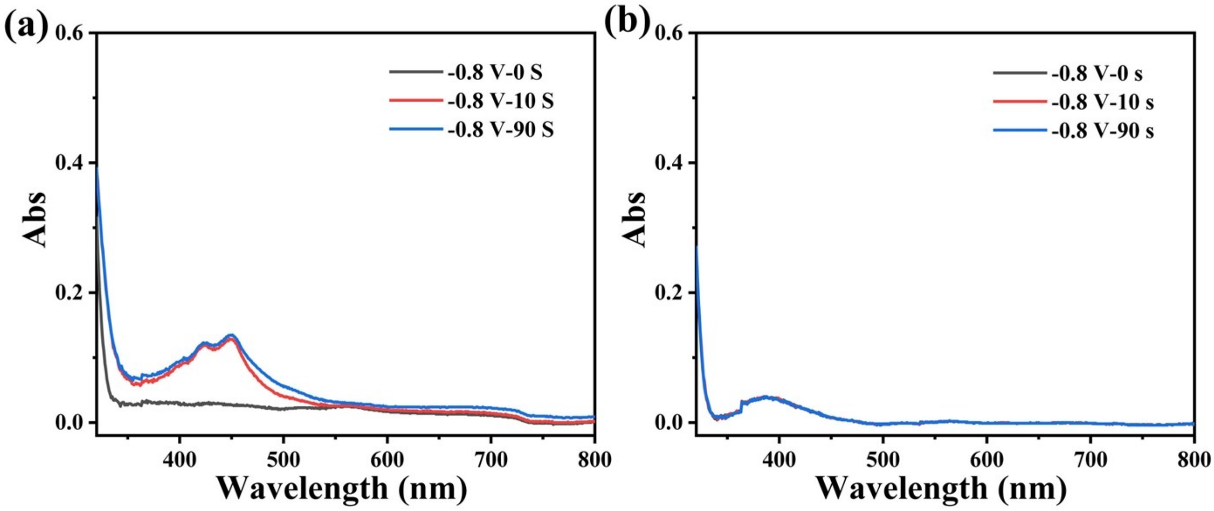


Figure S6. The UV-vis spectroelectrochemical spectra in situ of (a) p-BQ (1.0*10^{-3} M), (b) PR-Y (1.0*10^{-4} M) in acetone with 0.1 M TBAPF$_6$ when the voltage was set as -0.8 V with various time, respectively.

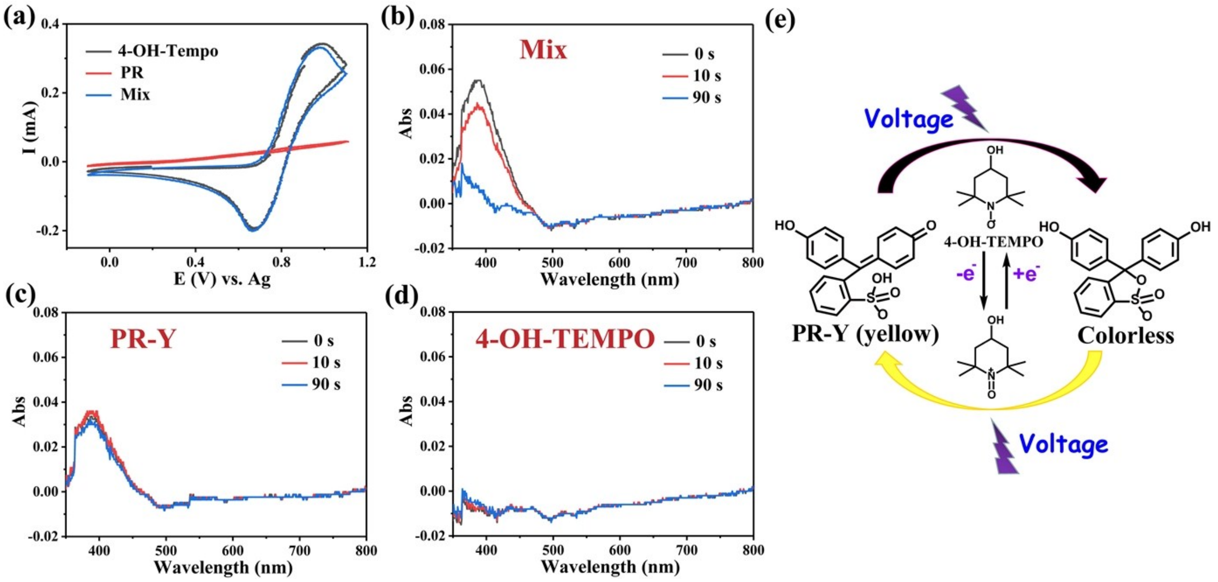


Figure S7. (a) Cyclic voltammetry diagrams of 4-OH-Tempo (1.0*10^{-3} M), PR (1.0*10^{-4} M) and 4-OH-TEMPO (1.0*10^{-3} M) & PR-Y (1.0*10^{-4} M) in 0.1 M TBAPF$_6$/acetone in situ. The UV-vis spectroelectrochemical spectra in situ of (b) 4-OH-TEMPO (1.0*10^{-3} M) & PR-Y (1.0*10^{-4} M), (c) PR-Y (1.0*10^{-4} M), (d) 4-OH-TEMPO (1.0*10^{-3} M) in acetone with 0.1 M TBAPF$_6$ when the voltage was set as +0.9 V with various time, respectively. (e) The mechanism of the conversion of yellow and colorless in the Magenta/yellow-EC layer ~~when the device was changed to cyan.~~

To verify the feasibility of the switch property from yellow to colorless by the combination of 4-OH-TEMPO and PR-Y, the acid-responsive property of PR-Y was tested firstly. As shown in **Figure S2**, the color of PR-Y solution was changed from yellow to colorless after the addition of acid. And the oxidation peak of 4-OH-TEMPO was at +0.9 V while PR-Y was above 1.15 V. The big gap between 4-OH-TEMPO and PR-Y ensured that the structure of PR-Y would not change while 4-OH-TEMPO was oxidized (**Figure S7a**). What's more, the UV-vis spectra of mixture and individual solutions of 4-OH-TEMPO and PR-Y respectively were investigated at +0.9 V. As shown in **Figure S7~~a–e~~**, the yellow was only disppeared when 4-OH-TEMPO and PR-Y coexisted in the solution. The color change indicated that the 4-OH-TEMPO could be served as reversible 'electroacid' to controlled the color and structure of RP-Y, as we expected.

5. Supplementary figure for devices

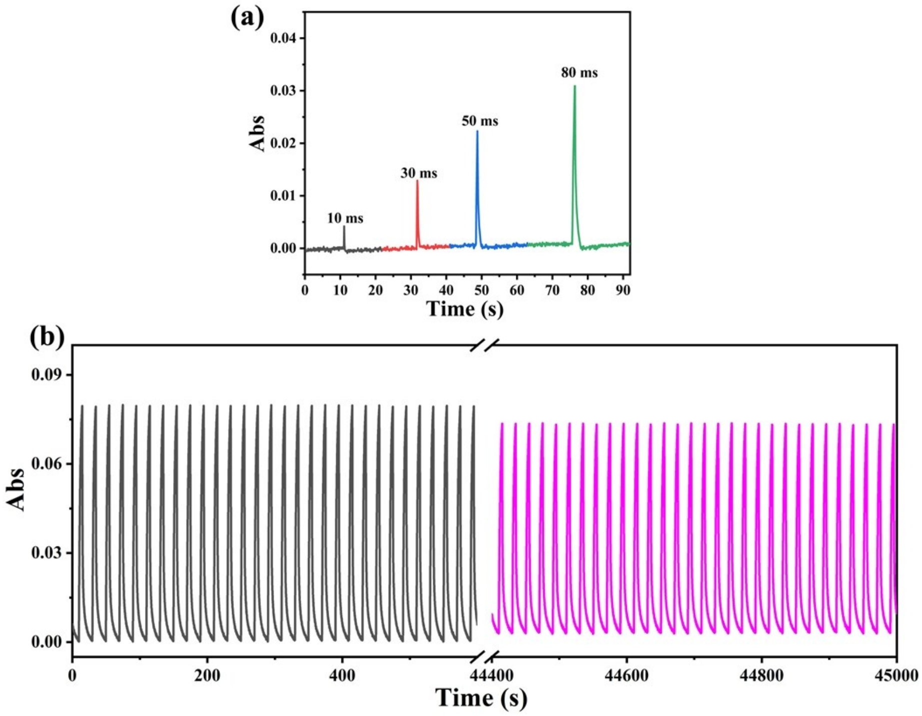


Figure S8. (a) Changes in absorption at 575 nm when added -1.5 V with various time. (b) The cycle stability of device at 575 nm (1.24 V-5 s, -0.36 V-15 s).