### **Supplement Information**

Electrochromic devices based on viologen derivatives with multiple color changes





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f e с d g b NH<sub>2</sub> h а g i d b | h а lef c 2.00H 00. 00.0 00. 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 f1 (ppm) 3.5 3.0 2.5 2.0 1.5 1.0 0.5 Figure S5: <sup>1</sup>H NMR spectrum of compound 5. -5.43  $\begin{array}{c} 7.01 \\ 6.99 \\ 6.88 \\ 6.81 \\ 6.81 \\ 6.79 \\ 6.79 \\ 6.20 \\ 6.20 \end{array}$ 

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Figure S10: High Resolution Mass Spectrometry of IV.









Figure S16: High Resolution Mass Spectrometry of BV.

#### 2. Fabrication of Electrochromic device



Figure S17: Electrochemical impedance spectroscopy (EIS) of (a) 2IV-based rigid ECD, (b) 2PV-based rigid ECD and (c) 2BV-based rigid ECD and (d) the corresponding analog equivalent circuit.



3. Optoelectrochemical properties of viologen derivatives

Figure S18: Cyclic voltammograms of (a) IV, (b) PV and (c) BV in PC solution containing 0.1 M TBAP at a scan rate of 50 mV/s.



Figure S19: UV-vis absorption spectra of (a) IV, (b) PV and (c) BV in PC solution.

Table S1: Optoelectrochemical properties of viologen derivatives

Compounds	$\lambda_{\max}$ (nm)	$\lambda_{_{ m edge}} \ (nm)$	E <sup>opt</sup> (eV)	E <sub>red</sub> onset (V)	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)
IV	361	496	2.50	-0.64	-6.26	-3.76
PV	394/424	564	2.20	-0.19	-6.41	-4.21
BV	333	433	2.86	-0.43	-6.83	-3.97



Figure S20: CVs of (a) IV-based rigid ECD, (b) PV-based rigid ECD and (c) BV-based rigid ECD at a scan rate of 50 mV/s.



Figure S21: Spectroelectrochemistry of (a) IV-based rigid ECD, (b) PV-based rigid ECD and (c) BV-based rigid ECD under different applied voltages and the image of corresponding devices.



Figure S22: Current-time curves of (a) IV-based rigid ECD, (b) PV-based rigid ECD and (c) BV-based rigid ECD (switched upon voltages between 0.0 V and -1.4 V with a switching interval of 120 s).



Figure S23: Properties in write-erase ability of (a) 2IV-based flexible ECD, (b) 2PV-based flexible ECD and (c) 2BV-based flexible ECD.



Figure S23: Properties in write-erase ability of (a) 2IV-based flexible ECD, (b) 2PV-based flexible ECD and (c) 2BV-based flexible ECD.

ECDs	Optical contrast (%)	Response time (s)	Coloring efficiency(cm <sup>2</sup> /C)	Stability (%)	
IV (ITO DET)	22.5 (5(4 mm))	46.0 (t <sub>c</sub> )	120 67 (564mm)	51.1 (1000 cycle)	
IV-(IIO-PEI)	55.5 (564 IIII)	4.9 (t <sub>b</sub> )	129.67 (5641111)		
PV (ITO PET)	37 4 (564 pm)	84.2 (t <sub>c</sub> )	87 78 (564pm)	97.6(1000  cycls)	
rv-(110-rE1)	37.4 (304 IIII)	9.9 (t <sub>b</sub> )	87.78 (3041111)	97.0 (1000 Cycle)	
BV (ITO DET)	45 8 (466 pm)	52.9 (t <sub>c</sub> )	107.22 (466nm)	72.7(1000  cycle)	
BV-(110-111)	45.8 (400 mm)	7.5 (t <sub>b</sub> )	107.22 (4001111)	72.7 (1000 Cycle)	
IV (ITO glass)	42 4 (582 pm)	22.0 (t <sub>c</sub> )	197 84 (582nm)	38.9 (1000 cycle)	
	42.4 (362 1111)	4.1 (t <sub>b</sub> )	197.64 (3621111)	56.9 (1000 Cycle)	
DV (ITO glass)	44 1 (584 pm)	35.2 (t <sub>c</sub> )	108 70 (584pm)	01.8 (1000 gycla)	
r v-(110-glass)	44.1 (384 1111)	2.4 (t <sub>b</sub> )	198.70 (3841111)	91.0 (1000 Cycle)	
BV (ITO glass)	44.0 (568 pm)	25.8 (t <sub>c</sub> )	201 50 (568nm)	88.8 (1000 cycle)	
DV-(11O-glass)	44.0 (308 IIII)	$3.2 (t_{\rm b})$	201.50 (5081111)		

Table S1 Electrochromic properties of ECDs based on IV, PV and BV.