Supplementary Materials for

Black electrochromic device based on CuI film for energy-efficient

applications

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Supplementary texts

Text S1. Materials.

Methacryloyl chloride (97%), methyl methacrylate (MMA) (99%), 2,2'-Azobis(2methylpropionitrile) (AIBN, 98%), Tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%), Hydroquinone (99%), 1,4-Benzoquinone (98%), Iodine (99.8%), Copper(II) chloride (98%), Copper(I) chloride (99.99%), Propylene carbonate (PC, 99.5%) were purchased from Energy Chemical, Poly (methyl methacrylate) (PMMA), Cupric carbonate basic (54%-57% Cu basis) were purchased from Aladdin, Potassium carbonate, Disodium dihydrogen ethylenediaminetetraacetate dehydrate (EDTA-2Na • 2H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd., Copper(I) chloride was purchased from Adamas, Ammonium nitrate (analytically pure), Sodium citrate ((analytically pure) were purchased from Beijing Beihua Fine Chemicals Co., Ltd., Tetrahydrofuran (THF) and Dichloromethane (DCM), Petroleum ether (PE) and Ethyl acetate (EA) were purchased from Titan, Triethylamine (TEA) was purchased from Yongsheng chemical works, Acetonitrile (ACN) was purchased from Thermo Fisher Scientific. Transparent indium tin oxideglass electrode (ITO, 10 Ω/sq) were purchased from CSG Holding Co. All reagents are not purified in advance except TBAPF₆. TBAPF₆ should be Recrystallized 3 times by EtOH before usage.

Text S2. Characterization instruments

UV-Vis absorption spectra were measured on a Shimadzu UV-2550 double-beam spectrophotometer. Nuclear magnetic resonance spectra (¹³C NMR and ¹H NMR) were conducted on and Wuhan Zhongke Niujin As 400 MHz(101MHz for ¹³C NMR and 400 MHz for ¹H NMR). ¹³C NMR (126 MHz) and ¹H NMR (500 MHz) spectra were conducted on a Bruker AVANCE500. Spectral data are performed in ppm relative to tetramethylsilane (TMS) as internal standard. The thickness of different layers was conducted on the step profiler DEKTAK 150. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) images were performed on field-emission scanning electronic microscopy (SU—8020/QUANT AX200) with an accelerating voltage of 100.0 kV. The electrochromic layer was performed on the spin coater AC 200. The ion storage layer and conducting layer was conducted on the automatic film application BEVS1811. The electrodeposition was performed by electrochemical workstation (CHI 760E, Shanghai Chenhua).

Text S3. Synthesis method



Synthesis route of ODBMA. The synthesis process and characterization data can be found in reference literature ^[1].

Synthesis of M2

Compounds M1 (5.48 g, 10 mmol), dichloromethane (DCM) (40 mL), and triethylamine (TEA) (4.17 mL, 30 mmol) were added to an oven dried round bottom flask under argon. Methacryloyl chloride (0.74 mL, 7.66 mmol), and 9.62 mL DCM was added in to another tube. The methacryloyl chloride solution was added dropwise in to schlenk flask under 0 °C The solution was then stirred under room-temperature for 24 h. After cooled to room temperature, the solution was washed by saturated sodium bicarbonate solution until it becomes alkaline. At last, the organic phase was dried over anhydrous Na₂SO₄, filtered, concentrated in vacuum and column chromatography was performed using PE/EtOAc as eluent to afford the product as deep grey powder. Yield: 40%. ¹H NMR (500 MHz, DMSO-d6) δ 10.21 (s, 1H), 8.45 (d, J = 8.2 Hz, 1H), 7.76 (t, J = 7.9 Hz, 1H), 7.46 (s, 1H), 7.26 (s, 1H), 7.01 – 6.96 (m, 2H), 6.65 – 6.58 (m, 2H), 6.56 (s, 1H), 6.54 – 6.49 (m, 2H), 6.46 – 6.40 (m, 2H), 5.98 (s, 1H), 5.67 (d, J = 1.8 Hz, 1H), 3.29 (t, J = 7.7 Hz, 4H), 2.49 (p, J = 1.9 Hz, 5H), 2.19 (s, 3H), 2.04 (t, J = 1.1 Hz, 3H), 1.50 (dq, J = 15.3, 8.3 Hz, 5H), 1.31 (h, J = 7.4 Hz, 4H), 0.91 (t, J = 7.3 Hz, 6H). LC-HRMS (ESI) calcd. for C₃₉H₄₂N₃O₄ [M+H]⁺: 616.3170, found: 616.3164. Melting point: 93.3 °C-94.8°C.

Synthesis of ODBMA

To an oven-dried, nitrogen 50 mL schlenk flask was added compound M2 (1 mmol), methacryloyl

chloride (2 mmol), triethylamine (7 mL). The solution was vigorously stirred for 24 h. The resulting solution was then evaporated. The solid was dissolved in DCM and then washed by water (3×40 mL), dried with Na₂SO₄ and filtered. The mixture solution was evaporated and then got the viscous liquid (yield = 90 %).

Text S4. Test method

- Sample of cyclic voltammentry: The solution of ODBMA was consisted of M10 20 mg, (TBAPF₆) 387 mg, 1mmol and CH₃CN 10mL. The solution of CuI was consisted of CuI 1.9 mg, 0.01 mmol, (TBAPF₆) 387 mg, 1mmol and CH₃CN 10mL. The work electrode is carbonglassy electrode, counter electrode is Pt wire, reference electrode is Ag wire.
- 2. Sample of in-situ absorption spectra: The solution of ODBMA was consisted of M10 20 mg, (TBAPF₆) 387 mg, 1mmol and CH₃CN 10mL. the working electrode was bare ITO electrode and ITO electrode covered by CuI film, respectively. the reference electrode was Ag wire, the counter electrode was Pt wire. The structure of test device as shown in Fig. 3a. The wavelength was set as 590 nm for CV-UV test, and the wavelength range of CA-UV test was 400 nm-800 nm.
- **3.** Sample of Fourier-transform infrared spectroscopy: compound was mixed with KBr, and the instrument of FT-IR was vacuumed during the testing period.

Text S4. Preparation of CuI film on ITO electrode.

- Preparation of Cu film on ITO electrode: Cu film was electrodeposited on ITO electrode. The fomular of electroplate liquid can be found in table S1. Both the working electrode and counter electrode were ITO electrode (3×3 cm). The beaker was used as plating bath, the distance between two ITO electrode was 5 cm. the potential of electrodeposition was -3 V. After electrodeposition, the ITO electrode with Cu film was immersed into deionized water and absolute ethyl alcohol, respectively.
- 2. Preparation of CuI film on ITO electrode: First, ITO electrode (5-6 pieces) with Cu film and Iodine (5-6 g) were put in culture dish, and seal with cling film. Then, the culture dish was heated under 60 °C by water bath. Iodine vapour could react with Cu film at such temperature.

The water bath was revoked once the Cu film turns to grey, which means the reaction between Cu film and iodine was finished. Finally, the ITO electrode with CuI was washed by dichloromethane, and dried by air.

Text S5. Preparation of the semi-solid device with the optimal component condition.

- Electrochromic solution: A mixture of ODBMA (40 mg), TBAPF₆ (38.7 mg) were dissolved in 1 mL THF.
- Ion conducting solution: A mixture of PMMA (2.4 g), TBAPF₆ (0.8 g) and PC (0.8 g) in 10 mL THF was stirred for 2 h under 60°C.
- 3. Ion storage solution: A mixture of PMMA (1.2 g), TBAPF₆ (0.4 g) and PC (0.4 g) in 10 mL THF with hydroquinone (0.1 mol/L) and benzoquinone (0.05 mol/L) was stirred for 2 h under 60°C.
- 4. Fabricated process of semi-solid film device: ITO electrodes were immersed in mixture of H₂O₂ and NH₃ H₂O (1: 3, volume ratio) for 30 min, and washed by isopropyl alcohol. Finally, the ITO electrode was dried under N₂ stream. The thin film (Ion conducting layer, and Ion storage layer) was fabricated through blade coating, the height of blade 1.4 mm (for ion storage layer), 1.7 mm and 1.8 mm (for ion conducting layer). The electrochromic layer was fabricated through spin-coating under different conditions. The scheme of device fabrication was shown in Fig. S1

Supplementary tables

Substance	Cu(OH) ₂ CO ₃	EDTA-2Na	Sodium citrate	NH ₄ NO ₃	H ₂ O
Weight (g)	22	150	32	4	Add to 1000

Table S1. The formula of electroplate liquid. The pH of solution was 13 which adjusted byNaOH.

Thickness of CuI (µm)	0	181.7	312.4	506.5	541.8
Resistance (Ω)	20	38	62	208	571

 Table S2. The Resistance of electrode with different thickness of CuI film are attached. The thickness "0" refers to the bare ITO electrode.

	L	a	b
Bleach state	61.143	0.447	13.07
Color state	30.980	0.520	2.407

 Table S3. CIE Lab value of electrochromic device based on CuI film during bleach state and color state, respectively.

Supplementary figures



Fig. S1 the process of electrochromic device based on CuI film. Cu thin film was fabricated by electrodeposition, CuI thin film was fabricated by chemical oxidation, the EC layer was fabricated by spin-coating, ion storage layer (IS layer) and ion conducting layer (IC Layer) was fabricated by blade coating.



Fig. S2. The trun on potential of electrochromic device with CuI film.



Fig. S3. The UV-vis spectrum and photos of electrochromic device based on CuI film and rhodamine derivatives. Such the device shows no absorption at initial state, and shows magenta under 1.5 V.



Fig. S4. The SEM image of Cu film electrodeposited without any additive. The Cu microparticles are irregular, and the Cu film is easy to exfoliation.



Fig. S5. The UV-vis spectra of different solution based on different substance or mixture. It can be found that only Cu^{2+} only the Cu^{2+} can change the color of ODBMA. Such the result is comply with the photos shown in Fig. 1b.



Fig. S6. The UV-vis spectra of electrochromic device under different voltage.



Fig. S7. The UV-vis spectra of electrochromic solution under different voltage.



Fig. S8. The cycle stability of electrochromic device based on CuI thin film. It can be observed that the optical modulation ability of device decreases extremely after 27 cycles.



Fig. S9. The bending cycle stability of flexible electrochromic device based on CuI thin film.



Fig. S10. The coloring rate and fading rate of electrochromic device based on CuI film.



Fig. S11. The coloring rate and fading rate of electrochromic solution based on ODBMA and CuI-

ITO electrode.



Fig. S12. Coloring efficiency (CE) of electrochromic device based on CuI film.