

Electronic-Supplementary-Information for

A Black Energy-saving Electrochromic Device based on a Dye

Copolymer-metal Complex

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The file includes:

Text S1. Materials

Text S2. Characterization instruments

Text S3. The strategy of component choosing

Text S4. Synthesis method

Text S5. Sample preparation and test method

Text S6. Preparation of the solid device with the optimal component condition.

Fig. S1 to S12.

Reference

Text S1. Materials.

Methacryloyl chloride (97%), methyl methacrylate (MMA) (99%), 2,2'-Azobis(2-methylpropionitrile) (AIBN) (98%), 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM] PF₆) (98%), Hydroquinone (99%), 1,4-Benzoquinone (98%) were purchased from Energy Chemical, Copper(II) chloride (98%), Potassium bromide (99.5%), Poly (methyl methacrylate) (PMMA) were purchased from Aladdin, Potassium carbonate was purchased from Sinopharm Chemical Reagent Co., Ltd., 5-Bromo-2,3'-bipyridine (BiPy) (95%) was purchased from Bidepharm, Copper(I) chloride was purchased from Adamas, Ethylene glycol (EG) was purchased from Beijing Beihua Fine Chemicals Co., Ltd., Tetrahydrofuran (THF) and Dichloromethane (DCM) were purchased from Titan, Triethylamine (TEA) was purchased from Yongsheng chemical works, Acetonitrile (ACN) was purchased from Thermo Fisher Scientific. Transparent indium tin oxide-glass electrode (ITO, 10 Ω/sq) were purchased from CSG Holding Co.

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 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. IR spectra studies were recorded on Vertex 80/80V FT-IR spectrometer with LN-MCT Mid DC detector using a KBr plate over the range of 4000-800 cm⁻¹. The melting points were performed on an SGW X-4B microscopy melting point apparatus (Shanghai). Gel permeation chromatography (GPC) analysis was performed on a Waters 1515 instrument equipped with two MIXED-C 7.5×300 columns, a guard column MIXED 7.5×50 mm PL column as well as a differential refractive index detector using THF as the eluent with a flow rate of 1 mL/min at 35 °C. The thickness of different layers was conducted on the step profiler DEKTAK 150. Scanning electron microscopy (SEM) images were performed on field-emission scanning electronic microscopy (SU8020, HITACHI; FE-

SEM) 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. Thermogravimetric analysis (TGA) was recorded with a TA 2050 in the temperature of 50-800°C with a heating rate of 10°C/min under a flow of nitrogen.

Text S3. The strategy of component choosing.

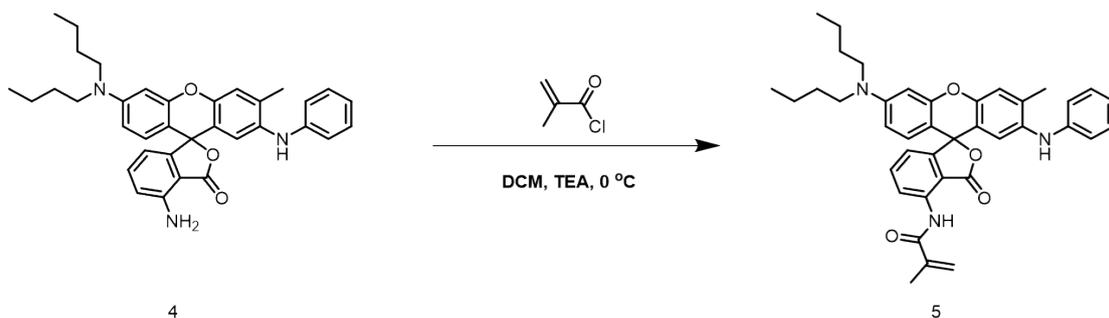
As mentioned above, the selected material ODB-Py-MA contains three parts: 1. Dye molecules (ODB-2) to show color, 2. Coordination sites (Py) to fix cupric ions and 3. Polymer backbones to restrain diffusion. ODB-2 is the most popular black dyes in numerous industry containing thermo-sensitive paper due to its high color density, high sensitivity and satisfying stability. The demand of ODB-2 can reach 10000 tons now. We were attracted by these impressive properties, and firmly believe that our material can show desirable properties,

With N atom on the fragment ring, pyridine is a kind of fine ligand for metal ions. With the presence of chelation, the coordination between metal ions and bipyridine is more stable, which is suitable for our material. The ligand such as EDTA-2Na is not suitable for our system because its strong coordination may limit the cupric ion reacts with ODB-2 under positive stimulation. And another reason is that the functional groups can be modified on bipyridine, which is beneficial to us to introduce double bond on it.

The polymer back bone is also important in our material. Polymethyl methacrylate is also known as “Acrylic” which was also known as “organic glass” for its high transmittance. We believe that our device will show better properties with this polymer backbone.

Text S4 Synthesis method

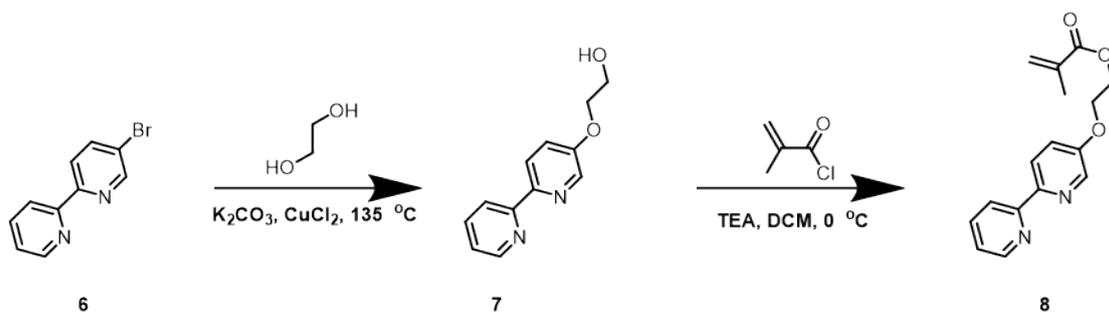
Synthesis method of M2, M3 and M4 have been reported in our previous work ^[1]



Synthetic route of M5

Synthesis of M5

Compounds M4 (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 Na_2SO_4 , 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, $\text{DMSO}-d_6$) 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 $\text{C}_{39}\text{H}_{42}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 616.3170, found: 616.3164. Melting point: 93.3 °C-94.8°C.



Synthetic route of M8

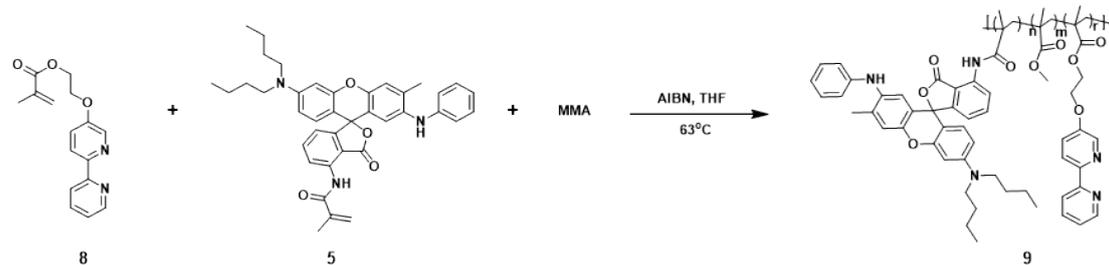
Synthesis of M7

To a round-bottomed flask charged with M6 (1.55 g, 6.6 mmol), CuCl₂ (35 mg, 0.3 mmol) and K₂CO₃ (2.74 g, 19.8 mmol) were added ethylene glycol (EG) (3.15 mL) under N₂ atmosphere. Then the reaction was carried out at reflux for 24 h. After the reaction was cooled down to room temperature, poured some water to the flask to wash the mixture in to another container under ultrasound shock. Then extract the reaction mixture with ethyl acetate, combine the organics and dry over anhydrous Na₂SO₄, concentrate under vacuum and then column chromatography was performed using petroleum ether and ethyl acetate as eluent to afford the product as pale yellow powder (yield = 44 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ(TMS,ppm) 8.64 (d, *J* = 4.8 Hz, 1H), 8.42-8.37 (m, 1H), 8.40-8.25 (m, 2H), 7.90 (t, *J* = 7.7Hz, 1H), 7.54(d, *J* = 8.8Hz, 1H), 7.38 (d, *J* = 7.5Hz, 1H), 4.96 (t, *J* = 5.5Hz, 1H), 4.14 (t, *J* = 4.9Hz, 2H), 3.76 (q, *J* = 5.1Hz, 2H). ¹³C NMR (126 MHz, DMSO) δ 155.50, 155.19, 149.10, 147.80, 137.34, 137.13, 123.24, 121.76, 121.19, 119.60, 70.13, 59.47. LC-HRMS (ESI) calcd. for C₁₂H₁₃N₂O₂ [M+H]⁺: 217.0972, found: 217.0985. Melting point: 117.2°C-117.8°C.

Synthesis of M8

Compound M7 (0.43 g, 2 mmol), triethylamine (0.56 mL, 4 mmol), and 10 mL DCM were added in an 50 mL oven-dried schlenk flask under argon. Methacryloyl chloride (0.38 mL, 4 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. Then, vigorously stirred for solution with 24 h under room temperature. After reaction, the resulting solution was evaporated. The solid was then dissolved in DCM and then washed by water (3×40 mL), dried with Na₂SO₄ and filtered. After concentrate under vacuum, column chromatography was performed using petroleum ether and ethyl acetate as eluent to afford the product as white wax powder (yield = 68 %). ¹H NMR (500 MHz, DMSO) δ 8.64 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.42 (d, *J* = 2.9 Hz, 1H), 8.35 (d, *J* = 8.8, 1H), 8.30 (d, *J* = 7.9, 1H), 7.91 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.39 (m, 1H), 6.08 - 6.03 (m, 1H), 5.71 (t, *J* = 1.6 Hz, 1H), 4.50-4.46 (m, 2H), 4.44-4.40 (m, 2H), 1.89 (t, *J* = 1.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.38, 155.87, 155.36, 149.24, 148.98, 137.62, 137.25, 136.00, 126.42,

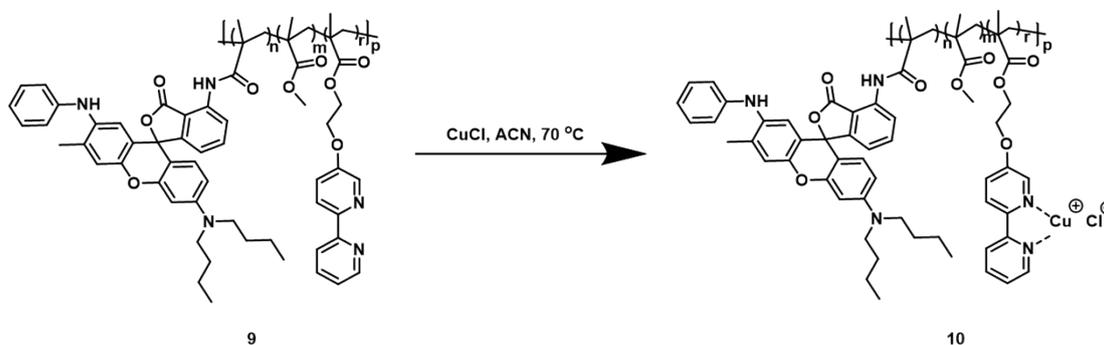
123.21, 121.94, 120.73, 66.63, 62.96, 18.43. LC-HRMS (ESI) calcd. for $C_{16}H_{17}N_2O_3$ $[M+H]^+$: 285.1234 found: 285.1253. Melting point: 67.2°C-67.5°C.



Synthesis route of copolymer M9

Synthesis of M9

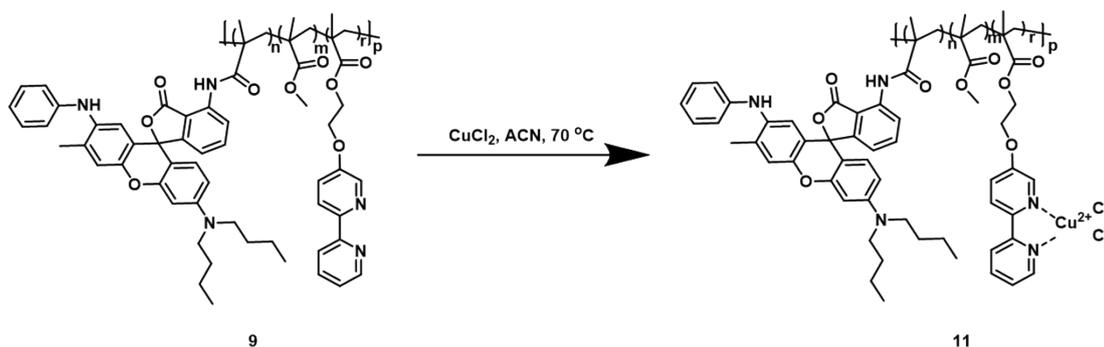
Compound M8 (0.28 g, 1 mmol), compound M5 (0.62 g, 1 mmol), methyl methacrylate (MMA) (0.21 mL, 2 mmol for 1: 2: 3, 0.52 mL, 5 mmol for 1: 2: 8, 1.05 mL, 10 mmol for 1: 2: 20, 1.6 mL, 15 mmol, for 1: 2: 40, respectively. The ratio was ODB: Py: MMA), azodiisobutyronitrile (AIBN) (26.13 mg, 0.16 mmol for 1: 2: 3, 45.73 mg, 0.28 mmol for 1: 2: 8, 78.4 mg, 0.48 mmol for 1: 2: 20, 111.06 mg, 0.68 mmol, for 1: 2: 40, respectively. The ratio was ODB: Py: MMA. Amount of AIBN was 4% of double bonds), and 10 mL of THF were put into a Schlenk flask. The solution was then degassed by four freeze-evacuate-thaw cycles. After the Schlenk flask was sealed, it was immersed in an oil bath at 63°C and kept stirring for 24 h. the mixture was then purified by precipitation in to excessive ethyl alcohol, filtered to collect the product, and dried under vacuum. M9 was obtained with a yield of 50%. Melting point: 140.2°C-143.8°C. molecular weight (test by Gel Permeation Chromatography, GPC) was 6883 for 1: 2: 3, 6014 for 1: 2: 8, 6829 for 1: 2: 20, and 6283 for 1: 2: 40, the ratio was ODB: Py: MMA. The mass of 1H NMR spectrum can be found in Fig. S1



Synthesis route of copolymer M10

Synthesis of M10

M9 (800 mg), Cuprous Chloride (62.37 mg, 0.63 mmol), and ACN (15 mL) were added in a 50 mL dried round bottom flask under argon atmosphere. The system was stirred for 24 h at 70 °C. After the reaction, the liquid was first evaporated under argon atmosphere, then the solid was dissolved in dichloromethane, and the unreacted CuCl was removed by filtration. The filtrate was again evaporated, and dichloromethane was added thereto until the solid just dissolved. The solution was added dropwise to a breaker containing 50 mL of diethyl ether and then filtered to get a precipitate. M10 was obtained with a yield of 76%. The evidence of coordination between cupric ions and M10 can be found in Fig.2 and Fig. 3.



Synthesis route of copolymer M11

Synthesis of M11 (ODB-Py (CuCl₂)-MA)

M9 (800 mg), Cuprous Chloride (84.73 mg, 0.63 mmol), and ACN (15 mL) were added in a 50 mL dried round bottom flask under argon atmosphere. The system was stirred for 24 h at 70 °C. After the reaction, the liquid was first evaporated under argon atmosphere, then the solid was dissolved in dichloromethane, and the unreacted CuCl₂ was removed by filtration. The filtrate was again evaporated, and dichloromethane was added thereto until the solid just dissolved. The solution was added dropwise to a breaker containing 50 mL of diethyl ether and then filtered to get a precipitate. M11 was obtained with a yield of 82%. The evidence of coordination between cupric ions and M11 can be found in Fig.3 and Fig. S6, S8 and S9.

Text S5. Sample of cyclic voltammetry and in-situ absorption spectrum:

The solution of M9 was consisted of M9 3.8 mg, Tetrabutylammonium Hexafluorophosphate (TBAPF₆) 387 mg (1 mmol), and CH₃CN 10 mL. The solution of M10 was consisted of M10 4.0

mg, TBAPF₆ 387 m, (1 mmol), and CH₃CN 10 mL. The solution of CuCl was consisted of CuCl 0.99 mg (0.01 mmol), TBAPF₆ 387 mg (1 mmol), and CH₃CN 10 mL. The work electrode is carbon-glassy electrode, counter electrode is Pt wire, reference electrode is Ag wire. All test results were correction by Ferrocene. For in-situ absorption spectrum, the wavelength was set as 590 nm except full-spectrum.

Text S6. Preparation of the solid device with the optimal component condition.

Electrochromic solution: A mixture of M10 (40 mg) and [BMIM]PF₆ (7 μL) in the mixture of 0.5 mL THF and 0.5 mL CH₃CN was stirred for 20 min.

Ion conducting solution: A mixture of PMMA (2.4 g) and [BMIM]PF₆ (0.6 g) in 10 mL acetonitrile was stirred for 2 h under 60°C.

Ion storage solution: A mixture of PMMA (1.2 g) and [BMIM]PF₆ (0.3 g) in 10 mL acetonitrile with hydroquinone (0.1 mol/L) and benzoquinone (0.05 mol/L) was stirred for 2 h under 60°C.

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 (electrochromic layer, Ion conducting layer, and Ion storage layer) was fabricated through blade coating, the height of blade was set as 1.25 mm (for electrochromic layer), 1.4 mm (for ion storage layer), 1.7 mm and 1.8 mm (for ion conducting layer). The scheme of device fabrication was shown in Fig. S9

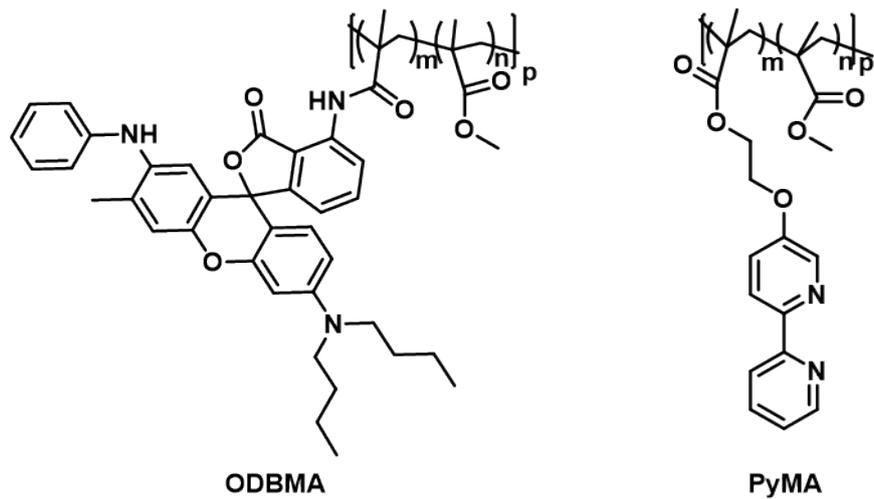


Figure S1. Structure of ODBMA and PyMA

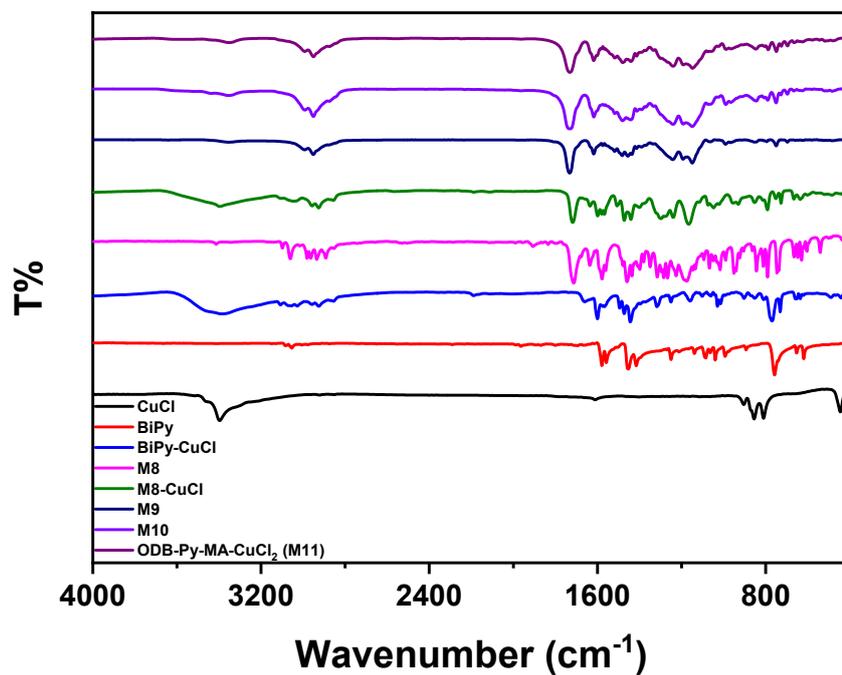


Figure S2 FT-IR of different substances. Black for CuCl, red for 2,2'-Bipyridine (BiPy), blue for 2,2'-Bipyridine-CuCl (BiPy-CuCl), magenta for M8, olive for M8-CuCl, navy for M9, violet for M10, and purple for ODB-Py (CuCl₂)-MA (M11).

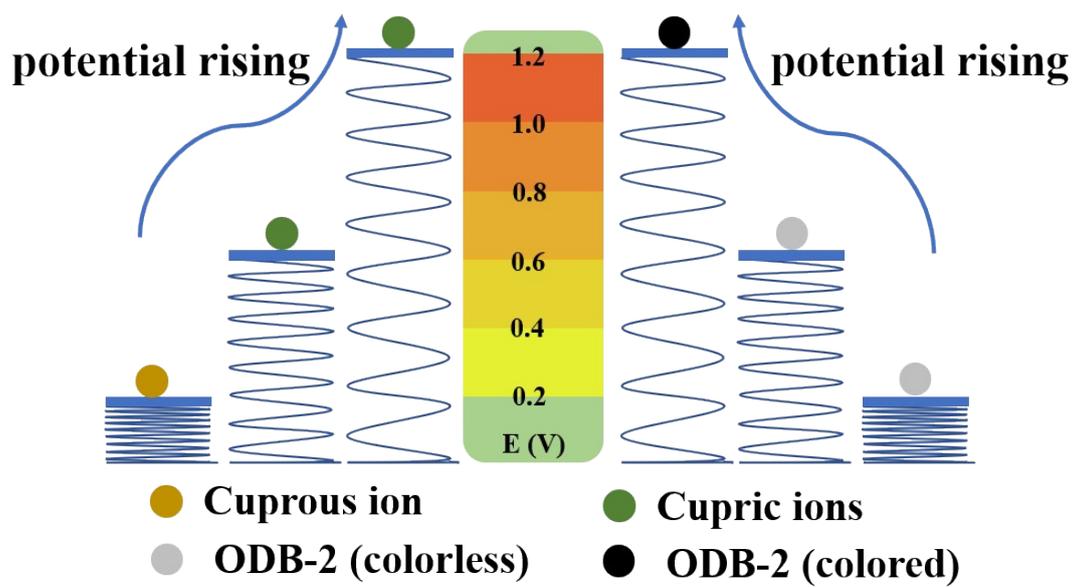


Figure S3. Schematic of Cuprous chloride and ODB under different potential.

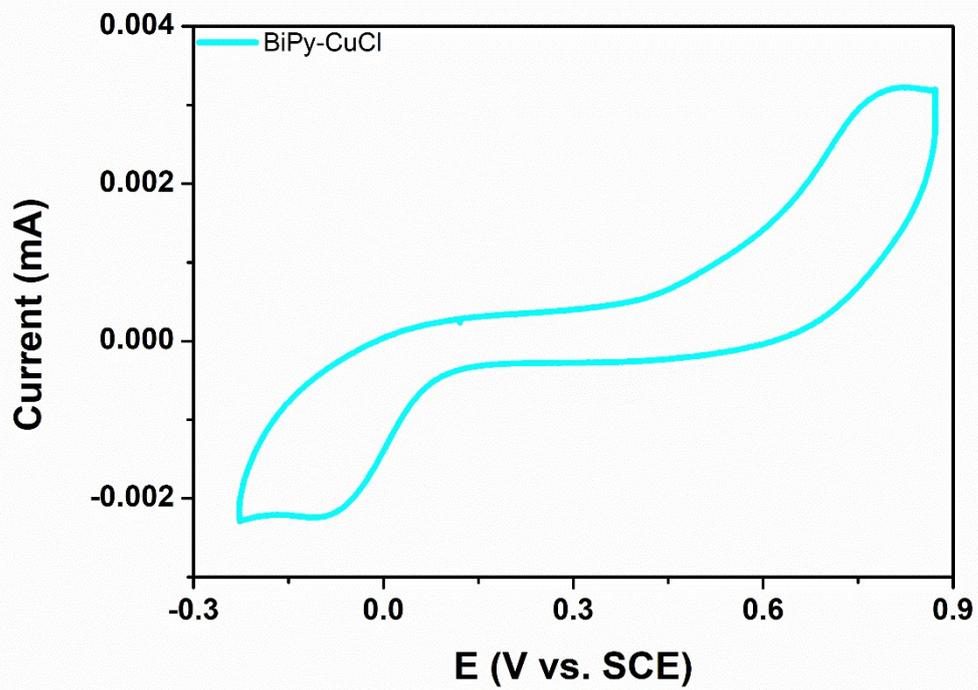


Figure S4. CV curve for BiPy-CuCl (cyan) from -0.23 V to 0.87 V.

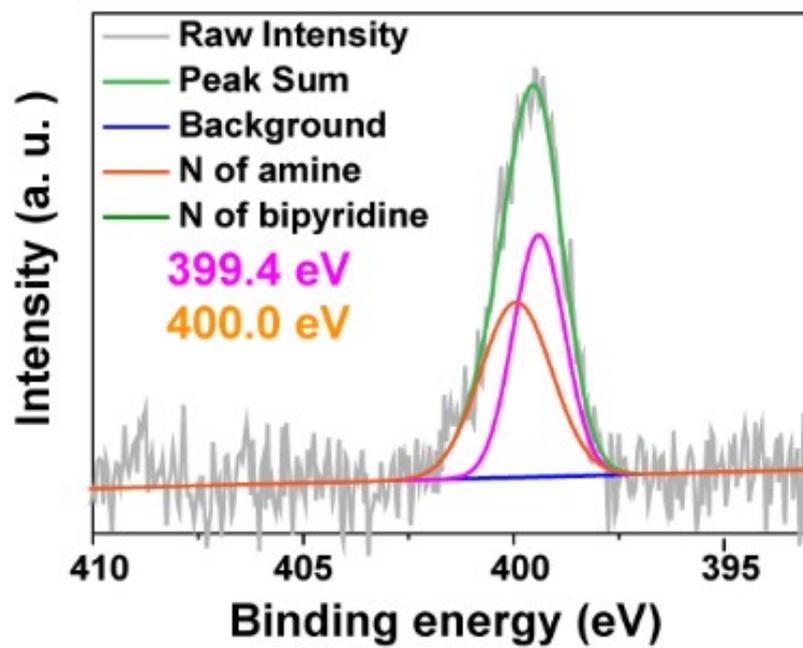


Figure S5. XPS spectrum of N in M11. The sample was separate from the thin film device after stimulate under 1.5 V.

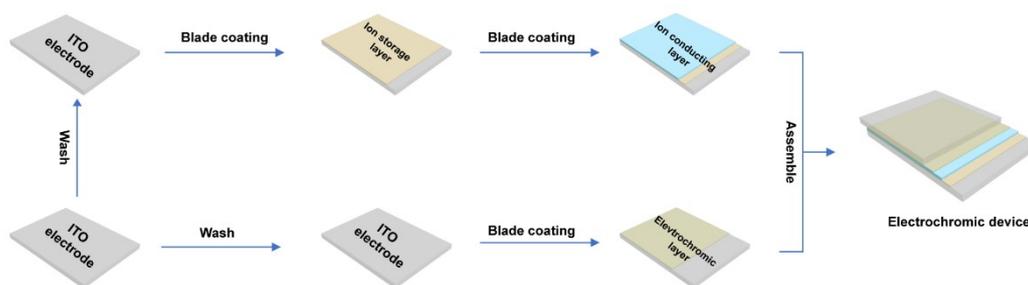


Figure S6. Fabrication progress of solid device based on M10.

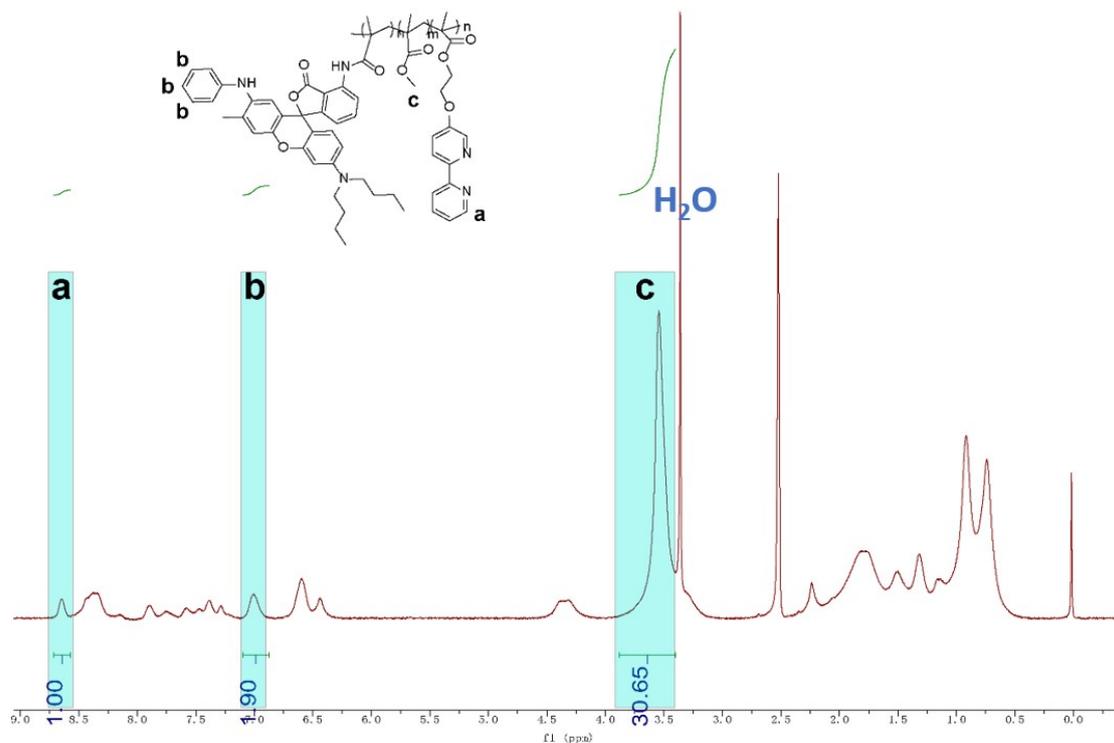


Figure S7. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) for M9. Characteristic hydrogen atoms of BiPy, ODB and PMMA have been noted.

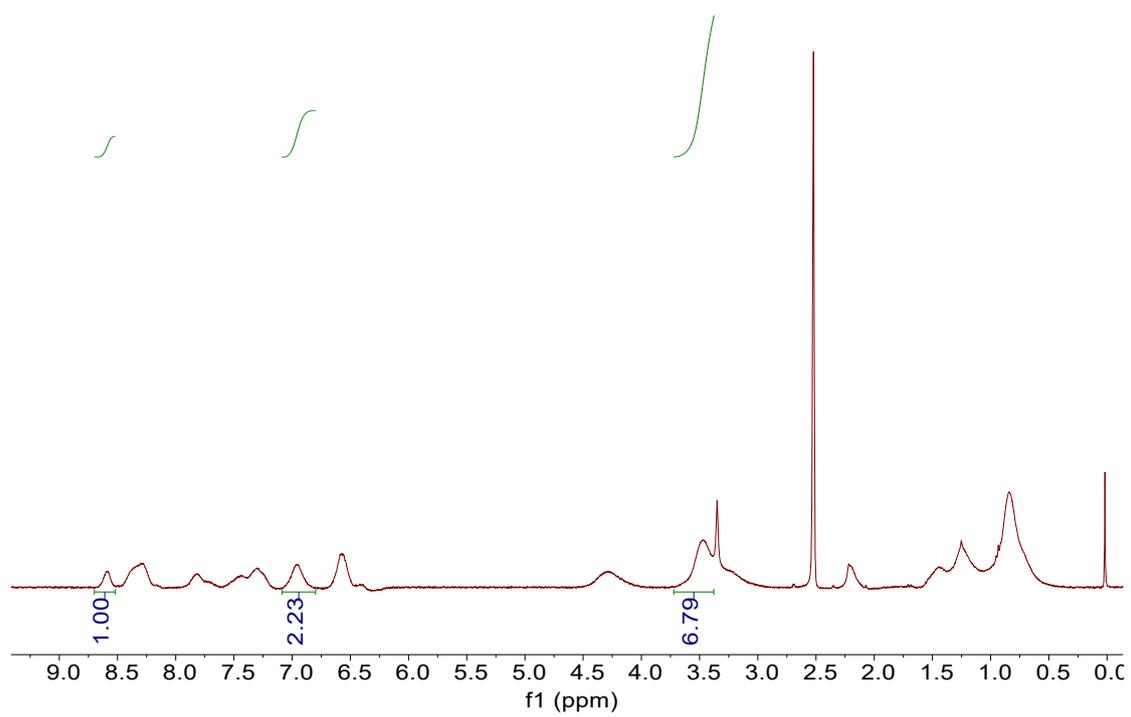


Figure S8. ¹H NMR (500 MHz, DMSO-*d*₆) for M9 with ODB: Py: MA= 1: 2: 3.

SRP-1-1-5, 1. f1d

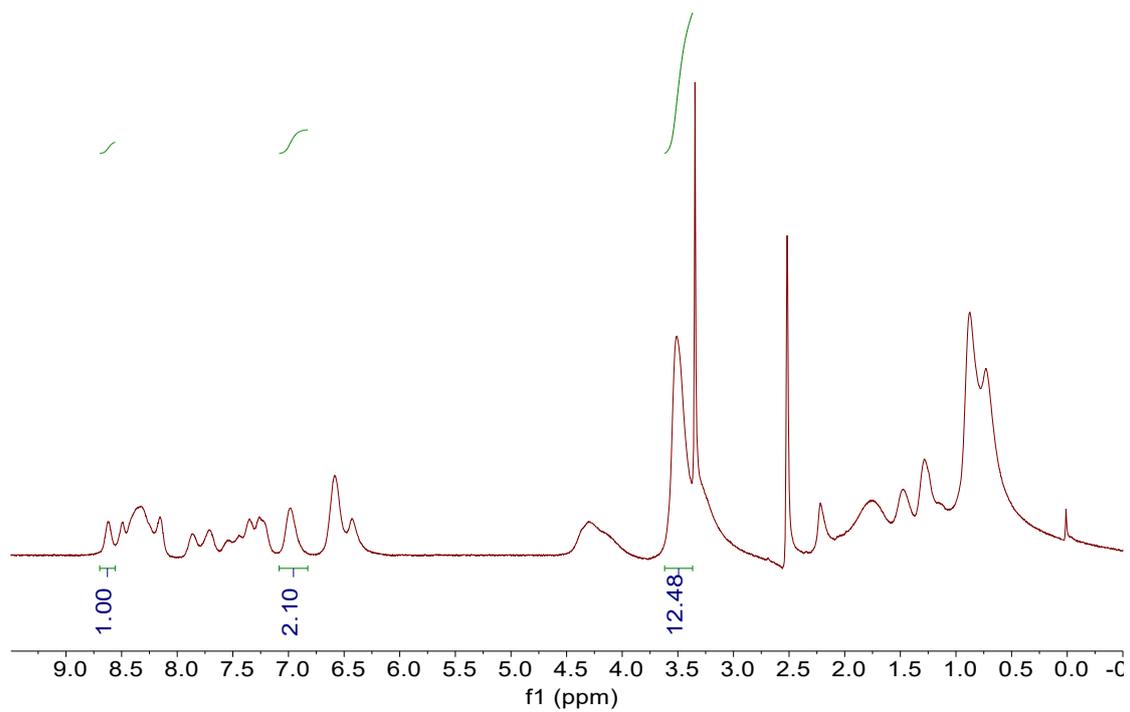


Figure S9. ¹H NMR (500 MHz, DMSO-*d*₆) for M9 with ODB: Py: MA= 1: 2: 8.

Srp-polymer-1-1-10-2021-7-15, 1. fid

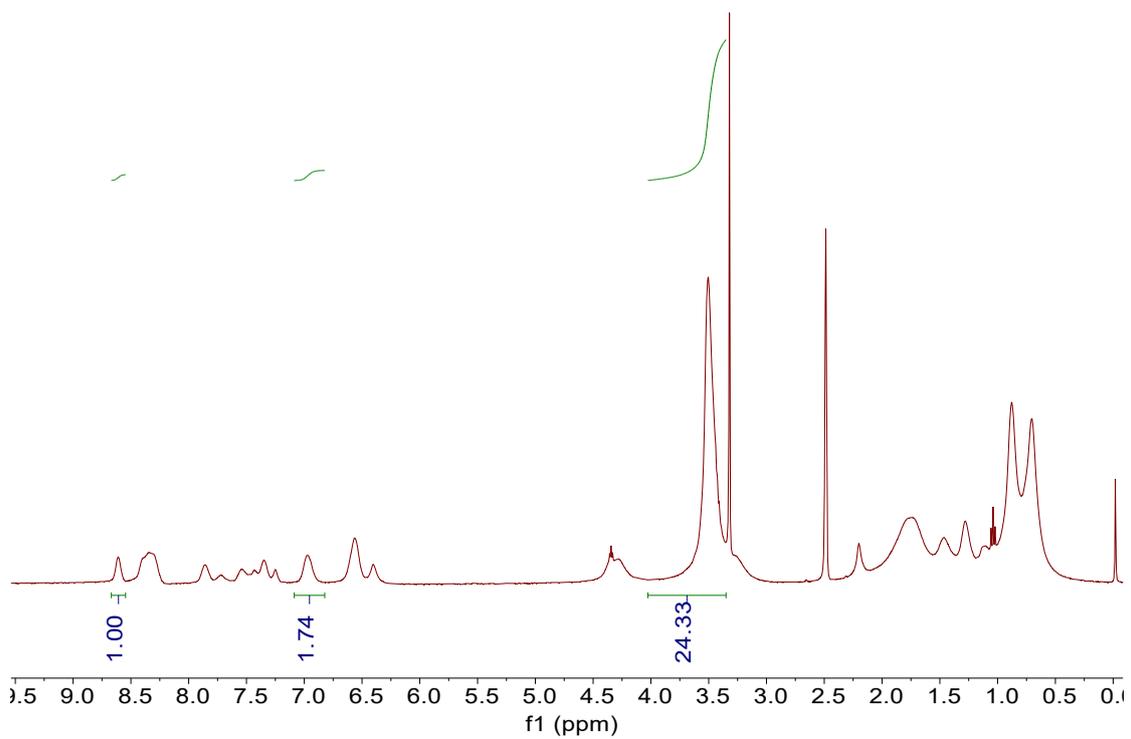


Figure S10. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) for M9 with ODB: Py: MA= 1:2:20.

SRP-1-1-15, 1, f1d

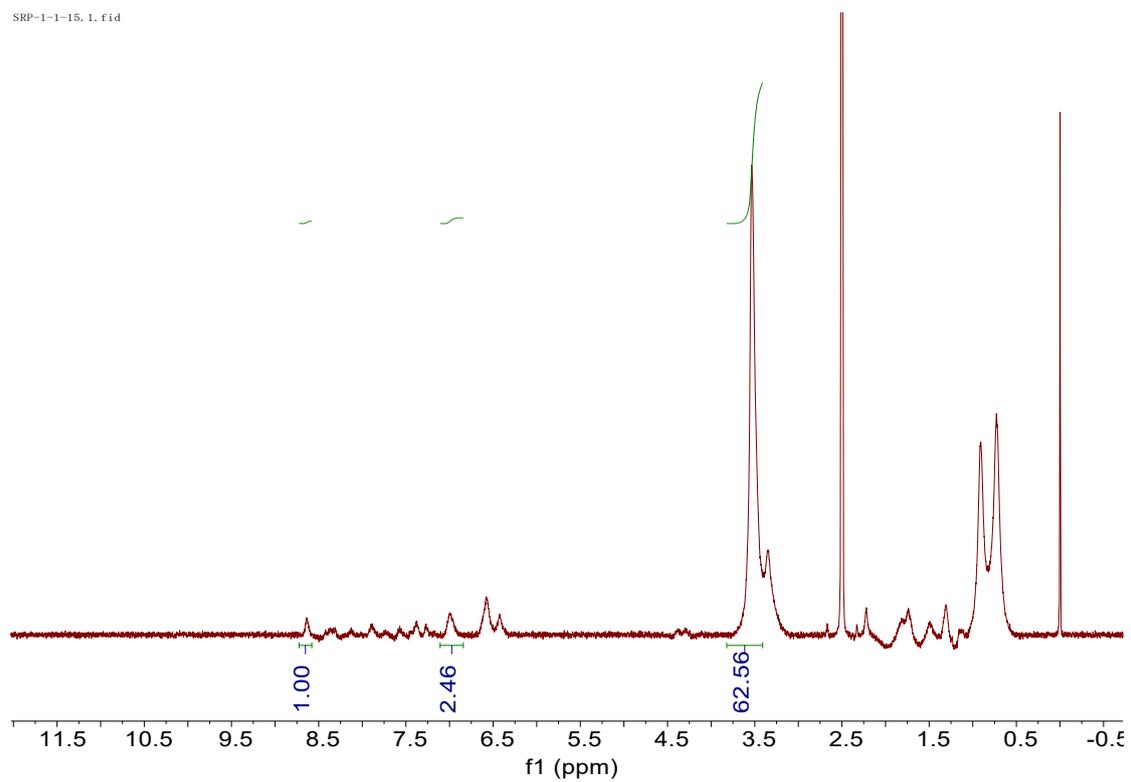


Figure S11. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) for M9 with ODB: Py: MA= 1: 2: 40.

Reference

1. Wang, YY. Et al. A multicolour bistable electronic shelf label based on intramolecular proton-coupled electron transfer, *Nat. Mater.*, **18**, 1335-1342, (2019).
2. Wang, YY., Shen, RP., Wang, S., Zhang, Y. M.; Zhang, S. X., Dynamic Metal-Ligand Interaction of Synergistic Polymers for Bistable See-Through Electrochromic Devices. *Adv. Mater.*, **34**, 2104413, (2022).