Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information

Steering ion transport direction for thin-film electrochromic energy storage device

Zhiqiang Yao,[a] Hengyuan Bai,[a] Yutong Tang,[a] Xiaochang Zou,[a] Jiaheng Gao,[a] Yu-Mo Zhang,*[a] and Sean Xiao-An Zhang*[a]

---

[a] Z. Yao, Prof. Y.-M. Zhang, Prof. S. X.-A. Zhang
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University
Changchun, 130012, P. R. China
E-mail: zhangyumo@jlu.edu.cn; seanzhang@jlu.edu.cn

Table of contents

Supplementary Figures

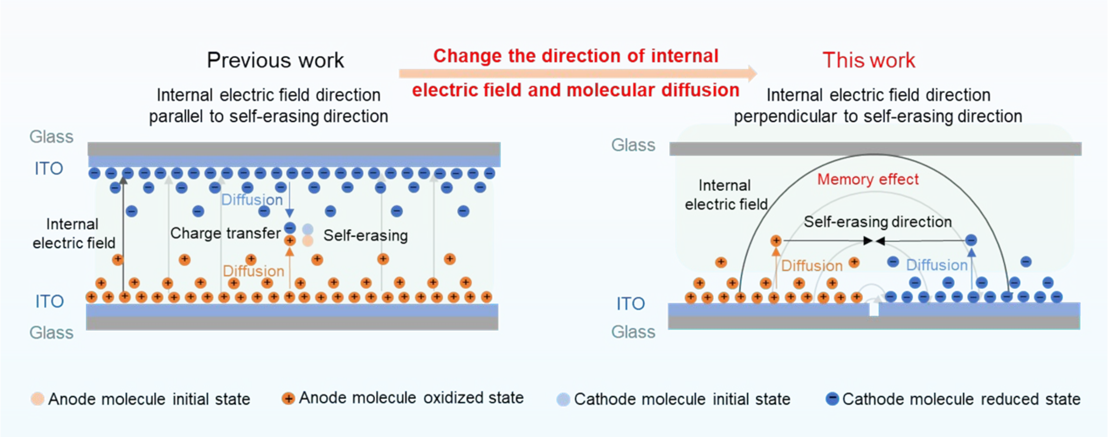


Figure S1. Schematic of the device architecture and the interplay between the internal electric field and molecular diffusion directions inside the device after power-off.

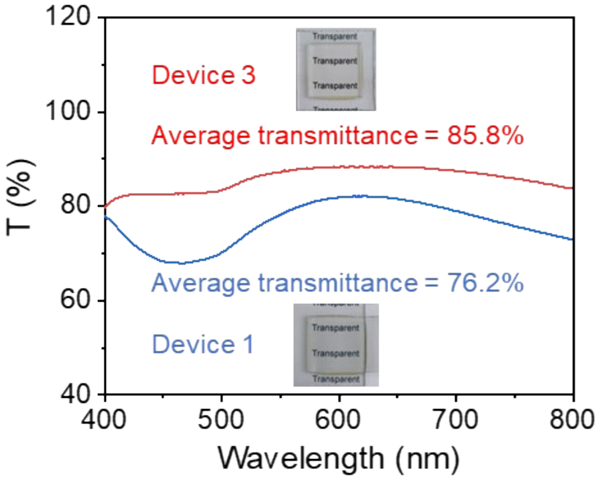


Figure S2. Transmittance spectra of Device 1 and Device 3 (with high transmittance glass as a covering) in their bleached state, along with the average transmittance and corresponding photographs.

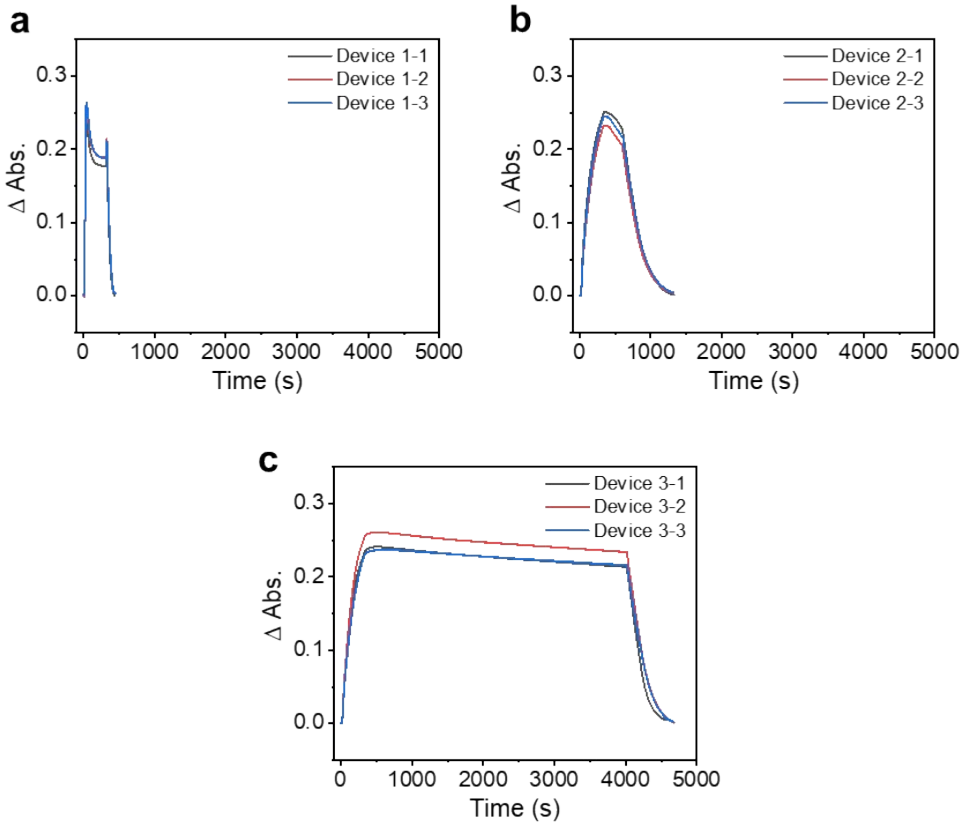


Figure S3. Parallel experiments of the absorbance changes at 605 nm for (a) Device 1, (b) Device 2, (c) Device 3 under electrical stimulation of −2.0 V for 300 s.

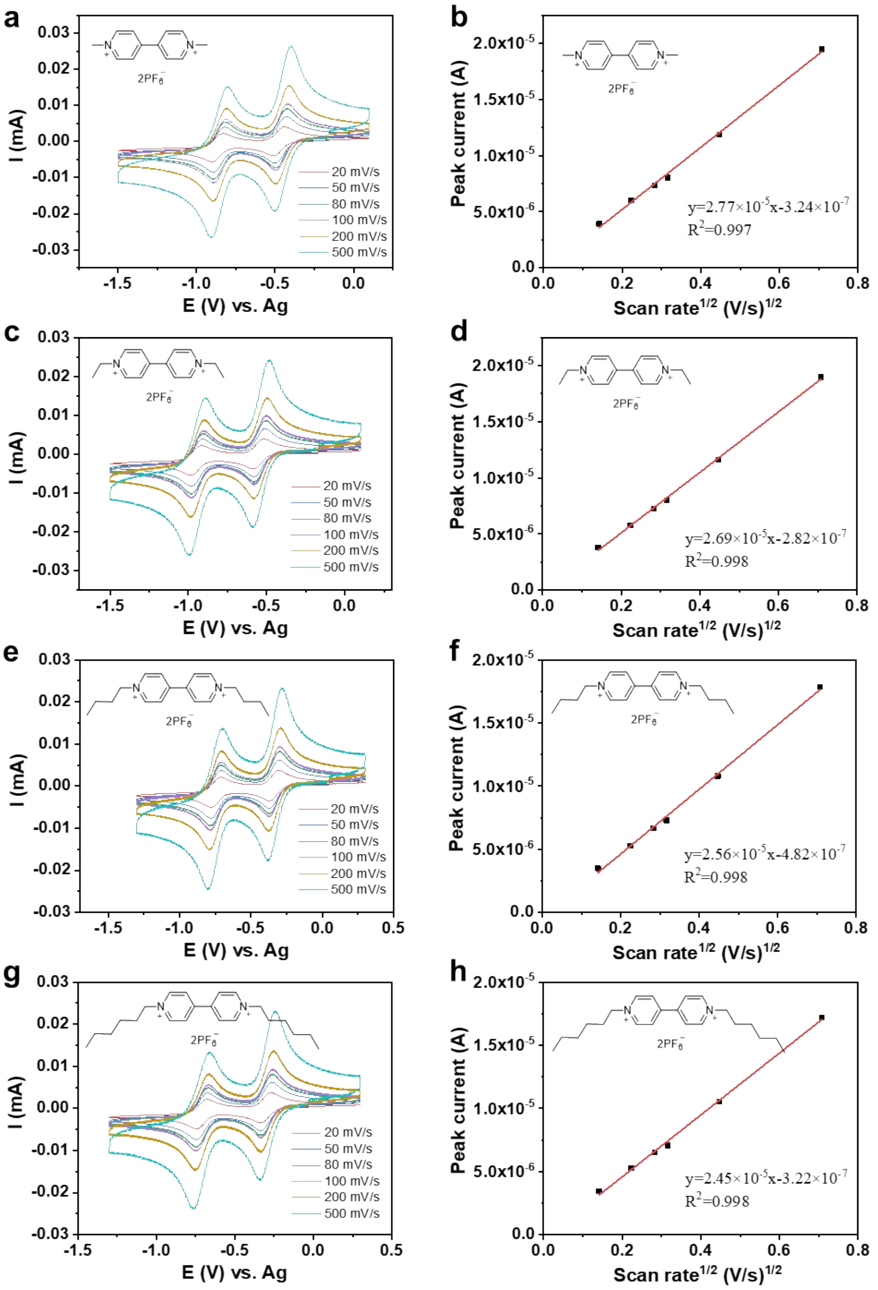


Figure S4. The cyclic voltammograms of (a) MV, (c) EV, (e) BV, (g) HV in PC with 0.1 M $TBAPF_6$ at different scan rate. Plot of peak current vs square root of scan rate for (b) MV, (d) EV, (f) BV, (h) HV.

The calculation of diffusion coefficients was based on the cyclic voltammograms of viologens with the known concentration and the surface of working electrode.

Randles-Sevcik equation calculation:

$I_p=2.69\times10^5An^{3/2}D^{1/2}v^{1/2}c$

I_p represents the redox peak current (A), A represents the area of effective surface of the working electrode (cm^2), n represents electrons transferred per molecule, D represents the diffusion coefficient (cm^2/s), v represents the scan rate (V/s), c represents the concentration of redox species (mol/cm^3).

According to each pair of redox peaks in viologens represents a single-electron transfer process (n=1), the area of effective surface of the working electrode ($A=0.0707\ cm^2$), the concentration of viologens ($c=1.0\times10^{-3}$ mol/L) and the slopes of the plots in Figures S2 (b), (d), (f), (h), the diffusion coefficients of different viologens can be calculated based on the Randles-Sevcik equation.

Diffusion coefficient of MV: $2.12\times10^{-6}\ cm^2/s$

Diffusion coefficient of EV: $2.01\times10^{-6}\ cm^2/s$

Diffusion coefficient of BV: $1.81\times10^{-6}\ cm^2/s$

Diffusion coefficient of HV: $1.66\times10^{-6}\ cm^2/s$

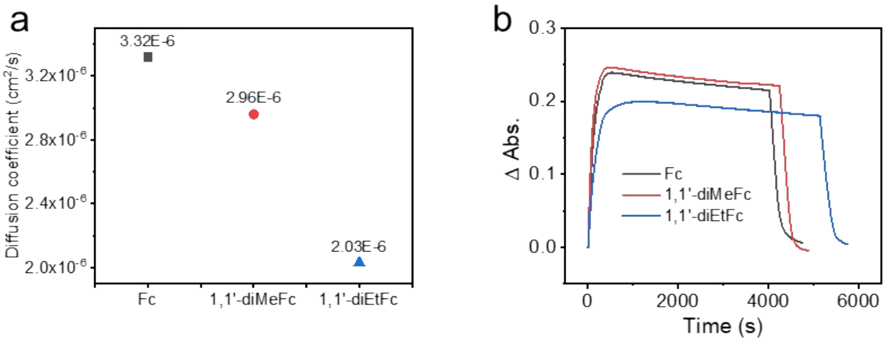


Figure S5. (a) Diffusion coefficients of ferrocene derivatives with various substituents. (b) Changes in absorbance at 605 nm for devices fabricated with different ferrocene derivatives.

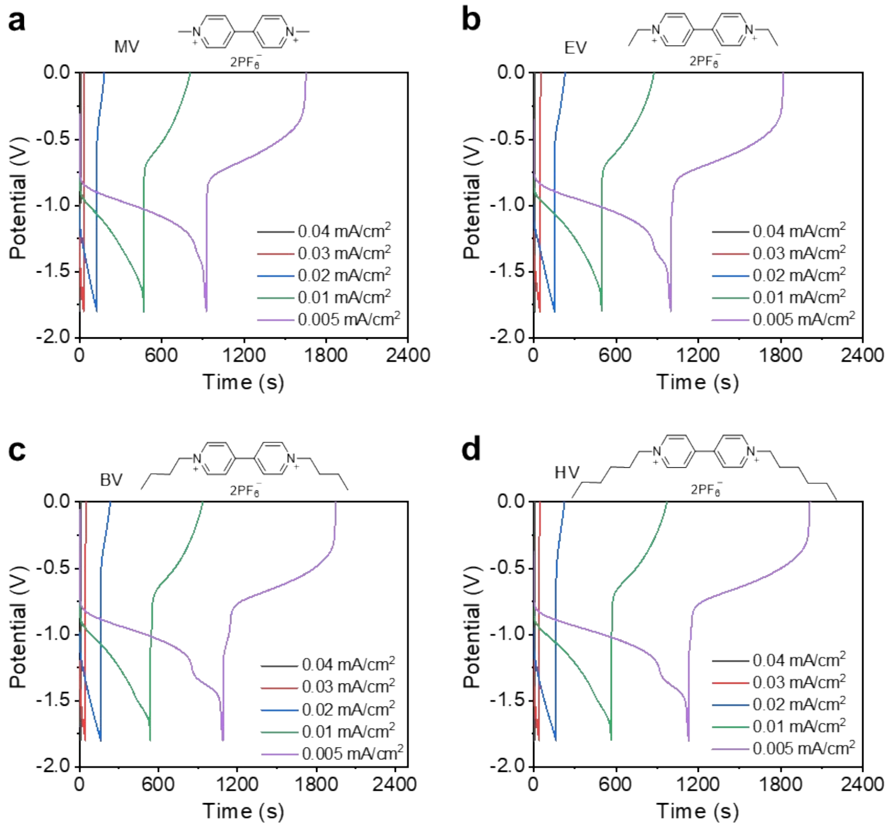


Figure S6. Galvanostatic charge-discharge (GCD) curves at different current densities of electrochromic energy storage devices with different viologens (a) MV, (b) EV, (c) BV, and (d) HV.

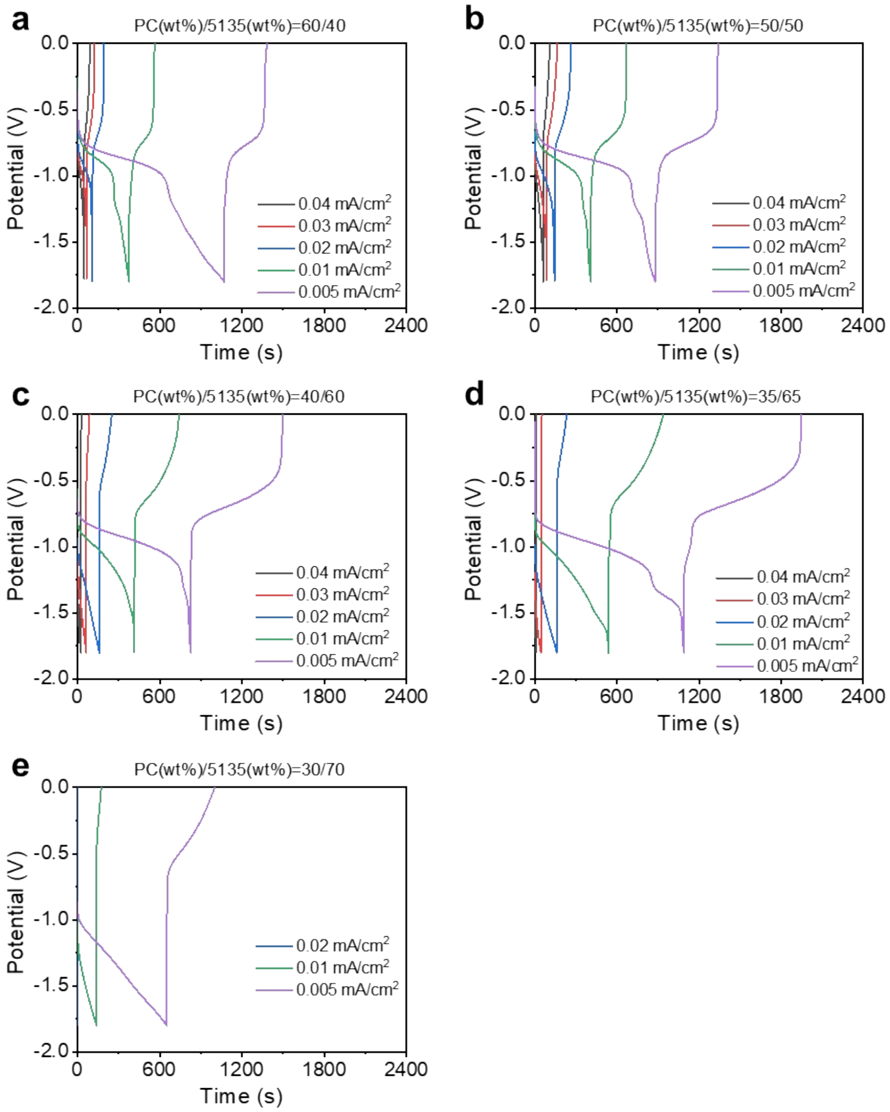


Figure S7. Galvanostatic charge-discharge (GCD) curves at different current densities of electrochromic energy storage devices with different plasticizer content (a) PC (wt%)/5135 (wt%)=60/40, (b) PC (wt%)/5135 (wt%)=50/50, (c) PC (wt%)/5135 (wt%)=40/60, (e) PC (wt%)/5135 (wt%)=35/65, and (e) PC (wt%)/5135 (wt%)=30/70.

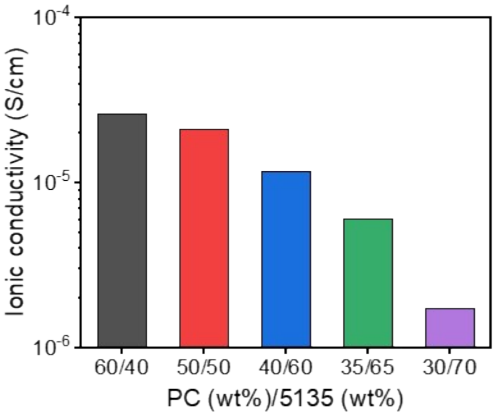


Figure S8. Ionic conductivity at different PC contents.

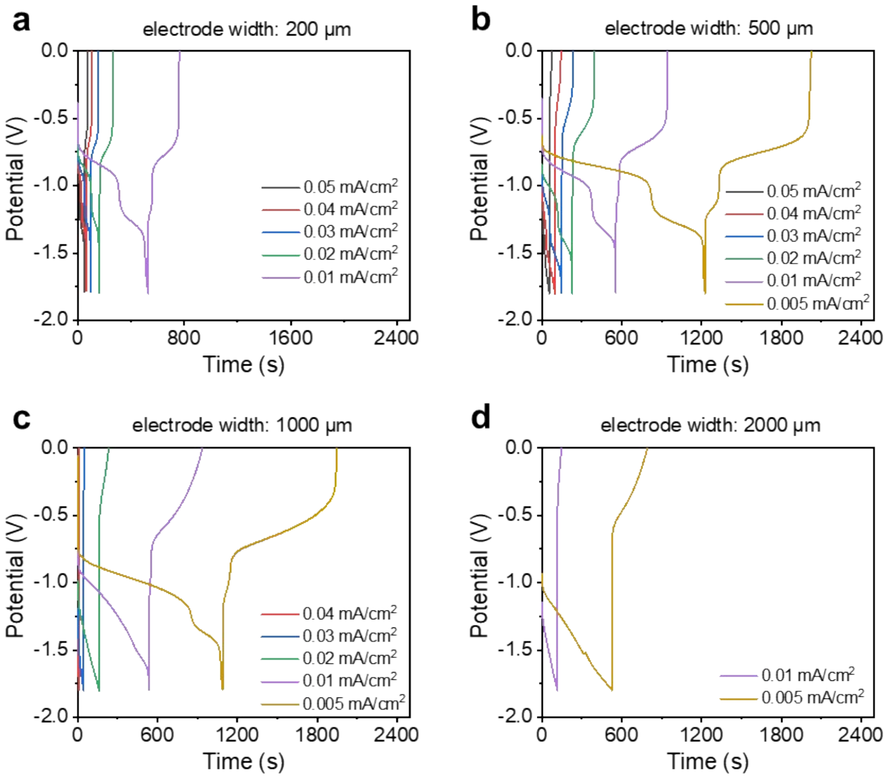
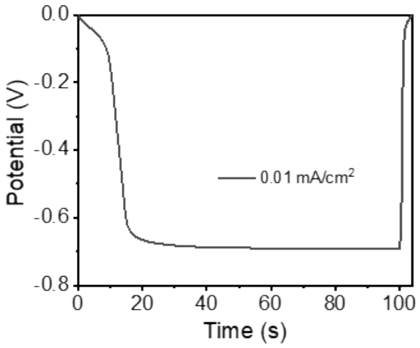


Figure S9. Galvanostatic charge-discharge (GCD) curves at different current densities of electrochromic energy storage devices with different electrode width (a) 200 μm, (b) 500 μm, (c) 1000 μm, and (d) 2000 μm.



Areal capacitance:

0.01 mA/cm^2 × 3.8 s / 0.692 V
= 0.055 mF/cm^2

Figure S10. Galvanostatic charge-discharge (GCD) curves at 0.01 mA/cm^2 of electrochromic energy storage device with traditional face-to-face electrode configuration (Device 1).

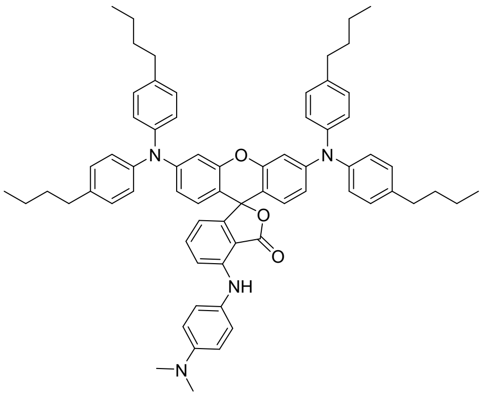


Figure S11. The oxidized electrochromic material (It was synthesized following a method previously reported by our group).[53]

Supplementary Notes

Note S1: Materials and Instrument information

Materials

4,4'-Bipyridine, iodomethane, iodoethane, 1-bromobutane, 1-bromohexane, potassium hexafluorophosphate (KPF_6), acetonitrile (CH_3CN), 1-hydroxycyclohexyl phenyl ketone (184), propylene carbonate (PC), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were purchased from Energy Chemical Company. Prepolymer 5135 was purchased from Jilin Huazhen Science & Technology Company. Ferrocene was purchased from Aladdin Chemicals, China. Polymer microspheres were purchased from Suzhou Nanomicro Technology Co., Ltd. Indium tin oxide (ITO) electrodes were purchased from South China Xiang Science & Technology Company. All the solvents were purchased in commercialized way and used without further purification. $TBAPF_6$ was recrystallized for three times in anhydrous ethanol and dried under vacuum overnight at 60 ^oC before using in the electrochemical measurements.

Instrument information

UV-vis spectra and kinetic data of absorption intensity were measured using a Shimadzu UV-2600i double-beam spectrophotometer or a SPECORD 210 PLUS from Analytikjena. Electrochemical data were measured by Bio-logic electrochemical workstation, Ivium electrochemical workstation and Chen Hua CHI770E electrochemical workstation and. ^1H and ^{13}C NMR spectra were measured by a ZhongkeNiujin AS 400 M NMR spectrometer. Chemical shift values were given relative to tetramethylsilane (TMS). In situ photocuring of electrochromic materials was performed with a UV LED lamp (365 nm, 200 mW/cm^2) from Yanxizao Factory, Zhongshan, China. Indium tin oxide (ITO) electrodes were etched by the Xi-Ai FB30-Z HPWU0300-SKS Laser marking machine.

Note S2: Electrochemistry

Cyclic voltammetry (CV) experiments were performed on a Bio-logic electrochemical workstation under room temperature (25 °C). Electrochemical experiments were measured using three-electrode system in chromatographic grade acetonitrile unless other mentioned, which contained $TBAPF_6$ (0.1 mol/L) as supporting electrolyte. Unless otherwise stated, the tested molecules were dissolved in chromatographic grade acetonitrile and the concentration was 1.0×10^{-3} mol/L. The three-electrode cell included a Pt (platinum) wire counter electrode (ida, China), a glass-carbon working electrode (3 mm diameters, ida, China), and an Ag wire reference electrode (ida, China). The surface of the working electrode was polished with 0.3 μm and 0.05 μm alumina (ida, China), and then followed by ultrasonic cleaning in deionized water for three times.

In addition, since the structure of the electrochromic device is a two-electrode system, the applied stimulation voltage is referred to the counter electrode.

Note S3: Synthesis of molecules

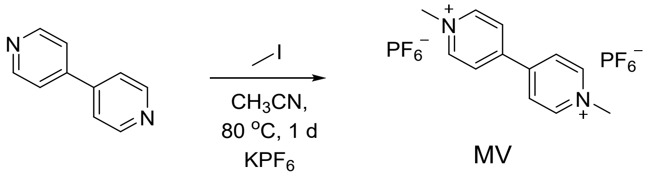


Figure. S12. Synthetic route of molecule MV.

4,4'-Bipyridine (1.56 g, 10 mmol), iodomethane (7.10 g, 50 mmol), and CH_3CN (20 mL) were placed into a round bottom flask. The reaction mixture was stirred at 80 °C for 1 d. The orange red precipitate was filtered and washed with CH_3CN. The solid was then dissolved in water and a saturated aqueous solution of KPF_6 was added until no further precipitation was observed. Then the product (yellowish white powder, yield = 60 %) was obtained by filtered and dried. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.28 (d, *J* = 6.2 Hz, 4H), 8.75 (d, *J* = 6.2 Hz, 4H), 4.43 (s, 6H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 148.19, 146.67, 126.05, 48.04.

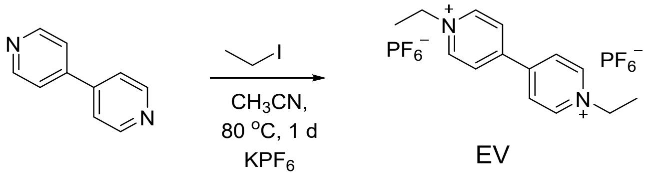


Figure. S13. Synthetic route of molecule BV.

4,4'-Bipyridine (0.78 g, 5 mmol), iodoethane (3.90 g, 25 mmol), and CH_3CN (10 mL) were placed into a round bottom flask. The reaction mixture was stirred at 80 °C for 1 d. The orange red precipitate was filtered and washed with CH_3CN. The solid was then dissolved in water and a saturated aqueous solution of KPF_6 was added until no further precipitation was observed. Then the product (white powder, yield = 84 %) was obtained by filtered and dried. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.38 (d, *J* = 6.7 Hz, 4H), 8.77 (d, *J* = 6.6 Hz, 4H), 4.72 (q, *J* = 7.3 Hz, 4H), 1.61 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 148.51, 145.29, 126.35, 56.43, 15.82.

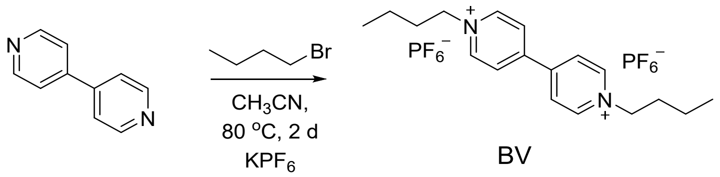


Figure. S14. Synthetic route of molecule BV.

4,4'-Bipyridine (3.12 g, 20 mmol), 1-bromobutane (6.85 g, 50 mmol), and CH_3CN (40 mL) were placed into a round bottom flask. The reaction mixture was stirred at 80 °C for 2 d. The orange precipitate was filtered and washed with CH_3CN. The solid was then dissolved in water and a saturated aqueous solution of KPF_6 was added until no further precipitation was observed. Then the product (white powder, yield = 70 %) was obtained by filtered and dried. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.38 (d, J = 6.3 Hz, 4H), 8.77 (d, J = 6.3 Hz, 4H), 4.69 (t, J = 7.4 Hz, 4H), 1.97 (p, J = 7.5 Hz, 4H), 1.34 (h, J = 7.3 Hz, 4H), 0.95 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.71, 145.77, 126.65, 60.77, 32.70, 18.83, 13.36.

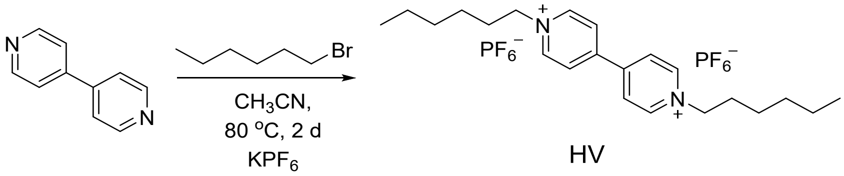


Figure S15. Synthetic route of molecule HV.

4,4'-Bipyridine (0.78 g, 5 mmol), 1-bromohexane (4.13 g, 25 mmol), and CH_3CN (20 mL) were placed into a round bottom flask. The reaction mixture was stirred at 80 °C for 2 d. The yellow precipitate was filtered and washed with CH_3CN. The solid was then dissolved in water and a saturated aqueous solution of KPF_6 was added until no further precipitation was observed. Then the product (white powder, yield = 75 %) was obtained by filtered and dried. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.38 (d, J = 6.7 Hz, 4H), 8.77 (d, J = 6.7 Hz, 4H), 1.98 (p, J = 7.3, 6.8 Hz, 4H), 1.30 (d, J = 5.7 Hz, 12H), 0.97 – 0.77 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.56, 145.43, 126.40, 60.84, 30.32, 30.23, 24.78, 21.48, 13.40.

Note S4: Preparation of the electrochromic devices

1. The in situ photocuring of electrochromic solution:

A mixture of propylene carbonate (PC), prepolymer (5135), BV, Fc, 184, $TBAPF_6$, polymer microspheres was used as electrochromic solutions for the in situ photocuring.

Electrochromic solutions with different contents of plasticizer (PC):

PC (60wt%)/5135 (40wt%): PC (600 mg), **5135 (400 mg)**, BV (28.0 mg), Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

PC (50wt%)/5135 (50wt%): PC (500 mg), **5135 (500 mg)**, BV (28.0 mg), Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

PC (40wt%)/5135 (60wt%): PC (400 mg), **5135 (600 mg)**, BV (28.0 mg), Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

PC (35wt%)/5135 (65wt%): PC (350 mg), **5135 (650 mg)**, BV (28.0 mg), Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

PC (30wt%)/5135 (70wt%): PC (300 mg), **5135 (700 mg)**, BV (28.0 mg), Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

Electrochromic solutions with different viologens (MV, EV, BV, HV):

MV: PC (350 mg), 5135 (650 mg), **MV (23.8 mg),** Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

EV: PC (350 mg), 5135 (650 mg), **EV (25.2 mg)**, Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

BV: PC (350 mg), 5135 (650 mg), **BV (28.0 mg)**, Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

HV: PC (350 mg), 5135 (650 mg), **HV (30.8 mg)**, Fc (9.3 mg), 184 (3.0 mg), $TBAPF_6$ (20.0 mg), polymer microspheres (diameter: 18 μm) (2.0 mg).

2. The preparation of electrochromic devices:

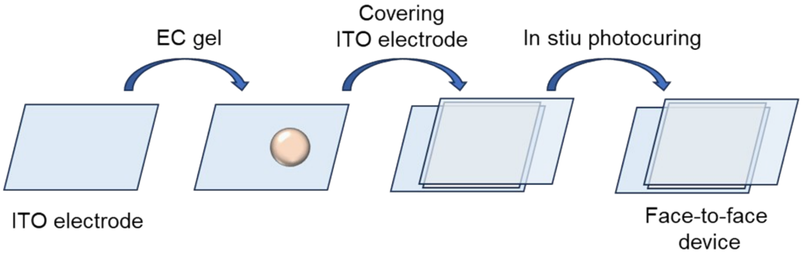


Figure S16. Fabrication schematic diagram of **Device 1**.

Device 1: First, the electrochromic (EC) gel was coated on the first ITO electrode. Then, another ITO electrode was covered and in-situ 365 nm ultraviolet photocuring was carried out for 5 minutes (Figure S11).

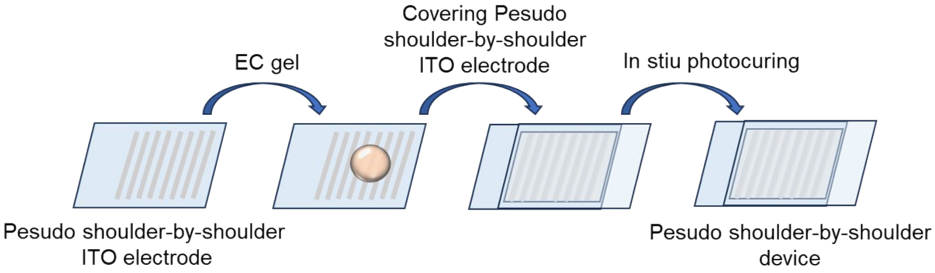


Figure S17. Fabrication schematic diagram of **Device 2**.

Device 2: First, the electrochromic (EC) gel was coated on the pesudo shoulder-by-shoulder ITO electrode. Then, another pesudo shoulder-by-shoulder ITO electrode was covered and in-situ 365 nm ultraviolet photocuring was carried out for 5 minutes (Figure S12).

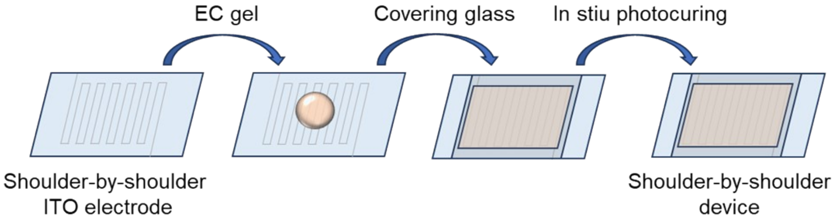


Figure S18. Fabrication schematic diagram of **Device 3**.

Device 3: First, the electrochromic (EC) gel was coated on the shoulder-by-shoulder ITO electrode. Then, another glass was covered and in-situ 365 nm ultraviolet photocuring was carried out for 5 minutes (Figure S13).

Note S5: ^{1}H and ^{13}C NMR spectra

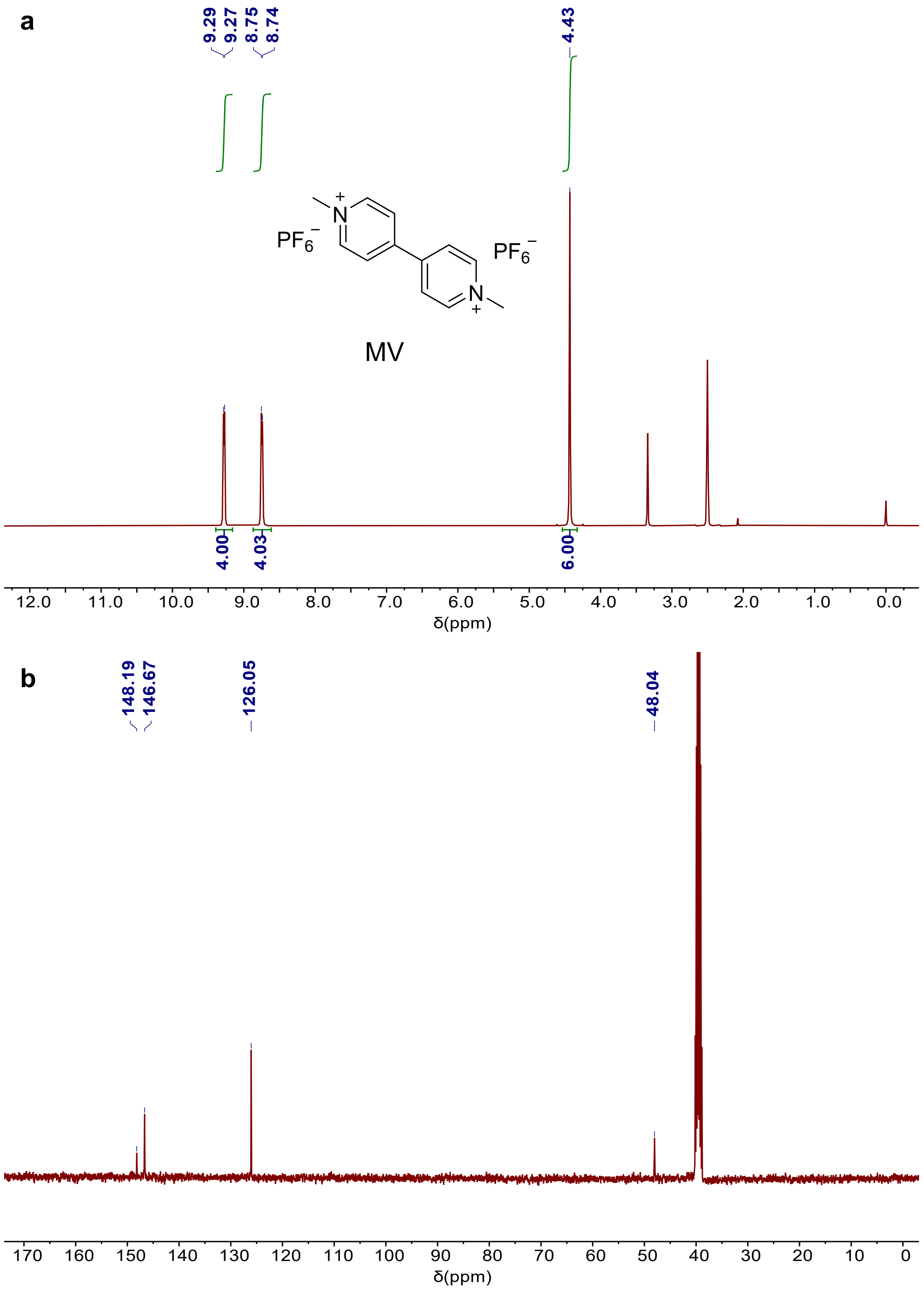


Figure S19. NMR of MV. (a) ^{1}H NMR (400 MHz, DMSO-d_6) and (b) ^{13}C NMR (101 MHz, DMSO-d_6).

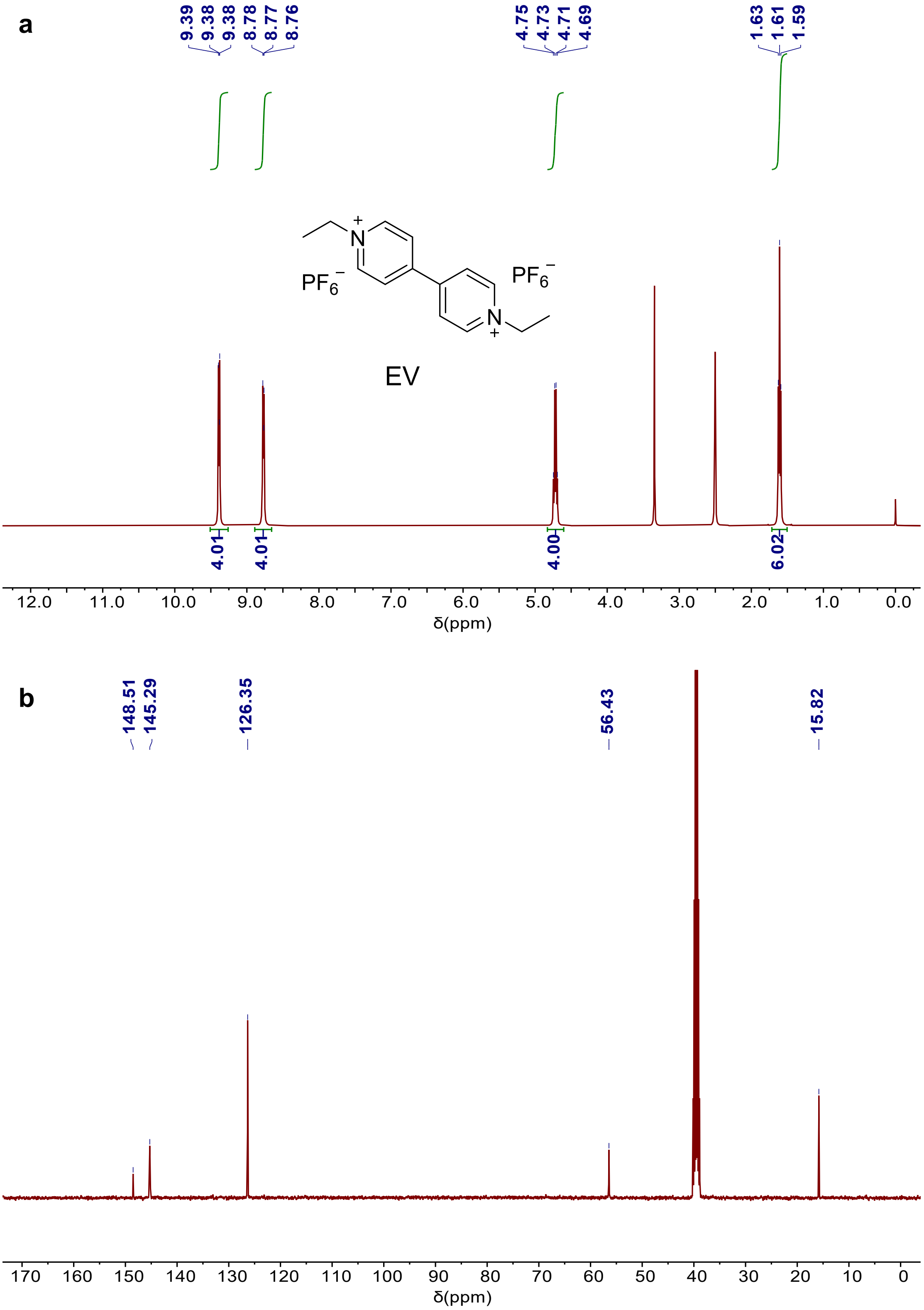


Figure S20. NMR of EV. (a) ^{1}H NMR (400 MHz, DMSO-d_6) and (b) ^{13}C NMR (101 MHz, DMSO-d_6).

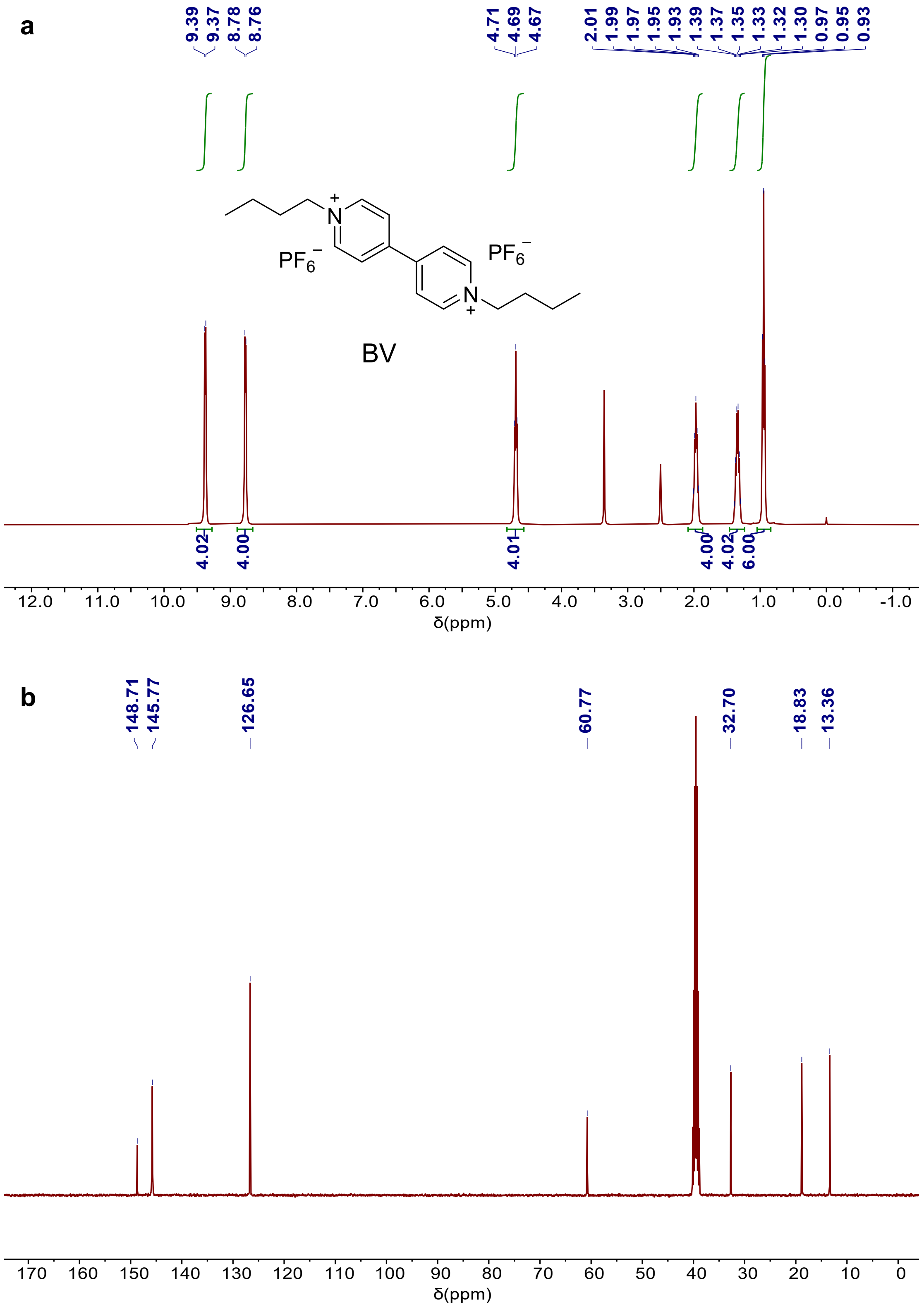


Figure S21. NMR of BV. (a) ^{1}H NMR (400 MHz, DMSO-d_6) and (b) ^{13}C NMR (101 MHz, DMSO-d_6).

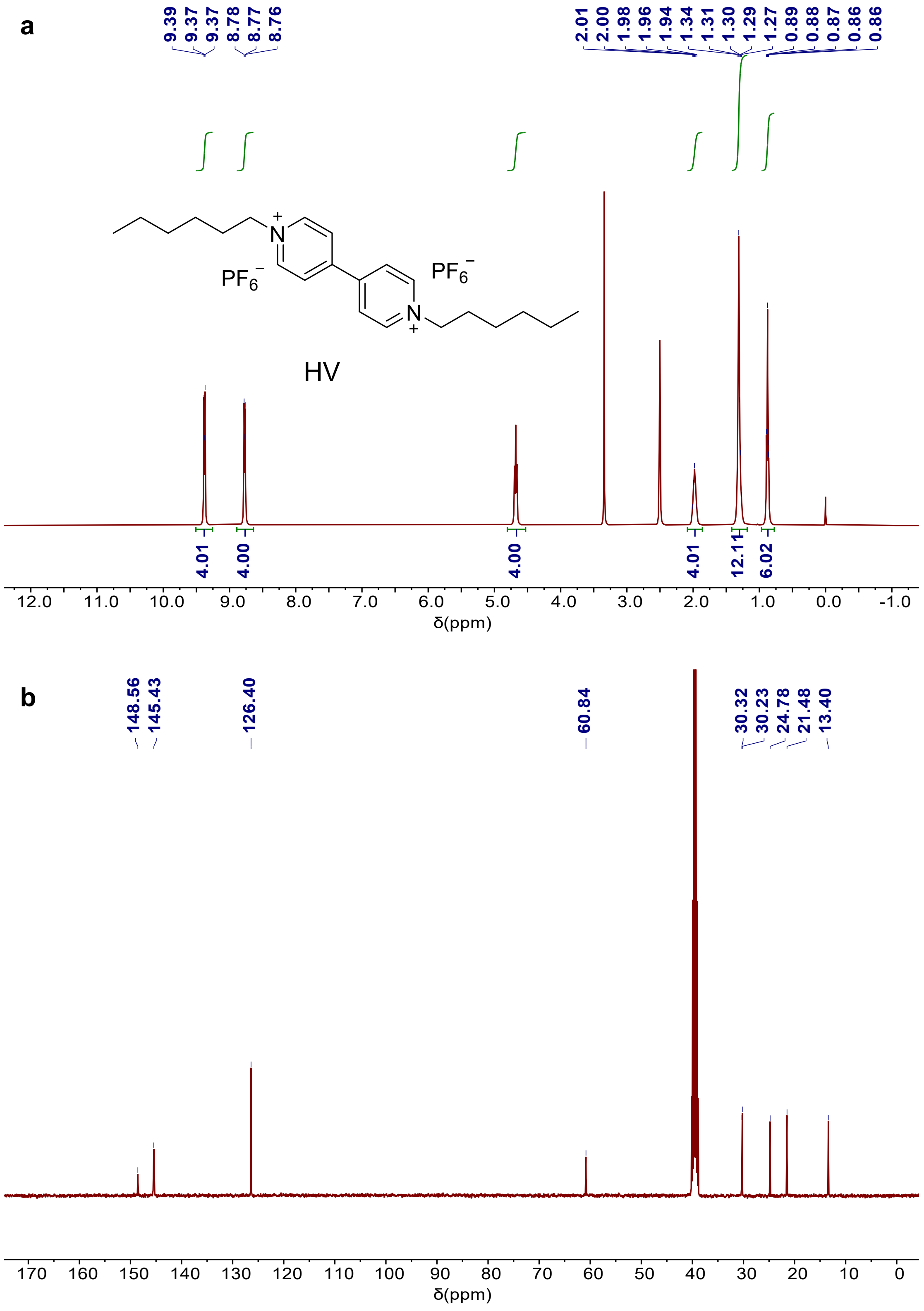


Figure S22. NMR of HV. (a) ^{1}H NMR (400 MHz, DMSO-d_6) and (b) ^{13}C NMR (101 MHz, DMSO-d_6).

Supplementary Movie S1 (separate file). Two fully charged electrochromic energy storage devices are connected in series to power a timer.

Supplementary Movie S2-S6 (separate file). Thin-film electrochromic energy storage devices that can be directly attached to any surface (such as marble, wood, plastic, ceramic, cloth, etc.) to power a timer.