

Supporting Information

A uniformly-coloring electrochromic device based on a Cardo fluorene-grafted viologen derivative with high dissolution stability

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1. General experimental details

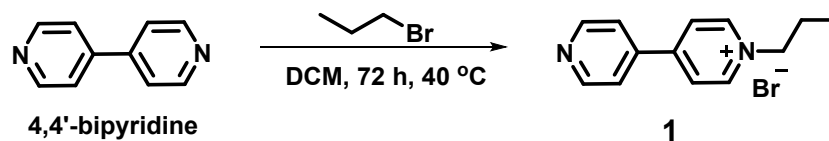
Materials

4,4'-Bipyridine, 4,4'-(9*H*-fluorene-9,9-diyl)diphenol, dichloromethane (DCM), bromopropane, 1,2-dibromoethane, potassium carbonate (K_2CO_3), 18-crown-6, acetonitrile (MeCN), ammonium hexafluorophosphate (NH_4PF_6), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), potassium chloride (KCl), propylene carbonate (PC), petroleum ether (PE), ethyl acetate (EA) and ethanol were purchased from Energy Chemicals, China. Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd. Ferrocene were purchased from Aladdin Chemicals, China. Indium tin oxide (ITO) electrodes were purchased from South China Xiang Science & Technology company. $TBAPF_6$ was recrystallized for three times in anhydrous ethanol and dried under vacuum overnight at 80 °C before using in the electrochemical measurements. The rest of all solvents were purchased in commercialized way and used without further purification.

Characterizations

UV-Vis absorption spectra and kinetic data of absorption intensity were measured using a Shimadzu UV-2600i double-beam spectrophotometer. Electrochemical data were measured by a Bio-logic SP-50e electrochemical work station. 1H NMR and ^{13}C NMR spectra were recorded by a Bruker AVANCE NEO 400 MHz nuclear magnetic resonance spectrometer with deuterated dimethyl sulfoxide (DMSO) as the solvent. Time of flight mass spectrometer (TOF-MS) analysis was determined by the AB Sciex 4600 spectrometer. Scanning electron microscope (SEM) images and scanning electron microscope-energy dispersive spectrometer (SEM-EDS) were measured by a Hitachi 8230 cold field emission scanning electron microscope. Metalloscope images were obtained by an Axio Observer 5 optical microscope.

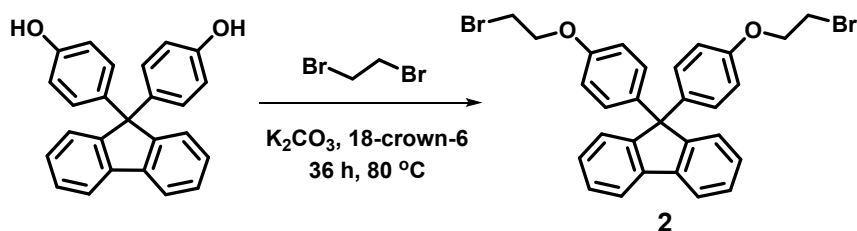
Synthesis of 1-propyl-[4,4'-bipyridin]-1-ium bromide (1)



Scheme S1. Synthetic route of the molecule 1.

4,4'-bipyridine (3.124 g, 0.020 mol) was dissolved in DCM (30 mL), then the bromopropane (2.460 g, 0.020 mol) was added, and stirred for 72 h at 40 °C. A large amount of yellow products precipitated from the reaction mixture, which was filtered, and dried in a vacuum oven. The target compound 1 was obtained as yellow power (5.025 g, 90% yield). The characterization was shown below (Figure S4). ^1H NMR (400 MHz, DMSO) δ 9.30 (d, $J=7.0$ Hz, 2H), 8.86 (dd, $J=4.5, 1.7$ Hz, 2H), 8.67 (d, $J=6.9$ Hz, 2H), 8.06 (dd, $J=4.5, 1.7$ Hz, 2H), 4.65 (t, $J=7.3$ Hz, 2H), 1.99 (dd, $J=14.7, 7.3$ Hz, 2H), 0.92 (t, $J=7.4$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 152.23 (s), 150.96 (s), 145.33 (s), 140.90 (s), 125.40 (s), 121.96 (s), 61.61 (s), 24.18 (s), 10.25 (s). TOF-MS: $m/z = 199.1235$, calculated 199.1230.

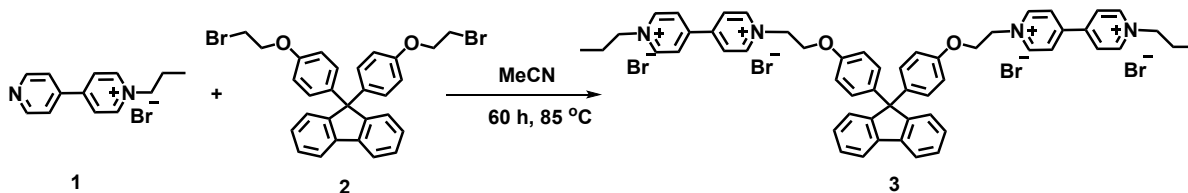
Synthesis of 9,9-bis(4-(2-bromoethoxy)phenyl)-9H-fluorene (2)



Scheme S2. Synthetic route of the molecule 2.

A suspension of 4,4'-(9-fluorenylidene) diphenol (1.752 g, 0.005 mol), finely powdered K_2CO_3 (1.780 g, 0.013 mol) and 18-crown-6 (0.265 g, 0.001 mol) in 1,2-dibromoethane (50 mL) was stirred at 80 °C for 36 h. After completion of reaction, the mixture was cooled, filtered, and washed with DCM. The filtrate was evaporated under vacuum to yield a residue that was purified by flash silica gel chromatography (EA:PE, 1:9 v/v) to yield pure dibromide 2 (2.483 g, 88%). The characterization was shown below (Figure S5). ^1H NMR (400 MHz, DMSO) δ 7.91 (d, $J=7.5$ Hz, 2H), 7.38 (dd, $J=11.7, 4.4$ Hz, 4H), 7.34–7.26 (m, 2H), 7.13–6.95 (m, 4H), 6.93–6.76 (m, 4H), 4.34–4.13 (m, 4H), 3.83–3.66 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 156.65 (s), 151.13 (s), 139.38 (s), 138.10 (s), 128.81 (s), 127.82 (s), 127.55 (s), 125.90 (s), 120.49 (s), 114.39 (s), 67.70 (s), 63.63 (s), 31.45 (s). TOF-MS: $m/z = 564.0120$, calculated 564.0123.

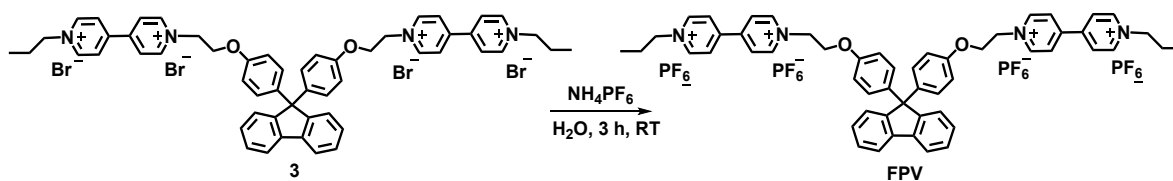
Synthesis of 1',1'''-(((9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy))bis(ethane-2,1-diyl))bis(1-propyl-[4,4'-bipyridine]-1,1'-dium) bromide (3)



Scheme S3. Synthetic route of the molecule 3.

The molecule 1 (2.792 g, 0.010 mol) and molecule 2 (1.693 g, 0.003 mol) were dissolved in MeCN (50 mL), and stirred for 60 h at 85 °C. A large amount of light yellow products precipitated from the reaction mixture, which was filtered, washed with MeCN, and dried in a vacuum oven. The target compound 3 was obtained as yellow power (2.896 g, 86% yield). The characterization was shown below (**Figure S6**). ¹H NMR (400 MHz, DMSO) δ 9.42 (dd, J=10.2, 6.7 Hz, 8H), 8.80 (t, J=6.1 Hz, 8H), 7.88 (d, J=7.5 Hz, 2H), 7.31 (qd, J=14.5, 7.1 Hz, 6H), 6.98 (d, J=8.8 Hz, 4H), 6.81 (d, J=8.8 Hz, 4H), 5.12 (s, 4H), 4.67 (t, J=7.2 Hz, 4H), 4.52 (s, 4H), 2.08–1.92 (m, 4H), 0.92 (t, J=7.3 Hz, 4H). ¹³C NMR (101 MHz, DMSO) δ 156.19 (s), 150.90 (s), 149.07 (s), 148.49 (s), 146.34 (s), 145.73 (s), 139.29 (s), 138.45 (s), 128.71 (s), 127.79 (s), 127.57 (s), 126.68 (s), 126.40 (s), 125.74 (s), 120.54 (s), 114.44 (s), 66.11 (s), 63.56 (s), 62.03 (s), 59.96 (s), 24.22 (s), 10.21 (s). TOF-MS: m/z = 200.6072, calculated 200.6056.

Synthesis of 1',1'''-(((9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy))bis(ethane-2,1-diyl))bis(1-propyl-[4,4'-bipyridine]-1,1'-dium) hexafluorophosphate (FPV)

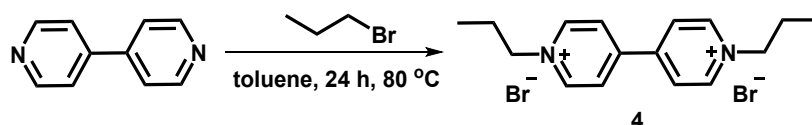


Scheme S4. Synthetic route of the molecule *FPV*.

The molecule 3 (2.245 g, 0.002 mol) was dissolved in water (30 mL), then the aqueous NH₄PF₆ (2.608 g NH₄PF₆ in 30 mL water) was added. The mixture was stirred at room temperature for 3 h, filtered under reduced pressure, washed with a small amount of cold water, and dried in a vacuum oven. The target compound *FPV* was obtained as light yellow power (2.600 g, 94% yield). The characterization was shown below (**Figure S7**). ¹H NMR (400 MHz, DMSO) δ 9.36 (dd, J=11.8, 6.8 Hz, 8H), 8.74 (t, J=5.7 Hz, 8H), 7.88 (d, J=7.5 Hz, 2H), 7.31 (qd, J=14.3, 7.0 Hz, 6H), 6.99 (d, J=8.9 Hz, 4H), 6.80 (d, J=8.9 Hz, 4H), 5.08 (d, J=4.4 Hz, 4H), 4.64 (t, J=7.3 Hz, 4H), 4.55–4.43 (m,

4H), 2.00 (dd, $J=14.7, 7.3$ Hz, 4H), 0.92 (t, $J=7.4$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 156.21 (s), 150.94 (s), 149.26 (s), 148.66 (s), 146.33 (s), 145.70 (s), 139.33 (s), 138.50 (s), 128.76 (s), 127.81 (s), 127.62 (s), 126.68 (s), 126.39 (s), 125.76 (s), 120.55 (s), 114.40 (s), 66.04 (s), 63.61 (s), 62.29 (s), 60.13 (s), 24.19 (s), 10.22 (s). TOF-MS: $m/z = 200.6072$, calculated 200.6056.

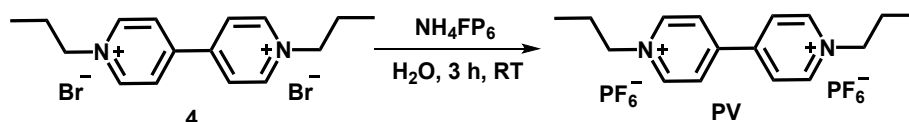
Synthesis of 1,1'-dipropyl-[4,4'-bipyridine]-1,1'-dium bromide (4)



Scheme S5. Synthetic route of the molecule 4.

4,4'-bipyridine (3.124 g, 0.020 mol) was dissolved in toluene (50 mL), then the bromopropane (7.380 g, 0.060 mol) was added, and stirred for 24 h at 80 °C. A large amount of yellow products precipitated from the reaction mixture, which was filtered, and dried in a vacuum oven. The target compound 4 was obtained as yellow power (7.722 g, 96% yield). The characterization was shown below (Figure S8). ^1H NMR (400 MHz, DMSO) δ 9.50 (d, $J = 6.9$ Hz, 4H), 8.88 (d, $J = 6.8$ Hz, 4H), 4.73 (t, $J = 7.3$ Hz, 4H), 2.01 (d, $J = 7.3$ Hz, 4H), 0.92 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 149.02 (s), 146.25 (s), 127.11 (s), 62.45 (s), 24.73 (s), 10.71 (s). TOF-MS: $m/z = 121.0882$, calculated 121.0886.

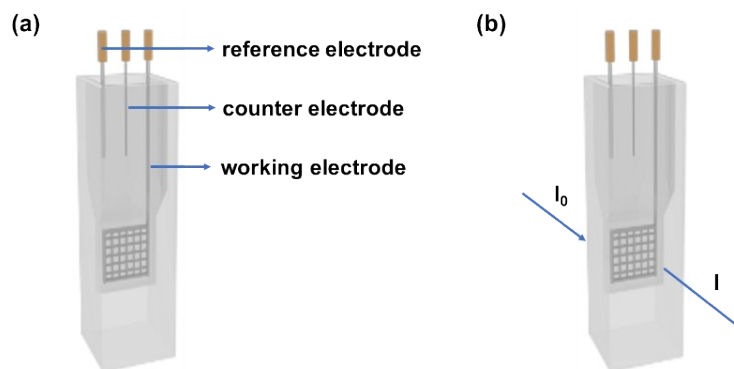
Synthesis of 1,1'-dipropyl-[4,4'-bipyridine]-1,1'-dium hexafluorophosphate (PV)



Scheme S6. Synthetic route of the molecule PV.

The molecule 4 (4.022 g, 0.010 mol) was dissolved in water (50 mL), then the aqueous NH₄PF₆ (13.040 g NH₄PF₆ in 30 mL water) was added. The mixture was stirred at room temperature for 3 h, filtered under reduced pressure, washed with a small amount of cold water, and dried in a vacuum oven. The target compound PV was obtained as light yellow power (5.057 g, 95% yield). The characterization was shown below (Figure S9). ^1H NMR (400 MHz, DMSO) δ 9.37 (d, $J = 6.7$ Hz, 4H), 8.77 (d, $J = 6.6$ Hz, 4H), 4.65 (t, $J = 7.3$ Hz, 4H), 2.01 (dd, $J = 14.6, 7.3$ Hz, 4H), 0.93 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 149.18 (s), 146.21 (s), 127.07 (s), 62.74 (s), 24.64 (s), 10.69 (s). TOF-MS: $m/z = 121.0881$, calculated 121.0886.

2. Spectroelectrochemical measurements *in situ*



Scheme S7. (a) The structure of a thin-layer quartz electrochemical cell which was used to measure the redox states in solution '*in situ*'. (b) The transmission route of ultraviolet (UV) and visible (Vis) lights.

As depicted in **Scheme S7**, the spectroelectrochemical measurements were conducted '*in situ*' using a thin-layer (1 mm) quartz glass electrochemical cell (ida, China). The three electrodes consisted of a Pt network working electrode, a Pt wire counter electrode, and an Ag reference electrode.

3. The EC mechanism of FPV

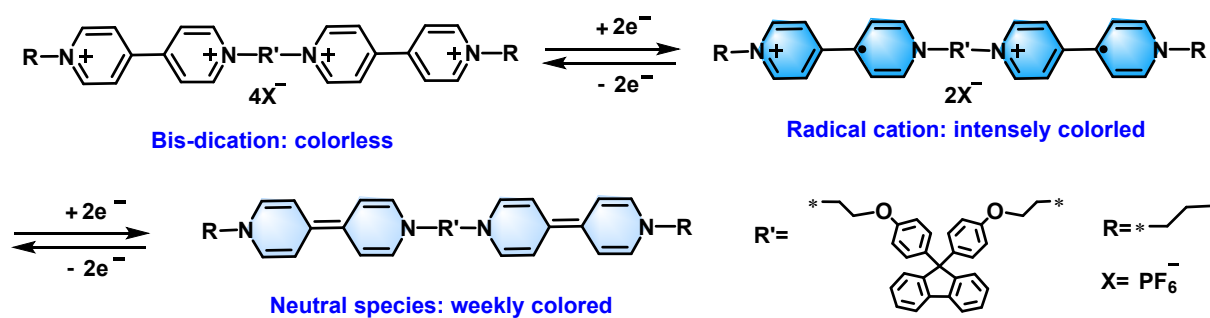


Figure S1. The EC mechanism of FPV

As shown in **Figure S1**, the viologens of FPV possess three reversible redox states: a dication (colorless), a radical cation (intensely colored) and a neutral form (weakly colored).

4. Supplementary Figures for devices

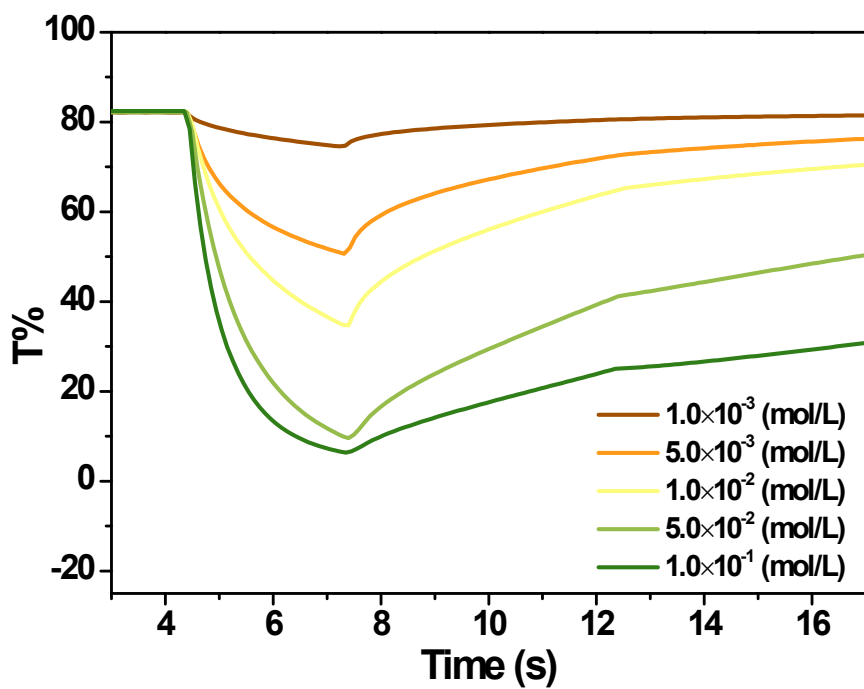


Figure S2. Transmittance spectra of device containing different concentrations of FPV.

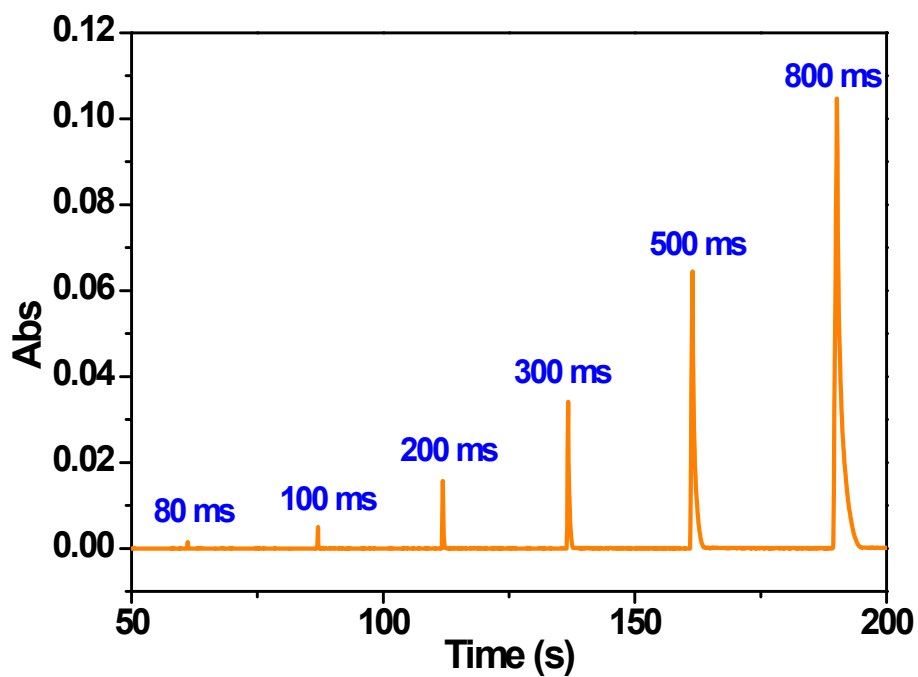


Figure S3. Changes of absorbance at 600 nm when the EC device was added -1.1 V with different time.

5. ^1H NMR and ^{13}C NMR spectra

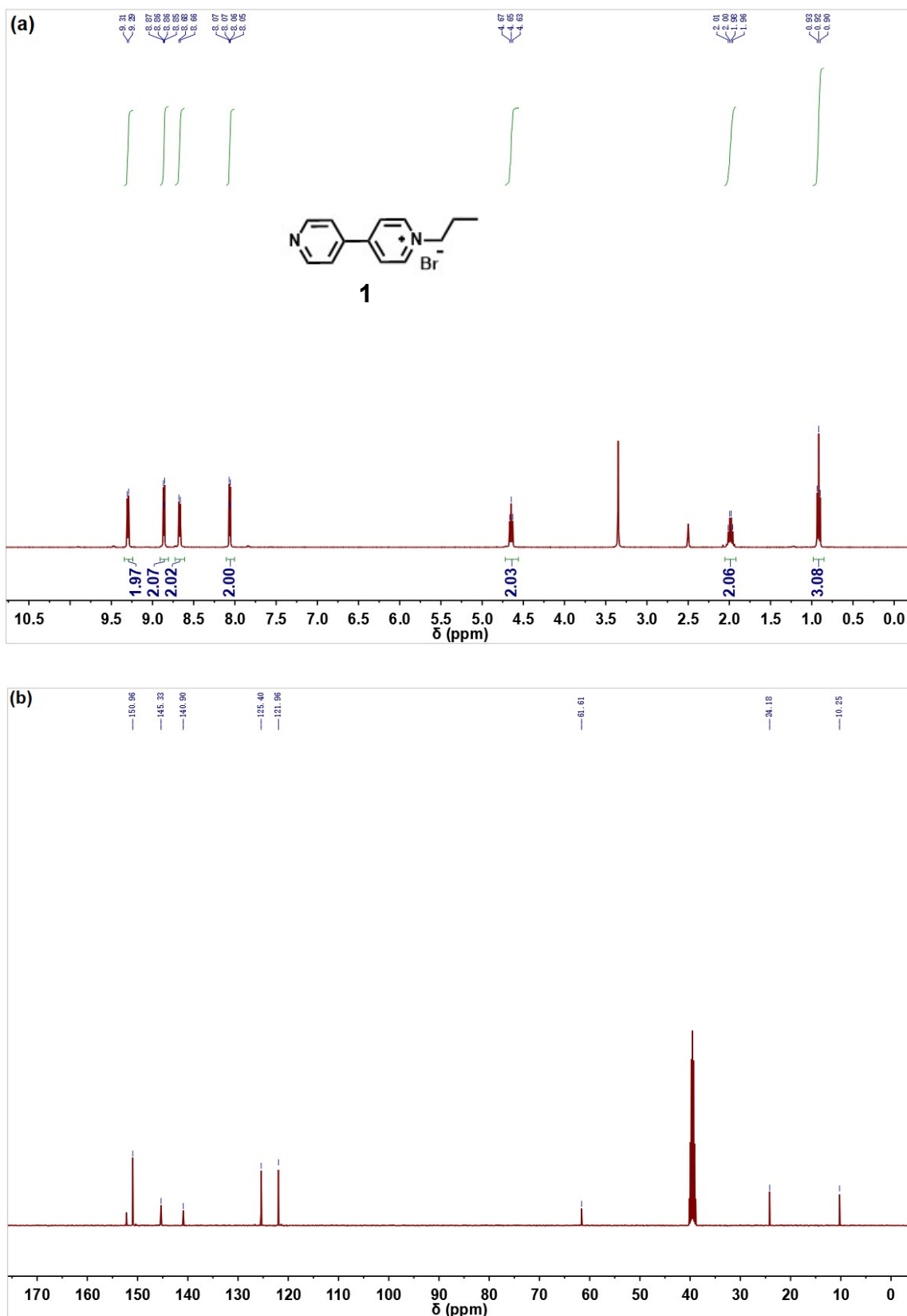


Figure S4. (a) ^1H NMR and (b) ^{13}C NMR spectra of molecule **1** in deuterated DMSO recorded at 400 MHz at room temperature.

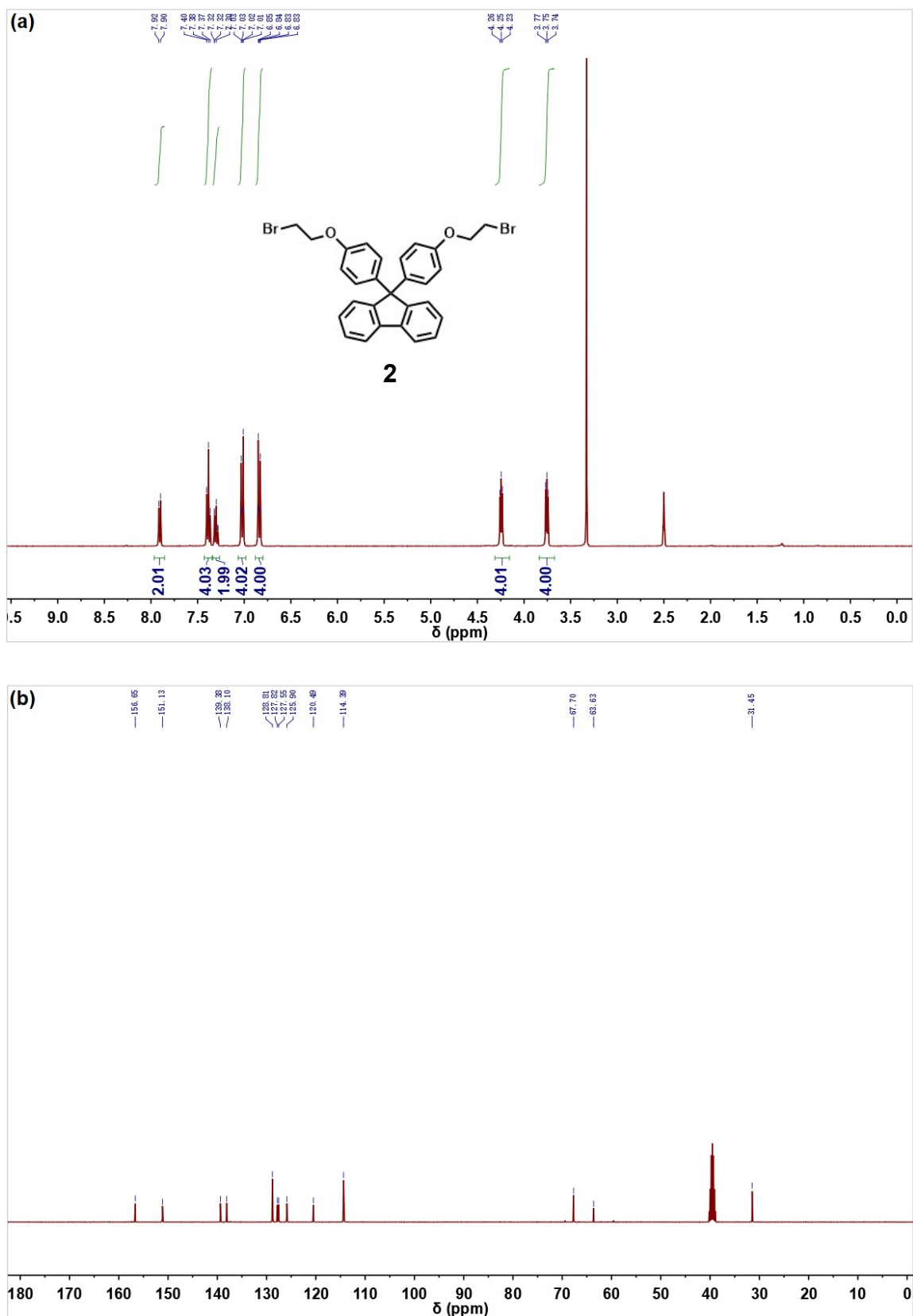
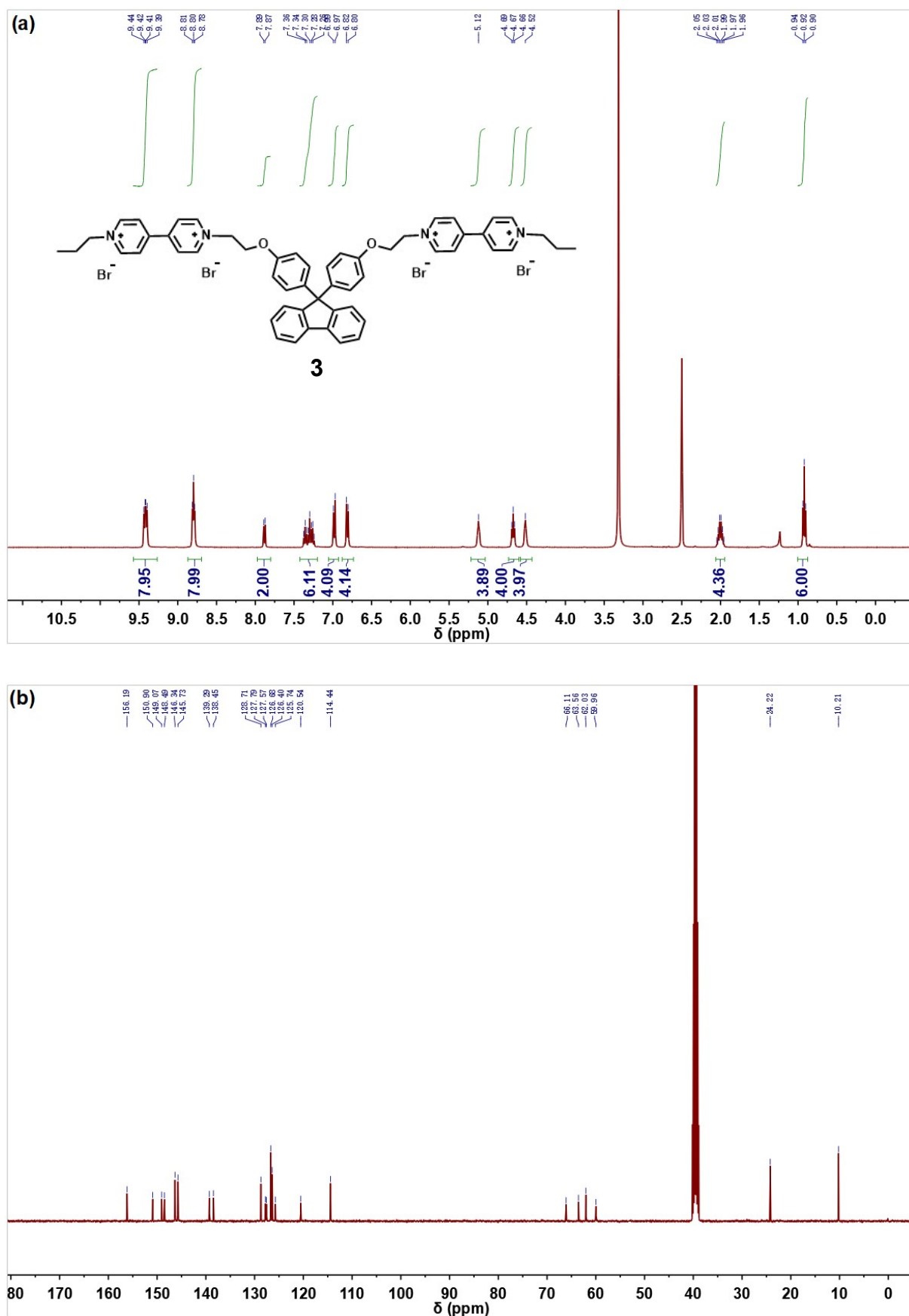


Figure S5. (a) ^1H NMR and (b) ^{13}C NMR spectra of molecule 2 in deuterated DMSO recorded at 400 MHz at room temperature.



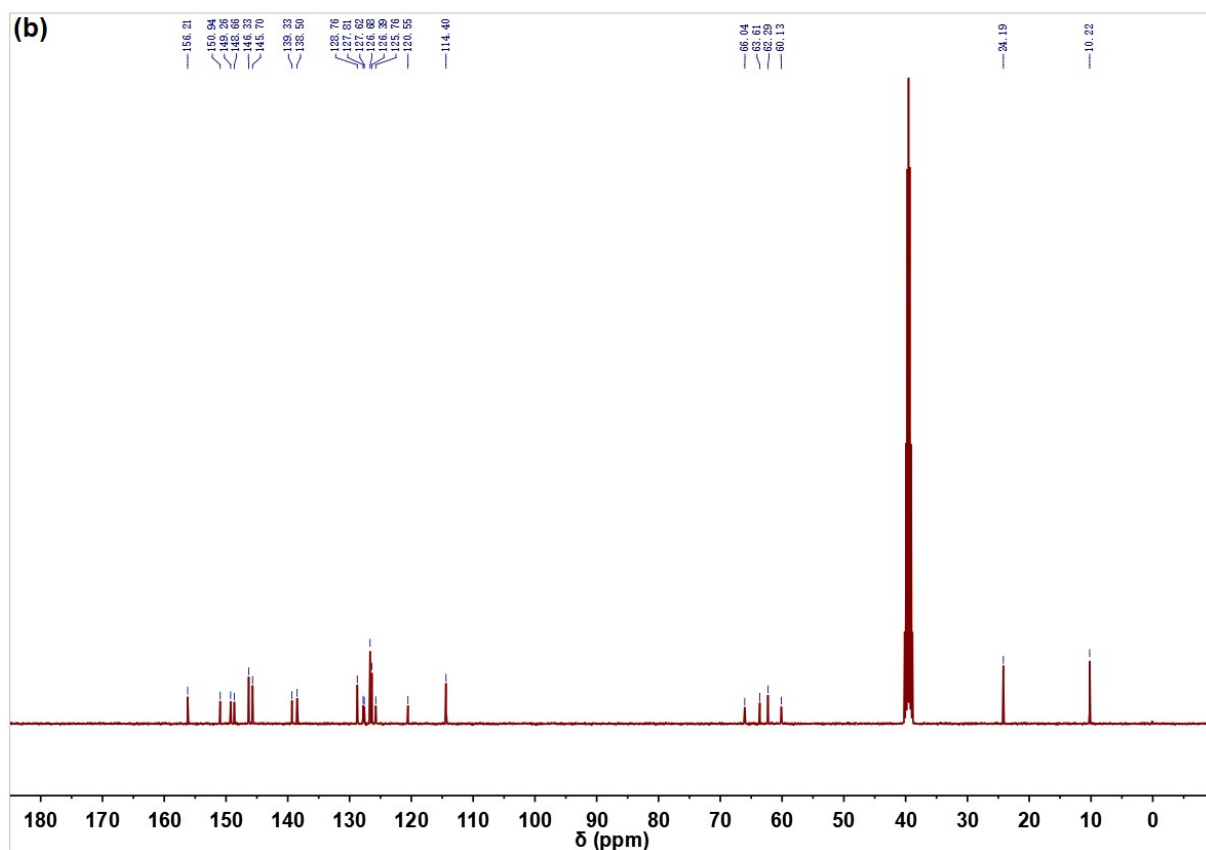
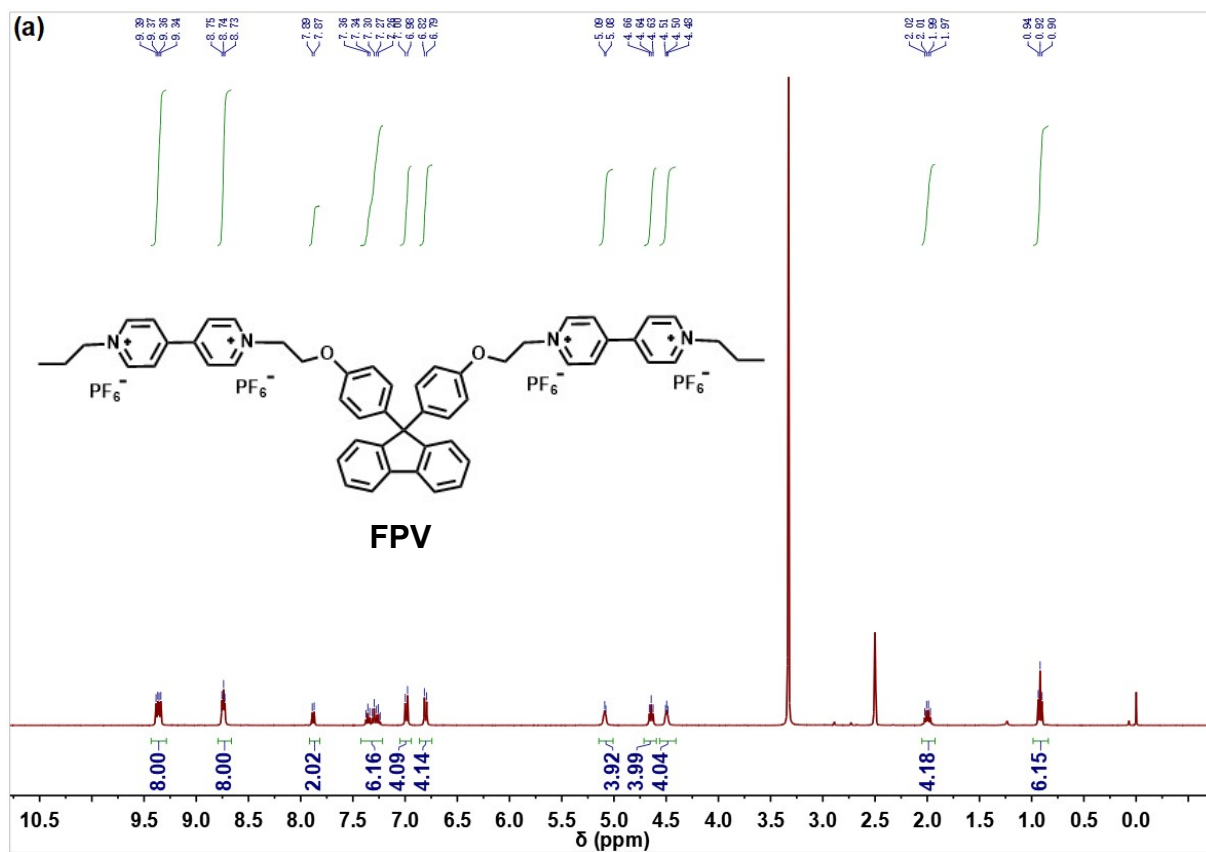


Figure S7. (a) ^1H NMR and (b) ^{13}C NMR spectra of molecule *FPV* in deuterated DMSO recorded at 400 MHz at room temperature.

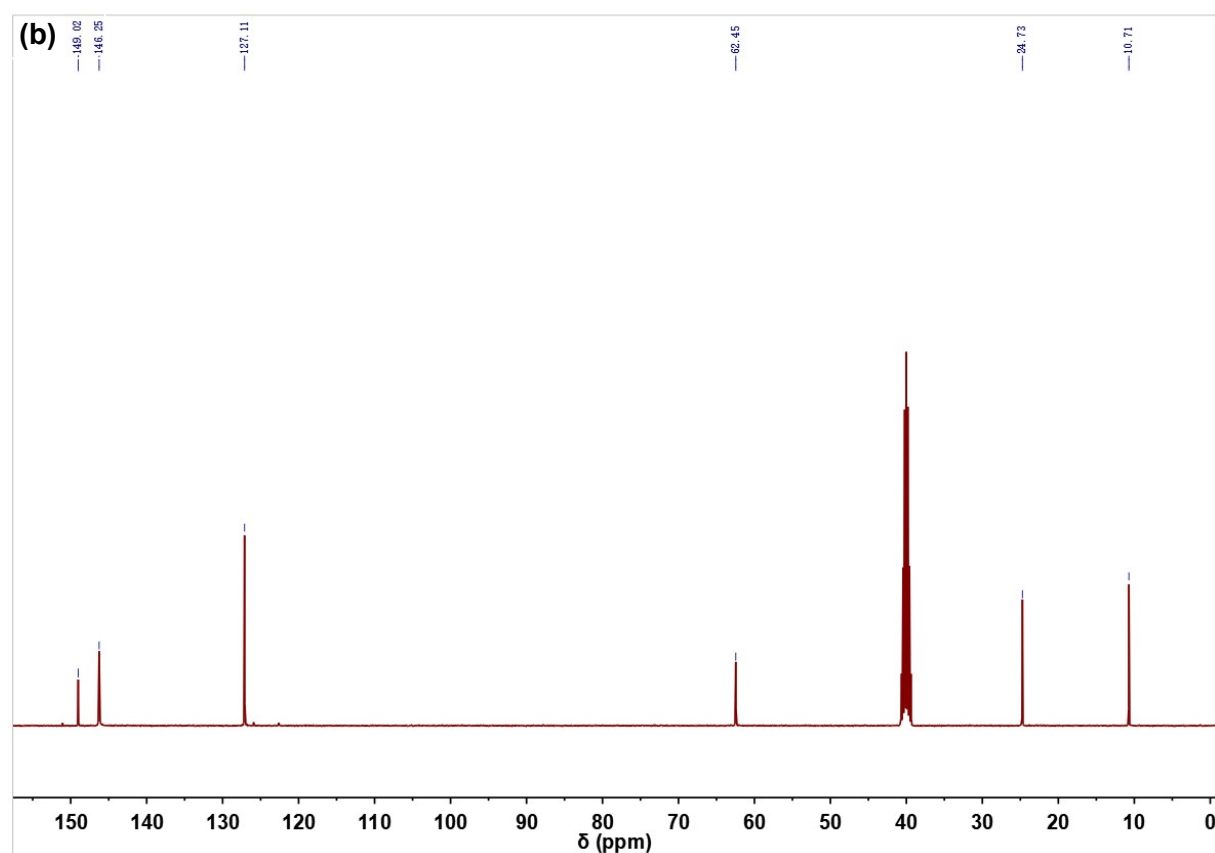
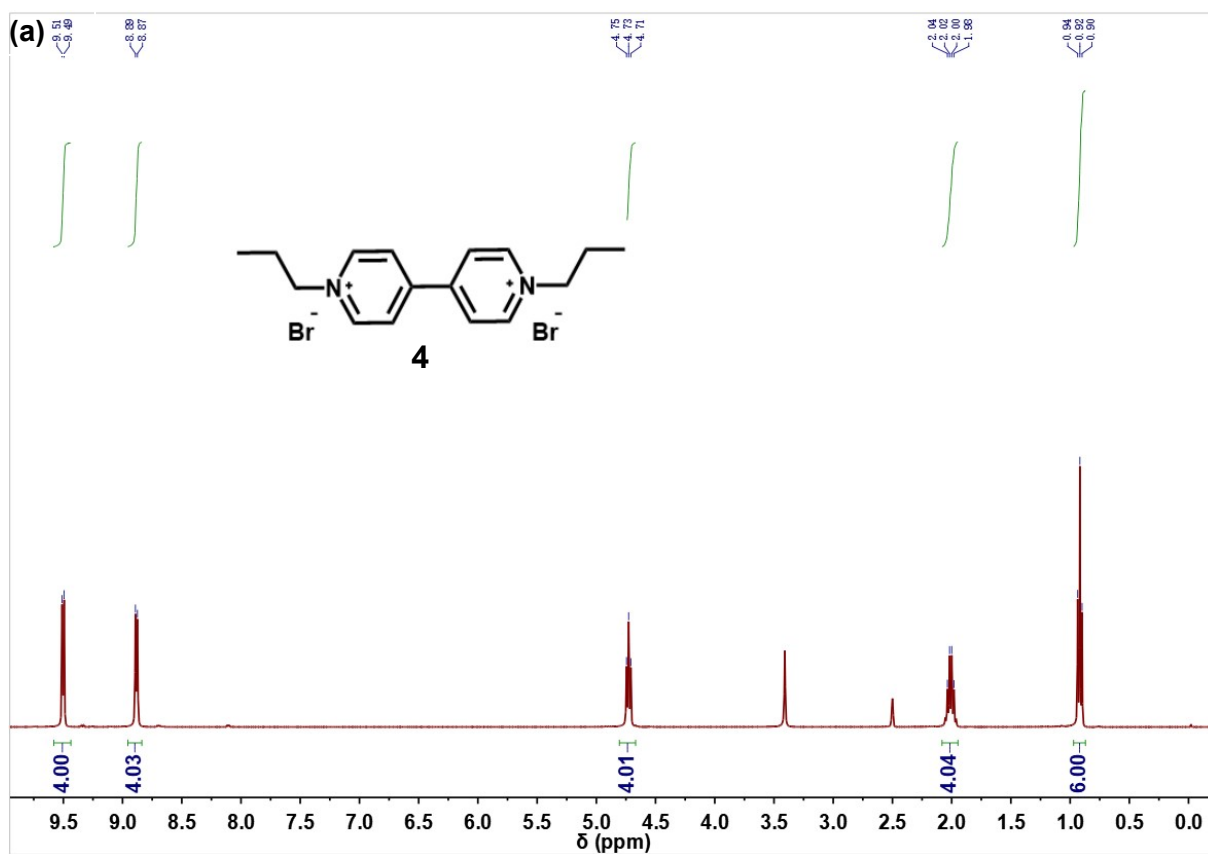


Figure S8. (a) ^1H NMR and (b) ^{13}C NMR spectra of molecule 4 in deuterated DMSO recorded at 400 MHz at room temperature.

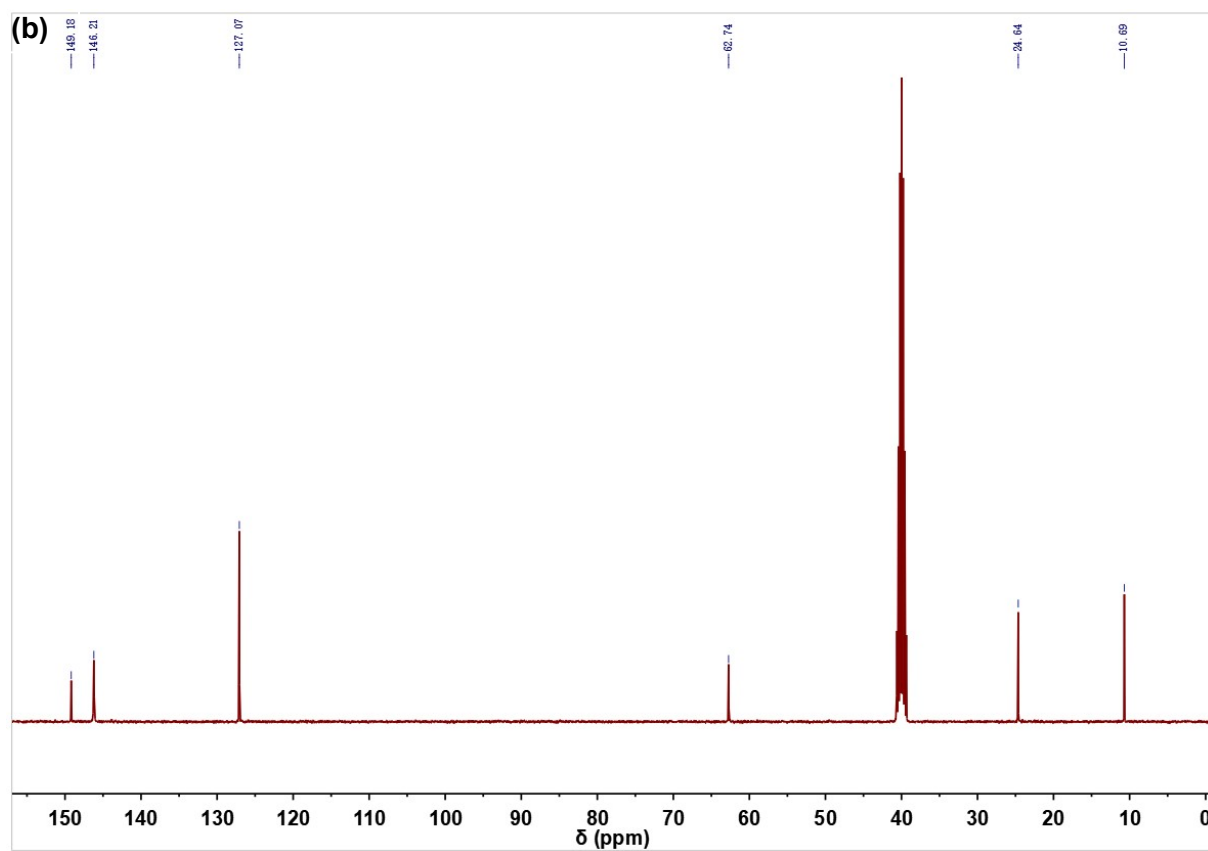
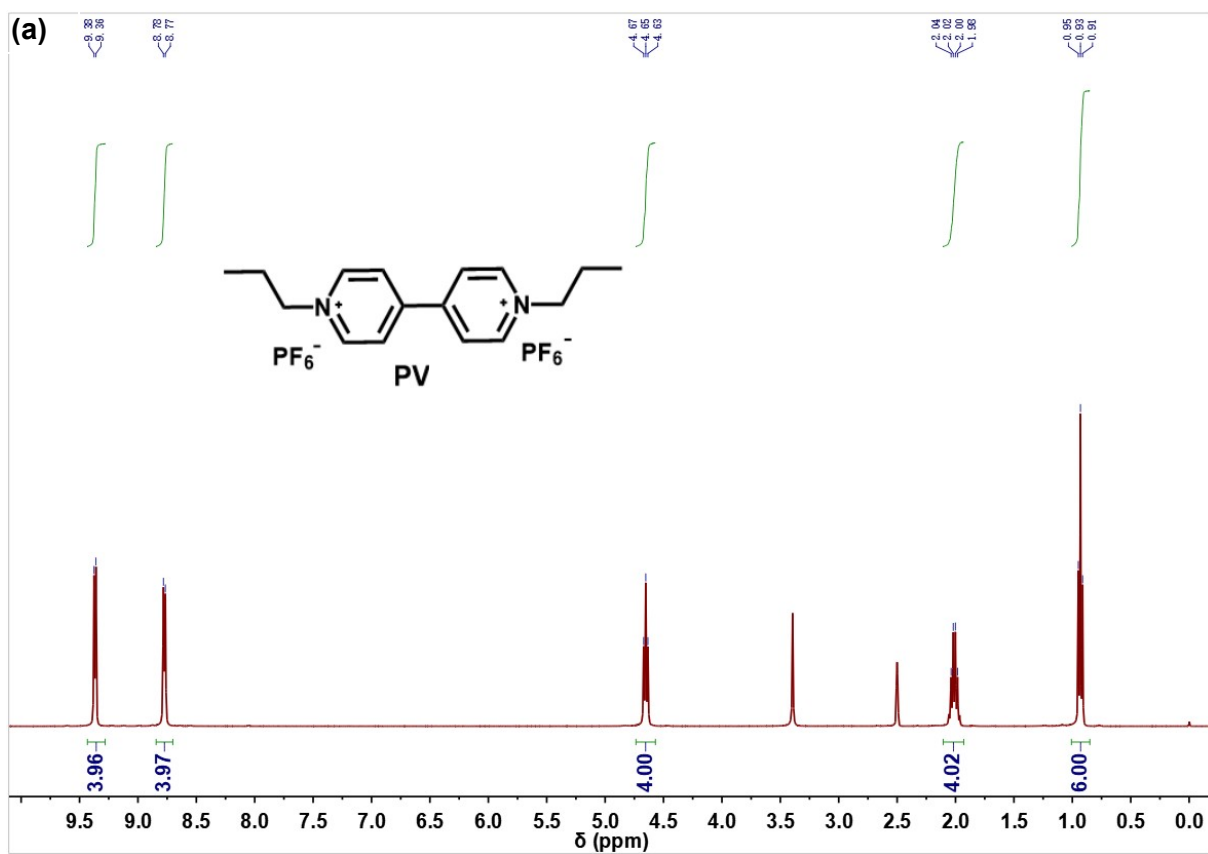


Figure S9. (a) ^1H NMR and (b) ^{13}C NMR spectra of molecule *PV* in deuterated DMSO recorded at 400 MHz at room temperature.

6. Supplementary Figures for smart windows

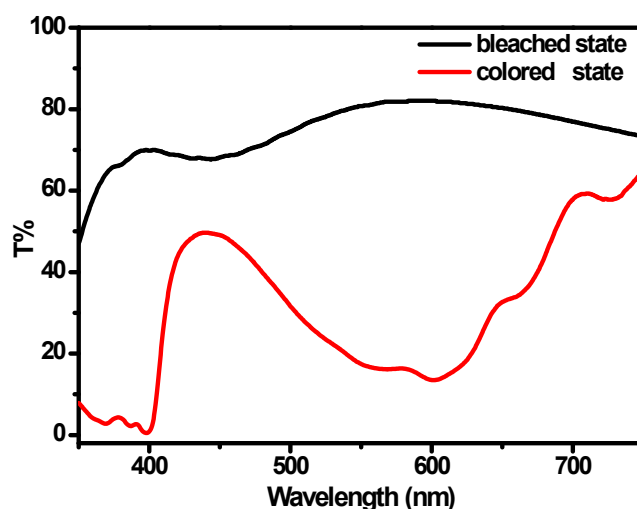


Figure S10. The spectra of transmittance changes of the electrochromic smart windows

Table S1. The comparison chart of the properties with some typical viologen-based EC materials

EC materials	λ_{\max}^a (nm)	ΔT^b (%)	t_b/t_c^c (s)	Stability (cycles)	CE ^d (cm ² C ⁻¹)	Ref.
FPV	602	69	4.4/0.9	1200	139.04	This work
VB-1	—	44	1.09/2.16	1000	121	1
VB-2	—	63	0.98/1.79	1000	199	1
VB-3	600/500	30	—	6000	—	2
VB-4	635	33	1.9/1.8	—	—	3
VB-5	650	28	0.54/2.18	1000	117	4
VB-6	610	56	5.9/2.6	3000	125.1	5
VB-7	—	96	9.7/1.7	1000	177	6
VB-8	—	76.9	56.7/9.5	1000	—	7

NOTE: ^amaximum absorbance wavelength; ^btransmittance change during coloration and bleaching process; ^cbleaching (t_b) and coloration time (t_c); ^dcoloration efficiency.

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