Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Flexible electrochromic device having remarkable color change from golden to green and their application on smart windows and electronic label

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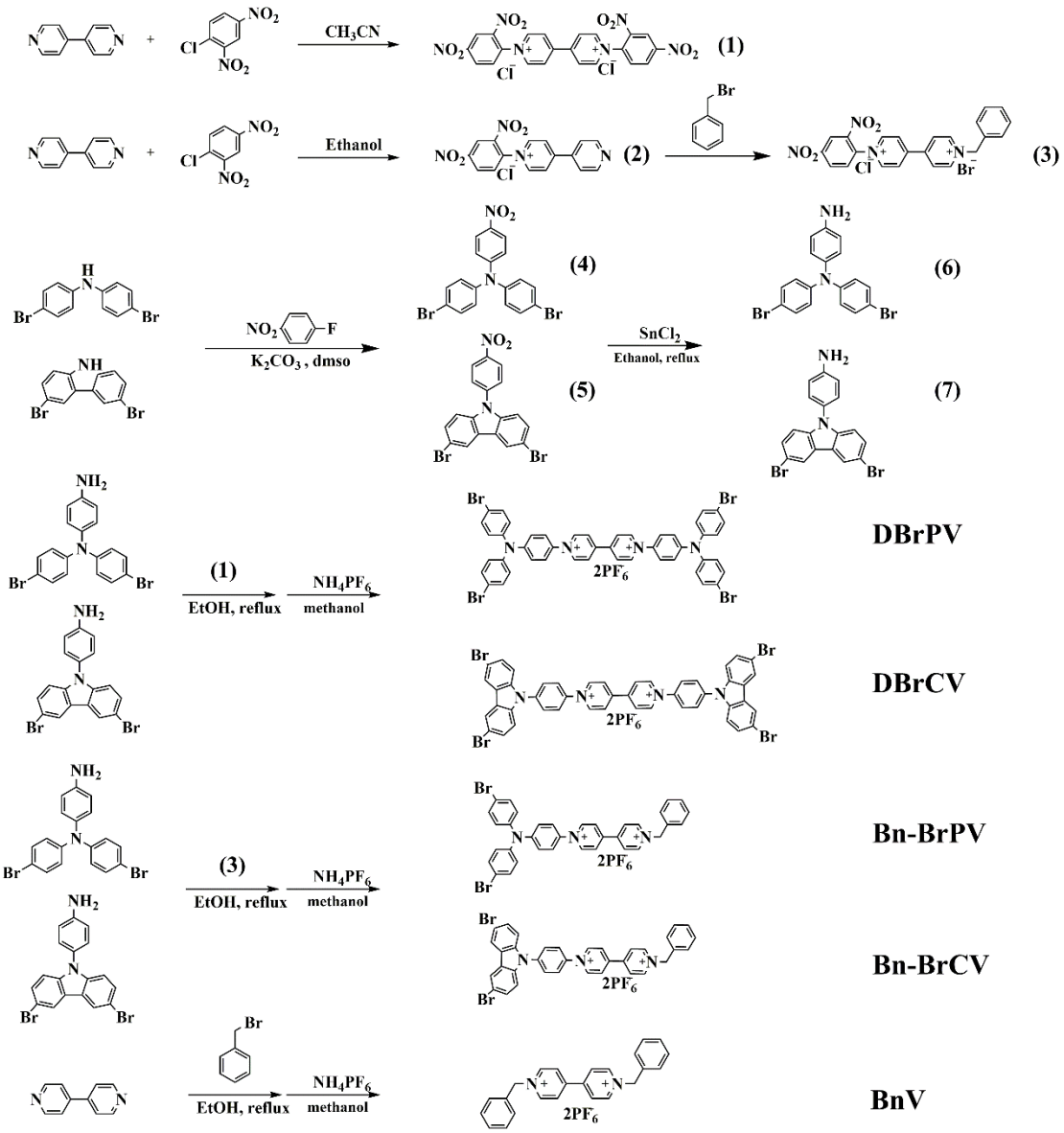
1. Synthesis

The synthetic routes to target compounds are shown in Scheme S1.



Scheme S1. The synthetic routes for the viologen derivatives.

Intermediate **(1)** was synthesized according to the previously reported procedure[1]. In brief, a mixture of 4,4'-bipyridine (3.28 g, 21 mmol), 1-chloro-2,4-dinitrobenzene (12.72 g, 63 mmol) and 60 ml acetonitrile were added in a three-necked flask. The mixture was refluxed for 24 hours. After the reaction is completed, it was cooled to room temperature and filtered to obtain the crude product. The crude product was

washed with dichloromethane and acetonitrile respectively and vacuum dried to obtain the white solid (8.96 g, yield 76%).[1]H NMR (600 MHz, D_2O) δ 9.43 (d, *J* = 6.1 Hz, 4H), 9.36 (d, *J* = 2.4 Hz, 2H), 8.91 – 8.88 (m, 6H), 8.27 (d, *J* = 8.6 Hz, 2H).

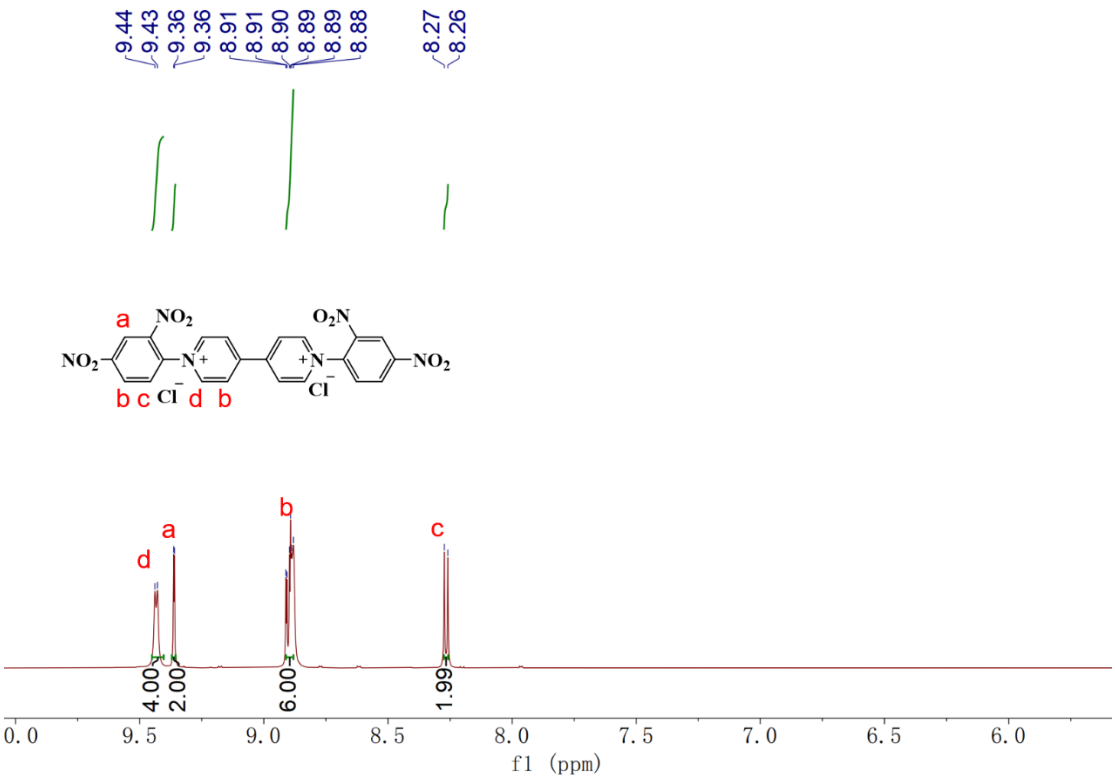


Figure S1 [1]H NMR spectrum of compound 1.

Intermediate **(2)** was synthesized by Zincke reaction according to previously reported procedure[1]. In brief, a mixture of 4,4'-bipyridine (4.68 g, 30 mmol), 1-chloro-2,4-dinitrobenzene (3.0 g, 15 mmol) and 60 ml ethanol were added a three-necked flask. The mixture was refluxed for 16 hours. After the reaction was completed, it was cooled to room temperature and filtered to obtain the crude product. The crude product was washed with dichloromethane and vacuum dried to obtain the green gray solid (3.82 g, yield 71%). [1]H NMR (600 MHz, D_2O) δ 9.41 (d, *J* = 2.5 Hz, 1H), 9.27 (d, *J* = 6.5 Hz, 2H), 8.96(d, *J* = 6.2 Hz, 1H), 8.84 (s, 2H), 8.70 (s, 2H), 8.31 (s, 1H), 8.04 (s, 2H).

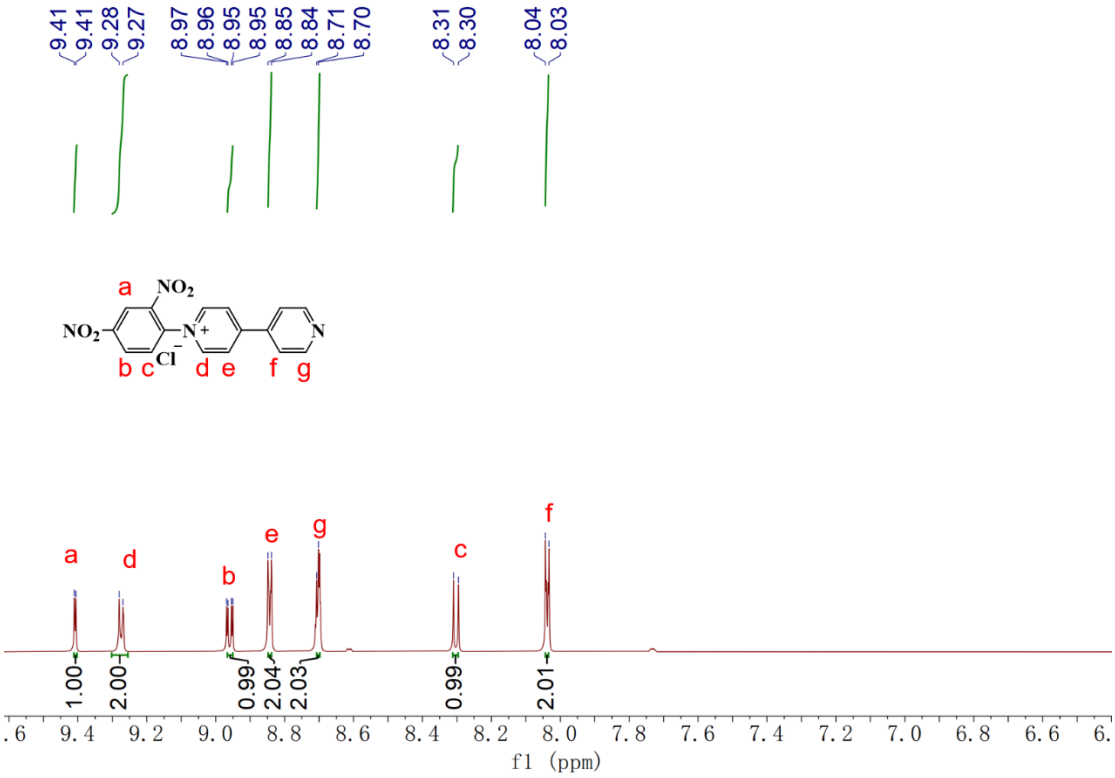


Figure S2 ^{1}H NMR spectrum of compound 2.

Intermediate **(3)** was synthesized as follows: a mixture of intermediate (2) (0.72 g, 2 mmol)), benzyl bromide (0.68 g ,4 mmol) and acetonitrile (100 ml) were added into a three-necked flask. The mixture was refluxed for 24 hours. After the reaction, it was cooled to room temperature, the organic solvent was removed by rotary evaporation. The crude product was washed repeatedly with dichloromethane to obtain the yellow powder (0.90 g, yield 85%). ^{1}H NMR (600 MHz, DMSO) δ 9.74 – 9.70 (m, 2H), 9.65 – 9.61 (m, 2H), 9.17 (d, *J* = 2.4 Hz, 1H), 9.09 – 9.05 (m, 2H), 9.03 (dd, *J* = 8.7, 2.6 Hz, 1H), 8.96 – 8.92 (m, 2H), 8.48 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.49 (dddd, *J* = 12.1, 7.0, 4.6, 2.3 Hz, 3H), 6.01 (s, 2H).

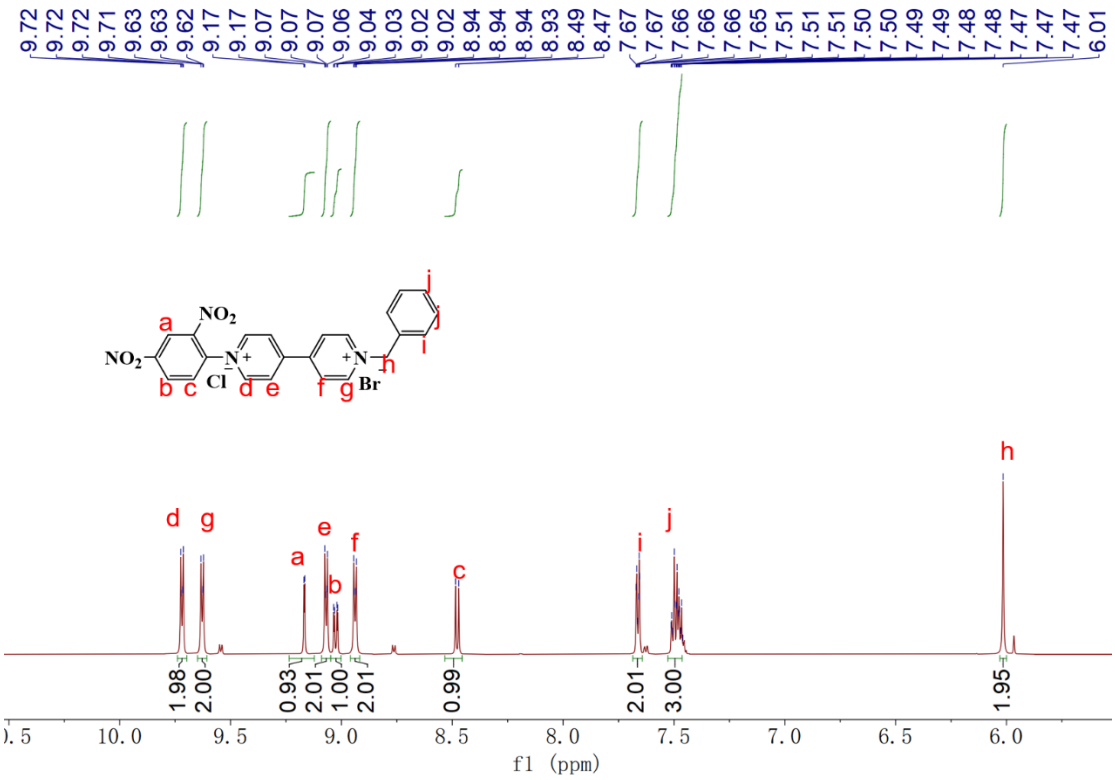


Figure S3 ^{1}H NMR spectrum of compound 3.

Intermediate **(4)** was synthesized as follows: a mixture of bis(4-bromophenyl)amine **(**3.27 g,10 mmol)**)**, , potassium carbonate (2.07 g, 15 mmol), 1-fluoro-4-nitrobenzene(2.12 g , 15 mmol) and 18 ml DMF were added into a three-necked flask. Reaction at 145 ℃ for 24 hours. After the reaction was completed, it was cooled to room temperature, stirred in 200 ml deionized water, filtered and collected precipitation, recrystallized precipitation with anhydrous ethanol to obtain the orange-red solid (3.63 g, yield 81%). ^{1}H NMR (600 MHz, DMSO) δ 8.15 – 8.02 (m, 2H), 7.69 – 7.55 (m, 4H), 7.24 – 7.14 (m, 4H), 6.97 – 6.86 (m, 2H).

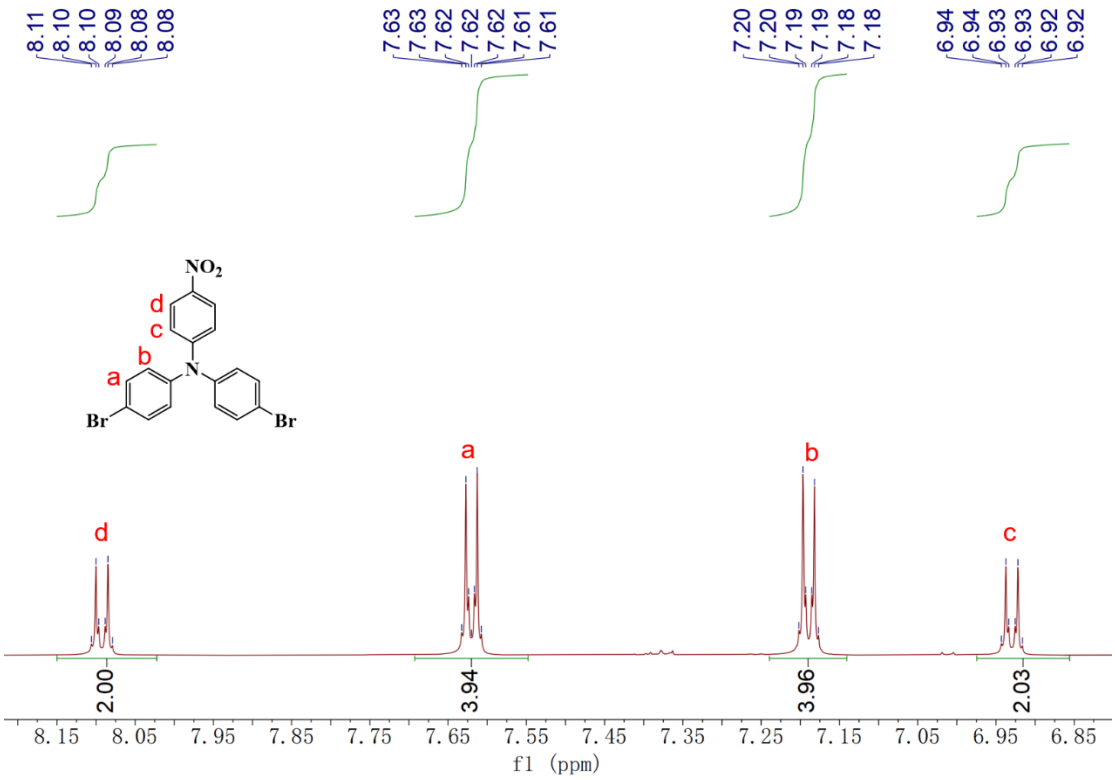


Figure S4 ^{1}H NMR spectrum of compound 4.

Intermediate **(5)** was synthesized as follows: a mixture of 3,6-dibromocarbazole(3.25 g,10 mmol), potassium carbonate(2.07 g, 15 mmol), 1-fluoro-4-nitrobenzene(2.12 g,15 mmol) and DMF (18 ml) were added into a three-necked flask, reacting at 145°C for 24 hours. After the reaction was completed, it was cooled to room temperature, stirred in 200 ml deionized water, filtered and collected precipitation, recrystallized precipitation with anhydrous ethanol to obtain the Orange-red solid (3.17 g, yield 71%).^{1}H NMR (600 MHz, DMSO) δ 8.63 (d, *J* = 2.0 Hz, 2H), 8.51 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.65 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H).

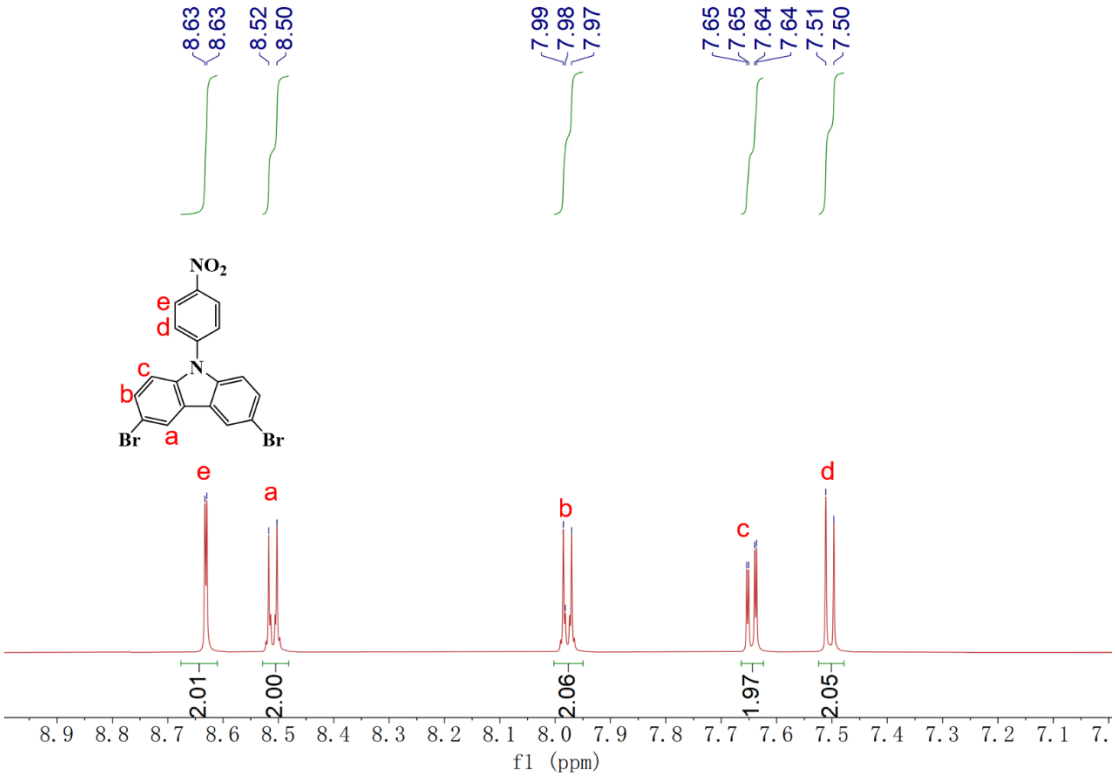


Figure S5 ^{1}H NMR spectrum of compound 5.

Intermediate **(6)** was synthesized as follows: Intermediate (4) (2.24 g, 5 mmol), stannous chloride (5.69 g, 30 mmol) and anhydrous ethanol (50 ml) were added into a three-necked flask. Reaction at 78℃ for 24 hours. After the reaction was completed, the crude product was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then it was dissolved with 50 mL dichloromethane, and the crude product was extracted with 3M sodium hydroxide solution, saturated sodium carbonate solution and deionized water successively. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (3:7, v/v) to obtain a pale yellow powder (1.61 g, yield 77%).^{1}H NMR (600 MHz, DMSO) δ 7.44 – 7.28 (m, 4H), 6.93 – 6.83 (m, 4H), 6.83 – 6.78 (m, 2H), 6.62 – 6.51 (m, 2H), 5.17 (s, 2H).

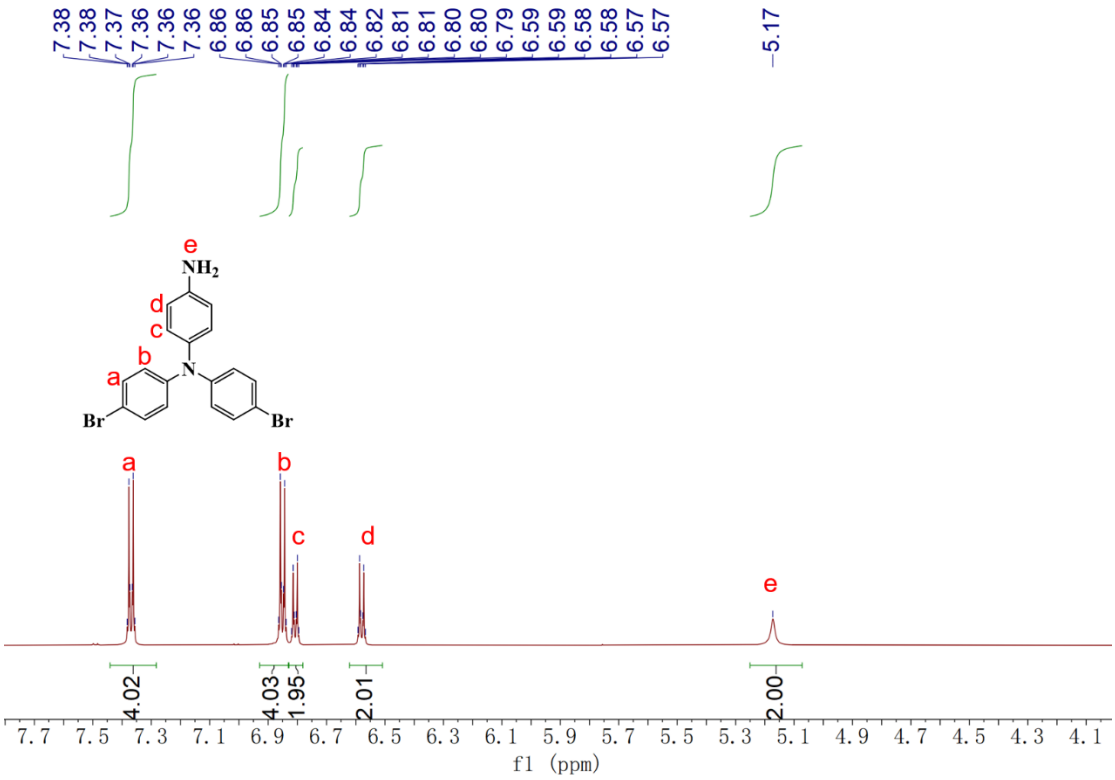


Figure S6 ^{1}H NMR spectrum of compound 6.

Intermediate **(7)** was synthesized as follows: Intermediate (5) (2.23 g, 5 mmol), stannous chloride (5.69 g,30 mmol) and anhydrous ethanol (50 ml) were added into a three-necked flask. Reaction at 78℃ for 24 hours. After the reaction was completed, the crude product was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then it was dissolved with 50 mL dichloromethane, and the crude product was extracted with 3M sodium hydroxide solution, saturated sodium carbonate solution and deionized water successively. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (3:10, v/v) to obtain a pale yellow powder (1.64 g, yield 79%).^{1}H NMR (600 MHz, DMSO) δ 8.54 (d, *J* = 2.0 Hz, 2H), 7.56 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.20 (dd, *J* = 13.9, 8.7 Hz, 4H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.69 (s, 2H).

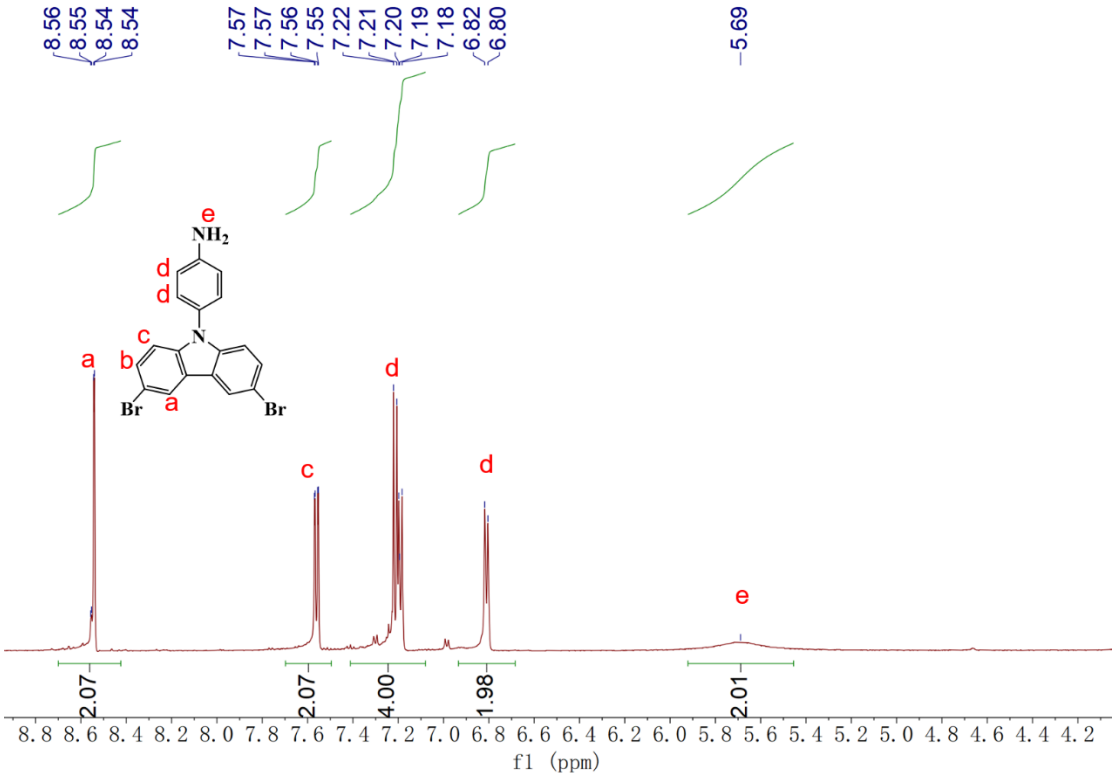


Figure S7 ^{1}H NMR spectrum of compound 7.

DBrPV was synthesized as follows: a mixture of Intermediate (6) (0.88 g, 2.1 mmol), Intermediate (1) (0.39 g ,0.7 mmol) and anhydrous ethanol (100 ml) were added into a three-necked flask. Reaction at 80℃ for 24 hours. After the reaction was completed, it was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then the crude product was repeatedly washed by using dichloromethane. The crude product was dissolved in methanol to obtain saturated solution. NH_4PF_6 (1.7 g, 10 mmol) was added to the solution. The mixture was stirred at room temperature for 3 hours, and then the mixture was filtered to obtain red solid (0.43 g, yield 49%). ^{1}H NMR (600 MHz, DMSO) δ 9.64 (d, *J* = 6.3 Hz, 4H), 9.04 (d, *J* = 6.5 Hz, 4H), 7.87 (d, *J* = 8.5 Hz, 4H), 7.72 – 7.44 (m, 8H), 7.26 (d, *J* = 8.6 Hz, 4H), 7.19 – 6.90 (m, 8H).^{13}C NMR (151 MHz, DMSO) δ 149.77, 148.61, 145.71, 145.63, 136.30, 133.43, 127.73, 126.97, 126.55, 122.67, 117.52.

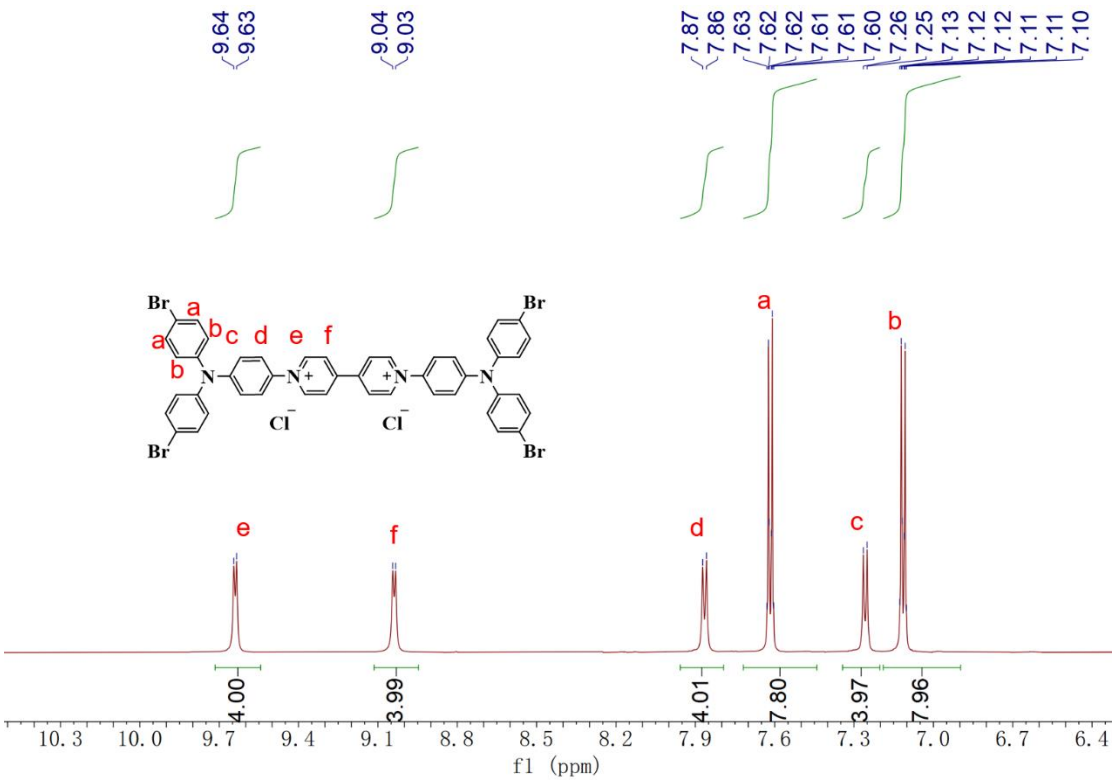


Figure S8 ^{1}H NMR spectrum of compound DBrPV.

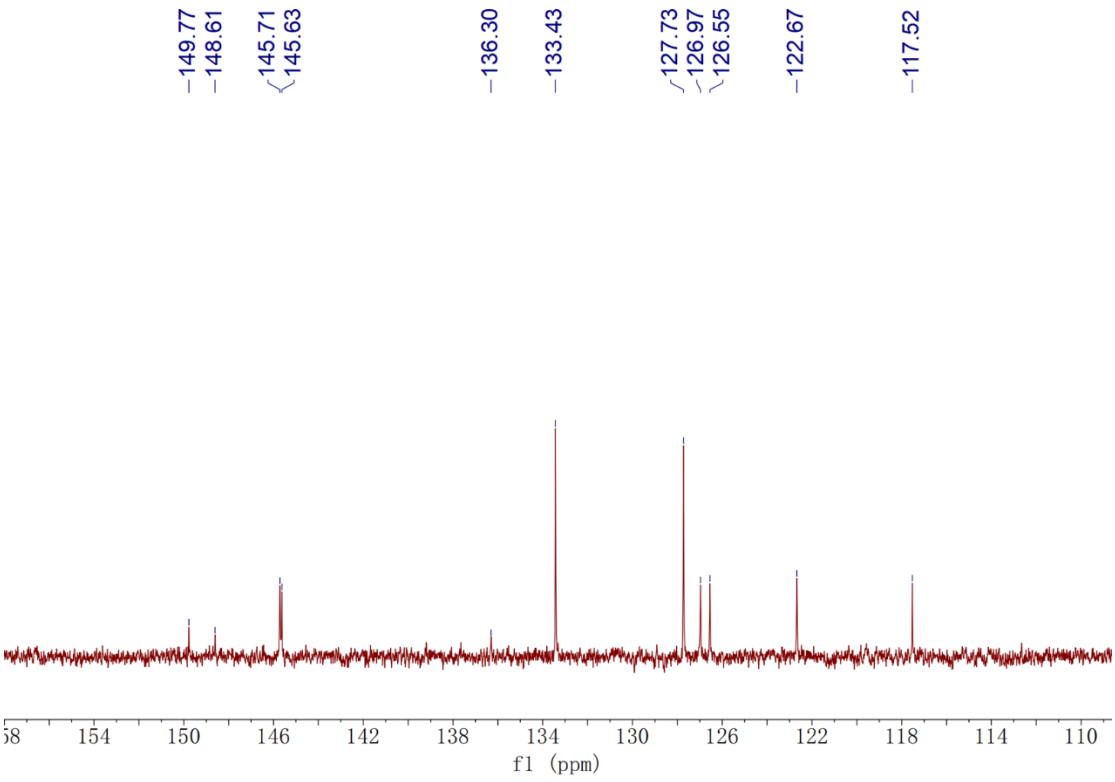


Figure S9 ^{13}C NMR spectrum of compound DBrPV

DBrCV was synthesized as follows: a mixture of Intermediate (7) (0.87 g, 2.1 mmol), Intermediate (1) (0.39 g ,0.7 mmol) and anhydrous ethanol (100 ml) were added into a three-necked flask. Reaction at 80℃ for 24 hours. After the reaction was completed, it was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then the crude product was repeatedly washed by using dichloromethane. The crude product was dissolved in methanol to obtain saturated solution. NH_4PF_6 (1.7 g, 10 mmol) was added to the solution. The mixture was stirred at room temperature for 3 hours, and then the mixture was filtered to obtain red solid (0.45 g, yield 52%).^{1}H NMR (600 MHz, DMSO) δ 9.86 (d, *J* = 6.4 Hz, 4H), 9.27 – 9.20 (m, 4H), 8.68 (d, *J* = 2.0 Hz, 4H), 8.35 – 8.30 (m, 4H), 8.18 – 8.13 (m, 4H), 7.72 (dd, *J* = 8.7, 2.0 Hz, 4H), 7.45 (d, *J* = 8.7 Hz, 4H).^{13}C NMR (151 MHz, DMSO) δ 149.53, 146.64, 141.52, 139.44, 130.29, 128.65, 127.64, 127.20, 124.56, 124.50, 113.63, 112.30.

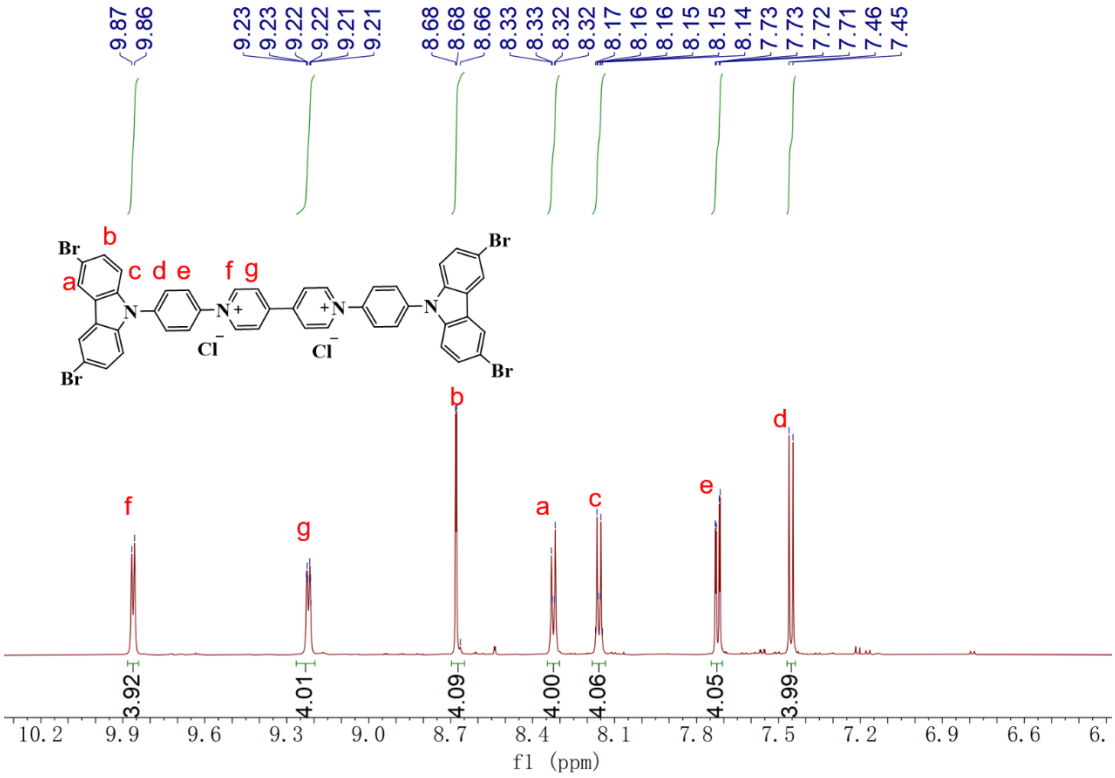


Figure S10 ^{1}H NMR spectrum of compound DBrCV

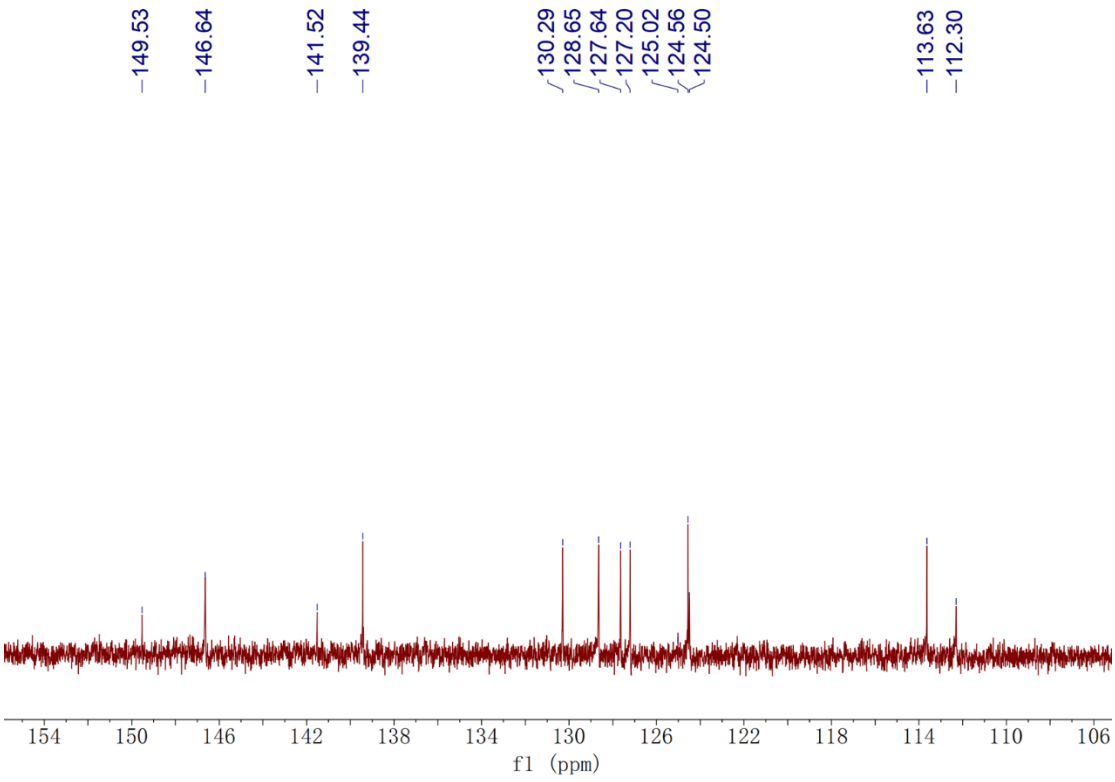


Figure S11 ^{13}C NMR spectrum of compound DBrCV

Bn-BrPV was synthesized as follows: a mixture of Intermediate (3) (1.10g, 2 mmol), Intermediate (6) (1.25 g ,3 mmol) and anhydrous ethanol (100 ml) were added into a three-necked flask. Reaction at 80℃ for 24 hours. After the reaction was completed, it was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then the crude product was repeatedly washed by using dichloromethane. The crude product was dissolved in methanol to obtain saturated solution. NH_4PF_6 (1.7 g, 10 mmol) was added to the solution. The mixture was stirred at room temperature for 3 hours, and then the mixture was filtered to obtain purple solid (1.03 g, yield 55%). ^{1}H NMR (600 MHz, DMSO) δ 9.62 (d, *J* = 6.8 Hz, 2H), 9.59 (d, *J* = 6.6 Hz, 2H), 8.93 – 8.87 (m, 4H), 7.88 – 7.83 (m, 2H), 7.67 (dt, *J* = 5.9, 1.5 Hz, 2H), 7.64 – 7.58 (m, 4H), 7.52 – 7.43 (m, 3H), 7.27 – 7.22 (m, 2H), 7.13 – 7.08 (m, 4H), 6.00 (s, 2H).^{13}C NMR (151 MHz, DMSO) δ 149.75, 149.28, 149.09, 146.24, 145.63, 136.32, 134.64, 133.42, 130.03, 129.77, 129.49, 127.71, 127.07, 126.53, 122.69, 117.50, 63.81.

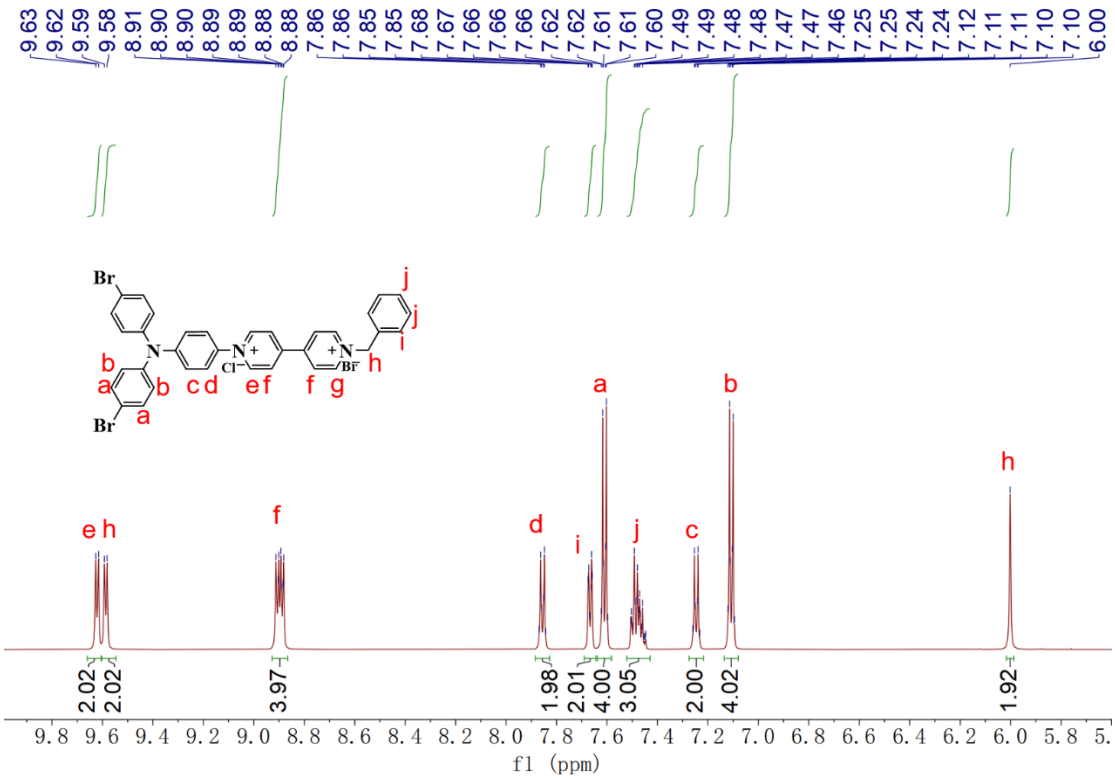


Figure S12 ^{1}H NMR spectrum of compound Bn-BrPV

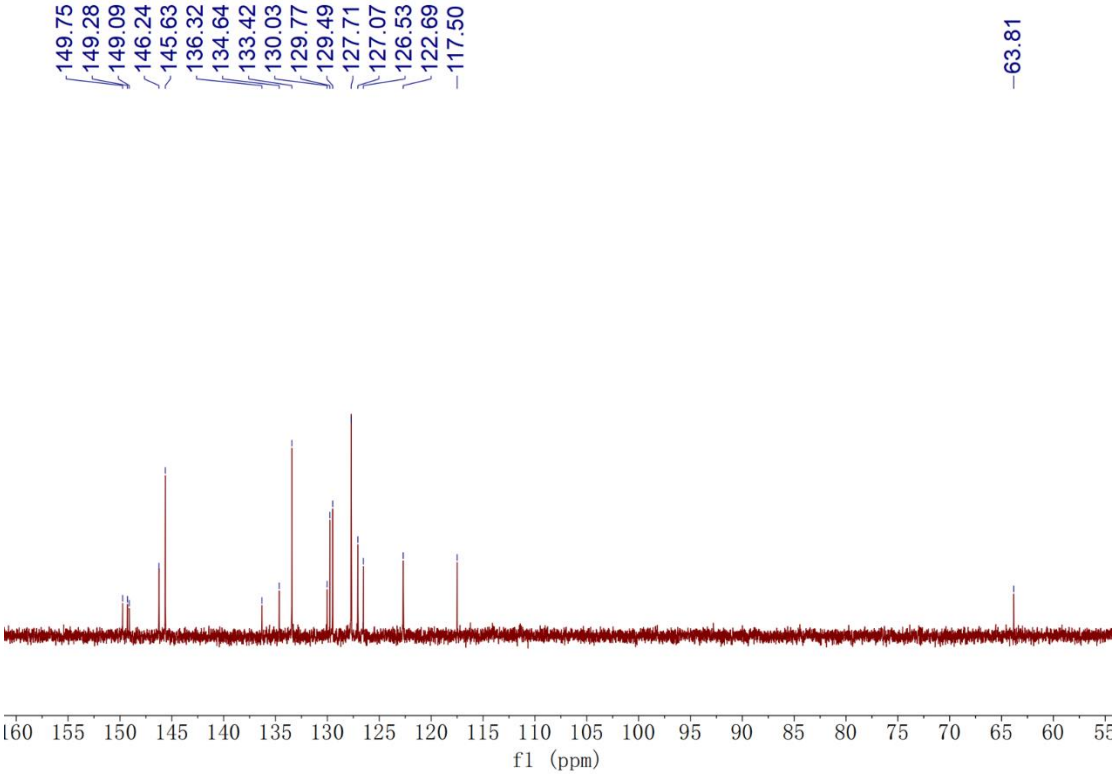


Figure S13 ^{13}C NMR spectrum of compound Bn-BrPV

Bn-BrCV was synthesized as follows: a mixture of Intermediate (3) (1.10 g ,2 mmol), Intermediate (7) (1.25 g ,3 mmol) and anhydrous ethanol (100 ml) were added into a three-necked flask. Reaction at 80℃ for 24 hours. After the reaction was completed, it was cooled to room temperature, and the organic solvent was removed by rotary evaporation. Then the crude product was repeatedly washed by using dichloromethane. The crude product was dissolved in methanol to obtain saturated solution. NH_4PF_6 (1.7 g,10 mmol) was added to the solution. The mixture was stirred at room temperature for 3 hours, and then the mixture was filtered to obtain orange solid (0.90 g, yield 48%). ^{1}H NMR (600 MHz, DMSO) δ 9.85 – 9.76 (m, 2H), 9.67 – 9.58 (m, 2H), 9.04 – 8.99 (m, 2H), 8.98 – 8.93 (m, 2H), 8.67 (d, *J* = 2.0 Hz, 2H), 8.33 – 8.25 (m, 2H), 8.17 – 8.10 (m, 2H), 7.70 (ddd, *J* = 9.6, 8.3, 1.6 Hz, 4H), 7.52 – 7.47 (m, 3H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.03 (s, 2H).^{13}C NMR (151 MHz, DMSO) δ 150.05, 149.24, 146.45, 146.32, 141.51, 139.42, 134.64, 130.27, 130.06, 129.79, 129.53, 128.63, 127.82, 127.60, 127.16, 124.53, 124.47, 113.61, 112.30, 63.88.

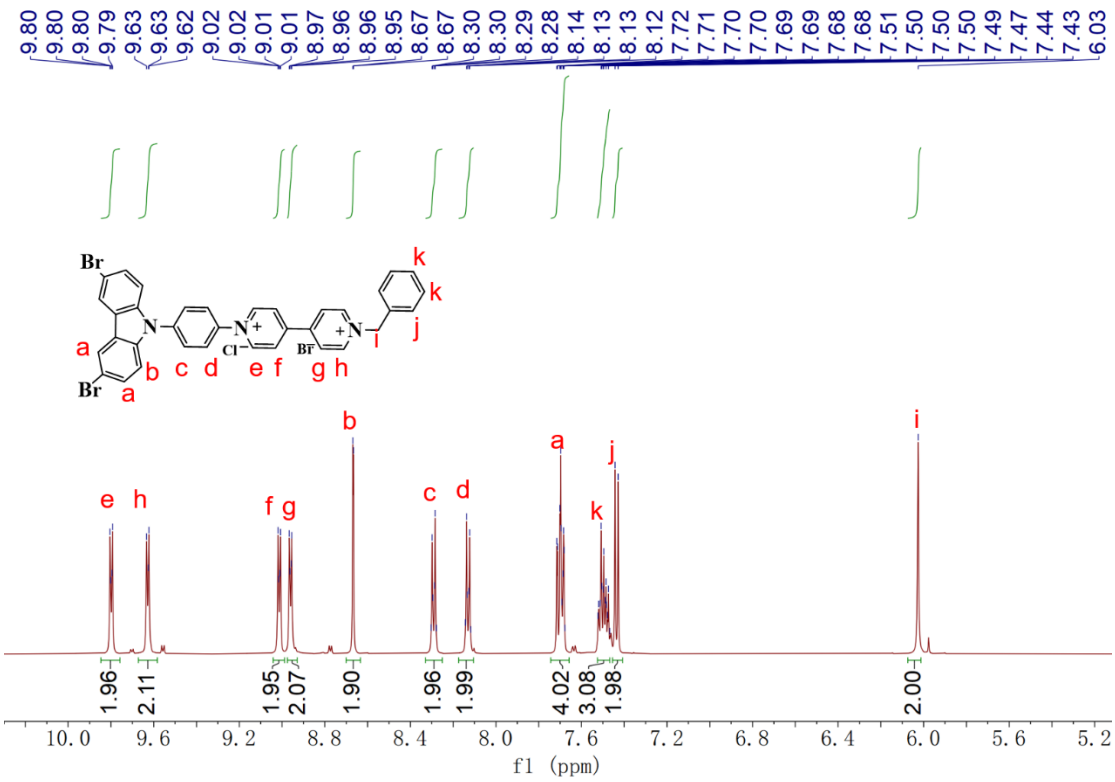


Figure S14 ^{1}H NMR spectrum of compound Bn-BrCV

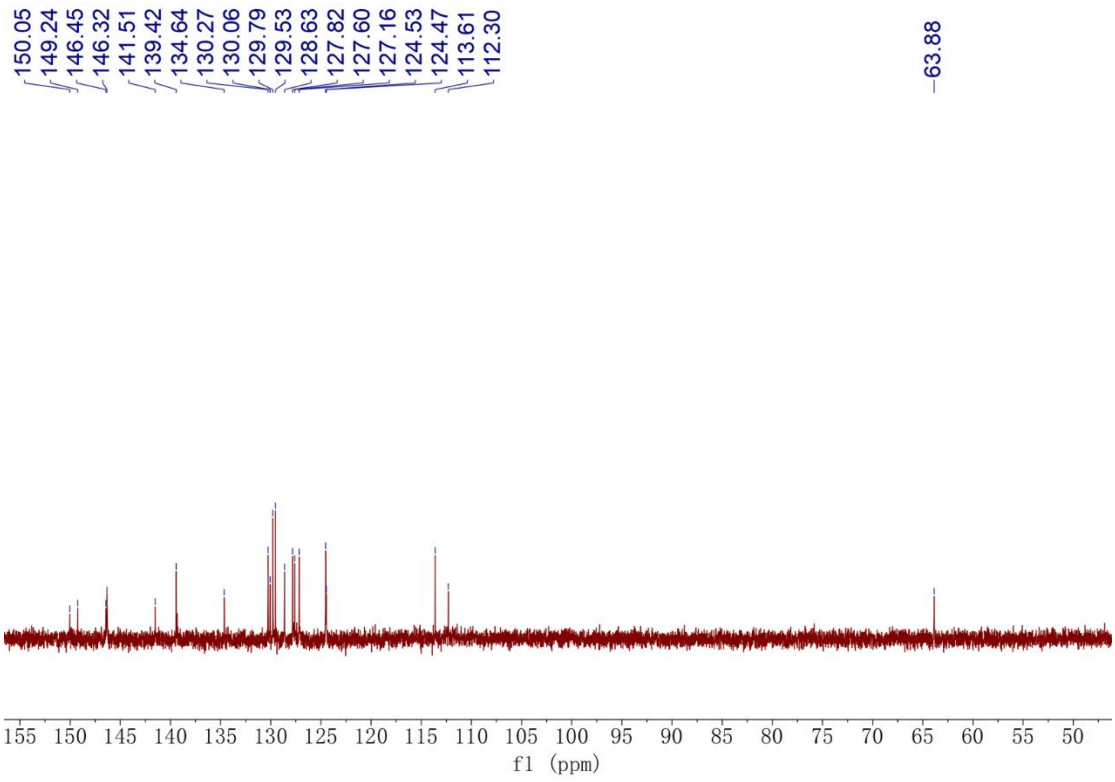


Figure S15 ^{13}C NMR spectrum of compound Bn-BrCV

BnV was synthesized according to literature[2]. ^{1}H NMR (600 MHz, DMSO) δ 9.62 – 9.39 (m, 4H), 8.86 – 8.59 (m, 4H), 7.83 – 7.54 (m, 4H), 7.53 – 7.27 (m, 6H), 5.93 (s, 4H).

2. Electrochemical impedance spectroscopy of flexible ECDs.

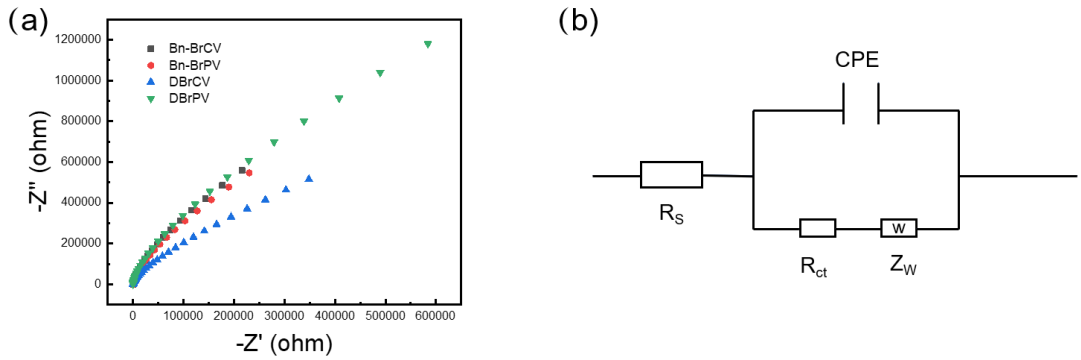


Figure S16 Electrochemical impedance spectroscopy (EIS) of (a) the flexible electrochromic devices based on DBrPV, Bn-BrPV, DBrCV and Bn-BrCV and (b) the corresponding analog equivalent circuit.

3 Optoelectrochemical properties of viologen derivatives

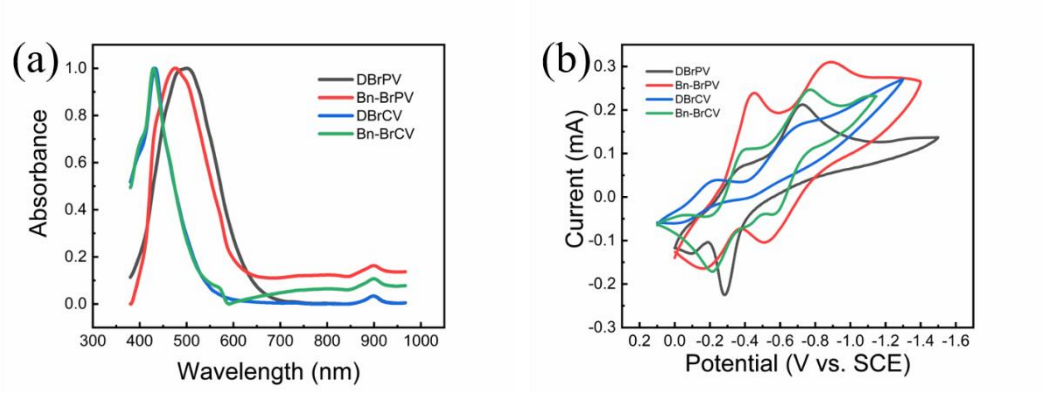


Figure S17 (a) UV–vis absorption spectra, and (b) Cyclic voltammograms of compounds.

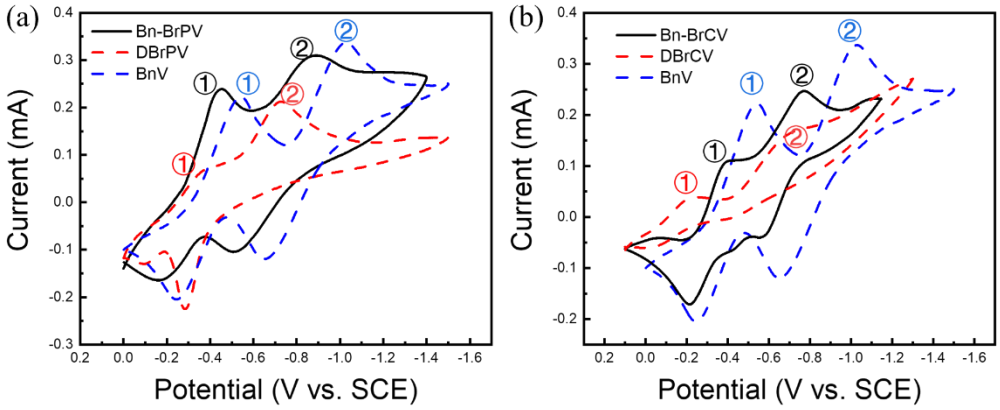


Figure S18 Cyclic voltammograms of compound (a) Bn-BrPV, DBrPV and BnV

(b) Bn-BrCV, DBrCV and BnV.

4 Electrochromic properties of devices based on viologen derivatives

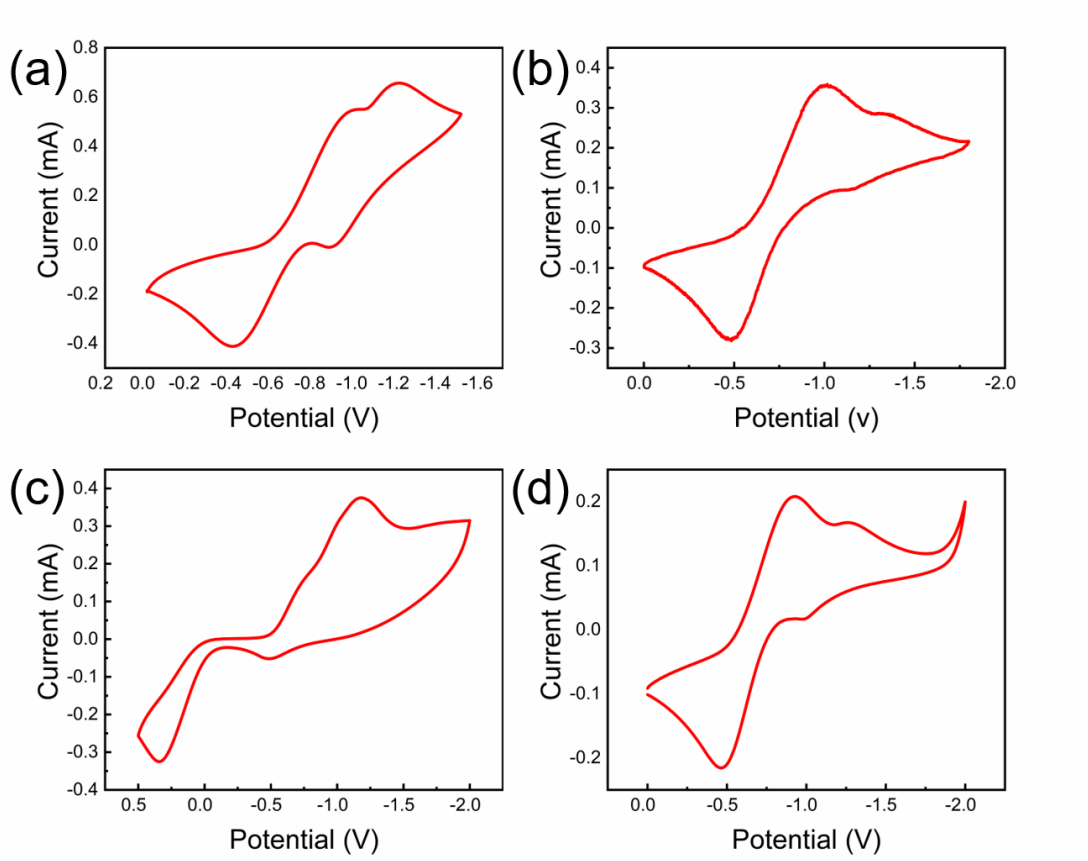


Figure S19 Cyclic voltammograms of flexible ECDs, (a) DBrPV–based flexible ECD, (b) Bn–BrPV–based flexible ECD, (c) DBrCV–based flexible ECD, (d)Bn–BrCV–based flexible ECD.

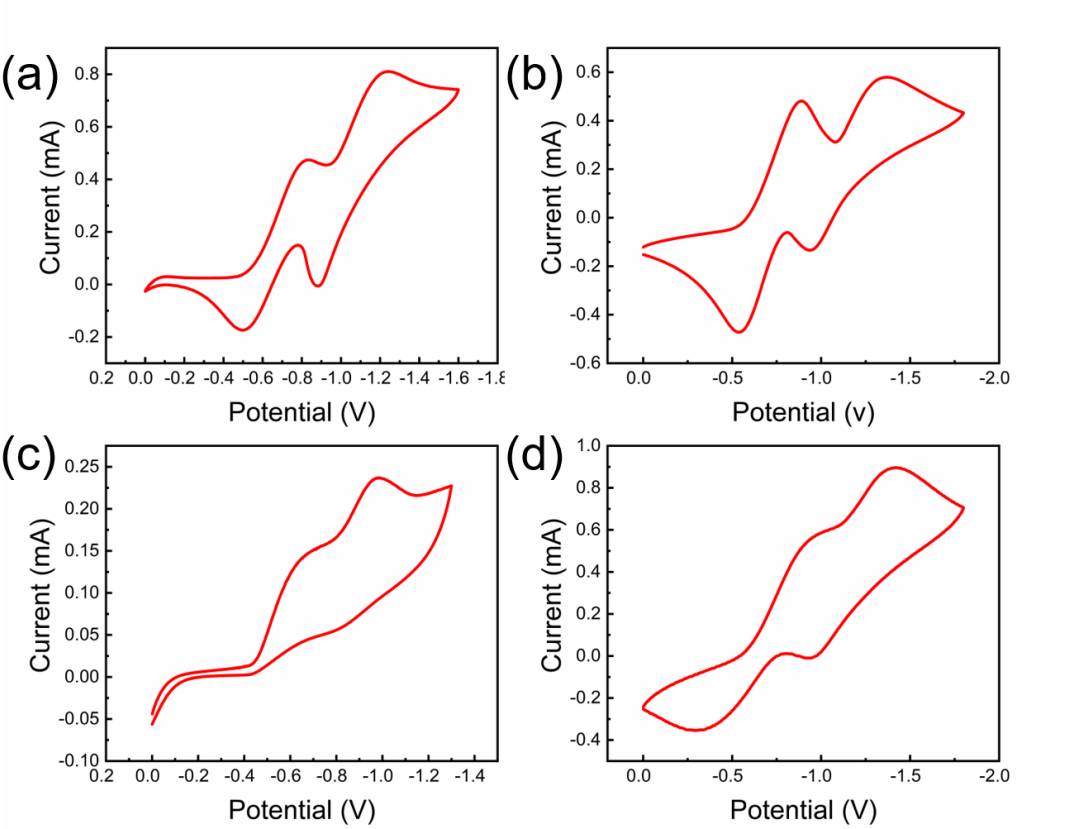


Figure S20 Cyclic voltammograms of rigid ECDs, (a) DBrPV–based rigid ECD, (b) Bn–BrPV–based rigid ECD, (c) DBrCV–based rigid ECD, (d)Bn–BrCV–based rigid ECD.

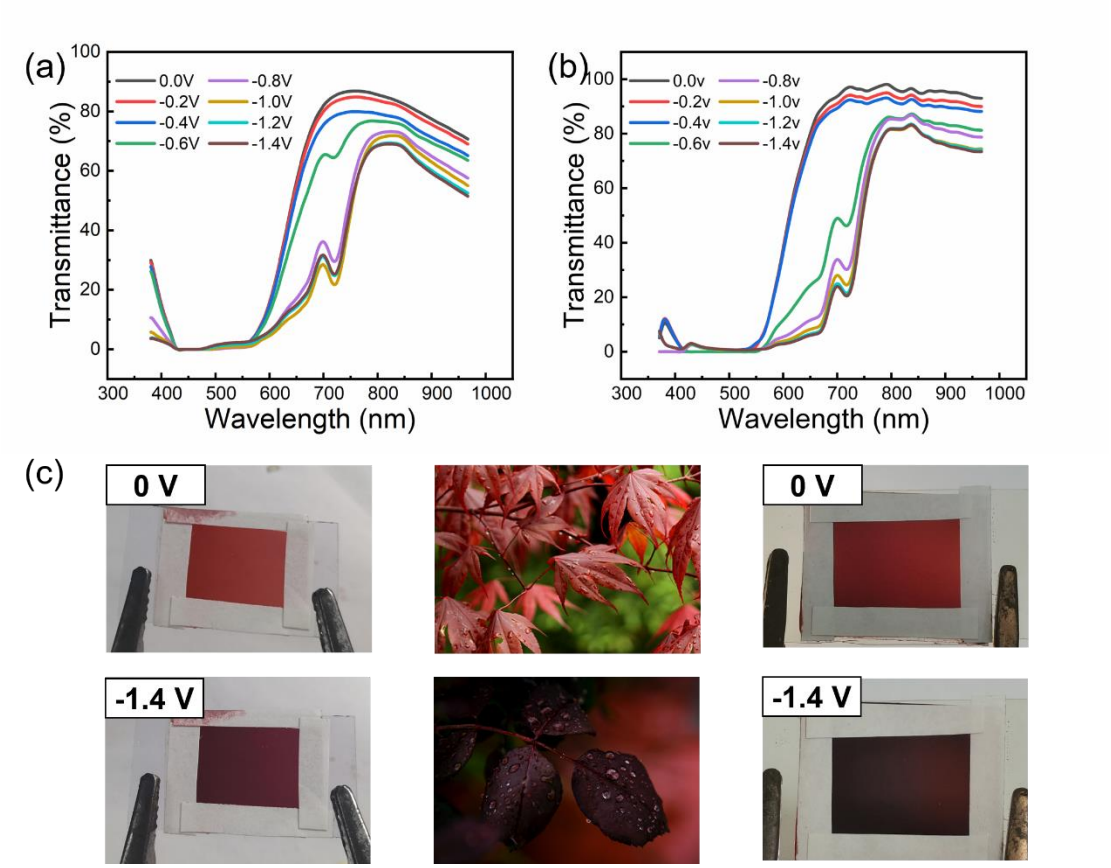


Figure S21 Transmittance spectra of ECDs, (a) DBrPV–based rigid ECD, (b) DBrPV–based flexible ECD, and (c) images of rigid device (left), colors of nature (middle), and flexible device (right).

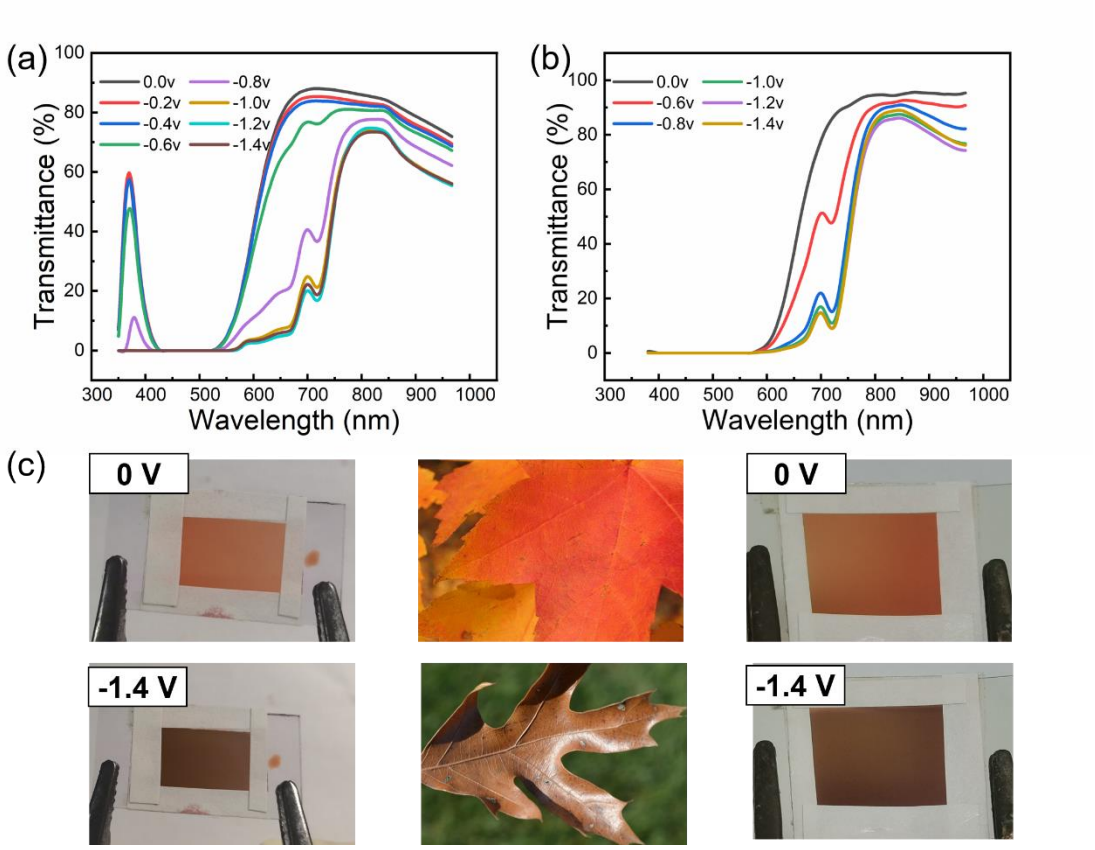


Figure S22 Transmittance spectra of ECDs, (a) Bn-BrPV–based rigid ECD, (b) Bn-BrPV–based flexible ECD, and (c) images of rigid device (left), colors of nature (middle), and flexible device (right).

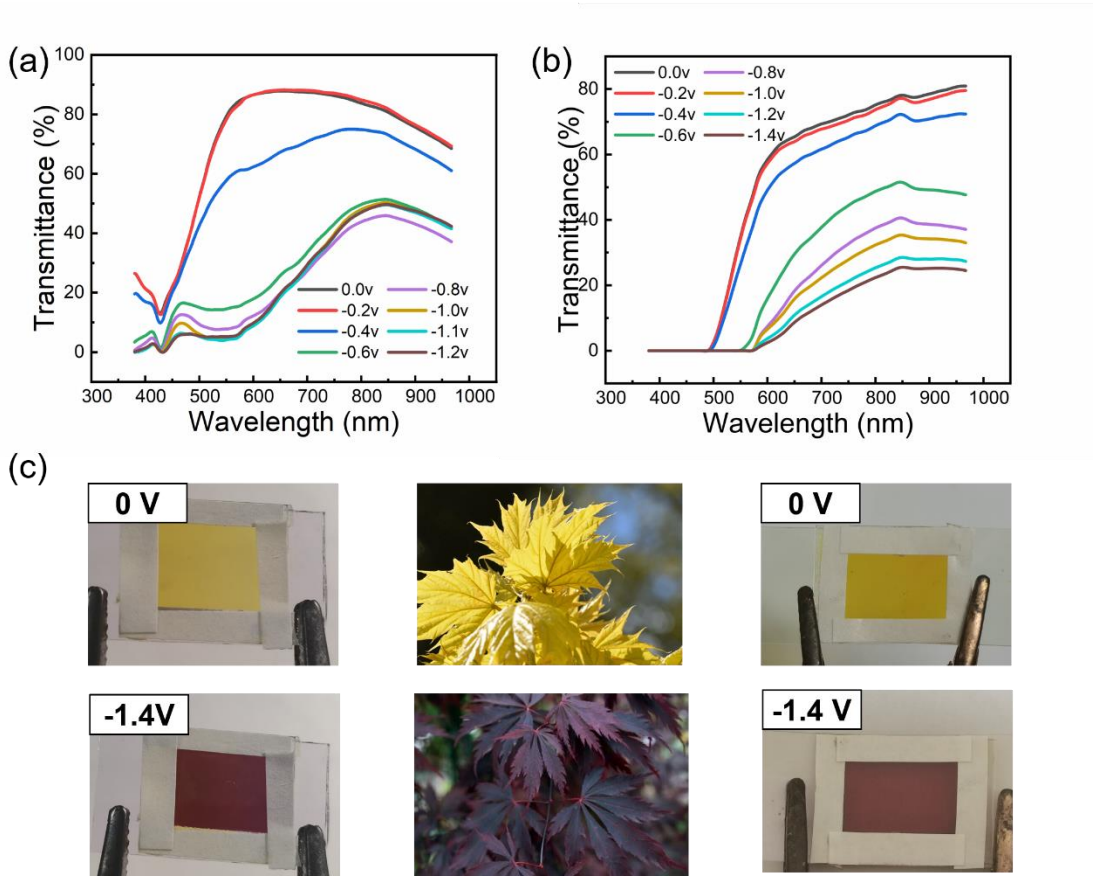


Figure S23 Transmittance spectra of ECDs, (a) DBrCV–based rigid ECD, (b) D BrCV–based flexible ECD, and (c) images of rigid device (left), colors of nature (middle), and flexible device (right).

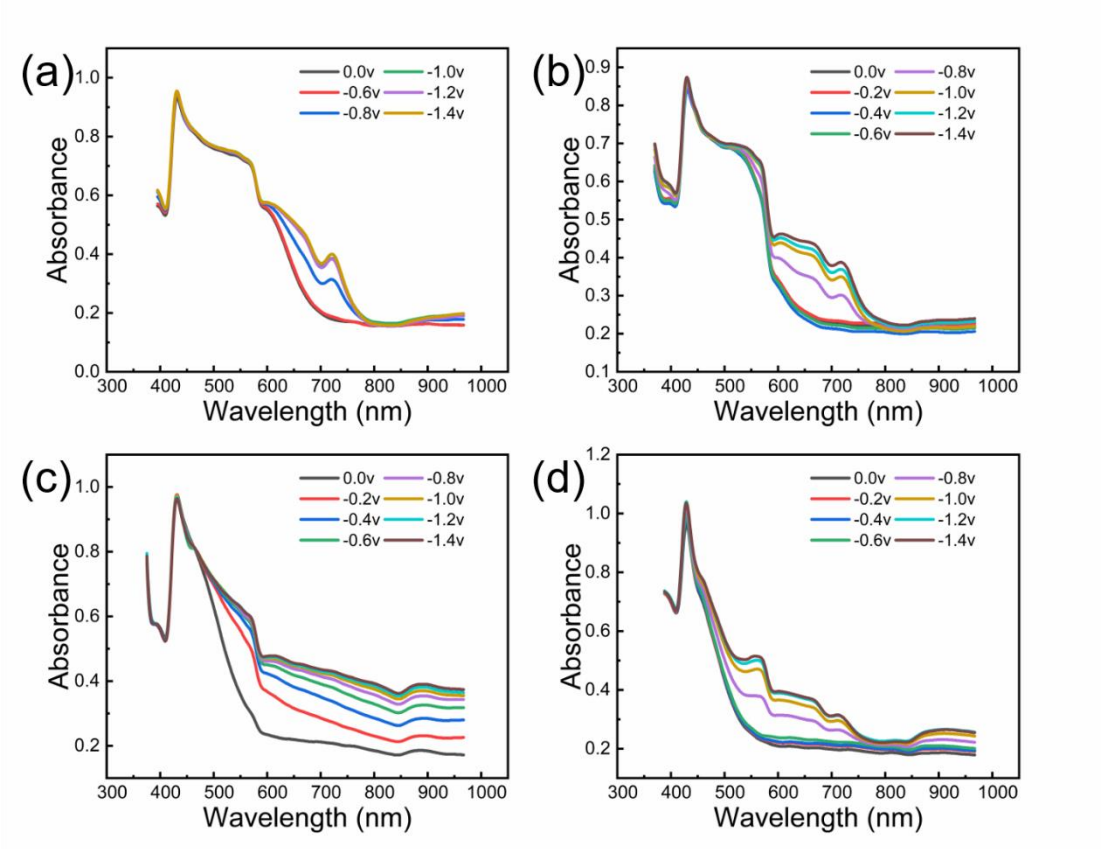


Figure S24 Absorbance spectra of flexible ECDs, (a) DBrPV-based flexible ECD, (b) Bn-BrPV-based flexible ECD, (c) DBrCV-based flexible ECD and (d) Bn-BrCV-based flexible ECD.

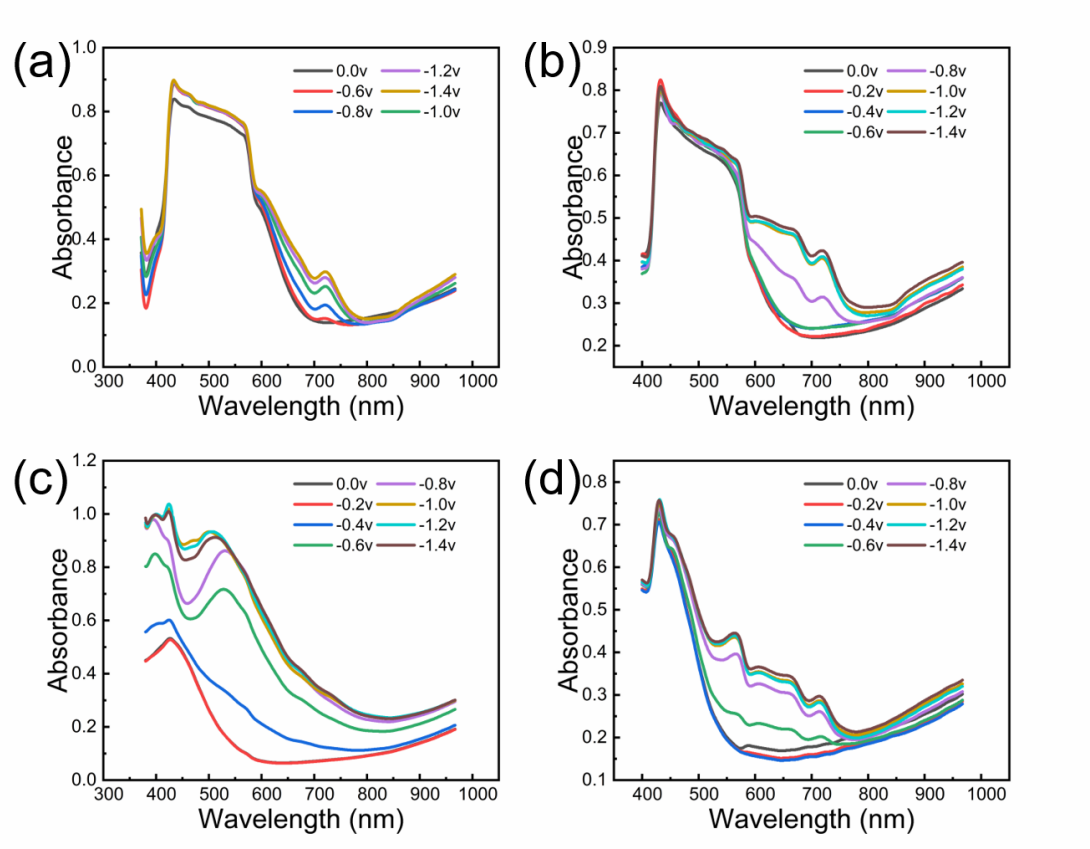


Figure S25 Absorbance spectra of the rigid ECDs, (a) DBrPV-based rigid ECD, (b) Bn-BrPV-based rigid ECD, (c) DBrCV-based rigid ECD and (d) Bn-BrCV-based rigid ECD.

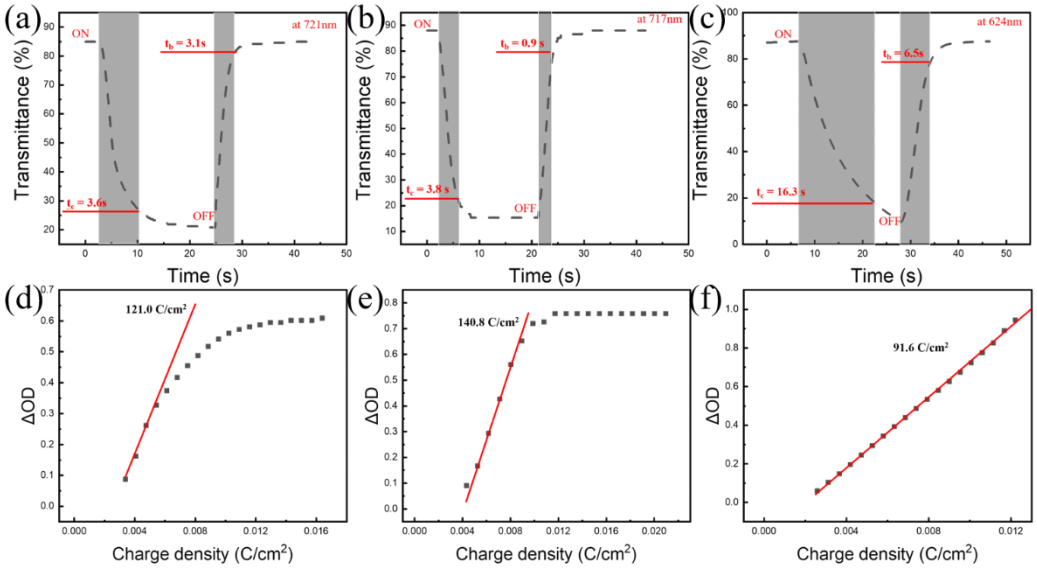


Figure S26 Response time and corresponding coloration efficiency of rigid ECDs, DBrPV-based rigid ECD (a, d), Bn-BrPV-based rigid ECD (b, e), DBrCV-based rigid ECD (c, f).

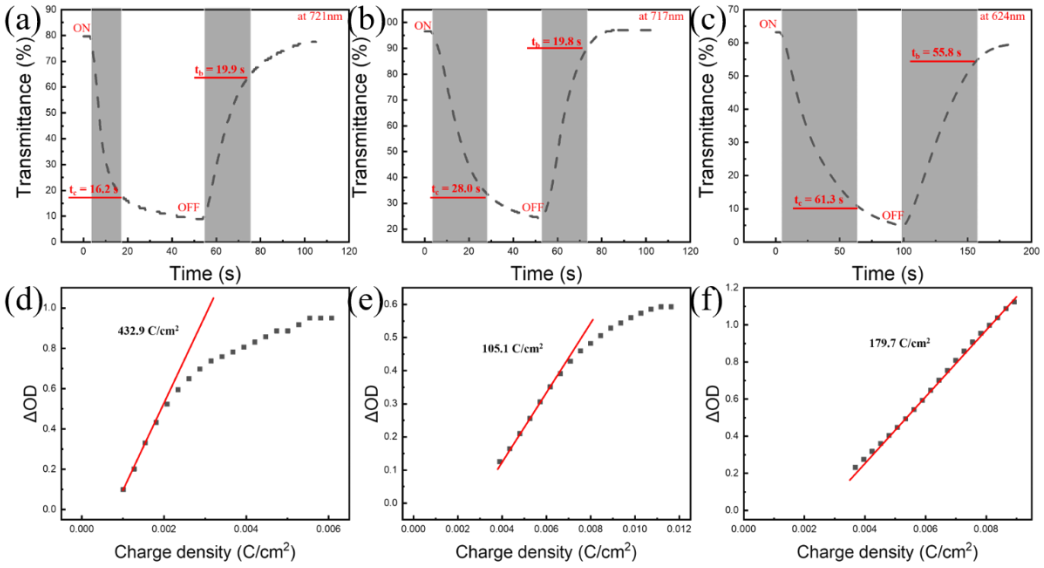


Figure S27 Response time and corresponding coloration efficiency of flexible ECDs, DBrPV-based flexible ECD (a, d), Bn-BrPV-based flexible ECD (b, e), DBrCV-based flexible ECD (c, f).

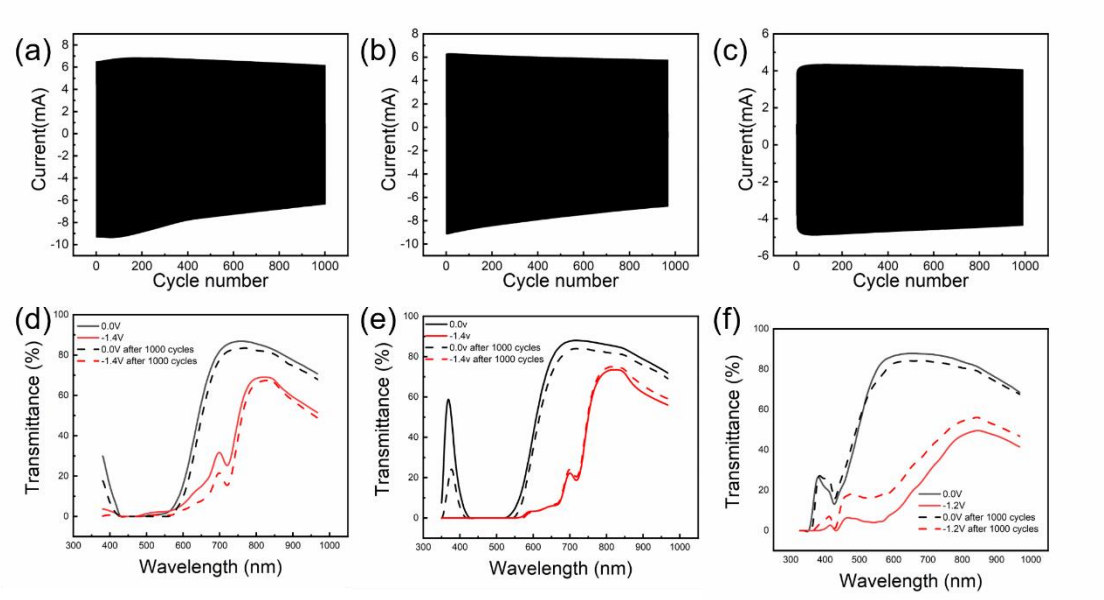


Figure S28 Chronoamperometry curve and corresponding transmittance curve of rigid ECDs, DBrPV-based rigid ECD (a, d), Bn-BrPV-based rigid ECD (b, e), DBrCV-based rigid ECD (c, f).

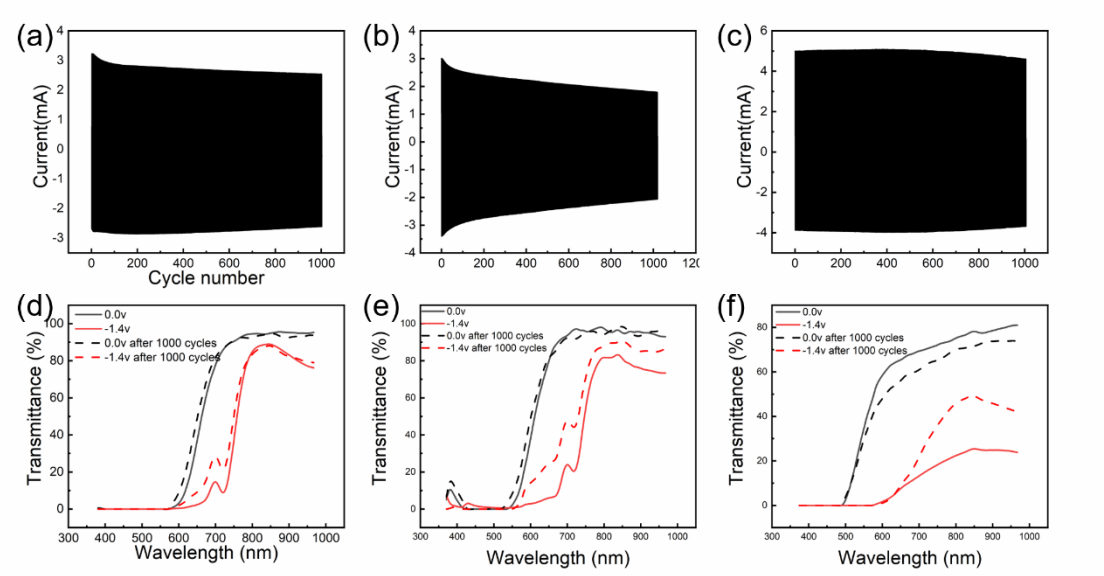


Figure S29 Chronoamperometry curve and corresponding transmittance curve of flexible ECDs, DBrPV-based flexible ECD (a, d), Bn-BrPV-based flexible ECD (b, e), DBrCV-based flexible ECD (c, f).

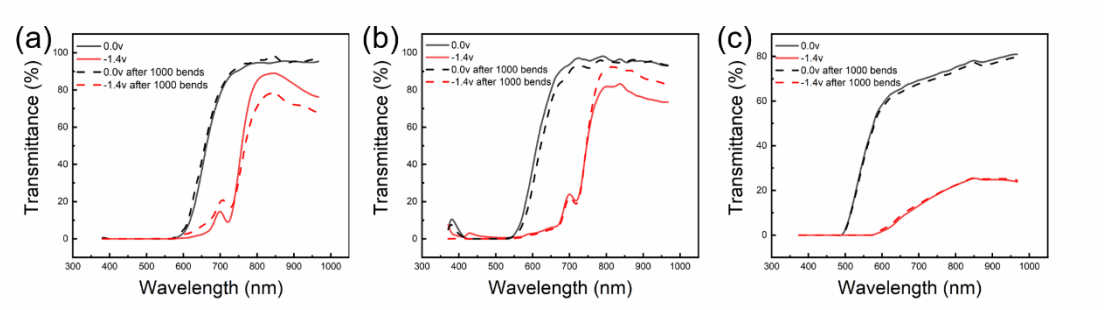


Figure S30 Transmittance curves of flexible ECDs under different applied voltages before and after 1000 bends (Bending radius, 3.12 cm), (a) DBrPV-based flexible ECD, BnBrPV-based flexible ECD, (c) DBrCV-based flexible ECD.

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