

Supporting Information

Colorless to Neutral-Color Electrochromic Devices Based on Asymmetric Viologens

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List of Supporting Information

- Synthesis of symmetric viologens pCNVio, EtVio and BnVio.
- Preparation of Gel formulations.
- Preparation of anhydrous formulations.
- Fabrication of Electrochromic Devices (ECDs).
- Characterization of 1-ethyl-1'-(p-cyanophenyl)-4,4'-bipyridinium dibromide (Et-pCNVio).
 - Figure S1. ^1H NMR spectra of Et-pCNVio.
 - Figure S2. ^{13}C NMR spectra of Et-pCNVio.
 - Figure S3. Anion chromatogram of Et-pCNVio.
- Characterization of 1-benzyl-1'-(p-cyanophenyl)-4,4'-bipyridinium dibromide (Bn-pCNVio).
 - Figure S4. ^1H NMR spectra of Bn-pCNVio.
 - Figure S5. ^{13}C NMR spectra of Bn-pCNVio.
 - Figure S6. Anion chromatogram of Bn-pCNVio.
- Figure S7. Spectroelectrochemical study of three-electrode ECD containing Gel electrolyte for comparative purposes.
- Figure S8. Cyclic voltammeteries of three-electrode ECDs containing Bn-pCNVio, pCNVio and BnVio gels.
- Table S1. % Transmittance, $\Delta\%T$ and color coordinates of three-electrode ECDs containing Bn-pCNVio gel at different applied potentials.

- **Figure S9. EC behavior of two-electrode ECDs containing Bn-pCNVio gel vs corresponding symmetric viologens and the mixture of them.**
- **Figure S10. EC behavior of two-electrode ECDs containing Et-pCNVio gel vs corresponding symmetric viologens and the mixture of them.**
- **Characterization of two-electrode ECDs containing Et-pCNVio and Bn-pCNVio gels.**
 - **Figure S11. UV/Vis transmittance profiles of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio gels.**
 - **Table S2. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio gels.**
- **Characterization of two-electrode ECDs containing EtVio, BnVio and pCNVio gels.**
 - **Figure S12. UV/Vis transmittance profiles of Two-electrode ECDs containing EtVio, BnVio and pCNVio gels.**
 - **Table S3. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing EtVio, BnVio and pCNVio gels.**
- **Characterization of two-electrode ECDs containing EtVio + pCNVio and BnVio + pCNVio gels.**
 - **Figure S13. UV/Vis transmittance profiles of Two-electrode ECDs containing EtVio + pCNVio and BnVio + pCNVio gels.**
 - **Table S4. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing EtVio + pCNVio and BnVio + pCNVio gels.**

- **Table S5. Evolution of the electrochromic performance of two-electrode ECD containing Et-pCNVio gel after 500 – 15 000 cycles.**
- **Evolution of switching and electrochromic performances of two-electrode ECD containing Bn-pCNVio gel.**
- **Figure S14. Evolution of the switching performance of two-electrode ECD containing Bn-pCNVio gel after 500 – 15 000 cycles.**
- **Table S6. Evolution of the electrochromic performance of two-electrode ECD containing Bn-pCNVio gel after 500 – 15 000 cycles.**
- **Characterization of two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**
- **Figure S15. UV/Vis transmittance profiles of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**
- **Table S7. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**
- **Figure S16. Transmittance profiles (UV/Vis transmittance response) of electrochromic devices containing Bn-pCNVio gel vs anhydrous formulation.**
- **Figure S17. Spectroelectrochemical study of three-electrode ECD containing Anhydrous electrolyte for comparative purposes.**
- **Characterization of two-electrode ECDs containing EtVio and BnVio anhydrous solutions.**
- **Figure S18. UV/Vis transmittance profiles of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**

- **Table S8. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**
- **Figure S19. UV/Vis transmittance response of electrochromic devices comprising gel-based formulations vs anhydrous formulations containing EtVio and BnVio symmetric viologens.**
- **Table S9. % Transmittance, $\Delta\%T$ and color coordinates of two-electrode ECDs containing different anhydrous formulations.**

- **Synthesis of symmetric viologens pCNVio, EtVio and BnVio**

Materials: 4,4'-bipyridyl (98%), 2,4-dinitrochlorobenzene (99%), *p*-cyanoaniline (98%), ethyl bromide (98%) and benzyl bromide (98%) were purchased from Sigma-Aldrich and used without further purification. Required solvents such as acetone, ethanol, methanol, diethyl ether, THF and acetonitrile were purchased from Scharlab and used as received.

Synthesis:

*1,1'-Bis-(*p*-cyanophenyl)-4,4'-bipyridilium dichloride (pCNVio)* was synthesized according to previously reported procedure.¹ ¹H NMR (500 MHz, DMSO-*d*₆, δ): 9.77 and 9.18 ppm (d of d, 4HJ = 4.00 Hz and 4HJ = 3.84 Hz, Ar H), 8.35 and 8.23 ppm (d of d, 4H J = 7.56 Hz and 4HJ = 7.26 Hz, bipyridine); IR (bulk ATR): ν (cm⁻¹) = 3091 (C-H olefin st), 2227 (-CNst), 1629(C=N st), 1603, 1508 (C=C), 831 (o-phenylene H); IC: % Cl⁻ calculated for C₂₄H₁₆N₄Cl₂: 16.4%, found 15.0%.

1,1'-Diethyl-4,4'-bipyridinium dibromide (EtVio) was synthesized according to previously reported procedure with minor modifications.² In brief, a mixture of 4,4'-bipyridyl (10 mmol) and ethyl bromide (80 mmol) was refluxed in acetonitrile (15 mL) for 16 hours. After cooling, the resulting yellowish solid was filtered and washed with acetonitrile and acetone. (Yield = 92%). ¹H NMR (500 MHz, DMSO-*d*₆, δ): 9.44 ppm (d, 4H, J = 6.75 Hz), 8.82 ppm (d, 4H, J = 6.55 Hz), 4.75 ppm (q, 4H), 1.61 ppm (t, 6H). IR (bulk ATR): ν (cm⁻¹) = 3031 (C-H olefin st), 2977 (C-H alkyl st), 1638 (C=N st), 1511 (C=C), 1439, (C-H alkyl δ) 853 (o-phenylene H); IC: % Br⁻ calculated for C₁₄H₁₈N₂Br₂: 42.7%, found 42.2%.

1,1'-Dibenzyl-4,4'-bipyridinium dibromide (BnVio) was synthesized as follows: a mixture of 4,4'-bipyridyl (10 mmol) and benzyl bromide (40 mmol) was refluxed in acetonitrile (15 mL) for 16 hours. After cooling, the resulting yellowish solid was filtered and washed with acetonitrile and acetone. (Yield = 93%). ¹H NMR (500 MHz, D₂O, δ): 9.18 ppm (d, 4H, J =

6.85 Hz), 8.55 ppm (d, 4H, $J = 6.78$ Hz), 7.55 ppm (s, 10H), 5.55 ppm (s, 4H); IR (bulk ATR): ν (cm^{-1}) = 3025 (C-H olefin st), 2994, 2946 (C-H alkyl st), 1629 (C=N st), 1492 (C=C), 1448, (C-H alkyl δ) 729 (o-phenylene H); IC: % Br⁻ calculated for C₂₄H₂₂N₂Br₂: 32.1%, found 32.4%.

- **Preparation of Gel formulations**

Preparation of EC gels (general procedure): all gels were prepared as follows: to a previously prepared 4% solution of PVA, aqueous solutions containing appropriate amounts of viologen and a 1:1 mixture of potassium ferrocyanide and potassium ferricyanide were added. The resulting mixtures were stirred until homogeneous solution was obtained. Then, each of these solutions were mixed with a 4% borax aqueous solution in a 4:1 volumetric ratio by vigorous stirring with a spatula, until a gel was formed. The formulations were left to settle on its own until a completely bubble-free materials were obtained.

Preparation of pCNVio, EtVio and BnVio gels: This electrochromic gels were fabricated keeping the final concentration of corresponding symmetricviologens 1,1'-bis-(*p*-cyanophenyl)-4,4'-bipyridilium dichloride (**pCNVio**), 1,1'-Diethyl-4,4'-bipyridinium dibromide (**EtVio**) and 1,1'-Dibenzyl-4,4'-bipyridinium dibromide (**BnVio**) respectively, at 10 mmolL⁻¹ and the concentration of the ferro/ferricyanide potassium pair at 5 mmolL⁻¹ value.

Preparation of Et-pCNVio gel: This electrochromic gel was fabricated keeping the final concentration of 1-ethyl-1'-(*p*-cyanophenyl)-4,4'-bipyridinium dibromide (**Et-pCNVio**) at 20 mmolL⁻¹ and the concentration of the ferro/ferricyanide potassium pair at 5 mmolL⁻¹ value.

Preparation of Bn-pCNVio gel: This electrochromic gel was fabricated keeping the final concentration of 1-benzyl-1'-(*p*-cyanophenyl)-4,4'-bipyridinium dibromide (**Bn-pCNVio**)

at 20 mmolL^{-1} and the concentration of the ferro/ferricyanide potassium pair at 5 mmolL^{-1} value.

Preparation of EtVio + pCNVio gel: This electrochromic gel was fabricated keeping the final concentration of both **EtVio** and **pCNVio** at 10 mmolL^{-1} and the concentration of the ferro/ferricyanide potassium pair at 5 mmolL^{-1} value.

Preparation of BnVio + pCNVio gel: This electrochromic gel was fabricated keeping the final concentration of both **BnVio** and **pCNVio** at 10 mmolL^{-1} and the concentration of the ferro/ferricyanide potassium pair at 5 mmolL^{-1} value.

Preparation of Gel electrolyte: This viologen-free gel was fabricated keeping the final concentration of the ferro/ferricyanide potassium pair at 5 mmolL^{-1} value.

- **Preparation of anhydrous formulations**

Preparation of anhydrous EC systems (general procedure): all liquid systems were prepared according to a procedure previously reported by our group.³⁻⁴ Briefly, a mixture of the corresponding viologen (0.12 mmol), hydroquinone (0.14 mmol) and 1-Butyl-3-methylimidazolium tetrafluoroborate (18 mmol) was dissolved in 5 g of propylene carbonate and stirred until homogeneous solution was obtained.

In the case of anhydrous electrolyte employed for comparative purposes the procedure was similar to the one described above without adding any viologen.

- **Fabrication of Electrochromic Devices (ECDs)**

Fabrication of Two-electrode Electrochromic Devices: The electrochromic devices were assembled according to previously reported procedure.⁵ The EC gel was spread on the FTO-coated side of one of the substrates provided with a $220 \mu\text{m}$ double-side adhesive tape frame used as spacer. Then it was covered with the other electrode substrate, applying slight pressure, and both electrodes were clipped using paper clip clamps. The EC gel flows and

adapts to the shape of the electrodes, providing uniform films with excellent contact to the upper and lower electrodes.

In the case of anhydrous liquid systems employed for comparison, the electrochromic formulations were introduced in a previously assembled cell by surface capillarity.

Fabrication of Three-electrode Electrochromic Devices: The electrochromic devices were prepared according to previously reported procedure.¹ In brief, 5 cm x 2.5 cm ITO-coated glass substrate was electrically insulated by laser scribing into two sections, having an approximate active area of 5 cm x 2 cm and 5 cm x 0.5 cm. Ag ink, purchased from Acheson (Electrodag PF-410), was employed to draw a layer on the 5 cm x 0.5 cm section which was employed as pseudo-reference electrode after being dried at 90 °C (RE). The wider section of the same substrate was employed as a working electrode (WE), while other ITO-coated glass substrate (without any laser treatment) was used as counter electrode (CE). The following steps required for device assembling were similar to those indicated for two-electrode electrochromic devices.

- **Characterization of 1-ethyl-1'-(p-cyanophenyl)-4,4'-bipyridinium dibromide (Et-pCNVio).**

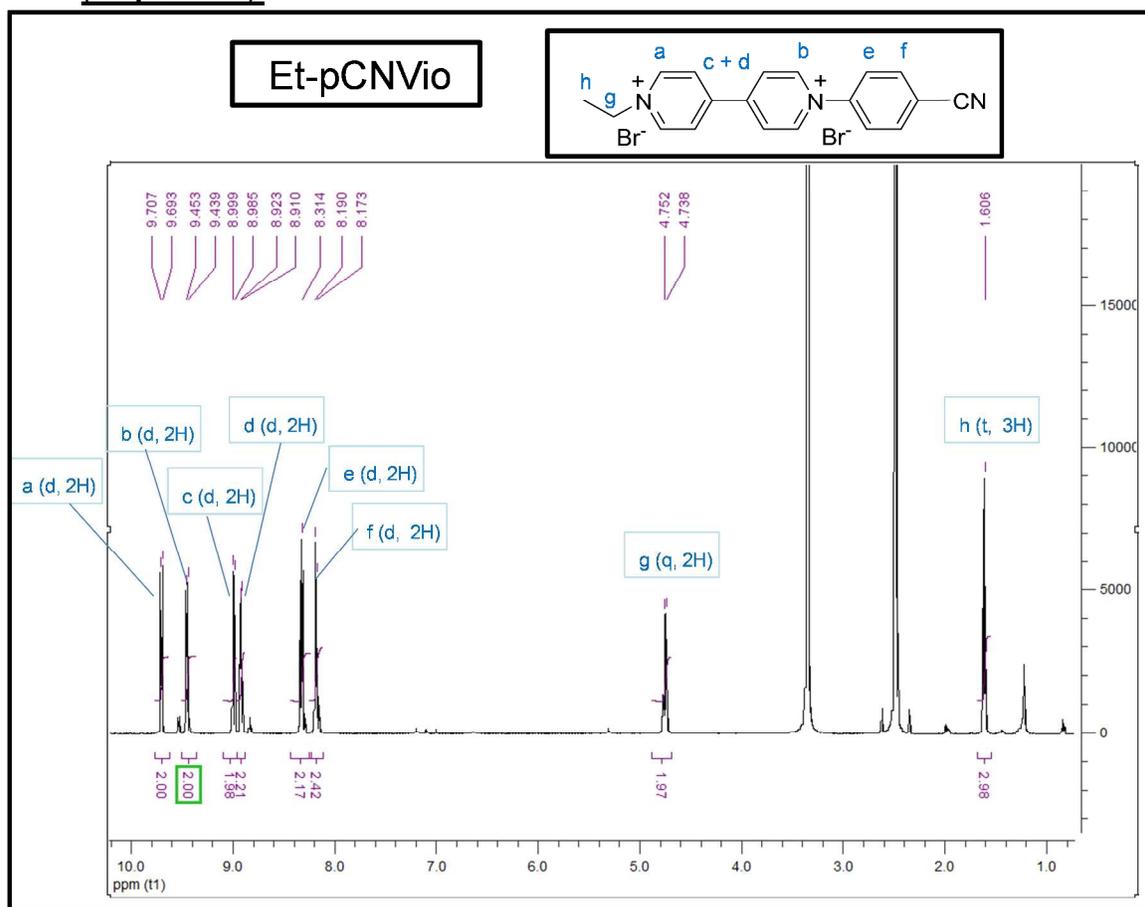


Figure S1. ¹H NMR spectra of Et-pCNVio.

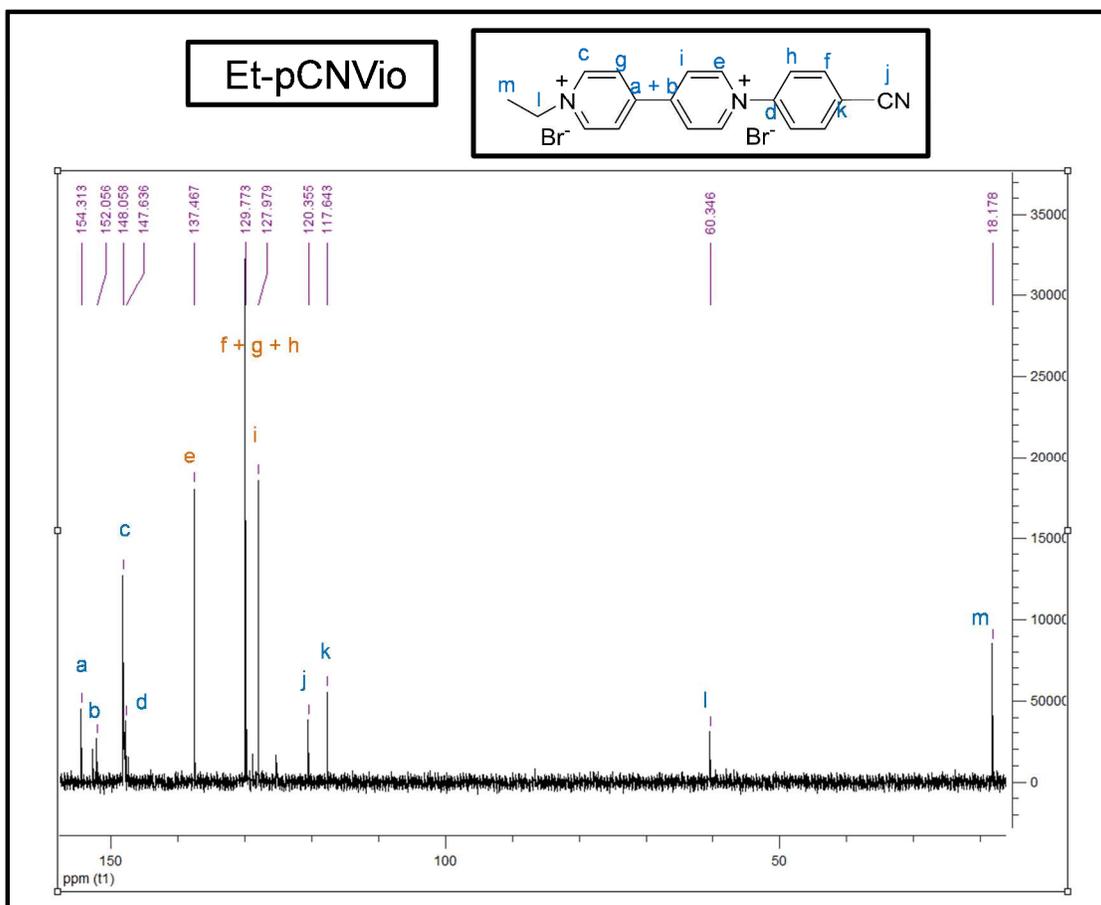


Figure S2. ^{13}C NMR spectra of Et-pCNVio. Estimation quality is indicated by color: good, rough.

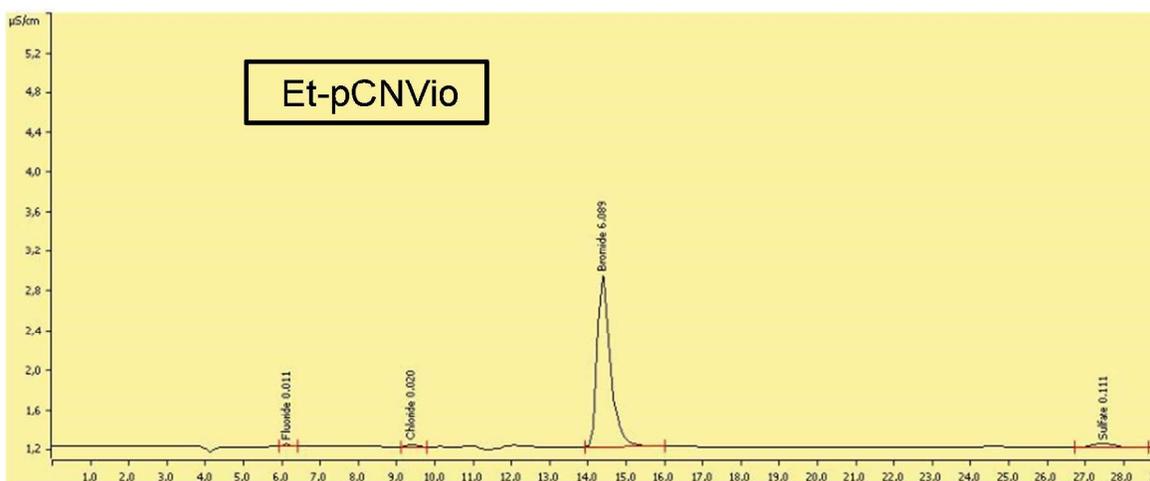


Figure S3. Anion chromatogram of Et-pCNVio.

Please note that the minor signals of other anions detected (Cl^- , F^- and SO_4^{2-}), were assigned to the traces present in the water employed in the dilution.

- **Characterization of 1-benzyl-1'-(p-cyanophenyl)-4,4'-bipyridinium dibromide (Bn-pCNVio).**

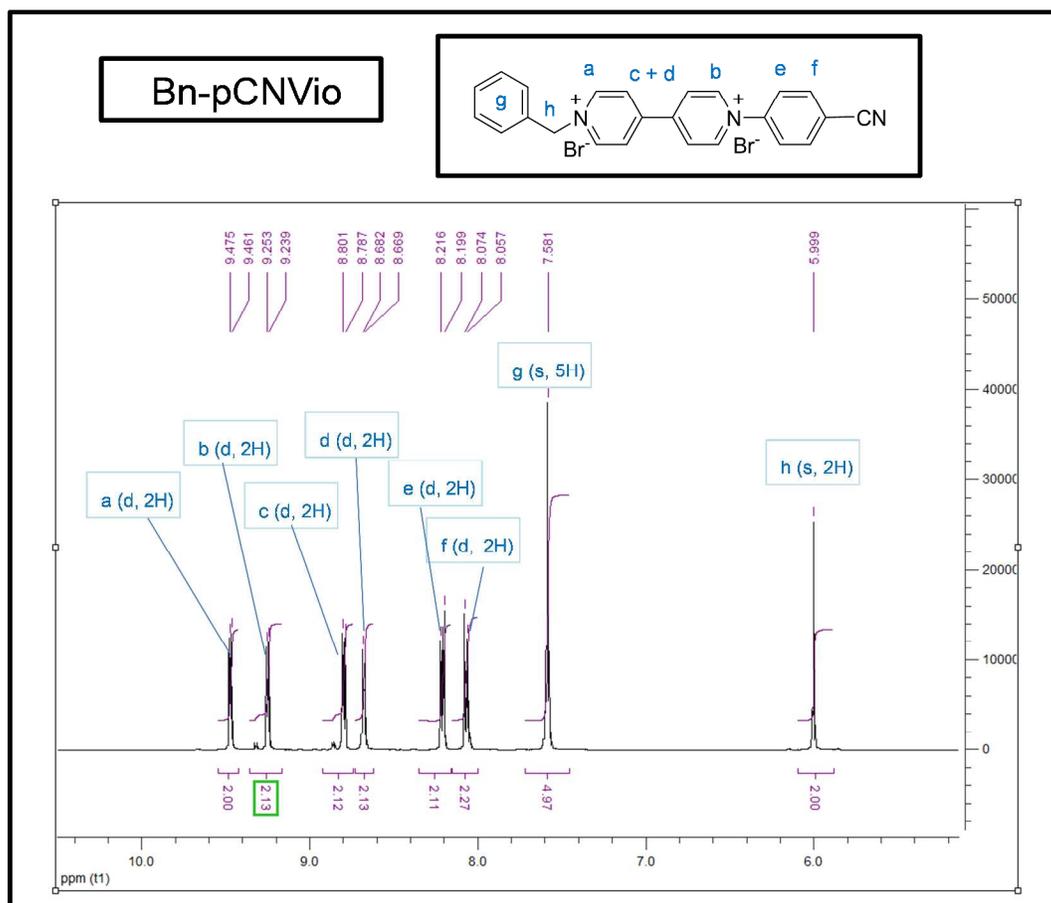


Figure S4. ¹H NMR spectra of Bn-pCNVio.

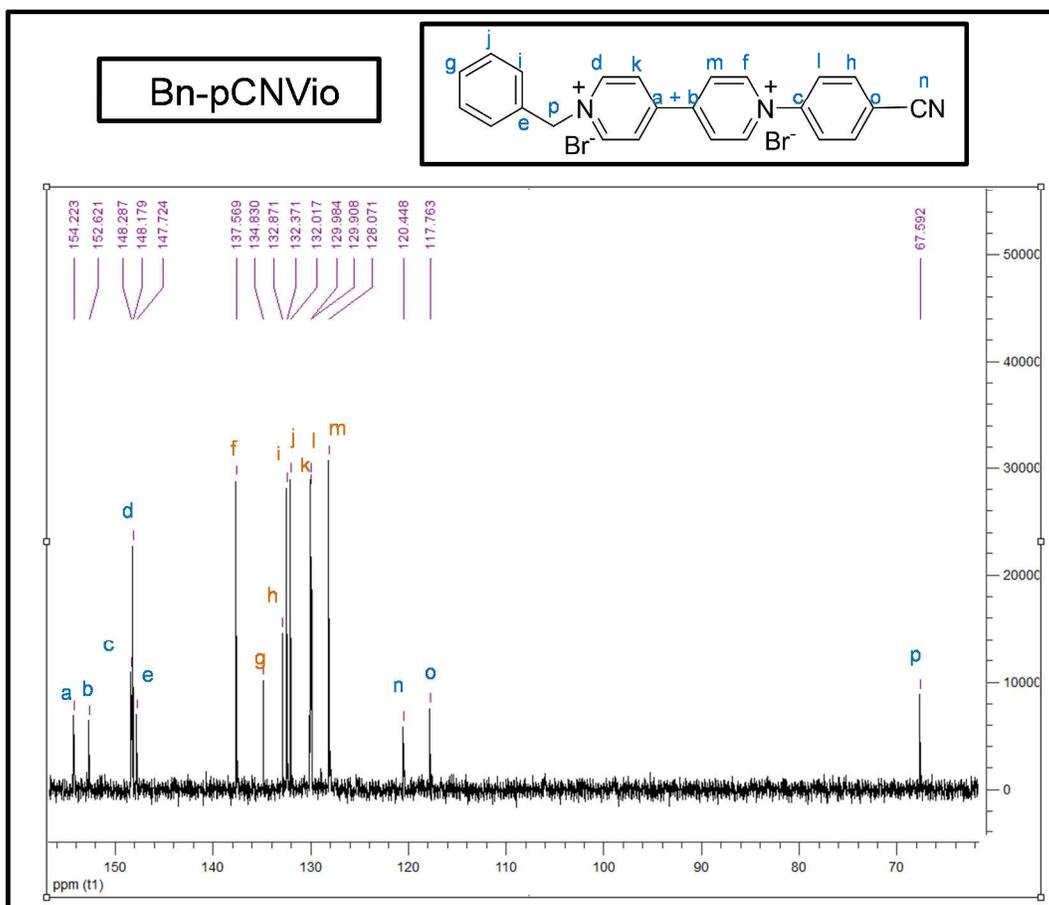


Figure S5. ^{13}C NMR spectra of Bn-pCNVio. Estimation quality is indicated by color: good, rough.

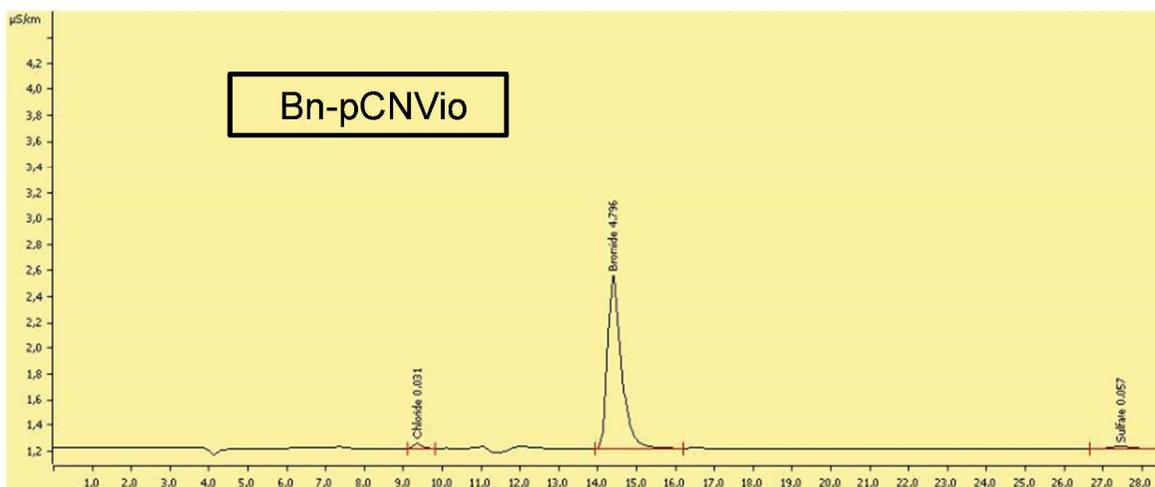


Figure S6. Anion chromatogram of Bn-pCNVio.

Please note that the minor signals of other anions detected (Cl^- , F^- and SO_4^{2-}), were assigned to the traces present in the water employed in the dilution.

- **Figure S7. Spectroelectrochemical study of three-electrode ECD containing Gel electrolyte for comparative purposes.**

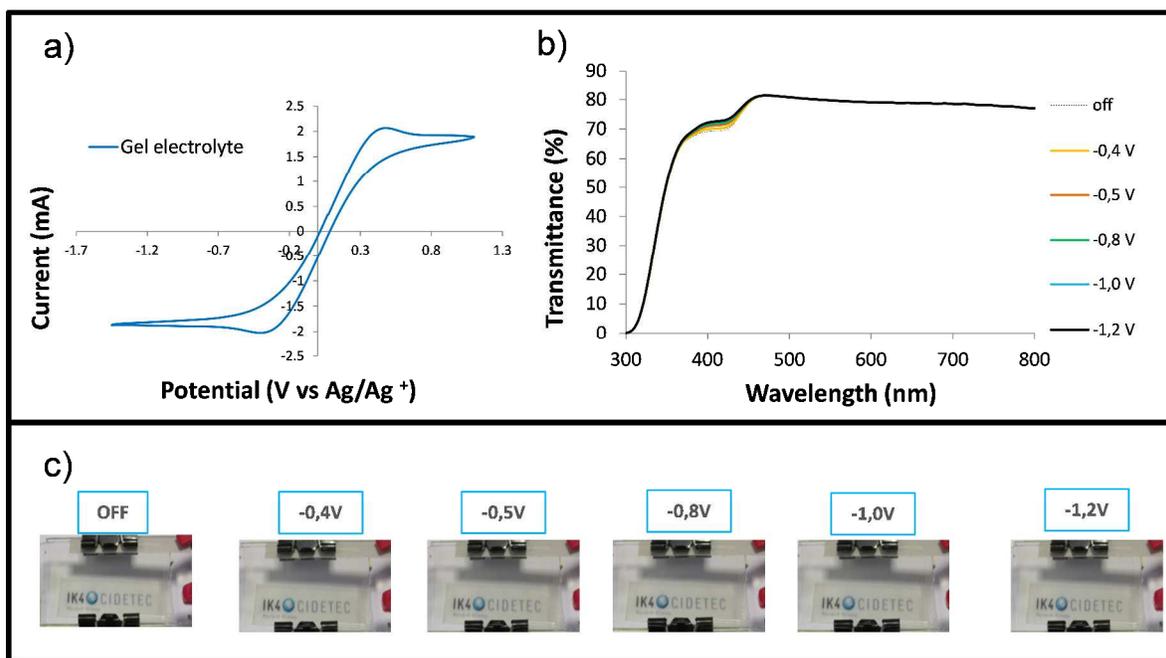


Figure S7. Spectroelectrochemical study of three-electrode ECD containing Gel electrolyte for comparative purposes. a) Cyclic voltammetry (CV); UV/vis transmittance responses as a function of wavelength (b) and photograph of the device (c) for different applied potentials from -0.4 to -1.2 V.

- **Figure S8. Cyclic voltammtries of three-electrode ECDs containing Bn-pCNVio, pCNVio and BnVio gels.**

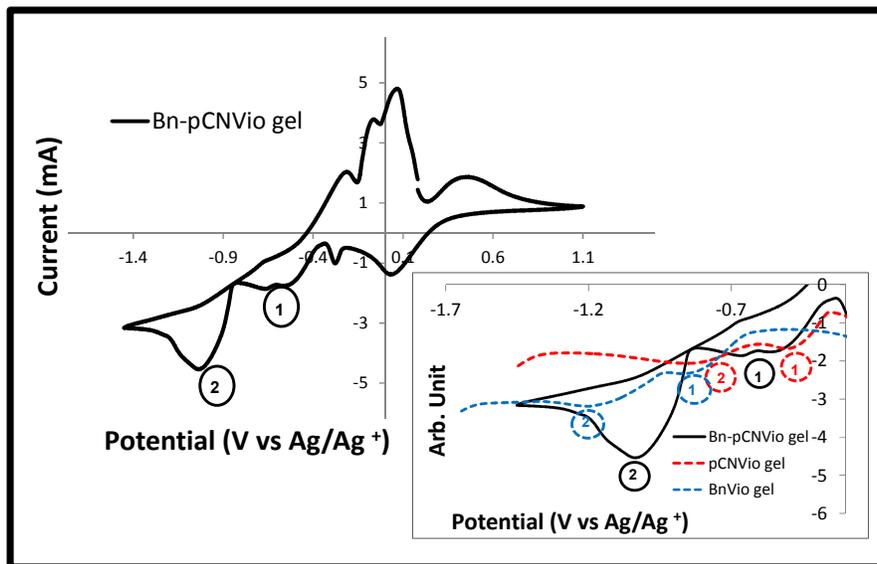


Figure S8. Cyclic voltammetry (CV) of three-electrode electrochromic device containing Bn-pCNVio gel and comparison with CVs of pCNVio gel and BnVio gel separately (inset).

- **Table S1. % Transmittance, $\Delta\%T$ and color coordinates of three-electrode ECDs containing Bn-pCNVio gel at different applied potentials.**

Potential (V)	$\%T_b$	$\%T_c$	$\Delta\%T^{(a)}$	$x^{(b)}$	$y^{(b)}$	$Y^{(b)}$	$L^{*(c)}$	$a^{*(c)}$	$b^{*(c)}$	Color ^(d)
off	67.1	-	-	0.309	0.326	67.9	86	0	-2	
-0.4		42.9	24.2	0.294	0.331	49.9	76	-9	-2	
-0.5		24.0	43.0	0.269	0.329	34.5	65	-17	-5	
-0.6		10.6	56.4	0.233	0.325	21.8	54	-27	-9	
-0.7		3.8	63.3	0.195	0.321	12.8	43	-35	-12	
-0.8		0.7	66.4	0.150	0.327	6.1	30	-43	-11	
-0.9		0.1	67.0	0.116	0.341	2.5	18	-42	-8	
-1.0		10.2	56.9	0.342	0.418	13.2	43	-12	20	

^{a)} Transmittance change at $\lambda = 600$ nm: ($\%T_b - \%T_c$) being T_b = transmittance at bleached state and T_c = transmittance at colored state.

^{b), c)} Color coordinates (D65):⁶⁻⁷ xyY_{1931} (x = blue / red; y = blue / green)^(b) and $L^*a^*b^*$ 1976 (a^* = green (-) / red (+); b^* = blue (-) / yellow (+))^(c).

^{d)} Color interpretation of the corresponding color coordinates ($L^*a^*b^*$) acquired through a color converter software (included to ease their interpretation).

- **Figure S9. EC behavior of two-electrode ECDs containing Bn-pCNVio gel vs corresponding symmetric viologens and the mixture of them.**

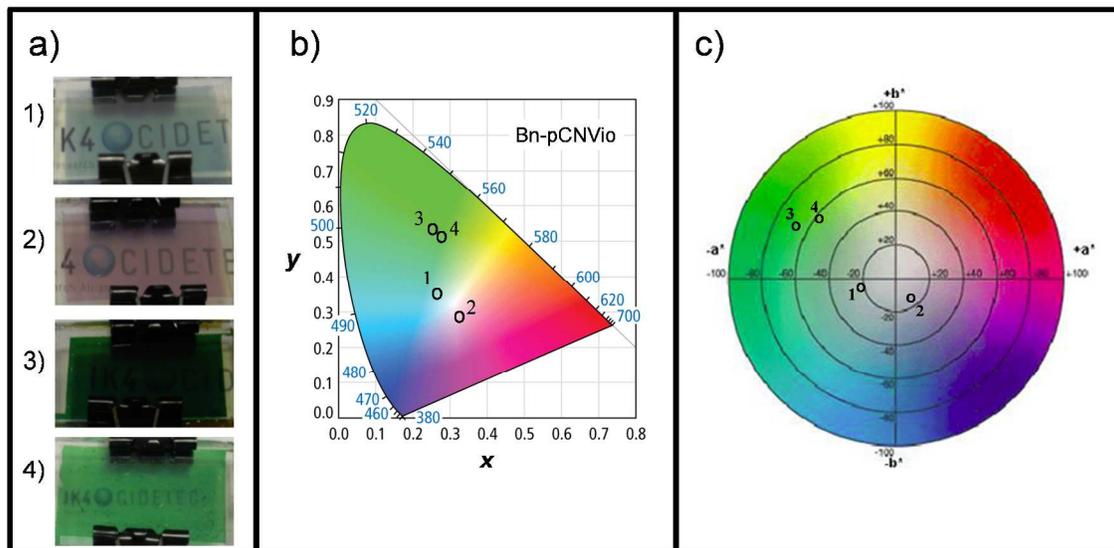


Figure S9. Two-electrode ECDs containing Bn-pCNVio gel (1) vs corresponding symmetric viologens BnVio (2) and pCNVio (3), and the mixture of them (BnVio + pCNVio gel) (4). Photographs of each device at their colored states (a) and the corresponding color coordinates represented in the chromaticity diagram (b) and in the L^*a^*b color space plot (c).

- **Figure S10. EC behavior of two-electrode ECDs containing Et-pCNVio gel vs corresponding symmetric viologens and the mixture of them.**

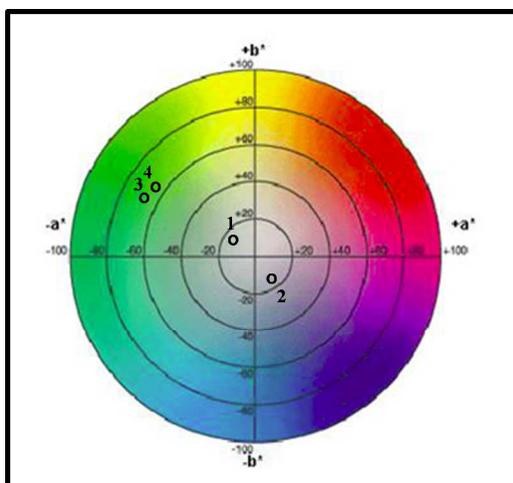


Figure S10. Two-electrode ECDs containing Et-pCNVio gel (1) vs corresponding symmetric viologens EtVio (2) and pCNVio (3), and the mixture of them (EtVio + pCNVio gel) (4): CIE color coordinates obtained at their colored states represented in the L^*a^*b color space.

- **Characterization of two-electrode ECDs containing Et-pCNVio and Bn-pCNVio gels.**

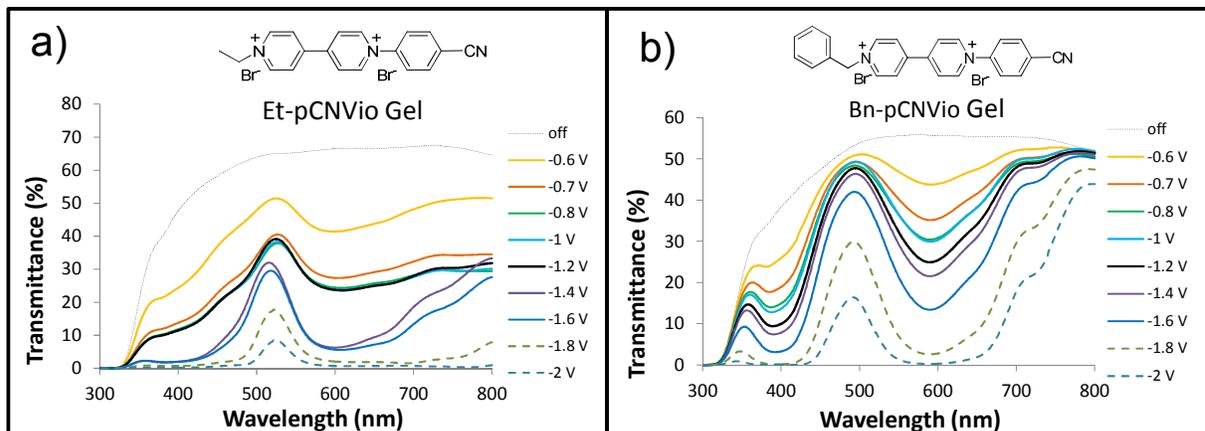


Figure S11. UV/Vis transmittance profiles of Two-electrode ECDs containing Et-pCNVio (a) and Bn-pCNVio (b) gels.

Table S2. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio gels. Values registered at the maximum contrast wavelength (600 nm) for different applied potentials.

Potential (V)	Et-pCNVio Gel			Bn-pCNVio Gel		
	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)
off	66.5	-	-	55.7	-	-
-0.6		41.4	25.1		43.9	11.7
-0.7		27.4	39.2		35.5	20.2
-0.8		24.4	42.1		30.8	24.9
-1.0		23.9	42.6		30.3	25.3
-1.2		23.7	42.8		25.4	30.3
-1.4		6.3	60.2		22.0	33.6
-1.6		5.7	60.9		13.9	41.8
-1.8		2.1	64.5		2.8	52.9

- **Characterization of two-electrode ECDs containing EtVio, BnVio and pCNVio gels.**

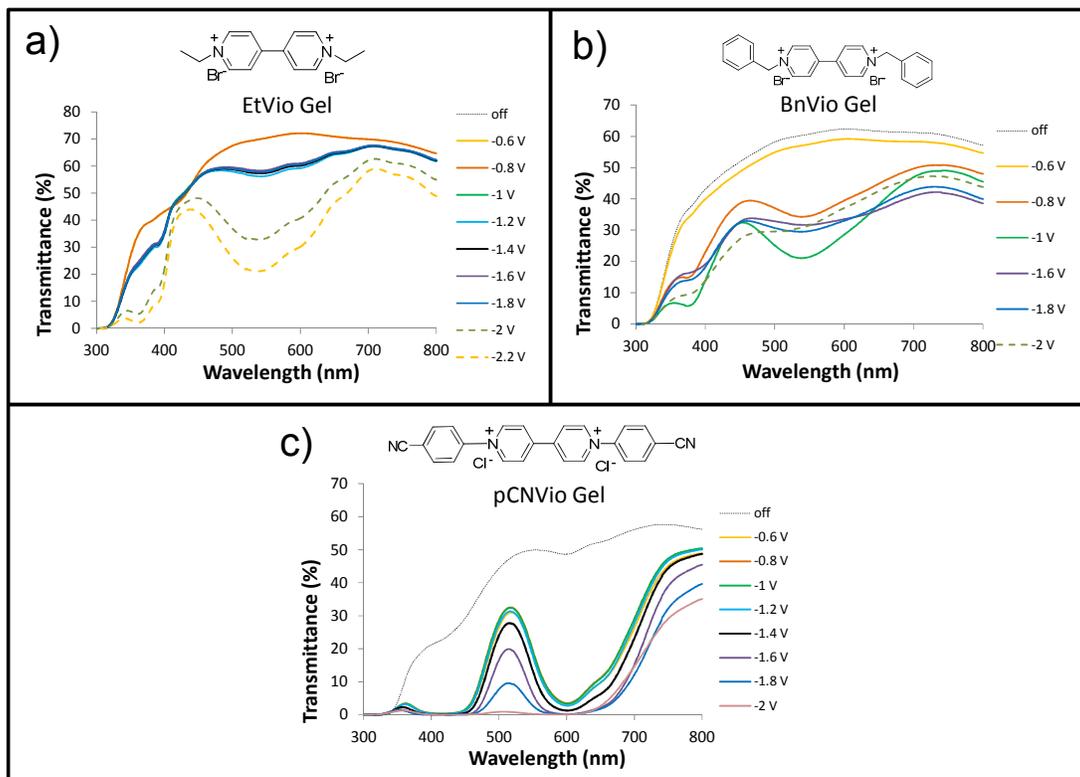


Figure S12. UV/Vis transmittance profiles of Two-electrode ECDs containing EtVio (a), BnVio (b) and pCNVio (c) gels.

Table S3. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing EtVio, BnVio and pCNVio gels. Values registered at the maximum contrast wavelength for different applied potentials.

Potential (V)	EtVio Gel			BnVio Gel			pCNVio Gel		
	%T off ($\lambda = 550\text{nm}$)	%T on ($\lambda = 550\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 550\text{nm}$)	%T off ($\lambda = 550\text{nm}$)	%T on ($\lambda = 550\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 550\text{nm}$)	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)
off		-	-		-	-		-	-
-0.6	70.3	70.3	0.0	60.7	57.5	3.2	48.6	3.2	45.4
-0.8		70.4	0.0		34.5	26.2		3.5	45.0
-1.0		57.8	12.5		21.4	39.3		3.3	45.2
-1.2		56.3	14.0		41.1	19.5		2.7	45.8
-1.4		57.5	12.9		42.4	18.3		1.3	47.3
-1.6		58.5	11.9		31.7	29.0		0.2	48.4
-1.8		57.9	12.4		29.7	31.0		0.1	48.4
-2.0		33.4	37.0		31.6	29.1		0.1	48.5

- **Characterization of two-electrode ECDs containing EtVio + pCNVio and BnVio +pCNVio gels.**

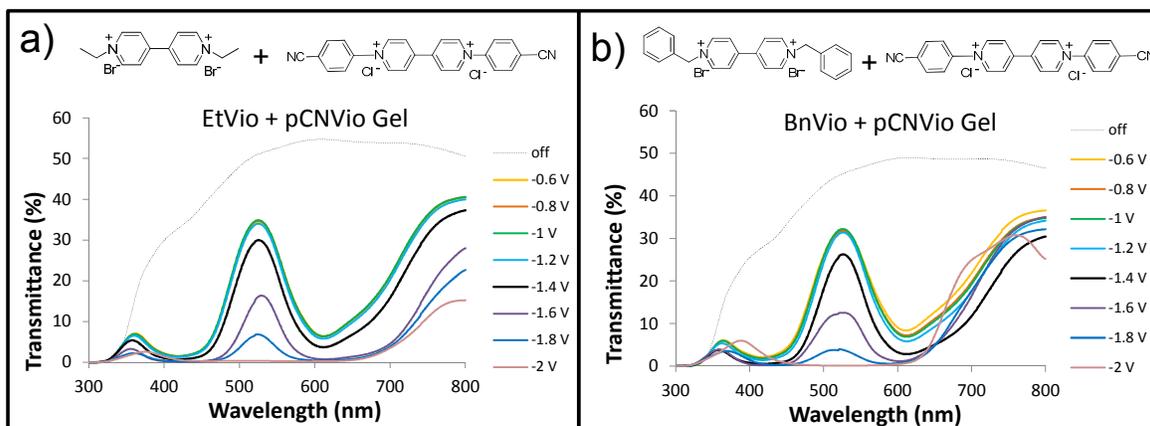


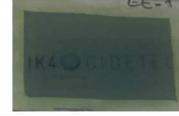
Figure S13. UV/Vis transmittance profiles of Two-electrode ECDs containing EtVio + pCNVio (a) and BnVio +pCNVio (b) gels.

Table S4. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing EtVio + pCNVio and BnVio +pCNVio gels. Values registered at the maximum contrast wavelength (600 nm) for different applied potentials.

Potential (V)	EtVio + pCNVio Gel			BnVio + pCNVio Gel		
	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)
off		-	-		-	-
-0.6	54.7	7.3	47.4	48.8	9.1	39.7
-0.8		7.1	47.5		8.0	40.9
-1.0		7.1	47.6		7.7	41.2
-1.2		6.5	48.2		6.5	42.3
-1.4		4.2	50.4		3.2	45.6
-1.6		0.9	53.7		1.2	47.7
-1.8		0.5	54.2		0.6	48.2
-2.0		0.3	54.4		0.4	48.4

- **Table S5. Evolution of the electrochromic performance of two-electrode ECD containing Et-pCNVio gel after 500 – 15 000 cycles.**

Table S5. Evolution of the electrochromic performance (%T, Transmittance changes ($\Delta\%T$) and visual appearance) of two-electrode ECD containing Et-pCNVio gel after 500 – 15 000 cycles. Values registered at the maximum contrast wavelength (600 nm) at off state and upon applying -1.0 V.

Cycles	%T off (t = 500s)	%T on (t = 554s)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)	Photographs OFF	Photographs ON
500	62,2	18,6	43,6		
1000	61,6	17,5	44,1		
1500	60,6	17,6	43,1		
2000	60,5	16,1	44,3		
7500	58,5	15,8	42,7		
10000	57,4	14,7	42,7		
15000	55,5	13,7	41,8		

- **Evolution of switching and electrochromic performances of two-electrode ECD containing Bn-pCNVio gel.**

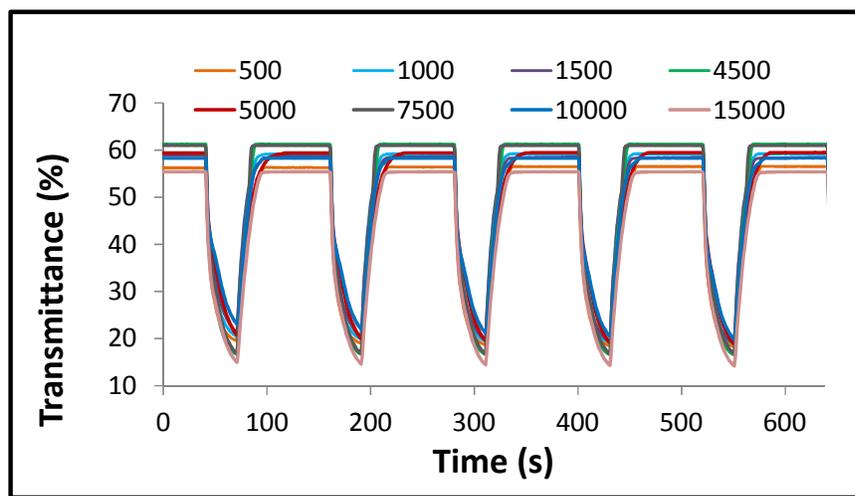


Figure S14. Evolution of the switching performance of two-electrode ECD containing Bn-pCNVio gel after 500 – 15 000 cycles. Values registered at the maximum contrast wavelength (600 nm) while square-wave potential-steps between bleached (0 V for 90 s) and colored state (-1.0 V for 30 s) were being applied.

Table S6. Evolution of the electrochromic performance (%T, Transmittance changes ($\Delta\%T$) and visual appearance) of two-electrode ECD containing Bn-pCNVio gel after 500 – 15 000 cycles. Values registered at the maximum contrast wavelength (600 nm) at off state and upon applying -1.0 V.

Cycles	%T off ($t = 520s$)	%T on ($t = 550s$)	$\Delta\%T$ off-on ($\lambda = 600nm$)	Photographs OFF	Photographs ON
500	56,5	18,3	38,2		
1000	59,2	18,9	40,3		
1500	58,4	19,0	39,5		
5000	59,5	18,7	40,7		
7500	61,0	16,8	44,2		
10000	58,3	19,9	38,5		
15000	55,4	14,2	41,2		

- **Characterization of two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions.**

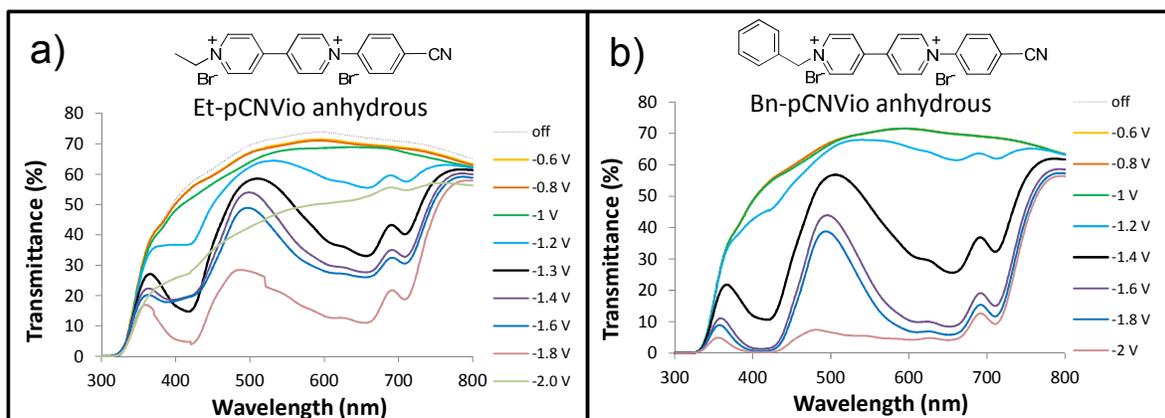


Figure S15. UV/Vis transmittance profiles of Two-electrode ECDs containing Et-pCNVio (a) and Bn-pCNVio (b) anhydrous solutions.

Table S7. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing Et-pCNVio and Bn-pCNVio anhydrous solutions. Values registered at 600 nm for different applied potentials.

Potential (V)	Et-pCNVio anhydrous			Bn-pCNVio anhydrous		
	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)
off		-	-		-	-
-0,6	73,8	71,4	2,3	71,5	71,5	0,0
-0,8		71,0	2,7		71,5	0,0
-1,0		68,6	5,2		71,5	0,0
-1,2		58,8	14,9		65,7	5,8
-1,4		30,7	43,1		31,9	39,6
-1,6		28,1	45,7		10,5	61,0
-1,8		13,3	60,5		7,0	64,5
-2,0		50,3	23,5		4,2	67,3

- **Figure S16. Transmittance profiles (UV/Vis transmittance response) of electrochromic devices containing Bn-pCNVio gel vs anhydrous formulation.**

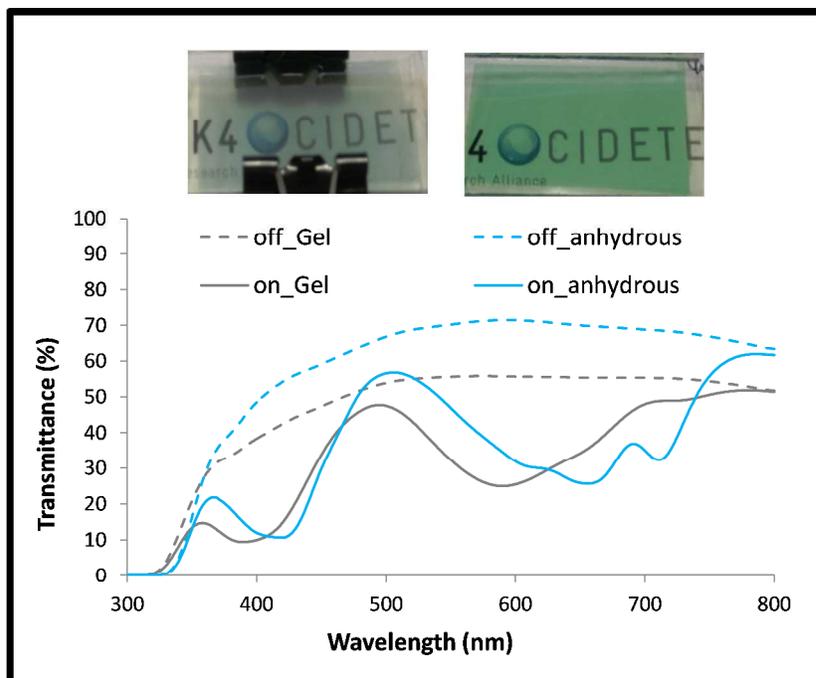


Figure S16. Transmittance profiles (UV/Vis transmittance response) of electrochromic devices containing Bn-pCNVio gel vs anhydrous formulation in their bleached and colored states. Photographs of the devices based on gel formulations (left) and anhydrous formulations (right) in their colored states (inset).

- **Figure S17. Spectroelectrochemical study of three-electrode ECD containing Anhydrous electrolyte for comparative purposes.**

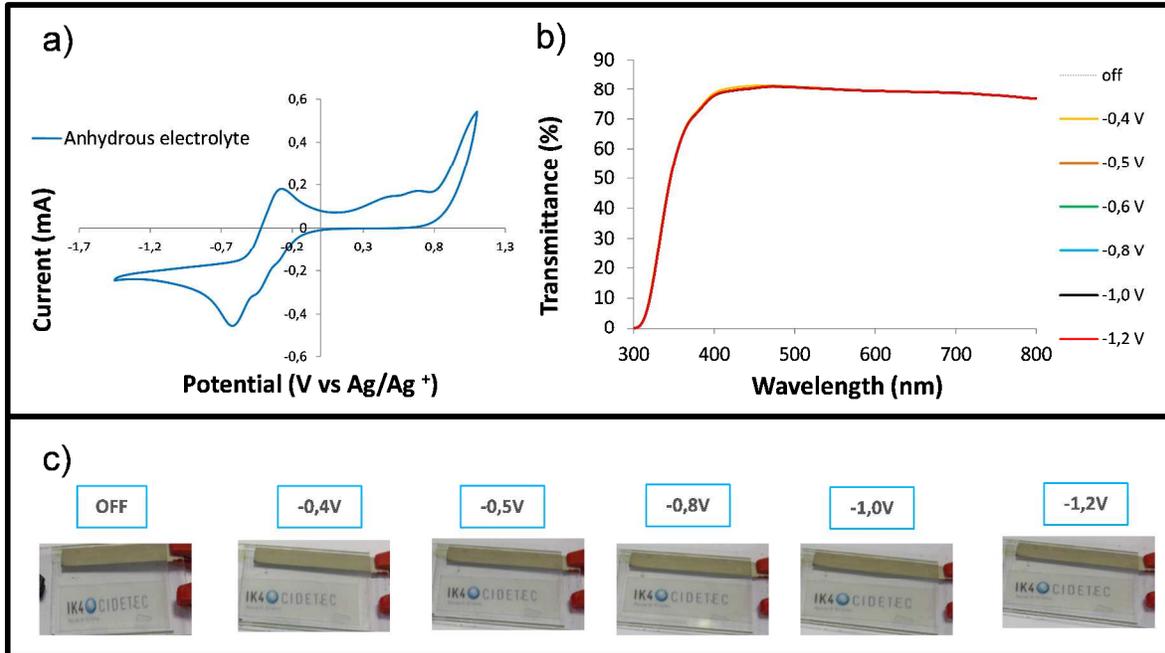


Figure S17. Spectroelectrochemical study of three-electrode ECD containing anhydrous electrolyte for comparative purposes. a) Cyclic voltammetry (CV); b) UV/vis transmittance responses as a function of wavelength and photograph of the device (c) for different applied potentials from -0.4 to -1.2 V.

- **Characterization of two-electrode ECDs containing EtVio and BnVio anhydrous solutions.**

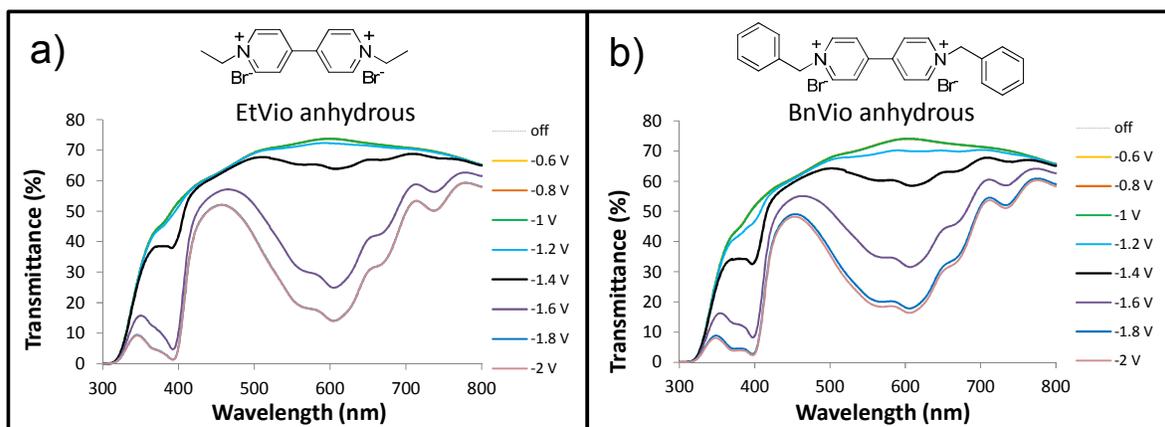


Figure S18. UV/Vis transmittance profiles of Two-electrode ECDs containing EtVio (a) and BnVio (b) anhydrous solutions.

Table S8. %T and Transmittance changes ($\Delta\%T$) of Two-electrode ECDs containing EtVio and BnVio anhydrous solutions. Values registered at the maximum contrast wavelength (600 nm) for different applied potentials.

Potential (V)	EtVio anhydrous			BnVio anhydrous		
	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)	%T off ($\lambda = 600\text{nm}$)	%T on ($\lambda = 600\text{nm}$)	$\Delta\%T$ off-on ($\lambda = 600\text{nm}$)
off		-	-		-	-
-0,6	73,8	73,8	0,0	74,1	74,0	0,0
-0,8		73,7	0,1		74,0	0,0
-1,0		73,7	0,1		74,0	0,0
-1,2		72,3	1,5		70,1	4,0
-1,4		64,1	9,7		58,9	15,2
-1,6		25,3	48,5		32,1	42,0
-1,8		14,4	59,4		18,2	55,9
-2,0		14,3	59,5		16,7	57,4

- **Figure S19. UV/Vis transmittance response of electrochromic devices comprising gel-based formulations vs anhydrous formulations containing EtVio and BnVio symmetric viologens.**

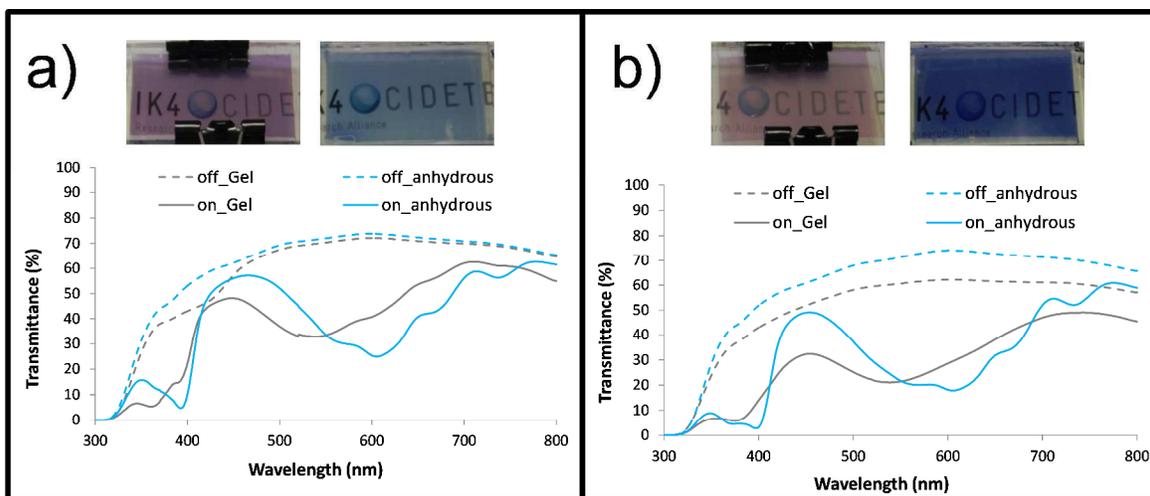


Figure S19. UV/Vis transmittance profiles of electrochromic devices comprising gel-based formulations vs anhydrous formulations containing EtVio (a) and BnVio (b) in their bleached and colored states. Photographs of the devices based on gel formulations (left) and anhydrous formulations (right) in their colored states (inset).

- **Table S9. % Transmittance, $\Delta\%T$ and color coordinates of two-electrode ECDs containing different anhydrous formulations.**

Anhydrous formulations	%T _b	%T _c	$\Delta\%T^{(a)}$	x ^(b)	y ^(b)	Y ^(b)	L* ^(c)	a* ^(c)	b* ^(c)
Et-pCNVio	73.8	30.7	43.1	0.286	0.365	40.1	70	-23	6
Bn-pCNVio	71.5	31.9	39.6	0.291	0.391	43.7	72	-29	14
EtVio	73.8	25.3	48.5	0.259	0.282	36.1	67	-4	-21
BnVio	74.1	32.1	42.0	0.277	0.296	39.0	69	-2	-14

^{a)} Transmittance change at $\lambda = 600$ nm: ($\%T_b - \%T_c$) being T_b = transmittance at bleached state and T_c = transmittance at colored state.

^{b), c)} Color coordinates (D65):⁶⁻⁷ xyY 1931 (x = blue / red; y = blue / green)^(b) and L*a*b* 1976 (a* = green (-) / red (+); b* = blue (-) / yellow (+))^(c).

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