

Supporting information

Reversible vis-NIR electrochromic/electrofluorochromic switching in dual-functional devices modulated by different benzothiadiazole-arylammine anodic components

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Table S1. Redox potential in Volts vs. AgCl/Ag of the benzothiadiazole arylamines^{a)} and ethylviologen dibromide^{b)}

Compound	$E_{\max}(1)$ (mV)	$E_{\max}(2)$ (mV)	$\Delta E_{1}^{b)}$ (mV)	K_c	E_g^{opt} (eV)
CS03	0.62	0.95	358.2	1.2×10^6	1.90
CS01	0.77	1.08	302.1	1.3×10^5	1.99
LCS01	0.78	0.87	86	29	2.19
EP02	0.87	0.98	96	42	2.3
EV	-0.63	-1.15	413		

^{a)}From Ref. 35. Measured at the maximum of the oxidation half-wave; ^{b)}From Ref. 38. Measured at the minimum of the reduction half-wave.

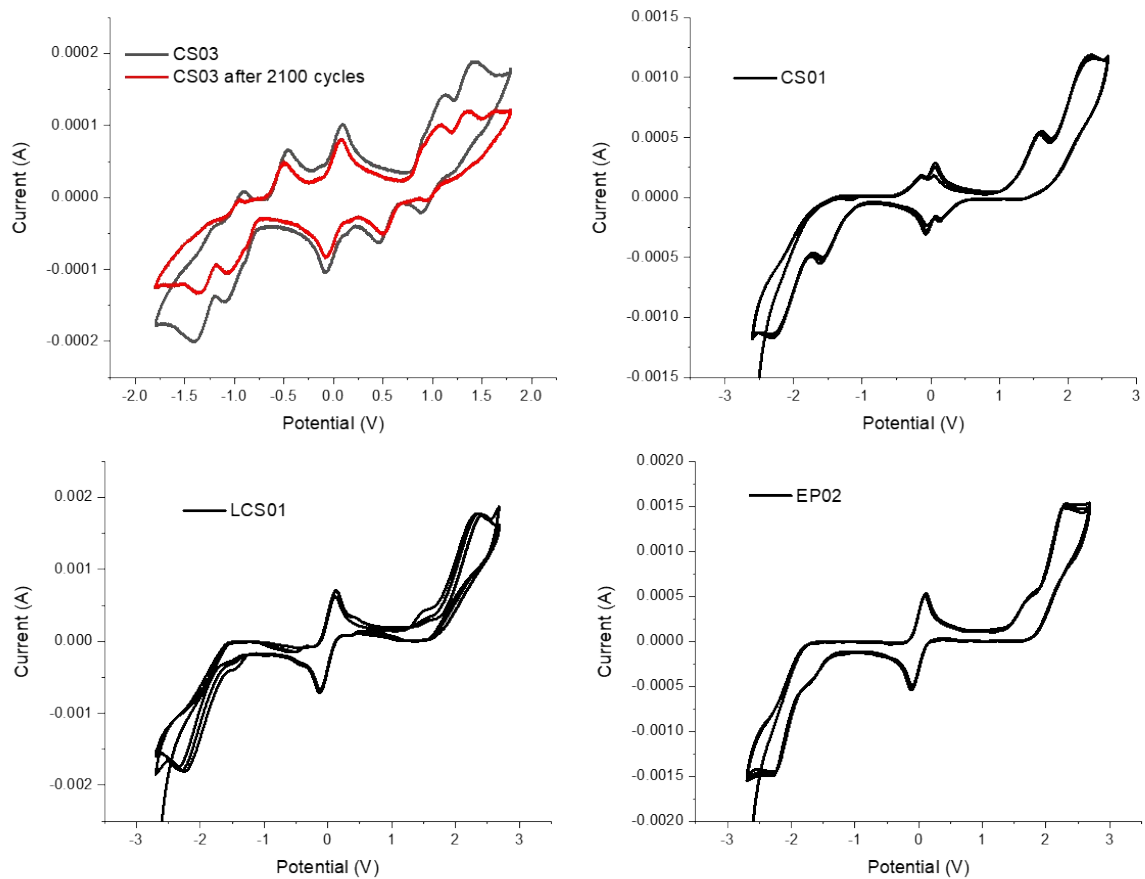


Figure S1. CVs covering the entire potential window of the BTDDPA and BTTPA devices. Please note that the peaks occurring at 0 V are not due to real electrochemical processes but are artifacts caused by the potential inversion.

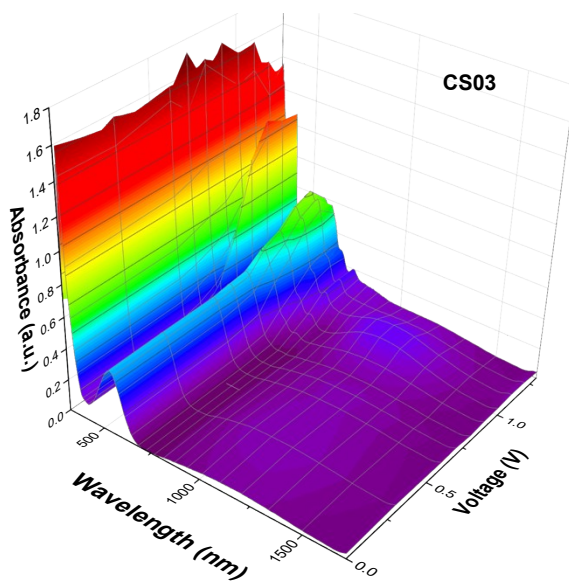


Figure S2. Spectroelectrochemistry in absorbance (3D plot) of the ITO/EC/ITO device with the anode CS03.

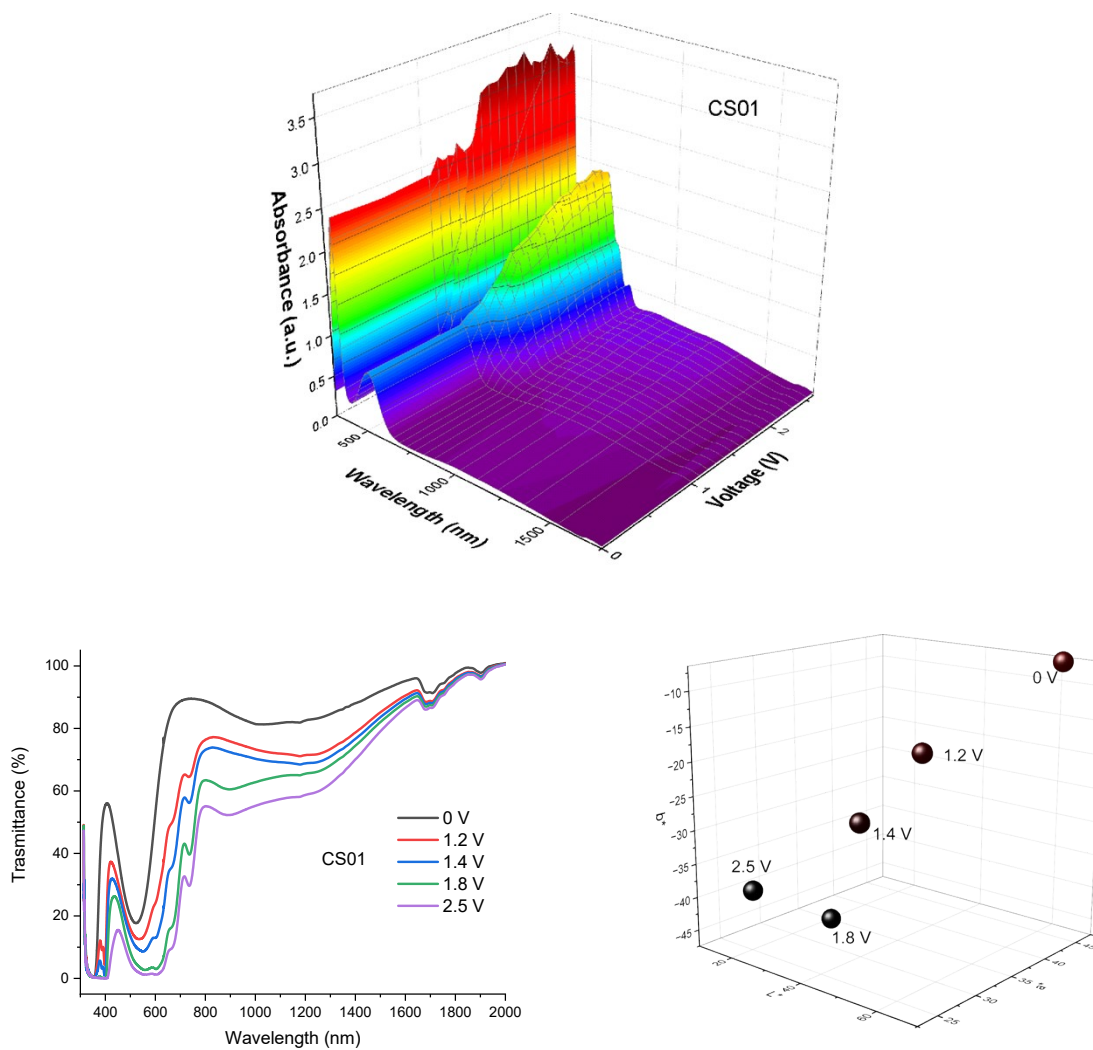


Figure S3. a) Spectroelectrochemistry in absorbance (3D plot) and b) in transmittance of the ITO/EC/ITO device with the anode CS01. c) 1976 CIE LAB coordinates as a function of the applied voltage for the device containing the CS01 anode.

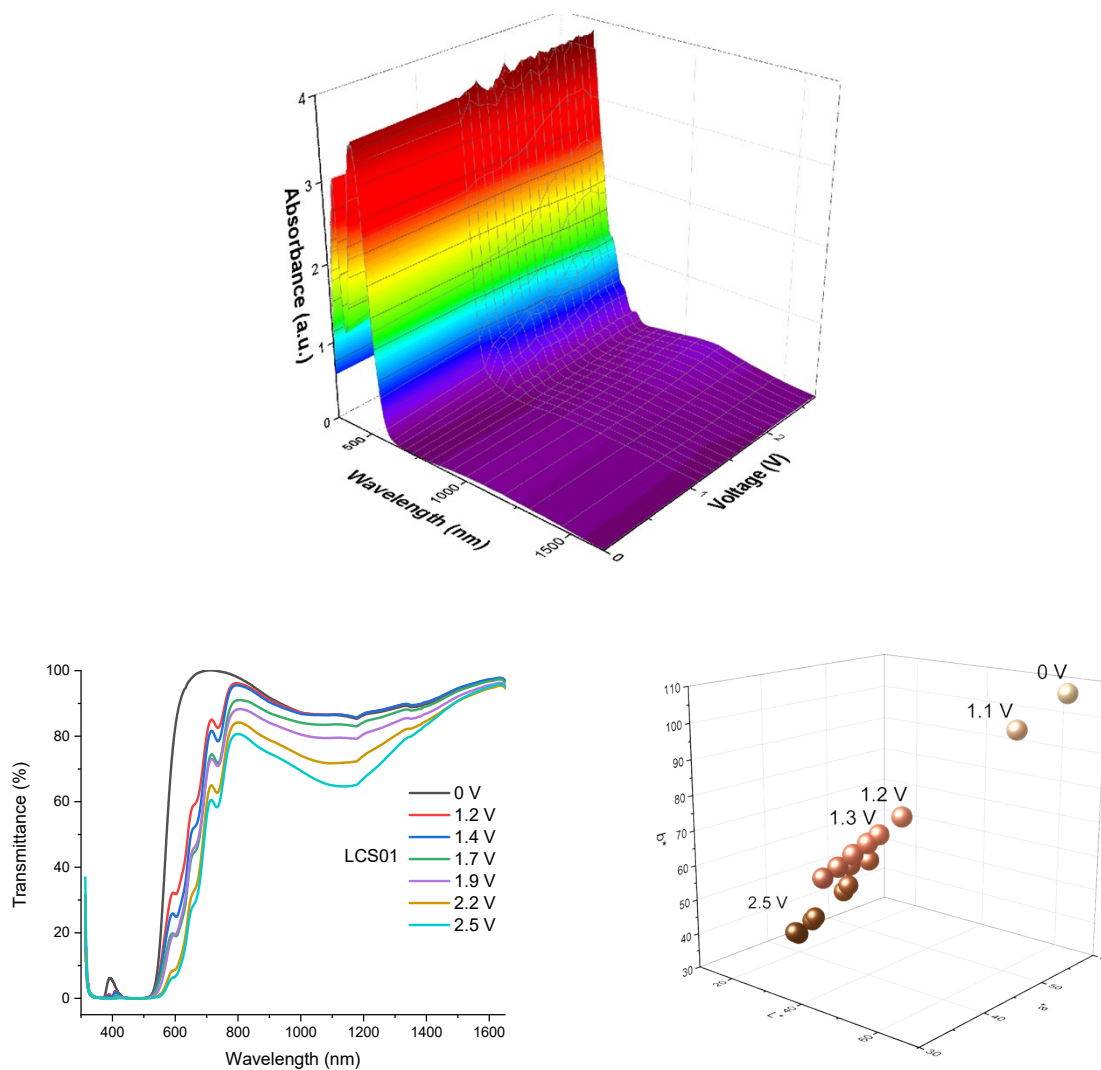


Figure S4. a) Spectroelectrochemistry in absorbance (3D plot) and b) in transmittance of the ITO/EC/ITO device with the anode LCS01. c) 1976 CIE LAB coordinates as a function of the applied voltage for the device containing the LCS01 anode.

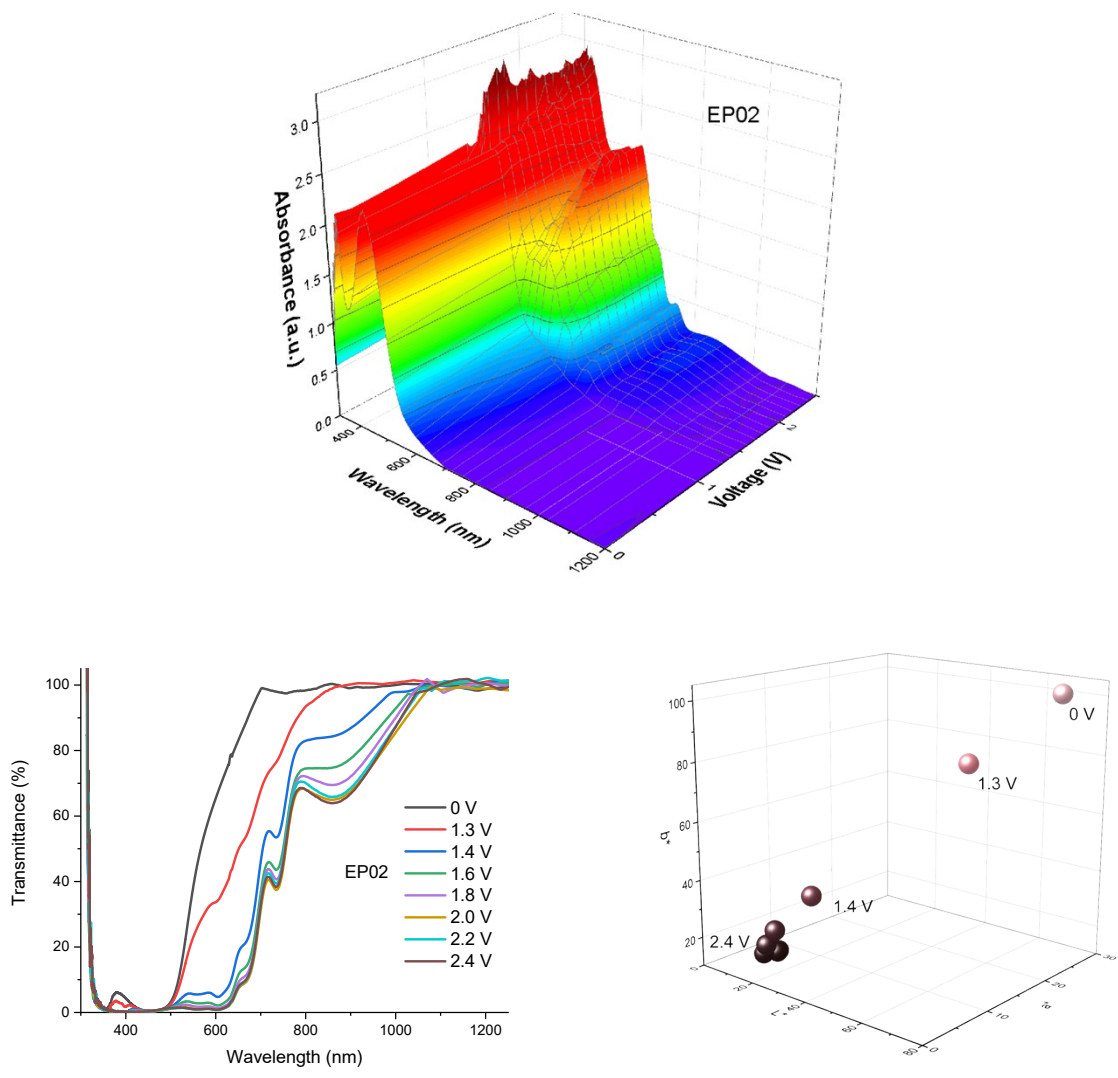


Figure S5. a) Spectroelectrochemistry in absorbance (3D plot) and b) in transmittance of the ITO/EC/ITO device with the anode EP02. c) 1976 CIE LAB coordinates as a function of the applied voltage for the device containing the EP02 anode.

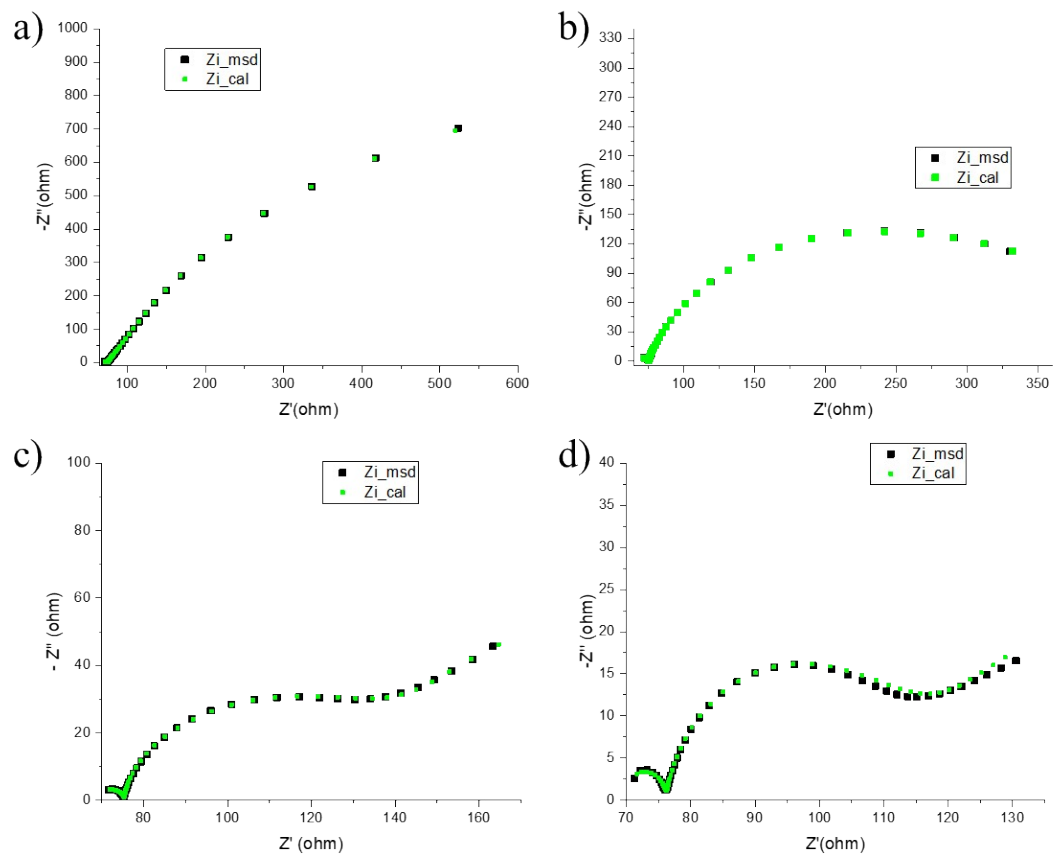


Figure S6. EIS experimental (black points) and calculated (green points) spectra of the CSO3-based device at the following voltages a) 0.6V, b) 0.8V, c) 1.2V and d) 1.6V.

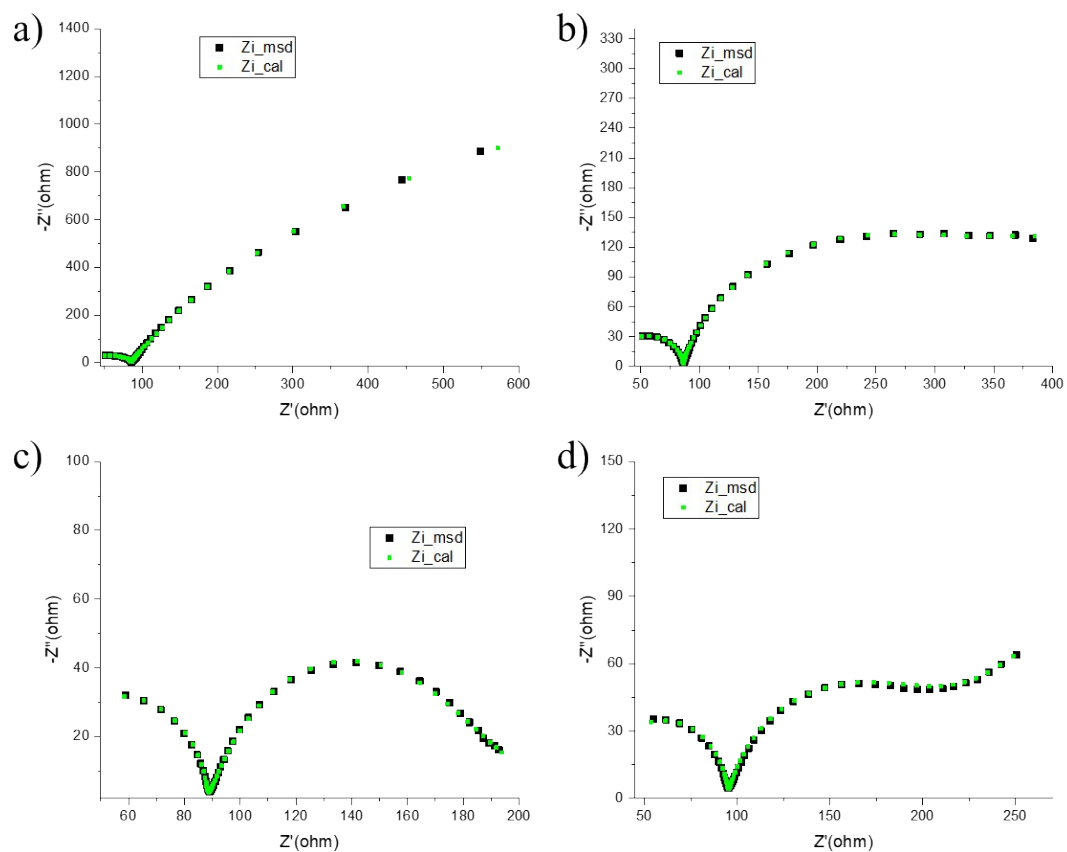


Figure S7. EIS experimental (black points) and calculated (green points) spectra of CS01-based device at the following voltages a) 0.8V, b) 1.2V, c) 1.9V and d) 2.4V.

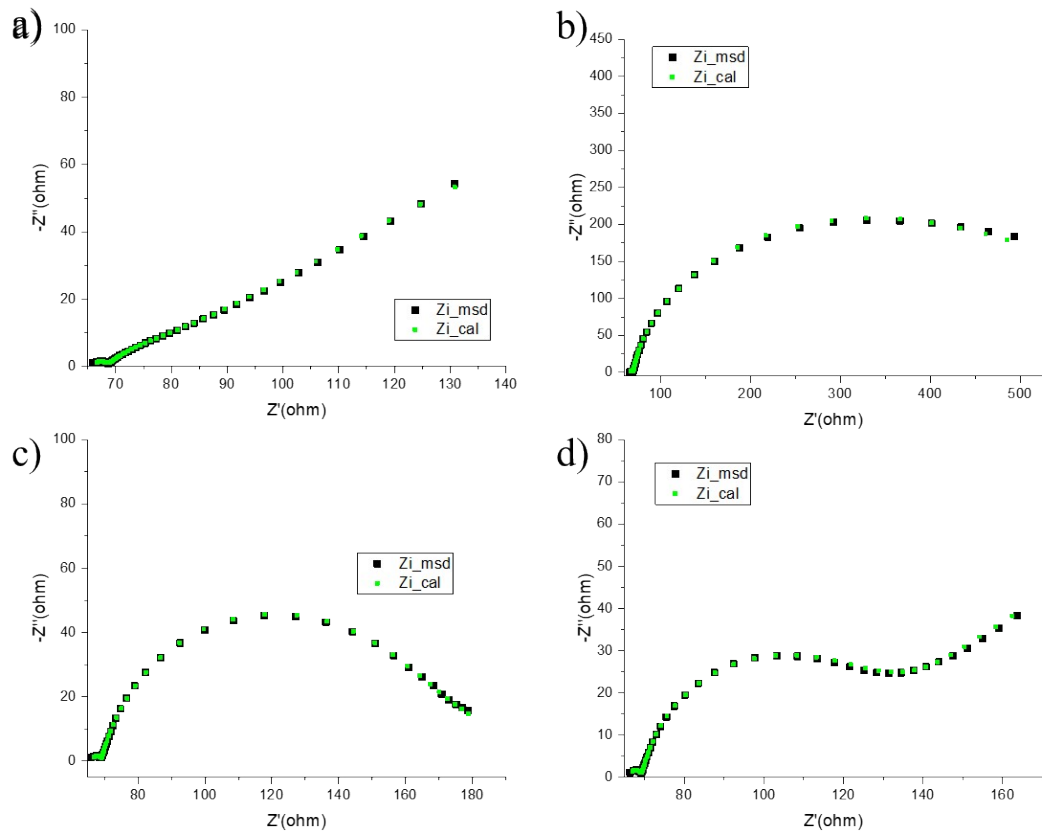


Figure S8. EIS experimental (black points) and calculated (green points) spectra of the EP02-based device at the following voltages a) 0V, b) 1.4, c) 1.6V and d) 2V.

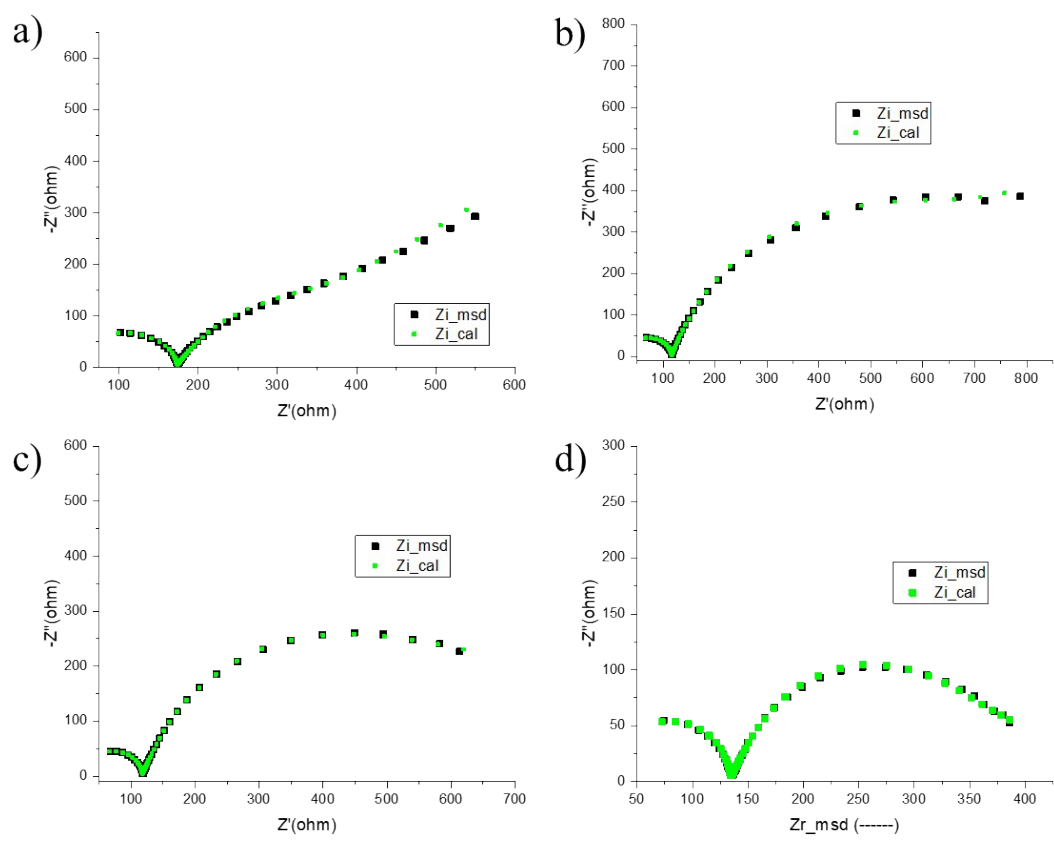


Figure S9. EIS experimental (black points) and calculated (green points) spectra of the LCS01-based device at the following voltages a) 0V, b) 1.4, c) 1.6V and d) 2.2V.

Table S2. EIS fitting parameters relative to the CS03 containing device as a function of the voltage.

BIAS (V)	C1 $\times 10^{-9}$ (F/cm ²)	R ₁ (Ω/cm ²)	C2 $\times 10^{-6}$ (F/cm ²)	R ₂ (Ω/cm ²)	W _{2FLY} $\times 10^{-4}$ (U [*])	W _{2FLB} (B ^{**})	W _{2Y} $\times 10^{-4}$ (U [*])	C3 $\times 10^{-6}$ (F/cm ²)	R ₃ (Ω/cm ²)	W _{3FLY} $\times 10^{-4}$ (U [*])	W _{3FLB} (B ^{**})	W _{3Y} $\times 10^{-4}$ (U [*])	χ ²
0.0	36.00	5.85	7.87	23250				5.24		4.70	0.22		1.4E-4
0.6	36.00	5.98	13.51	1226				13.51		4.36	0.18		8.4E-6
0.8	36.00	<u>6.20</u>	16.64	191.0				560	154	5.60	0.10		3.2E-6
1.0	36.00	6.23	<u>949</u>	36.92				<u>6.23</u>	85.47			1.58	1.2E-5
1.2	36.00	6.24	<u>233.2</u>	96.93				5.08	83.37			1.93	1.0E-5
1.4	36.00	<u>6.06</u>			30.45	0.39		5.57	59.18			1.85	7.1E-6
1.6	36.00	<u>6.44</u>			57.67	0.35		5.85	38.86			2.23	1.2E-5

The calculated value for R, the resistance of the polymeric bulk blend, was 69 Ω

*U= (F/sec^{0.5}cm²)

**B= (sec^{0.5}/cm²)

Table S3. EIS fitting parameters relative to the CS01 containing device as a function of the voltage.

BIAS (V)	C1 $\times 10^{-9}$ (F/cm ²)	R ₁ (Ω/cm ²)	C2 $\times 10^{-6}$ (F/cm ²)	R ₂ (Ω/cm ²)	W _{2FLY} $\times 10^{-4}$ (U [*])	W _{2FLB} (B [*])	W _{2Y} $\times 10^{-4}$ (U [*])	C3 $\times 10^{-6}$ (F/cm ²)	R ₃ (Ω/cm ²)	W _{3FLY} $\times 10^{-4}$ (U [*])	W _{3FLB} (B ^{**})	W _{3Y} $\times 10^{-4}$ (U [*])	χ ²
0.0	3.00	61.60	6.88	15180				7.27		5.25	0.17		8.7E-5
0.8	3.00	61.54	11.49	1751				4.75		3.29	0.17		1.3E-4
1.0	3.04	<u>61.84</u>	15.82	151.6				4.84	327	4.52	0.17		1.1E-4
1.2	3.10	<u>61.10</u>	18.36	119.1				5.66	559			3.79	7.1E-5
1.4	3.01	61.62	<u>18.06</u>	85.72				<u>3.97</u>	488			<u>3.40</u>	4.9E-5
1.7	2.96	62.27	<u>14.19</u>	73.58				<u>2.77</u>	125			<u>5.76</u>	4.0E-5
1.9	2.92	63.24	<u>12.17</u>	56.43				2.58	68.90			7.20	2.2E-5
2.15	2.91	<u>65.83</u>					31.82	5.11	13.95			1.48	5.3E-5
2.4	2.79	<u>68.27</u>					17.32	4.86	11.38			1.42	7.1E-5

The calculated value for R, the resistance of the polymeric bulk blend, was 25 Ω

*U= F/(sec^{0.5}cm²)

**B= (sec^{0.5}/cm²)

Table S4. EIS fitting parameters relative to the LCS01 containing device as a function of the voltage.

BIAS (V)	C1 x10 ⁻⁹ (F/cm ²)	R ₁ (Ω/cm ²)	C2 x10 ⁻⁶ (F/cm ²)	R ₂ (Ω/cm ²)	W2 _{FLY} x10 ⁻⁴ (U*)	W2 _{FLB} (B*)	W2 _Y x10 ⁻⁴ (U*)	C3 x10 ⁻⁶ (F/cm ²)	R ₃ (Ω/cm ²)	W3 _{FLY} x10 ⁻⁴ (U*)	W3 _{FLB} (B**)	W3 _Y x10 ⁻⁴ (U*)	χ ²
0.0	1.32	133.8	15.77	84.52				1.61				2.98	1.5E-4
1.0	2.03	<u>88.81</u>	10.86	74.09				4.11				3.31	1.1E-4
1.2	2.03	<u>89.21</u>	12.35	q				4.07				3.72	1.2E-4
1.4	1.98	<u>90.21</u>	10.81	410.4				3.06				3.08	1.3E-4
1.6	1.98	90.76	<u>9.51</u>	379.7				<u>2.67</u>	335	4.17	0.10		3.9E-5
1.8	1.97	<u>92.96</u>	<u>12.6</u>	217.9				3.88	340			3.64	1.0E-4
2.0	1.87	<u>97.94</u>	<u>12.23</u>	151.9				3.56	216			4.09	8.4E-5
2.2	1.72	<u>107.60</u>	<u>11.08</u>	139.1				2.03	200			4.85	7.9E-5

The calculated value for R, the resistance of the polymeric bulk blend, was 27 Ω

*U= F/(sec^{0.5}cm²)

**B= (sec^{0.5}/cm²)

Table S5. EIS fitting parameters relative to the EP02 containing device as a function of the voltage.

BIAS (V)	C1 x10 ⁻⁹ (F/cm ²)	R ₁ (Ω/cm ²)	C2 x10 ⁻⁶ (F/cm ²)	R ₂ (Ω/cm ²)	W2 _{FLY} x10 ⁻⁴ (U*)	W2 _{FLB} (B*)	W2 _Y x10 ⁻⁴ (U*)	C3 x10 ⁻⁶ (F/cm ²)	R ₃ (Ω/cm ²)	W3 _{FLY} x10 ⁻⁴ (U*)	W3 _{FLB} (B**)	W3 _Y x10 ⁻⁴ (U*)	χ ²
0.0	134.0	2.35			16.77	0.43		11.76	9.53			18.22	1.2E-5
1.1	<u>134.0</u>	<u>2.56</u>			20.69	0.35		8.06	5459			0.43	9.0E-6
1.4	<u>134.5</u>	<u>2.84</u>			32.70	0.15		6.49	550.4			0.68	4.3E-5
1.6	134.6	<u>2.91</u>	<u>9.14</u>	69.44				4.71	69.44			9.59	1.6E-5
1.8	<u>134.5</u>	2.68			27.77	0.38		5.29	66.31			1.10	3.2E-5
2.0	<u>134.4</u>	<u>2.53</u>			24.31	0.37		5.23	58.8			1.20	1.6E-5

The calculated value for R, the resistance of the polymeric bulk blend, was 67 Ω

*U= F/(sec^{0.5}cm²)

**B= (sec^{0.5}/cm²)

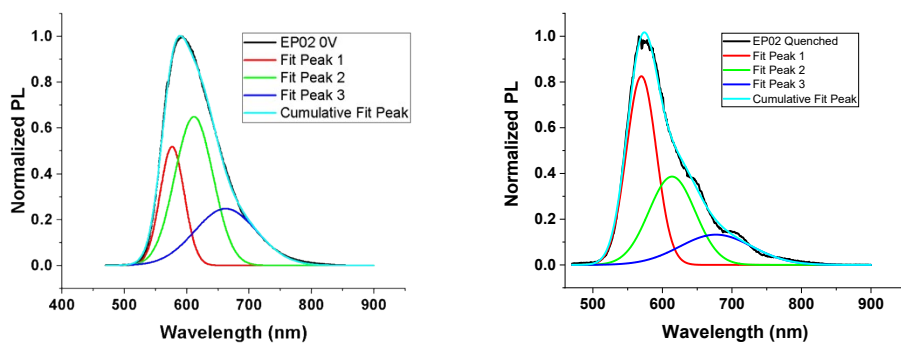


Figure S10. Deconvolution of the emission spectra of EP02-based device at 0.0V and 1.0V ($\lambda_{\text{ex}} = 450 \text{ nm}$).

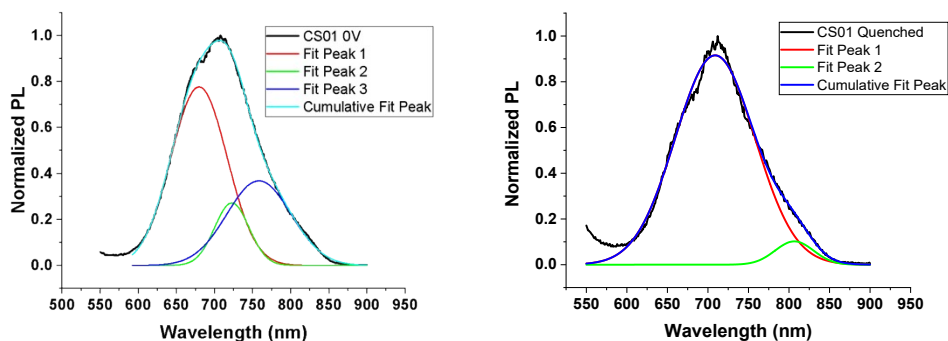


Figure S11. Deconvolution of the emission spectra of CS01-based device at 0.0V and 1.5V ($\lambda_{\text{ex}} = 520 \text{ nm}$).

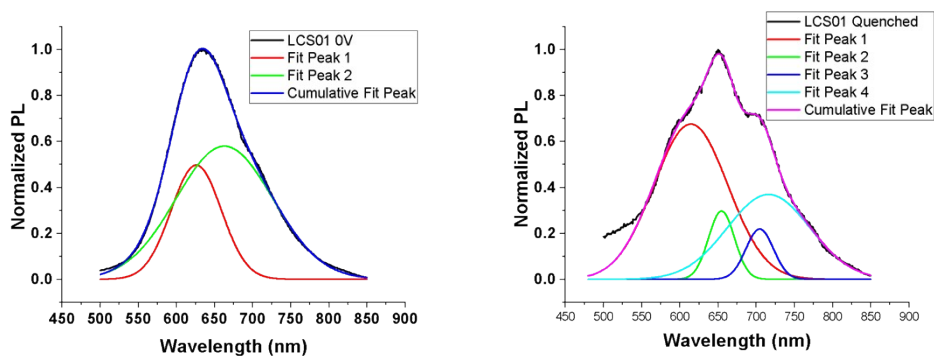


Figure S12. Deconvolution of the emission spectra of LCS01-based device at 0.0V and 1.6V ($\lambda_{\text{ex}} = 480 \text{ nm}$).

Table S6. Contribution of each fluorescence band to the overall emission of compounds in the gel phase, calculated by the spectral deconvolution at 0V and in the voltage induced quenched state.

		A% _{peak1} (λ nm)	A% _{peak2} (λ nm)	A% _{peak3} (λ nm)	A% _{peak4} (λ nm)	R ²	χ ²
EP02	0,0 V	24 (577)	47 (611)	29 (662)		0.9993	7.4*10 ⁻⁵
	Quenched	48 (570)	34 (614)	18 (677)		0.9977	2.1*10 ⁻⁴
CS01	0,0 V	57 (680)	12 (723)	31 (758)		0.9992	9.8*10 ⁻⁵
	Quenched	95 (709)	5 (807)			0.9849	1.5*10 ⁻³
LCS01	0,0 V	31 (626)	69 (663)			0.9993	8.1*10 ⁻⁵
	Quenched	54 (615)	8 (655)	6 (705)	32 (716)	0.9888	1.1*10 ⁻⁴