Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

A tunable color palette of electrochromic materials achieved through an ingenious stacking of ordinary conducting polymers

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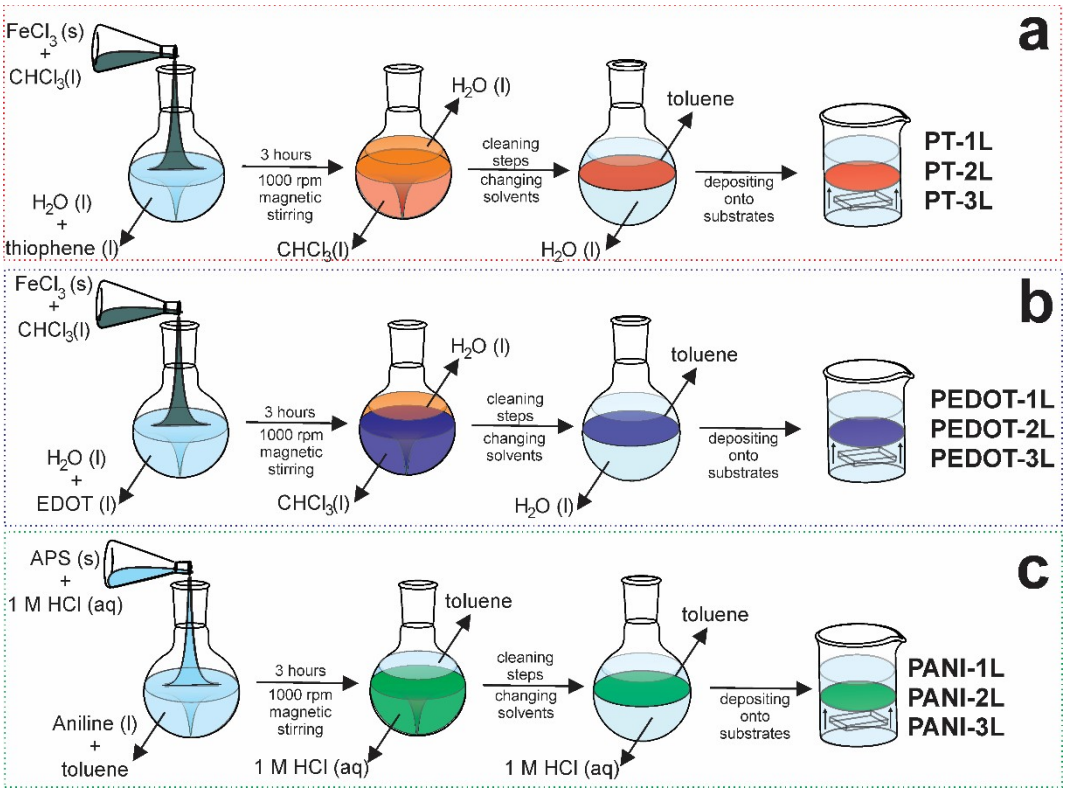

Figure S1. Synthesis of the ECPs. Schematic representation of liquid-liquid interfacial route to produce self-assembly thin film of a) polythiophene (PT), b) polydioxythiophene (PEDOT), and c) polyaniline (PANI).

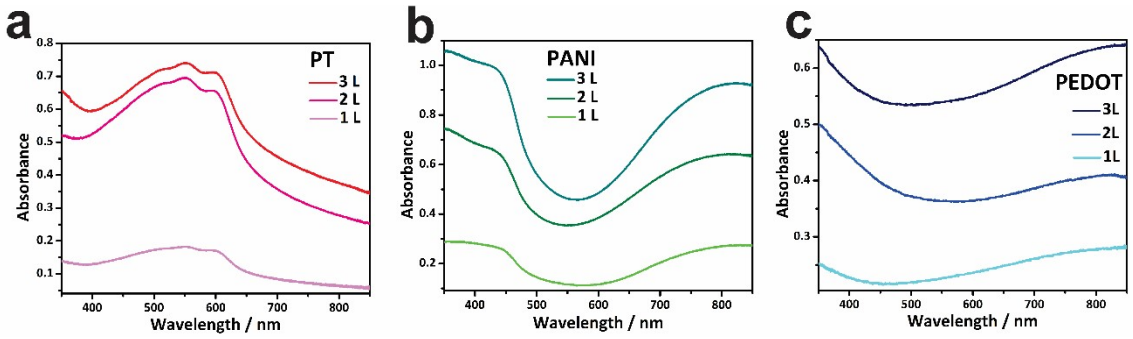

Figure S2. Absorbance spectra of the original ECP films with different number of layers.

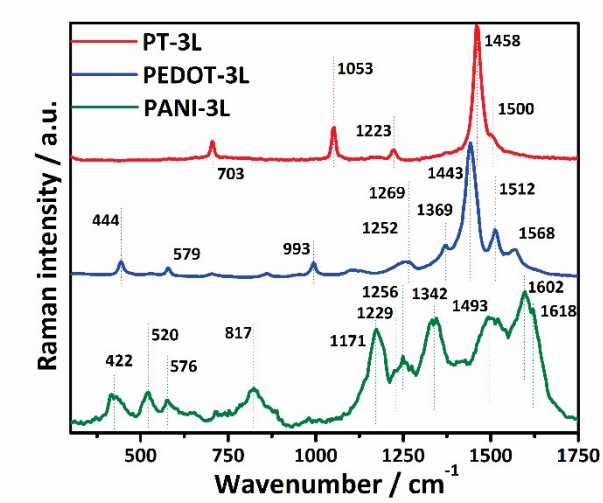

Figure S3. Raman spectra of the original ECPs films.

The Raman spectra of original ECPs films are presented in Figure S3: In the spectrum of the PT-3L sample it is noticing the presence of the fingerprint bands related to the neutral form of polythiophene at 703 cm^{-1} (C-S stretching and C-S-C deformation); 1053 cm^{-1} (C-C thiophene rings deformation); 1223 cm^{-1} (C-C thiophene rings stretching); 1458 cm^{-1} and 1500 cm^{-1} (the C=C symmetric A_g, and anti-symmetric B_{1g} stretching, respectively)[1,2]. The spectrum of the PEDOT-3L sample presents all the bands related to the oxidized form of the polymer, at 1568 cm^{-1} and 1512 cm^{-1} (asymmetric stretching C_α=C_β); 1443 cm^{-1} (symmetric stretching C_α=C_β);

1369 cm^{-1} (symmetric stretching C_β-C_β); 1269 cm^{-1} (inter-ring stretching C_α-C_α); 1104 cm^{-1} (deformation C-O-C), 993, 579 and 444 cm^{-1} (deformation of ethylenedioxy ring)[3,4]. The spectrum of the PANI-3L sample presents the bands of the semi-oxidized and protonated structure of polyaniline, the so-called emeraldine salt, at 1271 cm^{-1} (C-H quinoid ring deformation - bipolaronic structure); 1256 cm^{-1} (C-N stretching of polaronic unities); 1342 cm^{-1} (stretching of radical cations of delocalized polaron); 1493 cm^{-1} (C=N stretching in deprotonated diimine quinoid units); 1602 cm^{-1} (C=C stretching of the quinoid ring); 1618 cm^{-1} (C-C stretching of benzenoid rings), 817 cm^{-1} (C-H deformation of quinoid rings outside the plane); 576 cm^{-1} (reticulate portion of tertiary amines); 520 cm^{-1} and 422 cm^{-1} (C-C deformation)[5–9].

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Table S1. Chromaticity values.

	Sample	L*	a*	b*
1	PT-3L	50.40	23.36	12.66
2	PT-1L	74.76	12.63	2.18
3	PEDOT-1L/ PT-1L	54.63	7,57	-1.13
4	PEDOT-2L/PT-1L	53.84	6.65	-2.23
5	PEDOT-3L /PT-1L	42.91	5.96	0.51
6	PEDOT-3L	56.21	-0.75	-9.98
7	PEDOT-3L /PANI-1L	30.82	-6.13	-4,28
8	PEDOT-2L /PANI-1L	38,70	-8.68	-1.32
9	PANI-1L/PEDOT-1L	51.14	-12.21	0.86
10	PANI-3L	45.15	-20.07	7.13
11	PANI-1L	73.79	-9.80	4.11
12	PT-1L/ PANI-1L SD	68.83	-2.87	18.89
13	PT-2L/ PANI-1L SD	52.01	4.44	16.94

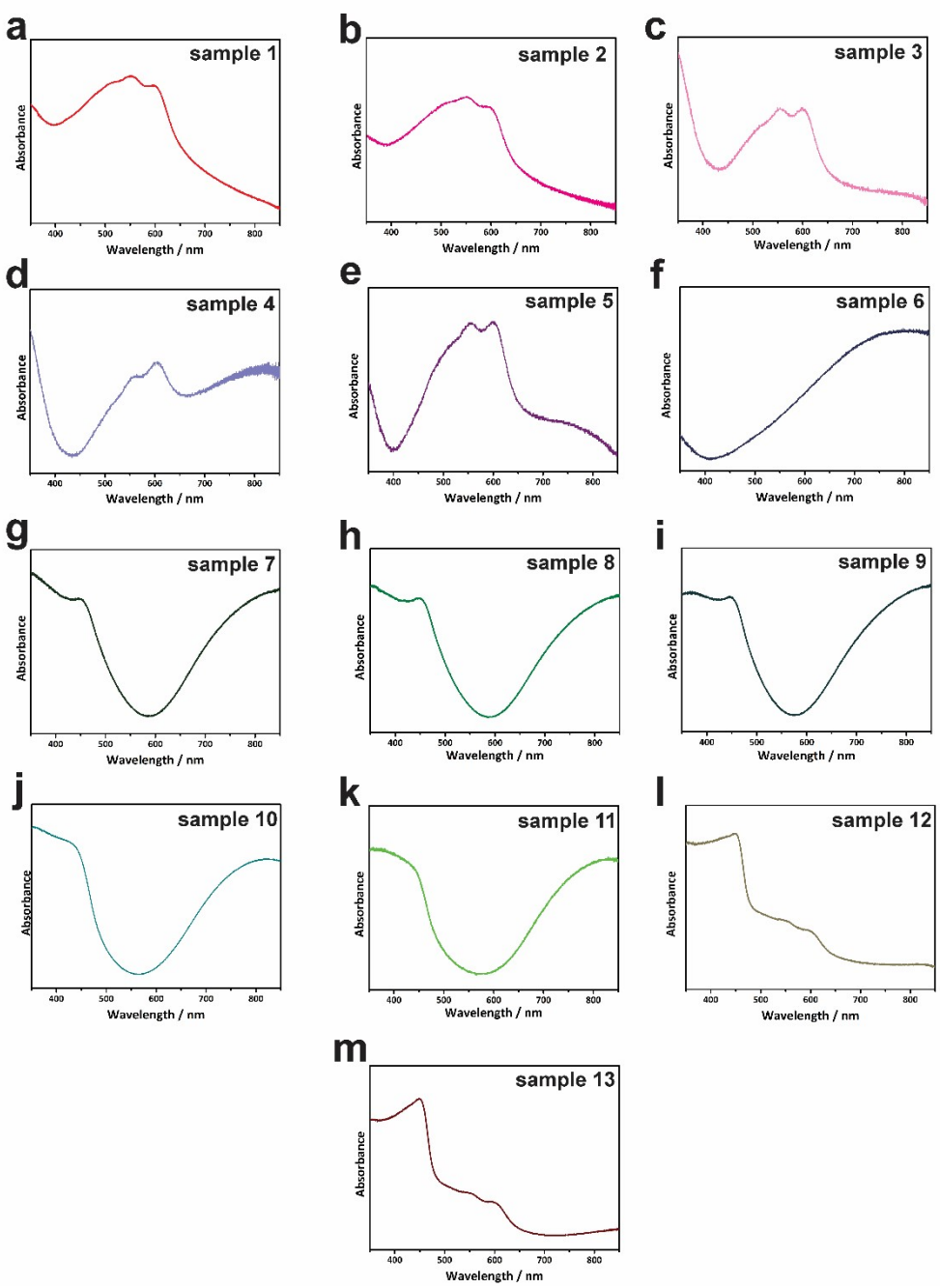

Figure S4. UV-Vis spectra of the 13 samples.

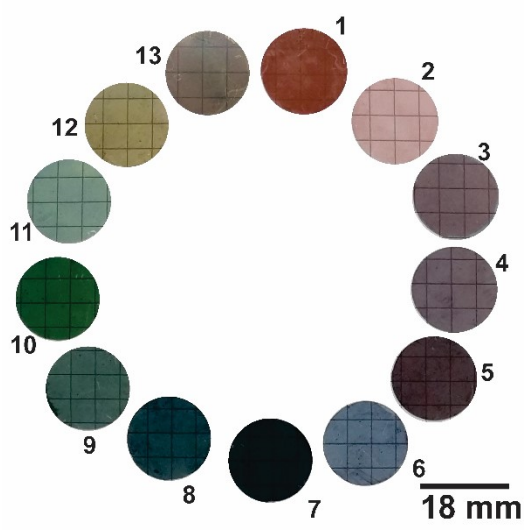

Figure S5. Color-palette films deposited over a glass substrate and photographed over a squared paper.

Table S2. Thickness (nm) and conductivity (S m^{-1}).

	Sample	Thickness / nm	σ / S m^{-1}
1	PT-3L	66 ± 8	not detectable
2	PT-1L	24 ± 6	not detectable
3	PEDOT-1L/ PT-1L	234 ± 47	0.15
4	PEDOT-2L/PT-1L	547 ± 71	0.22
5	PEDOT-3L /PT-1L	759 ± 89	0.60
6	PEDOT-3L	231 ± 25	1.37
7	PEDOT-3L /PANI-1L	629 ± 67	4.22
8	PEDOT-2L /PANI-1L	614 ± 55	15.13
9	PANI-1L/PEDOT-1L	293 ± 25	0.03
10	PANI-3L	503 ± 61	1.03
11	PANI-1L	116 ± 11	0.10
12	PT-1L/ PANI-1L SD	248 ± 17	1247.30
13	PT-2L/ PANI-1L SD	314 ± 13	1273.76

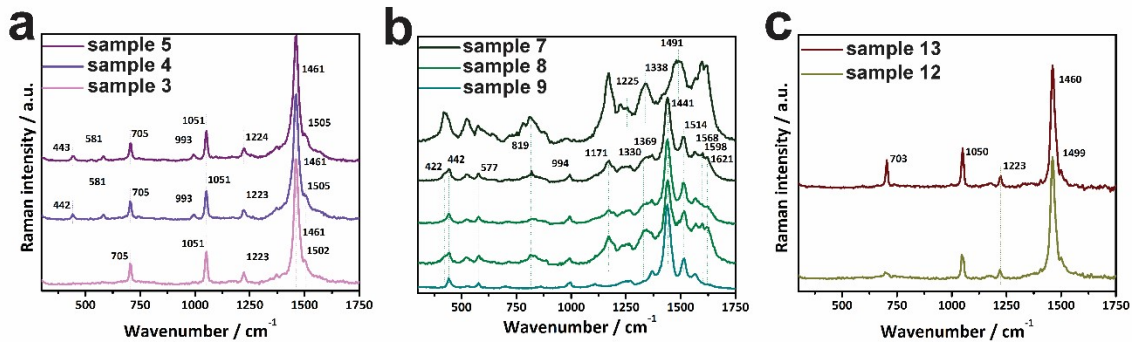

Figure S6. Representative Raman spectra of the color palette samples. (a) Sample 3 (light pink), sample 4 (violet), sample 5 (purple); (b) sample 9 (teal, one spectrum), sample 8 (green, two spectra), sample 7 (dark green, two spectra); (c) sample 12 (dark yellow), sample 12 (brown).

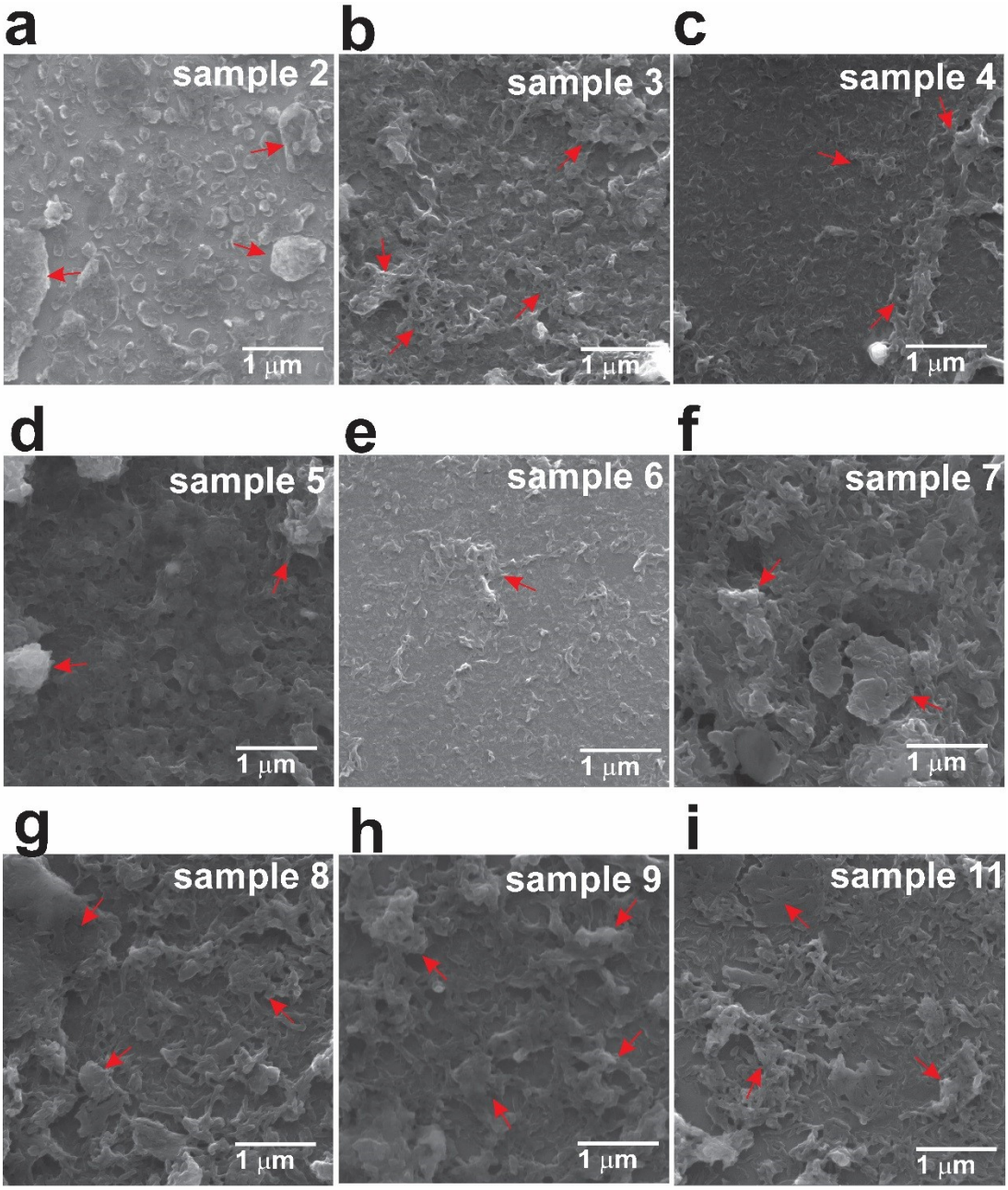

Figure S7. Scanning electron microscopy images of original and stacking samples. Red arrows point out the fibrillary aggregates of polymers.

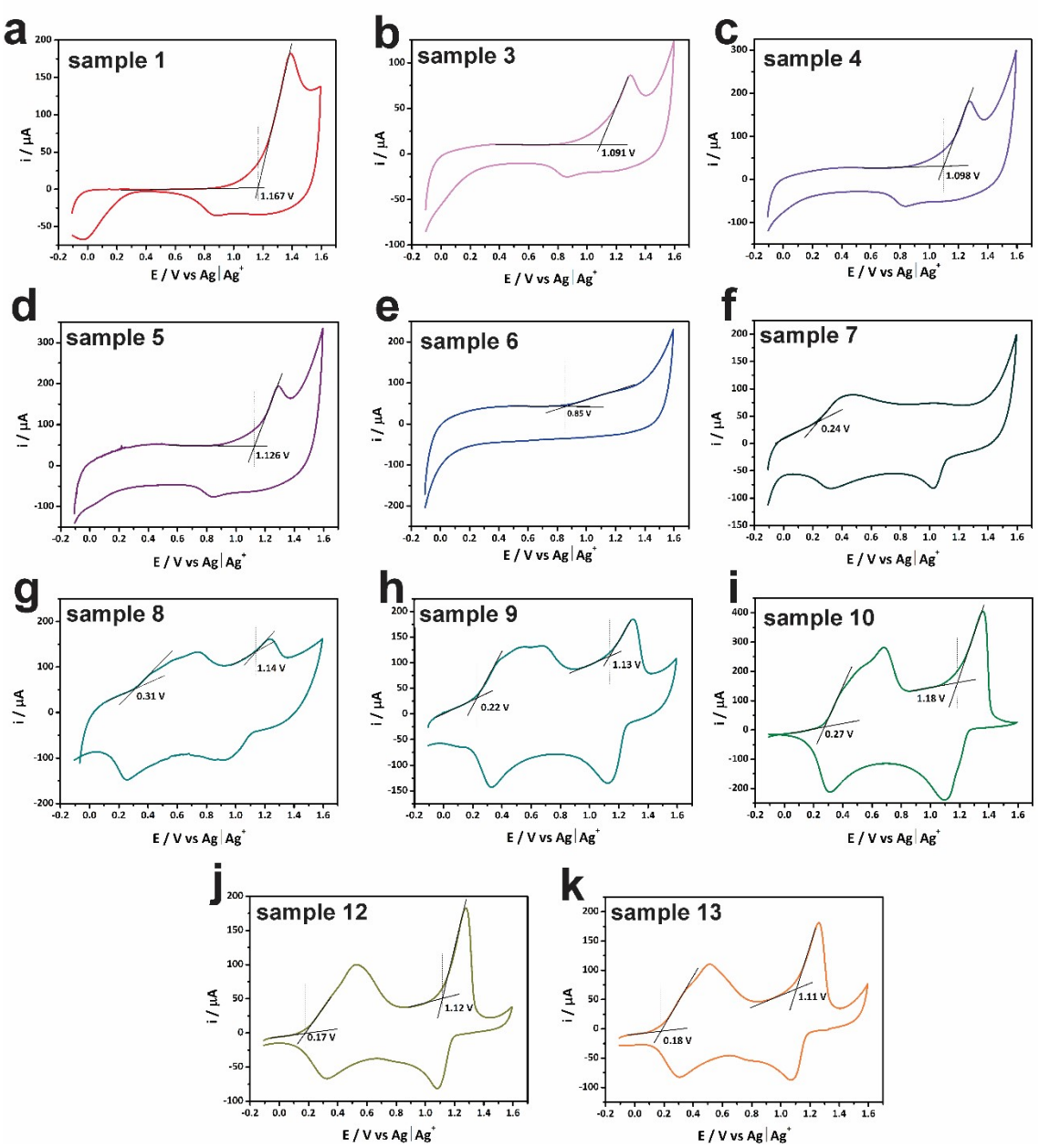

Figure S8. Cyclic voltammetry curves showing onset potentials were recorded at 10 mV s^{-1} in acetonitrile with lithium perchlorate 0.1 mol L^{-1}. The electrochemical potential was calibrated using the ferrocene/ferrocenium redox pair. The electrolyte was bubbling with N_2(g) for 10 minutes previously each measurement.

Table S3. Transmittance of the electrochromic samples in their reduced and oxidized state at highest/lowest wavelength absorption.

	Sample	T / % at -0.1 V	T / % at 1.5 V
1	PT 3L - 547nm	21	36
3	PEDOT-1L/PT-1L - 547nm	35	51
3	PEDOT-1L/PT-1L - 570nm	36	49
4	PEDOT-2L/PT-1L - 547nm	22	32
4	PEDOT-2L/PT-1L - 570nm	22	32
5	PEDOT-3L/PT 1L - 547nm	13	35
5	PEDOT-3L/PT-1L - 570nm	14	31
6	PEDOT-3L - 570nm	31	45
7	PEDOT-3L/PANI-1L - 570nm	15	18
7	PEDOT-3L/PANI-1L - 800nm	19	12
8	PEDOT-2L/PANI-1L - 605nm	20	34
9	PANI-1L/PEDOT-1L - 627 nm	40	42
10	PANI-3L - 669nm	27	16
11	PANI-1L - 669nm	67	49
12	PT-1L/PANI-1L - SD - 680nm	63	32
13	PT-2L/PANI-1L - SD - 680nm	70	28

Table S4. Electrochromic parameters for PEDOT-1L/PT-1L.

Cycle	Qoxi/ mC cm^{-2}	Qred/ mC cm^{-2}	CE/%	Toxi/%	Tred/ %	ΔOD	ηred/ cm^2 C^{-1}	ηoxi/ cm^2 C^{-1}	τred / s	τoxi / s
1	1,6	1,6	102	52,9	34,6	0,18	114,7	112,5	3,3	3,5
50	0,9	0,9	100	45,8	37,0	0,09	100,2	99,5	6,5	14,1

Electrode area = 1.4 cm^2; Qoxi is the charge of the oxidized state and Qred is the charge in the reduced state; CE is the Coulombic Efficiency, Toxi and Tred are the transmittances at the oxidized and reduced state, respectively; ΔOD is the optical density; ηred and ηoxi are the coloration efficiency at the reduced and oxidized state, respectively; τred and τoxi are the response time at the reduced and oxidized state, respectively.

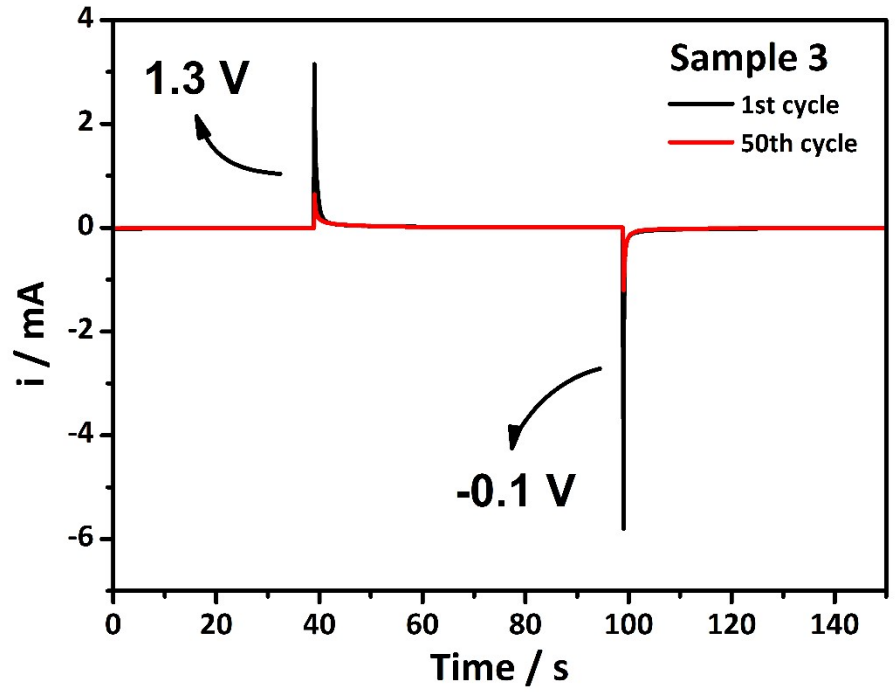

Figure S9. Chronoamperograms curves. Current response during time as a function of the applied potential for the 1st and 50th cycles for PEDOT-1L/PT-1L.