

A NEW STANDARD METHOD TO CALCULATE ELECTROCHROMIC SWITCHING TIME

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Experimental Section

Conjugated electrochromic polymers

P[ProDOT_m-BTD] films and devices

A black-to-clear 3,4-propylenedioxythiophene/benzothiadiazole-based P[ProDOT_m-BTD] random copolymer (M_n : 10 kDa, dispersity: 1.6) was synthesized using Stille cross-coupling [1]. P[ProDOT_m-BTD] films were deposited onto ITO glass substrates (PGO, 50mm x 7 mm x 0.7 mm, 8–10 Ω /sq) using an airbrush spray gun connected to a nitrogen line from a deposition solution of 5mg/ml polymer in toluene (ACS (99.5%), Alfa Aesar). Gas pressure and gun-substrate distance were kept fixed during all the experiments (0.2bar, 12cm). A silver wire was used as a pseudo-reference electrode (calibrated 0.1 V vs. NHE), a stainless steel plate as the counter electrode, and 0.1 M LiCF₃SO₃-propylene carbonate (PC, Sigma Aldrich, anhydrous, 99.7 %) as the electrolyte in all electrochemical measurements. The optical and electrochemical measurements were carried out in a cuvette sized glass cell (12 mm x 12 mm x 45 mm). A Cary 50 UV-Vis spectrophotometer was used for optical characterization and a Biologic SP-50 potentiostat was used for the electrochemical measurements. For both film and device measurements, the instrument was blanked vs. air. Potential pulse lengths applied were 30, 25, 20, 15, 10, 5, 3 and 1s. Transmittances in the bleached and colored states were recorded at λ_{max} , 500 nm (Fig. S1a).

For the devices, a minimally color changing dioxypyrrole polymer (MCCP) [2] was synthesized via dehalogenative polycondensation (M_n : 97.9; dispersity: 1.75). MCCP was dissolved at 5 mg/mL and spray coated onto 50mm x 7 mm x 0.7 mm (8–10 Ω /sq) ITO slides. Liquid electrolyte devices were assembled using MCCP films as counterelectrode with 0.1 M LiCF₃SO₃/PC as the electrolyte. Fixed redox capacity (4 mCcm⁻²) P[ProDOT_m-BTD] films were used for all cells, whereas variable redox capacity MCCP films, ranging from 2.8 to 5.6 mCcm⁻² were used. Devices were switched between 1 and -0.6 V. Redox capacities of the films were calculated from 20 mV/s cyclic voltammograms, 0.3 V and +1.3 V vs. NHE for P[ProDOT_m-BTD] films, 0.05 V and 1.15 V vs. NHE for MCCP.

PProDOT-(CH₂OEtHx)₂ films and devices

PProDOT-(CH₂OEtHx)₂ (M_n: 14.9 kDa; dispersity:1.3) was synthesized via direct arylation polymerization[3] and dissolved in toluene at 5 mg/mL. The films were deposited via spray coating using the same model spray gun as described above at approximately 20 psi onto ITO slides with a sheet resistance of 8-12 Ω/sq purchased from Delta Technologies Ltd. (25 mm x 75 mm x 0.7 mm for the two-electrode measurements and 7 mm x 50mm x 0.7 mm for the three-electrode measurements). Tetrabutylammonium hexafluorophosphate (TBAPF₆, Acros Organics 98%) was recrystallized from hot ethanol (2.5:1 w/w, ethanol:TBAPF₆) and dried overnight in a vacuum oven (60° C). PC (Acros Organics, 99.5%) was purified using a solvent purification system from Vac Atmospheres. Liquid electrolyte was prepared by dissolving 0.5 M TBAPF₆ in PC. Electrochemical measurements were performed using an EG&G PAR 273 potentiostat/galvanostat. Spectroscopic measurements were performed using an Ocean Optics USB2000+ spectrophotometer with a DH-2000-BAL fiber-optic light source. For film measurements, the instrument was blanked vs. the ITO substrate; for device measurements, the instrument was blanked versus air. PProDOT-(CH₂OEtHx)₂ films were tested in a cuvette size cell, with platinum flag counterelectrode and Ag/Ag⁺ as RE (0.55 vs. NHE). PProDOT-(OEtHx)₂ was spray coated to various thicknesses and the charge to switch was estimated from a CV at 50 mV/s from 0.05 V to 1.35 V vs. NHE. Switching kinetics were monitored at λ_{max} (ca. 550 nm) (Fig. S1b) for films switched between 0.05 V to 1.35 V vs. NHE in the second, using the following switching times: 30, 20, 15, 10, 5, 2, 1, 0.5, 0.25 s.

For the devices (ca. 5 cm²), MCCP [2] (synthesized via dehalogenative polycondensation (M_n: 97.9; dispersity: 1.75) was dissolved at 5 mg/mL and spray coated onto 25 mm x 75 mm x 0.7 mm (8–10 Ω/sq) ITO slides. MCCP was sprayed to a thickness that provided a comparable charge to switch (determined by CV at 50 mV/s, from 0.05 V to 1.15 V vs. NHE). Devices were assembled by first pre-oxidizing the MCCP film by applying 1.15 V for 30 s. A UV curable electrolyte was prepared according to a previously published procedure [4], sandwiched between the oxidized MCCP film, and the neutral PProDOT-(CH₂OEtHx)₂ film, and cured for 1 min at 365 nm in a UV chamber (UVP CL-1000). The switching kinetics of the devices were analyzed using the same pulse lengths as for the films between -1 V and + 1 V.

PProDOT-Et₂

3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (ProDOT-Et₂) (Sycon) films were electropolymerized onto ITO glass substrates in a two step method from a monomer solution containing 10 mM of ProDOT-Et₂, 0.1 M LiClO₄(Fluka, >98 %) in acetonitrile (Sigma-Aldrich). First, a potential of 2.1 V vs. NHE was applied for 0.05 s, followed by applying 1.6 V vs. NHE where the time was varied to control redox capacity of the obtained films. The redox capacities of the films were calculated from 20 mV/s CVs, between -0.2 V and 0.8 V vs. NHE. The switching kinetics were monitored by switching the potential between -0.2 V and 0.8 V for 30, 25, 20, 15, 10, 5, 3 and 1s. Transmittances in the bleached and colored states were recorded at λ_{max}, 566 nm (Fig. S1c).

Transition metal oxides

WO₃, NiO and V₂O₅ thin films were deposited on 2.5×2.5 cm²ITOcoated glasses (SOLEMS, ~30Ω/sq) by reactive RF magnetron sputtering. The targets (Neyco) were 75 mm diameter tungsten oxide (99.99%), pure nickel (99.99%), and pure vanadium (99.99%). The distance from the substrate to the target fixed at 8 cm. The gas-flow ratio of Ar (99.99 %) to O₂ (99.99 %) was fixed by mass flow controllers at 49:1 (sccm), 98:2 (sccm) and 80:20 (sccm), corresponding working pressure of 2 Pa, 4 Pa and 2 Pa for WO₃, NiO, V₂O₅, respectively. The power was maintained at 90 W for WO₃ and NiO, and at 200W for V₂O₅. Different deposition times were used to obtain various thicknesses, ranging from 11-12 nm/min, 18-20 nm/min and 7-12 nm/min for WO₃, NiO and V₂O₅, respectively.

The electrochemical properties of the films were characterized in liquid electrolyte in a three-electrode cell with Pt as counter electrode and Saturated Calomel Electrode as reference electrode (0.241V vs. NHE). Electrolytes used were 1:9 Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Solvionic) in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) (Solvionic) ionic liquid electrolyte for WO₃ and V₂O₅, 1 M H₃PO₄(Aldrich) (aq) for WO₃ and 1M KOH (Aldrich) (aq) for NiO. WO₃ films were tested between -0.6 V and 0.8 V in an aqueous electrolyte solution and between -0.8 V and 1.4 V in IL solution; NiO films were tested between -0.6 V and 0.6 V in aqueous solution; V₂O₅ films were tested between 1.1 and -0.3 V (all potentials referred to NHE).

Electrochemical characterization was performed using a Voltalab PG201 potentiostat. In situ optical transmittance measurements were carried using a Varian Cary UV-Visible-NIR spectrophotometer blanked vs. air.

2.5×2.5 cm² WO₃/V₂O₅ devices were assembled with a 0.3M LiTFSI-BMITFSI electrolyte incorporating 40% poly(methylmethacrylate) (PMMA). The transparent viscous mixture of ionic liquid with 40 % PMMA was spread under ambient atmosphere on the WO₃ and V₂O₅ electrochromic layers using a syringe and dried for 2 h at 80 °C under vacuum (~100 Pa), forming hydrophobic, sticky lithium conducting electrolyte membranes. Prior to device assembly, WO₃ and V₂O₅ thin films were cycled in 1:9LiTFSI–EMITFSI electrolyte for few cycles and assembled with the former in its bleached state and the latter in its colored one. Potentials applied to the devices were -1 V and 2 V.

The switching times were monitored at 550 nm for WO₃, NiO and V₂O₅ films (Figs. S1d, S1e, S1f), and 570 nm for WO₃/V₂O₅ devices. For the different films and devices nine switching times from the following set were applied: 1, 3, 5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 180, 300, 600 s.

Viologens

4,4'-bipyridyl (98%), ethyl bromide (98%), poly(vinyl alcohol) (PVA, Mw: 61 000), sodium tetraborate (borax, 99.5%), potassium ferrocyanide (98.5%), and potassium ferricyanide (99%),

were purchased from Sigma-Aldrich and used without further purification. Required solvents such as acetone and acetonitrile were purchased from Scharlab and used as received. Fluorine-doped tin oxide (FTO) coated glass substrates provided by Solems (R_s 6-8 Ωsq^{-1}) were washed with heated acetone before being used. 1,1'-Diethyl-4,4'-bipyridinium dibromide (ethyl viologen dibromide) was synthesized according to previously reported procedure[5]. ^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).

EC gels comprising varying concentration of ethyl viologen dibromide (EtVio) (2.5, 5.0, 7.5, 10.0 and 15.0 mmol L^{-1}) and a fixed concentration of complementary redox pair ferro/ferricyanide potassium salts (6 mmol L^{-1} of each) were prepared according to a previously reported procedure [6]. Briefly, appropriate amounts of potassium ferro/ferricyanide and EtVio were added to a 4% solution of PVA and stirred until complete homogenization was obtained. Afterwards, 4% sodium tetraborate solution was poured into the mixture in a 1:4 volumetric ratio (borax:PVA). The gel obtained after stirring with spatula was allowed to settle overnight.

The $2 \times 1.8 \text{ cm}^2$ two-electrode ECDs were prepared as follows: the EC gel was spread on the FTO-coated side of one of the substrates with a $220 \mu\text{m}$ double-side adhesive tape frame used as spacer. Then, it was covered with the other electrode substrate, applying light pressure, and both electrodes were clipped using paper clip clamps.

UV-Vis responses of the devices were obtained on a Jasco V-570 spectrophotometer using air as the background, while electrochemical measurements were performed with a Biologic MPG potentiostat-galvanostat.

Devices were submitted to 0 and -2 V steps using the following times: 60, 45, 30, 20, 10, 5 and 3s, while transmittance changes were registered at λ_{max} (532nm) (Fig. S1g). For asymmetrical switching the corresponding step was fixed to 55 s while varying the length of the opposite potential step between 70, 50, 40, 20, 10 and 5s.

Figures and tables

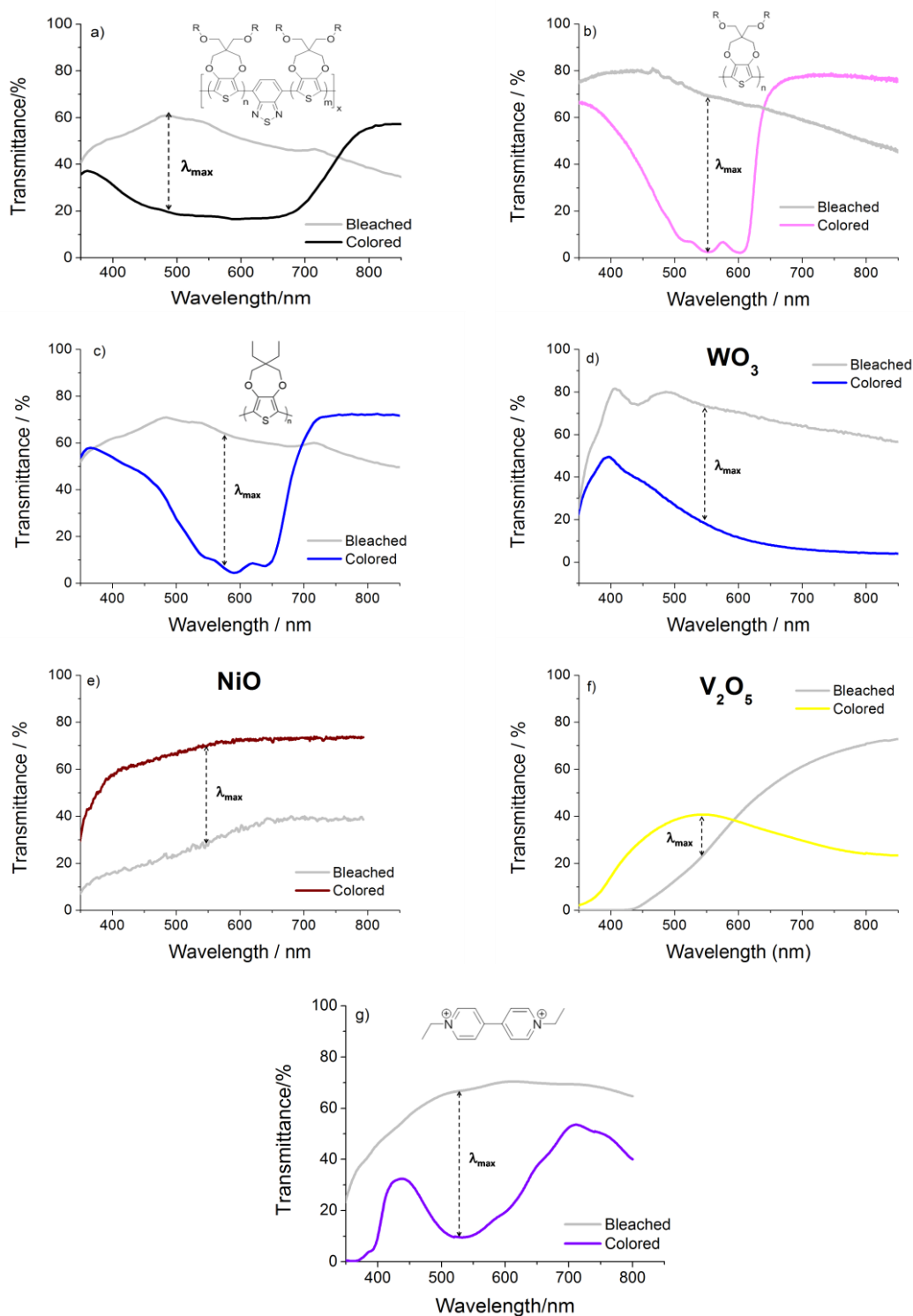


Figure S1. Transmittance spectra of the different materials tested in the study a) 4 mCcm⁻² P[ProDOT_m-BTD]film b) 2.89 mCcm⁻² PProDOT-(CH₂OEtHx)₂ film c) 1.9 mCcm⁻² PProDOT-Et₂ film d) 470 nm WO₃ film e) 350 nm NiO film f) 679 nm V₂O₅ film g) 15 mM EtViO device.

Table S1. Initial set of P[ProDOT_m-BTD] films with varying redox capacity. Contrast vs. step time fittings to a $f(t) = a(1 - e^{-bt})$ function were performed. Parameters a and b obtained for each film are shown in the second and third columns. The parameter τ is the inverse of b , and t_{90} is obtained as $t_{90} = \tau \ln 10$. The last column shows the regression coefficients obtained.

Redox capacity (mC/cm ²)	a (%T)	b (s ⁻¹)	τ (s)	t_{90} (s)	r^2
1.8	33.9	1.97	0.5	1.2	0.950
2.1	28.9	1.26	0.8	1.8	0.927
3.0	29.6	0.74	1.4	3.1	0.984
3.2	40.4	0.70	1.4	3.3	0.976
3.5	37.7	1.01	1.0	2.3	0.993
3.5	35.8	0.62	1.6	3.7	0.960
3.7	26.4	0.58	1.7	3.9	0.986
4.0	39.7	0.60	1.7	3.8	0.974
4.0	39.2	0.63	1.6	3.7	0.983
4.0	37.7	0.57	1.8	4.0	0.963
4.0	39.6	0.59	1.7	3.9	0.982
4.0	34.1	0.69	1.4	3.3	0.983
4.1	38.4	0.51	2.0	4.5	0.982
4.2	38.8	0.85	1.2	2.7	0.995
4.2	40.8	0.79	1.3	2.9	0.997
4.3	38.4	0.54	1.9	4.3	0.973
4.3	36.5	0.72	1.4	3.2	0.988
4.3	40.7	0.55	1.8	4.2	0.945
4.3	40.0	0.78	1.3	3.0	0.995
4.6	40.1	0.68	1.5	3.4	0.994
4.6	34.2	0.51	2.0	4.5	0.903
5.0	32.8	0.48	2.1	4.8	0.960
5.0	35.3	0.44	2.3	5.2	0.962
5.5	28.1	0.45	2.2	5.1	0.988
6.0	40.0	0.41	2.4	5.6	0.963
6.5	22.3	0.34	2.9	6.7	0.987
7.7	20.8	0.39	2.6	6.0	0.990

Table S2. Main experimental conditions for the materials and devices tested

Material	λ /nm	Electrolyte	Applied potential / V vs. NHE	Pulse lengths/s
P[ProDOT _m -BTD]	500	0.1 M LiCF ₃ SO ₃ -PC	+0.30 / +1.30	30-25-20-15-10-5-3-1
PProDOT-Et ₂	566	0.1 M LiCF ₃ SO ₃ -PC	-0.20 / +0.80	30-25-20-15-10-5-3-1
PProDOT-(CH ₂ OEtHx) ₂	550	0.1 M TBAPF ₆ -PC	+0.05 / +1.35	30-25-20-15-10-5-2-1-0.5-0.25
WO ₃	550	1M H ₃ PO ₄ -aq	-0.60 / +0.80	30-25-20-15-10-5-3-1
WO ₃	550	1:9 LiTFSI-EMITFSI	-0.60 / +1.60	300-120-60-30-15-10-5-3-1
V ₂ O ₅	550	1:9LiTFSI-EMITFSI	-0.30 / +1.10	90-60-40-20-15-10-5-3-1
NiO	550	1M KOH-aq	-0.60 / +0.60	30-25-20-15-10-5-3-1
Device	λ /nm	Electrolyte	Applied potential / V	Pulse lengths/s
P[ProDOT _m -BTD]/ MCCP	500	0.1 M LiCF ₃ SO ₃ -PC	-0.6 / +1.0	30-25-20-15-10-5-3-1
PProDOT-(CH ₂ OEtHx) ₂ / MCCP	550	0.5 M LiCF ₃ SO ₃ - PC-PMMA	-1.0 / +1.0	30-20-15-10-5-2-1-0.5-0.25
WO ₃ / V ₂ O ₅	570	LiTFSI-BMITFSI, 40% PMMA	-1.0 / +1.0	600-300-120-60-20-10-5-3-1
EtVio ²⁺ / [Fe(CN) ₆] ⁴⁻	532	EtVio Borax-PVA	-2.0 / +0.0	60-45-30-20-10-5-3

Table S3. Additional conjugated polymers tested. Full-switch contrast, time constant (τ), and regression coefficient obtained from $a\Delta T(t) = \Delta T_{max}(1 - e^{-\frac{t}{\tau}})$ fitting. t_{90} is obtained as $t_{90} = \tau \ln 10$

	Redoxcapacity (mC/cm ²)	Contrast (%T)	τ (s)	t_{90} (s)	r^2
PProDOT-(CH ₂ OEtHx) ₂	1.5	71.1	0.2	0.5	0.967
	2.0	71.8	0.2	0.5	0.995
	2.3	78.0	0.2	0.6	0.989
	2.9	66.7	0.4	0.9	0.973
	3.4	77.4	0.4	0.8	0.986
PProDOT-Et ₂	1.9	57.6	1.2	2.8	0.994

Table S4. Transition metal oxides tested. Full-switch contrast, time constant (τ), and regression coefficient obtained from a $\Delta T(t) = \Delta T_{max} \left(1 - e^{-\frac{t}{\tau}}\right)$ fitting. t_{90} is obtained as $t_{90} = \tau \ln 10$

	Thickness (nm)	Contrast(%T)	τ (s)	t_{90} (s)	r^2
WO₃					
Aqueous electrolyte	350	55.8	2.5	5.7	0.941
Ionic liquid electrolyte	80	17.4	3.5	8.1	0.995
	160	41.5	5.7	13.2	0.995
	240	54.0	10.2	23.4	0.992
	350	68.5	16.0	36.8	0.952
	360	42.2	7.7	17.7	0.997
	470	73.7	19.0	43.7	0.981
	570	77.1	24.6	56.7	0.919
V₂O₅					
	93	11.4	6.1	14.0	0.973
	313	27.3	10.1	23.3	0.945
	455	37.0	9.5	21.9	0.948
	679	39.8	26.6	61.2	0.963
	828	22.0	13.5	31.1	0.986
NiO					
	350	79.9	2.3	5.4	0.996

Table S5. Switching times for various EC devices. Full-switch contrast, time constant (τ), and regression coefficient obtained from a $\Delta T(t) = \Delta T_{max}(1 - e^{-\frac{t}{\tau}})$ fitting. t_{90} is obtained as $t_{90} = \tau \ln 10$

	Contrast (%T)	τ (s)	t_{90} (s)	r^2
PProDOT-(CH₂OEtHx)₂/MCCP				
Redox capacity (mC/cm²)				
0.85	48.8	0.2	0.5	0.979
0.98	46.5	0.3	0.6	0.904
1.18	52.5	0.2	0.5	0.881
1.24	52.9	0.3	0.7	0.949
2.08	42.5	0.6	1.4	0.915
P[ProDOT_m-BTD]/MCCP				
Redox capacity ratio MCCP/ P[ProDOT_m-BTD]^(*)				
0.7	34.5	2.0	4.7	0.984
0.9	38.0	2.4	5.4	0.983
1.2	36.7	4.9	11.3	0.993
1.4	38.5	3.8	8.7	0.986
WO₃ / V₂O₅				
Redox capacity (mC/cm²)				
11.0 ^(**)	47.3	16.4	37.9	0.956
3.6 / 33.1	34.1	6.2	14.2	0.966
EtVio²⁺ / [Fe(CN)₆]⁴⁻				
EtVioconcentration (mM)				
15	48.2	4.5	10.5	0.985
10	36.6	5.3	12.1	0.985
7.5	31.2	3.7	8.5	0.987
5	17.8	3.4	7.9	0.983
2.5	5.9	3.6	8.2	0.971

^(*)Redox capacity of P[ProDOT_m-BTD] films was fixed at 4mCcm⁻².

^(**)Redox capacities of both films were similar

Table S6. Comparison of full-switch contrast values obtained from the coloration and bleaching fitting functions between the asymmetrical pulse length method and the experimentally obtained ones.

Redox capacity / mCcm ⁻²	Contrast			
	Coloration		Bleaching	
	Experimental	Fitted	Experimental	Fitted
EtVio²⁺ / [Fe(CN)₆]⁴⁻ (*)	31.2	30.6	31.9	31.7
WO₃/V₂O₅				
11.0/11.0	45.1	45.6	49.7	50.1
3.6 / 33.1	23.6	23.5	24.6	24.9
PProDOT-Et₂				
1.9	56.2	56.6	57.0	57.0
PProDOT-(CH₂OEtHx)₂				
1.5	71.3	72.2	72.2	71.9
2.0	72.1	73.0	72.0	72.6
2.3	79.3	80.1	78.7	79.1
2.9	66.6	67.3	67.7	68.0
3.4	73.1	74.3	72.9	73.4
PProDOT-(CH₂OEtHx)₂/MCCP				
0.85	51.4	51.0	51.2	49.8
0.98	48.7	48.2	47.6	46.5
1.18	53.4	53.3	54.8	53.0
1.24	54.6	54.5	55.4	53.8
2.08	44.7	44.4	45.5	42.9

(*) EtViO concentration 7.5 mM

Table S7. Comparison of regression coefficients obtained from the coloration and bleaching fitting functions between the asymmetrical pulse length method and the symmetrical method

Redox capacity / mCcm ⁻²	Regression coefficient r ²		
	Symmetrical switching method	Asymmetrical switching method	
		Coloration	Bleaching
EtVio²⁺ / [Fe(CN)₆]⁴⁻ (*)	0.987	0.996	0.972
WO₃/V₂O₅			
11.0/11.0	0.956	0.995	0.999
3.6 / 33.1	0.966	0.981	0.954
PProDOT-Et₂			
1.9	0.994	0.951	0.978
PProDOT-(CH₂OEtHx)₂			
1.5	0.967	0.816	0.930
2.0	0.995	0.792	0.911
2.3	0.989	0.825	0.859
2.9	0.973	0.934	0.920
3.4	0.986	0.862	0.900
PProDOT-(CH₂OEtHx)₂/MCCP			
0.85	0.979	0.922	0.973
0.98	0.904	0.815	0.839
1.18	0.881	0.982	0.955
1.24	0.949	0.910	0.979
2.08	0.915	0.948	0.941

(*) EtVIO concentration 7.5 mM

Table S8. Comparison of t_{90} values calculated from the asymmetrical pulse length method, the symmetrical method, and the conventional method.

Redox capacity / mCcm ⁻²	t_{90}				
	Symmetrical variable steps method	Asymmetrical variable steps method		Conventional method	
		Coloration	Bleaching	Coloration	Bleaching
EtVio²⁺ / [Fe(CN)₆]⁴⁻ (*)	8.5	8.2	3.6	8.5	4.5
WO₃/V₂O₅					
11.0/11.0	37.9	11.5	51.2	10.7	36.4
3.6 / 33.1	14.2 ^(**)	5.2	3.2	4.4	5.9
PProDOT-Et₂					
1.9	2.8	3.3	3.4	2	2.3
PProDOT-(CH₂OEtHx)₂					
1.5	0.5	0.9	0.5	0.5	0.4
2.0	0.5	1	0.7	0.5	0.5
2.3	0.6	1.2	0.9	0.6	0.6
2.9	0.9	2	1.4	1.4	0.9
3.4	0.8	2	1.8	0.8	0.9
PProDOT-(CH₂OEtHx)₂/MCCP					
0.85	0.5	0.8	0.3	0.3	0.5
0.98	0.6	0.2	0.4	0.2	1.2
1.18	0.5	0.4	0.6	0.3	1.1
1.24	0.7	0.6	1	0.4	1.4
2.08	1.4	1.1	1.2	0.5	2.8

(*) EtVio concentration 7.5 mM

(**) Significant electrochemical degradation occurred in this device between the symmetrical and asymmetrical experiments. Full-switch contrast fell from 35 % to 24 %. Corresponding t_{90} calculated conventionally was, for the same experiment, 18.7 s, similar to 14.2 s obtained for the symmetrical steps method.

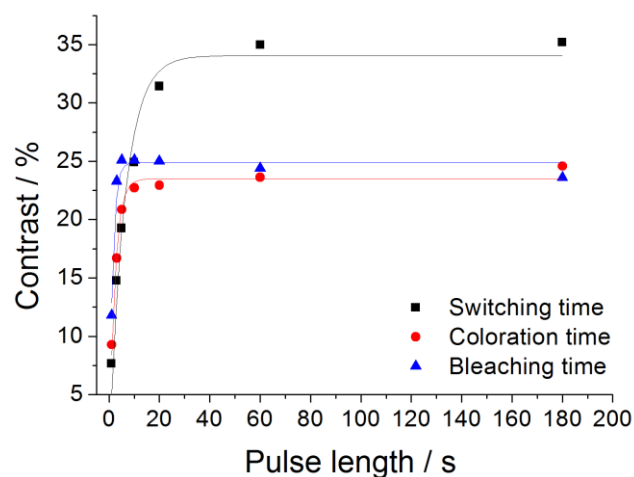


Figure S2. Contrast vs. pulse length plots for $\text{WO}_3/\text{V}_2\text{O}_5$ device (redox capacities $3.6/33.1 \text{ mCcm}^{-2}$) obtained first with the symmetrical method (to obtain switching time) followed by the asymmetrical switching method (to obtain coloration and bleaching times). Significant degradation (that reflects into lower contrast values) occurred between measurements.

References

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