Supplementary Materials

Limitations Imposed Using an Iodide/Triiodide Redox Couple in Solar-Powered Electrochromic Devices

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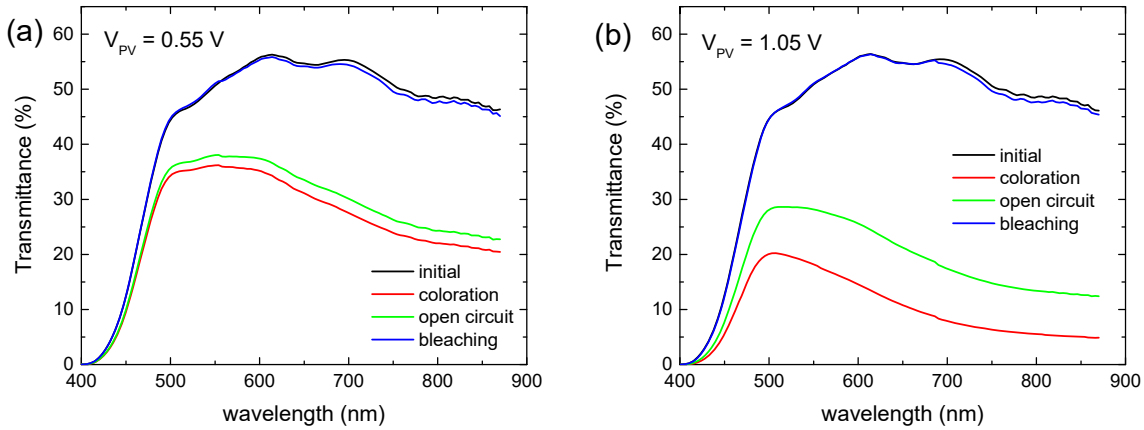
Table S1. Comparative table with hybrid ECDs having different redox electrolytes.

Redox Couple	Optical Modulation (ΔT)	Bias Potential	Switching Time (s)	Nr of Cycles/Operation Time	Ref.
I^- / I_3^-	61.8% (visual)	- 2V / +0.5 V	8*		[1]
Thiolate/disulphide (T^-/T_2)	52 % at 550 nm	- 2.5 V/ + 1.0 V	28 / 15**	50 cycles	[2]
I^- / I_3^-	45 % at 550 nm		5 / 23**		[2]
Fc^+ / Fc	52 %	- 1.5V / 0 V	10 / 22**	10 h	[3]
TMTU/$TMFDS^{2+}$	67.8 % at 648 nm	- 1.2 V / 1.0 V	7.3 / 5.9	> 100,000 cycles	[4]
I^- / I_3^-	44.3 % (vis)	- 1 V	-		[5]
TMTU/$TMFDS^{2+}$	68 % (vis)	- 1 V	-		[5]
TMTU/$TMFDS^{2+}$	55 % (vis)	- 1.5 V / 1.5 V	< 5 min		[6]
I^- / I_3^-	42.9 % (vis)	-0.72 V / 0.6 V	5 min		[7]
TMTU/$TMFDS^{2+}$	57.2 % (vis)	-0.795 V / 0.6 V			[7]
TEMPO/$TEMPO^+$	31.4 % (vis)	-1.035 V / 0.6 V			[7]
TMTU/$TMFDS^{2+}$	32 % (vis)	-2 V / 2 V			[8]
TTF	93 %	-0.9 V / no bias	12 / 28 **	200 cycles	[9]
I^- / I_3^-	30 – 35 % at 634 nm	- 1.5 V / 1.7 V	60 / 60	11,000 cycles	[10]
TMTU/$TMFDS^{2+}$	68.2 % at 603 nm	-1.5 V / 1.2 V	12.8 / 5.3**	10,000 cycles	[11]
I^- / I_3^-	59.4 %	- 1.8 V / 1.2 V	3.1 / 1.9**		[12]
I^- / I_3^-					Our work

*: the time to achieve a reduction of the transmittance by a factor of 10; **: τc and τb represents the time to modulate the 90% of the maximum ΔT.



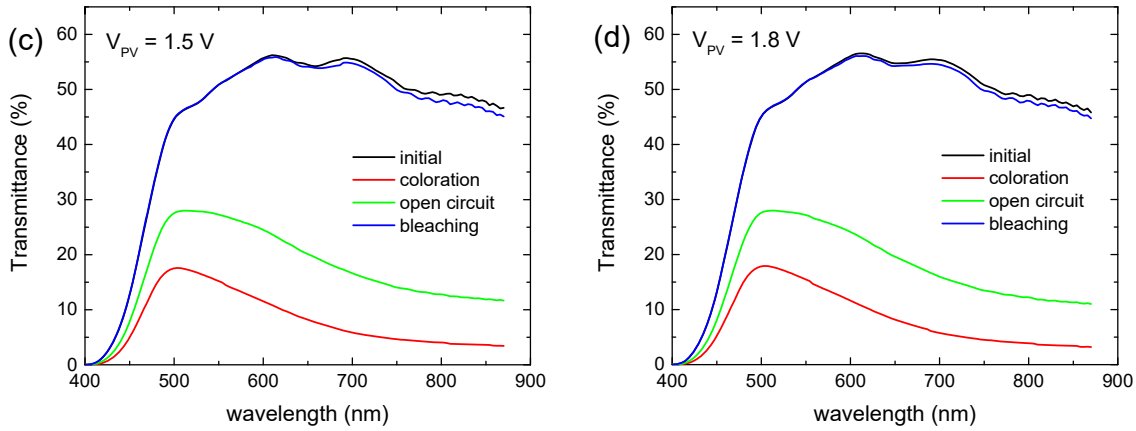


Figure S1. Transmittance spectra of a hybrid ECD during a coloration – bleaching cycle for the different values of the applied bias potential (V_{PV}), which was increased using series connected mini silicon solar cells: (**a**) 1 mini silicon solar cell, (**b**) 2 mini silicon solar cells, (**c**) 3 mini silicon solar cells and (**d**) 4 mini silicon solar cells.

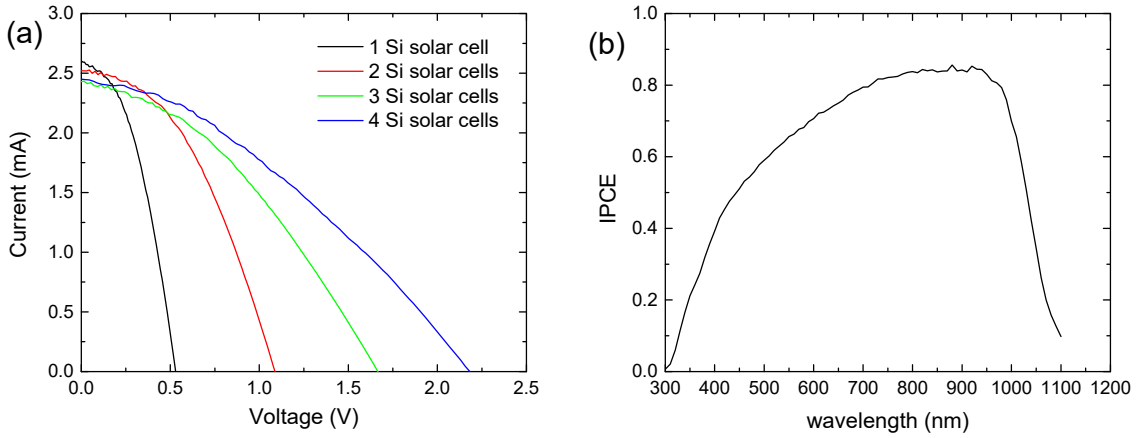


Figure S2. (**a**) Typical I-V curves of up to 4 series connected BPW34 mini-Si solar cells and (**b**) a typical IPCE spectrum.

Table S2. Characteristic photovoltaic properties of series connected BPW34 mini silicon solar cells.

	Voc (V)	Isc (mA)	FF	PCE (%)
1 Si solar cell	0.532	2.60	0.421	12.9
2 Si solar cells	1.09	2.52	0.421	13.0
3 Si solar cells	1.68	2.43	0.366	12.1
4 Si solar cells	2.19	2.45	0.345	11.1

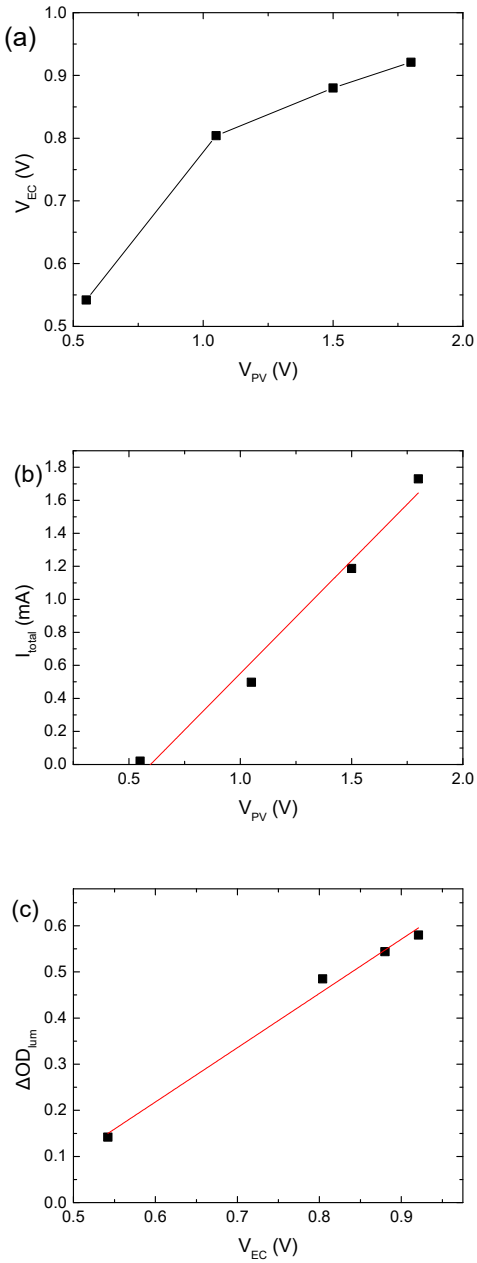


Figure S3. (**a**) Variation in the voltage at the ECD terminals (V_{EC}) with respect to the applied bias potential (V_{PV}), (**b**) linear increment in I_{total} passing through of the ECD with the applied bias potential (V_{PV}), (c) linear increment in the luminous optical density modulation with the voltage at the ECD terminals (V_{EC}).

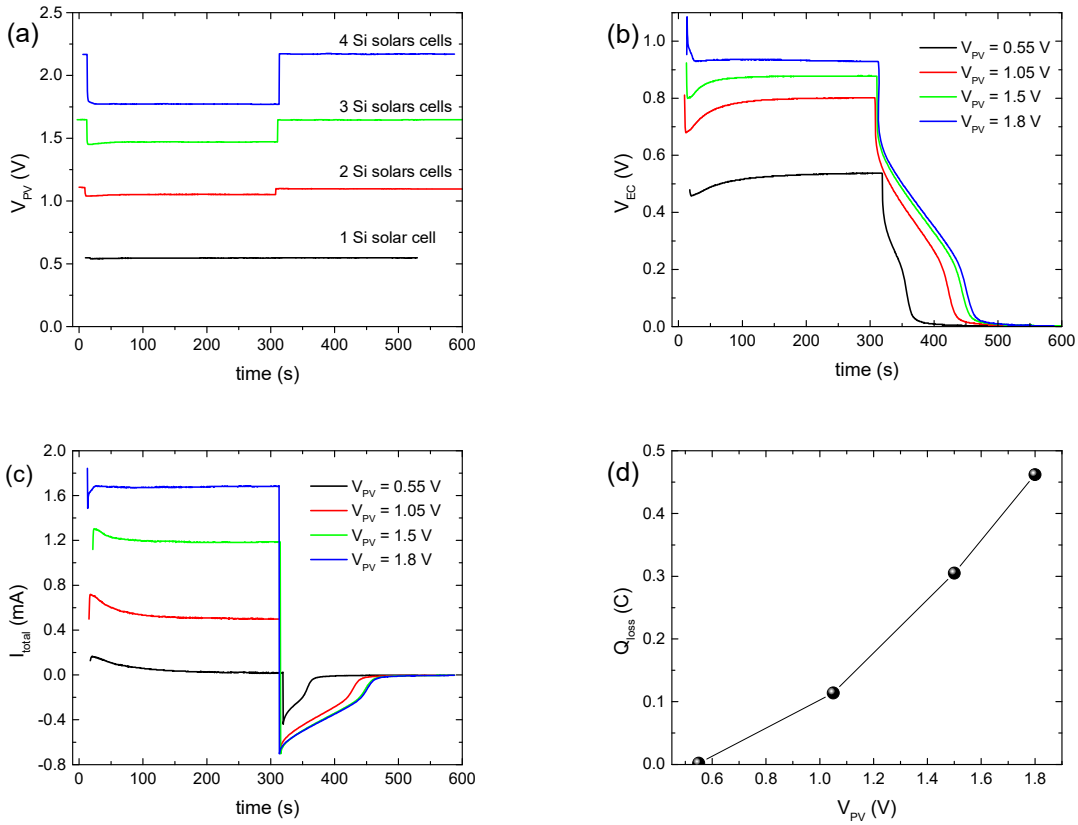


Figure S4. Variation in the applied bias potential V_{PV} (**a**), the potential at the terminals of the ECD (V_{EC}) (**b**) and the total current density (I_{total}) passing through the ECD (**c**) during a coloration–bleaching cycle, (**d**) variation in Q_{loss} with the applied bias potential (V_{PV}).

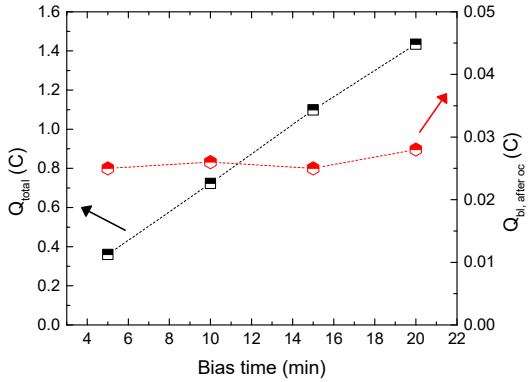


Figure S5. Variation in the total charge (Q_{total}) and the charge released from the WO_3 layer during bleaching ($Q_{bl,\ after\ oc}$) with the bias time, after an open circuit step.

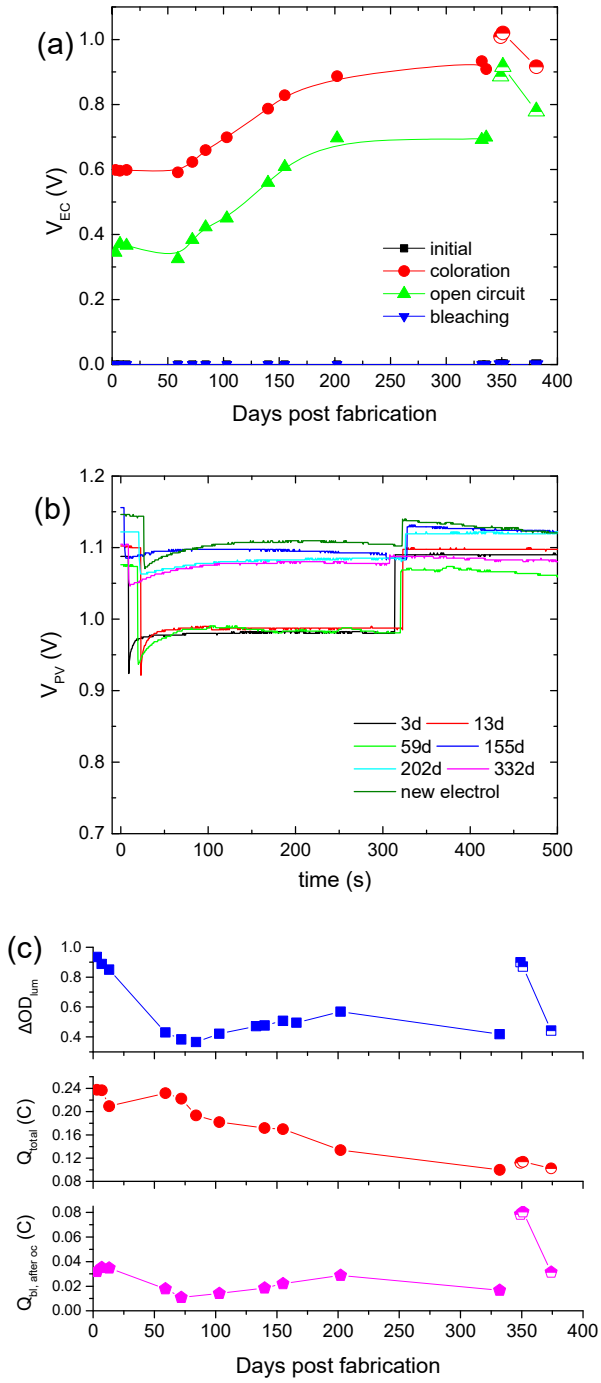


Figure S6. (**a**) Variation in the potential at the terminals of the ECD (V_{EC}) at the end of each step during a coloration–bleaching cycle with days post-fabrication, (**b**) variation in the applied bias potential (V_{PV}) for specific days post-fabrication during coloration of the ECD, (**c**) variation in ΔOD_{lum}, Q_{total} and $Q_{bl,\ after\ oc}$ with days post-fabrication. (open symbols are used in the case of the fresh electrolyte).

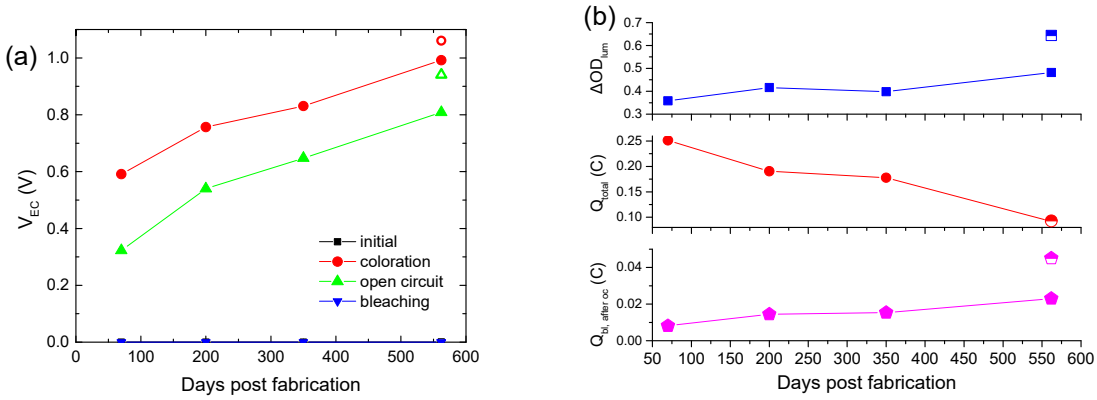


Figure S7. (**a**) Variation in the potential at the terminals of the ECD (V_{EC}) at the end of each step during a coloration–bleaching cycle with days post-fabrication, (**b**) variation in ΔOD_{lum}, Q_{total} and $Q_{bl,\ after\ oc}$ with days post-fabrication. (open symbols are used in the case of the fresh electrolyte).

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