Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Synergetic Interfacial Conductivity Modulation Dictating Hysteresis Evolution in Perovskite Solar Cells under Operation

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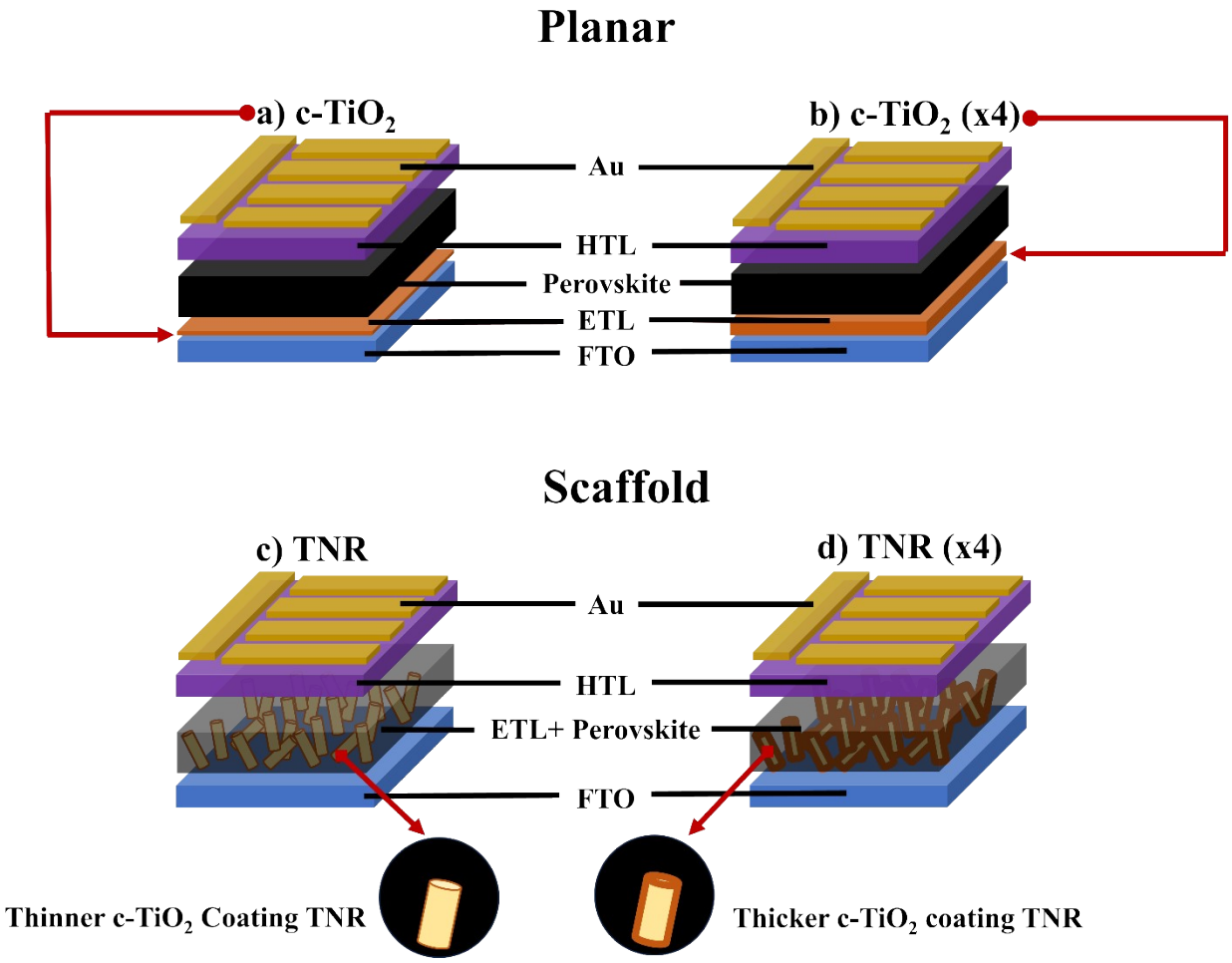

Figure S1: Schematic illustration of *n-i-p* PSCs studied in this work based on the ETL configuration: (a) planar c-TiO_2, b) planar c-TiO_2 (x4), (c) TNR and (d) TNR(x4).

Table S1- Valence band energy (E_{VB}) and work function (Φ) values of different ETL structures

	c-TiO_2	c-TiO_2 (x4)	TNR	TNR (x4)
IE (eV)	6.90	6.94	6.82	6.93
Φ (eV)	3.21	3.18	3.19	3.20

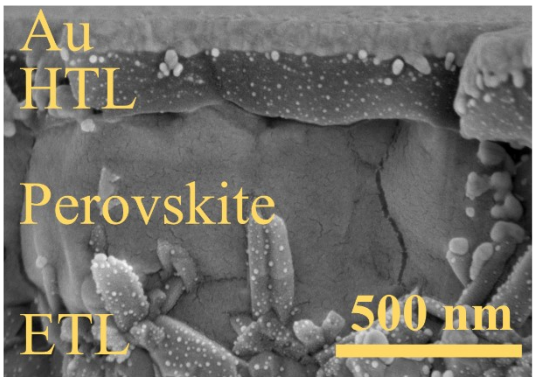

Figure S2- Cross-section SEM image of the full stack PSC in *n-i-p* architecture, using TNR as ETL

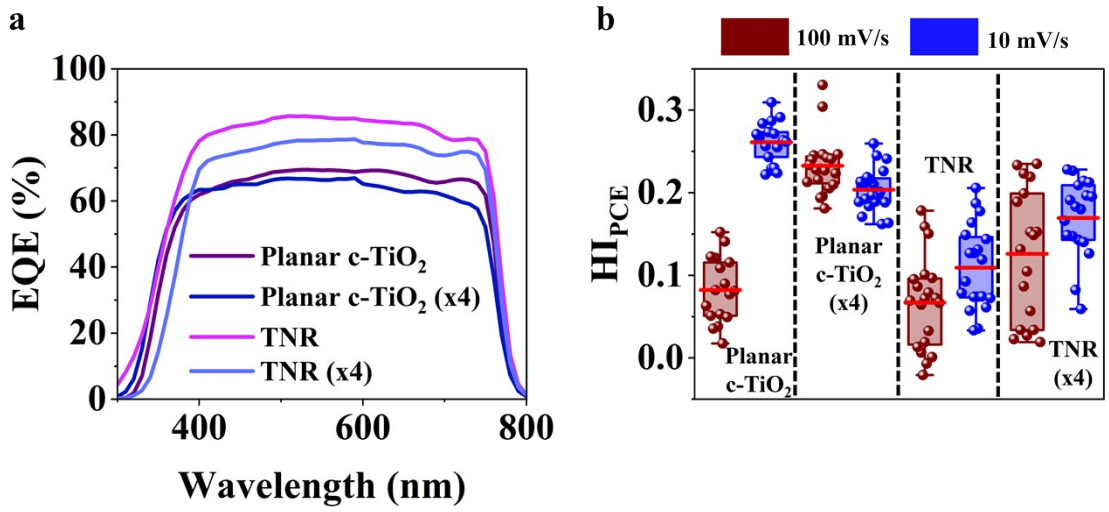

Figure S3- External quantum efficiency (EQE) spectra and (b) hysteresis index (HI_{PCE}) for PSCs based on different ETL structures.

Table S2- Change of PV metrics for PSCs based on Planar c-TiO_2 before and after 60 minutes light soaking. In each column, 100 and 10 denote the scan speeds of 100 mV/s and 10 mV/s, respectively. Additionally, LS stands for light soaking.

	100 RS w/o	100 FS w/o	10 RS w/o	10 FS w/o	100 RS LS	100 FS LS	10 RS LS	10 FS LS
J_{SC} (mA.cm^{-2})	17.77	17.88	16.88	16.55	17.11	17	16	15.55
V_{OC} (V)	1.058	1.018	1.069	1.051	1.037	1.001	1.050	1.034
FF (%)	64.98	59.00	57.72	41.37	67.62	64.18	65.27	50.70
PCE (%)	12.22	10.73	10.41	7.19	11.99	10.92	10.96	8.15
HI_{PCE}	0.12		0.3		0.08		0.25	

Table S2- Change of PV metrics for PSCs based on Planar c-TiO_2 (x4) before and after 60 minutes light soaking. In each column, 100 and 10 denote the scan speeds of 100 mV/s and 10 mV/s, respectively. Additionally, LS stands for light soaking.

	100 RS w/o	**100 FS w/o**	**10 RS w/o**	**10 FS w/o**	**100 RS LS**	**100 FS LS**	**10 RS LS**	**10 FS LS**
J_{SC} (mA.cm^{-2})	17.44	17.33	15.55	16.44	17.44	17.66	16.11	16.11
V_{OC} (V)	1.027	0.983	1.025	1.015	0.985	0.959	1.003	1.009
FF (%)	62.63	49.88	64.04	51.26	64.53	52.66	66.00	51.45
PCE (%)	11.22	8.49	10.21	8.55	11.08	8.91	10.66	8.36
HI_{PCE}	0.24		0.15		0.19		0.21	

Table S4- Change of PV metrics for PSCs based on TNR before and after 60 minutes light soaking. In each column, 100 and 10 denote the scan speeds of 100 mV/s and 10 mV/s, respectively. Additionally, LS stands for light soaking.

	100 RS w/o	**100 FS w/o**	**10 RS w/o**	**10 FS w/o**	**100 RS LS**	**100 FS LS**	**10 RS LS**	**10 FS LS**
J_{SC} (mA.cm^{-2})	22.77	22.11	21.88	22.00	22.66	22.88	21.77	21.88
V_{OC} (V)	1.080	1.045	1.088	1.065	1.039	1.027	1.045	1.033
FF (%)	75.88	73.09	75.58	71.13	71.71	70.9	72.25	67.32
PCE (%)	18.66	16.88	17.99	16.65	16.88	16.66	16.44	15.22
HI_{PCE}	0.09		0.07		0.01		0.07	

Table S5- Change of PV metrics for PSCs based on TNR (x4) before and after 60 minutes light soaking. In each column, 100 and 10 denote the scan speeds of 100 mV/s and 10 mV/s, respectively. Additionally, LS stands for light soaking.

	100 RS w/o	100 FS w/o	10 RS w/o	10 FS w/o	100 RS LS	100 FS LS	10 RS LS	10 FS LS
J_{SC} (mA.cm^{-2})	18.33	18.66	17.88	17.88	17.33	17.33	16.33	16.44
V_{OC} (V)	1.062	1.017	1.075	1.046	0.973	0.936	1.007	0.990
FF (%)	71.33	57.12	70.48	57.30	61.59	57.32	66.33	54.73
PCE (%)	13.88	10.83	13.54	10.71	10.38	9.29	10.90	8.91
HI_{PCE}	0.21		0.20		0.10		0.18	

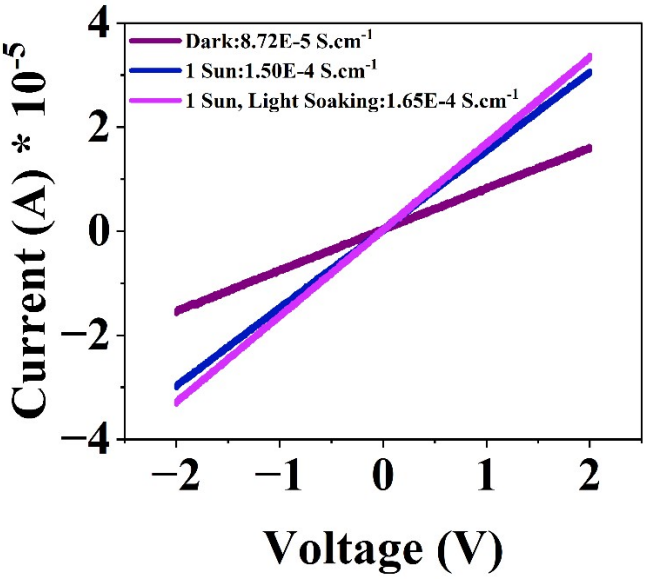

Figure S4- Results of the conductivity measurements on glass/spiro-OMeTAD film under dark, illumination and light soaking for 60 minutes.

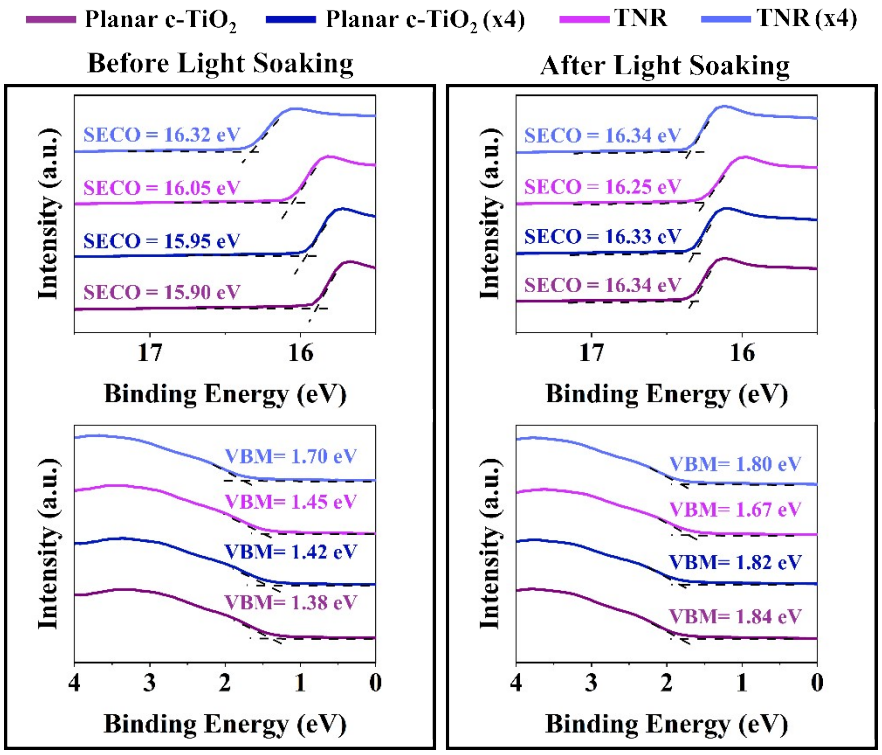

Figure S5- Comparison of the high binding energy part (a,b), as well as the low binding energy segment (c,d) of the UPS spectra of perovskite layer interfacing each ETL configuration for before and after light soaking.

Table S6- Valence band energy E_{VB} and Φ values of perovskite layer interfacing different ETL structures. LS stands for light soaking.

	c-TiO_2	c-TiO_2 (x4)	TNR	TNR (x4)
IE- Before LS (eV)	6.70	6.69	6.62	6.60
IE- After LS (eV)	6.72	6.71	6.64	6.68
Φ - Before LS (eV)	5.32	5.27	5.17	4.9
Φ - After LS (eV)	4.88	4.89	4.97	4.88

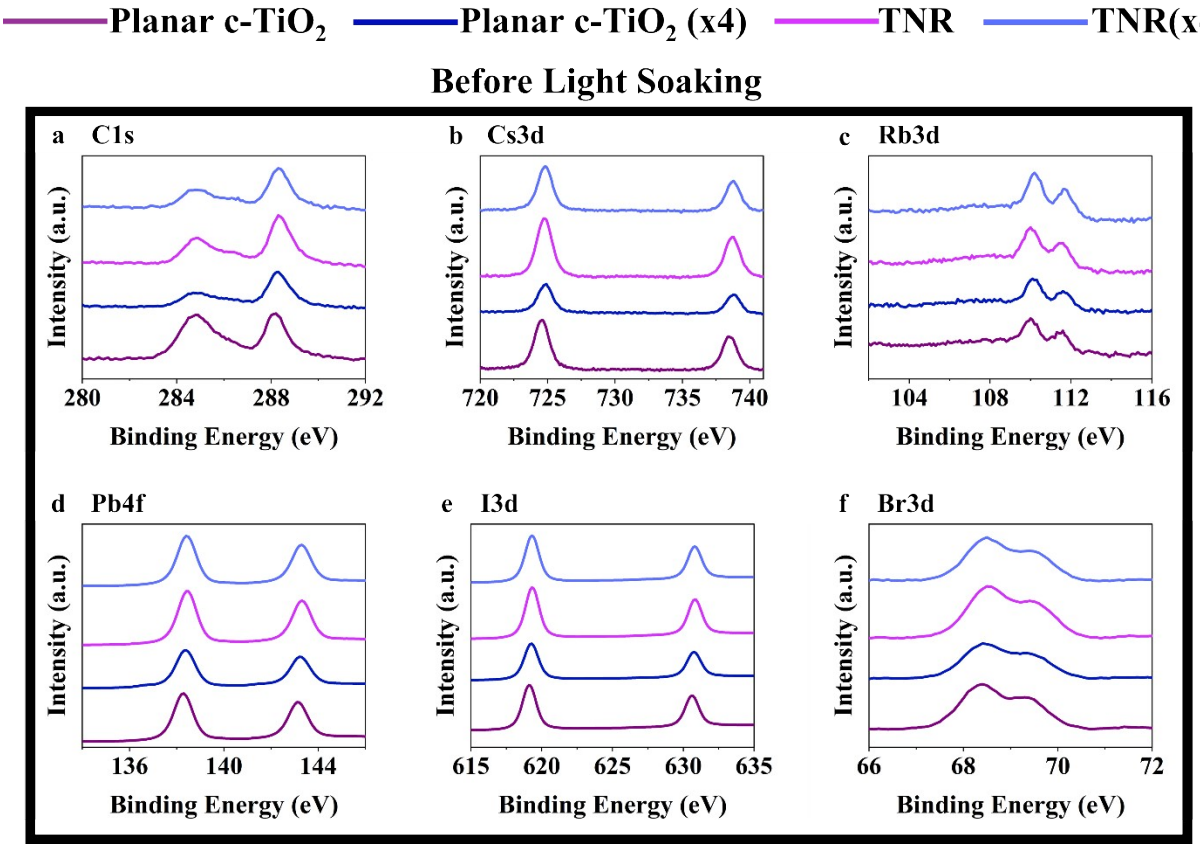

Figure S6- Comparison of the XPS core-level spectra for perovskite layers interfacing different ETLS before light soaking: (a) C1s, (b) Cs3d, (c) Rb3d, (d) Pb4f, (e) I3d and (f) Br3d.

Table S7- Summary of the values obtained through fitting the XPS spectra displayed in Figure S6.

		c-TiO_2		c-TiO_2 (x4)		TNR		TNR (x4)	
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
C1s	1	284.9	1.94	284.7	1.14	284.62	1.67	284.8	1.44
	2	287.6	0.77	286.1	1.42	286.4	1.58	286.39	1.5
	3	288.2	0.75	288.3	1.56	288.3	1.08	288.33	1.04
	4	288.8	0.52	290.4	0.75	289.3	1.25	289.7	1.04

Cs3d	1	724.6	1.77	724.9	1.17	724.7	1.33	724.8	1.25
	2	738.4	1.25	738.8	2.87	738.7	2.42	738.8	2.56
Rb3d	1	107.8	3.08	107.32	3.65	107.46	2.56	107.7	3.02
	2	110	1.29	110.1	0.93	110	1.06	110.2	1.06
	3	111.6	0.87	111.6	1.27	111.6	1.29	111.7	0.94
Pb4f	1	138.3	1.04	138.4	1.08	138.5	1.04	138.4	1.04
	2	143.1	0.94	143.2	0.96	143.3	0.93	143.3	0.94
I3d	1	619.1	1.19	619.3	1.23	619.3	1.19	619.3	1.21
	2	630.6	1.14	630.7	1.15	630.8	1.14	630.8	1.14
Br3d	1	68.4	0.96	68.4	1.15	68.5	0.98	68.5	1
	2	69.3	0.77	69.49	0.58	69.4	0.58	69.4	0.58

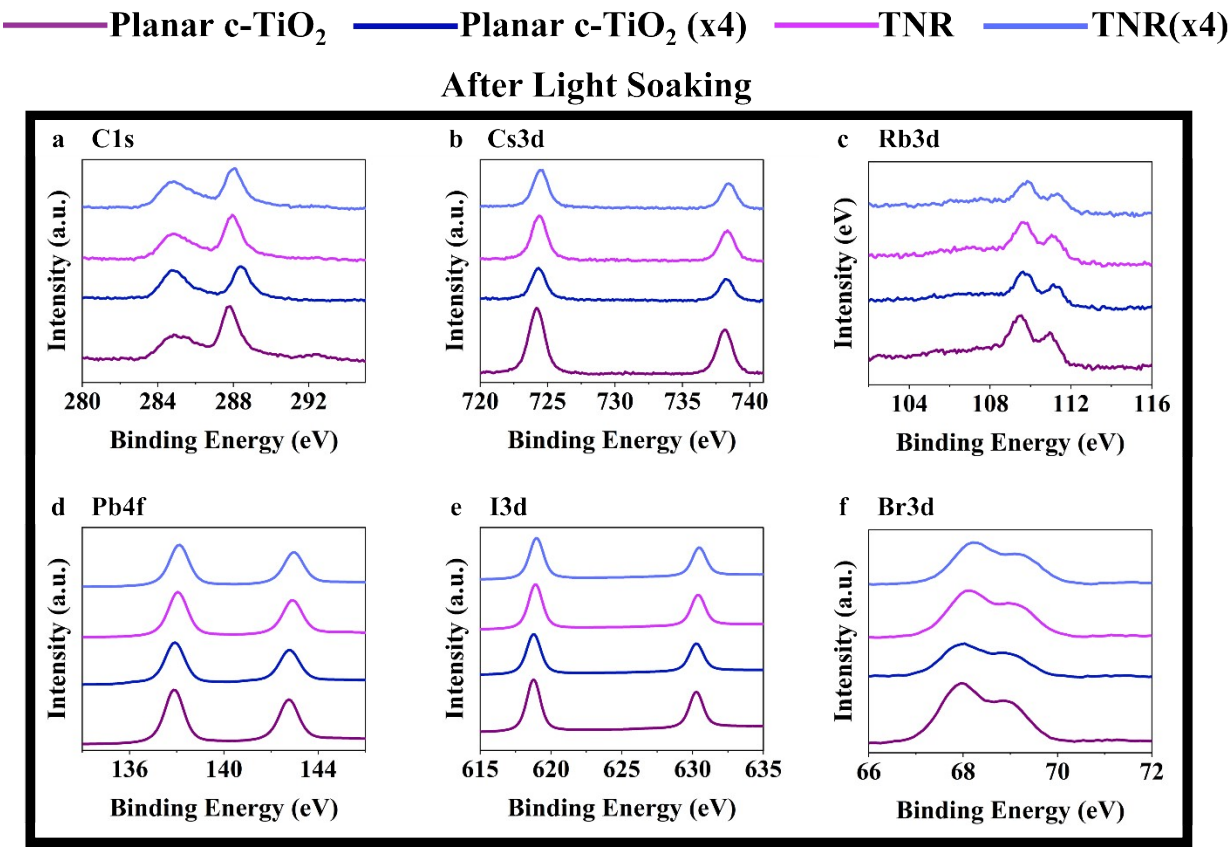

Figure S7- Comparison of the XPS core-level spectra for perovskite layers interfacing different ETLS after light soaking: (a) C1s, (b) Cs3d, (c) Rb3d, (d) Pb4f, (e) I3d and (f) Br3d.

Table S8- Summary of the values obtained through fitting the XPS spectra displayed in Figure S7.

		c-TiO_2		c-TiO_2 (x4)		TNR		TNR (x4)	
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
C1s	1	284.9	2.14	284.7	1.58	284.8	1.75	284.8	2.19
	2	286.1	0.98	286.2	1.27	286	1.04	286.5	0.43
	3	287.9	1.48	288.3	1.42	287.9	1.42	288	1.38
	4	290	1.79	289.8	0.47	289.5	1.85	289.8	1.67
	5	292.4	1.17	-	-	-	-	-	-
Cs3d	1	724.2	2.44	724.9	1.21	724.3	1.27	724.4	1.27
	2	738.2	1.31	738.8	2	738.3	2.31	738.4	2.62
Rb3d	1	106.55	2.71	108.2	1.9	107.1	2.46	107.5	3.25
	2	109.6	1.23	110.2	1.15	109.6	1.23	109.8	1.1
	3	110.88	1.23	111.75	1.15	111	1.14	111.3	1.37
Pb4f	1	137.9	1.04	138.5	1.08	138	1.06	138.1	1.06
	2	142.8	0.94	143.3	0.98	142.9	0.96	142.9	0.96
I3d	1	618.8	1.19	619.3	1.23	618.9	1.21	618.9	1.23
	2	630.3	1.12	630.8	1.15	630.3	1.14	630.4	1.15
Br3d	1	68.9	0.58	68.6	0.98	68.1	0.96	68.1	1
	2	68	1	69.4	0.58	68.9	0.58	69	0.58

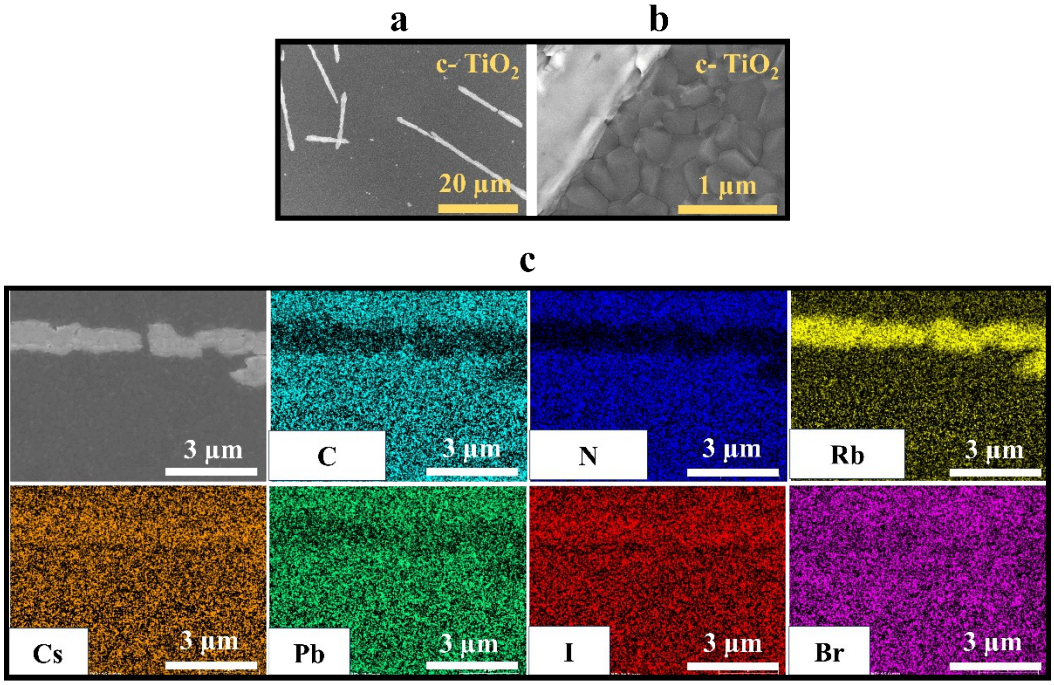

Figure S8- Top-view SEM image of the perovskite layer, interfacing c-TiO_2 as ETL, after light soaking at (a) 15k and (b) 50k magnification, as well EDS mapping (c) obtained over the precipitate displaying similar morphology and composition to Figure 2a.

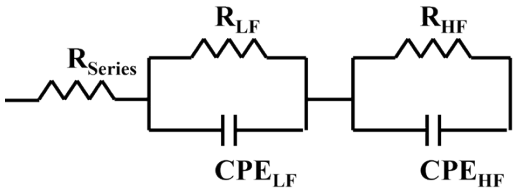

Figure S9- Equivalent circuit used in fitting the EIS patterns of Figure 5.

Table S9- The extracted parameters from fitting the Nyquist plots of Figure 5a with the equivalent circuits of Figure S9, for PSCs based on c-TiO_2.

	R_{Series} (Ω)	R_{LF} (Ω)	C_{LF} (F)	R_{HF} (Ω)	C_{HF} (F)
Before JV	28.15	20.32	0.02	54.47	2.49E-8
After JV	26.3	19.75	0.01	97.73	2.89E-8
LS-Before JV	22.58	20.01	0.02	39.85	2.31E-8
LS-After JV	27.34	24.08	0.01	67.23	9.10E-9

Table S10- The extracted parameters from fitting the Nyquist plots of Figure 5b with the equivalent circuits of Figure S9, for PSCs based on c-TiO_2 (x4).

	R_{Series} (Ω)	R_{LF} (Ω)	C_{LF} (F)	R_{HF} (Ω)	C_{HF} (F)
Before JV	28.69	34.63	0.000585	64.78	1.61E-8
After JV	26.24	26.79	0.000498	60.82	1.39E-8
LS-Before JV	21.84	31.69	0.000566	48.97	1.90E-8
LS-After JV	22.66	34.42	0.00072	55.31	1.59E-8

Table S11- The extracted parameters from fitting the Nyquist plots of Figure 5c with the equivalent circuits of Figure S9, for PSCs based on TNR.

	R_{Series} (Ω)	R_{LF} (Ω)	C_{LF} (F)	R_{HF} (Ω)	C_{HF} (F)
Before JV	14.66	7.97	0.012	27.65	2.89E-8
After JV	15.07	6.81	0.026	25.87	2.61E-8
LS-Before JV	15.44	11.49	0.028	28.34	2.17E-8
LS-After JV	15.74	11.24	0.034	29.94	1.54E-8

Table S12- The extracted parameters from fitting the Nyquist plots of Figure 5d with the equivalent circuits of Figure S9, for PSCs based on TNR (x4).

	R_{Series} (Ω)	R_{LF} (Ω)	C_{LF} (F)	R_{HF} (Ω)	C_{HF} (F)
Before JV	32.15	16.67	0.00462	52.35	3.51E-8
After JV	28.11	13.53	0.00361	45.76	3.78E-8
LS-Before JV	21.31	24.91	0.000858	54.61	3.83E-8
LS-After JV	21.83	27.35	0.000984	61.94	3.18E-8