Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Shelf Lifetime Analysis of Organic Solar Cells Combining Frequency and Time Resolved Techniques

Alfonsina Abat Amelenan Torimtubun,[a] Maria Méndez,[b] José G. Sánchez,[b] Josep Pallarès,[a] Emilio Palomares,*[b,c] and Lluis F. Marsal*[a]*

A. A. A. Torimtubun, Prof. J. Pallarès, Prof. L. F. Marsal
[a] Department of Electric, Electronic and Automatic Engineering
Universitat Rovira i Virgili
Av. Països Catalans 26, 43007 Tarragona, Spain
E-mail: josep.pallares@urv.cat, lluis.marsal@urv.cat

Dr. M. Méndez, Dr. J. G. Sánchez, Prof. E. Palomares
[b] Institute of Chemical Research of Catalonia (ICIQ-BIST)
Av. Països Catalans 16, 43007 Tarragona, Spain
E-mail: epalomares@iciq.es
[c] ICREA. Passeig Lluís Companys, 23. Barcelona. E-08010. Spain

EXPERIMENTAL SECTION

Materials. PTB7-Th (poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b′]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]-thiophene)-2-carboxylate-2,6-diyl] polymer donor and $PC_{70}BM$ ([6,6]-phenyl-C_{70}-butyric acid methyl ester) fullerene acceptor were purchased from One-Material Inc. 1,8-diiodooctane was obtained from Alfa Aesar. PFN (poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)], titanium (IV) isopropoxide and zinc acetate dyhydrate were purchased from One-Material Inc. Vanadium oxide (V_2O_5) and a high purity silver (Ag) wire (99.99%) were purchased from Sigma-Aldrich and Testbourne Ltd., respectively. Other chemical reagents were supplied from Sigma-Aldrich and used as received.

Device fabrication. OSC devices were fabricated with the inverted structure of ITO/ETL/PTB7-Th:$PC_{70}BM$/V_2O_5/Ag as shown schematically in Fig. 1a. The patterned ITO coated glass substrate with the sheet resistance of 10 Ω cm^{-2} were cleaned with deionized water/detergent and then sonicated in acetone, methanol and isopropanol solution in a sequence for 10 min, respectively. The cleaned ITO-glass substrates were dried under nitrogen stream and transferred to an oven for 5 min at 100ºC. Before fabrication, substrates were treated in ultraviolet-ozone for 15 min to remove any organic residues. To fabricate ETL, the diluted precursor solutions of PFN, titanium sub-oxide (TiO_x) and zinc oxide (ZnO), prepared according to our previous work[14,18,40], were spin-coated onto the cleaned ITO-glass substrates at 4000, 6000 and 3000 rpm, respectively. The ETL-coated ITO substrates were brought to a nitrogen-filled glove box for the active layer deposition. The active layer solution was prepared by dissolving PTB7-Th and $PC_{70}BM$ (1:1.5 weight ratio) in chlorobenzene and 1,8-diiodooctane (97:3% v/v) with a total concentration of 25 mg mL^{-1}. The solution was stirred and heated on a hotplate at 40ºC overnight. The active layer solution was spin-coated onto the ETL at 750 rpm for 30 s, resulting in an active layer thickness around 100 nm. The substrates were finally transferred into an evaporation chamber inside the glove box where 5 nm of V_2O_5 and 100 nm Ag were sequentially deposited under high vacuum conditions ($\leq 1 \times 10^{-6}$ mbar). The effective area of devices was 0.09 cm^2. The area of the tested solar cells was determined by an optical microscope.

Device measurement and characterization. The current density – voltage (*J-V*) characteristics, namely the short circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE), were extracted using a Keithley 2400 Source Measure Unit with a solar simulator (Abet Technologies model 11000 class type A, Xenon arc) as an artificial light source. The standard light intensity of the AM 1.5G spectrum was calibrated by an NREL certified monocrystalline silicon photodiode. The devices were tested under illumination at light intensity of 100 mW cm^{-2}. Moreover, dark measurements were performed to obtained *J-V* dark curves. All the *J-V* characteristics were performed at room temperature. *J-V* curves were measured in the forward direction from –1 to 1 V, with a scan step of 0.01 V and a dwell time of 2 ms. V_{OC} and J_{SC} over different light intensity were obtained by *J-V* measurements under the solar simulator using a set of optical density filters. The external quantum efficiency (EQE) measurement were taken place using Lasing IPCE-DC model with the series number of LS1109-232 under a forward wavelength sweep direction from 300 nm to 800 nm. Impedance spectroscopy (IS) measurements were carried out under simulated AM 1.5G illumination using an HP-4192A impedance analyzer. Impedance data were extracted at three different dc levels: short-circuit current point, near maximum powerpoint, and close to open-circuit point, superimposing an ac signal with 1 mV amplitude in the frequency range between 5 Hz to 5 MHz. The IS experimental data were fitted using Ivium software analyzer. Charge extraction (CE), transient photovoltage (TPV) and transient photocurrent (TPC) measurements were carried out using a white light LED ring LUXEON® Lumileds controlled by a programmable power supply and a control box that switches from open to short-circuit states. All the signals are recorded in an oscilloscope Yokogawa DLM2052 registering voltage drops. All devices were measured in a sealed holder under room temperature (RT, i.e. 25–30 °C) in an N_2 atmosphere. Light perturbation pulses for TPV and TPC were provided by a nanosecond PTI GL-3300 nitrogen laser. To study the degradation, the nonencapsulated devices were stored under dark illumination in ambient environment (RT and 35 – 50% relative humidity) in open circuit condition, corresponding to the International Summit on Organic Photovoltaic Stability (ISOS) standard D–1 shelf.[27] To accurately describe the decay behavior, the ISOS protocols require to present four pairs of the device parameters (J_{SC}, V_{OC}, *FF, and* PCE) over storage time. The initial testing measurement, E_0, was performed immediately after the device fabrication at time= 0, T_0. The subsequent testing measurement was carried out after the device has decayed 20% form the initial testing measurement, E_{80}. T_{80} is the time it took to decay to E_{80}.

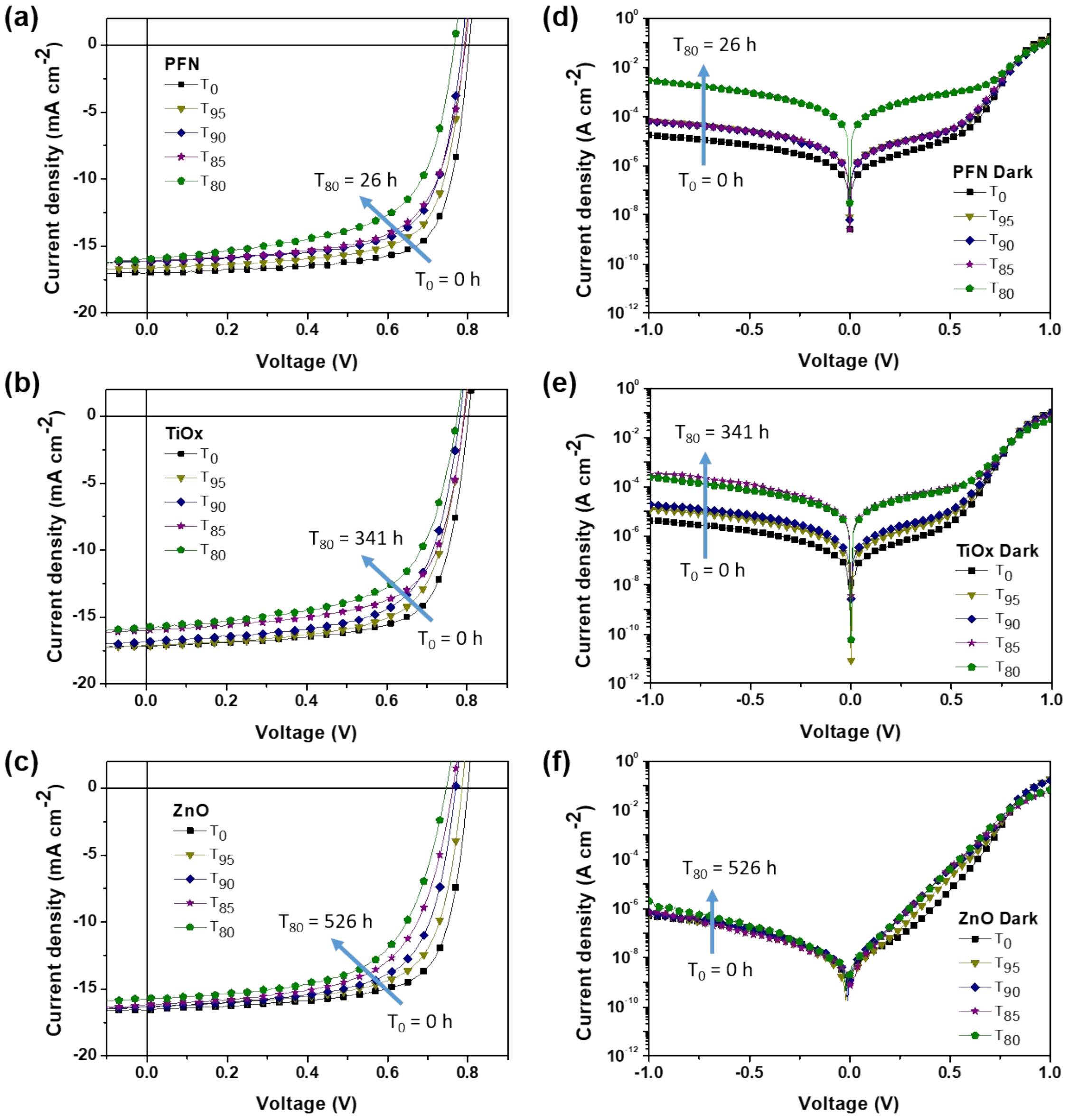

Figure S1. **a–c**, Light illumination and **d–f**, dark *J-V* characteristic of PTB7-Th:PC$_{70}$BM-based device with different ETLs: **a,d**, PFN, **b,e**, TiO$_x$, and **c,f**, ZnO exposed to ambient conditions over storage time. T_0 is the initial time for the initial testing measurement of the fresh device and T_{80} is the time the devices took to decay 20% from its initial measurement.

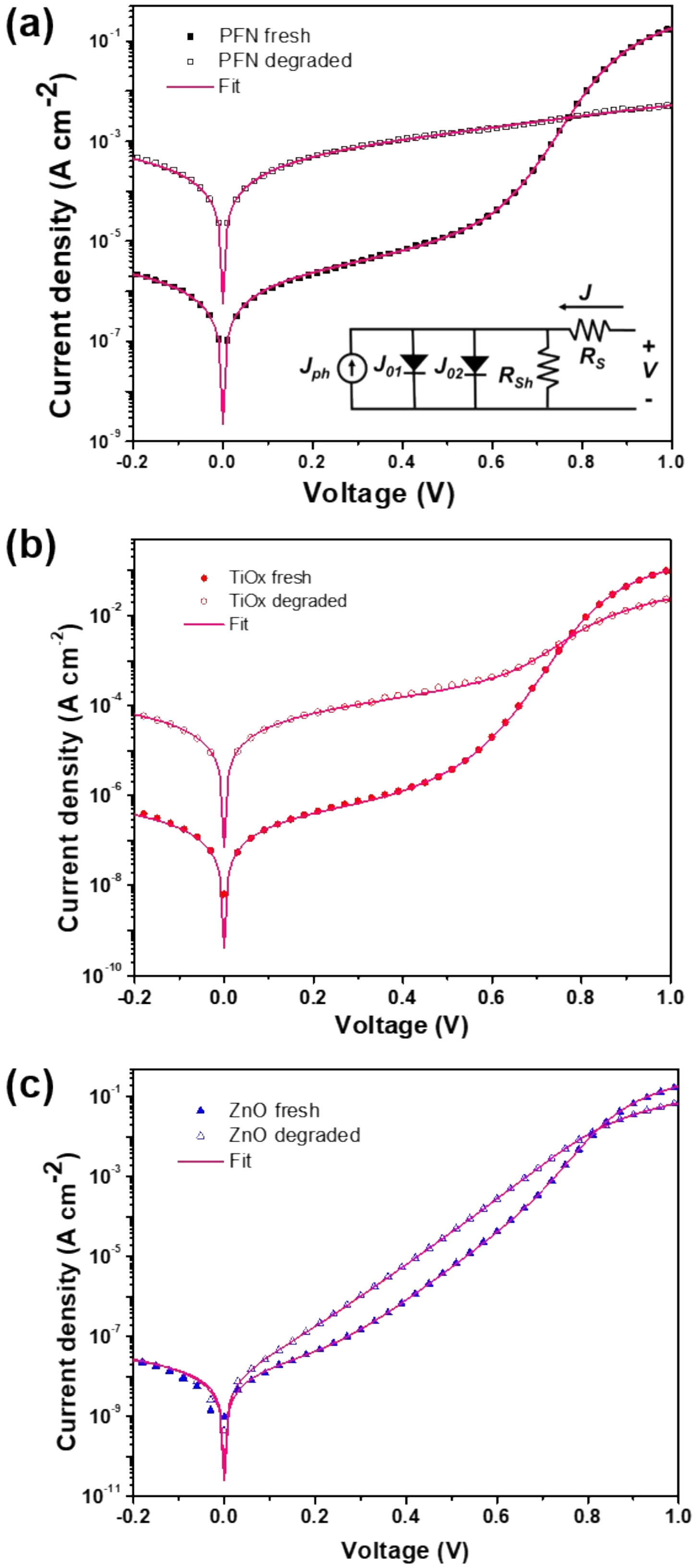

Figure S2. Fitting dark *J*-*V* curves of fresh and degraded cells at 526 h for **a**, PFN-, **b**, TiOx-, **c**, ZnO-iOSCs using two-diode electrical circuit model.

Table S1. Extracted series resistance and shunt resistance values from experimental and modeled data from dark *J-V* curves Figure 1d for fresh and degraded devices after 526 h exposure time.

Device Parameters	**PFN Fresh**	**PFN Deg**	**TiO_X Fresh**	**TiO_X Deg**	**ZnO Fresh**	**ZnO Deg**
R_S^{exp} (Ω cm^2)	11.92	204	19.22	67.50	11.71	28.96
R_S^{fit} (Ω)	0.62	69	1.24	7	0.64	2
R_{Sh}^{exp} (Ω cm^2)	9.24×10^4	4.30×10^2	5.16×10^5	3.16×10^3	9.09×10^6	8.16×10^6
R_{Sh}^{fit} (Ω)	9.22×10^4	4.00×10^2	5.35×10^5	3.15×10^3	7.45×10^6	9.36×10^6
J_{01}^{fit} (A cm^{-2})	8.42×10^{-15}	4.67×10^{-9}	5.95×10^{-15}	1.84×10^{-12}	1.88×10^{-15}	1.42×10^{-11}
n_1	1.11	1.91	1.09	1.37	1.05	1.50
J_{02}^{fit} (A cm^{-2})	2.28×10^{-8}	4.10×10^{-5}	1.58×10^{-9}	7.30×10^{-7}	3.68×10^{-10}	4.34×10^{-9}
n_2	3.35	6.4	2.64	4.12	2.00	2.12

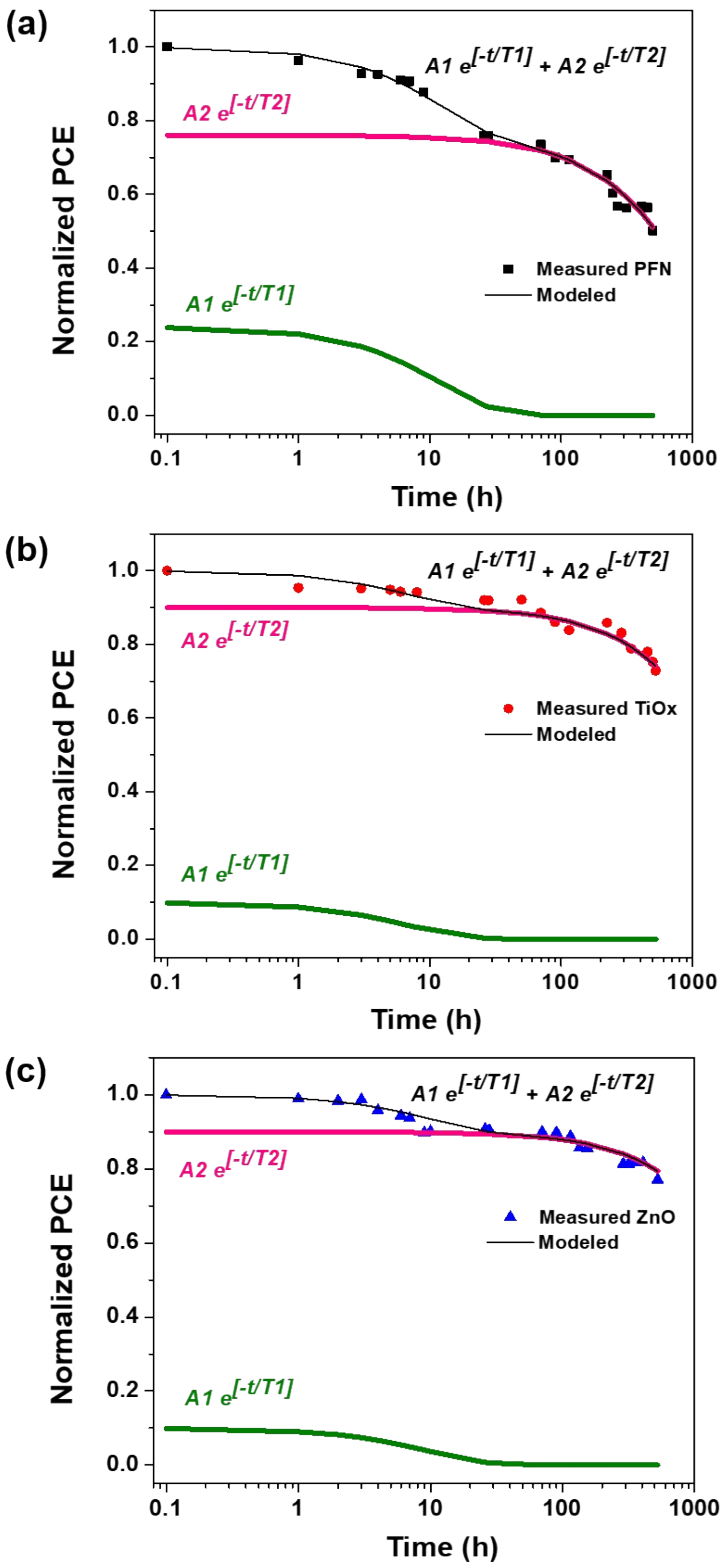

Figure S3. The modeled normalized PCE of **a**, PFN-, **b**, TiOx- and **c**, ZnO-ETLs iOSCs over storage time using Eq. (1). The filled symbols are the experimental data and the lines are the fitting curves. The green line represents the fast initial decay and the pink line shows the slow decay, the black line is the total decay observed.

Table S2. Parameters obtained from fit the normalized PCE by equation (1) with different ETLs. T1 and T2 are the time constants, A1 and A2 are the degradation power factors and r is the ratio of A1/A2.

ETL	A1 (%/%)	A2 (%/%)	T1 (h)	T2 (h)	r = A1/A2
PFN	0.24	0.76	12	1260	0.32 (r <1)
TiOx	0.06	0.92	6	2526	0.07 (r <1)
ZnO	0.11	0.89	9	4000	0.12 (r <1)

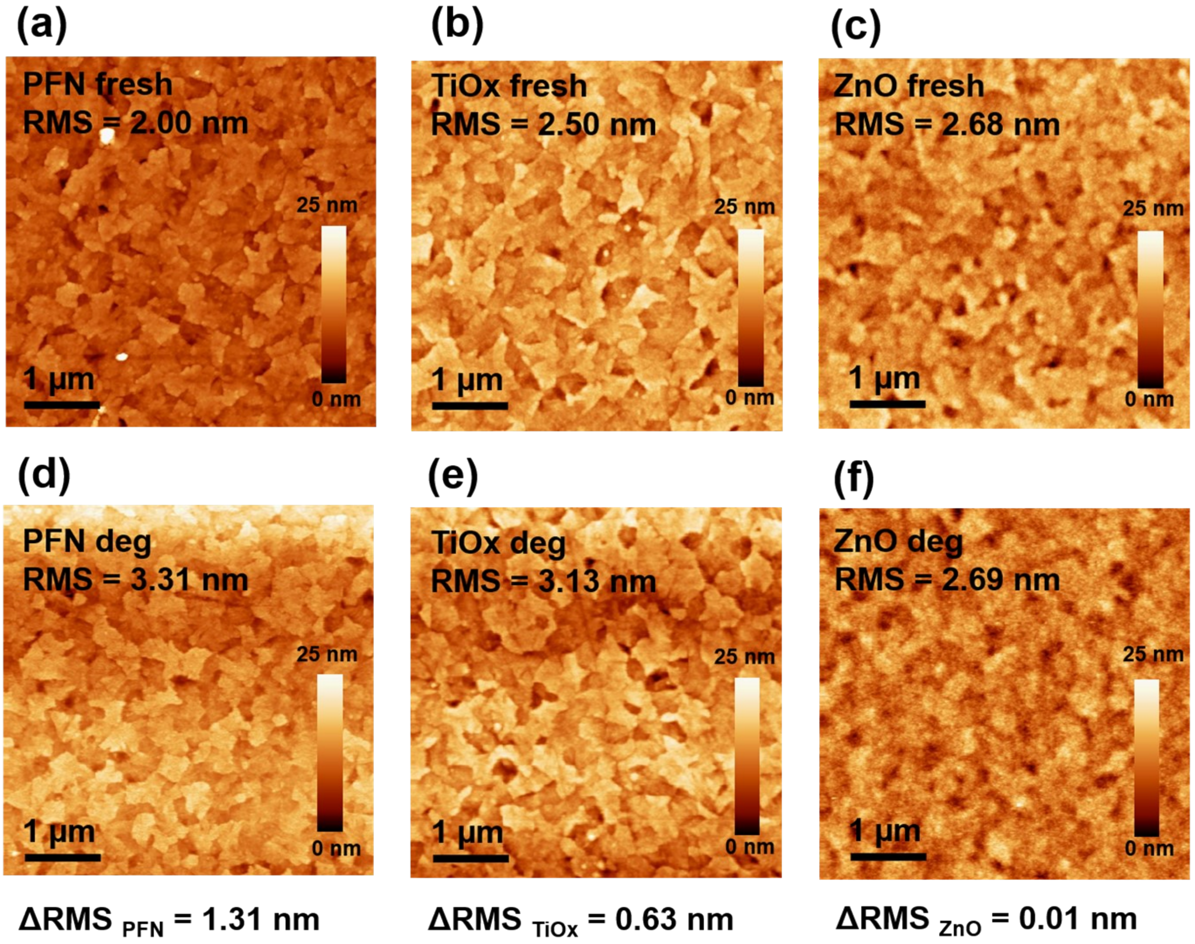

Figure S4. AFM height images of **a-c**, fresh and **d-f**, degraded ETL films. The ETLs used are **a,d**, PFN, **b,e**, TiOx, and **c,f**, ZnO. The delta root-mean-square (ΔRMS = RMS degraded – RMS fresh) roughness values are extracted.

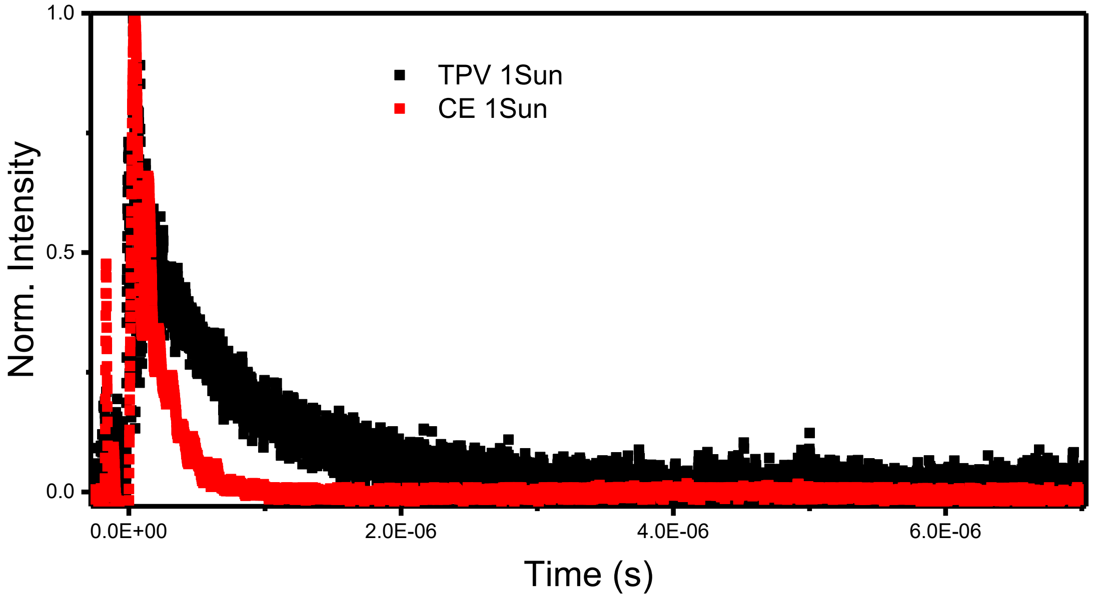

Figure S5. The CE and TPV decays under 1 Sun illumination conditions for OSC using TiOx as ETL.

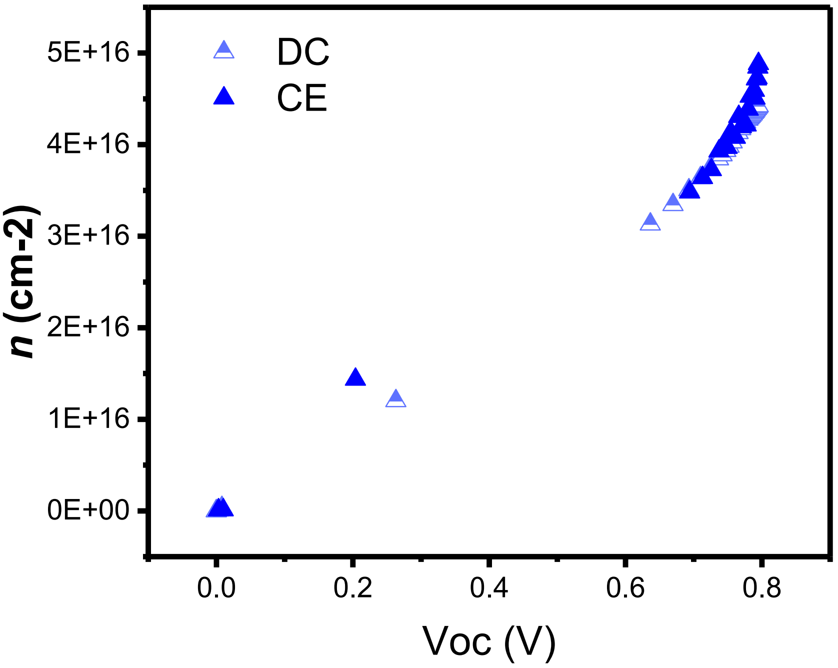

Figure S6. Comparison between the charge density measured by using charge extraction (CE) and differential capacitance (DC) techniques for a device using ZnO as ETL.

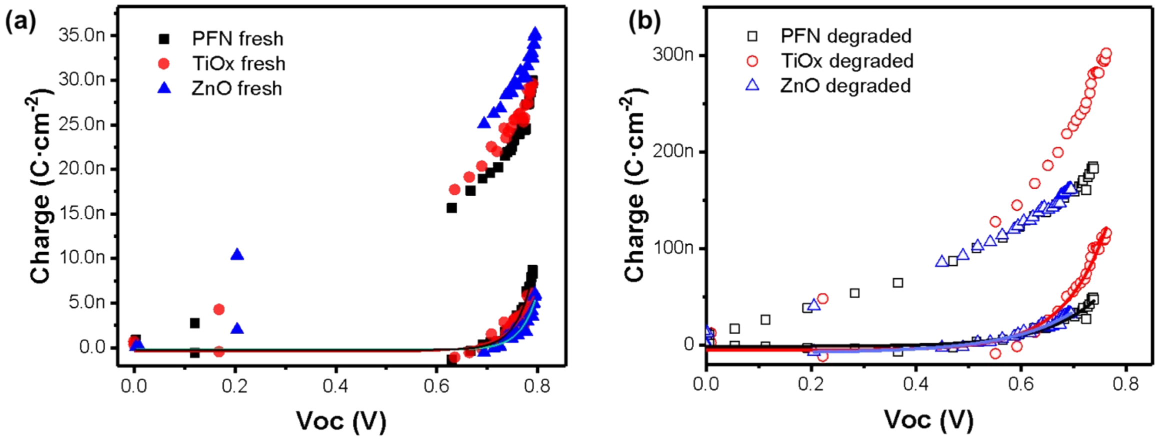

Figure S7. Charge measured at different light bias for OSCs with different ETL. The solid lines at the graph bottom represents only the exponential part of the fits: $y=Be^{Cx}$ (chemical capacitance) for fresh (**a**) and degraded (**b**) devices after subtracting the linear part (geometrical capacitance).

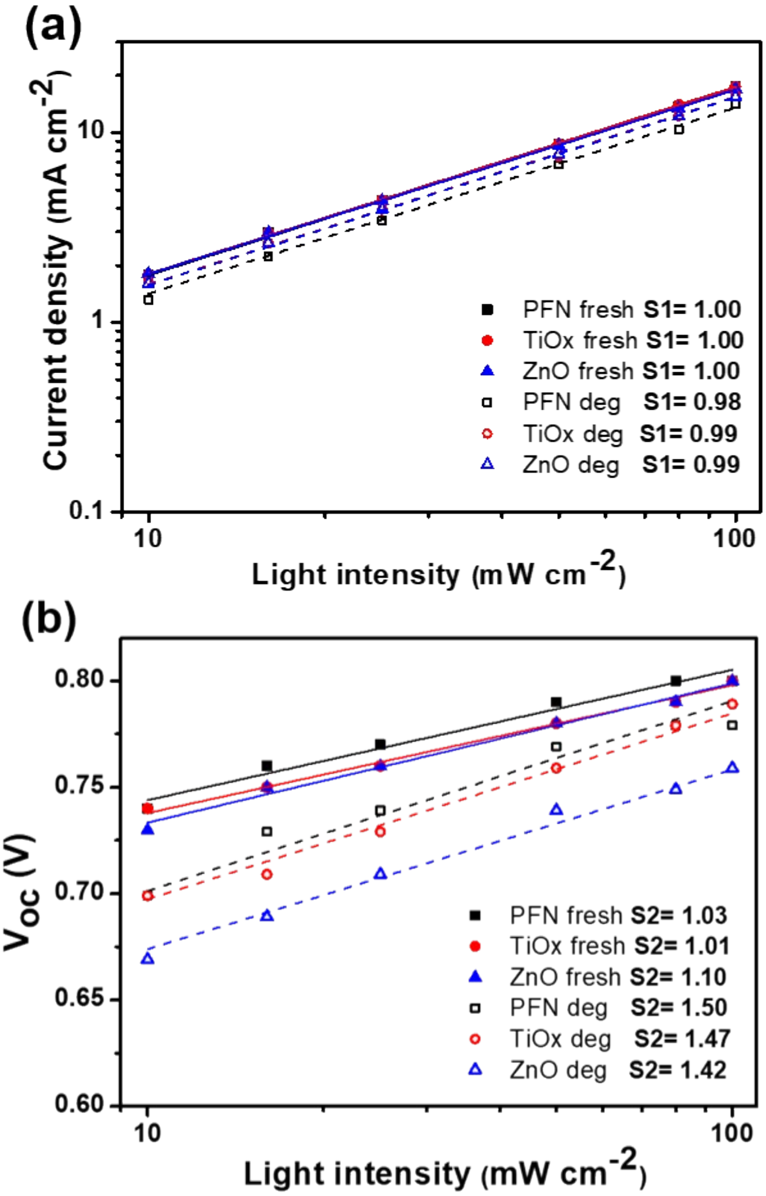

Figure S8. J_{SC} **a-c**, and V_{OC} **d-f**, dependence on light intensity over storage time of PTB7-Th:$PC_{70}BM$–based OSCs with different ETLs: **a,d**, PFN, **b,e**, TiO_x, and **c,f**, ZnO. It is worth noting that the ideality factor values, *n* (*n* = S2/S1) of this measurement is in good agreement with the n_1 values obtained from the dark *J-V* fitting parameters in Table S1.[1]

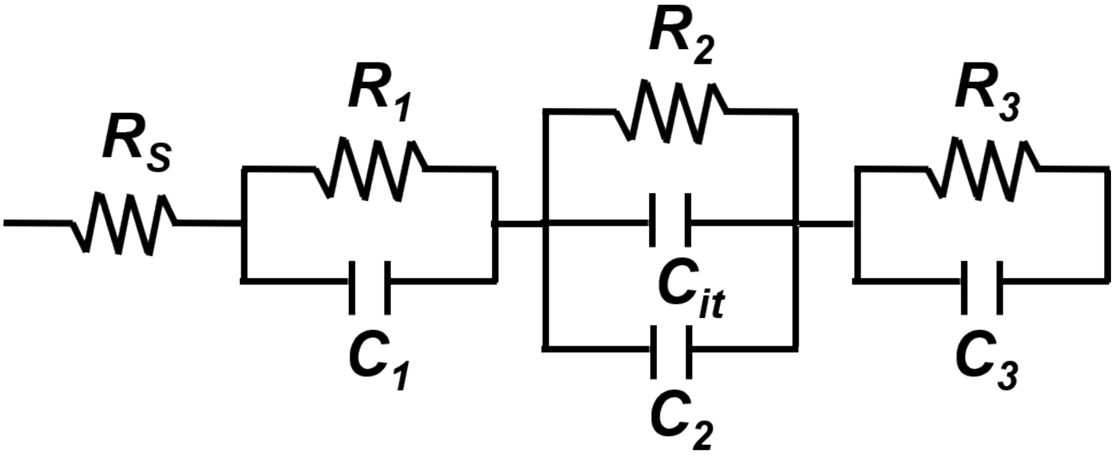

Figure S9. The schematic illustration of three resistor/capacitance ladder equivalent circuit model with interface capacitance (C_{it}) used for the fitting of impedance spectra. Notice that C_X denotes the geometrical capacitance of layer X.

The theoretical geometrical capacitance value of each layer in Fig. S9 is calculated using this equation:

$$C_{geo} = \varepsilon_0 \varepsilon_{layer} \frac{A}{d_{layer}} \tag{1}$$

where ε_0 is the vacuum dielectric permittivity, the ε_{layer} is the relative dielectric permittivities (ε_{bulk}, ε_{ETL}, and ε_{V2O5}), d_{layer} is the thickness of each layer (d_{bulk}, d_{ETL}, and d_{V2O5}) and A is the active area.

Table S3. Dielectric constant, thickness, and calculated capacitance for each layer.

Layers	ε_{layer}	d_{layer} (nm)	Capacitance (nF)
Bulk	3.9 [2]	100	3
V_2O_5	5 [3]	5	78
PFN	3.5 [4]	10	28
TiO_x	50 [5]	15	200
ZnO	4 [2]	15	21

Table S4. Capacitance and resistance values of each layer for different ETLs used under AM 1.5G for fresh (T_0) and T_{80} degraded devices. For PFN devices, the values for 526h are also shown (in parenthesis). The values were extracted by using the circuit model shown in Supplementary Figure 9 at open-circuit voltage.

ETLs	Layers	Capacitance (nF)		Resistance (Ω)	
		Fresh	Degraded	Fresh	Degraded
PFN	R_s	-	-	7	10 (53)
	PFN	28	28 (28)	11	17 (54)
	Bulk	10	11 (14)	7	13 (23)
	V_2O_5	78	78 (78)	7	12 (13)
TiO_x	R_s	-	-	14	21
	TiO_x	200	200	3	17
	Bulk	9	12	15	32
	V_2O_5	78	78	9	13
ZnO	R_s	-	-	6	12
	ZnO	21	21	4	25
	Bulk	12	13	15	18
	V_2O_5	78	78	8	17

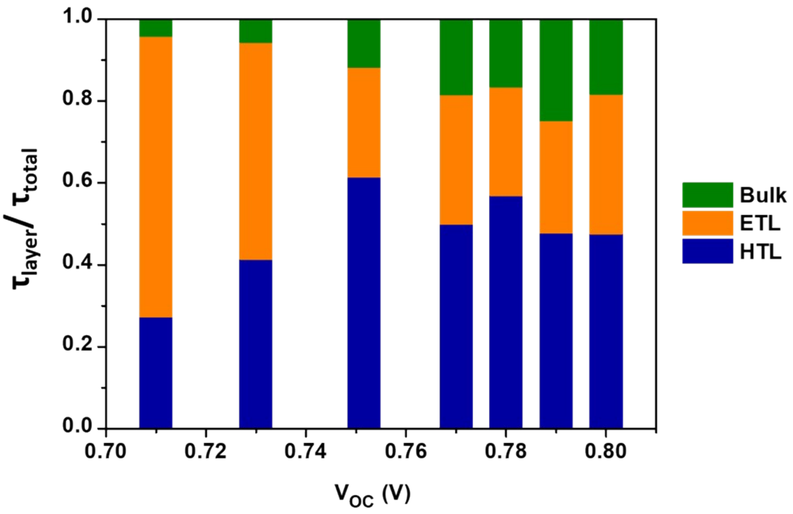

Figure S10. The relative contribution of each layer to the total τ value at different degradation time.

SUPPLEMENTARY REFERENCES

[1] A. A. A. Torimtubun, J. G. Sánchez, J. Pallarès, L. F. Marsal, *Sustain. Energy Fuels* **2020**, *4*, 3378.

[2] J. G. Sánchez, V. S. Balderrama, S. I. Garduño, E. Osorio, A. Viterisi, M. Estrada, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, *RSC Adv.* **2018**, *8*, 13094.

[3] S. Thiagarajan, M. Thaiyan, R. Ganesan, *New J. Chem.* **2015**, *39*, 9471.

[4] Z. Peng, Y. Zhang, Y. Xia, K. Xiong, C. Cai, L. Xia, Z. Hu, K. Zhang, F. Huang, L. Hou, *J. Mater. Chem. A* **2015**, *3*, 20500.

[5] E. Osorio, J. G. Sánchez, L. N. Acquaroli, M. Pacio, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, *ACS Omega* **2017**, *2*, 3091.