Study of light-induced degradation of Polymer:Fullerene Solar Cells

Abhishek Sharma[1,2 #], Mihirsinh Chauhan[3 #], Jessica Patel[4], Manoj Kumar Pandey[4], Brijesh Tripathi[4], J. P. Tiwari[1,2,], Suresh Chand[1,2]*

[1]Advanced Materials and Devices Division, CSIR-National Physical Laboratory New Delhi 110012 (India).

[2]Academy of Scientific and Innovative Research (AcSIR), CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg New Delhi 110012 (India)

[3]Department of Solar Energy, School of Technology, Pandit Deendayal Energy University, Gandhinagar 382426 (India).

[4]Department of Physics, School of Technology, Pandit Deendayal Energy University, Gandhinagar 382426 (India).

[#]Authors contributed equally.

[*]Corresponding Author: Ph. +91 9013301619, +91 1145608640, Fax +91 11 45609310

Email: jai_ti2002@yahoo.com, tiwarijp@nplindia.org

Supplementary Information

Device Fabrication:

Five device structures are fabricated stated as below:

1. ITO/PEDOT:PSS(~ 40 nm)/P3HT:$PC_{71}BM$(~100 nm)/Al(~120 nm)
2. ITO/PEDOT:PSS(~ 40 nm)/PTB7:$PC_{71}BM$ (~90 nm) /Al (~120 nm)
3. ITO/PEDOT:PSS(~ 40nm) /P3HT:$PC_{71}BM$(~100 nm) /Ca (~20 nm) /Al (~120 nm)
4. ITO/MoO_3 (~10 nm) /P3HT:$PC_{71}BM$ (~100 nm) /Ca(~20 nm)/Al (~120 nm)
5. ITO/MoO_3 (~10 nm)/PTB7:$PC_{71}BM$ (~90 nm)/Ca(~20 nm)/Al (~120 nm)

The patterned ITO glass substrates (sheet resistance = 15 Ω/□) were sonicated in a soap solution, acetone, and isopropanol for device fabrication. Cleaned ITO glasses were then exposed to ultraviolet-ozone irradiation for 20 min. In all the devices, the thickness of MoO_3 was ~ 10 nm, and PEDOT:PSS was spin-coated at 4000rpm to give a thickness of ~40nm. The active layer is made from the spin coating of (P3HT:$PC_{71}BM$ (1:1) and PTB7:$PC_{71}BM$ (1:1.5) blend, which was dissolved (25mg/ml in both the cases) in dichlorobenzene. Finally, the Ca (20nm)/Al (120nm) electrode is thermally deposited in a high vacuum (~8×10^{-6} mbar), over the active layer through a shadow mask. In all the cases, the active area of the devices was 4 mm^2. Further, for the encapsulation of the device, glass sheet, and epoxy is used. The Current-Voltage (I-V) characteristics were measured using a Keithley 2420 under 100 mW/cm^2 simulated AM 1.5 G solar illumination. The light intensity was measured using a calibrated Si photodetector.

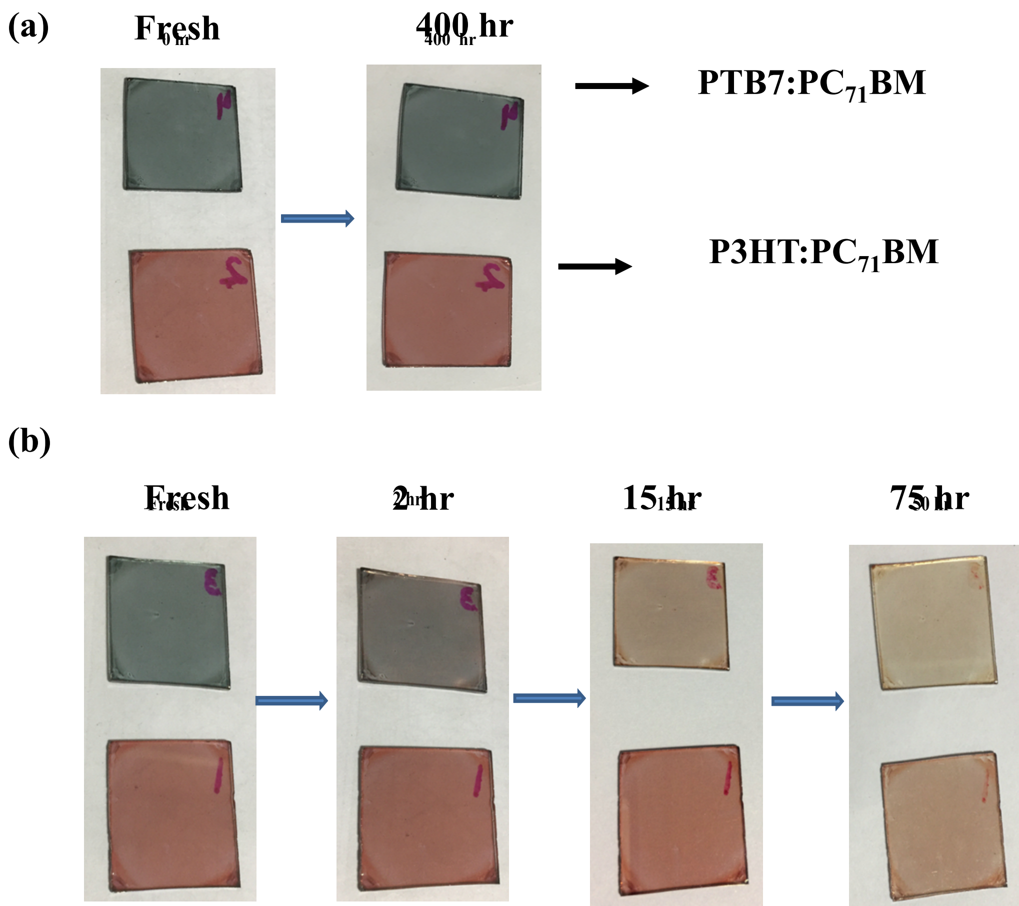

Figure S 1: The images of active layer (P3HT:PC_{71}BM, PTB7:PC_{71}BM) films on a glass substrate in the dark (a) as well as in sunlight (b) with time.

In the dark, there is no change in the color of the active layer, which supports the negligible dark degradation in the absorption of the active layer films. There is bleaching of polymer with time due to photodegradation, as discussed above in sunlight. This bleaching of the polymer can be seen from the figure, especially in PTB7:PC71BM, which occurs rapidly compared to P3HT:PC_{71}BM. Hence the degradation in active layer absorption is mainly happening due to the photodegradation.

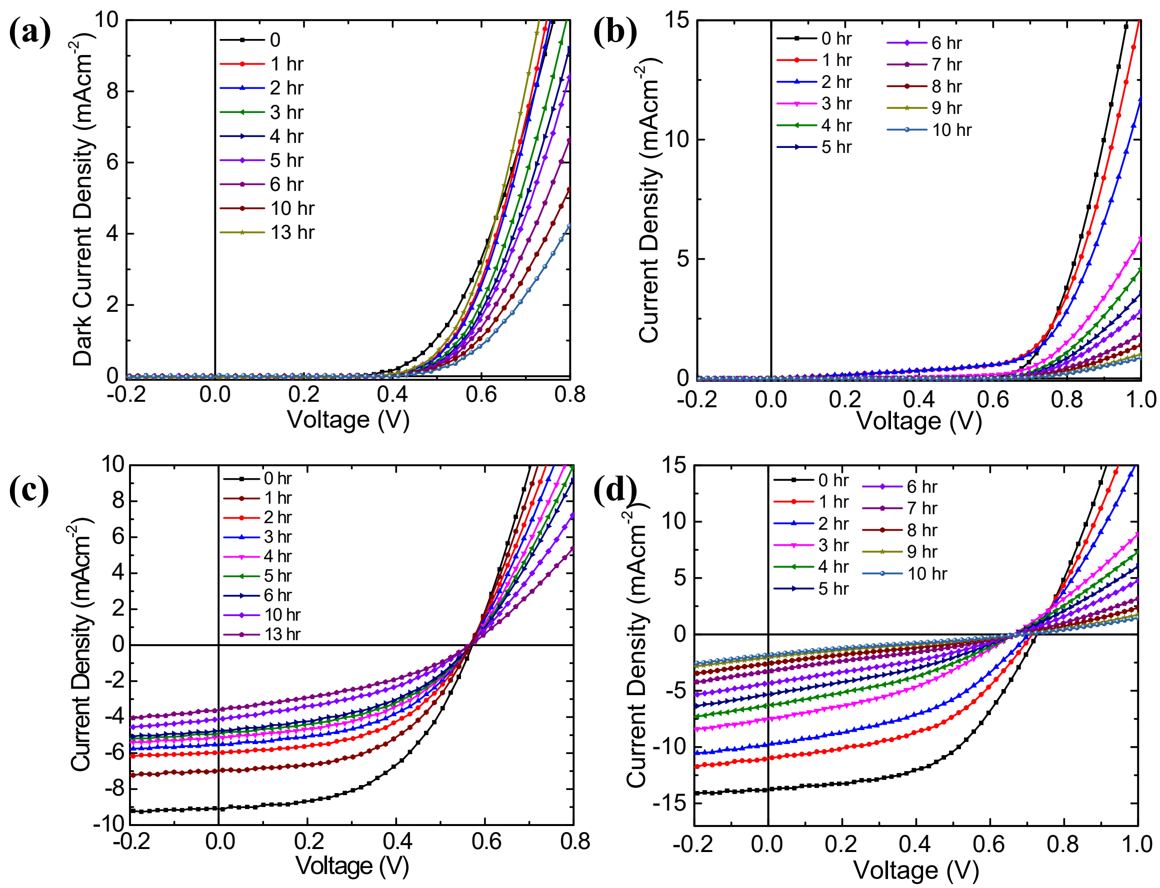

Figure S 2. (a) and (c) Dark and Light Current-voltage characteristics of P3HT:PC_{71}BM, (b) and (d) Dark and Light Current-voltage characteristics of PTB7:PC_{71}BM with PEDOT: PSS

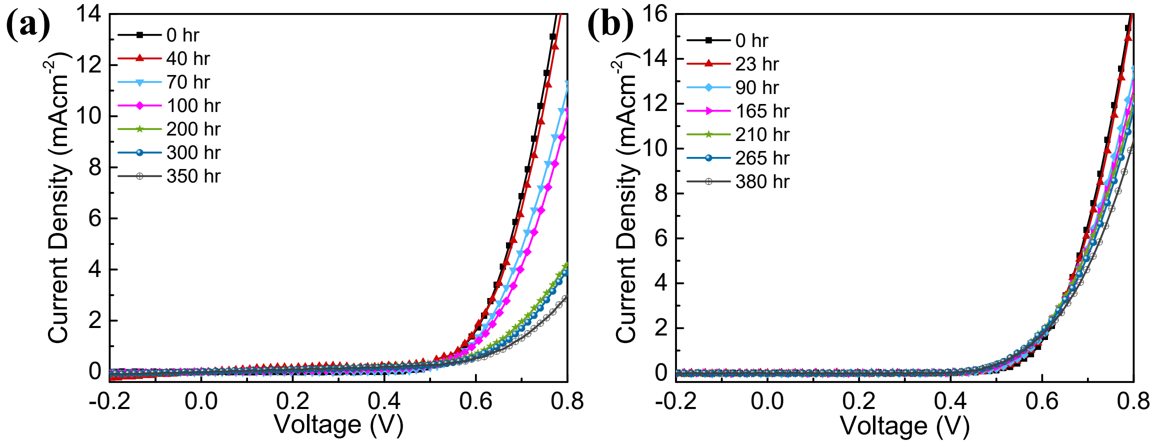

Figure S 3. Dark Current-voltage characteristics of P3HT:$PC_{71}BM$ with (a) PEDOT:PSS, (b) MoO_3

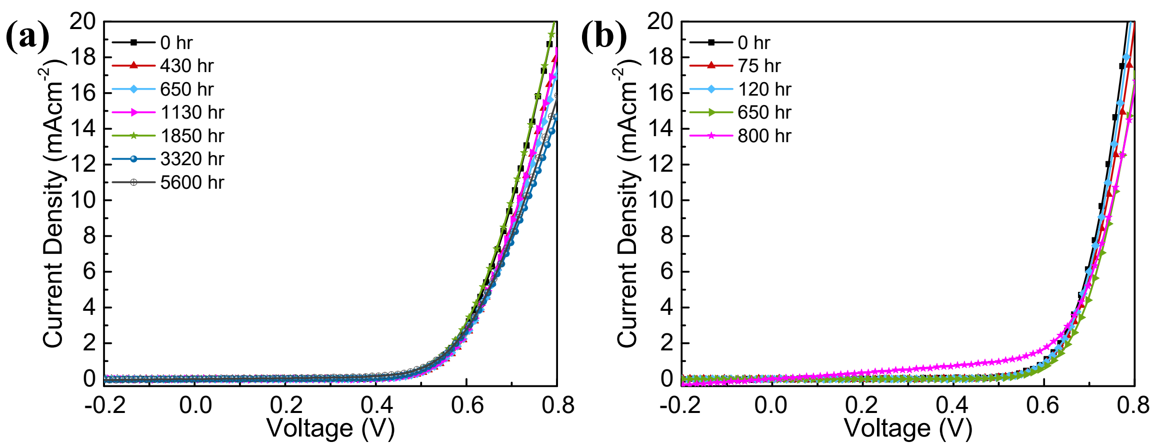

Figure S 4. Dark Current-voltage characteristics of encapsulated devices with MoO_3 as HTL for (a) P3HT:$PC_{71}BM$ and (b) PTB7:$PC_{71}BM$ devices

Table S 1. Photovoltaic parameters for P3HT:PC_{71}BM with PEDOT:PSS as HTL (Device C)

P3HT:PC_{71}BM/PEDOT:PSS	**J_{sc} (mA/cm^2)**	**Voc (V)**	**FF (%)**	**PCE (%)**
0 hr	7.68	0.61	58.27	2.73
40 hr	6.65	0.61	54.72	2.22
70 hr	5.55	0.60	53.75	1.79
100 hr	4.03	0.60	50.45	1.22
200 hr	1.86	0.585	45.95	0.5
300 hr	1.31	0.57	44.19	0.33
350 hr	1.08	0.564	37.75	0.23

Table S 2. Photovoltaic parameters for P3HT:PC_{71}BM with MoO_3 as HTL (Device D)

P3HT:PC_{71}BM/MoO_3	**J_{sc} (mA/cm^2)**	**Voc (V)**	**FF (%)**	**PCE (%)**
0 hr	6.46	0.60	59.16	2.34
23 hr	6.76	0.59	56	2.24
90 hr	6.18	0.59	55.6	2.03
165 hr	5.53	0.576	53.3	1.70
210 hr	5.35	0.576	52.3	1.61
265 hr	4.63	0.561	52.6	1.37
380 hr	3.48	0.560	51.8	1.01

Table S 3. Fitting parameters for Device C

	Device C		
Parameters	**Fitted Equation**	**b1**	**b2**
J_{SC}	$J_{SC1}(t) = J_{SC1}(0) + b_1 t + b_2 t^2$	-0.0056	8×10^{-6}
V_{OC}	$V_{OC1}(t) = V_{OC1}(0) + b_1 t$	-2×10^{-4}	
FF	$FF_1(t) = FF_1(0) + b_1 t$	-8.8×10^{-4}	
PCE	$PCE_{SC1}(t) = PCE_{SC1}(0) + b_1 t + b_2 t^2$	-0.00618	1×10^{-5}

Table S 4. Fitting parameters for device D

Device D			
Parameters	**Fitted Equation**	**b1**	**b2**
J_{SC}	$J_{SC2}(t) = J_{SC2}(0) + b_1 t$	-0.00125	
V_{OC}	$V_{OC2}(t) = V_{OC2}(0) + b_1 t + b_2 t^2$	-2×10^{-4}	4×10^{-7}
FF	$FF_2(t) = FF_2(0) + b_1 t + b_2 t^2$	-6.5×10^{-4}	9.8×10^{-7}
PCE	$PCE_{SC2}(t) = PCE_{SC2}(0) + b_1 t$	-0.00147	

Table S 5. Photovoltaic parameters for encapsulated P3HT:PCBM with MoO_3 as HTL (Device E)

Encapsulated P3HT:$PC_{71}BM/MoO_3$	**J_{sc} (mA/cm^2)**	**Voc (V)**	**FF (%)**	**PCE (%)**
0 hr	7.57	0.57	58.17	2.51
430 hr	7.17	0.57	56.3	2.3
650 hr	6.77	0.57	57	2.2
1130 hr	6.7	0.564	56.8	2.15
1850 hr	6.07	0.561	56.6	1.93
3320 hr	5.9	0.557	56.5	1.86
5600 hr	5.37	0.547	56.8	1.67

Table S 6. Photovoltaic parameters for encapsulated PTB7:$PC_{71}BM$ with MoO_3 as HTL (Device F)

Encapsulated PTB7:$PC_{71}BM/MoO_3$	**J_{sc} (mA/cm^2)**	**Voc (V)**	**FF(%)**	**PCE (%)**
0 hr	11.25	0.696	59.3	4.64
75 hr	11.17	0.690	60.0	4.66
120 hr	10.24	0.686	60.1	4.22
650 hr	10.10	0.680	60.0	4.18
800 hr	8.41	0.670	51.3	2.89

Simulation study:

The transport limited photovoltaic response can be described in terms of the quasi-Fermi level splitting by replacing external voltage with internal voltage ($V_{internal}$) through [1][1],

$$V_{internal} = V - \left(\frac{dJ}{\sigma}\right) \tag{S1}$$

The electrical conductivity σ depends on the position of the quasi-Fermi level, which is defined by [1],

$$\sigma = 2q\mu_d N_i \exp\left(\frac{V_{internal}}{2V_{TH}}\right) \tag{S2}$$

Where, N_i is intrinsic charge carrier density, q is Coulombic charge, V_{TH} is thermal voltage defined as k_BT/q

Therefore, a closed-form expression of the J-V curve under transport limited condition can be derived using well-known relations, $V_{OC} = V_{TH}\ln\left(\frac{J_{PH}+J_S}{J_S}\right)$ with the assumption $J_0 << J_G$ [2],

$$J = J_{PH}\left\{\exp\left[\frac{(V_{internal} - V_{OC})}{V_{TH}}\right] - 1\right\} \tag{S3}$$

So, we can rewrite the Eq. (S1) as,

$$V = V_{internal} + \left(\frac{dJ_{PH}}{\sigma}\left\{\exp\left[\frac{(V_{internal} - V_{OC})}{V_{TH}}\right] - 1\right\}\right)$$

$$= V_{internal} + \left(\frac{dJ_{PH}}{2q\mu_d N_i}\exp\left(-\frac{V_{internal}}{2V_{TH}}\right)\left\{\exp\left(\frac{V_{internal}}{V_{TH}}\right)\exp\left(-\frac{V_{OC}}{V_{TH}}\right) - 1\right\}\right)$$

$$= V_{internal} + \left(\frac{dJ_{PH}}{2q\mu_d N_i}\left\{\exp\left(\frac{V_{internal}}{2V_{TH}}\right)\exp\left(-\frac{V_{OC}}{V_{TH}}\right) - \exp\left(-\frac{V_{internal}}{2V_{TH}}\right)\right\}\right)$$

$$= V_{internal} + \left(\frac{dJ_{PH}}{2q\mu_d N_i}\exp\left(-\frac{V_{OC}}{2V_{TH}}\right)\left\{\exp\left(\frac{V_{internal}}{2V_{TH}}\right)\exp\left(-\frac{V_{OC}}{2V_{TH}}\right) - \exp\left(-\frac{V_{internal}}{2V_{TH}}\right)\exp\left(\frac{V_{OC}}{2V_{TH}}\right)\right\}\right)$$

$$= V_{internal} + \left\{\frac{dJ_{PH}}{2q\mu_d N_i}\exp\left(-\frac{V_{OC}}{2V_{TH}}\right)2\sinh\left(\frac{1}{2V_{TH}}(V_{internal} - V_{OC})\right)\right\}$$

$$= V_{internal} + \left\{ \frac{dJ_{PH}}{2q\mu_d N_i} \exp\left(-\frac{V_{OC}}{2V_{TH}}\right) \frac{(V_{internal} - V_{OC})}{V_{TH}} \right\} \quad \text{(Using the simplification } \sinh(x) \to x \text{)}$$

$$= V_{internal} + \alpha (V_{internal} - V_{OC}) \tag{S4}$$

where,

$$\alpha = \frac{J_{PH} d}{2k_B T \mu_d N_i} \exp\left(\frac{-V_{OC}}{2V_{TH}}\right) \tag{S5}$$

Inserting the value from Eq. (S4) into Eq. (2) leading finally [2],

$$J = J_{PH} \left\{ \exp\left(\frac{(V - V_{OC})}{(1+\alpha)V_{TH}} \right) - 1 \right\} \tag{S6}$$

As we know that at open circuit condition V = V_{int} = V_{OC}. Using this condition, Equation 2 leads to a well-known expression $V_{OC} = V_{TH} \ln\left(\frac{J_{PH}}{J_S}\right)$. This is reasonable because the current density is zero at open circuits, and transport issues are irrelevant.

Finally, putting the value of $\exp\left(-\frac{V_{OC}}{V_{TH}}\right) = \frac{J_S}{J_{PH}}$, where $J_S = qdk_L N_i^2$, α can be rewritten as,

$$\alpha = \frac{d^2 \sqrt{k_L G_{eh}}}{2\mu_d V_{TH}} \tag{S7}$$

Table S 7. Value of α for different devices understudy

Time (hr)	Device C	Time (hr)	Device D	Time (hr)	Device E	Time (hr)	Device F
0	3.05	0	3.1	0	2.8	0	3.3
40	3.8	23	4	430	2.9	75	3.34
70	3.92	90	4.1	650	2.95	120	3.4
100	4.7	165	4.7	1130	3	650	3.85
200	5.95	210	4.8	1850	3.05	800	4
300	6.4	265	4.9	3320	3.1		
350	6.8	380	5.05	5600	3.12		

(1) Neher, D.; Kniepert, J.; Elimelech, A.; Koster, L. J. A. A New Figure of Merit for Organic Solar Cells with Transport-Limited Photocurrents. *Sci. Rep.* **2016**, *6*, 24861.
(2) Abhishek Sharma, PhD Thesis (Supervisor J. P. Tiwari) , Awarded in 2019.