Supplementary material

Photo-induced degradation of organic light-absorbing materials measured through changes in infrared absorption

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1. Anneal of PTB7:PCBM films for different anneal times:

(a) (b)

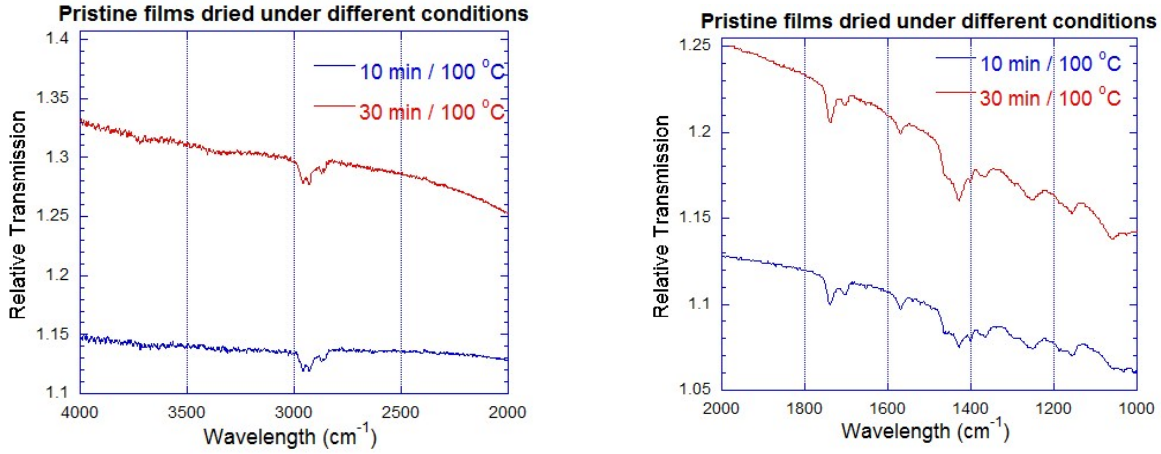


Fig. S1. Measured infrared (IR) transmission spectra of pristine PTB7:PCBM films that were annealed at 100 °C for 10 minutes (blue) and 30 minutes (red). The absorption is divided into a) high frequency (4000 cm^{-1} to 2000 cm^{-1}), and b) low frequency (2000cm^{-1} to 1000cm^{-1}).

2. **Environmental chamber for light induced degradation studies.**

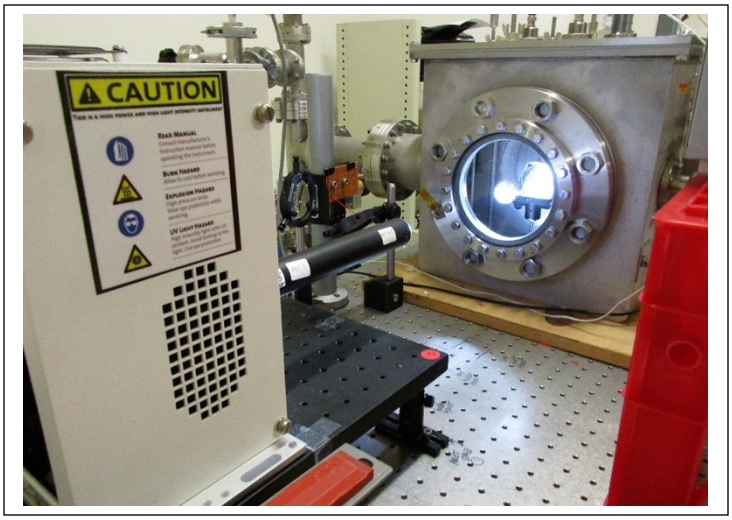


Fig. S2. Shown on the right side is the environmental chamber for measurement of light induced degradation of organic solar cell, that was filled with i) inert N_2 flow ii) dry air flow (N_2;O_2 70:30), or iii) ambient atmosphere (containing O_2 and moisture). Light is incident on a mirror inside the chamber that directs the light to the sample. The ABET solar simulator is on the left.

3. **Infrared spectroscopy of PTB7 films (without the blend)**

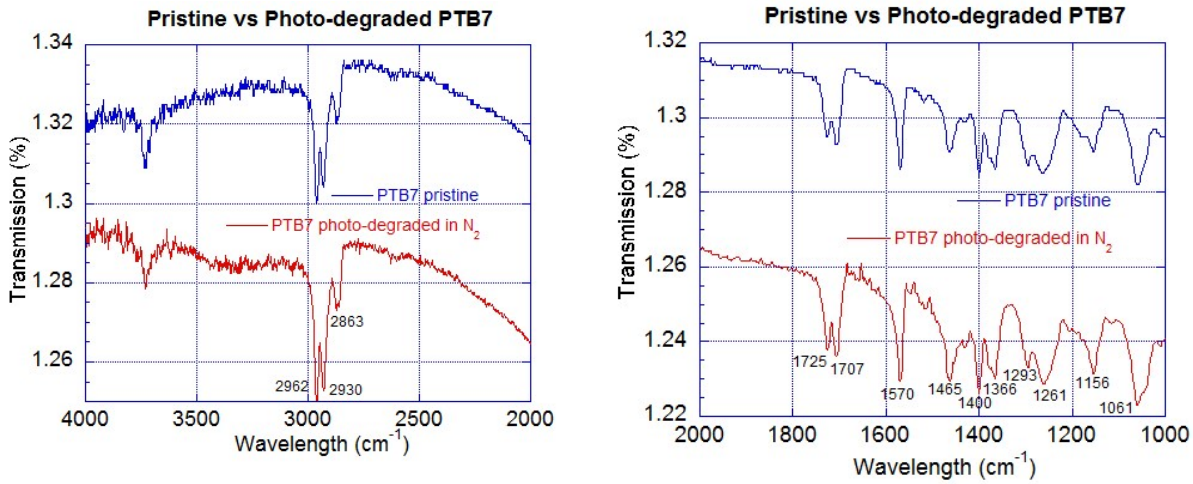


Fig. S2. Measured infrared (IR) transmission spectra of PTB7 film after photo-degradation in inert N_2 atmosphere. Pristine and photo-degraded film at a) high frequency (4000 cm^{-1} to 2000 cm^{-1}), and b) low frequency (2000cm^{-1} to 1000cm^{-1}).

Table S1. FTIR absorption features measured for pristine and photo-degraded (in N_2) PTB7 polymer films with the vibrational modes identified.

	pristine PTB7	**Photo degraded PTB7 in N_2**
Mode	Peak (cm^{-1})	Peak (cm^{-1})
CH2 asymm stretch	2960	2962
CH2 asymm stretch	2930	2933
CH2 symm stretch	2860	2862
C=O str. (aldehyde)	1725	1725
C=O str. (ester)	1707	1707
C=C aromatic str.	1570	1570
CH3 asym. bend	1465	1465
CF stretch	1400	1400
CH3 symm. bend	1366	1366
Asymm. C-O-C stretch+ CH2 twist	1293	1293
Asymm. C-O-C str; + CH2 twist	1261	1261
CH2 wag	1153	1153
C-O-C symm. stretch	1062	1066

In order to de-convolute the relative contributions of PTB7 and PCBM in the FTIR spectrum of the blend, we measured the absorption of PTB7 and PCBM films separately.

The PTB7 film in both pristine state and after light-degraded in N_2 shows (Fig. S2, Table S1) the stretch and bending vibrations similar to that in observed in the blend. Most of the IR-active modes observed in the PTB7:PCBM blend (Table 1), including the high frequency modes (above 2000 cm $^{-1}$), occur from the PTB7 component. No significant changes in absorption occur after light degradation in inert N_2, similar to the result observed with the blend.

4. **Infrared spectroscopy of PCBM films (without the blend)**

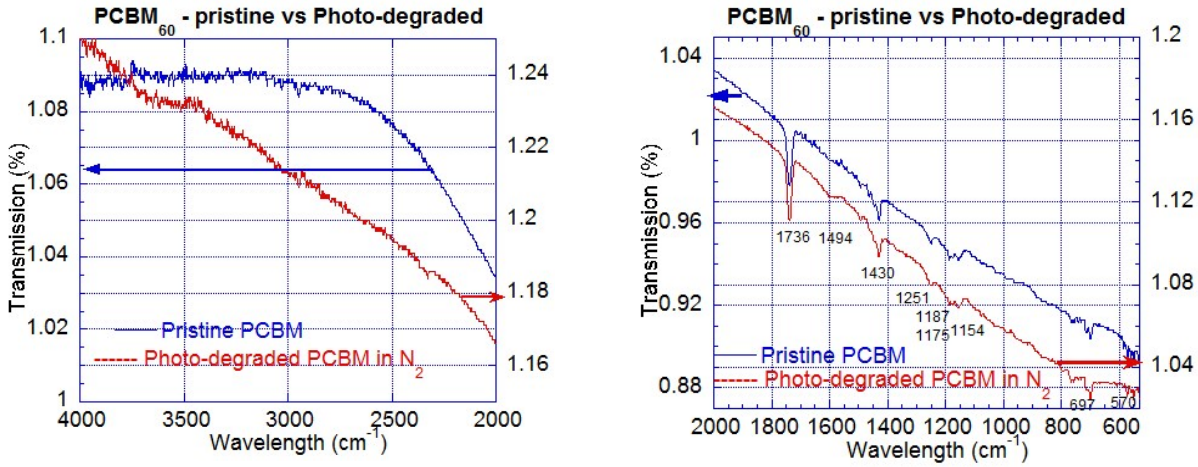


Fig. S3. Measured infrared (IR) transmission spectra of a PCBM film after photo-degradation in inert N_2 atmosphere. Pristine and photo-degraded film at a) high frequency (4000 cm^{-1} to 2000 cm^{-1}), and b) low frequency (2000 cm^{-1} to 1000 cm^{-1}).

Table S2. FTIR absorption features measured for pristine and photo-degraded (in N_2) PCBM films with the vibrational modes identified.

	Pristine PCBM	**Photo degraded PCBM in N_2**
Mode	Peak (cm-1)	Peak (cm-1)
C=O str. (ester)	1736	1736
CH bend (phenyl)	1494	1494
CH_3 bend (methyl)	1430	1430
C-H bend (into alkyl)	1251	1251
C-O stretch (ester)	1187,1175,1154	1187,1175,1154
C-C stretch fullerene	697,570	697,570

The high frequency regions (4000 – 2000 cm^{-1}) is featureless since there are very few ethyl (CH_2) groups in PCBM, compared to PTB7. At lower frequencies we observe C=O modes (1736 cm^{-1}), C-H bend (phenyl) (1494 cm^{-1}), CH_3 bend of the capping methyl group (1430 cm^{-1}), the C-H bend into the alkyl group (1251 cm^{-1}) and the C-O stretch modes of the ester group (1187,1175,1154 cm^{-1}) in both pristine and light degraded PCBM, similar to previous studies of PCBM (Ref. 28). We also observe the characteristic C-C fullerene modes of the C60 at 697 and 570 cm^{-1}.

5. **Atomic configuration of the PTB7 monomer**

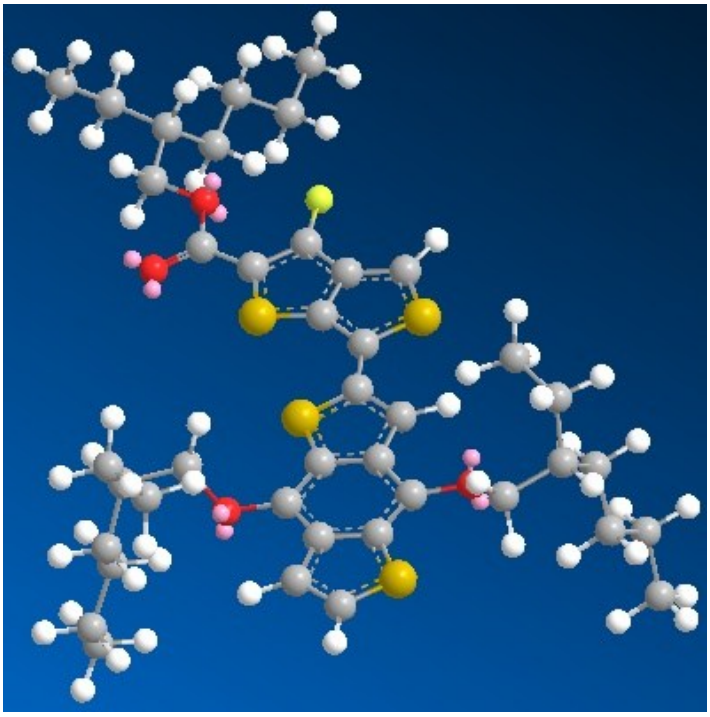


Fig. S4. Atomic configuration of the PTB7monomer, with C(grey), H(white), O(red); S(yellow) and F(green). Lone pair electrons (pink) are shown. The monomer has been capped by H atoms at the two ends. The aromatic backbone (dashed) is connected to alkyl chains through O bridging atoms.

6. Optical Absorption spectrum

We measured the optical absorption of PTB7-PCBM blends before and after light-soaking in N2 (Fig. S5 (a)); and before and after light-soaking in dry air (Fig. S5 (b). Negligible changes were observed. The band edge at 760 nm is consistent with the experimental band gap of 1.59 eV.

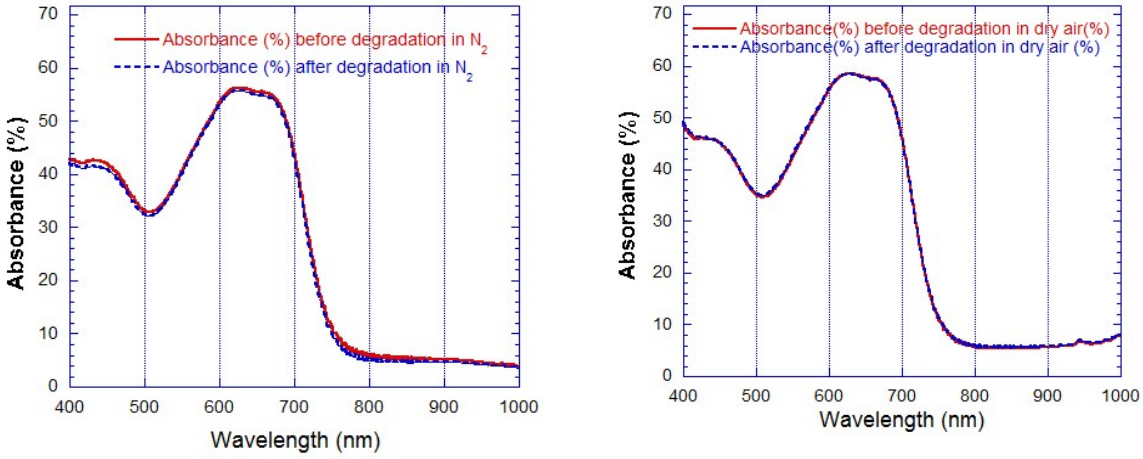
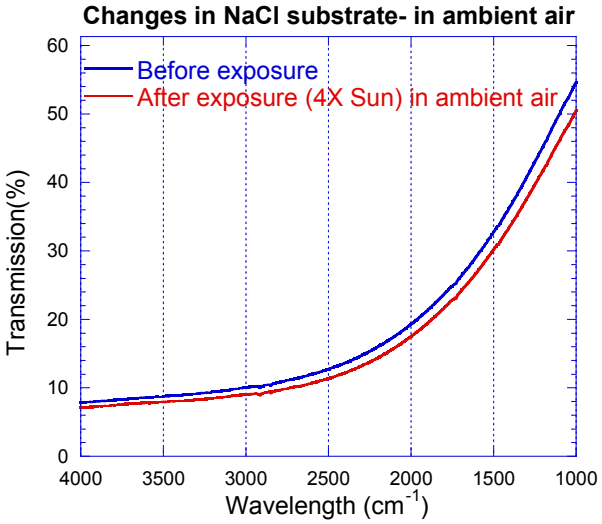


Fig. S5 The optical absorption of PTB7-PCBM blends a) before and after light-soaking in N2, and b) before and after light-soaking in dry air.

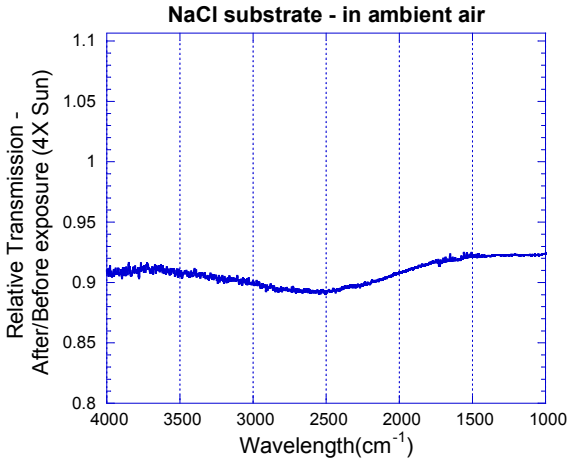
7. Analysis of photo-exposure of NaCl substrates

We examined the role of the NaCl substrate by photo-exposure of the bare substrates in ambient atmosphere (Fig. S6 (a,b)) and in dry air (Fig. S6 (c,d)), and comparing their IR absorption with the pristine salt substrate. No new IR absorption features were induced in the NaCl on photo-exposure. By plotting the ratios of the light exposed sample to the pristine sample, we observed an overall decrease of the IR transmission by ~ 8% after exposure to dry air (Fig. S6 (c) and between 0-10% for ambient atmosphere depending on the wavelength (Fig. S6 (d)).

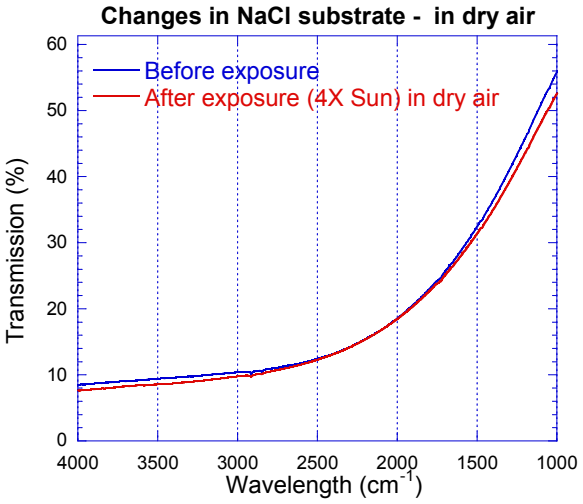
(a)



(b)



(c)



(d)

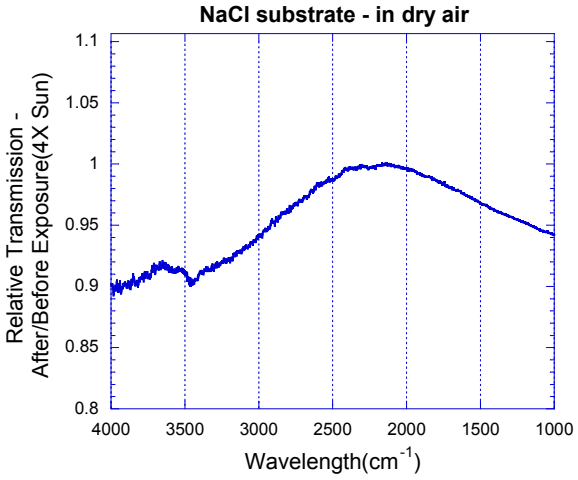


Fig. S6 a) Measured infrared (IR) transmission spectra of the bare uncoated substrate (NaCl) before light exposure (pristine) and after light exposure in ambient. b) Ratio of IR transmission of the photo-exposed in ambient and pristine NaCl. c) Measured infrared (IR) transmission spectra of the bare uncoated substrate (NaCl) before light exposure (pristine) and after light exposure in dry air. d) Ratio of IR transmission of the photo-exposed in dry air and pristine NaCl.