Supporting Information

Influence of traces of oxidized polymer on the performances of bulk heterojunction solar cells

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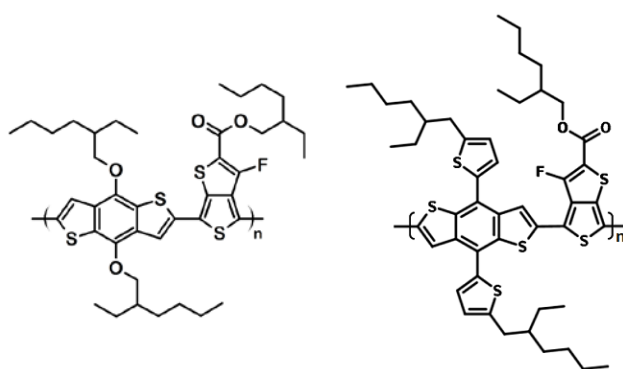
Figure S1. Chemical structure of polymers PTB7 (left) and PTB7-Th (right)
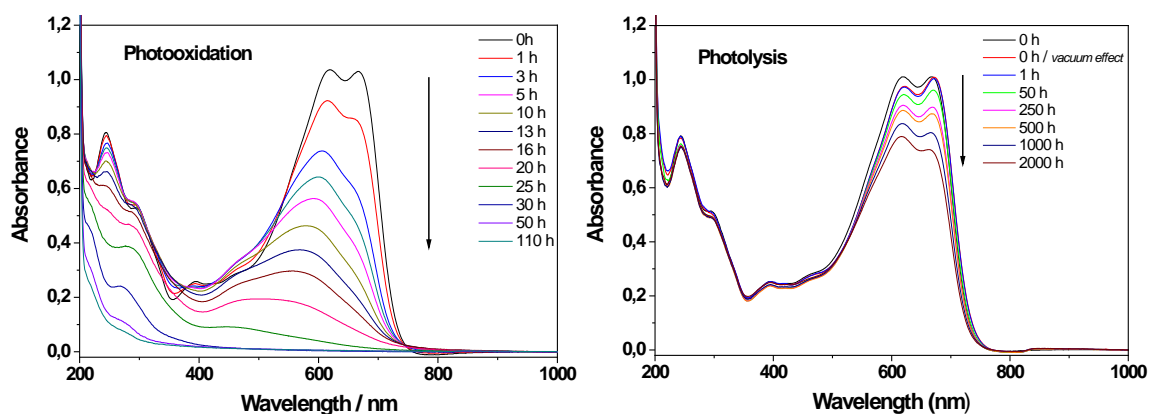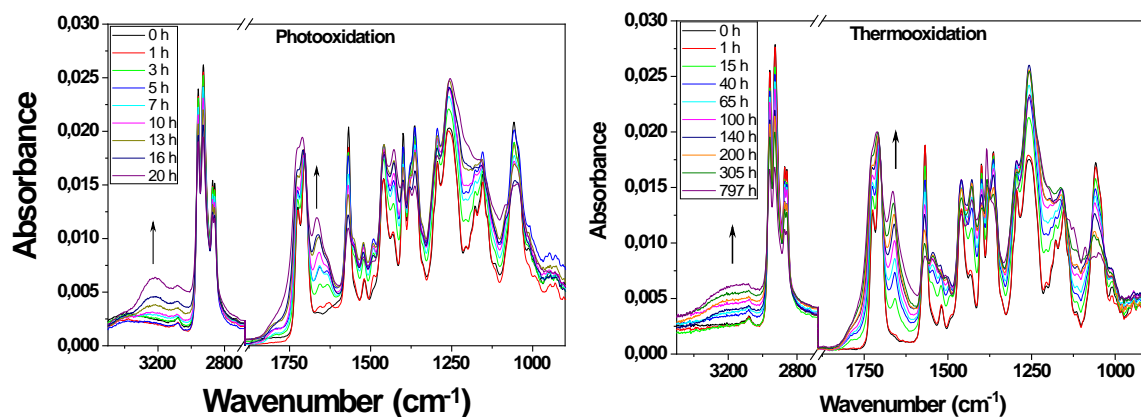

Figure S2. Evolution of the UV-Vis spectra of PTB7 films submitted to irradiation in ambient air (left) and in deoxygenated atmosphere (right).
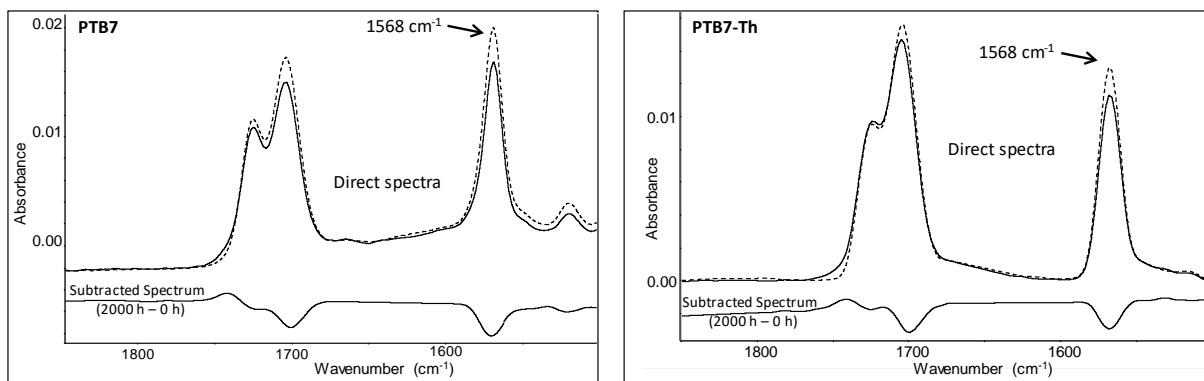
Figure S3. IR spectra of PTB7 (left) and PTB7-Th (right) submitted to photolysis. (top) direct spectra : before (dotted line) and after (full line) 2000 h exposure. (bottom) subtracted from initial spectra of 2000 h photolyzed sample
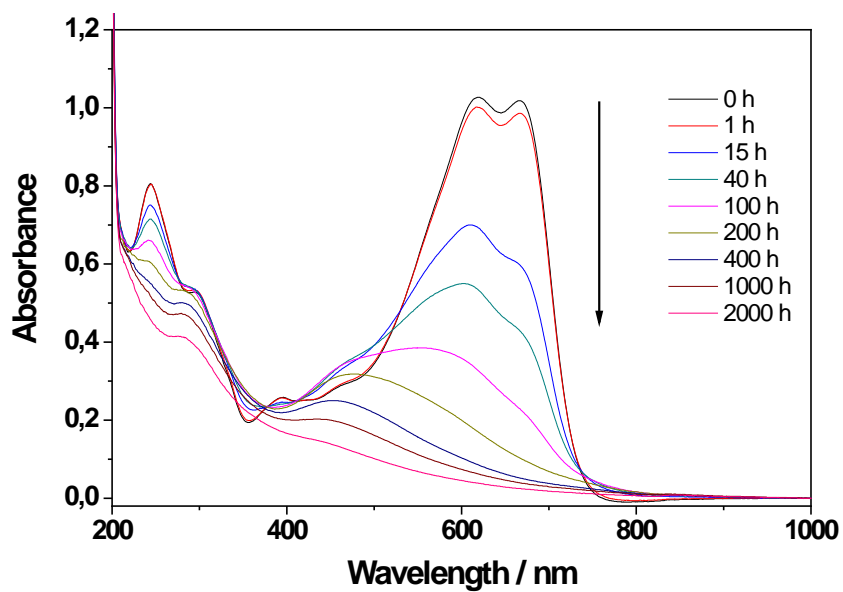
Figure S4. Evolution of the UV-Vis spectra of PTB7 films submitted to thermooxidation in a ventilated oven at 100°C.
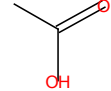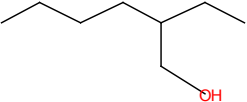
Figure S5. Evolution of the direct infrared spectra of PTB7. Photooxidation between 0 and 20h (left); Thermo-oxidation at 100°C between 0 and 797h (right).
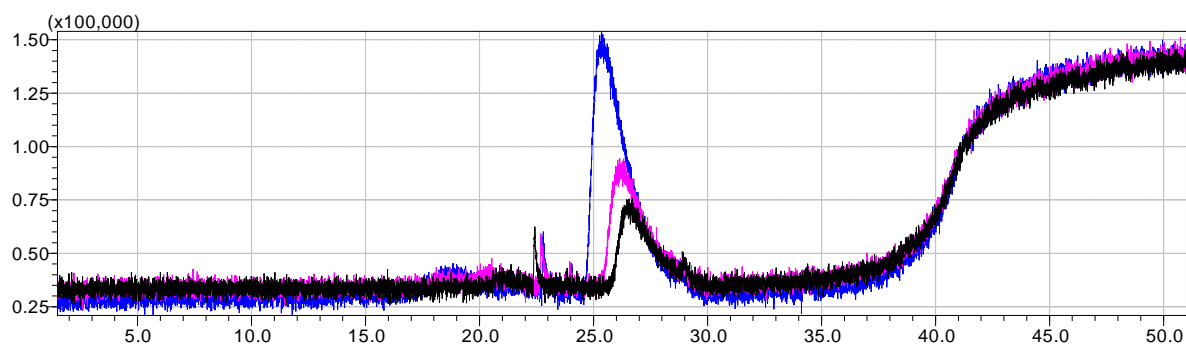
Figure S6. Total Ion Count chromatogram corresponding to HS-SPME-GC-MS analysis of a PTB7 sample irradiated for **Black = 0h, Pink =1h, Blue = 5h**. Refer Table S1 for peak identification.

Table S1. Main Volatile Organic Compounds released from irradiated PTB7 Films, identified by HS-SPME-GCMS (see also Fig. S4).

Retention time (min)	Identification	Chemical structure
22.695	Acetic acid	
26.145	1-Hexanol, 2-ethyl-	
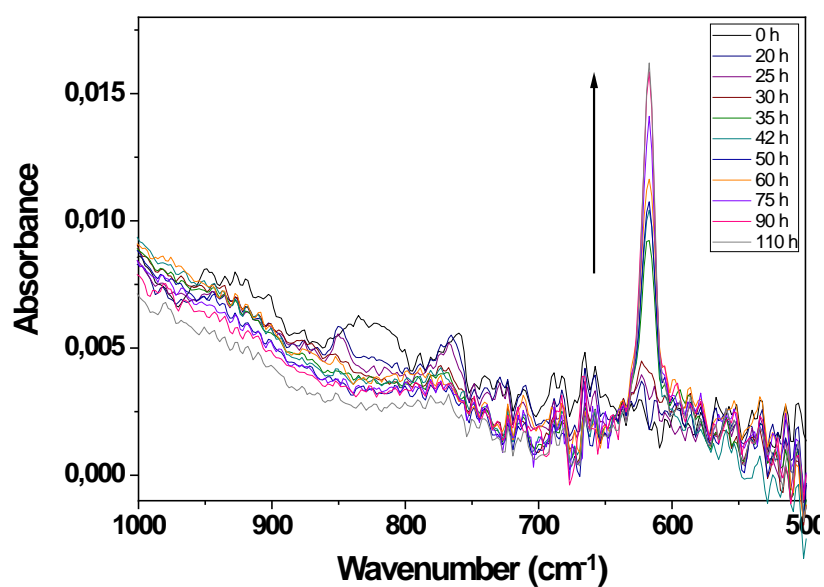
Figure S7. Evolution during photo-oxidation of the infrared spectra of PTB7 in the 1000-500 cm^{-1} region.
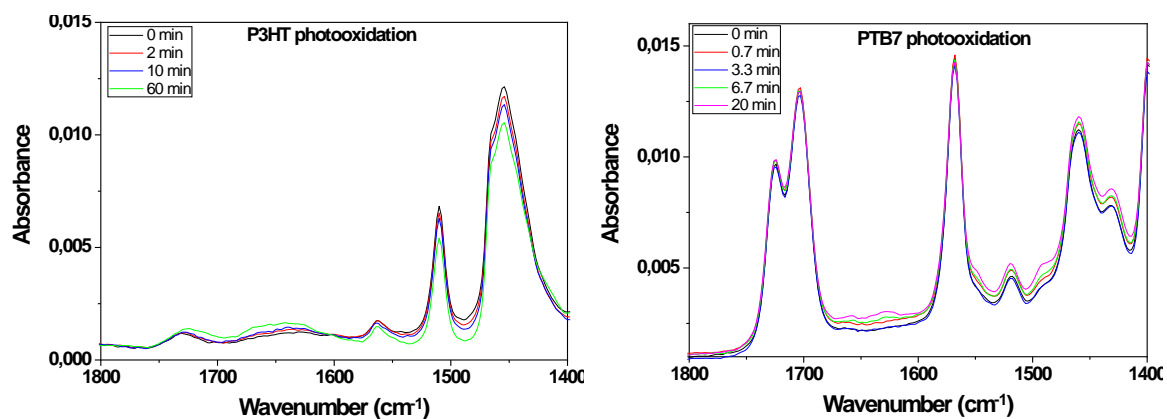
Figure S8. Evolution of the infrared spectra of PTB7 and P3HT submitted to short duration photooxidation. P3HT photo-oxidized between 0 and 60 min(left). PTB7 photo-oxidized between 0 and 20 min (right).
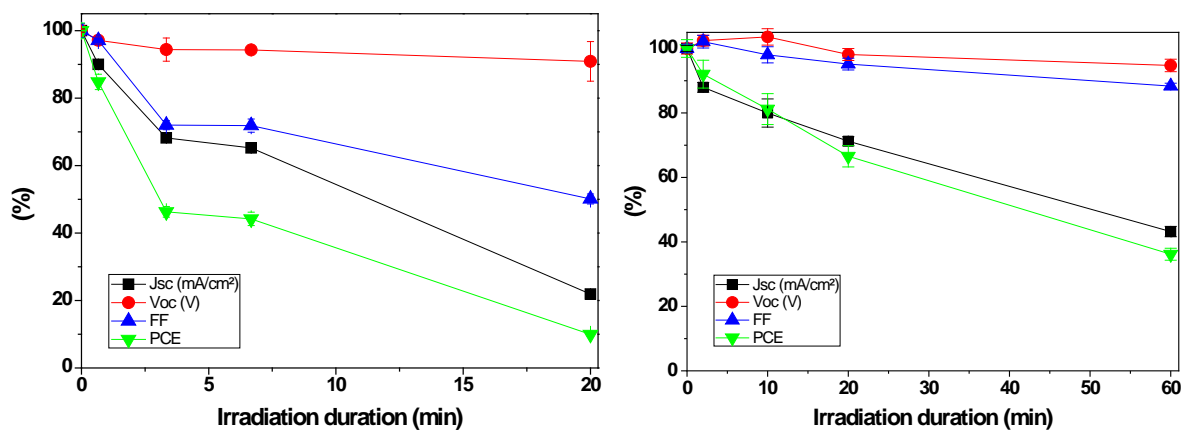
Figure S9. Normalized photovoltaic characteristics of solar cells based on previously photooxidized PTB7:PCBM from 0 to 20 min (left) and photo-oxidized P3HT:PCBM from 0 to 60 min(right).

Bond dissociation energies for all the possible hydrogen atoms of the studied structures

Be the following convention for labelling hydrogen atoms across the studied structures:

   A# - lateral chain of donor moiety

   B# - lateral chain of acceptor moiety

   C# - aromatic hydrogen atoms

And the following coding for each hydrogen # is illustrated below:

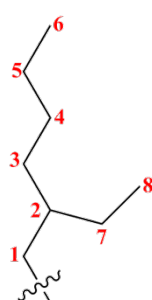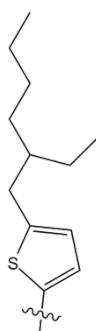| 2EH lateral chain | Secondary scission (*see below*) | Secondary scission (*see below*) |
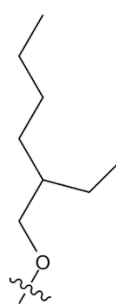
The following **Table S2** presents all the bond dissociation energies.

Besides individual hydrogen atoms, we also present the bond dissociation energies for the whole lateral chains for some of the compounds (if the same moiety exists in another different molecule, than it is studied only once).

We also studied two possible mechanisms for the dissociation of the lateral chain: a homolytic and a heterolytic one. Clearly, the homolytic is the most probable.

For PTB7, we studied a secondary scission of the lateral chain: instead of cleaving the COO-R bond, we now cleaved it as CO-OR, forcing a CO molecule to leave and the remaining radical now can be found on the thiophene cycle of the acceptor moiety. This is presented in the table under the label **2EHCO.**

Similarly, for PTB7-Th, the scission was performed firstly between the first carbon of the lateral chain of the donor moiety and the lateral thiophene ring. We then tested a secondary scission between the donor moiety and the lateral thiophene ring. This is presented under the label **T2EH.**

The weakest points are highlighted in red.

Concerning hydrogen atoms, as most of them are in alpha of an alkoxy group, they are not labile. However, the one of PTB7-Th is because there is no oxygen between the lateral thiophene and the 2EH chain.

Alcoxy 2EH lateral chains attached to the donor moiety have a low bond dissociation energy. This indicates that this can be a weak point of the molecule. Upon dissociation, one would have:

$$2EH^\bullet + P\text{-}O^\bullet$$
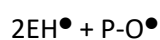
Table S2. Calculated bond dissociation energies in PTB7 and PTB7-Th within B3LYP/6-31G** theory level.

	BDE (kcal/mol)	
	PTB7	PTB7-Th
A1	101,30	82,88
A2	104,41	97,98
A3	105,03	103,41
A4	106,01	104,61
A5	104,75	108,37
A6	108,83	108,37
A7	104,88	102,43
A8	108,11	107,13
B1	106,27	101,03
B2	98,91	98,16
B3	106,89	102,52
B4	105,19	100,17
B5	106,10	105,39
B6	110,27	107,04

B7	107,32	104,01
B8	108,45	105,77
C1	121,09	117,91
C2	-	119,99
C3	-	119,30
R(donor)-radical	55,34	108,66
R(acceptor)-radical	93,58	86,70
R(donor)-ionic	146,56	-
R(acceptor)-ionic	148,35	-
R'(donor)-radical	126,52	-

R' PTB7 = **2EHCO_acc_rad**

R' PTB7-Th = **T2EH_don_rad**

Electrophilic character of the studied structures

The chemical potential can measure how eager is a molecule to accept an electron from its surroundings. It is calculated as the average between the electron affinity and the ionization potential in the same way that Pauli's electronegativity is. The hardness can measure how difficult is to the molecule to lose the electron that it has taken back to the environment. It means, it measures the ability of the molecule to acquire and to keep the additional charge. In an analogy to the electrical equation of power P dissipated over a resistance by a voltage ($P=V^2/R$), Paar and coworkers have defined the electrophilicity index **ω** as the measure of the electrophilic power of a molecule. The higher the value of this value, the more electrophilic is the molecule and, by consequence, the less propitious it is to undergo an electrophilic attack from another molecule. It means that, as the molecule is already electrophilic enough, it will be harder to another molecule (molecular oxygen, for example) to take an electron away of the molecule in question.

	IP_v (eV)	EA_v (eV)	η (eV)	μ (eV)	ω (eV)
PTB7	6,19	0,77	5,42	-3,48	1,12
PTB7-Th	6,07	0,84	5,23	-3,46	1,14

Index *v* stands for a vertical transition from ground to ionic state. IP stands for Ionization potential. EA stands for Electron affinity. **η** stands for the hardness. **μ** stands for the chemical potential and **ω** for the electrophilicity calculated for a single monomer.

	% more stable against electrophilic attack
PTB7	0,00
PTB7-Th	1,79

Calculated in reference to PTB7 as it is the less stable based on electrophilicity results.

Calculated for a single monomer.