Supplementary Information

The Critical Role of Interfacial Dynamics for the Stability of Organic Photovoltaic Devices

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Fig. S1 Absorption spectra of neat PCPDTBT (black line) and of the PCPDTBT:PCBM 1:3 (blue symbols).
Fig. S2 Black line: trEPR spectrum recorded 0.5 μs after the laser pulse of neat PCPDTBT spin coated film. Spectrum recorded at T=120 K. Green line: calculated triplet spectrum using the following parameters: D = -0.0326 cm⁻¹, E = 0.0039 cm⁻¹. Abs.= absorption, Em.= emission.

Fig. S3 Black line: experimental LEPR spectrum (light on-light off) of PCPDTBT:PCBM film. Green line: calculated EPR spectrum of two radicals with g factors of 2.0021 and 1.9997. The spectrum has been recorded at 120K under Xe lamp illumination of the film.

The spectrum in Figure S3 shows the presence of two radical species whose isotropic g-factors correspond to the typical values for a semiconducting polymer cation (g_c = 2.0021) and for the PCBM anion (g_a = 1.9997). For a better simulation of the spectrum, anisotropic g-tensor has to be used for both radicals and the corresponding g-tensor principal values are reported in Table S1.

Table S1 Principal values of g-tensors of the radicals observed in LEPR spectrum of the PCPDTBT:PCBM blend. The values are obtained from the best fit of experimental spectrum.

<table>
<thead>
<tr>
<th>Radical</th>
<th>g_1</th>
<th>g_2</th>
<th>g_3</th>
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<tbody>
<tr>
<td>Radical 1 (PCPDTBT⁺)</td>
<td>2.0032</td>
<td>2.0021</td>
<td>2.0011</td>
</tr>
<tr>
<td>Radical 2 (PCBM⁻)</td>
<td>2.0004</td>
<td>1.9999</td>
<td>1.9986</td>
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</tbody>
</table>

The g-factors for the two radicals correspond to the values reported in other polymer:PCBM blends.¹⁻³
**Fig. S4** TrEPR spectra recorded at 0.5 µs after the laser pulse of pristine PCPDTBT film. Black spectrum: sample sealed under vacuum. Red spectrum: sample exposed to air. Abs. = absorption, Em. = emission.

**Fig. S5** CW-PA spectra of the PCPDTBT measured in Nitrogen (dotted line) and in air (black solid line) atmosphere.
Fig. S6 TD-(U)DFT computed T1→Tn vertical excited state transitions at different XC DFT functional. TD-(U)B3LYP (red bars) gives the most reliable results if compared to the experimental (Figure 1.a) transient absorption spectra of the pristine PCPDTBT.

REFERENCES