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

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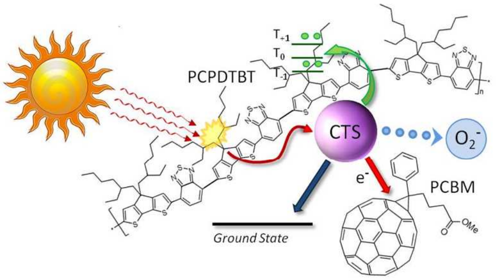
By combining optical and magnetic spectroscopy we found that the long-living emissive interfacial CT state is responsible in the generation of reacting and harmful species, affecting the robustness of the photovoltaic active layer.



Understanding the stability and degradation mechanisms of organic solar materials is required to achieve long device lifetimes. Here we study photodegradation mechanisms in (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]) : [6,6]-phenyl-C61-butyric acid methyl ester (PCPDTBT:PCBM) low band gap-based photovoltaic blend. We apply quasi steady state Photo-induced Absorption Optical Spectroscopy, time-resolved Electron Spin Resonance Spectroscopy and theoretical modeling to investigate the dynamics of long-lived photoexcited species. The role of the interfacial physics on the efficiency and robustness of the photovoltaic blend is clarified. We demonstrate that the polymer triplet state (T), populated through the interfacial charge transfer (CT) state recombination, coexists with charge carriers. However, contrarily to previous suggestions, it has no role in the degradation process caused by air exposure. Instead, the long-living emissive interfacial CT state is responsible for the blend degradation in air. It mediates direct electron transfer to contaminants, leading to the formation of reactive and harmful species, such as the superoxide.

## Introduction

Recent reports on organic solar cells presenting power conversion efficiencies exceeding 10% [1] have made compelling the need of improving the device stability in order to push this technology in the market of distributed and portable energy sources. By and large instability is caused by the combination of light and atmospheric agents, with major role of oxygen and water. The detrimental effects are electron trapping and photo-oxidation that break polymer conjugation and bleaches the absorption.[2, 3] Substantial efforts have been devoted to the development of efficient barrier materials which can protect the active photovoltaic layers from environmental agents.[4] However, so far, no effective solution preserving low cost and flexibility has been achieved. Perhaps one reason is that degradation mechanisms are still unknown. At one side, understanding the physical-chemistry behind the degradation issues can drive an educated synthesis of optimized materials; on the other side it can help in the optimization of the device architecture, e.g. targeting the right barrier responding to the right requirements. In the past years, two mechanisms have been identified as the main responsible for organic molecules degradations in presence of oxygen.[5-8] Oxygen sensitization is one of them, mediated by long lived triplet states with energy level higher than the differential energy between the oxygen singlet state and its ground triplet state, i.e. 0.98 eV.[9]

Alternatively, electron transfer could happen from the photo-excited polymer to molecular oxygen, generating the superoxide, $O_2$-, that is a very reactive anionic radical. It must be noticed that hydrated forms of molecular oxygen become easier to reduce, because their electron affinity becomes larger,[10] thus, even if water on its own seems to have small effect, it can accelerate the rate of degradation when $O_2$ is present.

As often highlighted when investigating the working mechanisms of excitonic solar cells, the interface physics rules the device macroscopic behavior, and this is the case also for degradation processes. In fact, degradation of a single component can be substantially affected when it is blended to have the photovoltaic composite. A few concomitant phenomena are suggested, i.e. light screening, singlet exciton quenching and radical scavenging, where the latter is supposed to be the dominant one.[5] In fact, this mechanism is affected when tuning the electron affinities of the electron acceptor compound in order to improve the device photo-voltage.[6] *Distler et al.* [5] also identified a destabilizing role of the electron acceptor molecule in the PCPDTBT:PCBM blend which has been generalized on the base of interface physics.[5, 7] When the interfacial CT state energy level is above the triplet level of the electron donor compound, the population of the latter becomes more efficient with consequent enhancement of photodegradation of the photovoltaic compound.[8, 9]

However, this conclusion is based on the unverified hypothesis that the triplet state is involved in the photodegradation reaction by oxygen sensitization.

Here, by combining optical and magnetic spectroscopic techniques sensitive to long living photoexcited paramagnetic species, i.e. quasi steady state photo-induced absorption (PIA) spectroscopy and Electron Spin resonance (EPR) spectroscopy, with theoretical calculations, we reveal the degradation dynamics in a prototypal photovoltaic blend, PCPDTBT:PCBM. We unambiguously show that the polymer triplet state is populated via recombination of the interfacial CT state. However, we also demonstrate that such a triplet state is not involved in the photodegradation kinetics of the photovoltaic blend when exposed to ambient conditions. We find that critical role is instead played by the long lived interfacial emissive CT state which triggers the formation of radicals through an electron transfer mechanism to the contaminant species.

## Results and discussion

Fig. 1 shows the CW photoinduced absorption (CW-PA) spectra of the pristine PCPDTBT and of the PCPDTBT:PCBM blend, in nitrogen atmosphere. The pristine polymer presents the photobleaching (PB, $\Delta OD<0$) of the ground state absorption ($S_0$) for probing energy above 1.35 eV (920 nm), and a PA band ($\Delta OD>0$) for probing energy below 1.35 eV, peaking at ~ 1 eV. In literature this feature has been assigned to triplet state PA generated in the pristine polymer upon inter-system crossing (ISC) from the photoexcited singlet state ($S_1$).[9, 11]

The spectrum of the blend reveals a broader and slightly red shifted PA band, peaking at ~0.95 eV (1305 nm). Previous studies have assigned the feature at ~ 0.95 eV to the PA of the polymer positive polarons. [9, 11-14]

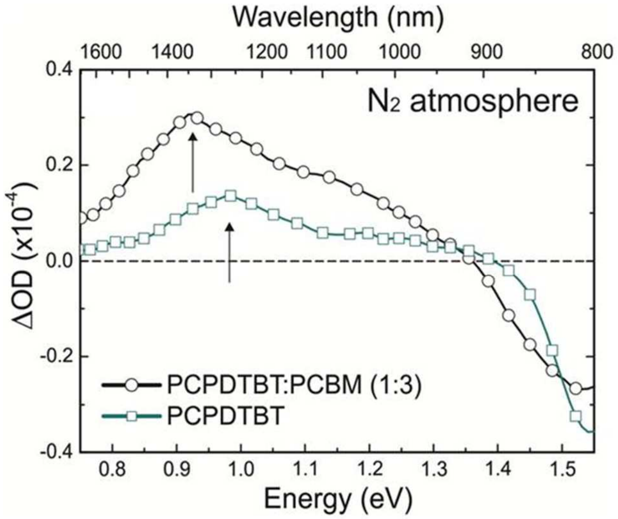


**Fig. 1** CW-PA spectra of the pristine PCPDTBT film (blue squares) and PCPDTBT:PCBM (1:3) blend (black dots) measured under Nitrogen atmosphere at room temperature. The arrows indicate the probe energies corresponding to the excited state triplet to triplet (T1→Tn) photoinduced absorption (PA) transition (at 1 eV/ 1240 nm) and to charge PA (at 0.9 eV/ 1370 nm).

It is however hard to exclude a co-existence of both polarons and triplets states just on the base of optical measurements and this issue has been debated for PCPDTBT based blends.[9, 11-15]

To settle the debate we performed time-resolved EPR (trEPR) measurements, which allow distinguishing species with different spin multiplicity (Triplets, CT states and free charges) in a time window between 150 ns and a few ms.[16, 17]

Fig. 2a shows the trEPR spectrum of the pristine polymer at 500 ns time delay after the photoexcitation (thin film and solution samples show identical spectra, see Fig. S2 in Supplementary Information, SI) which extends over about 800 Gauss and shows a complex pattern, with a signal partially in emission and partially in absorption. These are common features for transient photogenerated paramagnetic species and depend on the non-equilibrium population of electron spin states (spin-polarization, indicated in the following as T+1 and T-1), controlled by spin-selective generation and decay processes.[16] The relevant parameters characterizing the magnetic interactions in the triplet state are the zero-field splitting parameters $D$ and $E$, related to the mean electron-electron distance (D) and the deviation from axial symmetry of electron distribution in the triplet state (E). They can be extracted from spectral simulation[18] which, in our case, provides the best fit values of $D = -0.0326\ cm^{-1}$ and $E = 0.0039\ cm^{-1}$ (the sign of D is assumed to be negative as in other conjugated oligomers and polymers.[18] The good fit of the experimental trEPR spectrum (green line in Fig. 2a) allows us to infer that the triplet state, T, in the pristine polymer, is populated via spin-orbit promoted inter-system crossing (ISC) from the singlet excited state (S). ISC is a spin-selective process which generates a non-equilibrium distribution of the spin sublevel populations with different rates (see sketch in Fig. 2d).

Fig. 2b presents the trEPR spectrum of the PCPDTBT:PCBM blend at 500 ns time delay. It shows a signal extended over about 800 Gauss and a pattern that exhibits double emission/absorption peaks both at low field and high field-side. The shape and the spectral width of the spectrum suggest the assignment to the triplet T state of the polymer, but with an *anomalous* spin polarization. The difference in the absorption/emission pattern with respect to the neat polymer is due to different spin sublevels populations. It can be rationalized by considering different pathways for triplet generation. In the pristine PCPDTBT the T state is solely populated via ISC from S, whereas in the donor-acceptor blend the triplet state can be populated by two concurrent mechanisms: the ISC and a spin-selective charge recombination mechanism. Accordingly, the EPR spectrum can be simulated by using the same zero field parameters of the PCPDTBT triplet, but using an excess population on the T+1 and T-1 states. The best-fit calculated spectrum is shown in Fig. 2.b (solid orange line). The T±1 excess population can be explained by considering the possible spin states of a correlated polaron pair (named CT state in the following): there are four spin levels, one with singlet character (S) and three with triplet character (T-1 T0, T+1). The S and T0 levels are mixed by several mechanisms such as g-factor differences, electron-electron magnetic dipolar interaction and hyperfine interactions. The CT state possesses initially only singlet character. Due to the g-factor differences, hyperfine or dipolar interactions, the CT state evolves into triplet T0 within a time scale shorter than our time resolution.[15]

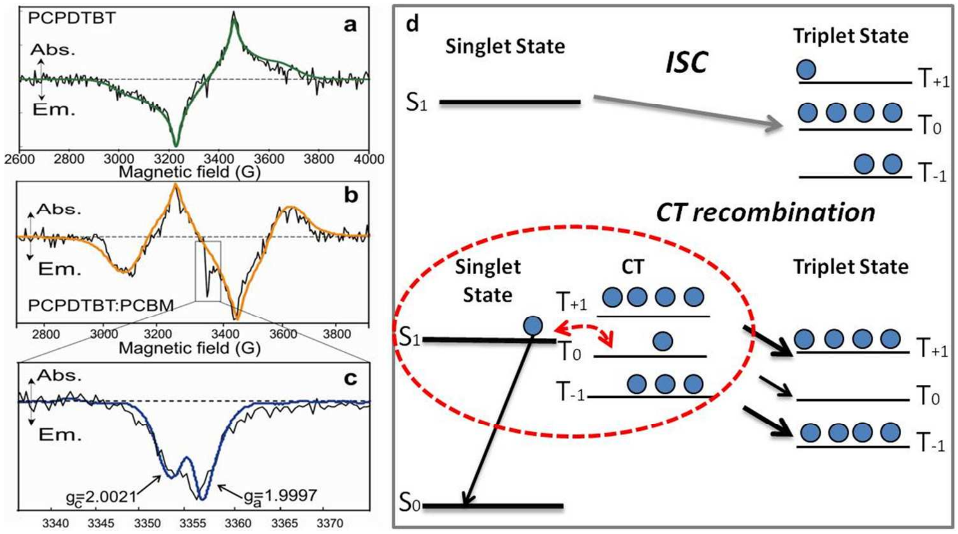


**Fig. 2** a) trEPR spectrum for the pristine PCPDTBT solution in *o*-DCB recorded at 0.5 µs after the laser pulse (black line: experimental data; green line: calculated triplet spectrum from ISC). b) trEPR spectrum of the PCPDTBT:PCBM film recorded at 0.5 µs after the laser pulse (black line: experimental data; orange line: calculated triplet spectrum derived from both ISC and recombination processes). c) trEPR spectrum in the narrow central magnetic field range (black lines: experimental spectrum), integrated LEPR spectrum (blue line), sensitive only to long living photo-induced radical species. All trEPR spectra are recorded at 120 K. (Abs. = absorption, Em. = emission). d) Representation of the main processes leading to triplet population.

Spin relaxation processes slowly transfer population from T0 to the T-1 and T+1 states of the CT pair. If the CT state in the singlet state recombines geminately, it leaves an excess of pairs in the triplet states T+1 and T-1, since the T0 is partially depleted (see sketch in Fig. 2d). Triplet recombination pathways for the CT state have been already reported in the literature,[9, 15, 20] leading to either the triplet state on the donor (the polymer) or on the acceptor (PCBM), with a spin-conserving process that projects the triplet sublevels population from the source state (the CT in the triplet state) to the final triplet state.[21, 22] Therefore, we conclude that the polymer triplet state acts in this photovoltaic blend, at room temperature, as a sink state where a fraction of CT state population can decay. When focusing in the spectral range between 3340 and 3370 Gauss (Fig. 2c) we note also the presence of a narrow emissive peak. The sharp feature is the result of two partially overlapped emissive peaks. The solid blue line represents the steady state Light-Induced EPR (LEPR) spectrum, integrated and normalized, taken in the same spectral range (see Fig. S3 in the SI for the derivative spectrum and simulation). The spectrum extends over ~20 Gauss and shows two lines, 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).[23] The emissive character of free charges has been already observed and interpreted in terms of a spin-selective decay pathway of the CT state by a partial mixing of S and T0 spin levels of the pairs.[24] The trEPR spectrum does not indicate any appreciable interaction between the two spins which could modify the spectral shape giving rise to a spin-correlated radical pair spectrum, as already described in other polymer: fullerene based blends.[24, 25] Therefore, we conclude that on µs timescale both triplets and charges coexist.

Having clarified the photophysical scenario under inert conditions, we explore the effect of air exposure. We have measured the trEPR spectra of the PCPDTBT:PCBM film taken in vacuum ($10^{-5}$ mbar) and in air (Fig. 3a, black and red lines, respectively). The results show no alteration of the spectral features related to triplet species, clearly indicating, contrary to what previously proposed in the literature, that the oxygen has virtually no effect on the polymer triplet population. Minor changes have been also observed for the pristine PCPDTBT film (see Fig. S4 and S5 in the SI). This experimental result has been rationalized by computing at the DFT/TDDFT level of theory the triplet energy levels (Tn) for a finite size chain oligomer, i.e. four repeat units, of PCPDTBT. Fig. 3b shows the computed electronic states for singlets and triplets manifold at the UB3LYP level, the one that better features the triplet energies in molecular systems with strong intra-chain charge transfer character. We find the lowest triplet state located 0.78 eV above the ground state. It may be considered as an upper limit since larger conjugation length or solid state effects (e.g. polarization) will lower the actual triplet energy of the polymer. Thus, reminding that the oxygen triplet level is at 0.98 eV, the calculations suggest that the $T_1$ state has very little chance to undergo oxygen sensitization, supporting our experimental evidences. We have to mention that in Ref. [9] a higher energy for the $T_1$ state has been estimated when the polymer is dissolved in solution (just above 0.98 eV).We conjecture that solvent effects on the energetic of the donor-acceptor polymer can likely change the scenario when comparing solid states and solution samples.

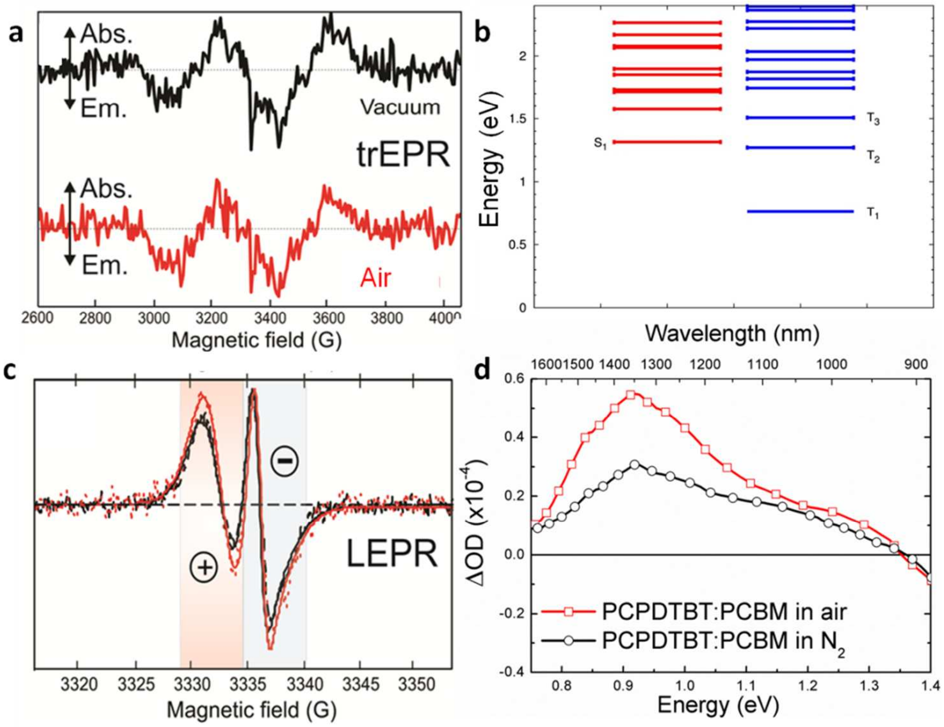


**Fig. 3** a) trEPR spectra at 0.5 μs after excitation of the PCPDTBT:PCBM blends in absence of oxygen (black), and in air (red); Abs.=absorption, Em.=emission. b) Computed singlet (red lines) and triplet (blue lines) excited state energies (vertical transitions) at the B3LYP/6-31G** level for the PCPDTBT tetramer. c) LEPR spectra of PCPDTBT:PCBM blend in absence of oxygen (black) and in air (red); dotted lines: experimental data, solid lines: best fit, calculated spectra. The + and – symbols and the shadowed areas are located at the spectral positions of the cation and anion radicals (polarons) d) CW-PA spectra of PCPDTBT: PCBM (1:3) measured under Nitrogen (black dots) and air (red squares) atmosphere.

On the other hand, different scenarios appear when we look at the effect of air exposure on the charged species.

Upon air exposure, the LEPR spectra (see Fig. 3c) show a relative increase of the spectral feature related to the positive charge (PCPDTBT cation) with respect to the one of the negative charges (PCBM anion). This information retrieved from EPR spectroscopy is confirmed by optical spectroscopy measurements. The CW PA spectrum (Fig. 3d) shows that the PA band peaking at 0.95 eV increases with air exposure. Thus we conclude that upon air exposure the charge population in the photovoltaic blend remains unbalanced in favor of positive charge. Though dry $O_2$ or pure $H_2O$ clusters may be poor electron acceptors, hydrated $O_2$ $(H_2O)_n$ clusters present in atmosphere show a larger electro negativity which can foster p-photo-doping of the organic blend[10] as we observe in our experimental result, leaving behind a $PCPDTBT^+$. Of course, the presence of reactive radical species such as $O_2^-$ can initiate the organic compound degradation.[5, 6]

Having clarified what is the degrading mechanism, the question that remains to be answered regards the nature of the photoexcited state acting as the intermediate state for such a process. The triplet population is not affected both in pristine and blend samples. We conjecture that both the triplet generation mechanisms in both samples and the formation of the interfacial CT state just upon photoexcitation of the blend are faster phenomena than any photo-induced electron transfer to the accepting contaminating species introduced by the environment (e.g. OH•, OOH•, or hydrated $O_2(H_2O)n$ species). Though it is clear that the degradation mechanism is somehow related to the interface dynamics, whether is the anion on the PCBM molecule (also generated upon photoinduced charge transfer) interacting with the doping species or a bound species cannot be fully assessed on the basis of the previous observations. Some indications can be obtained by the recent work of A. Rao *et al.*[15] They demonstrated that free carriers recombination partially populates the triplet state. Thus, direct involvement of the PCBM anion would have affected the triplet population too, which we do not observe.

The quenching behavior of the photoluminescence (PL) of pristine polymer and luminescent CT state may help answering this question. Fig. 4 shows the steady state PL spectra from a pristine PCPDTBT thin film (Fig 4a) and the blend PCPDTBT/PCBM (Fig. 4b) in vacuum and upon air exposure. The PL of the pristine sample, peaking at about 900 nm (1.37 eV), arises from the radiative recombination ($S_1 \rightarrow S_0$) of the polymer exciton. When the polymer is blended with PCBM, the excitonic PL is completely quenched, while an emissive band at longer wavelength (around 1100 nm/ 1.12eV) appears, which has been assigned to the radiative recombination of interfacial CT states.[26] While the intensity of the pristine sample is unaffected by air exposure, the emission intensity in the blend is quenched by oxygen.

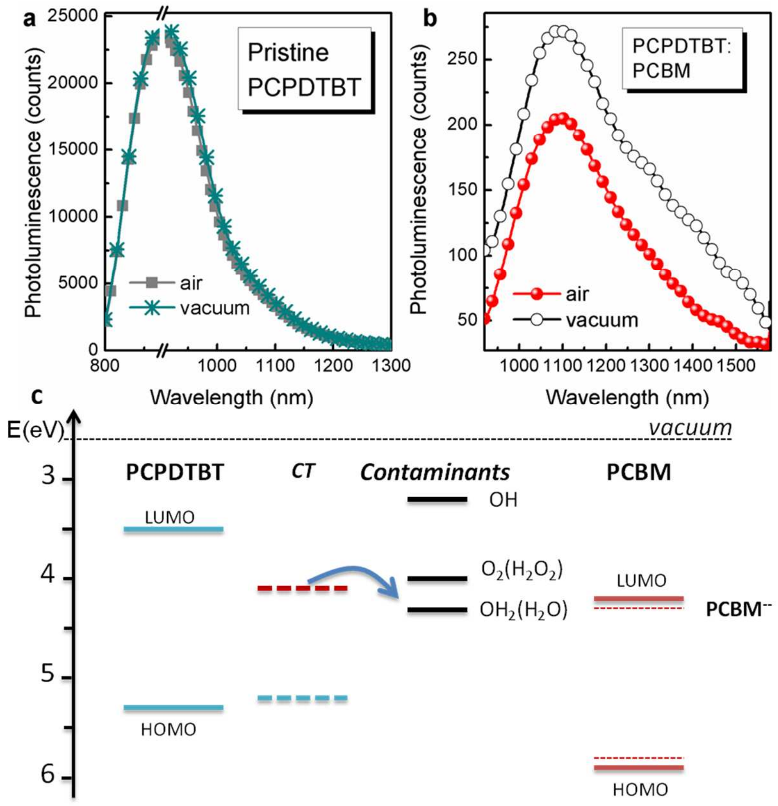


**Fig. 4** CW-Photoluminescence spectra of a) the pristine PCPDTBT (S1→S0) and b) the PCPDTBT:PCBM blend (CT1→CT0) upon excitation at 700 nm. c) Energy levels diagram of the system components. The arrow indicates the photo-degradation mechanism occurring through the interfacial CT state.

This observation is in accordance with the short fluorescence lifetime of the pristine polymer film of 200 ps, [26] which suggests that the deactivation of the pristine singlet excitons by radiative and non-radiative recombination is much faster than electron transfer to oxygen centered contaminant species. On the other hand, the excited state lifetime of the CT complex (≥ 1 ns [11]) is long enough to allow for collisional quenching by oxygen involving electron transfer to the latter. Moreover, from PL emission we can estimate the CT energy level to be around 1.1 eV (1127 nm), thus prone to interacts with oxygen species.

Therefore we conclude that the formation of long lived interfacial CT states mediates electron transfer to the contaminant species in competition with radiative and non radiative recombination processes occurring on faster timescale (see sketch in Fig. 4c).

## Conclusions

In summary, by combining EPR and optical spectroscopy with theoretical calculations, we have investigated the dynamics of paramagnetic species, i.e. triplet and radical species in a prototypal photovoltaic blend. We find that in the pristine PCPDTBT the triplet state is populated via ISC from the singlet state, while in the PCPDTBT:PCBM blend, the interfacial CT state partially recombines into the polymer triplet state. We show that upon air exposure the photophysical properties are virtually unaffected in the pristine polymer, but change dramatically in the blend with electron acceptor. Contrarily to previous suggestions, we demonstrate that the triplet state has no role in the degradation process. Instead we reveal the critical role of the photoexcited interfacial CT state in the generation of reacting and harmful species, such as the superoxide, upon electron transfer to contaminants such as OH•, OOH•, or hydrated $O_2(H_2O)n$ clusters present in atmosphere. Through this study we have being able to shed light on the crucial aspects of the interface physics, which so far has been mainly investigated to improve the overall device power conversion efficiency, in regard of the solar cell stability. The sensitivity of the CT state to contaminants will depend on its lifetime and its energetic. The first one is more difficult to forecast, though recent studies have highlighted how the interface local morphology can facilitate the charge separation; on the other end the latter can be easily tuned by designing polymers and fullerenes with larger electron affinities. Our results reveal that robust photovoltaic blends require an educated design of the interface energetic not only for charge separation but also for stability.

## Experimental

### Materials

PCPDTBT (Mw = 55.7 kg mol−1, PD =2.28) was synthesized according to the published route[27] $PC_{60}BM$ was obtained from Solenne. Thin films of PCPDTBT and PCPDTBT:PCBM blend were prepared under ambient conditions by doctor blading on soda lime glass. PCPDTBT films were prepared from 1% (w/v) polymer solutions in chlorobenzene, respectively. Blend films were processed from analogous solutions (same solvents and polymer concentrations) with PCBM in the optimized ratio (1:3.6). Prior to polymer deposition, the substrates were cleaned for 15 min in acetone and 15 min in 2-propanol using an ultrasonic bath. After deposition, the samples were annealed in a nitrogen atmosphere.

### CW Photoinduced Absorption

Quasi-cw Photoinduced absorption (PA) spectroscopy was used to investigate the absorption of photo-generated long-lived species (from µs to ms). Pump excitation was provided by a HeNe laser at 632 nm modulated by a mechanical chopper. A 8 mm diameter laser beam was made using a telescope in order to guarantee a good overlap with the probe beam. The probe was generated from a 100 W halogen lamp. The changes in transmission under photoexcitation were detected by a silicon photodiode and measured by a lock-in amplifier referenced to the modulation frequency in order to measure the signal in phase and out of phase with respect to the laser pump. Finally, the signal was normalized to the un-modulated transmission for every wavelength ($\Delta T/T$), from which the differential optical density (ΔO.D.) was calculated. The samples were measured in a vacuum chamber filled with nitrogen atmosphere; to study the effect of degradation, the chamber was then opened to let ambient air in.

### CW Photoluminescence

For quasi-cw Photoluminescence a spectrofluorimeter (HORIBA Jobin Yvon Nanolog) has been used. A 450 W xenon short-arc lamp coupled with single-grating excitation and emission monochromator has been used to excite the system. The emission spectra has been registered by a VIS Si-based (400-800 nm) and IGA-020 near-IR solid-state photodiode (800–1500 nm).

### EPR Spectroscopy

For the EPR measurements, PCPDTBT:PCBM blend films were prepared into quartz tubes (4 mm o.d.) from mixed solution of polymer and fullerene in ODCB (1:2 by weight, 1 mg/ml each component). The solvent was eliminated from the solutions in the tubes by slow (about 1/2 hour) evaporation under vacuum and finally the tubes were flame sealed under vacuum ($<10^{-3}$ mbar).

Spin-coated sample were prepared depositing a solution of PCPDTBT:PCBM (1:2 by weight, 10 mg/ml each component) onto a PET substrates and successively inserted into quartz tubes. The EPR spectra were recorded with a Bruker ER200D X-band spectrometer equipped with a nitrogen flow cryostat for sample temperature control. LEPR spectra have been obtained by subtracting the EPR spectrum recorded before illuminating the sample from the spectrum recorded under illumination of the sample. A 300 W Xenon lamp, IR filtered and focused onto a quartz optical fiber was used as the source of photoexcitation, delivering about 100 mW/cm$^2$ to the sample.

TrEPR experiments were performed using a modified Bruker ER200D X-band spectrometer with an extended detection bandwidth (6 MHz) and direct detection of the signal without magnetic field modulation. Sample photoexcitation was obtained using the second harmonic of a pulsed Nd:YAG laser Quantel Brilliant, λ= 532 nm, pulse length = 5 ns; E/pulse ≅ 5 mJ, 50 Hz repetition rate. The EPR direct-detected signal was recorded with a LeCroy LT344 digital oscilloscope, triggered by the laser pulse. The overall response time of the instrument was about 150 ns. At each magnetic field position, an average of 200 transient signals was usually recorded. All the TREPR and LEPR spectra were usually recorded at T=120 K. Spectral simulations were carried out using Easyspin, a Matlab TM toolbox.

### Computational Details

DFT ground state optimizations of a four-units oligomer of PCPDTBT [13, 28] in the singlet ground S0 state and triplet T1 state have been carried out at the restricted and unrestricted level of theory. Vertical excited state transitions have been evaluated at the TD-DFT level for both singlet and triplet states. Hybrid GGA B3LYP, BHandHLYP and range separated CAM-B3LYP and ωB97XD [29] functional have been considered. For each functional, geometry optimizations (for S0 and T1) and excited state calculations (S0→Sn and T1→Tn) have been carried out (see SI for details). The double split Pople basis set 6-31G** has been considered and all calculations have been conducted in vacuum. For all calculations Gaussian 09 program [30] has been used.

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## Notes and references

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