Supplemental Information

Matter of minutes degradation of Poly(3-hexylthiophene) under illumination in air.

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Streak camera results for a P3HT film in air.

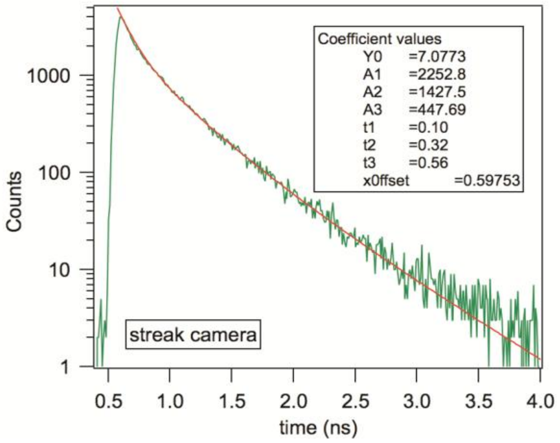

***Figure S1**: Streak camera results for a film of P3HT exposed to air under laser illumination at 532 nm (2x10^{12} incident photons cm^{-2}).*

The importance of the streak camera result is simply that the fluorescent lifetime of a P3HT film in air can be measured at all and that emission lifetime is not shortened with each subsequent laser pulse. When measured the lifetime appears stable (even under laser illumination) with a typical lifetime of around 350 ps. In the above data, to get the average fluorescent lifetime, the decay is fitted to a tri-exponential fit, giving approximate lifetimes of 0.10 ns, 0.32 ns and 0.56 ns. The first exponential decay is assigned to annihilation of P3HT singlet states[1] and ignored while the second and third lifetimes represent the fluorescent lifetime of the P3HT and give a weighted average of τ_{av} ~380 ps [0.32*1428/(1428+448)+0.56*448/(1428+448)]. Other examples of a similar fluorescence lifetime data exist in the literature[2] .

Fitting data in Fig.2 to Eq.3

Figure S2*: (left) Fitting of the data in Fig.2 to Eq.3. As the rate of defect formation depends on time, only the first 3 data points are used in the fits in order to extract a value for the rate of defect formation for a pristine film. (right) The dependence on time for the value of B.*

Fit to the data in Fig.2 using Eq.3 (left). The fit moves away from the data points at later times and this we believe is because the fit assumes a fixed rate of defect formation with time (*B*). The poor fit suggests however that *B* does vary with time, or in other words, with progress of the degradation. The change in *B* as a function of time is shown (right).

Absorption spectra changes after degradation.

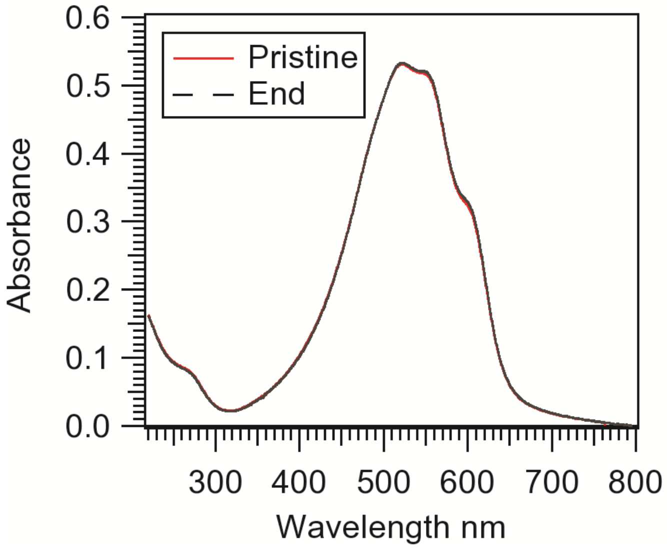

Figure S3*. Absorption spectra for the P3HT used in Fig1 & 2 before and after testing.*

Absorption spectra suggests no change to the absorption spectra of the film after testing. Results for other films also show no change within error.

Fourier Transform Infrared data

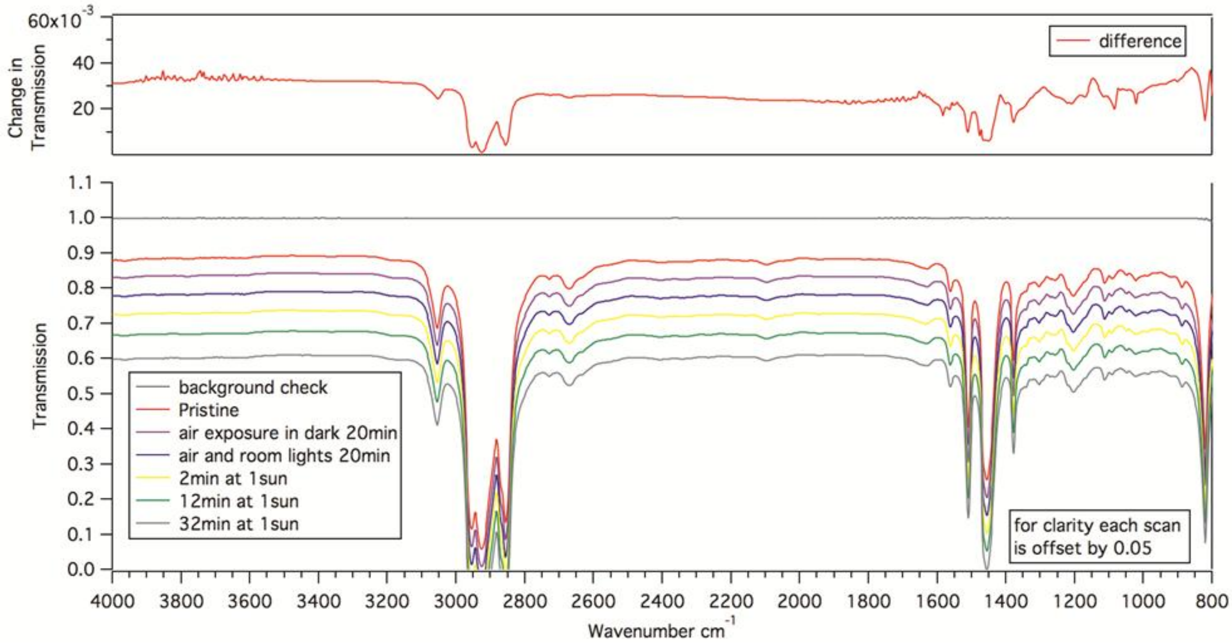

Figure S4. *FTIR data for a film of P3HT degraded under different conditions up to 1 sun illumination for 32 min. The 'difference' spectra in the top part of the graph represents the difference between the initial and final spectrum. No new absorption peaks are observed in the difference spectra (only minor changes to those already present) and so no new species can be identified.*

FTIR data taken after various degradation treatments. The scans are an average of 32 scans and are offset for clarity. No change to the shape of the FTIR curve is observed with time as can be exemplified by the positive change in transmission (e.g. more light transmitted) in the difference spectra between final and initial scans of the film. The background positive increase in transmission is probably due to a slight rise in the light output of the lamp with time. Some potential FTIR peaks we would have hoped to have seen are in Refs [3,4].

EXTRA THOUGHTS

On the positive polaron interaction with O_2...There are some interesting potential parallels between the reported interaction between the positive polaron of P3HT and ground state oxygen and the reaction here of the polymer excited state and ground state oxygen. In both cases they presumably involve oxygen interaction with the P3HT radical cation where there is a missing HOMO electron (Figure S5). Initial attack by oxygen might involve a dative bond to the positively charged carbon possibly creating a more stable positive species (Figure S6). Presumably the reaction is reversible, returning to the polythiophene radical cation, hence explaining the reversible doping effect of oxygen on P3HT. The oxygen bonded intermediate could also be an intermediate in the degradation reaction. Note that other reports suggest that O_2 can form a bond to each of the two sulphur bonded carbons in ground state P3HT and that this can also yield a degradation product (a similar reaction happens with Furan also). This configuration however is unlikely to yield any stabilisation to the cation state.

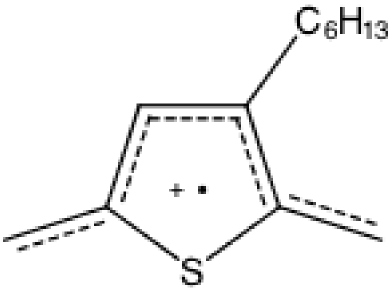

***Figure S5**. Polythiophene radical cation – interacts strongly with ground state O_2?*

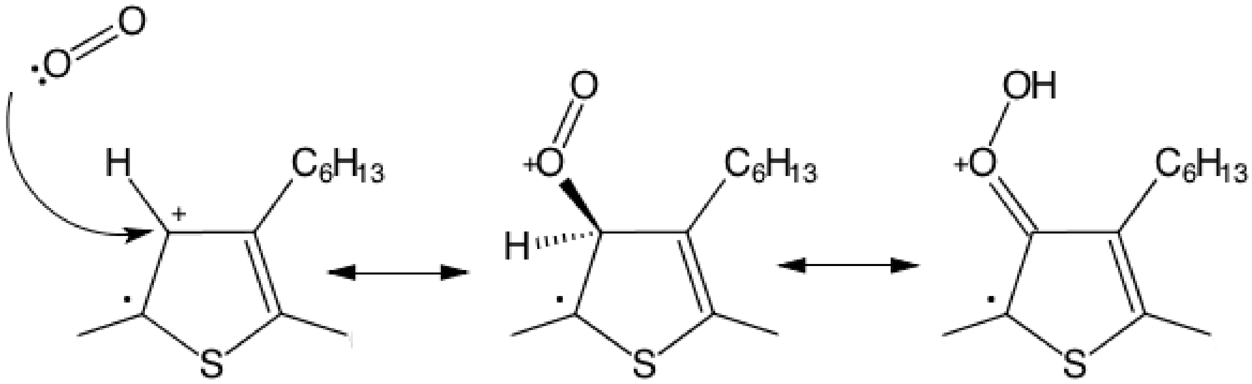

***Figure S6**. Possible reaction where the positive charge is moved off the polythiophene radical cation onto the molecular oxygen, stabilising the charge. The intermediate could be even further resonance stabilised by interaction with the conjugation system. Note that attack at any position of the ring is possible to give the first two equilibrium positions, however only attack at position 4 yields the rightmost isomer form.*

On the excited state mechanism... An important part of the mechanism in Fig.5 that is yet to be resolved is why exactly the degradation mechanism stops, or at least appears to stop, while the fluorescence lifetime of P3HT is still relatively long at around 350 ps. The reasonably long lifetime means there should still be sufficient collision between oxygen and a singlet state and hence more reactions and defect formation. A plausible explanation is that as films of P3HT are physically inhomogeneous, with regions of both crystalline tightly-packed chains and regions of amorphous and much less dense chain packing. While oxygen could be expected to permeate through the amorphous regions, crystalline regions may be relatively impermeable to oxygen (or oxygen permeation could be slower)[5] , and therefore stable to illumination. If the crystalline regions were air impermeable then it would explain why film P3HT emission could not be quenched entirely. A kinetically limited rather than diffusion limited reaction is also a potential solution. If the charge transfer state was slow in forming (took many collisions or required re-arrangement perhaps) and that this required time became slower than the P3HT effective emissive lifetime, then no (further) degradation via this mechanism could occur. If this was the case then interestingly the same behaviour may be observed in solution, unfortunately no information on the minimum lifetime of P3HT fluorescence in solution exists, and so this deserves further investigation.

On the reaction mechanism in Figure 5...Note that transient absorption studies show no evidence of triplet formation in P3HT films so the excited state involved in the reaction with oxygen should principally be singlet in character.[6]

On degradation in general...Rather surprisingly we cannot find any assessment of the potential harm trace amounts of metal catalysts left over from synthesis may play in any degradation reactions.

On the potential degradation of P3HT:PCBM blend films... As an aside, previously, transient absorption spectroscopy has been used to reveal the presence of roughly 1 - 4 x 10^{17} per cm^3 trap states in P3HT:PCBM blend films. By the above argument, it follows that these states are not related to oxygen defects in P3HT sites, and instead could be due to structural traps (such as grain boundaries etc) in P3HT. This assignment is in accord with observations that the the number of traps depends on annealing conditions and polymer regioregularity.[7]

References

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