

Characterization of the photochemical stability of all-polymer solar cells

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Summary of Key Findings

The effect of light soaking (ISOS-L-1) on the optical and electronic properties of all-polymer solar cell systems has been assessed. A large variation in photobleaching lifetime of common materials was found, with neat PTB7 and PTB7-Th exhibiting half-lives of less than 10 hours, while neat J51 and J52 exhibit half-lives of over 300 hours. Importantly, the commonly used electron accepting polymer N2200 was found to be relatively robust with a photobleaching half-life of over 600 hours. Complicated photobleaching behaviour was observed in blends. The stability of N2200 was found to be enhanced in the blend with P3HT, while blending with PTB7 and PTB7-Th led to a more rapid degradation of N2200 compared to neat N2200 films. J51:N2200 and J52:N2200 blends exhibited relatively good photochemical stability, as did the P3HT:N2200 blend; these three blends were selected for further analysis of the effect of light soaking on electronic properties. The TRMC signal of P3HT:N2200, J51:N2200, and J52:N2200 blends was found to be more rapidly affected than light absorption. Curiously the lifetime of TRMC traces was not found to be significantly altered by light soaking even though the overall magnitude of the TRMC signal was. The overall power conversion efficiency of unencapsulated P3HT:N2200, J51:N2200, and J52:N2200 solar cells was found to degrade by ~ 50% over a period of 16 hours.

Introduction

As polymer solar cells come closer to commercialisation, the photochemical stability of the active layer materials is becoming an increasingly critical and limiting issue. While new materials continue to be developed propelling the record power conversion efficiency of all-polymer solar cells past 11%¹ (along with the record power conversion efficiency of polymer/non-fullerene acceptors past 15%²) little attention is given the stability of these materials. Although record efficiency figures attract attention and many citations, these record breaking materials will be of little practical usage if they quickly degrade under solar illumination. Device stability covers thermal stability (changes in performance as the result of heating) and photochemical stability (changes in performance as a result of the photochemical degradation of the materials in the device).³ Degradation in the performance of solar cells can result from degradation of the active layer itself as well as degradation of interfaces, electrode materials, and encapsulating materials. While device stability needs to be treated holistically, a basic starting point is characterising the photochemical stability of the active layer itself. Clearly materials that are inherently more robust are attractive and should be preferred to active layer materials that are inherently unstable to degradation under ambient conditions.

This report investigates the photochemical stability of thin films of common donor and acceptor materials used in all-polymer solar cells. As well as characterising the stability of neat films, the stability of blends is also characterised since a mixture of two materials may show enhanced or reduced stability relative to the unmixed materials. Finally, the effect of photochemical degradation on the electronic properties of all-polymer blends is studied by looking at the effect of light soaking on the time-resolved microwave conductivity (TRMC) response of blends, and the effect of light soaking on the device parameters of unencapsulated all-polymer solar cells.

Methodology

Light soaking

Light soaking was performed following the ISOS-L-1 protocol.⁴ Simulated sunlight is used as the light source under ambient temperature and ambient relative humidity. For solar cell devices, cells are kept at maximum power point or open circuit voltage in between testing. Samples for optical (UV-Vis spectroscopy) and time-resolved microwave conductivity (TRMC) measurement were prepared on quartz glass substrates with thickness of ~ 100 nm. Samples were all as deposited and had no encapsulation. Light soaking experiments at Macquarie University (samples for UV-Vis and TRMC) used an in-house setup using 4 Solux lamps, a cooling fan, a rotating stage and powered through an uninterrupted power supply unit as shown in figure 1. The intensity of the light was measured using a power meter with a calibrated Si detector to be close to 100 mW/cm^2 at the point of placement of samples. The sample stage was rotated to allow for uniform irradiation. Light soaking experiments at Monash University (unencapsulated solar cells) utilised a Photo Emission Tech model SS50AAA solar simulator, simulating an AM1.5G radiation spectrum with 100 mW/cm^2 . The intensity of the simulator was calibrated with a silicon reference cell with a KG3 glass filter. The spectral profiles of the two lamps used (compared to the AM1.5G spectrum) are provided in figure 2.

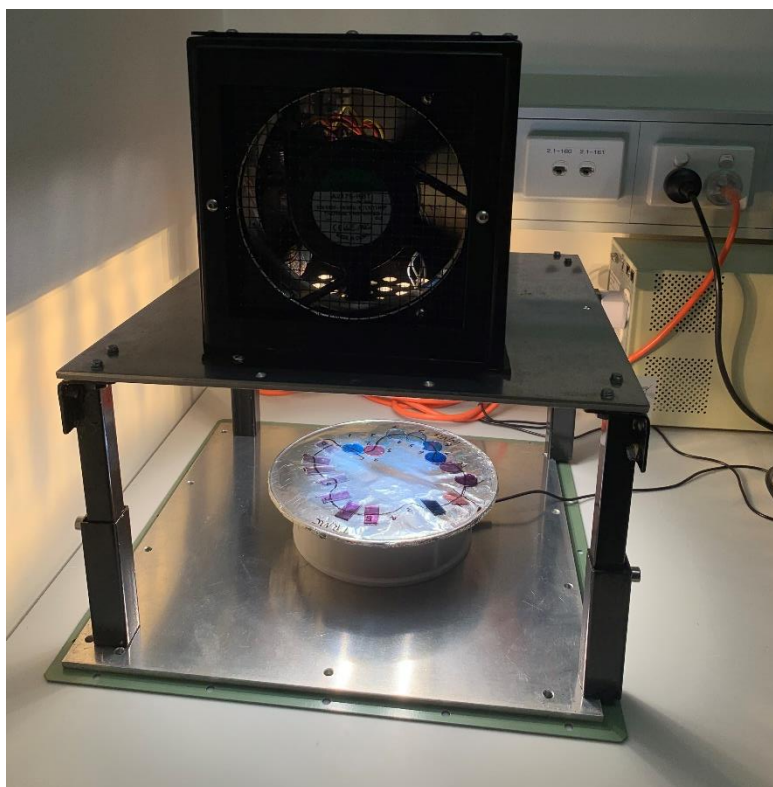


Figure 1. Photograph of the bleaching set up at Macquarie university used for this study showing a set of samples being bleached.

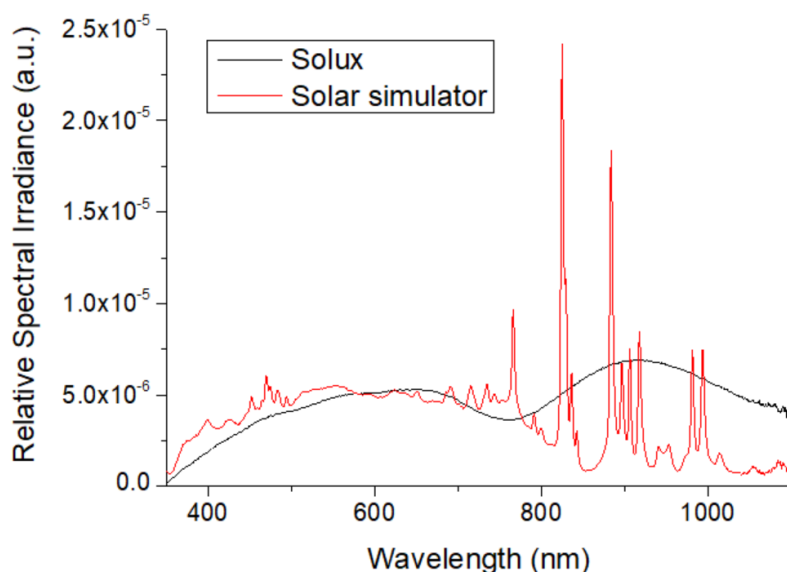


Figure 2. Spectral irradiance vs. wavelength for the lamps used in the study with comparison to the AM1.5G spectrum.

Materials

The chemical structures of the polymers used in this study are shown in figure 3. The polymers selected include 5 common donor polymers, P3HT, PTB7, PTB7-Th, J51, and J52 along with two acceptor polymers, N2200 and F-N2200. P3HT was sourced from Rieke Metals. PTB7, PTB7-Th, J51, J52, F-N2200 were purchased from 1-Material Inc. N2200 (also known as P(NDI2OD-T2)) was purchased from Raynergy Tech. N2200 is the most common acceptor polymer used in all-polymer solar cells with efficiencies of 11% achieved in combination with the donor polymer PTzBI-Si.¹ Although PTzBI-Si is not included in this study, PTB7-Th, J51 and J52 have all be utilised in blends with N2200 yielding efficiencies of over 8% with J51 as donor.⁵ Good efficiencies can also be achieved with F-N2200 (over 6%)⁶ and is included to study the effect of fluorination on photochemical stability. All samples were spin-coated from solution onto quartz glass substrates for UV-Vis and TRMC studies. Details of solar cell preparation is provided below.

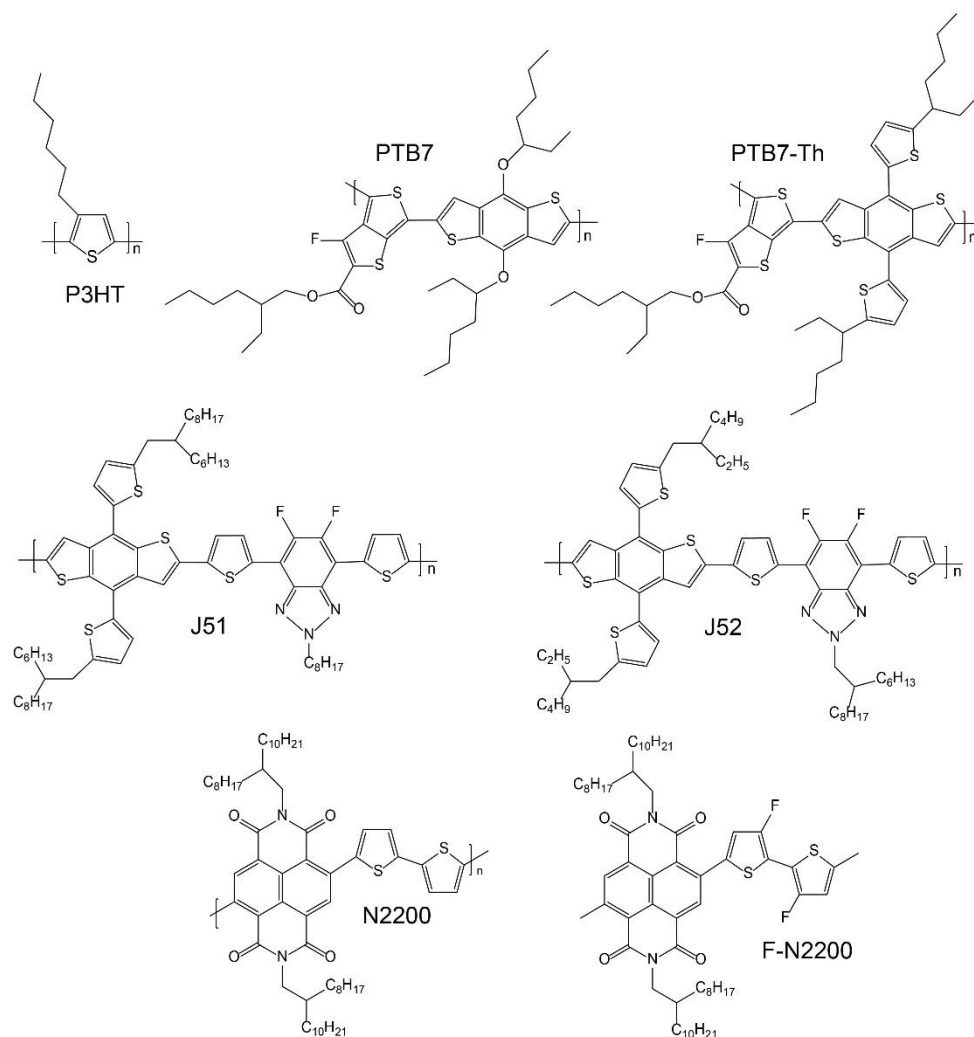


Figure 3. Chemical structures of polymers used in this study.

UV-Vis spectroscopy

Photobleaching (reduction in light absorption due to light soaking) was characterised using a CARY Agilent UV-Vis Spectrometer (CARY 8454).

Time-resolved microwave conductivity (TRMC)

TRMC measurements were performed using a home-built setup. Samples for TRMC were prepared on quartz substrates. The same weight ratio and casting solvent was used, with thickness altered where necessary to increase the optical density at the probe wavelength to at least 0.7. The TRMC response was measured by placing sample under test in the resonance cavity of an X-band microwave waveguide, which is located within a laser enclosure. Within the laser enclosure, a 5 ns pulse from a Nd:YAG laser is used to excite the carriers, with microwaves used to probe the relative population of the excited carriers. A wavelength of 532 nm is used with a frequency of 10 Hz. The relative change in the absorbed microwave power from the dark signal to the excited signal, is directly proportional to the photoconductance ΔG :

$$\Delta G = \beta q_e I_0 F_A (\phi \sum \mu) \quad (1)$$

The product ($\phi\sum\mu$), which is the product of the quantum yield and sum of the mobilities of the electrons and holes, is the figure of merit extracted from the TRMC measurements. All other parameters are measurable quantities. β is the geometric factor for the X-band waveguide ($\beta=2.2$ (W/H)), q_e is the elementary charge, I_0 the incident photon flux from the laser excitation and F_A is the fraction of light absorbed at the excitation wavelength which in our case is 532 nm. Further details can be found in another report.⁷

Device fabrication and characterisation

Solar cells were fabricated with an inverted architecture: ITO/ZnO/PEIE/active layer/MoO_x/Ag. ITO-coated glass substrates were cleaned firstly by sonication for 10 minutes in acetone, followed by sonication for another 10 minutes in isopropanol before oxygen plasma cleaning for 10 minutes. A 0.1 M ZnO precursor solution was prepared by dissolving 160 mg of zinc acetate dehydrate in 61 mg of ethanolamine and 10 mL of 2-methoxyethanol with vigorous stirring for 12 hours for the hydrolysis reaction at 60 °C. A 0.073 M ZnO precursor solution was then spin-coated onto cleaned ITO-coated glass at 3000 rpm for 30 s and annealed on a hot plate at 200 °C for 30 minutes to form a thin conducting layer. A PEIE layer was subsequently spin coated on top of the ZnO layer at 5000 rpm for 30 s and annealed on a hot plate at 110 °C for 15 mins to form a thin hole-blocking layer. The active layers of the solar cells were spin coated from blend solutions at different spin speed for 60 s. Finally, a 15 nm MoO_x layer with a 100 nm Ag layer was thermally deposited. All top electrode layers were deposited via thermal evaporation in vacuo ($\sim 10^{-6}$ mbar) through a shadow mask to define electrodes with an active area of 4.5 mm². Devices were encapsulated with epoxy resin and glass cover slides before being moved from the glove box for testing. Current–voltage (J–V) characteristics for all devices were measured using a Keithley 2635 source meter. A Photo Emission Tech model SS50AAA solar simulator, simulating an AM1.5G radiation spectrum with 100 mW/cm² irradiance, was used. The intensity of the simulator was calibrated with a silicon reference cell with a KG3 glass filter.

Results

Photobleaching of neat samples

As a reference, the photobleaching of neat films was first characterised. The photobleaching data for neat P3HT, PTB7, PTB7-Th, J51, J52, N2200 and F-N2200 are shown in figures 4 through 10. To compare the rates of photobleaching, plots of normalised absorbance vs. time were prepared, see figure 11. For each sample, the peak optical density in the visible to near infrared region of the spectrum was extracted as a function of time. This value was normalised to the initial value and then plotted against time as shown in figure 11. For P3HT the absorbance at 515 nm was used; for PTB7 the absorbance at 670 nm; for PTB7-Th, 700 nm; for J51, 550 nm; for J52, 550 nm; for N2200, 700 nm; and for F-N2200, 680 nm. From figure 11 it is clear that the different neat samples have vastly different photobleaching rates. To provide a quantitative calculation, the half-life ($t_{1/2}$) for photobleaching was determined as the time taken for absorbance to reach 50% of its initial value. The calculated values are tabulated in table 1.

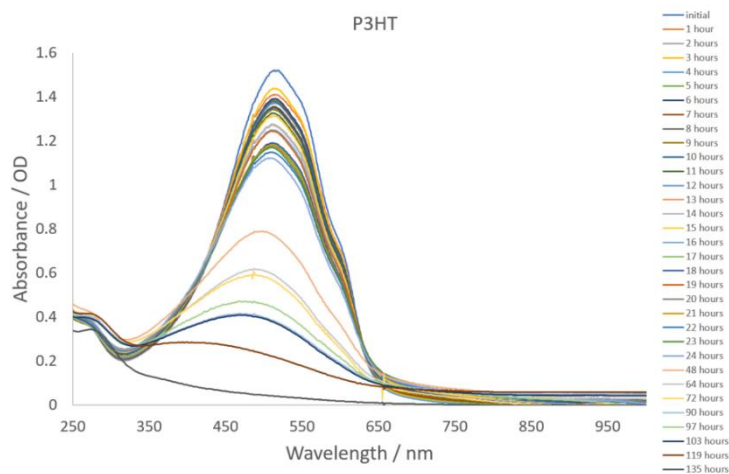


Figure 4. Photobleaching of neat P3HT

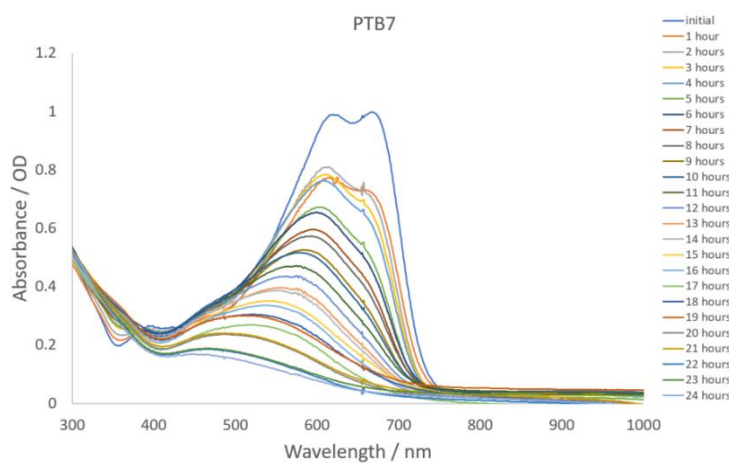


Figure 5. Photobleaching of neat PTB7

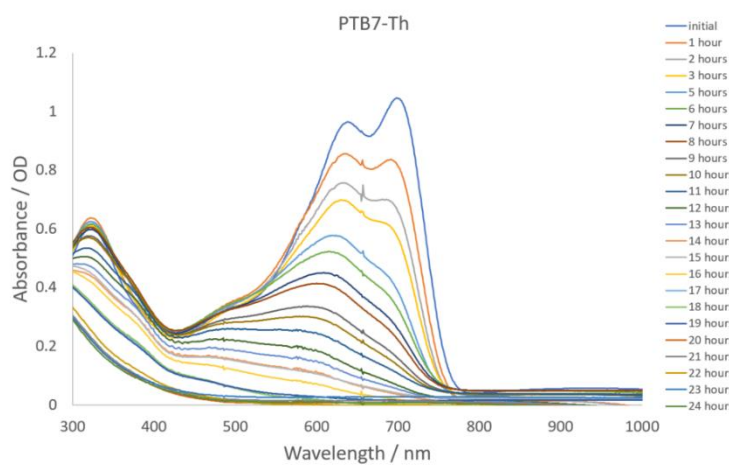


Figure 6. Photobleaching of neat PTB7-Th

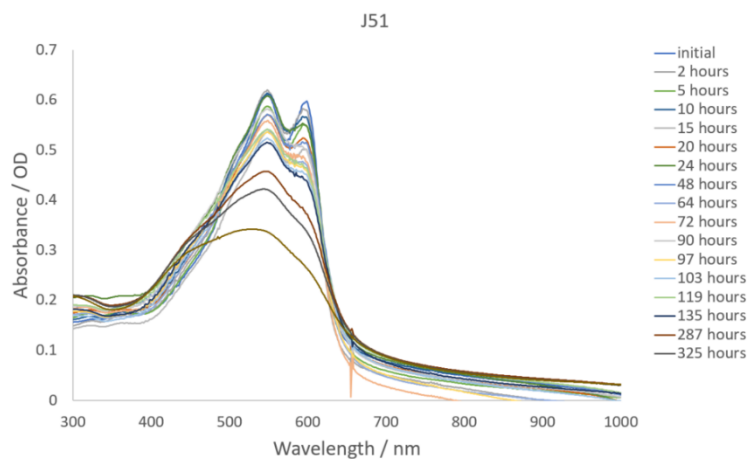


Figure 7. Photobleaching of neat J51

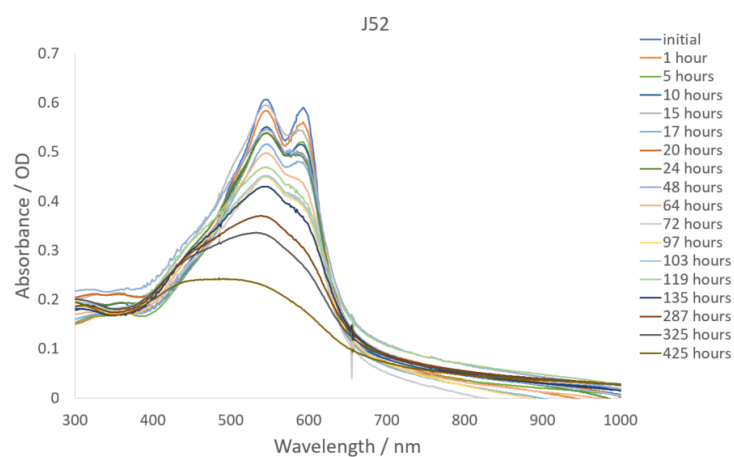


Figure 8. Photobleaching of neat J52

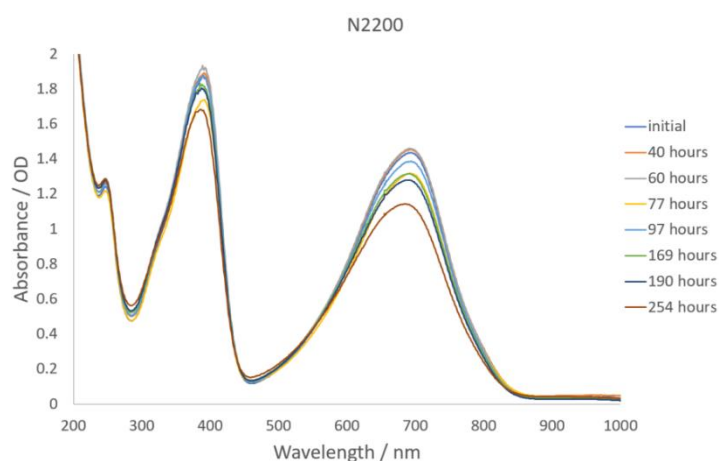


Figure 9. Photobleaching of neat N2200

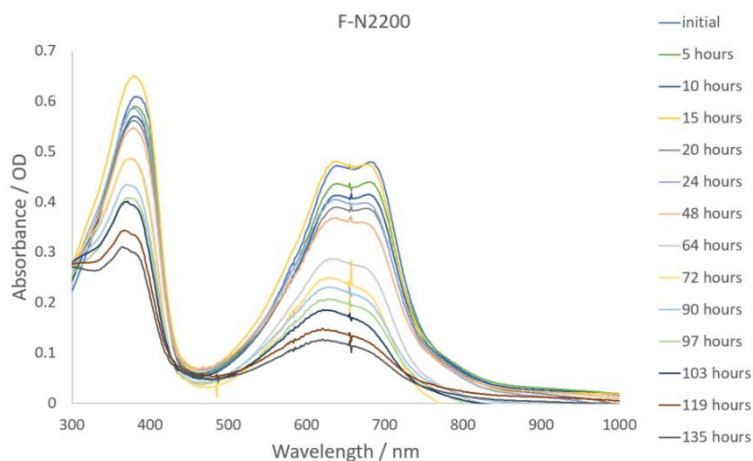


Figure 10. Photobleaching of neat F-N2200

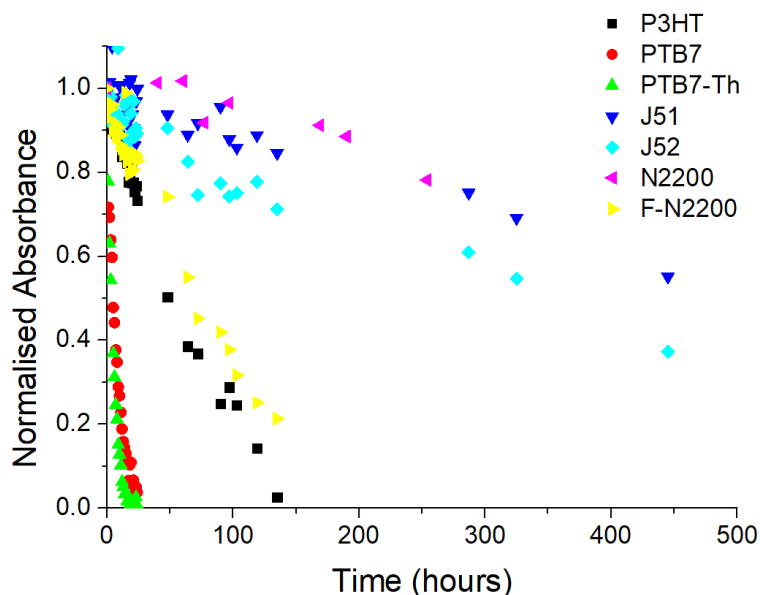


Figure 11. Plot of normalised absorbance vs. time for neat samples demonstrating the different bleaching rates of the different neat films.

Table 1: Photobleaching half-lives determined for the 7 neat polymers studied.

Polymer	$t_{1/2}$ (hours)
P3HT	61
PTB7	8
PTB7-Th	3
J51	510
J52	335
N2200	620
F-N2200	75

From table 1, it is clear that PTB7 and PTB7-Th have very poor photochemical stability, with half-lives of 8 hour and 3 hours respectively. In contrast the donor P3HT has a half-life of 61 hours, while J51 and J52 have significantly longer half-lives of 510 hours and 335 hours respectively. The

commonly used donor polymer N2200 is found to have a remarkably long half-life of over 600 hours. The half-lives of J52 and N2200 are longer than the testing time and are based on projections. F-N2200 has a shorter half-life of 75 hours. These results show that the different polymers used have vastly different half-lives. In particular PTB7 and PTB7-Th despite being widely used donor materials are very unstable and should not be used. In contrast J51 and J52 are inherently more stable and can yield similar efficiencies. While fluorination to produce F-N2200 appears to cause a reduction in photochemical stability, fluorination itself does not necessarily lead to poor photochemical stability with both J51 and J52 being fluorinated polymers.

Photobleaching of blends

Figures 12 through 17 present the photobleaching data of blends based on P3HT:N2200 (figure 12), PTB7:N2200 (figure 13), PTB7-Th:N2200 (figure 14), J51:N2200 (figure 15), J52:N2200 (figure 16), and J52:F-N2200 (figure 17). The analysis of the photobleaching data of the blends is made more complicated by the fact the spectrum is made of contributions by two materials. This makes quantitative extraction of half-life values difficult, although qualitative comparisons can be made.

For the P3HT:N2200 blends, figure 12, it is clear that P3HT degrades faster than N2200 in the blend, with the peak at 550 nm characteristic of P3HT decaying with a half life of ~ 60 hours while the peaks at 400 nm and 750 nm do not show significant degradation over the time period analysed (371 hours). While P3HT degrades in the blend with N2200 at a similar rate as in the neat sample, N2200 in the blend with P3HT does not show significant degradation suggesting that its lifetime may be prolonged in the blend with P3HT.

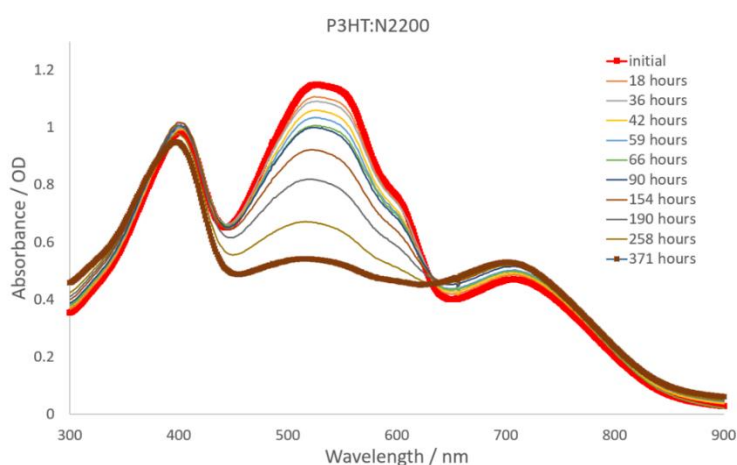


Figure 12. Photobleaching of the P3HT:N2200 blend.

For the PTB7:N2200 and PTB7-Th:N2200 blends, figures 13 and 14, there is a two-stage degradation process corresponding to the fast degradation of PTB7/PTB7-Th followed by a slower degradation of N2200. While the fast degradation of PTB7/PTB7-Th in the blend with N2200 is consistent with degradation of neat PTB7/PTB7-Th, N2200 degrades faster in blends with PTB7 and PTB7-Th exhibiting complete photobleaching within 150 hours.

Turning now to the J51:N2200 and J52:N2200 blends, improved stability seen compared to blends with PTB7/PTB7-Th as donor. However both J51 and N2200 as well as J52 and N2200 appear to degrade faster when blended compared to when neat. In particular J51 and J52 exhibit half-lives of ~ 150 to 200 hours compared to over 300 hours in neat films. N2200 also has a half-life of ~ 300 hours in blends with J51 and J52 compared to ~ 600 hours in neat films.

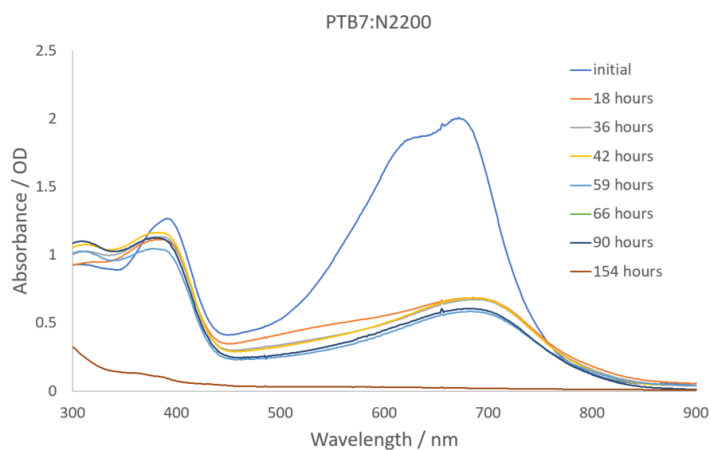


Figure 13. Photobleaching of the PTB7:N2200 blend.

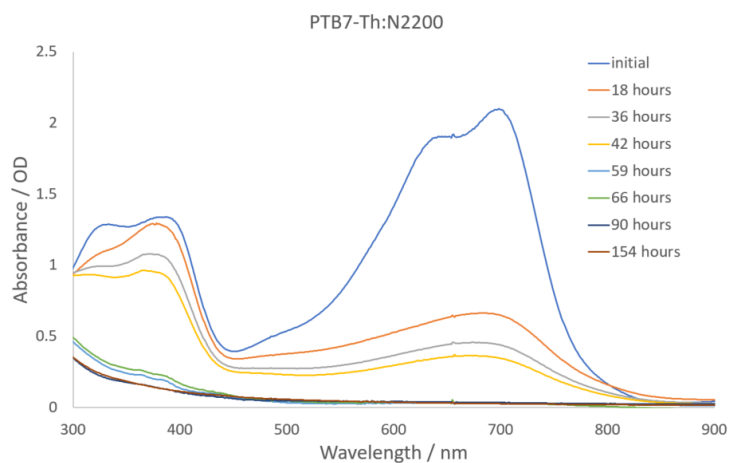


Figure 14. Photobleaching of the PTB7:N2200 blend.

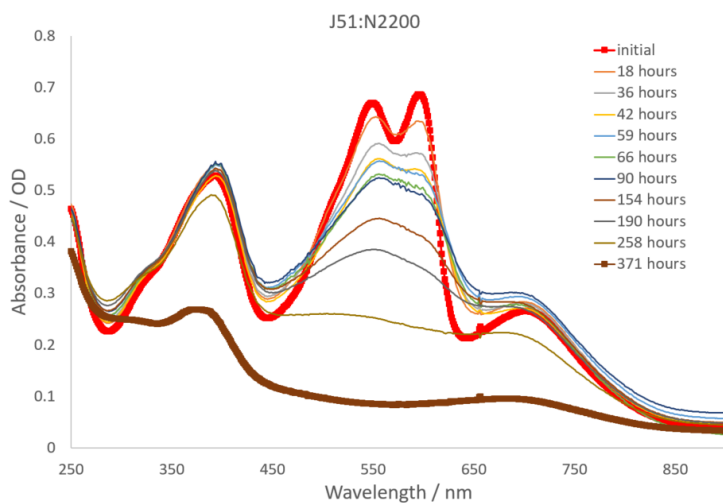


Figure 15. Photobleaching of the J51:N2200 blend.

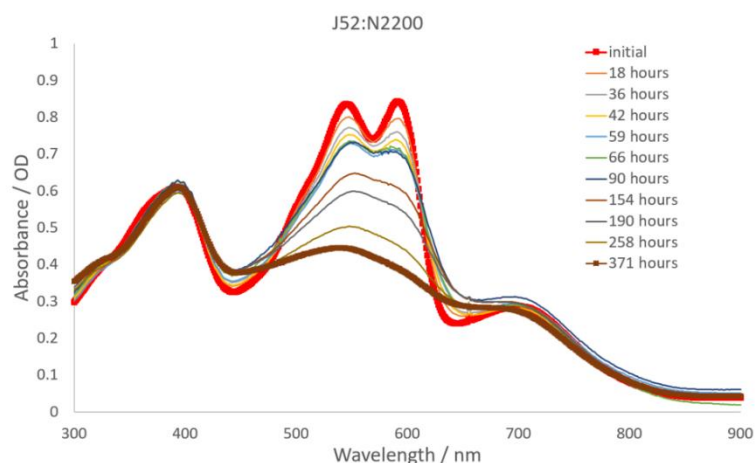


Figure 16. Photobleaching of the J52:N2200 blend.

Finally, for the PTB7-Th:F-N2200 blend shows a similar behaviour to PTB7-Th:N2200, with complete photobleaching of the sample after ~ 100 hours. The overlapping absorption spectra of the two materials makes separating the degradation kinetics particularly difficult, however it is clear that the fluorinated N2200 derivative does not fare any better when blended with PTB7-Th than N2200.

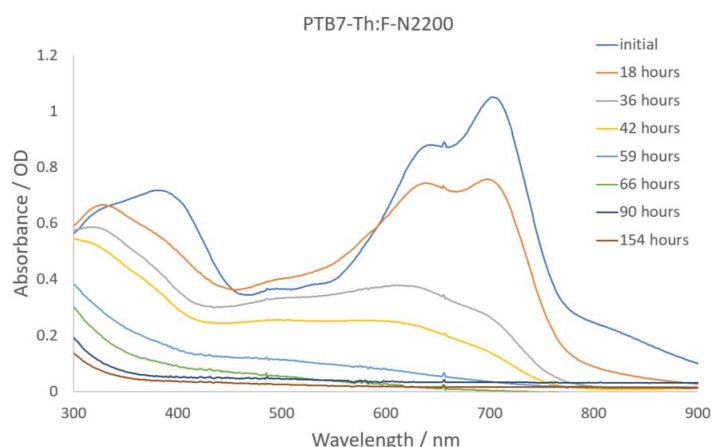


Figure 17. Photobleaching of the PTB7-Th:F-N2200 blend.

Assessment of changes in electronic properties with ageing

The impact of ageing under simulated sunlight on the electronic properties of blends was studied by measuring the change in TRMC response of films as well as the change in current-voltage characteristics of unencapsulated solar cells. The three most stable blends identified from the photobleaching study above were chosen to be studied, namely P3HT:N2200, J51:N2200 and J52:N2200. Figures 18, 19, and 20 plots for the blends the change in $\phi\sum\mu$ peak TRMC figure of merit as a function of laser pulse intensity. Examining the data for P3HT:N2200 (figure 18) it is clear that the $\phi\sum\mu$ peak value decays substantially faster than the optical absorbance. While the absorbance at 550 nm for the P3HT:N2200 blend decays by $\sim 15\%$ after ~ 40 hours, the TRMC signal has decayed by over 80%. This indicates that the processes governing photocarrier generation (and hence TRMC signal) are more sensitive to the chemical defects produced by photochemical degradation than is optical absorption.

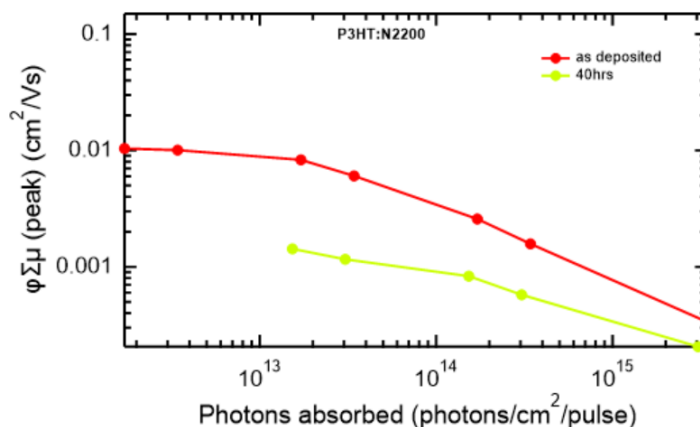


Figure 18. Impact of light soaking on the TRMC response of P3HT:N2200.

A similar decrease in the TRMC peak signal is seen for J51:N2200 and J52:N2200 (figures 19 and 20 respectively). The TRMC response for J51:N2200 decays by $\sim 90\%$ after 40 hours of light soaking while the TRMC response of J52:N2200 decays by $\sim 75\%$. Note that at higher hours of light soaking the TRMC signal at low pump fluence becomes difficult to reliably determine as the signal becomes too noisy.

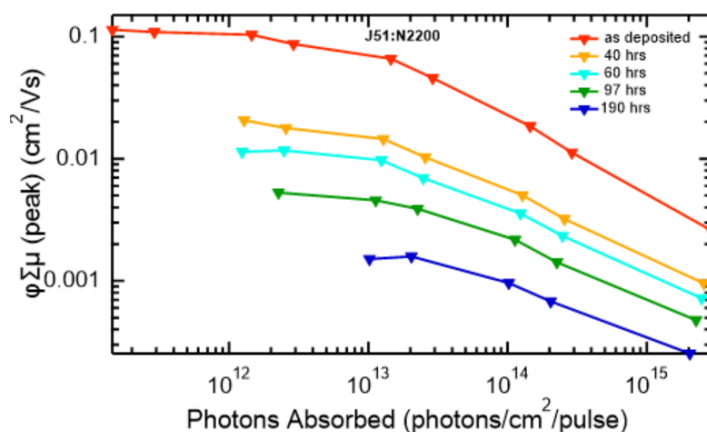


Figure 19. Impact of light soaking on the TRMC response of J51:N2200.

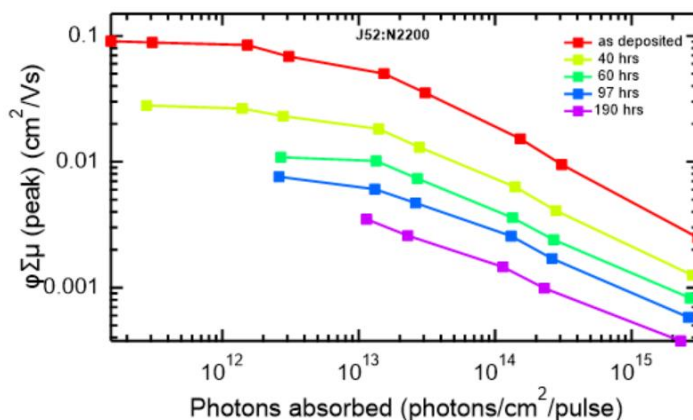


Figure 18. Impact of light soaking on the TRMC response of J52:N2200.

The effect of light soaking of the lifetime of photogenerated charges was next examined. The transient responses were fitted using a double exponential decay fit:

$$y = A_1 \exp(-\ln v \tau_1 \cdot x) + A_2 \exp(-\ln v \tau_2 \cdot x) \quad (2)$$

With values of τ_1 , τ_2 , and A_1 , A_2 , extracted. Figure 19(a) plots τ_1 (slow decay time) and τ_2 (fast decay time) vs. laser flux for fresh (solid lines) and samples aged for 190 hours (dashed). Figure 19(b) then plots A_1 (fast fraction) and A_2 (slow fraction) vs. laser flux for fresh (solid lines) and samples aged for 190 hours (dashed). Remarkably little change in the lifetimes and weightings with ageing are seen, suggesting that the lifetime of those charge that are generated in aged samples are not significantly affected, with photobleaching mainly impacting the yield of photogenerated charges.

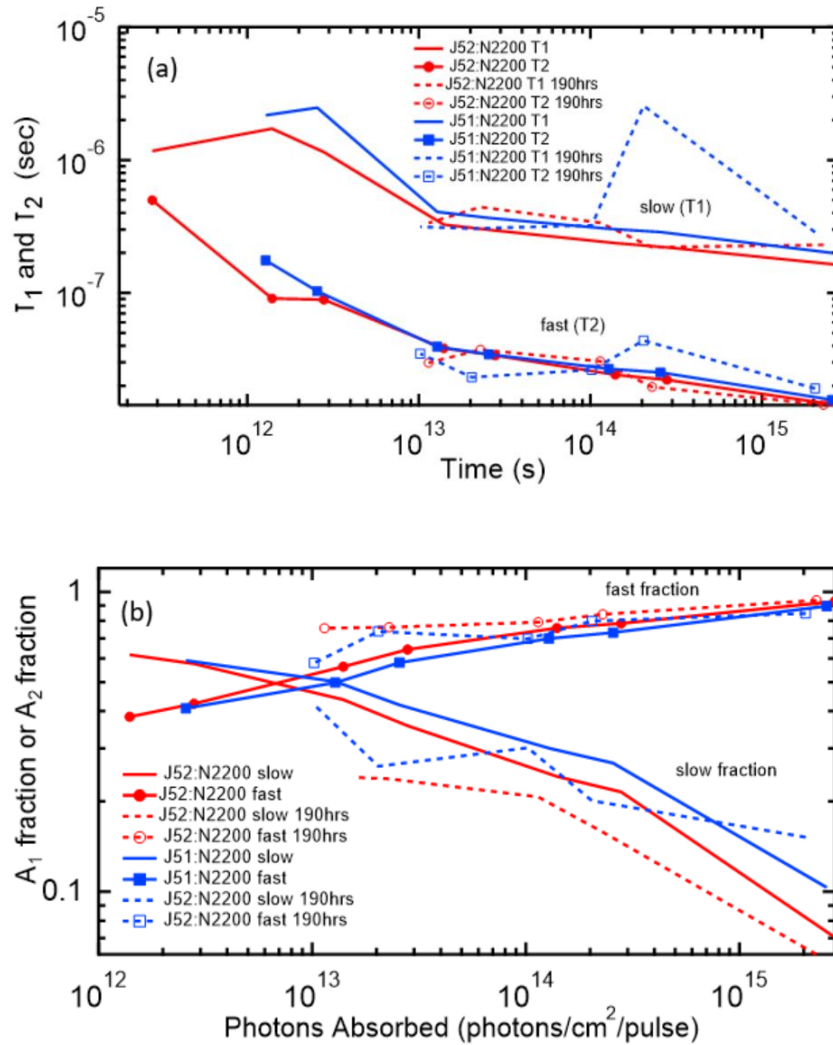


Figure 19. Impact of ageing on the slow and fast lifetimes (a) and relative weightings (b) for pristine (solid) and aged (dashed) samples.

Figures 20, 21, and 22 show the effect of light soaking on the performance of unencapsulated P3HT:N2200, J51:N2200, and J52:N2200 solar cells. J_{SC} , V_{OC} , FF and PCE parameters have been extracted from the plots of figures 20 to 22 and plotted as a function of ageing time in figure 23. These three solar cells show similar decay kinetics with the overall PCE decaying to about 50% after 16 hours.

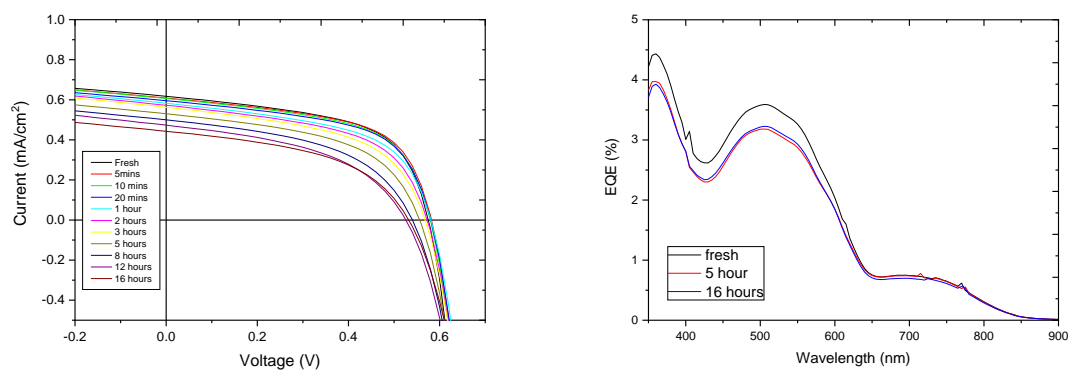


Figure 20. Impact of light soaking on the current-voltage curves and EQE spectrum of unencapsulated P3HT:N2200 solar cells.

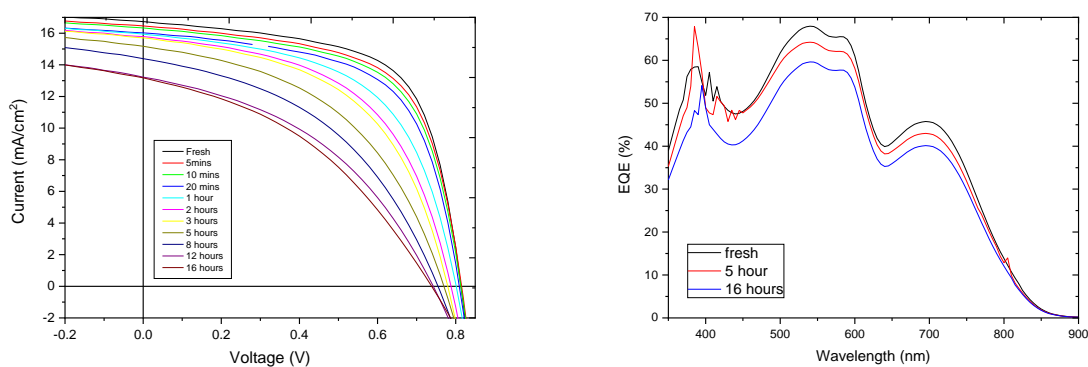


Figure 21. Impact of light soaking on the current-voltage curves and EQE spectrum of unencapsulated J51:N2200 solar cells.

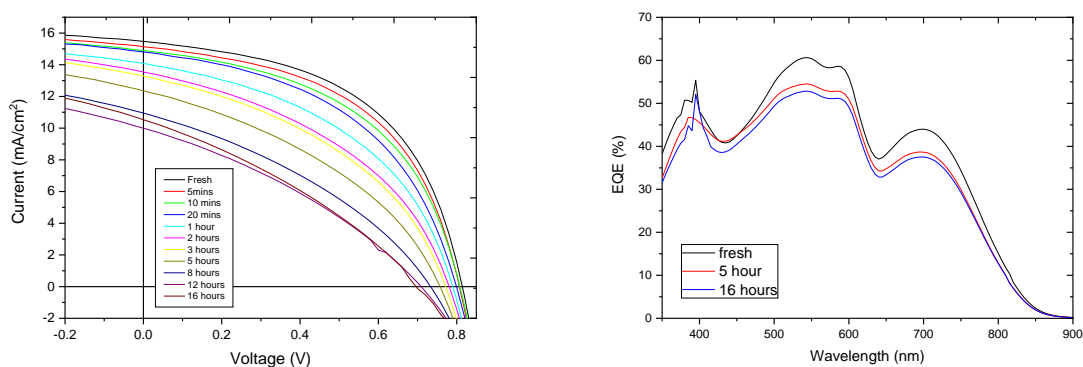


Figure 22. Impact of light soaking on the current-voltage curves and EQE spectrum of unencapsulated J52:N2200 solar cells.

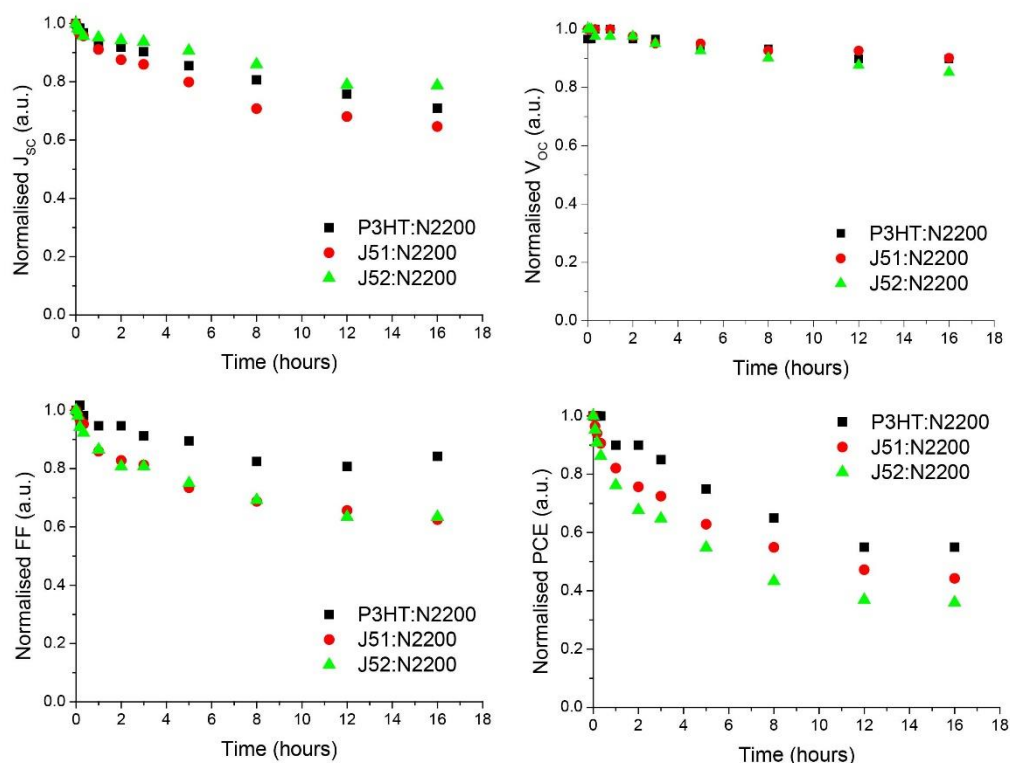


Figure 23. Summary of the degradation of solar cell parameters with ageing (ISOS-L-1).

Conclusions

The effect of light soaking (ISOS-L-1) on the optical and electronic properties of all-polymer solar cell systems has been assessed. A large variation in photobleaching lifetime of common materials was found, with neat PTB7 and PTB7-Th exhibiting half-lives of less than 10 hours, while neat J51 and J52 exhibit half-lives of over 300 hours. Importantly, the commonly used electron accepting polymer N2200 was found to be relatively robust with a photobleaching half-life of over 600 hours. Complicated photobleaching behaviour was observed in blends. The stability of N2200 was found to be enhanced in the blend with P3HT, while blending with PTB7 and PTB7-Th led to a more rapid degradation of N2200 compared to neat N2200 films. J51:N2200 and J52:N2200 blends exhibited relatively good photochemical stability, as did the P3HT:N2200 blend; these three blends were selected for further analysis of the effect of light soaking on electronic properties. The TRMC signal of P3HT:N2200, J51:N2200, and J52:N2200 blends was found to be more rapidly affected than light absorption. Curiously the lifetime of TRMC traces was not found to be significantly altered by light soaking even though the overall magnitude of the TRMC signal was. The overall power conversion efficiency of unencapsulated P3HT:N2200, J51:N2200, and J52:N2200 solar cells was found to degrade by ~ 50% over a period of 16 hours.

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