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Material Crystallinity as a Determinant of Triplet Dynamics and Oxygen Quenching in Donor Polymers for Organic Photovoltaic Devices

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This paper is concerned with the photophysics of triplet excitons in conjugated donor polymers, and their quenching by molecular oxygen. These photophysics are assayed by transient absorption spectroscopy, and correlated with X-ray diffraction measurements of relative material crystallinity. Eleven different donor polymers are considered, including representatives from several classes of donor polymers recently developed for organic solar cell applications. Triplet lifetimes in an inert (nitrogen) environment range from <100 ns to 5 μs. A remarkably quantitative correlation is observed between these triplet lifetimes and polymer XRD strength, with more crystalline polymers exhibiting shorter triplet lifetimes. Given the broad range of polymers considered, this correlation indicates that material crystallinity is the dominant factor determining triplet lifetime for the polymers studied herein. The rate constant for oxygen quenching of these triplet states, determined from a comparison of transient absorption data under inert and oxygen environments, also show a correlation with material crystallinity. Overall these dependencies result in the yield of oxygen quenching of polymer triplet states increasing strongly as the crystallinity of the polymer is reduced. These photophysical data are compared with photochemical stability of these donor polymers, assayed by photobleaching studies of polymer films under continuous light exposure in an oxygen environment. A partial correlation is observed, with the most stable polymers being the most crystalline, exhibiting negligible oxygen quenching yields. These results are discussed in terms of the likely origins of the correlations between material crystallinity and photophysics, and in terms of their implications for the environmental stability of such donor polymers in optoelectronic devices.

1. Introduction

Triplet excitons are a key consideration for the function of many plastic optoelectronic devices including organic light emitting diodes (OLEDs) and photovoltaic cells (OPVs). In fluorescent OLEDs, charge recombination to form triplet exciton states is a key loss pathway which can reduce device photoluminescence efficiency. The decay of such triplet states is primarily non-radiative, and spin statistics indicate that triplet exciton formation is three times more probable than singlet excitons.[1] Substantial progress has been made to harness these triplet excitons to achieve near 100% internal electroluminescence quantum efficiencies using phosphorescent molecules.[2] In such phosphorescent OLEDs devices, triplet–triplet annihilation is however found to be a significant loss mechanism leading to quantum efficiency roll-off at high current densities.[2] In OPV devices, triplet exciton formation has been found to be a significant loss pathway, with charge recombination to triplet excitons resulting in loss of photocurrent generation.[3–5] Conversely, triplet excitons typically have longer lifetimes than singlet excitons; this longer lifetime can result in longer exciton diffusion lengths and can facilitate their ability to drive photoinduced charge separation.[6] The longer triplet lifetimes, and high triplet yields have been a key factor behind the success of ruthenium based coordination dyes in dye sensitized solar cells[7] whilst there have been considerable attempts to utilise the longer diffusion length of triplet excitons to reduce the nanomorphology requirement of donor/acceptor films for organic solar cells.[8] Recent studies have also shown the possibility of doubling internal quantum yields by creating two triplet excitons from each singlet exciton via a singlet–triplet fission process.[9] This is analogous to the multiple exciton generation demonstrated in inorganic photovoltaic devices.[10] In addition to the possible effects of triplet states on device efficiency,

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triplet excitons may also play a role in the photochemical stability of organic electronics.[11,12] Such triplets may be generated either by direct intersystem crossing from singlet excitons or by charge recombination such as those active in OLEDs.[9,23] As we and others have recently demonstrated, triplet mediated singlet oxygen generation can cause significant photochemical degradation on polymers of interest for organic photovoltaics.[5,13] Therefore, predicting and controlling triplet dynamics is of significant impact to the development of organic electronics.

In this paper, we report the triplet exciton decay dynamics for a broad range of polymers recently developed for OPV applications, demonstrate that these triplet dynamics, and the efficiency of their quenching by molecular oxygen, are strongly correlated with polymer crystallinity, and discuss these results in relation to polymer photochemical stability.

The photophysics of triplet states in conjugated polymers has been studied previously using techniques including optically detected magnetic resonance, time-resolved electron paramagnetic resonance and photomodulation spectroscopy.[14] Solid-state studies of triplet photophysics using these techniques need to be conducted under very low temperature (to increase the triplet lifetime) and/or high excitation densities in order to obtain good triplet signals. However, low temperature conditions are less relevant to practical device applications, whilst high excitation densities typically invoke bimolecular triplet-triplet annihilation processes, rather than the monomolecular decay of triplet states normally of most relevance for solar irradiation conditions. Additionally, most early studies of polymer triplet excitons have focused on conjugated polymers developed for OLED applications.Studies of triplet photophysics of polymers for OPV applications have been relatively limited to date, as has been reported previously.[15–18]

The crystallinity of donor polymers is known to affect the morphology of OPV and OLED active layers, their charge transport and other functional properties, and hence device performance.[19,20] Several studies have reported limited studies of the relationship between a polymer's crystallinity and its triplet exciton dynamics. It has been reported that more planar conjugated structures can reduce spin-orbit coupling,[21] which can have direct impact on the rate of triplet formation and decay. Both Janssen et al.[22] and Becker et al.[23] have also shown that the photophysics of triplet states are considerably affected by aggregation and conjugation lengths of α-oligothiphenes. More recently, Cadby et al.[17] observed significantly lower yield of triplet excitons in thermally annealed poly(9,9-dioctyl)fluorene (PFO) films compared to the unannealed PFO films, while Ohkita et al.[4] have observed the presence of triplet states in amorphous polythiophene films but not in the more crystalline ones. However, comparative studies of triplet exciton dynamics between different donor polymers have been very limited to date, and therefore the relative importance of the dependence upon material crystallinity compared to other aspects of molecular design has not previously received significant attention.

The development of new, lower bandgap donor polymer has recently led to impressive advances in OPV device efficiency. However, relatively few studies have compared the relative stabilities of these donor polymers. Some such studies have investigated the main photodegradation pathways of such donor polymers in neat and blend films, including in particular triplet mediated singlet oxygen generation, or anion mediated superoxide radical anion formation, although at present there is not a clear consensus on the relative importance of these pathways.[5,13,24] Triplets are known to be able to sensitise the formation of singlet oxygen via energy transfer to molecular oxygen. The resultant singlet oxygen is highly reactive and can attack polymer chain leading to degradation.[25] Studies by Ma et al. have, for example, shown that formation of triplet states may be a key step leading to photodegradation in poly(p-phenylenevinylenes) (PPVs).[12] However direct comparisons between polymer triplet yields/lifetimes and photochemical stability have been very limited to date.

In this paper, we employ a broad range of polymers (**Figure 1**), mainly of donor/acceptor type recently developed for OPV device applications. We measure the triplet yields and decay dynamics in neat films of these polymers in both inert and oxygen atmospheres, and correlate these photophysical data with X-ray diffraction (XRD) measurements of polymer crystallinity. Our study employs transient absorption spectroscopy (TAS) which allows the determination of monomolecular triplet decay dynamics in conjugated polymers under room temperature, which is closer to the normal operating condition of OLEDs and OPVs. The high sensitivity of our TAS system enables the detection of transient signals at low laser intensities (~1–3 μJ cm^{-2}), which ensures that contributions from triplet-triplet annihilation are excluded. Our studies focus on the microsecond timescale, allowing us to address the quenching of these triplets states by molecular oxygen.[26] Finally we measure the photochemical stability of these polymers under accelerated degradation conditions in oxygen and discuss the correlation between this photochemical and stability and oxygen quenching of photogenerated triplet states.

2. Results

Transient absorption data were collected for neat films of all the polymers studied herein (see Figure 1 for polymer structures). Typical data for one such polymer, GeIDT-BT, is presented in **Figure 2**. This polymer film exhibited a photoinduced transient absorption band peaking at approx. 1050 nm (see insert), which decayed monoexponentially with a lifetime of 1.60 μs under nitrogen environment, accelerating to 0.2 μs under oxygen environment. The oxygen sensitivity of this transient absorption signal, and its monoexponential microsecond decay dynamics, allow us to assign this signal to GeIDT-BT triplet exciton $T_1 \rightarrow T_n$ absorption. These triplets states most likely derive from intersystem crossing from the corresponding polymer singlet excitons.

Figure 3a shows these triplet exciton decay kinetics as a function of laser excitation intensity. As seen from the inset, there is a linear dependence between the initial triplet signal amplitude and excitation intensity for intensities <7 μJ cm^{-2}, whereas saturation of the triplet signal amplitude occurs at higher excitation intensities. At low excitation intensities, all decays exhibited a monoexponential, 1.60 ± 0.1 μs decay, whilst at higher excitation intensities, an additional faster decay is observed, resulting in biexponential decay dynamics, as illustrated in

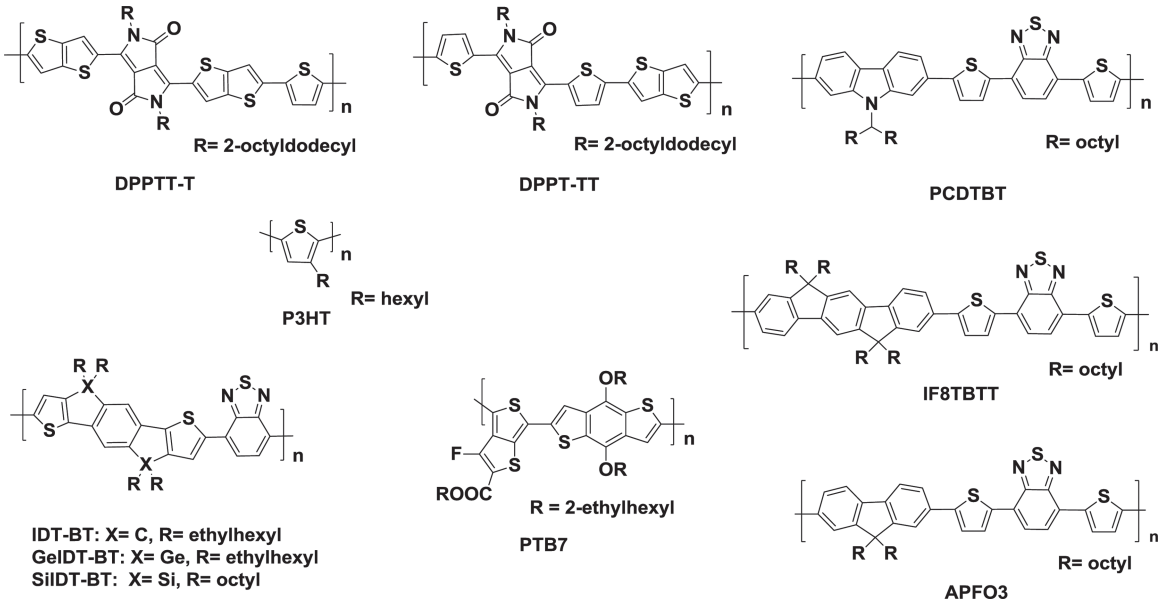

Figure 1. Structures of the polymers used in this study.

Figure 3b. This additional decay phase (and saturation of initial signal amplitude) is assigned to the presence of triplet–triplet annihilation at high excitation intensities.[22,27,28] As such, all triplet lifetimes reported herein were obtained from decay kinetics at low excitation energies (typically ~3 μJ cm^{-2}), well into the linear region where only monomolecular decay of triplet excitons is observed.

Analogous data (see Supporting Information, Figure S1) to that shown in Figures 2 and 3 were collected for neat films of all the polymers shown in Figure 1. Large variations in transient data were observed between the polymers studied. Some polymers showed strong triplet signals with long triplet lifetimes (up to 5 μs) whereas others showed no triplet exciton signal beyond the time resolution of our transient spectrometer (~100 ns). For some neat polymers, an additional, slower, low amplitude power law decay phase was observed when using high excitation densities, assigned to formation of polymer polarons. The relatively low amplitude of this signal, and requirement for high excitation densities, indicates the yield of these polarons is relatively low, consistent with the expected low charge separation yields in neat polymer films; these polarons are not considered further in this paper. Polymer triplet exciton lifetimes in inert atmosphere as determined from these data are listed in **Table 1**, and ranged from 0.1 to 5 μs.

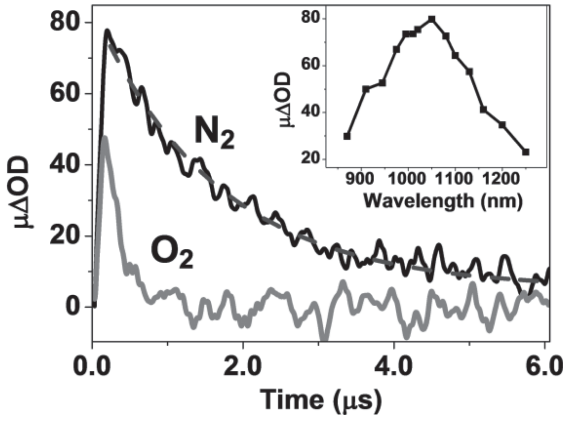

Figure 2. The transient absorption decay kinetics of a GeIDT-BT neat film under nitrogen and oxygen environments, measured using 3.5 μJ cm^{-2} excitation at 640 nm and a probe wavelength of 1050 nm. The broken line represents fitting curve with a monoexponential equation: $\Delta OD \propto \exp(-t/\tau)$. The inset shows the normalised transient absorption spectrum measured at 1 μs.

In addition to yielding triplet lifetimes, a comparison of the transient absorption decay kinetics determined in inert and oxygen atmospheres (τ_{N2} and τ_{O2} respectively) allows us to determine the rate constant, k_{O2} and quantum yield, Φ_{O2} of oxygen quenching of the polymer triplet from:

$$k_{O2} = \frac{1}{\tau_{O2}} - \frac{1}{\tau_{N2}} \quad (1)$$

$$\Phi_{O2} = \left(1 - \frac{\tau_{O2}}{\tau_{N2}}\right) \times 100\% \quad (2)$$

These oxygen quenching rate constants and quantum yields are also listed in Table 1. k_{O2} varies between polymers from 0.28×10^6 to 3.7×10^6 s^{-1}. Φ_{O2} ranges from 0 to 84 ±2% polymers, with this variation arising both from variations in triplet lifetime where polymers with longer triplet lifetimes exhibit higher oxygen quenching yields, and from variations in oxygen quenching rate constant.

We investigated the possibility of a correlation between the polymer triplet decay kinetics (and oxygen quenching) and the polymer singlet exciton energies, as assayed by their optical absorption band gaps, also listed in Table 1. No such correlation could be observed (see Supporting Information, Figure S2), suggesting that the pronounced differences in triplet photophysics and oxygen quenching among the polymers studies are

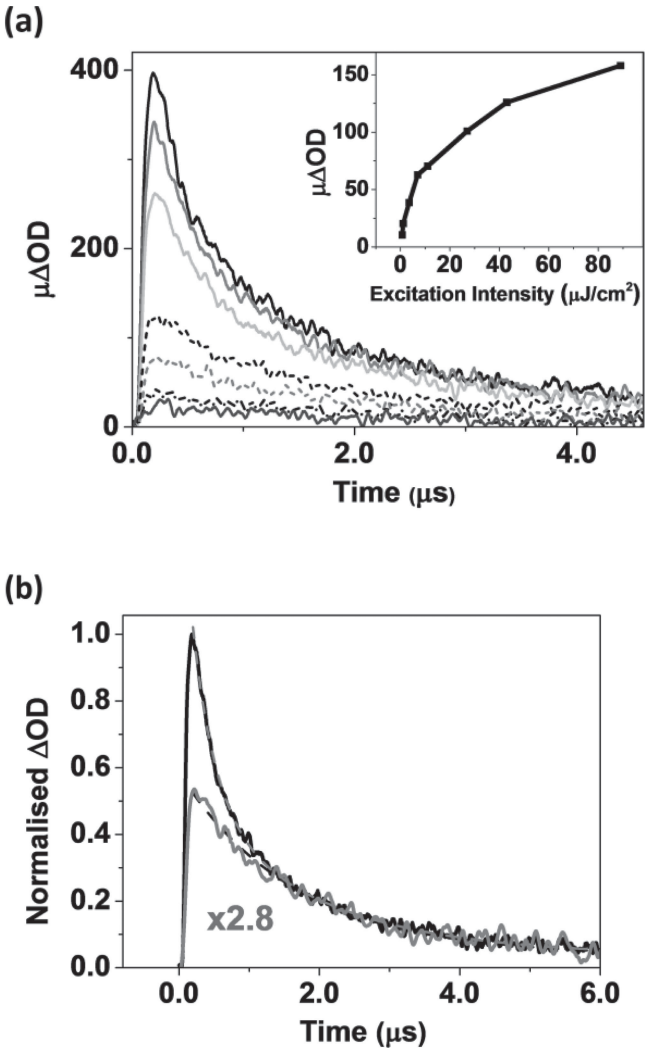

Figure 3. a) The transient absorption decay kinetics of a GeIDT-BT neat film as a function of laser excitation intensity, from top to bottom, E = 89, 43, 27, 7, 3.5, 1.1, 0.7 μJ cm^{-2}. The inset shows monoexponential decay amplitude against laser excitation intensity. b) Decay kinetic at 89 μJ cm^{-2} (solid black line) is fitted to a biexponential equation, $\Delta OD \propto A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ while decay kinetic at 7 μJ cm^{-2} (solid grey line) is fitted to a monoexponential equation, $\Delta OD \propto \exp(-t/\tau)$.

Table 1. Photophysical properties of neat films. (The pump and probe wavelengths for each polymer are listed in the Supporting Information.)

Polymers	τ_{N2} [μs]	k_{O2} [$\times 10^6$ s^{-1}]	Φ_{O2} [%]	E_s [a)] [eV]
Ra-P3HT	5.0	1.2	84	2.3
GeIDT-BT	1.6	3.7	80	1.8
IF8TBTT	1.3	2.6	79	2.0
APFO3	0.9	1.4	55	2.0
PCDTBT	0.9	1.4	55	1.9
PTB7	0.8	0.4	25	1.7
SiIDT-BT	0.4	0.3	10	1.9
IDT-BT	0.1	0	0	1.8
DPPTT-T	–	–	-	1.4
DPPT-TT	–	–	–	1.4
Rr-P3HT	–	–	–	2.0

[a)]Optical bandgaps, E_s, are estimated from the first vibrational band of absorption and emission spectra.

unlikely to be explained by the energies of singlet (and by inference triplet) excitons.

Wide-angle X-ray scattering data was employed to assay the diffraction strength and thereby the relative crystallinity of drop cast films of the polymers employed in this study. Typical data are shown in **Figure 4**, normalised for film thickness, showing scattering peaks at around q = 0.4 $Å^{-1}$ and 1.6 $Å^{-1}$, assigned as previously[29] to out-of-plane lamellar stacking and π–π stacking peaks respectively. It is apparent that the polymers used in this study exhibit a highly varying degree of XRD scatter intensity and peak widths, indicative of varying crystallinity between the polymers studied. We note the relative magnitudes of these scatter peaks is not only dependent on film crystallinity but also on any preferred orientation of the polymer crystalline domains within the film. Three of the polymers studied, regioregular P3HT (Rr-P3HT), DPPT-TT and DPPTT-T exhibit intense and narrow lamellar scattering peaks at around q = 0.4 $Å^{-1}$ consistent with their previously reported high degree of crystallinity.[20,30] These polymers exhibited relatively weak π–π stacking scatter peaks, attributed to these polymers being primarily oriented edge-on to the substrate (with π–π stacking parallel to the substrate), as indicated for both Rr-P3HT and DPPT-TT from previous grazing incidence X-ray scattering (GIXS).[20,30] The remaining polymers films exhibited weak and broad scattering peaks at around q = 0.4 $Å^{-1}$ and additionally at q = 1.6 $Å^{-1}$. For these polymers, the relative film crystallinities were estimated from integration of the diffraction intensities over the relevant bands following literature procedures.[31] Similar relative crystallinities

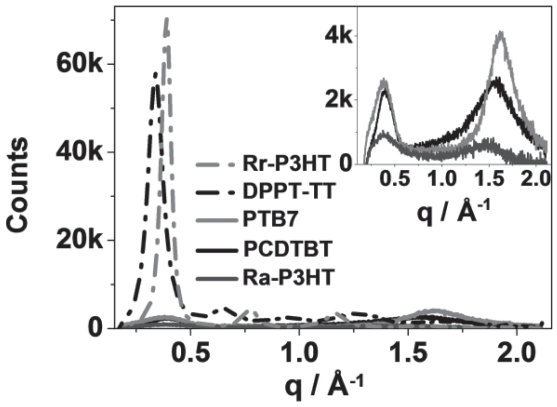

Figure 4. Wide-angle X-ray scattering data on neat films showing polymers with different degree of diffraction strength. The inset shows an expansion of scattering data for the more amorphous polymers. The scattering vector q was determined from the scattering angle by $q = (4\pi/\lambda)\sin(\theta)$. Film thicknesses are (4.1, 7.5, 4.2, 4.9, 3.7) nm for Rr-P3HT, DPPT-TT, PTB7, PCDTBT, and Ra-P3HT respectively.

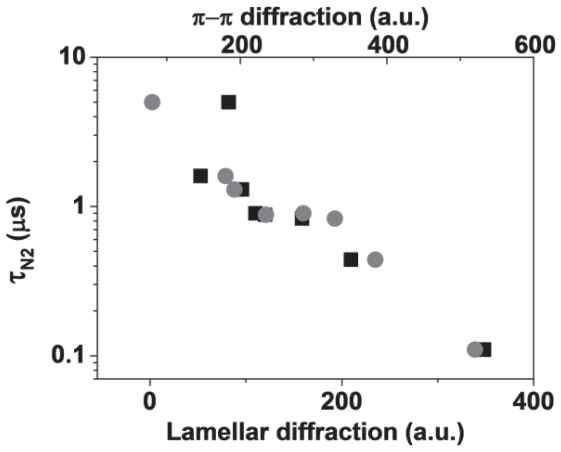

Figure 5. Triplet exciton lifetimes (as estimated from triplet decay kinetics) as a function of lamellar (black square) and π–π (grey circle) diffraction strength, determined from integration of XRD peaks.

were obtained for these polymers from analysis of either the lamellar stacking or π–π stacking peaks, indicating that both these peaks were effective assays of polymer crystallinity, and consistent with relatively random crystal orientations within these more amorphous films.

Figure 5 shows a plot of polymer triplet exciton lifetimes as a function of relative polymer crystallinity measured from the strength of either the lamellar or π–π XRD peaks. No triplet signals were observable for the three polymers exhibiting high crystallinity and evidence of orientated films; these polymers are therefore not included in this analysis. It is apparent that for the remaining, more amorphous polymers, the polymer triplet lifetime shows a strong correlation with both the lamellar and π–π assays of film crystallinity, with the polymers with low fractional crystallinity showing longer triplet lifetimes. This correlation is particularly clear for the π–π stacking XRD peak, strongly indicating that the strength of polymer π–π stacking (and the associated increase in polymer crystallinity) is a key determinant of triplet exciton lifetime.

We also considered whether there was a correlation between polymer crystallinity and the yield of polymer triplet excitons, as assayed by the initial amplitude of the transient absorption signal assigned polymer triplet T_1–T_n absorption (see Supporting Information, Figure S3). This assay is less quantitative than the lifetime data due to likely variations in polymer T_1–T_n absorption coefficient, and due to difficulty in measuring this amplitude for triplets with lifetimes approaching our instrument response. For the polymers where the initial signal amplitude could be clearly measured, we observed rather similar triplet signal amplitudes (±50%) for all the polymers studied, with only a limited correlation with polymer crystallinity (a weak trend of decreasing triplet signal amplitude with increasing polymer crystallinity, see Figure S2, consistent with Cadby et al.[17] It thus appears that whilst the triplet exciton lifetime is strongly correlated with polymer crystallinity (varying by >50 fold as a function of relative polymer crystallinity), the yield of these triplets is not so strongly correlated, at least within the limits of our experimental assay.

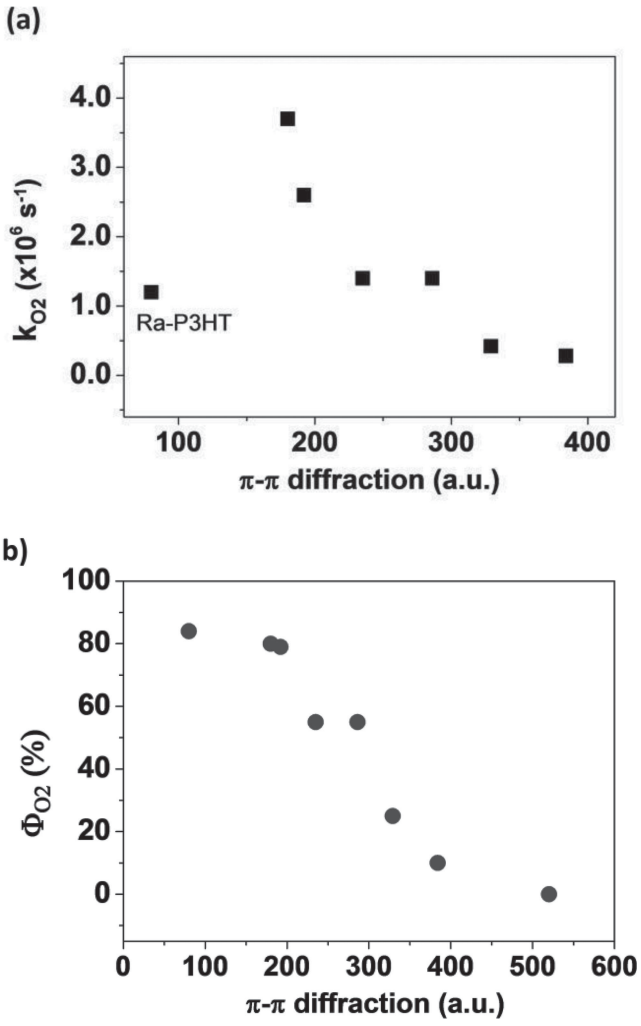

Figure 6. Plot of a) rate constants and b) yields of oxygen quenching against π–π diffraction strength.

In terms of oxygen quenching, a correlation was observed between oxygen quenching rate constant and polymer crystallinity, with more crystalline polymers showing a slower rate constant (**Figure 6**a), with the exception of regiorandom P3HT (Ra-P3HT), which shows an anomalously slow rate constant for oxygen quenching given its low crystallinity (discussed further below). The yield of oxygen quenching showed a particularly strong correlation with polymer crystallinity (Figure 6b). For more amorphous polymers such as Ra-P3HT or GeIDT-BT, more than 80% of triplet excitons are effectively quenched by oxygen, whereas more crystalline polymers such as IDT-BT showed negligible oxygen quenching yield. This correlation can be attributed both to the longer triplet lifetime of more amorphous polymers giving the triplets more time to interact with oxygen, and the higher oxygen quenching rate constant observed for the more amorphous polymers. For the three crystalline polymers, no oxygen quenching data could be obtained, although the absence of any triplet exciton signal on timescales >100 ns, and the trend of decreasing oxygen

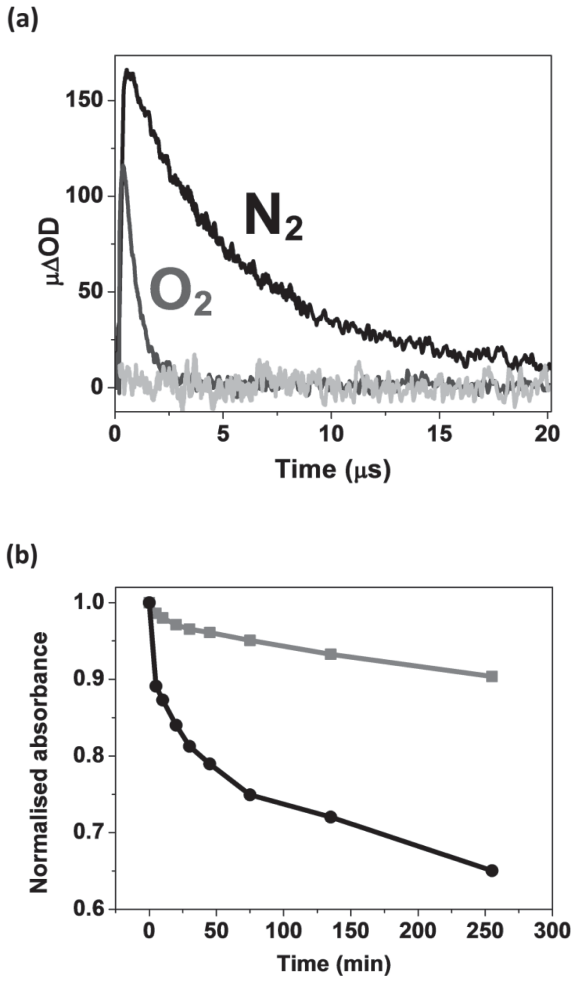

Figure 7. a) The transient absorption decay kinetics of a regiorandom P3HT neat film under nitrogen and oxygen environments, excited at 440 nm and probed at 980 nm. Transient decay kinetic of regioregular P3HT neat film (light grey) showed no observable signal on the same timescale. b) The rate of degradation of regioregular (black circle) and regiorandom (grey square) P3HT neat films when exposed to white light and pure oxygen environments.

This photochemical stability was assayed by monitoring the rate of photobleaching of ground state absorption spectra of each polymer film as a function of white light illumination time in pure oxygen.[13] No photobleaching was observed in the absence of either light or oxygen.

We first of all consider the photostability of Rr-P3HT and Ra-P3HT, as these polymers are chemically almost identical, but differ significantly in crystallinity. **Figure 7**a shows the transient absorption data for these two polymers, with Ra-P3HT showing a long lived triplet signal, strongly quenched by oxygen (oxygen quenching yield of 84%), whilst Rr-P3HT showed no triplet transient absorption signal on the timescales measured, and therefore is expected to have a negligible oxygen quenching yield. A comparison of the rates of photodegradation of Rr-P3HT and Ra-P3HT is presented in Figure 7b, showing that Rr-P3HT is much more stable than Ra-P3HT (~3.5 fold) under the same conditions. This striking difference in photochemical stability is consistent with the difference in triplet photophysics between these two polymers.

Figure 8 compares the rates of photodegradation of the polymers in our study. The two most photostable polymers in this study are DPPTT-T and Rr-P3HT, the two polymers which exhibited particularly high crystallinity and negligible triplet signals. On the other hand, the more amorphous polymers with longer triplet lifetimes, and significant oxygen quenching yields, are relatively less stable. The superior photostability of the highly crystalline polymers may stem from the absence of long-lived triplet excitons which could drive singlet oxygen generation. However there is not a clear quantitative correlation between photodegradation rate and oxygen quenching yield, with for example PCDTBT exhibiting a higher stability than PTB7, but a lower (although still significant) oxygen quenching yield. Similarly Ra-P3HT exhibits the highest polymer triplet yield (see Supporting Information, Figure S3), and highest oxygen quenching yield, but superior stability to PTB7. Hence, whilst these data are consistent with triplet exciton generated singlet oxygen being a key photodegradation pathway of these neat polymer films, the yield of singlet oxygen is clearly not the only factor determining the rate of photochemical degradation.

quenching rate constant with increased crystallinity suggests that their oxygen quenching yield will be negligible. Oxygen quenching of molecular triplet states has been previously shown to proceed by energy transfer to molecular oxygen, resulting, at least in part, in excitation of molecular oxygen from its $^3O_2$ triplet ground state to its $^1O_2$ singlet state.[32]

As discussed above, oxygen quenching of triplet excitons, leading to singlet oxygen generation, is known to be a key photodegradation pathway for organic materials. We therefore now turn to the photochemical stability of the polymers studied herein, and the extent to which this stability correlates with triplet photophysics and polymer crystallinity.

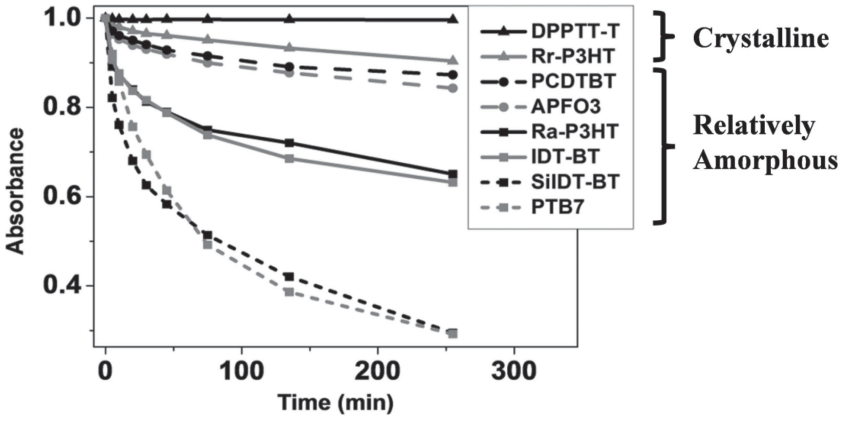

Figure 8. The rate of degradation of polymers when exposed to white light and pure oxygen environments, as monitored by the decay of their peak absorption strength.

3. Discussion

First we summarise the correlation we observe between polymer triplet photophysics and material crystallinity, and then address the basis and implications of this correlation. Herein, polymers studied are categorised according to their relative film crystallinity, as estimated by the strengths of their lamellar and π–π stacking XRD peaks. For the more amorphous polymers, PCDTBT, PTB7, SiIDT-BT, GeIDT-BT, APFO3, IF8TBTT, Ra-P3HT, and IDT-BT, optical excitation is observed to result in long lived triplet excitons with lifetimes ranging from 0.1 to 5 μs. These triplets are observed to be quenched under oxygen on the timescales measured, with the oxygen quenching efficiency increasing with longer triplet lifetime. On the other hand, Rr-P3HT, DPPTT-T and DPPT-TT all exhibited substantially higher film crystallinity, and no observable transient species on the microsecond timescale.

For the more amorphous polymers, where we are able to quantify both the relative material crystallinity and triplet exciton lifetime, we observed a good correlation between triplet lifetime and polymer crystallinity, with the triplet exciton lifetime decreasing at least 50-fold with increasing polymer crystallinity. This correlation is consistent with previous studies which have indicated some correlation between triplet photophysics and material crystallinity for single material studies.[15,17,22] Our observation herein that this correlation can be observed even for a broad range of structurally different polymers indicates this correlation is quite general, and suggests that polymer crystallinity is the primary determinant of triplet lifetime for such polymers.

We now consider the likely physical origin of this correlation between polymer crystallinity and triplet lifetime. Molecular aggregation/crystallisation has been reported to result in quenching of molecular singlet excited states due to an acceleration of non-radiative decay processes (a process often referred to as 'concentration quenching').[33] However, for the polymers studied herein, only a weak correlation was observed between fluorescence decay time (determined from time correlated single photon counting) and film crystallinity (see Supporting Information Figure S4). Similarly the polymer triplet yield, as approximately assayed by the amplitude of the T_1–T_n transient absorption signal, did not strongly correlate with polymer crystallinity (see Figure S2). This suggests that the strong correlation between triplet lifetime and polymer crystallinity reported here should not be assigned primarily to such concentration quenching effects. It appears more likely that this correlation is associated with a lower triplet exciton mobility in the more amorphous polymers reducing the probability of triplet excitons reaching quenching sites, hence contributing to an increase in triplet lifetimes.[34]

The rate constant for oxygen quenching of polymer triplet excitons was observed to correlate well with polymer crystallinity. This correlation can most probably be attributed to higher oxygen solubility in more amorphous polymers.[35,36] Ra-P3HT, however, appears to be an anomaly to this correlation (Figure 6a), showing a rather slow oxygen quenching rate constant. In the case of Ra-P3HT, the nature and density of the short alkyl chains may act to impede oxygen diffusion. The yield of oxygen quenching is also found to correlate well with polymers' crystallinity. The higher yield of oxygen quenching observed for more amorphous polymers results primarily from the increased triplet lifetimes, as well as from increased oxygen quenching rate constant.

From the rate of photodegradation of the polymers shown in Figure 8, it is apparent that the most stable polymers are highly crystalline, with no observable triplet formation. Other than the absence of triplet mediated degradation pathway, the photostability of crystalline polymers may also be enhanced by the lower oxygen solubility which can reduce the rate of photooxidation.[35,37] In a recent work,[13] we have compared the photodegradation pathways of two polymers (DPPTT-T and PTB7) which exhibit very different photochemical stability. It was demonstrated from studies employing a molecular singlet oxygen probe that the PTB7 film showed a high yield of singlet oxygen generation under white light irradiation, consistent with the observed high PTB7 triplet yield and efficient oxygen quenching, and rapid photochemical degradation. As such it seems reasonable that the faster photochemical degradation observed for the more amorphous polymers studied herein is associated with the observed oxygen quenching of the polymer triplet excitons, leading to singlet oxygen generation. However we do not observe a quantitative correlation between oxygen quenching yield and photochemical degradation rate, suggesting another factor is also influencing the rate of photochemical degradation. For all the neat polymer films studied herein, only very low polaron yields were observed, suggesting that anion mediated superoxide generation[24,38] is unlikely to be a significant degradation pathway. Most probably the variations in photodegradation rates observed for the relatively amorphous polymers are associated with the specific chemistry of the interaction of singlet oxygen with the donor polymers, especially the electron density and steric nature of the conjugated diene groups along the backbone. For example, it is known that singlet oxygen is particularly reactive with electron-rich diene units when strong electron-donating group such as sulphur is present, for example in thiophenes.[25] In addition, the particular instability of SiIDT-BT may be associated with ability of silicon to form strong silicon-oxygen bonds,[39] whilst the instability of PTB7 may be associated with the high electronegativity of its fluorine substituent which may accelerate the reaction with singlet oxygen. As reported by Son et al.,[40] the introduction of more fluorine atoms into polymer backbone can increase its susceptibility to singlet oxygen attack.

For the study reported here in, we do not see any significant correlation between exciton energetics and photophysics/ photochemical stability (see for example Table 1). Consistent with this observation, we note that polymer triplet excitons are typically reported to be 0.4–0.7 eV below the singlet exciton,[41] suggesting that for all the polymers studied apart from DPPTT-T and DPPT-TT (which in any case does not exhibit long lived triplet states), the polymer triplet exciton has sufficient energy to drive singlet oxygen generation (0.98 eV).

The oxygen quenching of polymer triplet exciton reported herein was obtained for neat polymer films. In polymer/ fullerene blend films employed in organic solar cells, triplet formation by direct intersystem crossing from polymer singlet excitons is likely to be suppressed by photoinduced charge separation. However recombination of these

photoinduced charges can also result in triplet exciton generation.[18,27,42] Indeed we have reported that PTB7:$PC_{71}BM$ blend films actually exhibit higher singlet oxygen generation yields than neat PTB7 films.[13] Furthermore it is widely reported that electron/hole recombination in OLED devices can lead to high yields of triplet excitons.[43] Therefore, whilst the specific impact of triplet mediated singlet oxygen generation will depend upon the details of device operating conditions, and the extent of encapsulation of the device from oxygen ingress, it appears likely that the neat polymer stability reported herein will have some relevance to the long term stability of OPV and OLED devices. The design of materials to avoid triplet mediated singlet oxygen generation is therefore likely to be an important consideration for stable optoelectronic devices.[13] The results we report herein suggest that one strategy to address this requirement is to employ relatively crystalline donor polymers, as these exhibit (at least for the materials studied herein) triplet lifetimes too short for efficient singlet oxygen generation.

4. Conclusion

The results we report herein indicate that materials crystallinity is a key determinant of the lifetime and oxygen quenching efficiency of polymer triplet states. This dependence appears to be the dominant determinant of triplet lifetime for a broad range of polymer structures. This conclusion is clearly of relevance to optoelectronic devices where photochemical stability under irradiation is of concern when considering encapsulation requirements to prevent oxygen ingress. It is also of relevance to device design strategies where triplet exciton states play a key role in device function, such as singlet fission based photovoltaic devices and OLED devices utilising triplet excitons. As such, these results suggest that the impact of materials crystallinity upon triplet photophysics is a key materials design consideration likely to be of importance for many organic optoelectronic devices applications.

5. Experimental Section

Materials: The polymers DPPTT-T,[44] DPPT-TT,[20] APFO3,[45] IF8TBTT,[46] GeIDT-BT,[47] SiIDT-BT[48] and IDT-BT[49] were synthesised as reported elsewhere. Both PCDTBT and PTB7 were purchased from 1-Material and purified before use as detailed previously.[13] Regioregular P3HT (Rr-P3HT) was purchased from Merck whereas regiorandom P3HT (Ra-P3HT) from Sigma Aldrich, and both were used as received.

Film Fabrication: Solutions for films were prepared with dichlorobenzene (18 mg/mL) for GeIDT-BT, SiIDT-BT, IDT-BT and IF8TBTT; with chlorobenzene (12 mg/mL) for Rr-P3HT, Ra-P3HT, APFO3 and DPPT-TT; and with chloroform (10 mg/mL) for PCDTBT and DPPTT-T. For PTB7 films, solutions were prepared with a mixture of 97% chlorobenzene and 3% 1,8-diodoctane at ~15 mg/mL. The choice of solvents were as used in the optimised blend photovoltaic devices. The solutions were heated on a hot plate at ~50 °C (except for chloroform solutions) and stirred continuously overnight to ensure complete dissolution. All polymer films were then fabricated by spin coating the solutions onto glass substrates at 2000–3000 rpm for 1 min. Before spin coating, the substrates were cleaned by sonication in acetone and isopropanol for 15 min respectively.

Measurements: Transient absorption data were collected on films with a microsecond transient absorption system under nitrogen (or oxygen) atmosphere as detailed previously.[50]

Wide-angle X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu Kα1 beam and X'CELERATOR detector, using current I = 40 mA and accelerating voltage U = 40 kV. Samples were prepared by drop casting ~0.25 mL of solutions onto 2 cm x 1 cm substrates and left to dry at room temperature.

For stability study, films were degraded by exposing to white light irradiation from Luxeon Star white LED (~80 mW cm^{-2}) under pure oxygen environment. Ground state absorption spectra were then obtained as a function of illumination time using a UV-1601 Shimadzu uv-vis spectrophotometer. Control data in the absence of illumination showed no measureable degradation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[2] a) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4; b) X. Yang, D. Neher, D. Hertel, T. K. Däubler, *Adv. Mater.* **2004**, *16*, 161; c) E. L. Williams, K. Haavisto, J. Li, G. E. Jabbour, *Adv. Mater.* **2007**, *19*, 197.
[3] M. A. Baldo, C. Adachi, S. R. Forrest, *Phys. Rev. B* **2000**, *62*, 10967.
[4] a) C. Dyer-Smith, L. X. Reynolds, A. Bruno, D. D. C. Bradley, S. A. Haque, J. Nelson, *Adv. Funct. Mater.* **2010**, *20*, 2701; b) D. Veldman, S. C. J. Meskers, R. A. J. Janssen, *Adv. Funct. Mater.* **2009**, *19*, 1939.
[5] H. Ohkita, S. Cook, Y. Astuti, W. Duffy, S. Tierney, W. Zhang, M. Heeney, I. McCulloch, J. Nelson, D. D. C. Bradley, J. R. Durrant, *J. Am. Chem. Soc.* **2008**, *130*, 3030.
[6] A. Distler, P. Kutka, T. Sauermann, H.-J. Egelhaaf, D. M. Guldi, D. Di Nuzzo, S. C. J. Meskers, R. A. J. Janssen, *Chem. Mater.* **2012**, *24*, 4397.
[7] J. E. Kroeze, T. J. Savenije, J. M. Warman, *Adv. Mater.* **2002**, *14*, 1760.
[8] A. Listorti, B. O'Regan, J. R. Durrant, *Chem. Mater.* **2011**, *23*, 3381.
[9] a) S. T. Roberts, C. W. Schlenker, V. Barlier, R. E. McAnally, Y. Zhang, J. N. Mastron, M. E. Thompson, S. E. Bradforth, *J. Phys. Chem. Lett.* **2010**, *2*, 48; b) Y. Shao, Y. Yang, *Adv. Mater.* **2005**, *17*, 2841; c) W. A. Luhman, R. J. Holmes, *Appl. Phys. Lett.* **2009**, *94*, 153304.
[10] a) A. Rao, M. W. B. Wilson, J. M. Hodgkiss, S. Albert-Seifried, H. Bässler, R. H. Friend, *J. Am. Chem. Soc.* **2010**, *132*, 12698; b) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891; c) V. K. Thorsmølle, R. D. Averitt, J. Demsar, D. L. Smith, S. Tretiak, R. L. Martin, X. Chi, B. K. Crone, A. P. Ramirez, A. J. Taylor, *Phys. Rev. Lett.* **2009**, *102*, 017401.

[11] a) M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, A. J. Nozik, *Nano Lett.* **2007**, *7*, 2506; b) A. J. Nozik, *Nano Lett.* **2010**, *10*, 2735.
[12] a) B. H. Cumpston, K. F. Jensen, *Synth. Met.* **1995**, *73*, 195; b) H. Hintz, H. J. Egelhaaf, L. Lüer, J. Hauch, H. Peisert, T. Chassé, *Chem. Mater.* **2010**, *23*, 145.
[13] L. Ma, X. Wang, B. Wang, J. Chen, J. Wang, K. Huang, B. Zhang, Y. Cao, Z. Han, S. Qian, S. Yao, *Chem. Phys.* **2002**, *285*, 85.
[14] Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch, J. R. Durrant, *Chem. Commun.* **2013**, *49*, 1291.
[15] a) P. A. Lane, S. V. Frolov, Z. V. Vardeny, *Semiconducting Polymers*, Wiley-VCH, Weinheim, Germany **2000**; b) M. D. E. Forbes, *Photochem. Photobiol.* **1997**, *65*, 73; c) G. Possamai, M. Maggini, E. Menna, G. Scorrano, L. Franco, M. Ruzzi, C. Corvaja, G. Ridolfi, P. Samorì, A. Geri, N. Camaioni, *Appl. Phys. A Mater. Sci. Process.* **2004**, *79*, 51; d) M. Wohlgenannt, C. P. An, Z. V. Vardeny, *J. Phys. Chem. B* **2000**, *104*, 3846.
[16] J. Guo, H. Ohkita, H. Benten, S. Ito, *J. Am. Chem. Soc.* **2009**, *131*, 16869.
[17] a) B. Kraabel, D. Moses, A. J. Heeger, *J. Chem. Phys.* **1995**, *103*, 5102; b) J. J. Benson-Smith, H. Ohkita, S. Cook, J. R. Durrant, D. D. Bradley, J. Nelson, *Dalton Transactions* **2009**, 10000.
[18] A. J. Cadby, P. A. Lane, H. Mellor, S. J. Martin, M. Grell, C. Giebeler, D. D. C. Bradley, M. Wohlgenannt, C. An, Z. V. Vardeny, *Phys. Rev. B* **2000**, *62*, 15604.
[19] H. Ohkita, S. Cook, Y. Astuti, W. Duffy, M. Heeney, S. Tierney, I. McCulloch, D. D. Bradley, J. R. Durrant, *Chem. Commun.* **2006**, *37*, 3939.
[20] a) A. Zen, J. Pflaum, S. Hirschmann, W. Zhuang, F. Jaiser, U. Asawapirom, J. P. Rabe, U. Scherf, D. Neher, *Adv. Funct. Mater.* **2004**, *14*, 757; b) Z. M. Beiley, E. T. Hoke, R. Noriega, J. Dacuña, G. F. Burkhard, J. A. Bartelt, A. Salleo, M. F. Toney, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 954; c) C. L. Donley, J. Zaumseil, J. W. Andreasen, M. M. Nielsen, H. Sirringhaus, R. H. Friend, J.-S. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 12890; d) J. Jo, S.-I. Na, S.-S. Kim, T.-W. Lee, Y. Chung, S.-J. Kang, D. Vak, D.-Y. Kim, *Adv. Funct. Mater.* **2009**, *19*, 2398.
[21] X. Zhang, L. J. Richter, D. M. DeLongchamp, R. J. Kline, M. R. Hammond, I. McCulloch, M. Heeney, R. S. Ashraf, J. N. Smith, T. D. Anthopoulos, B. Schroeder, Y. H. Geerts, D. A. Fischer, M. F. Toney, *J. Am. Chem. Soc.* **2011**, *133*, 15073.
[22] D. Beljonne, Z. Shuai, G. Pourtois, J. L. Bredas, *J. Phys. Chem A* **2001**, *105*, 3899.
[23] R. A. J. Janssen, L. Smilowitz, N. S. Sariciftci, D. Moses, *J. Chem. Phys.* **1994**, *101*, 1787.
[24] R. S. Becker, J. Seixas de Melo, A. L. Maçanita, F. Elisei, *J. Phys. Chem.* **1996**, *100*, 18683.
[25] E. T. Hoke, I. T. Sachs-Quintana, M. T. Lloyd, I. Kauvar, W. R. Mateker, A. M. Nardes, C. H. Peters, N. Kopidakis, M. D. McGehee, *Adv. Energy Mater.* **2012**, *2*, 1351.
[26] a) M. S. A. Abdou, S. Holdcroft, *Can. J. Chem.* **1995**, *73*, 1893; b) N. Dam, R. D. Scurlock, B. Wang, L. Ma, M. Sundahl, P. R. Ogilby, *Chem. Mater.* **1999**, *11*, 1302; c) R. D. Scurlock, B. Wang, P. R. Ogilby, J. R. Sheats, R. L. Clough, *J. Am. Chem. Soc.* **1995**, *117*, 10194.
[27] B. A. Baldwin, H. W. Offen, *J. Chem. Phys.* **1968**, *49*, 2933.
[28] T. A. Ford, I. Avilov, D. Beljonne, N. C. Greenham, *Phys. Rev. B* **2005**, *71*, 125212.
[29] M. Westerling, C. Vijila, R. Osterbacka, H. Stubb, *Chem. Phys.* **2003**, *286*, 315.
[30] T. J. Prosa, M. J. Winokur, J. Moulton, P. Smith, A. J. Heeger, *Macromolecules* **1992**, *25*, 4364.
[31] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.
[32] J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Salleo, M. F. Toney, *Chem. Rev.* **2012**, *112*, 5488.
[33] a) W. Shi, J. Barber, Y. Zhao, *J. Phys. Chem. B* **2013**, *117*, 3976; b) E. Z. M. Ebeid, S. T. Abdel-Halim, M. H. Abdel-Kader, *J. Phys. Chem.* **1988**, *92*, 7255.
[34] a) J. Cornil, D. Beljonne, J. P. Calbert, J. L. Brédas, *Adv. Mater.* **2001**, *13*, 1053; b) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, M. Ree, *Nat Mater* **2006**, *5*, 197.
[35] J. F. Rabek, *Photodegradation of Polymers*, Springer-Verlag, New York **1996**.
[36] A. S. Michaels, H. J. Bixler, *J. Polym. Sci.* **1961**, *50*, 393.
[37] a) A. Dupuis, P. Wong-Wah-Chung, A. Rivaton, J.-L. Gardette, *Polym. Degrad. Stab.* **2012**, *97*, 366; b) N. C. Billingham, P. Prentice, T. J. Walker, *J. Polymer Sci.: Symposium* **1976**, *57*, 287.
[38] S. Chambon, A. Rivaton, J.-L. Gardette, M. Firon, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6044.
[39] D. F. Shriver, P. W. Atkins, *Inorganic Chemistry*, Oxford University Press, Oxford **2006**.
[40] H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li, L. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 1885.
[41] a) K. Sakurai, H. Tachibana, N. Shiga, C. Terakura, M. Matsumoto, Y. Tokura, *Phys. Rev. B* **1997**, *56*, 9552; b) A. Köhler, D. Beljonne, *Adv. Funct. Mater.* **2004**, *14*, 11.
[42] D. Veldman, O. Opek, S. C. J. Meskers, J. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. v. Bavel, J. Loos, R. A. J. Janssen, *J. Am. Chem. Soc.* **2008**, *130*, 7721.
[43] A. P. Monkman, *ISRN Materials Science* **2013**, *2013*, 19.
[44] H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. Shakya Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney, I. McCulloch, *J. Am. Chem. Soc.* **2011**, *133*, 3272.
[45] M. A. Faist, T. Kirchartz, W. Gong, R. S. Ashraf, I. McCulloch, J. C. de Mello, N. J. Ekins-Daukes, D. D. C. Bradley, J. Nelson, *J. Am. Chem. Soc.* **2011**, *134*, 685.
[46] Y. W. Soon, T. M. Clarke, W. Zhang, T. Agostinelli, J. Kirkpatrick, C. Dyer-Smith, I. McCulloch, J. Nelson, J. R. Durrant, *Chem. Sci.* **2011**, *2*, 1111.
[47] Z. Fei, R. S. Ashraf, Z. Huang, J. Smith, R. J. Kline, P. D'Angelo, T. D. Anthopoulos, J. R. Durrant, I. McCulloch, M. Heeney, *Chem. Commun.* **2012**, *48*, 2955.
[48] R. S. Ashraf, Z. Chen, D. S. Leem, H. Bronstein, W. Zhang, B. Schroeder, Y. Geerts, J. Smith, S. Watkins, T. D. Anthopoulos, H. Sirringhaus, J. C. de Mello, M. Heeney, I. McCulloch, *Chem. Mater.* **2010**, *23*, 768.
[49] H. Bronstein, D. S. Leem, R. Hamilton, P. Woebkenberg, S. King, W. Zhang, R. S. Ashraf, M. Heeney, T. D. Anthopoulos, J. d. Mello, I. McCulloch, *Macromolecules* **2011**, *44*, 6649.
[50] H. Xin, S. Subramaniyan, T.-W. Kwon, S. Shoaee, J. R. Durrant, S. A. Jenekhe, *Chem. Mater.* **2012**, *24*, 1995.