Journal of Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2014, 2, 20189

Photochemical stability of high efficiency PTB7:$PC_{70}BM$ solar cell blends†

Joseph Razzell-Hollis,[a] Jessica Wade,[a] Wing Chung Tsoi,[a] Ying Soon,[b] James Durrant[b] and Ji-Seon Kim*[a]

Received 21st October 2014
Accepted 22nd October 2014

DOI: 10.1039/c4ta05641h

www.rsc.org/MaterialsA

Thieno[3,4 b]thiophene-*alt*-benzodithiophene (PTB7) is a promising donor–acceptor copolymer that has achieved high efficiencies (7–9%) in organic solar cells but suffers from poor stability and degrades when exposed to light and oxygen. Using resonant Raman spectroscopy to examine the nature of this photo-oxidation, three main changes to the vibrations of the conjugated backbone are observed: (1) shift of the benzodithiophene (BDT) C=C stretch peak at ~1489 cm^{-1} up to ~1499 cm^{-1}; (2) increase in the relative intensity of coupled fused thiophene and benzene C=C stretch peaks at ~1535 and ~1575 cm^{-1}; (3) appearance of a new peak at ~1650 cm^{-1}; which suggest oxidation takes place on the BDT unit without loss of conjugation. *In situ* accelerated photo-degradation reveals that the observed oxidation is the initial step of degradation, which is followed by reductions in absorption and Raman scattering intensities that indicate the loss of chromophores by a second, more extensive oxidation step. Blending PTB7 with $PC_{70}BM$ is found to accelerate the polymer's degradation, and further shift the BDT peak to ~1509 cm^{-1}. Using density functional theory to simulate Raman spectra for several possible oxidised products, the initial oxidation is best described by hydroxylation of 3rd and 7th positions on the BDT donor unit.

Introduction

Organic photovoltaics (OPVs) based on blend films of organic semiconductors such as conjugated polymers and fullerenes have attracted significant interest as a potential lightweight, low-cost renewable energy source.[1–5] Low band-gap donor–acceptor polymers and modified fullerenes developed specifically for OPV devices have recently achieved power conversion efficiencies of ~9%, approaching the ~12% threshold for commercial viability.[3,6] However, these high-performance conjugated polymers tend to photochemically degrade when exposed to light in the presence of water and/or oxygen,[7,8] limiting the operating lifetime of OPV devices and raising the levelised cost of OPV as an energy source.[5] As a result, understanding their stability, in particular how semiconducting polymers degrade is an increasingly important aspect of OPV research and is critical to making a high-efficiency device that does not need to be replaced every few years. As such, several studies have been published in recent years discussing stability and degradation mechanisms specific to individual polymers such as poly(3-hexylthiophene) (P3HT), or classes of polymer like poly-*p*-phenylenevinylenes (PPVs).[9–11]

The donor–acceptor copolymer thieno[3,4-b]thiophene-*alt*-benzodithiophene (PTB7) has achieved efficiencies of up to 9% in an optimised device architecture,[6,12] but a recent study by Soon *et al.* demonstrated that PTB7 degrades rapidly under accelerated conditions (exposure to ~1 sun of white light in a pure O_2 atmosphere), showing a rapid loss of absorption compared to other polymers such as P3HT and DPP-TT-T.[13] Their investigation identified that PTB7 degrades *via* photo-oxidation by the highly reactive singlet $^1O_2$ species, which is generated when ambient O_2 quenches triplet excited states on the polymer, and not the generation of anionic radical O_2^- superoxide by charge transfer from the polymer, which is an established degradation mechanism for some other polymers including PPV. Here we probe the effect of photo-oxidation on the molecular structure of PTB7, in order to understand how the polymer chain reacts with $^1O_2$ at the molecular level. To this end we have used Raman spectroscopy, a method that is sensitive to the vibrations of conjugated systems comprised of C–C and C=C bonds, and has previously been used to detect changes in structure resulting from chemical alteration or conformational twisting of the polymer chain.[14–19] By comparing experimentally observed Raman spectra to theoretical spectra obtained from Density Functional Theory (DFT) simulations of likely degradation products, we identify the nature of photo-oxidised PTB7. This information can assist the development of

[a]Department of Physics and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, UK. E-mail: ji-seon.kim@imperial.ac.uk

[b]Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, UK

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c4ta05641h

analogue polymers modified to hinder or avoid that degradation process, potentially allowing the fabrication of high-efficiency long-lifetime OPV devices based on modified PTB7.

Results and discussion

Fig. 1 shows the molecular structure of PTB7, comprising alternating thienothiophene (TT) and benzodithiophene (BDT) units that act as an intramolecular electron donor–acceptor system with low band-gap (~1.6 eV). PTB7 exhibits a distinctive Raman spectrum with major peaks from vibrational modes of the conjugated backbone (Fig. 1). Peak 1 (1489 cm^{-1}) was assigned to the C=C stretching mode of the BDT unit's fused thiophenes, Peak 2 (1549 cm^{-1}) is a coupled vibration of the same mode to the C=C stretching mode of the non-fluorinated thiophene of the TT unit, and Peak 3 (1578 cm^{-1}) is the quadrant stretching mode coupled to the C=C stretching mode of the fluorinated thiophene of TT. A weak peak at ~1720 cm^{-1} (Peak 4) corresponds to the less Raman-active C=O stretching mode of the TT unit's ester side chain. Assignments were made according to DFT simulated Raman spectra for individual TT, BDT units and PTB7 oligomers (see Fig. S1†).

Degradation of neat PTB7 films

Fig. 2 shows the absorption spectrum of PTB7, which has a distinctive peak at ~680 nm with an onset at ~750 nm, demonstrating the low band-gap nature of the donor–acceptor polymer. Soon *et al.* measured the extent of degradation by the reduction of this absorption peak, as is observed for a neat PTB7 film degraded by 4 hours exposure to white light and oxygen (see Fig. 2), indicative of the loss of chromophores resulting from broken conjugation and chain scission reported as degradation mechanisms for other polymers.[9–11] Our chosen Raman excitation wavelength (488 nm) is resonant with the absorption band of PTB7, in order to exploit electron-phonon coupling and enhance Raman scattering from vibrational modes associated with the conjugated backbone (Peaks 1 to 3). This is intended to increase sensitivity to any structural changes to that backbone caused by degradation, and as such four spectral changes were observed (shown by arrows in Fig. 2): Peak 1 was up-shifted by ~8 cm^{-1} to 1497 cm^{-1}; the relative intensity of Peak 2 to Peak 1 was increased from 0.54 to 0.75; the relative intensity of Peak 3 was also increased from 0.28 to 0.47; and a new but weak peak at ~1645 cm^{-1} has appeared. These changes provide a qualitative description of degradation: the three major modes of PTB7 associated with C=C stretches

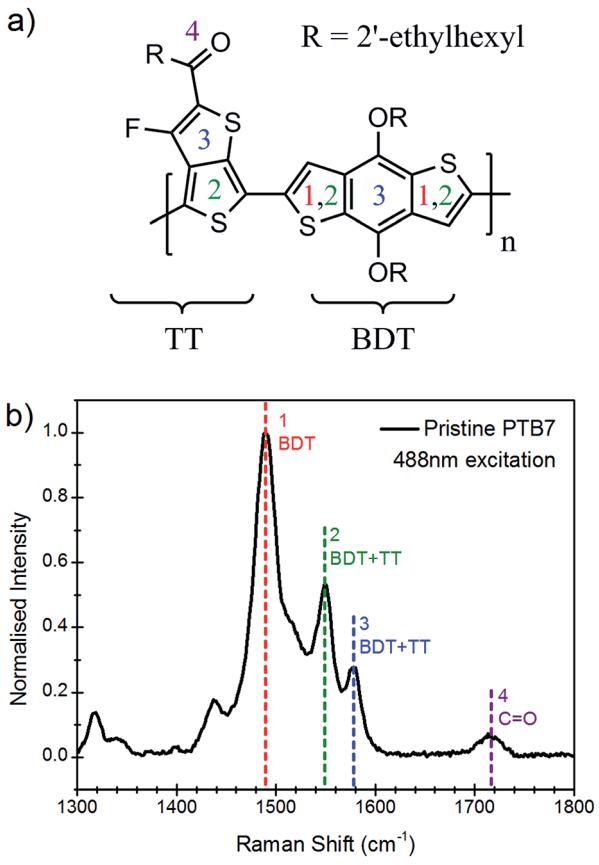


Fig. 1 (a) Chemical structures of the repeat unit for the polymer donor PTB7, coloured numbers indicate assignment of Raman modes to vibrations of C=C and C=O bonds on PTB7. (b) Raman spectrum of PTB7 under 488 nm excitation and purging with N_2.

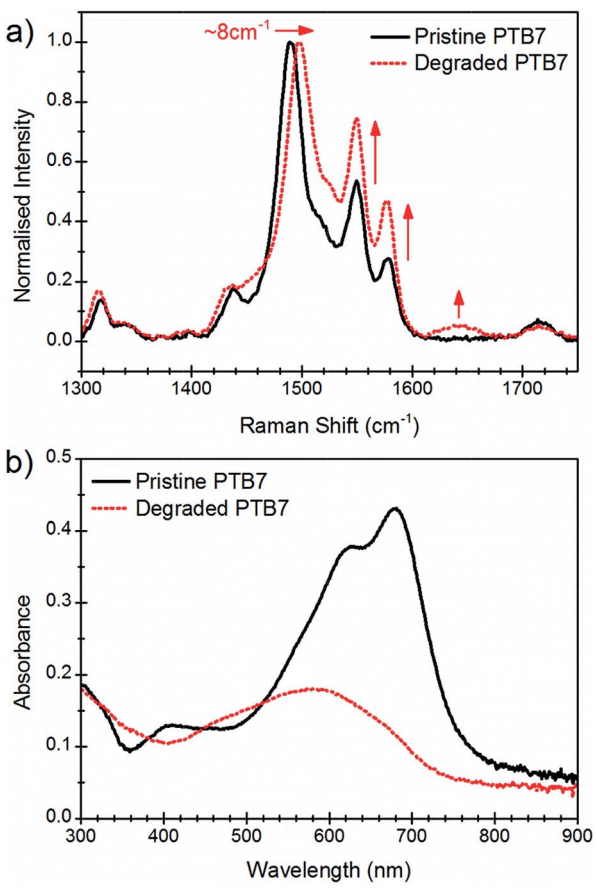


Fig. 2 Normalised Raman spectra (a) and absorption spectra (b) for films of neat PTB7, before and after 4 hours of degradation under white light (~1 sun) and O_2 purging.

along the polymer's conjugated backbone are altered, indicating that the degradation is taking place on the main backbone. In particular, the ~8 cm^{-1} shift of Peak 1 to higher wavenumbers means that the C=C bonds of the BDT unit's fused thiophenes are vibrating at higher frequency, suggesting a change in bond lengths on the BDT unit after photo-oxidation, possibly due to insertion of an electron-withdrawing oxygen group onto the unit. The retention of Raman scattering intensity despite extensive degradation indicates that the observed Raman changes are from molecules that have been oxidised without the loss of conjugation or the chromophore (which would no longer be resonant if broken). Therefore, we must be probing an initial stage of photo-chemical degradation rather than the final product, revealing the nature of early oxidised species that are further broken down by continued exposure.

Degradation of PTB7:$PC_{70}BM$ blend films

Fig. 3 shows the Raman spectrum of a PTB7:$PC_{70}BM$ blend film, exhibiting peaks from both molecules. The strongest Raman peaks of $PC_{70}BM$ (at ~1570 and ~1460 cm^{-1}, assigned to anti-symmetric and symmetric C=C stretching modes)[16] overlap with the 3 main modes of PTB7, with the former obscuring PTB7's Peak 3 and the latter creating a shoulder on Peak 1. Subtraction of the $PC_{70}BM$ spectrum from the blend reproduced the original PTB7 spectrum, including Peak 3 (see Fig. S2†), confirming that the vibrations of PTB7 are not altered by blending with fullerene, unlike those of P3HT.[14] Fig. 3 shows the effect of degradation on the Raman spectrum of the blend, which exhibits several changes caused by degradation. The strongest peak is now at 1470 cm^{-1}, at first suggesting an unexpected ~20 cm^{-1} down-shift of PTB7's Peak 1 to lower wavenumbers but in fact corresponds to the symmetric C=C mode of $PC_{70}BM$ (marked by grey dotted line in Fig. 3b). Instead we observe a new peak at 1509 cm^{-1} (indicated by *) that appeared to line up with the high-energy shoulder of PTB7's Peak 1 but was concluded to be Peak 1 shifted to higher wavenumbers (confirmed during *in situ* degradation of the blend, by the gradual evolution of Peak 1 from a Raman shift of 1489 cm^{-1} to ~1509 cm^{-1}, shown in Fig. 4d). This ~20 cm^{-1} up-shift greatly exceeds the ~8 cm^{-1} observed for degraded neat PTB7, suggesting that degradation is more extensive for the blend under the same conditions. This agrees with the conclusions of Soon *et al.* who observed that blending PTB7 with $PC_{70}BM$ resulted in a more rapid degradation as a result of faster singlet oxygen production.[13] Although a neat film of $PC_{70}BM$ did not show any evidence of degradation under the same conditions, the poorer signal : noise ratio of the degraded blend spectrum meant that it was not possible to deconvolute PTB7 and $PC_{70}BM$ spectra from the blend, and thus it is difficult to comment on changes in the intensity ratio of Peaks 2 or 3 to Peak 1 due to their overlap with the ~1570 cm^{-1} peak of $PC_{70}BM$.

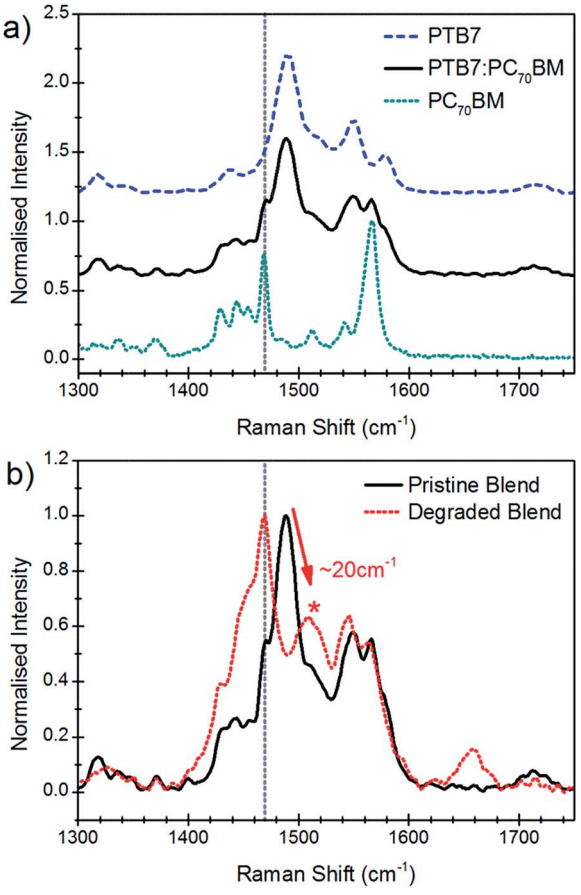


Fig. 3 Normalised Raman spectrum for the pristine PTB7:$PC_{70}BM$ blend film, superimposed over (a) stacked spectra for neat PTB7 and neat $PC_{70}BM$ films, (b) the blend after 4 hours of degradation under white light (~1 sun) and O_2 purging.

In situ accelerated degradation

To better understand the effect of degradation on the molecular structure of PTB7, we intentionally degraded pristine films of neat and blended PTB7 *in situ* by cumulative exposure to the 488 nm excitation laser. Under N_2 purging, there was no change in the Raman spectra (see Fig. 4) of either the neat PTB7 film or the blended PTB7:$PC_{70}BM$ film even after 1 hour of light exposure. This is in agreement with our understanding that the photo-degradation process requires combined exposure to both light and oxygen. Under ambient conditions, the Raman shift of Peak 1 from neat PTB7 changed significantly over the first 10 minutes of exposure (see Fig. 5), exhibiting a ~3 cm^{-1} up-shift to higher wavenumbers after the first 30 seconds of exposure with respect to a stable spectrum collected under N_2. After 3.5 min Peak 1 reached a stable Raman shift of ~1499 cm^{-1} (an up-shift of ~10 cm^{-1}) and did not change further. This is comparable to the ~8 cm^{-1} up-shift observed for samples degraded *ex situ*, and a simultaneous increase in the relative intensities of Peaks 2 and 3 confirm that our *in situ* degradation explores the same mechanism. Therefore the ~10 cm^{-1} up-shift of Peak 1 is characteristic the oxidised state of PTB7. The PTB7:$PC_{70}BM$ blend film exhibited the same ~10 cm^{-1} up-shift after only 2 min, compared to 3.5 min for neat PTB7, confirming that blending PTB7 with $PC_{70}BM$ accelerates the polymer's

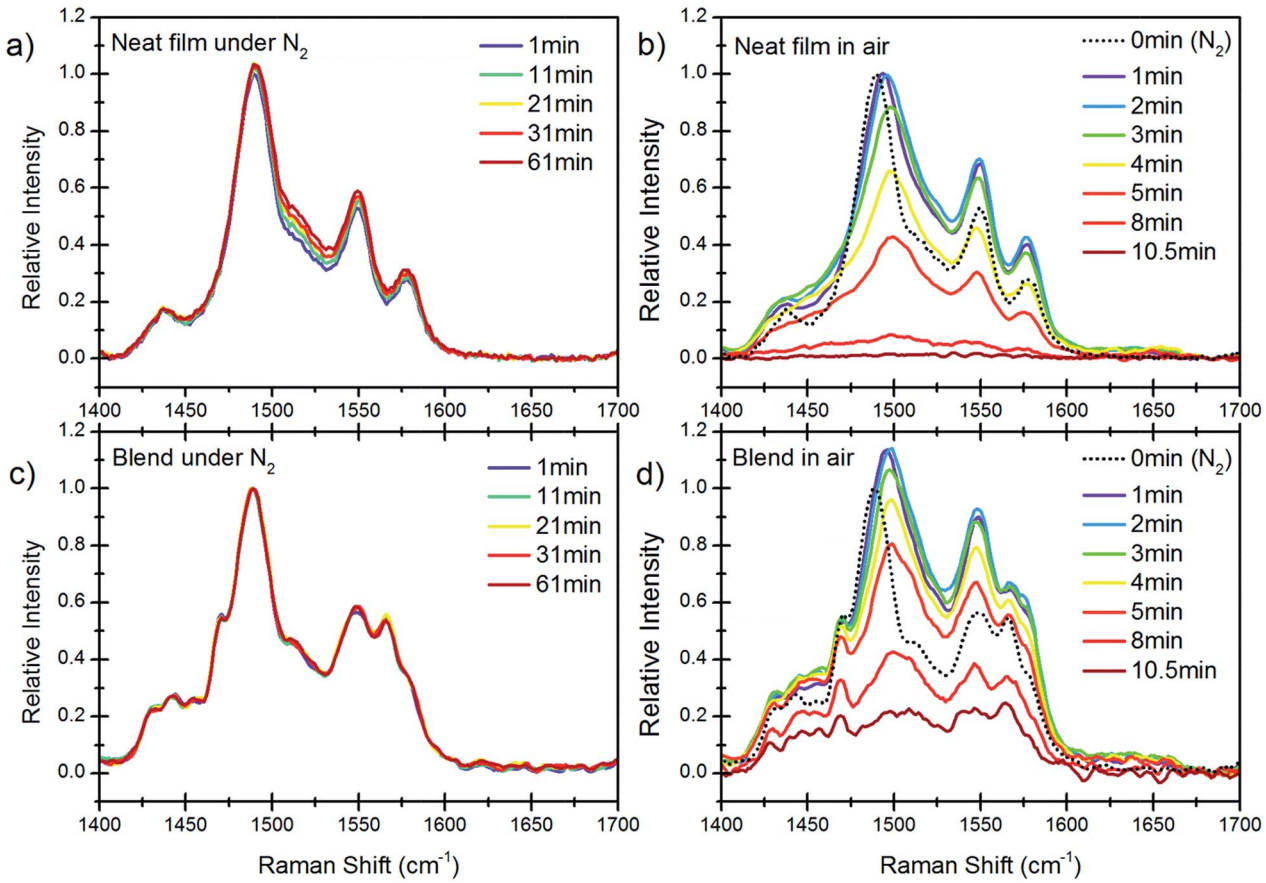


Fig. 4 Raman spectra of neat PTB7 (a and b) and blended PTB7:$PC_{70}BM$ (c and d) films during *in situ* degradation under N_2 purging (a and c) or in air (b and d), according to total *in situ* laser exposure time. Intensities are relative to the pristine value of Peak 1.

degradation. With prolonged exposure (>6 min) Peak 1 shifted to even higher wavenumbers and broadened to overlap with the high-energy shoulder, reaching a ~20 cm^{-1} up-shift (to ~1509 cm^{-1}) after 10 min. This was in agreement with the observed up-shift for the *ex situ* degraded blend, demonstrating that the star-marked peak in Fig. 3b is due to an up-shifted Peak 1. This confirms that blending PTB7 with $PC_{70}BM$ increases both the rate and the extent of photochemical degradation. The accelerated nature of *in situ* degradation, occurring in minutes compared to hours for *ex situ*, is due to the greater irradiance achieved by focusing a ~0.9 mW laser onto a μm-scale area.

We found that beyond a total exposure time of ~2 min Raman intensity across the whole spectrum began to decrease (plotted in Fig. 5 as the maximum intensity of Peak 1 relative to its original value) for both neat PTB7 and blended PTB7:PC_{70}BM films. After 10.5 min the spectrum of the neat film is almost completely lost, while the blend retains ~33% of its original peak intensity. As described earlier, a loss of PTB7 chromophores (*i.e.* loss of absorption) was observed for samples degraded for 4 hours *ex situ* and is identified qualitatively for *in situ* degradation by optical microscopy of the exposed area, which revealed a marked discolouration (see Fig. S3†). Such a process is also expected to reduce Raman scattering intensity, as any chains present that have broken conjugated systems are no longer resonant with the excitation laser and will not contribute to Raman scattering. Consequently Fig. 5 demonstrates that we can observe this more pronounced destructive stage of degradation (marked in blue), and infer from its onset at the ~2 min mark that it occurs only once sufficient amount of PTB7 has been oxidised to the initial degradation state (which is achieved after 2–4 minutes, marked in yellow in Fig. 5). This leads us to propose that PTB7 degradation is a 2-step process: the initial photo-oxidation of the polymer, which causes the observed vibrational changes but preserves conjugation; followed by a more destructive photo-oxidation process that further oxidises the molecule, breaking conjugation of the chromophore and reducing intensities of both absorption and Raman scattering.

Theoretical simulations using DFT

So far we have described the photo-oxidation of PTB7 according to changes to its measured Raman spectrum, without identifying the specific oxidised products responsible for those changes. We used density functional theory to simulate the Raman spectrum of a given molecular structure, as demonstrated in Fig. 6 for a symmetric PTB7 oligomer comprised of a donor BDT unit between two acceptor TT units (an ADA oligomer). Vibrational modes with simulated Raman shifts of 1490,

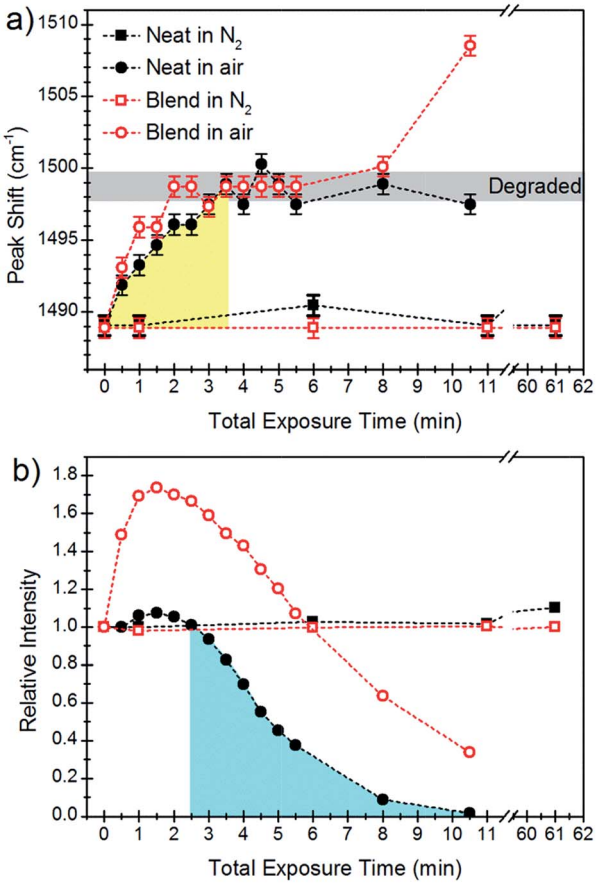


Fig. 5 Evolution of PTB7's Peak 1 Raman shift (a) and relative intensity (b) plotted against total *in situ* laser exposure time, for both neat PTB7 and blended PTB7:$PC_{70}BM$ films. 1st and 2nd degradation stages marked in yellow and blue respectively.

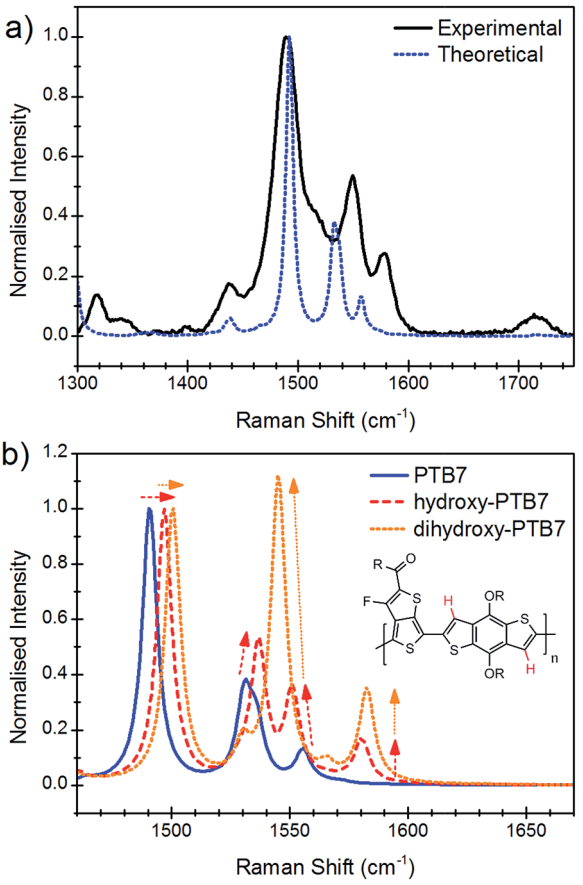


Fig. 6 (a) Theoretical Raman spectrum of an ADA oligomer of PTB7, compared to the experimental spectrum of neat PTB7. (b) Theoretical spectra for PTB7 oligomers, pristine and with oxidation of the coloured C–H bonds to C–OH groups.

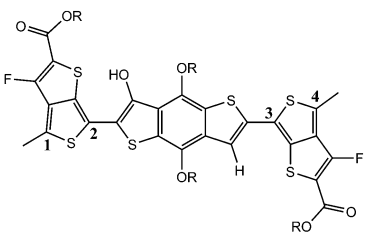
1532 and 1555 cm^{-1} are an approximate match to the three main peaks observed experimentally at 1489, 1555 and 1575 cm^{-1}, with a comparable pattern of relative intensities. We note that DFT appears to underestimate the frequency of the TT-BDT coupled vibrations (Peaks 2 and 3) but not that of the BDT-only mode (Peak 1).

In order to identify how the molecular structure of PTB7 is altered by degradation, we then simulated several possible degradation products. These were chosen based on established information that PTB7 degrades *via* a photo-oxidation mechanism that involves the conjugated system,[13] and on previously reported degradation processes for similar semiconducting polymers.[7,20] A common oxidation mechanism, abstraction of H from the α-position of a side chain, is unlikely in PTB7 as ester and ether side chains are reported to protect PTB7 from α-abstraction compared to analogue polymers with alkyl side chains.[11] Instead, we propose that oxidation of PTB7 will take place *via* electrophilic insertion of oxygen into any C–H bonds present on the sp^2-hybridised system, the only possible sites being the 3rd and 7th positions of electron-rich BDT (marked in red in the inset diagram of Fig. 6). We simulated two oligomers with either one or both C–H bonds on the BDT unit oxidised to C–OH groups (named hydroxyl-PTB7 and dihydroxy-PTB7 respectively); the resulting theoretical Raman spectra are plotted in Fig. 6. When compared to the simulated spectrum of a pristine oligomer, the spectral changes resulting from a single oxidation of the BDT unit are comparable to those observed experimentally: (1) Peak 1 is up-shifted to higher wavenumbers by ~7 cm^{-1} to 1497 cm^{-1}; (2) the intensities of Peaks 2 and 3 relative to Peak 1 are increased from 0.38 to 0.53 and 0.13 to 0.36 respectively; (3) a new higher-energy but low-intensity peak appears at ~1580 cm^{-1}, assigned to the stretching mode of the C=C bond adjacent to the OH group. There were no major structural changes along the conjugated backbone, bond lengths on the BDT unit varied by <1 pm from their original values (see Fig. S4†), confirming that this oxidised product has an otherwise intact conjugated system. Oxidation of the second C–H bond to C–OH (dihydroxy-PTB7) caused Peak 1 to up-shift by a further 3 cm^{-1} to ~1500 cm^{-1} and significantly increased the relative intensity of the modes at ~1545 and ~1580 cm^{-1}, effectively continuing the trend described for hydroxy-PTB7. This second hydroxylation may explain why the PTB7:$PC_{70}BM$ blend exhibited a second shift to higher wavenumbers beyond 5 min of *in situ* degradation, with increased production of singlet O_2 in the

blend resulting in further oxidation of hydroxy-PTB7 to dihydroxy-PTB7.

We also considered several other possible oxidation products for PTB7, including further oxidation of the C–OH groups to C=O (ketone-PTB7) or the insertion of O_2 across the benzene ring of the BDT unit to form a bridging *endo*-peroxide (peroxy-PTB7), as well as oxidation of the thiophene sulfur atom to produce sulfones and sulfoxides. These products involve significant changes to the conjugated backbone, resulting in large vibrational changes (see Fig. S5† for their spectra) that could not correspond to what was observed experimentally. Likewise, a [2 + 4] cycloaddition reaction between the thiophene ring and singlet O_2, which has been reported by Yu *et al.* based on IR measurements of PTB7 after prolonged photo-oxidation,[21] would result in breaking of conjugation and thus does not explain our experimental observations of the initial photo-oxidised species. Instead, it may represent the product of the 2nd, more destructive oxidative step that occurs once the BDT unit has been hydroxylated. To investigate this possibility, we examined the effect of hydroxylation on electron density across the TT non-fluorinated thiophene ring, particularly at the 2nd and 5th positions (see Table 1) that would react with electrophilic O_2 during a [2 + 4] cycloaddition. We find that hydroxylation of the adjacent BDT unit increases the predicted overall negative charge of the non-fluorinated thiophene closest to the hydroxyl group, making the ring more electron rich and potentially more reactive (similar to what was described by Yu *et al.* for PTB7 analogues containing fluorinated BDT). Therefore it seems likely that the initial hydroxylation we have observed using Raman spectroscopy is indirectly responsible for the loss of chromophores that occurs with prolonged degradation, as it alters the distribution of electron density across the molecule and increases its reactivity towards conjugation-breaking oxidative mechanisms.

Table 1 Calculated negative charges of the 2nd and 5th atoms of the non-fluorinated thiophene ring of each TT unit of an ADA oligomer, for both pristine PTB7 and hydroxy-PTB7



Atom	Pristine PTB7	Hydroxy-PTB7
1	−0.200	−0.214
2	−0.247	−0.245
3	−0.227	−0.228
4	−0.188	−0.187

Experimental

Film Preparation and *ex situ* degradation: PTB7 (1-Material, purified) and $PC_{70}BM$ (Solenne b.v.) were dissolved in solutions of Chlorobenzene (97% by volume) and 1,8-diiodooctane (3%) to make up solutions of neat PTB7 (~15 mg mL^{-1}) and blended PTB7:$PC_{70}BM$ (~25 mg mL^{-1}, 1 : 1.25 weight ratio). Thin films were deposited from solution by spin-coating (2000 rpm for 2 min) onto glass substrates. Samples were then degraded *ex situ* by exposure to ~1 sun of white light ($\lambda > 410$ nm) from a Luxeon Star LED for 4 hours, under an atmosphere of pure O_2.

Spectroscopy and *in situ* degradation: Raman measurements were done using a Renishaw inVia microscope with a 50× objective in a back-scattering configuration. The excitation source was a 488 nm (Ar ion) laser, spectra were obtained with a laser power of ~0.9 mW and an acquisition time of 60 s. To reduce laser induced photo-degradation of the sample, the laser-spot was defocused to ~18 μm and measurements were done in an N_2 environment. For *in situ* degradation, each sample was exposed to the ~0.9 mW laser in a series of 60 s acquisitions up to a total exposure time of 61 min under N_2 purging, or 30 s acquisitions up to a total of 10.5 min in air. UV-Vis absorption spectroscopy was done using a Shimadzu UV-2550 spectrophotometer.

DFT simulations: theoretical simulations of PTB7 oligomers and oxidised products were calculated using the Gaussian 09 software package, using a B3LYP 6-31G(d,p) basis set.[22] Molecular structures were first optimised in the gas phase, with alkyl side-chain reduced to methyl groups to aid computation time, and then theoretical Raman spectra were calculated for the optimised structures. Theoretical Raman shifts were adjusted using an empirically obtained 0.9615 scaling factor according to the chosen basis set.[23]

Conclusions

In conclusion, we have used Raman spectroscopy to probe the vibrational modes of PTB7 during photo-chemical degradation (exposure to light and O_2), identifying spectral changes indicative of conversion to an oxidised species. *In situ* degradation confirmed that blending PTB7 with $PC_{70}BM$ causes the polymer to degrade faster due to increased production of singlet O_2, achieving the oxidised state earlier, and more extensively. Loss of absorption and Raman intensity with prolonged exposure revealed further degradation that occurs after this initial oxidation, resulting in a loss of chromophores. Consequently we propose that the degradation of PTB7 is a 2-step process, starting with formation of an initial oxidised species that retains conjugation. Using DFT, we simulated the Raman spectra of several possible 1st-step products and found that formation of hydroxyl groups at the 3rd and 7th positions on the BDT unit was most representative of our experimental observations, and is predicted to alter electron density on the neighbouring TT unit that renders it more reactive to conjugation-breaking cycloaddition reactions with O_2. This knowledge can guide the synthesis of modified polymers that are more

resistant to that initial photo-oxidation step, maintaining high efficiencies over longer lifetimes.

Acknowledgements

This work was funded by the EPSRC through the Plastic Electronics Doctoral Training Centre (EP/G037515/1), the Scalable Low Cost Organic Photovoltaic Solar Cells (SCALLOPS) Project (EP/J500021/1, TP no. 100897). We thank Dr M. Heeney for valuable comments.

Notes and references

1 B. D. Wöhrle and D. Meissner, *Adv. Mater.*, 1991, 129–138.
2 H. Spanggaard and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 125–146.
3 C. Brabec, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 273–292.
4 L. M. Peter, *Philos. Trans. R. Soc., A*, 2011, **369**, 1840–1856.
5 B. Azzopardi, C. J. M. Emmott, A. Urbina, F. C. Krebs, J. Mutale and J. Nelson, *Energy Environ. Sci.*, 2011, **4**, 3741.
6 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 593–597.
7 M. Jørgensen, K. Norrman and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 686–714.
8 M. Jørgensen, K. Norrman, S. a. Gevorgyan, T. Tromholt, B. Andreasen and F. C. Krebs, *Adv. Mater.*, 2012, **24**, 580–612.
9 M. O. Reese, A. J. Morfa, M. S. White, N. Kopidakis, S. E. Shaheen, G. Rumbles and D. S. Ginley, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 746–752.
10 G. Griffini, S. Turri and M. Levi, *Polym. Bull.*, 2010, **66**, 211–222.
11 S. Alem, S. Wakim, J. Lu, G. Robertson, J. Ding and Y. Tao, *ACS Appl. Mater. Interfaces*, 2012, 2–7.
12 Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
13 Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch and J. R. Durrant, *Chem. Commun.*, 2013, **49**, 1291–1293.
14 W. C. Tsoi, D. T. James, J. S. Kim, P. G. Nicholson, C. E. Murphy, D. D. C. Bradley, J. Nelson and J.-S. Kim, *J. Am. Chem. Soc.*, 2011, **133**, 9834–9843.
15 W. C. Tsoi, D. T. James, E. B. Domingo, J. S. Kim, M. Al-Hashimi, C. E. Murphy, N. Stingelin, M. Heeney and J.-S. Kim, *ACS Nano*, 2012, **6**, 9646–9656.
16 W. C. Tsoi, W. Zhang, J. Razzell Hollis, M. Suh, M. Heeney, I. McCulloch and J.-S. Kim, *Appl. Phys. Lett.*, 2013, **102**, 173302.
17 J. Razzell-Hollis, W. C. Tsoi and J.-S. Kim, *J. Mater. Chem. C*, 2013, **1**, 6235–6243.
18 S. Wood, J. S. Kim, D. T. James, W. C. Tsoi, C. E. Murphy and J.-S. Kim, *J. Chem. Phys.*, 2013, **139**, 064901.
19 S. Wood, J. B. Franklin, P. N. Stavrinou, M. A. McLachlan and J.-S. Kim, *Appl. Phys. Lett.*, 2013, **103**, 153304.
20 Y. Aoyama, T. Yamanari, N. Koumura, H. Tachikawa, M. Nagai and Y. Yoshida, *Polym. Degrad. Stab.*, 2013, **98**, 899–903.
21 H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li and L. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 1885–1894.
22 M. J. Frisch, *et al.*, *Gaussian 09, rev. A.02*, Gaussian Inc., Wallingford CT, 2009.
23 J. P. Merrick, D. Moran and L. Radom, *J. Phys. Chem. A*, 2007, **111**, 11683–11700.