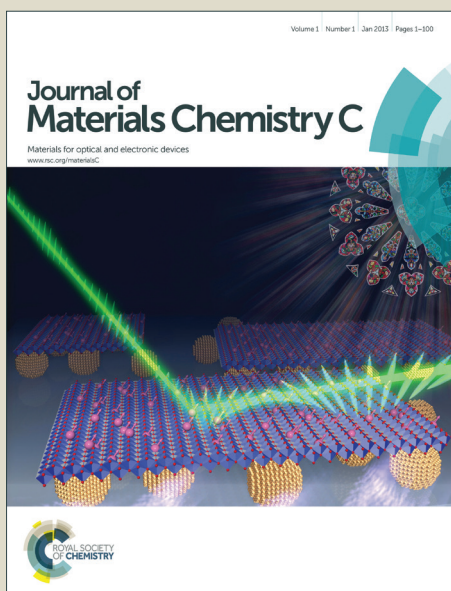


Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Oxygen diffusion dynamics in organic semiconductor films

Safa Shoaee,^{†} and James R. Durrant^{*}*

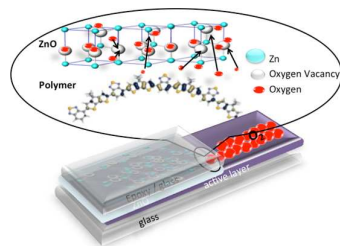
Dr Safa Shoaee, Prof. James R. Durrant Centre for Plastic Electronics, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom
s.shoaee06@imperial.ac.uk and j.durrant@imperial.ac.uk

Present Addresses

[†]Centre for Organic Photonics & Electronics, The University of Queensland, Brisbane, Queensland 4072, Australia

Abstract

Transient absorption spectroscopy is commonly used to probe the yield and kinetics of excited states of materials. We present a transient absorption spectroscopic assay of oxygen diffusion in a series of solution-processed polymer films. The films were partially encapsulated with an epoxy/glass top barrier as a simple model system for organic photovoltaic and light emitting devices with metal top contacts. The results presented herein show that this spectroscopic approach can be a versatile and quantitative in situ assay of local oxygen concentrations in such organic semiconductor films. With our current apparatus, the approach has a time resolution of 5 seconds, thereby enabling direct measurement of oxygen diffusion kinetics into a semiconductor film. The versatility of this approach suggests it could be widely applicable to measurement of oxygen diffusion into organic optoelectronic devices, including for example oxygen diffusion through encapsulation and barrier layers. Employing this approach, we demonstrate significant differences in oxygen diffusion kinetics between different semiconducting polymers. We furthermore demonstrate the impact of an additional getter (ZnO) and light exposure upon the local oxygen concentration, providing new insights into role of oxygen diffusion kinetics in determining the environmental stability of organic semiconductors.

TOC

Organic electronic devices, including light emitting diodes, transistors and photovoltaic cells, are receiving extensive academic and commercial interest. With advances in device performance, and

expansion of the organic electronics market, strategies to enhance and measure the stability of the organic semiconductors employed in such devices are receiving increasing attention. Most organic semiconductors exhibit only limited ambient stability, particularly in the presence of light, due to the tendency of organic materials to undergo (photo)induced reactions with the ambient oxygen and moisture.¹⁻³ As such, devices based upon organic semiconductors typically require careful encapsulation against oxygen and water ingress, as well as often the inclusion of getters to absorb infiltrated water or oxygen, adding significantly to device costs. In this regard, the measurement of the local oxygen and water content within organic semiconductor film is key assay of the effectiveness of any encapsulation or getters employed. In addition, most organic semiconductors are employed in devices as thin films sandwiched between flat barrier layers; as such the lateral diffusion kinetics of oxygen or water within the organic layer from the device edges or point of barrier failure is also an important consideration for technological application.

Our study herein reports a simple, in situ approach to measure the local oxygen content, and the lateral oxygen diffusion kinetics, within a series of organic semiconductor thin films sandwiched between glass barrier layers. The approach is based upon the use of transient absorption spectroscopy to measure the kinetics of oxygen quenching of triplet states photogenerated in these semiconductor films. Measurements of oxygen concentration and diffusion in polymer films have typically employed phosphorimetry – monitoring the phosphorescence quenching of added molecular phosphors.^{4,5} This approach is however difficult to employ with semiconducting polymers due to potential electronic interactions between the phosphor and the semiconductor polymer. Studies of oxygen diffusion in semiconductor polymers have primarily employed fluorescence quenching studies at elevated pressures.^{6,7} Comparative studies of oxygen diffusion kinetics between organic semiconductor thin films have been very limited to date, with studies primarily focused on P3HT. The approach we employ herein exploits the previously reported sensitivity of the triplet exciton states of many organic semiconductors to quenching by molecular oxygen. Oxygen induced quenching of molecular triplet states has previously been used to assay oxygen concentrations in solution,⁸ but has not, to the best of our knowledge, been applied as an in-situ assay of oxygen diffusion in organic films.

Transient absorption studies of the decay dynamics of triplet excitons in organic semiconductor thin films, and the acceleration of these decay dynamics in presence of oxygen has been widely reported.⁹⁻¹² We have recently correlated such oxygen quenching with measurements of singlet oxygen generation and the kinetics of film photobleaching.¹⁰ In the study reported herein, we demonstrate that this experimental approach can also be used as an in-situ assay of the local oxygen concentration in the film as a function of time after oxygen exposure. This approach thus allows us to measure directly the oxygen diffusion constant for different organic semiconductor films, as well to assay the effect of an incorporated getter layer and light exposure in reducing the local oxygen concentration. Our study is focused upon a series of polymer semiconductors of interest for organic photovoltaic (OPV) applications, however the approach should be generally applicable to any organic semiconductor exhibiting long-lived triplet excitons upon photoexcitation.

It has been widely reported that most unencapsulated organic semiconductor thin films exhibit rapid photobleaching, typically on timescales of minutes to a few hours, when exposed to the combination of light and oxygen. This photodegradation has been attributed to the generation of either singlet oxygen or superoxide radical anions.^{2,10,13} Our study reported herein was particularly motivated by

the observation that, following the deposition of a metal top contact (as present in organic photovoltaic or light emitting devices), such organic semiconductor film can become much more stable with respect to photodegradation by light and oxygen,^{10,14,13,15,16} Figure 1 shows typical data in this regard of direct relevance to organic photovoltaic devices, comparing the rapid photobleaching of a representative donor polymer: fullerene blend film with the strikingly more stable photovoltaic performance of an unencapsulated solar cell fabricated with the same blend film composition by deposition of a metal top electrode. This difference in stability is most obviously due to the metal top electrode functioning as a barrier layer to oxygen diffusion into the film top surface. In such partially encapsulated structures, lateral oxygen diffusion from the device edges into semiconductor layer (or indeed from pinholes in the metal electrode) is likely to be a key consideration for device stability. It is this lateral oxygen diffusion, and the impact of polymer molecular structure, gettering and light exposure on the resultant local oxygen concentration, which is the subject of this study.

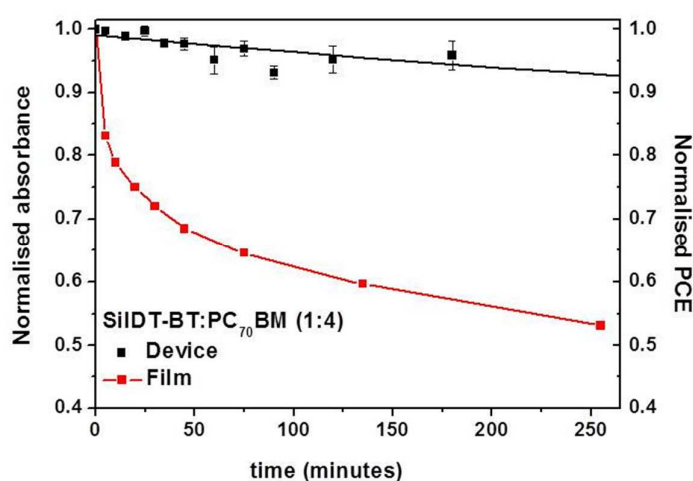
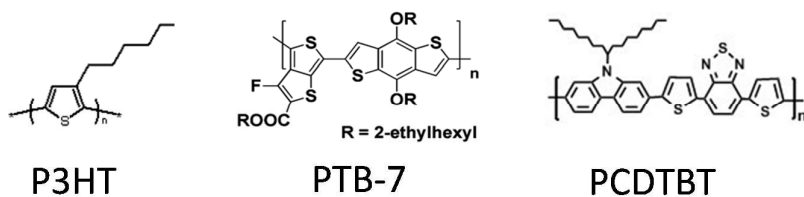


Figure 1 Photodegradation of a polymer:fullerene blend film under light and oxygen exposure compared to the performance of an unencapsulated organic photovoltaic device with analogous photoactive layer. Samples were kept under oxygen atmosphere and white light irradiation ($\lambda > 410$ nm, 80 mWcm^{-2}) over the same timescale. Data is adapted from Ref¹⁷, and employs the donor polymer SiIDT-BT in a 1:4 blend with PC₇₀BM. Film and device fabrication as reported previously, employing a silver metal electrode.

In the study reported herein, we address the oxygen diffusion kinetics for thin films of three semiconducting polymers - regiorandom P3HT (RRa-P3HT), PCDTBT and PTB-7 (see Scheme 1 for polymer molecular structures). These donor polymers were selected as they exhibit long lived triplet excitons which are quenched by molecular oxygen,¹⁸ and are polymers widely used in OPV studies. We also include analysis of the gettering effect of incorporating an additional ZnO thin film into the structure. Samples were studied as a function of time after oxygen (1 atmosphere) and / or light exposure. Experiments employed partially encapsulated 1 cm^2 thin films - sandwiched between glass slides but exposed around their edges to ambient oxygen (with an epoxy glue ensuring adhesion of the top glass – see SI for details). Control experiments employed un-encapsulated thin films on glass substrates without any top cover. Transient absorption measurements interrogated the central 0.25 cm^2 of the sample, such that in these partially encapsulated films, oxygen had to diffuse $\sim 0.5 \text{ cm}$ through the semiconductor film to reach the measured sample area.



Scheme 1 presents the chemical structures of the semiconducting polymers employed in this study.

Transient absorption spectroscopy on the microsecond timescale was employed to assay triplet exciton lifetime at room temperature. These studies employed low excitation densities so as to avoid bimolecular triplet quenching processes^{19,20} (as confirmed by our observation of exponential, intensity independent decay profiles). Data were collected at the $T_1 \rightarrow T_n$ absorption maxima in the near infrared, determined previously to be ~ 980 nm for RRa-P3HT and PCDTBT and 1100 nm for PTB-7.^{10,18} Each decay kinetic required ~ 5 seconds of signal averaging (at an excitation repetition rate of 20 Hz); our assay of local oxygen concentration therefore is limited to this 5 s time resolution.

Figure 2a illustrates typical transient absorption decays for an un-encapsulated RRa-P3HT film, under nitrogen and oxygen atmospheres. It is clear that whilst the decay lifetime of the film is immediately quenched (i.e.: within 5 s) following exposure to an O_2 atmosphere, the decay dynamics recover back to the original signal once the film is purged with N_2 (even after long periods of O_2 exposure), consistent with low light exposures employed in our studies causing negligible photodegradation.

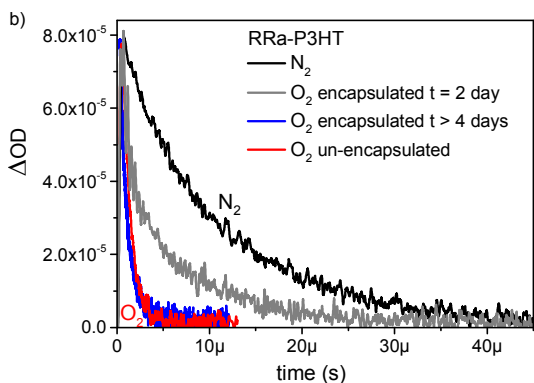
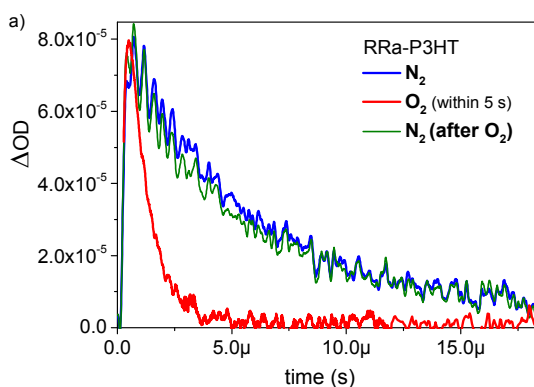


Figure 2 a) Transient absorption decay dynamics of a RRa-P3HT film under N₂ and O₂ atmospheres. b) Transient absorption decay dynamics of a partially encapsulated RRa-P3HT film under O₂ atmosphere as a function of time, until fully saturated. Films were excited at 460 nm at a laser intensity of 4 μJ cm⁻², and probed at 980 nm.

Figure 2b contrasts data obtained for an un-encapsulated RRa-P3HT film (red trace, under O₂ for 5 s) with those obtained for a partially encapsulated film, where oxygen can only diffuse into the film laterally from the film edges (a distance of ~ 0.5 cm, see SI for details). The transient decay dynamics of this partially encapsulated film were studied as a function of time after exposure to an O₂ atmosphere in the dark (Figure 2b). It is apparent that even after 2 days oxygen exposure, the triplet decay dynamics are significantly slower than those observed for the un-encapsulated film after 5 s of oxygen exposure. The partially encapsulated film required over 4 days of oxygen exposure to achieve similar decay dynamics to the un-encapsulated film. This clearly indicates that the partially encapsulated film takes several days for the local oxygen concentration to reach equilibrium with the ambient oxygen environment, indicative of strikingly slow oxygen diffusion kinetics on the days timescale.

The triplet decay dynamics such as those plotted in Figure 2b were measured as a function of time (t) after exposure to oxygen. From these data, the time dependence of the local oxygen concentration, [O₂](t) was determined:

$$\frac{[O_2](t)}{[O_2]_{eqm}} = \frac{\frac{1}{\tau(t)} - \frac{1}{\tau_0}}{\frac{1}{\tau_{eqm}} - \frac{1}{\tau_0}} \quad (1)$$

where $\frac{[O_2](t)}{[O_2]_{eqm}}$ is the ratio of concentration of oxygen at time t to the concentration of

oxygen at equilibrium (measured for an oxygen saturated film), $\tau(t)$ is the lifetime of triplets under oxygen as a function of time, τ_0 is the lifetime of the triplet excitons under nitrogen environment and τ_{eqm} is triplet lifetime at equilibrium (see Supporting information of derivation of this equation). Using equation 1, the relative local oxygen concentration was determined as a function of oxygen exposure time for a partially encapsulated RRa-P3HT, as plotted in Figure 3 (black squares). It is apparent that the oxygen saturation half-time (the time taken for the local O₂ in the centre of the film to reach 50% of dark equilibrium) for RRa-P3HT is ~ 10 hours.

Analogous experiments were carried out for two further polymer films; namely, PTB-7 and PCDTBT, as well as for a RRa-P3HT film in a bilayer structure with a ZnO thin film. In all cases, qualitatively the same behaviour was observed, with the triplet decay dynamics of partially encapsulated devices slowly accelerating with time, reaching the same kinetics as un-encapsulated films after several days of dark oxygen exposure (see SI). Following equation 1 above, these data were employed to determine the local oxygen concentration as a function oxygen exposure time, as also plotted in Figure 3. It is apparent the oxygen diffusion kinetics varied significantly between the samples studied, being the fastest for PTB-7 ($t_{1/2} \sim 4.5$ hours) and slowest for RRa P3HT / ZnO ($t_{1/2} \sim 17$ hours). The faster half-time for PTB-7 is indicative of faster oxygen diffusion kinetics, whilst the slower half-time observed with ZnO is attributed to the oxygen getter properties of ZnO, as we discuss further below.

Mathematically, the diffusion of molecular oxygen through the organic film can be characterized by the diffusion equation:

$$\frac{\partial C(\vec{r}, t)}{\partial t} = \nabla^2(DC(\vec{r}, t)) - G \quad (2)$$

where C is the concentration of the diffusing oxygen, D is the diffusion coefficient and G is absorption of the oxygen by the getter (if present). This can be simplified for one-dimensional diffusion from the film edge, neglecting gettering to:

$$C(t) = C_0 \left(1 - \frac{x}{2\sqrt{Dt}} \right) \quad (3)$$

where x is the distance from the film edge. The smooth lines in figure 3 correspond to fits of the experimental data to equation 3. In all cases, reasonable fits were obtained, supporting the validity of this simple physical model. Values of oxygen diffusion constants obtained from these analyses for the three polymers studied are detailed in Table 1, with PTB-7 showing the largest diffusion constant, and RRa-P3HT the smallest. These values are of similar order of magnitude to those reported previously for organic polymers,^{21,22} with for example previous studies reporting an oxygen diffusion constant for regioregular P3HT of $3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.^{6,7} The values of the estimated diffusion coefficients of oxygen in the three polymers studied increase in the polymer order PTB7 < PCDTBT < RRa-P3HT. We note the polymers have different polarity which may influence the diffusion of oxygen, although a detailed analysis of origin of these differences between polymers is beyond the scope of this study. However we do note this trend shows a weak correlation with the polymer crystallinity (with PCDTBT being the most crystalline and RRa-P3HT the least)¹⁸ and with polymer density: 1.12 g cm^{-3} ,²³ 1.13 g cm^{-3} ²⁴ and 1.15 g cm^{-3} .²⁵ The longest saturation time is observed for the ZnO/RRa-P3HT sample, which we attribute to the ZnO acting as a temporary oxygen getter, absorbing some of the oxygen as it diffuses into the sample. This is consistent with previous literature indicating ZnO can function as an oxygen getter.²⁶

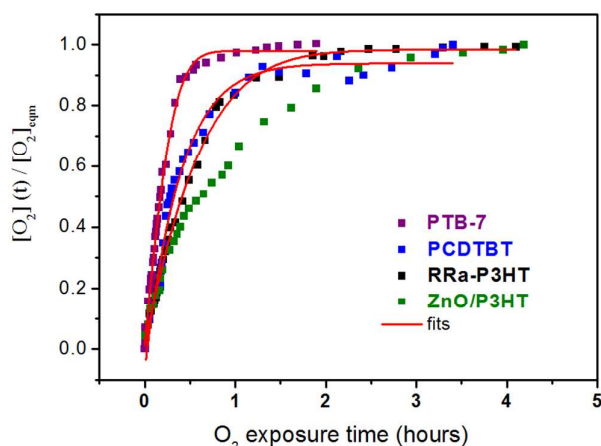


Figure 3 Local oxygen concentration of partially encapsulated polymer films as a function of time, as measured by transient absorption. The partially encapsulated films were kept in dark and exposed to oxygen atmosphere until saturated. Red lines shows fits to equation 3.

Table1 Oxygen diffusion half-times ($t_{1/2}$) and diffusion coefficients (D) determined from the data in Figure 3, using equations 1 and 3, for the four samples studied herein.

Material system	$t_{1/2}$ (hours)	$D / \text{cm}^2\text{s}^{-1}$
PTB7	4.52	1.2×10^{-8}
PCDTBT	7.60	7.3×10^{-9}
RRa-P3HT	10.01	5.5×10^{-9}
RRa- P3HT/ZnO	16.96	-

The data reported above indicate that for partially encapsulated films, analogous in geometry to unencapsulated OPV devices with a metal top contact, the oxygen concentration in the polymer layer reaches the saturated equilibrium value in the dark after a few days. Whilst this observation clearly demonstrates that lateral oxygen diffusion into the active layer is relatively slow, this observation alone does not explain how some OPV devices without further encapsulation can be relatively stable in air for periods of weeks or months.^{27,28} In order to address this issue, we now turn to the impact of irradiation upon the local oxygen concentration of the partially encapsulated films employed in this study. A partially encapsulated RRa-P3HT was exposed to an oxygen atmosphere in the dark for several days, such that the local oxygen concentration reached saturation. The film was then exposed to white light irradiation ($\sim 70 \text{ mWcm}^{-2}$), still in an oxygen atmosphere, and the triplet decay dynamics were measured as a function of light exposure time to determine the impact of light exposure upon the local oxygen concentration. Typical data are plotted in Figure 4, with the transient absorption kinetics shown in insert. It is apparent that even a few minutes of light exposure results in a significant reduction of local oxygen concentration, with a half-time for oxygen depletion under these irradiation conditions of ~ 2 minutes. It can be concluded that light exposure results in a rapid consumption of molecular oxygen in the film, resulting in a reduction in the local oxygen concentration. Indeed after prolonged light exposure, the triplet decay dynamics actually became slightly longer than those observed for a nitrogen control, indicative of this light activated oxygen consumption being particularly efficient in consuming even residual oxygen remaining in the film.

The light activated oxygen consumption demonstrated in figure 4 can be most simply assigned to the photoactivated oxidation of the polymer by singlet oxygen, with this singlet oxygen deriving from oxygen quenching of the polymer triplet state.¹⁰ It is striking however that this light exposure of the partially encapsulated, oxygen-saturated film did not cause measurable photodegradation of the film, with the film optical absorption spectrum being almost unchanged by 30 minutes light exposure. This contrasts to the impact of analogous oxygen / light exposure of unencapsulated RRa-P3HT films, where 30 minutes of light exposure resulted in a $\sim 20\%$ bleaching of film optical absorption. This difference in stability can be understood as resulting from the relatively small amount of oxygen present in an oxygen-saturated film, and, for the partially encapsulated film, the slow diffusion kinetics of oxygen into the film to replenish the oxygen consumed by light exposure. Literature estimates of oxygen solubility in PVOH films, which has a density similar to that of our conjugated polymers, give an oxygen solubility of $\sim 10^{-4}$ per polymer unit cell²⁷, consistent with the steady state amount of oxygen present in such polymer films being insufficient to cause substantial photobleaching. As such, light exposure initially results in a rapid, but marginal, photodegradation.

This light exposure also results in a rapid reduction in the local oxygen concentration, greatly reducing the rate of further photoinduced degradation. As such, further degradation requires oxygen diffusion into the organic film, which due to the very slow lateral oxygen diffusion kinetics, can result in a greatly extended film lifetime. It follows that the stability of partial encapsulated organic films, such as OPV devices with metal top contact without further encapsulation, is likely to be strongly dependent upon the kinetics of lateral oxygen diffusion within the organic photoactive layer of the device.

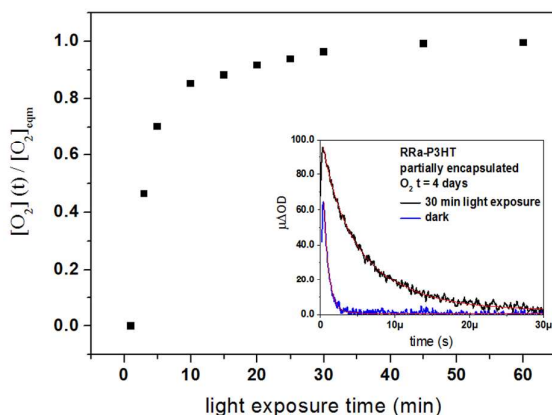


Figure 4 Plot of the relative local oxygen concentration of partially encapsulated polymer films as a function of light exposure time, as measured by transient absorption. The partially encapsulated films were initially equilibrated in an oxygen atmosphere for 4 days. They were subsequently exposed to light (70 mW cm^{-2} white light) for up to 60 minutes in this atmosphere. Inset: transient absorption decay kinetic of partially encapsulated RRa-P3HT film, fully saturated in oxygen in dark and after exposure to light for 30 minutes.

In conclusion, we have presented a transient absorption spectroscopic assay of oxygen diffusion in a series of solution-processed polymer films. The films were partially encapsulated with an epoxy/glass top barrier as a simple model system for organic photovoltaic and light emitting devices with metal top contacts. The results presented herein show that this spectroscopic approach can be a versatile and quantitative in situ assay of local oxygen concentrations in such organic semiconductor films. With our current apparatus, the approach has a time resolution of 5 seconds, thereby enabling direct measurement of oxygen diffusion kinetics into a semiconductor film. The versatility of this approach suggests it could be widely applicable to measurement of oxygen diffusion into organic optoelectronic devices, including for example oxygen diffusion through encapsulation and barrier layers.^{31,32} Employing this approach, we demonstrate significant differences in oxygen diffusion kinetics between different semiconducting polymers. We furthermore demonstrate the impact of an additional getter (ZnO) and light exposure upon the local oxygen concentration, providing new insights into role of oxygen diffusion kinetics in determining the environmental stability of organic semiconductors.

Experimental Section

Materials and Methods:

P3HT and PCDTBT were purchased from Merck whilst PTB-7 was purchased from Solamer. All polymers were used as purchased.

Solutions were prepared from chlorobenzene at a concentration of 15mg/ml, by dissolving the solute at room temperature and left to stir in glovebox.

Glass substrates were washed sequentially in: deionised water (with 0.1 % detergent); acetone and iso-propanol for 15 mins each with ultrasonication, followed by blow-drying with nitrogen.

Neat films were fabricated by spin coating the polymer solution onto glass substrate at 1100 rpm for 45 seconds.

Bilayer films: ZnO was first spun onto the clean glass substrate, which was then annealed at 150 °C (for 1h in N₂). The polymer solution was subsequently spin coated on top of the pre-coated annealed substrates.

Partial glass encapsulation: a glass substrate with 2/3rd of length dimensions as the sample substrate was cleaned as described above. Using epoxy glue, the desired area of the sample was glued for encapsulation. The glass substrate was placed on top and the entire sample was then placed under UV light for 20 minutes, to ensure complete adhesion.



Transient absorption: decays were measured under nitrogen and oxygen atmosphere, by exciting the sample film pumped with a Nd:YAG laser (Lambda Photometrics). The excitation wavelengths used were: 460 nm (RRa-P3HT), 560 nm (PCDTBT) and 630 nm (PTB-7) with a pump intensity of 4 μJcm^{-2} and a repetition frequency of 20 Hz. A 100 W quartz halogen lamp (Bentham, IL 1) with a stabilised power supply (Bentham, 605) was used as the probe light source at 980nm (RRa-P3HT and PCDTBT) and 1100 nm (PTB-7). The probe light passing through the sample film was detected with a silicon photodiode (Hamamatsu Photonics, S1722-01). The signal from the photodiode was pre-amplified and sent to the main amplification system with an electronic band-pass filter (Costronics Electronics). The amplified signal was collected with a digital oscilloscope (Tektronics, TDS220), which was synchronised with a trigger signal of the pump laser pulse from a photodiode (Thorlabs Inc., DET210). To reduce stray light, scattered light and sample emission, monochromator and appropriate optical cut-off filters were placed before and after the sample.

From the measured transient absorption signal, each decay was fitted to a mono-exponential kinetic, from which the lifetime of the triplets was extracted. These lifetimes were plotted as a function of time.

Derivation of local oxygen concentration

$$1/\tau(t) = \frac{1}{\tau_0} + K_{O_2} [O_2]$$

at equilibrium

$$K_{O_2} [O_2] = \frac{1}{\tau(t)} - \frac{1}{\tau_0}$$

$$K_{O_2} [O_2] = \frac{1}{\tau(t)_{eqm}} - \frac{1}{\tau_0}$$

$$[O_2](t) / [O_2]_{eqm} = \frac{\frac{1}{\tau(t)} - \frac{1}{\tau_0}}{\frac{1}{\tau_{eqm}} - \frac{1}{\tau_0}}$$

Acknowledgements

We thank Solvay SA and the EPSRC (project EP/101927/8) for financial support.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- (1) Jorgensen, M.; Norrman, K.; Gevorgyan, S. A.; Tromholt, T.; Andreasen, B.; Krebs, F. C. *Advanced Materials* **2012**, *24*, 580.
- (2) Jorgensen, M.; Norrman, K.; Krebs, F. C. *Solar Energy Materials and Solar Cells* **2008**, *92*, 686.
- (3) Krebs, F. C.; Carle, J. E.; Cruys-Bagger, N.; Andersen, M.; Lilliedal, M. R.; Hammond, M. A.; Hvidt, S. *Solar Energy Materials and Solar Cells* **2005**, *86*, 499.
- (4) Klumbies, H.; Karl, M.; Hermenau, M.; Roesch, R.; Seeland, M.; Hoppe, H.; Mueller-Meskamp, L.; Leo, K. *Solar Energy Materials and Solar Cells* **2014**, *120*, 685.
- (5) Unterleitner, F. C.; Hormats, E. I. *The Journal of Physical Chemistry* **1964**, *69*, 2516.
- (6) Abdou, M. S. A.; Orfino, F. P.; Son, Y.; Holdcroft, S. *Journal of the American Chemical Society* **1997**, *119*, 4518.
- (7) Hintz, H.; Egelhaaf, H. J.; Luer, L.; Hauch, J.; Peisert, H.; Chasse, T. *Chemistry of Materials* **2011**, *23*, 145.
- (8) Grewer, C.; Brauer, H.-D. *Journal of Physical Chemistry* **1994**, *98*, 4230.

- (9) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Heeney, M.; Tierney, S.; McCulloch, I.; Bradley, D. D. C.; Durrant, J. R. *Chemical Communications* **2006**, 3939.
- (10) Soon, Y. W.; Cho, H.; Low, J.; Bronstein, H.; McCulloch, I.; Durrant, J. R. *Chemical Communications* **2013**, 49, 1291.
- (11) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1973**, 69, 708.
- (12) Arbogast, J. A.; Darmany, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *Journal of Physical Chemistry* **1991**, 95, 11.
- (13) Hoke, E. T.; Sachs-Quintana, I. T.; Lloyd, M. T.; Kauvar, I.; Mateker, W. R.; Nardes, A. M.; Peters, C. H.; Kopidakis, N.; McGehee, M. D. *Advanced Energy Materials* **2012**, 2, 1351.
- (14) Reese, M. O.; Nardes, A. M.; Rupert, B. L.; Larsen, R. E.; Olson, D. C.; Lloyd, M. T.; Shaheen, S. E.; Ginley, D. S.; Rumbles, G.; Kopidakis, N. *Advanced Functional Materials* **2010**, 20, 3476.
- (15) Kawano, K.; Pacios, R.; Poplavskyy, D.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Solar Energy Materials and Solar Cells* **2006**, 90, 3520.
- (16) Peters, C. H.; Sachs-Quintana, I. T.; Mateker, W. R.; Heumueller, T.; Rivnay, J.; Noriega, R.; Bailey, Z. M.; Hoke, E. T.; Salleo, A.; McGehee, M. D. *Advanced Materials* **2012**, 24, 663.
- (17) Soon, Y. W. **2013**, *Doctrate of Philiosophy Thesis*, p.108.
- (18) Soon, Y. W.; Shoaee, S.; Ashraf, R. S.; Bronstein, H.; Schroeder, B. C.; Zhang, W.; Fei, Z.; Heeney, M.; McCulloch, I.; Durrant, J. R. *Advanced Functional Materials* **2014**, 24, 1474.
- (19) Koehler, A.; Baessler, H. *Materials Science & Engineering R-Reports* **2009**, 66, 71.
- (20) Kelper, R. G.; Avakian, P.; Caris, J. C.; Abramson, E. *Physical Review Letters* **1963**, 10, 400.
- (21) Kaptan, Y.; Pekcan, O.; Guven, O. *Journal of Applied Polymer Science* **1992**, 44, 1595.
- (22) Hormats, E. I.; Unterleitner, F. C. *Journal of Physical Chemistry* **1965**, 69, 3677.
- (23) Collins, B. A.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. *Advanced Energy Materials* **2013**, 3, 65.
- (24) Clulow, A. J.; Armin, A.; Lee, K. H.; Pandey, A. K.; Tao, C.; Velusamy, M.; James, M.; Nelson, A.; Burn, P. L.; Gentle, I. R.; Paul, M. *Langmuir* **2014**, 30, 1410.
- (25) Kiel, J. W.; Kirby, B. J.; Majkrzak, C. F.; Maranville, B. B.; Mackay, M. E. *Soft Matter* **2010**, 6, 641.
- (26) Gossman, R. D.; Feldman-Peabody, S. D.; Knapp, J. T. *Patentdocs* **2013**, *Primestar Solar, INC* 20130019934.
- (27) Krebs, F. C. *Solar Energy Materials and Solar Cells* **2008**, 92, 715.
- (28) Chu, T.-Y.; Tsang, S.-W.; Zhou, J.; Verly, P. G.; Lu, J.; Beaupre, S.; Leclerc, M.; Tao, Y. *Solar Energy Materials and Solar Cells* **2012**, 96, 155.