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ARTICLE TYPE

Polaron stability in semiconducting polymer neat films

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We describe a spectroelectrochemical approach
 10 to accelerated electrochemical stability studies of conjugated
 polymers under oxidative stress. The polaron stabilities of
 alternating copolymers based on (i) thiophene and thiazole,
 namely PTTz, and (ii) bithiophene and thiazole are compared
 in neat films with that of P3HT. P3HT is found to be the most
 15 stable whilst PTTz is found to be the least stable.

Although there are several successful examples of
 commercialised organic electronic applications, particularly in
 the organic light emitting diode (OLED) area, the durability of
 organic electronic devices remains for many applications a
 20 significant concern. Several approaches to increasing device
 lifetime have been adopted including optimisation of electrode
 materials, encapsulation techniques and device architecture.[1]
 However, elucidating the intrinsic stability limitations of the
 organic materials used in the active layer remains a significant
 25 challenge. Such active layer materials are susceptible to a range
 of degradation pathways, including photochemical [2],

	$E_{\text{HOMO}}^a/\text{eV}$	$E_{\text{HOMO}}^b/\text{eV}$	$E_{\text{onset}}^c/\text{V}$	$E_{\text{probe}}^d/\text{V}$
P3HT	-4.8	-4.7	-4.8	-5.01
PTTTz	-5.1	-5.0	-4.9	-5.16
PTTz	-5.2	-5.2	-5.1	-5.41

Table 1 ^a HOMO energy level as determined by CV; $E_{\text{HOMO}} = -(E^{1/2}_{\text{ox vs Fc}} + 4.8)$. ^b HOMO energy level as determined by PESA. ^c HOMO energy level calculated from onset of spectroelectrochemical response. ^d Energy level equivalent of probing potential.

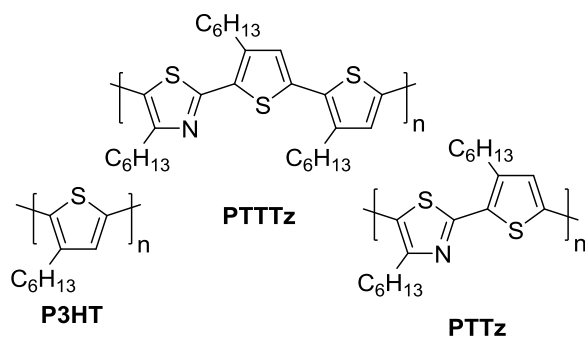


Fig. 1 Chemical structures of the three studied polymers.

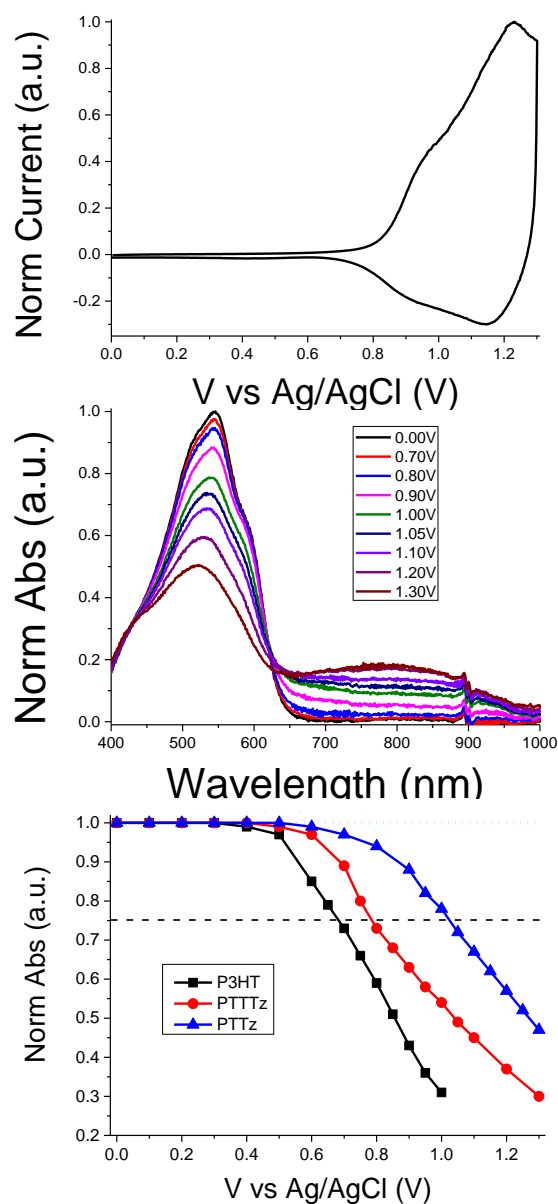


Fig. 2 (A) Cyclic voltammogram of a neat film of PTTz spun on FTO glass. (B) Spectroelectrochemistry of a neat film of PTTz spun on FTO glass. Absorption spectra were measured in-situ as a function of working electrode potential; background of FTO glass submerged in 0.1 M TBAPF₆/CH₃CN electrolyte solution was subtracted from spectra. (C) Comparison of change in normalised maximum absorption for films of P3HT, PTTTz and PTTz, as a function of working electrode potential. Horizontal dashed line shows the potential leading to a 25% reduction in absorption. All potentials are quoted with respect to Ag/AgCl reference electrode. Data taken from spectroelectrochemical data in Fig. W (ESI).

morphological [3] and electrochemical [4]. Understanding the relationship between materials design and active layer stability is therefore essential for technological application.

A thermodynamic evaluation by de Leeuw [5] considered the susceptibility of organic semiconductors to electrochemical reactions in the presence of oxygen and water as a function of their ionisation potential. This study predicted that a low energy HOMO (below -4.9 eV) is necessary for a neutral p-type material such that electrochemical oxidative reactions involving oxygen and saturated water are thermodynamically unfavourable. However this study only considered the stability of the initially neutral polymer, and thus was relevant for understanding shelf-life stability. The impact of a steady state concentration of hole polarons upon the operational stabilities of such organic electronic devices was not considered and is addressed herein. One approach addressing this issue in organic field effect transistors (OFETs) focusses on the reliability of device parameters such as threshold voltage when subjected to a gate bias stress.[6] Siringhaus et al. has developed a new optical spectroscopy approach to investigating this degradation in OFETs, referred to as charge accumulation spectroscopy, which monitors polaron-induced absorptions as a function of time.[7]

For the majority of organic electronic devices, the conjugated polymers are partially oxidised under operation, with bulk hole polaron densities ranging from $10^{15-17} \text{ cm}^{-3}$ for organic solar cells and OLEDs to $>10^{18} \text{ cm}^{-3}$ for OFETs (in the surface accumulation layer). We are interested in evaluating the relative stabilities of different semiconducting polymers under bulk oxidative stress conditions particularly relevant for OLED and organic solar cells, and specifically the relationship between polaron stability and polymer ionisation potential.

In this communication, we describe a novel methodology for the investigation of polaron stability in conjugated polymer films and present a comparison of three conjugated polymers; the well-studied P3HT and two analogous polymers with similar structures but lower HOMO energy levels, PTTTz and PTTz – see structures in Fig. 1.[8] Before we can discuss the relative polaron stabilities of these conjugated polymers, it is essential to understand their oxidative properties. HOMO energy levels of polymers in thin films have been estimated here by cyclic voltammetry (CV) and photoemission spectroscopy in air (PESA) measurements (see Table 1). The cyclic voltammogram in Fig. 2A shows an onset current at a potential of *ca.* +0.70 V, which represents the onset of oxidation of the polymer film and is used to estimate the HOMO energy level of PTTz. Spectroelectrochemical measurements represent an alternative way of viewing the oxidation wave of a conjugated polymer in a similar experimental set-up to that used in cyclic voltammetry. Chronoamperometry is used to control the degree to which a film is oxidised, i.e. to control how much positive charge is injected into a polymer film. The film is held in a controlled oxidised state while absorption spectra are recorded to produce spectroelectrochemistry data like that in Fig. 2B. In the case of PTTz, an absorption peak is observed at 540 nm in its neutral state. When a sufficiently oxidising ($V > +0.70 \text{ V}$) potential is applied to PTTz, two observations are made; (i) a reduction in absorption intensity at 540 nm, and (ii) the appearance of a broad absorption around 800 nm. These observations are attributed to

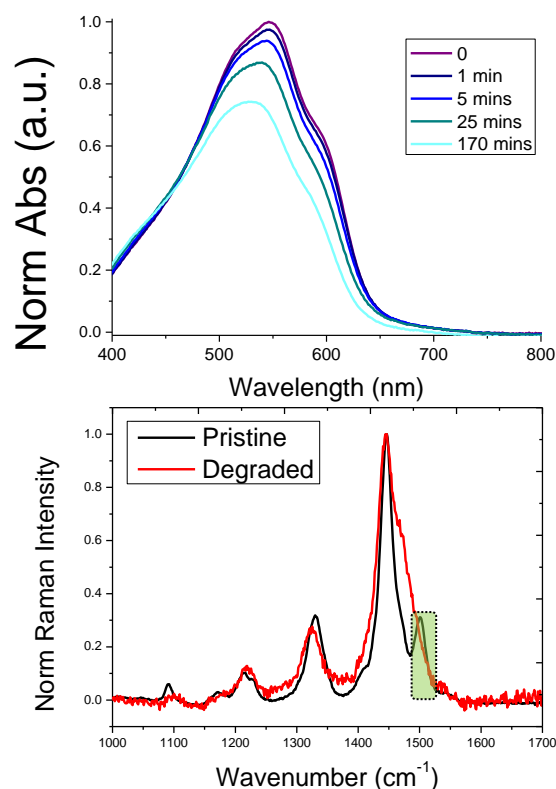


Fig. 3 (A) Ground state absorption spectra of a neat film of PTTz spun on FTO glass as a function of electrochemical charge injection time. A potential of +1.05 V was used to electrochemically degrade the film. Spectra were measured in-situ; background of FTO glass submerged in 0.1 M TBAPF₆/CH₃CN electrolyte solution was subtracted from spectra. (B) Background corrected and normalised Raman spectra of pristine and degraded films of PTTz.

the oxidation of the PTTz film leading to an increase in the population of hole polarons at the expense of neutral polymer. Fig. 2C is a comparative plot of the normalised absorption at the initial wavelength maximum as a function of probing potential for P3HT, PTTTz and PTTz (see ESI Figure S1 for spectroelectrochemical data). The onset in the spectroelectrochemical response is used to estimate a HOMO energy level, similar to the technique of cyclic voltammetry. [9] Table 1 shows that all three methods of determining HOMO levels (CV, PESA and spectroelectrochemistry) are quite consistent. PTTz has the lowest energy HOMO and therefore requires the most positive potential for hole injection. On the contrary, P3HT has the highest HOMO and therefore requires the least positive potential for hole injection. This data is consistent with the expected stabilisation effect of the HOMO as the more electron deficient thiazole unit content is increased along the polymer backbone.

The presence of hole polarons under device operation is found to make polaron degradation pathways accessible. Electrochemical degradation is tracked for a neat PTTz film in Fig. 3A by measuring the absorption spectrum of the neutral film as a function of oxidative stress time. An oxidising potential (+1.05 V) is applied to the working electrode, which results in oxidation of the film, such that the injected polaron concentration is approx. 10^{20} cm^{-3} . This oxidising potential is referred to as the probing potential (Table 1), and is expressed as an absolute

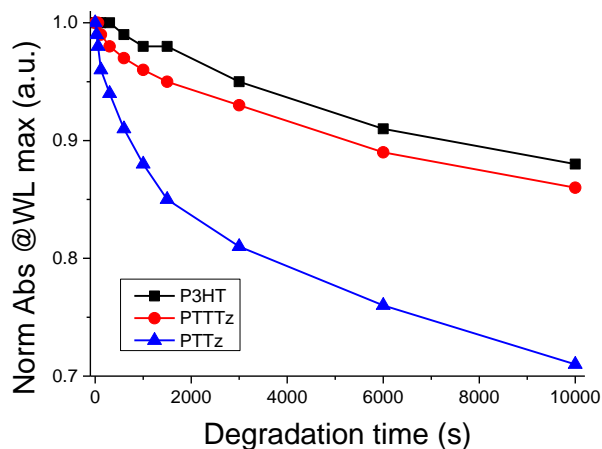


Fig. 4 Change in normalised absorption intensity at the initial maximum absorption wavelength of film as a function of electrochemical charge injection time. Data is for films of P3HT, PTTTz and PTTz held at +0.65 V, +0.80 V and +1.05 V, respectively.

energy level. The film is held in this oxidised state, under Argon, for a defined period of time in what is called the oxidative stress stage. This is a relatively high polaron concentration compared to that experienced in organic electronic devices, and so accounts for the accelerated degradation rates observed herein. At intervals, the film is reduced to its neutral state by removing the oxidising potential, allowing for ground state absorption spectra to be recorded. The extent to which the absorption spectrum recovers is therefore a direct probe into the extent of polaron induced degradation.

Typically, a blue shift and a reduction in intensity of the absorption maxima were observed. These changes are attributed to a reduction in conjugation length which is speculated to arise from a degradation of the C=N double bond, as suggested by the Raman evidence described below. In the absence of an oxidising potential, the absorption spectrum of a PTTz film is observed to be stable over the timescale of this experiment (see Fig. S2 in ESI). Thus, degradation is attributed to chemistry occurring due to the presence of polarons. It is also observed that the rate at which this degradation occurs increases when polaron concentration is increased (Fig. S3 ESI).

Raman spectroscopy was used to determine whether there were any polymer structural differences between pristine PTTz films and PTTz films that had been subjected to 3 hours of oxidative stress (Fig. 3B). Vibrational modes were assigned to oligomers of P3HT, PTTTz and PTTz using DFT with a B3LYP Hybrid Functional and a 6-31 G(d,p) basis set.^[10] Two signals are observed at 1330 cm^{-1} and 1450-1490 cm^{-1} which are assigned to C-C skeletal stretching and C=C ring stretching, respectively, for both pristine and degraded films. A third signal at 1500 cm^{-1} is observed in pristine PTTz films which is attributed to the C=N stretch. This signal is quenched after degradation suggesting that the C=N bond is broken in the degradation step. An increase in luminescence background signal in the raw Raman data under 488 nm excitation and an increase in the high energy component of the C=C bond producing a significant increase in its FWHM (indicated by the green box in Fig. 3B) are indicative of enhanced polymer conformational

disorder which might result from an increase in shorter effective conjugation lengths after degradation. This is consistent with the observations made in the absorption spectroscopy data where the absorption peak blue shifts as a function of oxidative stress time.

P3HT and PTTTz were investigated using a similar procedure to PTTz to determine the relative polaron stability across the series. One requirement of this methodology was to ensure that different polymers are subjected to the same extent of oxidative stress, i.e. the polaron concentration injected into the polymer film is the same across the series – approx. 10^{20} cm^{-3} . Polaron concentration is controlled by the probing potential selected in the chronoamperometry set-up. The extent of oxidation that a given probing potential will impose on a polymer film is affected by the HOMO energy level of that film. All three polymers used in this study have different HOMO energy levels, and so a different probing potential must be selected for each polymer, in order to subject each polymer to the same extent of oxidative stress. The probing potential to be used in the degradation stage was defined as that potential which caused a 25% reduction in absorption at the polymer peak wavelength (Fig. 2C). Chronoamperometry curves were then integrated to confirm an injected polaron concentration of 10^{20} cm^{-3} . Hence, the increasingly oxidising probing potentials across the series (+0.65 V, +0.80 V, +1.05 V, respectively) track the deepening of HOMO energy level across the series (-4.8 eV, -5.1 eV, -5.2 eV, respectively), reasonably well. We note the relationship between probing potential and HOMO energy level is not exact as molecular orbital energies are generally not well defined.

The absorption spectrum of P3HT degrades in a similar fashion, and yet a lesser extent to that of PTTz, with a blue shift in peak absorption and a reduction in intensity. The degradation of the absorption spectrum of PTTTz is more pronounced than P3HT, and not as pronounced as PTTz. Fig. 4 shows a plot of normalised peak absorption for all three polymers as a function of oxidative stress time, all measured with matched densities of injected polarons. Over the timescale of this experiment, P3HT is seen to be most stable, and is followed by PTTTz, and then PTTz.

In the Raman study of P3HT, signals at 1375 cm^{-1} and 1460 cm^{-1} are observed, which are assigned to C-C skeletal stretching and C=C ring stretching, similar to the case of PTTz. Raman signals of pristine and degraded P3HT films overlap reasonably well (Fig. S4, ESI) which is consistent with absorption spectra that suggest P3HT is a relatively stable polymer under these oxidative stress conditions. The Raman study of PTTTz (Fig. S4, ESI) shows that it degrades in a similar fashion to PTTz, but to a lesser extent, which is again consistent with absorption spectroscopy measurements. The degradation rate correlates with the amount of thiazole unit content within the conjugated backbone.

When considering HOMO energy levels, our results indicate that polaron stability in the polymer series including P3HT, PTTTz and PTTz decreases as HOMO energy level is lowered, such that increasing the thiazole content along the polymer backbone leads to a reduction in polaron stability. It has already been reported that the oxidative stability of neutral polymers (i.e.: their resistance to dark oxidation) is enhanced for lower lying HOMO energy level polymers.⁵ The results herein suggest that when considering the stability of the polymer when partially

oxidised, the opposite trend is observed, with the polymer with the deepest HOMO showing the fastest degradation. In other words, the more oxidising the polarons, the more likely they may cause degradation. This study is clearly limited to a single polymer series, and therefore caution should be taken on the generality of the trend observed. Nevertheless, the results do suggest, at least for the materials studies herein that whilst low-lying HOMO polymers may have better storage stability and resistance to oxidation by water and oxygen, they may have poorer stability in the presence of charge carriers (holes), which may have important implications for device operational lifetimes.

Conclusions

We have developed a new methodology for evaluating the polaron stabilities of conjugated polymers in neat films. It consists of probing the absorption properties of the conjugated polymers after the injection of a relatively high polaron concentration. We have compared the polaron stability of three structurally similar conjugated polymers, P3HT, PTTTz and PTTz in neat films. Our results suggest that polaron stability is improved in higher lying HOMO polymers.

Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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