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# A study on stability of active layer of polymer solar cells: effect of UV–visible light with different conditions

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**Abstract**  The objective of this study is to investigate the stability of the active layer of polymer solar cells from the effect of UV–visible light irradiation using different conditions with respect to time. The active layers were composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM), deposited on conductive glass substrates through spin coating. These samples are placed in a UV–visible light exposure chamber using different conditions (heat and water) over the specific periods of time. The samples are analyzed by UV–visible absorption spectroscopy, X-ray photoelectron spectroscopy and Fourier transforms infrared spectroscopy (FTIR) measurements. The results indicate that after continuous exposure to UV irradiation for 72 and 120 h, the sample shows a significant decrease in absorption of the main peak. The sample shows around 25% loss in absorption (main peak) after 72 h of irradiation. The FTIR results illustrate a progressive decrease in intensities of all typical absorption peaks owing to P3HT ring scission, side chain oxidation as well as degradation of the side groups of PCBM.

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**Graphical abstract**

UV-Vis absorption of P3HT: PCBM blends
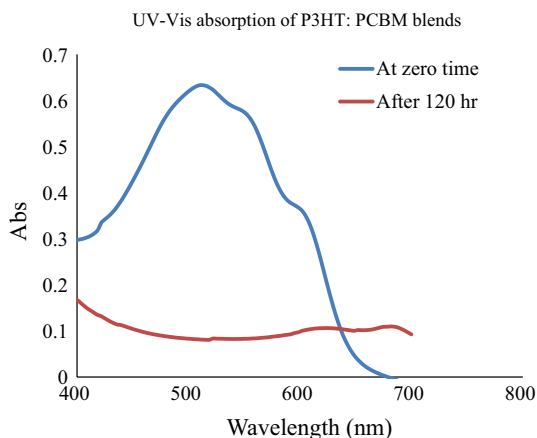
## Introduction

A tremendous progress has been achieved in polymer solar cells (PSCs) in recent decades because of their low-cost [1, 2], highly scalable [3–5], flexible [6], light-weight [6], with a short energy payback time [7, 8], and consequently of high commercial interest. A progressive research is being made to improve the power conversion efficiency (PCE) and the stability of the device since both are major factors [9–12] in the evaluation of PSCs performance. The most recent efficiencies of PSCs are reported as 10.8% (single junction cells) and 11.5% (multiple junctions), with an estimated lifetime of 1000 h [13–15]. Still, improving the stability of the devices remains a serious issue that has to be resolved in order to make them commercially feasible. Their organic nature makes them more susceptible to chemical degradation from light, oxygen, heat and water.

A number of studies showed that the stability/degradation phenomena are rather complicated and certainly not yet fully understood, though good progress has been made [16, 17]. Highly delocalized π-electrons of the conjugated polymers generate large electronic polarization, which eventually enables the photon absorption in the visible region and transfer of electrical charges along the polymer backbone. This charge transfer occurs along the short, continuous fragments of the polymeric chain by thermally induced bounding [18, 19]. Crystallization effects and polymer molecular weight influence the charge transport process and hence the improvement of the performance of PV cells [20]. Any chemical reaction that causes chain scission, termed as polymer degradation, affects the charge transport properties. Reduced charge transport causes a decrease in current density, and this directly affects the

efficiency of PSCs. Sunlight triggers the photochemical reaction in polymers, which leads to chain scission, i.e., polymer degradation.

One of the widely accepted mechanisms of photooxidation and thermooxidation of P3HT in solution claims that degradation originates from singlet oxygen photosensitization [6, 7]. Once formed, this singlet oxygen undergoes a Diels–Alder cycloaddition with the thinly unit of P3HT, ultimately forming an unstable endoperoxide. The latter subsequently decomposes into sulfine and ketone, among others, which leads to disruption of the π-conjugation [8]. For the bulk polymer, it was clearly demonstrated by Manceau et al. [9] that singlet oxygen is most probably the main intermediate responsible for the degradation. Based on the identification of degradation products by IR and UV spectroscopy, i.e., carbonyl and sulfur moieties which come from the degradation of the side chains (α-carbon atom of the hexyl group of P3HT which is the chemically weakest C–H bond) and of the backbone (S-ring) of the polymer, respectively. They proposed three types of degradation paths [9]: (i) the "H" abstraction reaction of alkoxy radicals leading to the formation of an α-unsaturated alcohol; (ii) the cage reaction of alkoxy radicals with OH leading to the formation of an aromatic ketone and (iii) β-scission leading to the formation of an aromatic aldehyde that rapidly oxidizes into carboxylic acids. The consequences of all these reactions are conjugation loss and/or chain scissions that lead to a decrease in UV–Vis absorbance and hole mobility reduction [10–12].

Here, we have made an attempt to study the degradation mechanism of the photoactive layers of P3HT/PCBM blend effectively by using different conditions and time periods. The samples were placed in a UV–visible light exposure chamber using different conditions (heat and water) over the specific periods of time. The samples are analyzed by UV–visible absorption spectroscopy, X-ray photoelectron spectroscopy, Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) measurements. We observed the different rate of degradation with respect to environment conditions and periods of exposure and discussed the degradation mechanism in detail below.

## Experimentation and characterization

ITO glass substrates were washed with acetone, iso-propanol and distilled water. First, glass substrates are sonicated (BRANSON 3510) in acetone for ten minutes. Subsequently, these substrates are sonicated in iso-propanol for ten minutes. Finally, substrates are rinsed with distilled water and dried in an oven at 100 °C. A conducting layer of ZnO is deposited on a glass substrate using plasma deposition technique. The thin film of P3HT/PCBM (1:1 in chlorobenzene) blend was next deposited using spin coating in a glove box. Finally, the coated substrates are annealed at 100 °C for 30 min. These samples are then placed in a UV–visible light exposure chamber for 24, 48, 72 and 120 h. The wavelength and intensity of incident radiation were 340 nm and 0.30 W/m$^2$, respectively.

The degradation due incident irradiation in these samples was analyzed by JASCO-670 UV/VIS spectrophotometer and FTIR. The XPS system used in the analysis of these samples is ESCA LAB 250 Xi from Thermo Scientific. The

samples were mounted over a sampling stage through double-sided graphite tape and insert into the vacuum chamber where the base pressure in the analysis chamber is $10^{-10}$ mbar. The equipment uses Al-Kα radiation for analysis. The pass energy used for survey scan is 100, while 50 eV pass energy used for high-resolution scans. The surface of each sample was lightly etched for 5 s with $Ar^+$ ions prior to the surface analysis to remove surface contamination. Also, an electron flood gun was used during the experiment to compensate for surface charging. Data from core level spectra S 2p, O 1s and C 1s were collected and analyzed using "Advantage version 5.932" software.

## Result and discussion

### XPS analysis

Figure 1 shows high-resolution S 2p spectra for all samples. It is clear from the figure that there are two main peaks one at a binding energy (BE) around 164 eV and the other at a BE around 169 eV. The intensity of the peak at 164 eV decreases with increase in illumination time, while the intensity of the peak at 169 eV increases with increase in illumination time. The peak at BE 164 eV is assigned to sulfur atoms in P3HT bonding environment as indicated in a recent study [13]. The peak at BE 169 eV is assigned to sulfur atoms in SOx bonding environment, where O are oxygen atoms absorbed from the atmosphere and reacted with sulfur atoms on the surface of sample [13]. The results of the XPS analysis are summarized in Table 1. It is clear that the duration of the UV light illumination of the sample affects the structure of the sample surface and induces modifications such as more sulfur atoms in the SOx bonding environment are formed and there is a disappearance of sulfur atoms in P3HT bonding environment. Figure 2 shows the curve fitted S 2p spectra of the four samples investigated in this study. Each main peak is fitted with the usual S $2p_{3/2}$ and S $2p_{1/2}$ spin–orbit doubled. The results of the fitting are summarized in



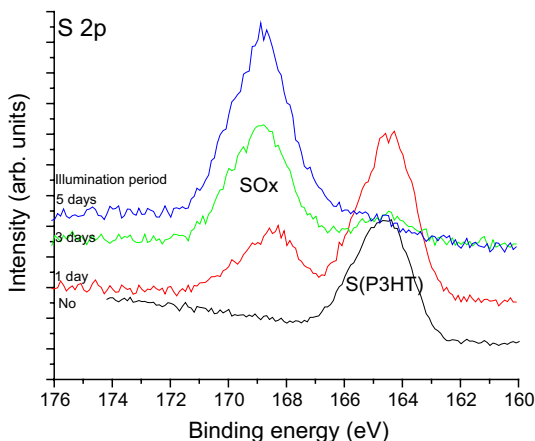**Fig. 1** S 2p core level spectra for all samples investigated in this study

**Table 1** Analysis of S 2p core level peak for the four samples analyzed

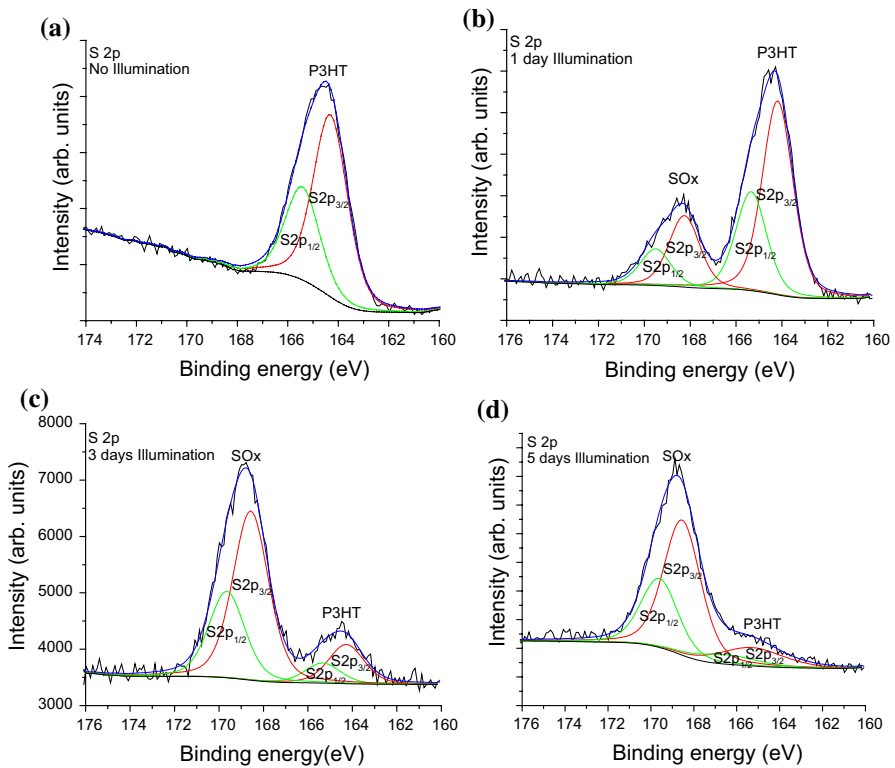| Sample | XPS peak | BE (eV) | FWHM(eV) | % |
|---|---|---|---|---|
| No irradiation | S2p$_{3/2}$ (P3HT) | 164.3 | 1.6 | 100 |
| | S2p$_{1/2}$ (P3HT) | 165.4 | 1.6 | |
| 1 day | S2p$_{3/2}$ (P3HT) | 164.3 | 1.6 | 72.8 |
| | S2p$_{1/2}$ (P3HT) | 165.4 | 1.6 | |
| | S2p$_{3/2}$ (SOx) | 168.4 | 1.6 | 27.2 |
| | S2p$_{1/2}$ (SOx) | 169.6 | 1.6 | |
| 3 days | S2p$_{3/2}$ (P3HT) | 164.3 | 1.8 | 18.5 |
| | S2p$_{1/2}$ (P3HT) | 165.3 | 1.8 | |
| | S2p$_{3/2}$ (SOx) | 168.5 | 1.8 | 81.5 |
| | S2p$_{1/2}$ (SOx) | 169.6 | 1.8 | |
| 5 days | S2p$_{3/2}$ (P3HT) | 165.3 | 3.5 | 18.6 |
| | S2p$_{1/2}$ (P3HT) | 166.6 | 3.5 | |
| | S2p$_{3/2}$ (SOx) | 168.4 | 2.0 | 81.4 |
| | S2p$_{1/2}$ (SOx) | 169.6 | 2.0 | |



**Fig. 2** S 2p spectra fitted with two contributions, namely S from P3HT and S in SOx bonding environment

Table 1. We see that in Fig. 2a (No illumination), only a single peak at BE 164 eV is fitted and is due to sulfur atoms in the P3HT bonding environment, while in Fig. 2d for the sample illuminated for 5 days with UV light, 81% of the sulfur atoms are in SOx bonding environment and only 19% of the sulfur atoms are in P3HT bonding environment. These results give a clear indication of the degradation of the P3HT sample as a function of the duration of UV light illumination.

Figure 3 shows high-resolution C 1s spectra for all samples investigated in this study. There are two main peaks in each spectrum with a strong peak at a BE around 284.6 eV. The other low-intensity peaks are located at different lower BE than the strong peak for the UV illuminated samples. For the sample without illumination, a low-intensity peak appears at a BE around 287 eV, while it is located at a BE around 289 eV for the samples with 1 and 3 days UV illumination. As for the sample with 5 days illumination, the low-intensity peak appears at a BE around 290 eV. According to the literature, the strong peak is assigned to carbon atoms in C–C bonding environment. The other small peaks are due to carbon atoms in C–O/C–S and O–C=O bonding environments [13]. Figure 4 shows the fitting of the C 1s spectra of all four samples. Carbon atoms exist in two environments in the non-illuminated sample, namely C–C and C–O/C–S bonding environments. The amount of carbon in C–O/C–S environment is small (10%). For the illuminated samples, the carbon atoms exist in three different bonding environments, namely C–C, C–S/C–O and O–C=O. The peaks assignments are clearly shown in the figure, and the results of the fittings are summarized in Table 2.

## Ultra Violet–Visible (UV–Vis) absorption analysis

Figure 5 presents the evolution of the UV–Vis spectrum of a P3HT/PCBM sample after various exposure times. As seen from the figure, the sample observed a maximum absorbance at 520 nm, and the two distinct shoulder peaks around 550 and 600 nm before irradiation. The two shoulder peaks attribute to the inter-chain absorption of the sample coming from highly ordered domains [11, 14]. The

**Fig. 3** C 1s core level spectra for all samples investigated in this study
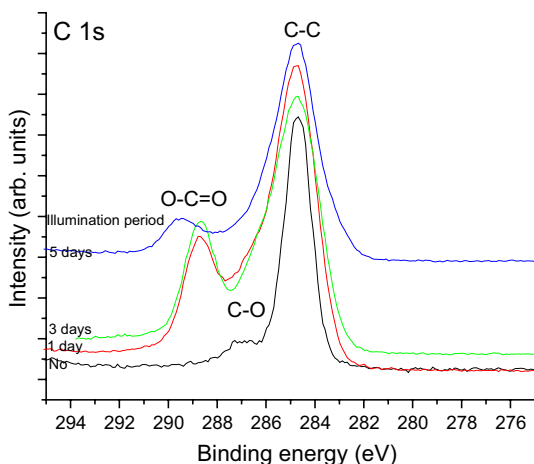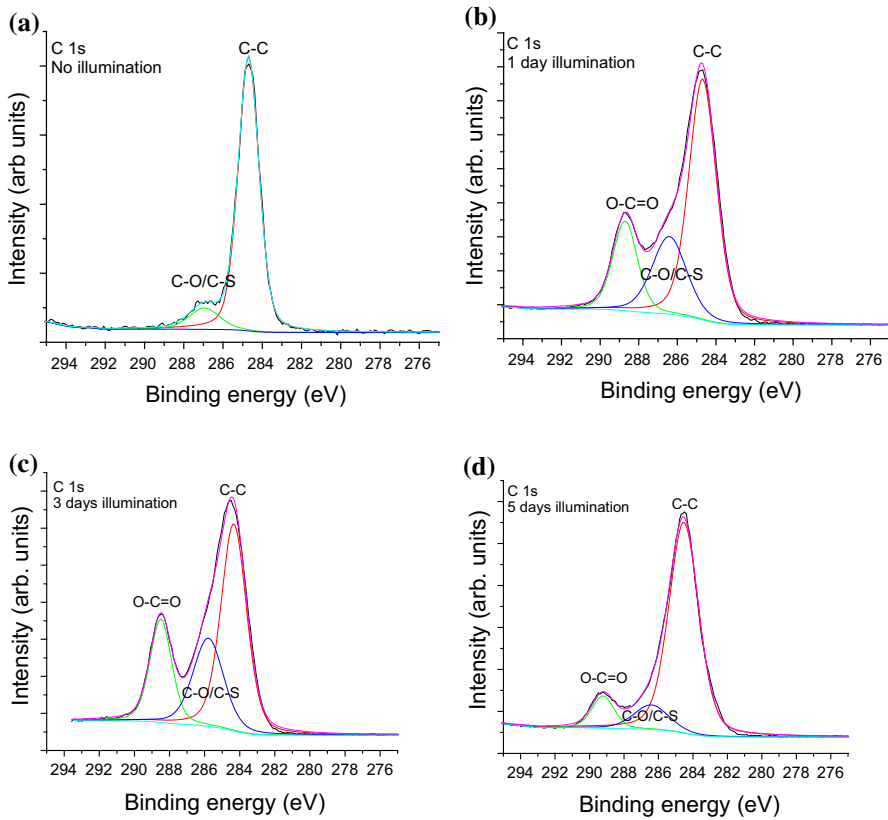
**Fig. 4** C 1s spectra fitted with the possible contributions, namely C–C, C–O/C–S and O–C=O bonding environments

**Table 2** Analysis of C1s core level peak for the four samples analyzed

| Sample | XPS peak | BE (eV) | FWHM(eV) | % |
|---|---|---|---|---|
| No irradiation | C1s (C–O) | 284.7 | 1.8 | 89.7 |
| | C1s (C–O/C–S) | 286.95 | 1.8 | 10.3 |
| 1 day | C1s (C–O) | 284.7 | 1.8 | 57.6 |
| | C1s (C–O/C–S) | 286.6 | 1.6 | 19.2 |
| | C1s (O-C=O) | 288.7 | 1.8 | 23.2 |
| 3 days | C1s (C–O) | 284.6 | 1.7 | 52.0 |
| | C1s (C–O/C–S) | 286.0 | 1.6 | 26.0 |
| | C1s (O–C=O) | 288.8 | 1.8 | 22.0 |
| 5 days | C1s (C–O) | 284.5 | 1.7 | 79.9 |
| | C1s (C–O/C–S) | 286.4 | 1.6 | 10.9 |
| | C1s (O–C=O) | 288.9 | 1.8 | 9.2 |

**Fig. 5** UV–Vis absorption of
P3HT/PCBM blends
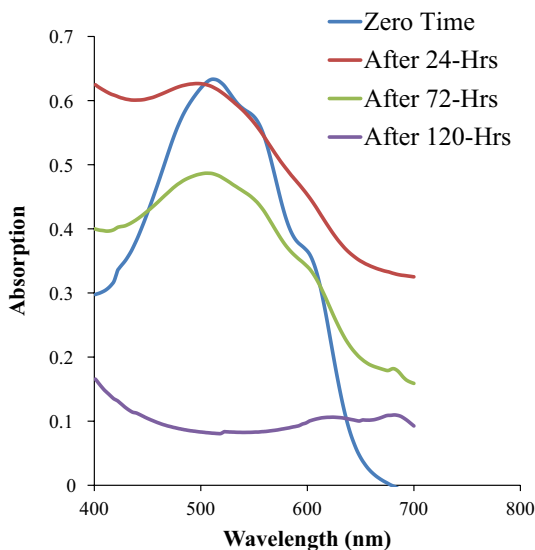


intensity of these signals is therefore dependent on polymer region-regularity and packing of the P3HT chains [11, 14]. The additional absorption at 400 nm could be due to the presence of PCMB contents in blends. Because PCBM absorbs/ gives an efficient absorption at near UV part, which may be due to $\pi$-$\pi^*$ transitions of the conjugated system. During irradiation, a continuous decrease in the intensity of the absorption band accompanied by a blue shift is observed. This suggests a reduction in the conjugation length in the macromolecular backbone, which leads to the photo-bleaching of the polymer. It was observed that there is a little decrease in absorption of the main peak after 24 h irradiation, which implies that the UV irradiation did not destruct much $\pi$-conjugation system during this period. After continuous exposure of UV irradiation to a similar dose for 72 and 120 h, the sample shows significant decrease in absorption of the main peak. The sample shows around 25% loss in absorption (main peak) after 72 h of irradiation. However, the shoulder peaks did not disappear which indicates that UV irradiation for 72 h did not alter the degree of inter-chain order in the microcrystalline domains of P3HT [11]. The extended period of UV irradiation for 120 h provoked a complete loss of the UV–Vis absorbance, and this indicates that the $\pi$-conjugated backbone was totally broken in the sample. The UV irradiation for 120 h has also altered the degree of inter-chain order in the microcrystalline domains P3HT, as evidenced by the disappearance of the shoulders at 550 and 600 nm. The conclusion drawn from this study is that P3HT/PCBM blend is unstable upon UV irradiation over extended periods of time (> 24 h). However, other researchers [15, 16] reported that the presence of PCBM in the blend decreases the degradation rate, compared to P3HT only using the same exposure condition.

**Fourier transformation infrared (FTIR) spectroscopy analysis**

The various exposure times of UV irradiation on P3HT/PCBM sample are studied using FTIR analysis, and the results are shown in Fig. 6a–d. As shown in Fig. 2a prior to irradiation, the spectrum of P3HT/PCBM sample shows the characteristic absorption peaks at 3087 and 2843–2992 $cm^{-1}$ which correspond to C–H bond stretching vibration on thiophene ring [17]; the peaks at 1459–1577 $cm^{-1}$ are the stretching vibration of C=C bond, the peak at 1384 $cm^{-1}$ is the stretching vibration for $CH_2$, the peak at 825 $cm^{-1}$ is the bending vibration of C–H bond. The peak at 1746 $cm^{-1}$ results from C=O ester stretch and the peak at 1091 $cm^{-1}$ belongs to the O–$CH_3$ stretching vibration in the PCBM [17, 18]. The peak at 729 $cm^{-1}$ is the characteristic absorption of S atom on polythiophene ring. Upon UV irradiation, a progressive decrease in the various functional groups of the polymer is observed. Decreased intensities of all typical absorption peaks point to P3HT ring scission and side chain oxidation as well as degradation of the PCBM's side group. During the 24 h of irradiation, the intensity of the signals characteristic of the thiophene (1459–1577 $cm^{-1}$) and PCBM (1091 and 825 $cm^{-1}$) moieties decreases insignificantly (Fig. 6b). During this period of exposure, there is no change in the intensity of the signals characteristic of the alkyl moieties of P3HT (2843–2992 $cm^{-1}$). Continuing the exposure for 72 h, new absorption bands in the carbonyl and hydroxyl regions developed. The increase in the intensity of absorption band around 3460 $cm^{-1}$ is characteristic of the hydrogen-bonded OH stretching of alcohols and hydrogen peroxides [19]. The other peaks for thiophene ring and fullerene moieties become wider and weaker (Fig. 2c). The properties of fullerene to trap the radicals by photoreaction during UV irradiation and lead to the formation of sites radicalize which can initiate its own degradation, and thus bringing out new carbonyl products [20]. The intensity of the peak for C=O group increased continuously while increasing UV irradiation up to 120 h during irradiation. After 120 h, an increase in the degradation rate of fullerene moieties is observed in Fig. 2d and the rate of disappearance of the thiophene band is reduced. However, Tournebize et al. [15] reported that reorganization of the blend (increase in the P3HT/PCBM interface area) results in a stabilization of P3HT by PCBM, but with an enhancement of the oxidation rate of the fullerene cage. The oxidized PCBM molecules are known to act as deep traps, thus decreasing the overall device electron mobility. Similar observations have already been made for polysulfone photodegradation [21].

**Conclusion**

We investigated the influence of UV–visible light irradiation on the stability of P3HT/PCBM blend in controlled UV–visible light for different periods of exposure time. The results indicate that the degradation of the P3HT/PCBM blend is strongly accelerated by UV light. Results show that the UV irradiation significantly reduces the absorption intensity of the main peak. The sample exhibited around 25% loss in absorption (main peak) after 72 h of irradiation. The FTIR results illustrated a
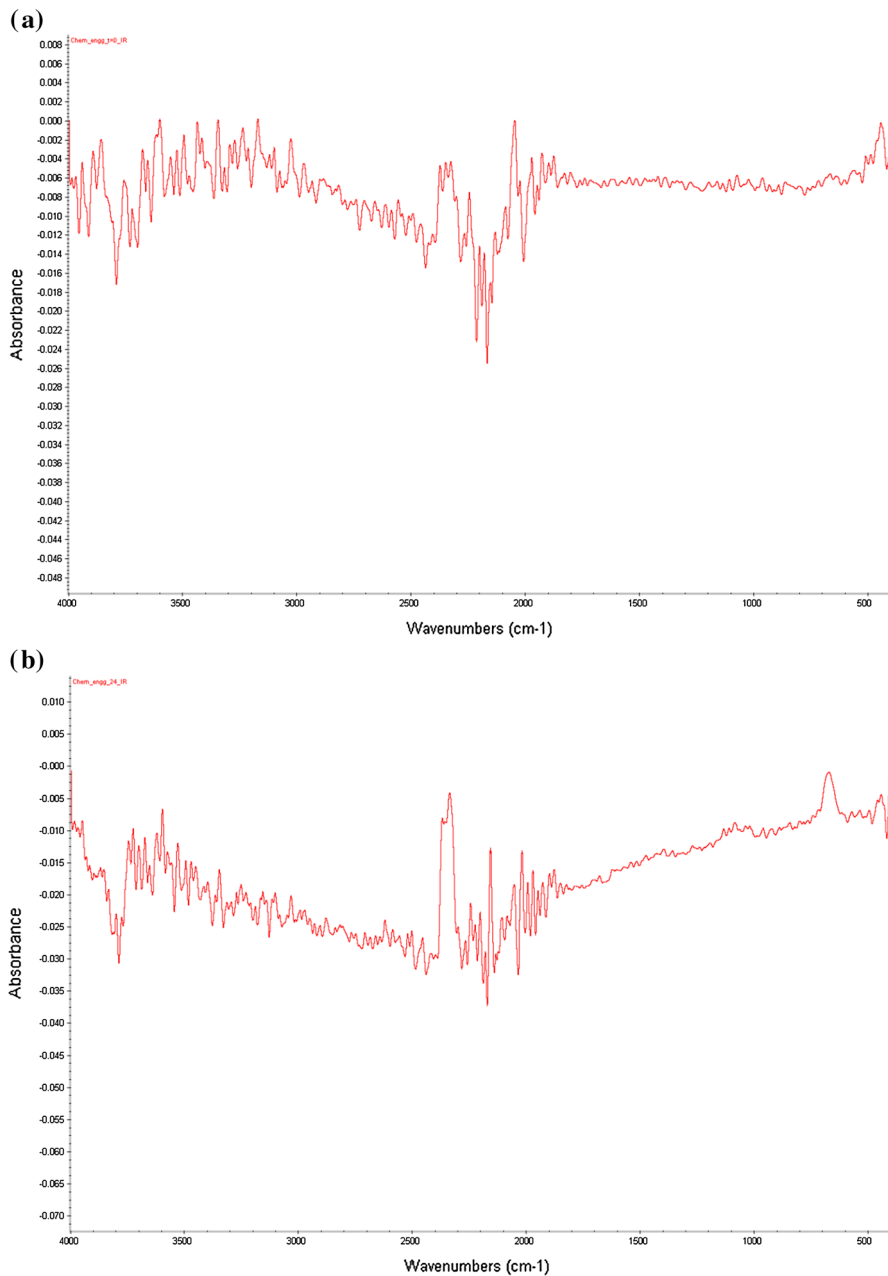
**(a)**



**(b)**



**Fig. 6**  **a** Zero time of exposure, **b** 24 h of exposure, **c** 72 h of exposure and **d** 120 h of exposure
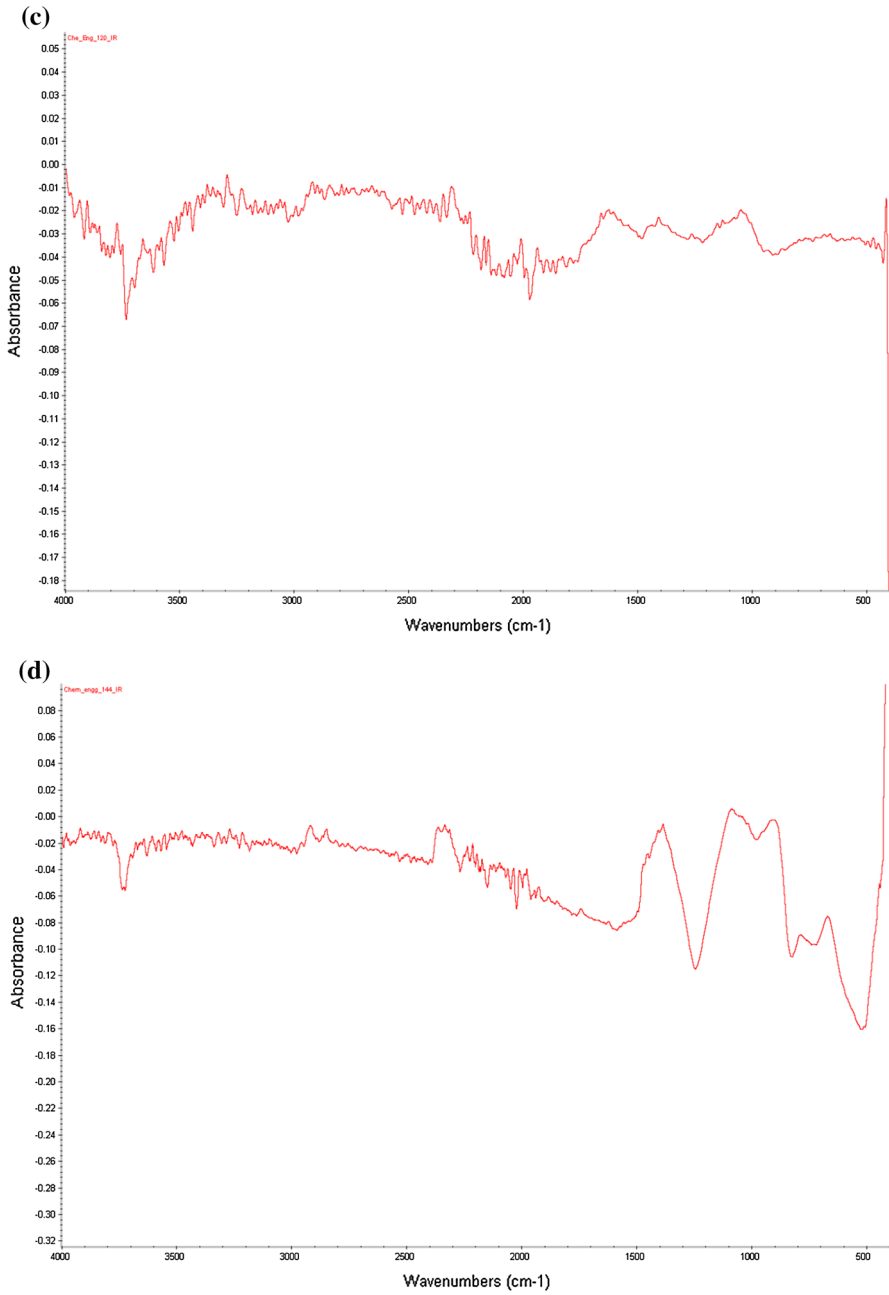
**(c)**



**(d)**



**Fig. 6** (continued)

progressive decrease in intensities of all typical absorption peaks owing to P3HT ring scission, side chain oxidation as well as degradation of the side groups of PCBM.

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