

# Excited state spectroscopy in polymer fullerene photovoltaic devices under operation conditions

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## Abstract

The discovery of a photoinduced charge transfer interaction between conjugated polymers and fullerenes led to intensive spectroscopic investigations as well as to high efficiency photovoltaic devices. Up to now, most spectroscopic investigations were performed on thin films, whereas little is known about the behavior of the charge carriers under working conditions of the device with an applied electric field.

In this work, we investigated thin film photovoltaic devices by means of photoinduced absorption spectroscopy. Significant changes were observed for the polaron signal as well as the lifetime of the positive polaron on the conjugated polymer backbone upon changing the applied voltage on the device. The results are discussed in comparison with current–voltage characteristics of the devices.

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## 1. Introduction

The photophysics of conjugated polymers shows an interesting photoinduced charge transfer interaction with fullerenes [1]. The forward reaction, i.e. the transfer of a photoexcited electron from the polymer onto the fullerene, is known to occur in a timescale of around 45 fs [2], whereas the backward reaction is slow and happens in a timescale of  $\mu\text{s}$  to ms [1,3]. At low temperatures, photoinduced charges can even live for several seconds up to metastability [4]. Commonly used techniques to study this phenomenon are photoinduced absorption techniques in steady state as well as time-resolved operation.

Photovoltaic cells are a potential device application of this photoinduced charge transfer. The long living photoinduced, separated charges can be quantitatively extracted to electrodes. Power conversion efficiency exceeding 2.5% has been reported [5–8].

Here we report on a photoinduced absorption study on a photovoltaic device, with an active layer of a poly-paraphenylene-vinylene/fullerene blend. When applying an external voltage on the device, a significant increase of the photoinduced signal is observed. Additionally, a decrease of the mean lifetimes of the charged species is observed. These phenomena are discussed in comparison with current voltage curves of the device.

## 2. Experimental

The photovoltaic devices were prepared from a blend of poly[2-methoxy, 5-(3,7)-dimethyl-octyloxy]-*p*-phenylene-vinylene (MDMO-PPV) and [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) as reported by Shaheen et al. [6]. The active layer thickness was approximately 120 nm. As top electrode, 0.6 nm of LiF and subsequent a layer of Au or Al was evaporated. LiF is known to improve the electron injection between Al or Au and organic materials [9]. Au and Al show similar behavior as top electrode material in bulk heterojunction devices [10]. Thirty nanometer of Au

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or Al were used as top electrodes for semi-transparent devices. Whereas thin Au devices show good stability, thin Al devices show degradation after short time. Al electrodes with a thickness over 60 nm show sufficient stability.

Photoinduced absorption spectra PIA were measured at 80 K in two different setups: in transmission with the semi-transparent devices and in reflection with thick electrode devices. PIA in transmission was measured with a tungsten lamp as probe and a chopped laser light from an  $\text{Ar}^+$  laser as pump. Typical chopping frequency for recording spectra was 73 Hz. The probe was recorded with a Si–InGaAsSb sandwich detector, after passing a monochromator and detected with a lock-in amplifier. The PIA signal was corrected for the photoluminescence, photoinduced absorption spectra also for the lamp spectrum.

For the reflection measurement, a tungsten lamp was used and the monochromator was set in front of the device. A  $\text{N}_2$  cooled Ge detector with a cutoff filter at 1.8 eV was used. The signals were also corrected for the photoluminescence.

The bias voltage was applied between the ITO and Al electrode, which was on mass.

### 3. Results

Fig. 1 shows the PIA spectrum, measured in transmission geometry, of a photovoltaic device with thin Al top electrode. The spectrum shows an absorption peak at 1.3 eV and a second peak arising below 0.6 eV. The two peaks have been attributed earlier to the absorption of the photoexcited

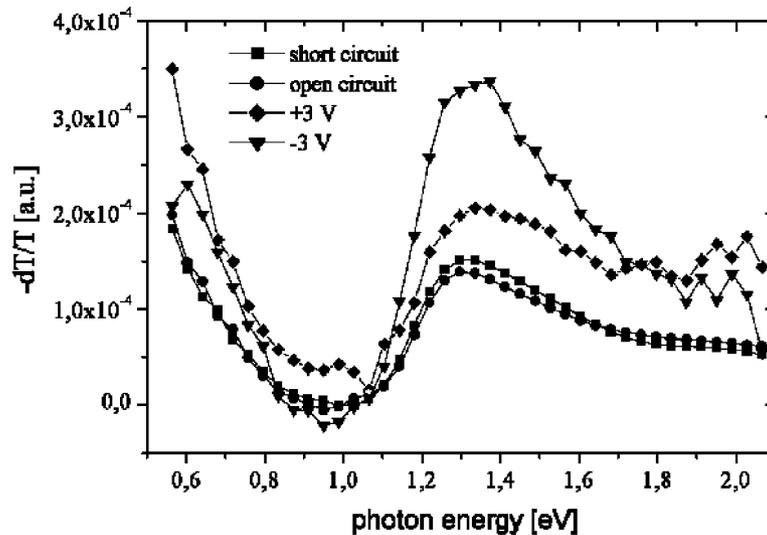


Fig. 1. PIA signal ( $-dT_x/T$ ) in transmission geometry of a photovoltaic device with a thin Al electrode under different external applied voltages.

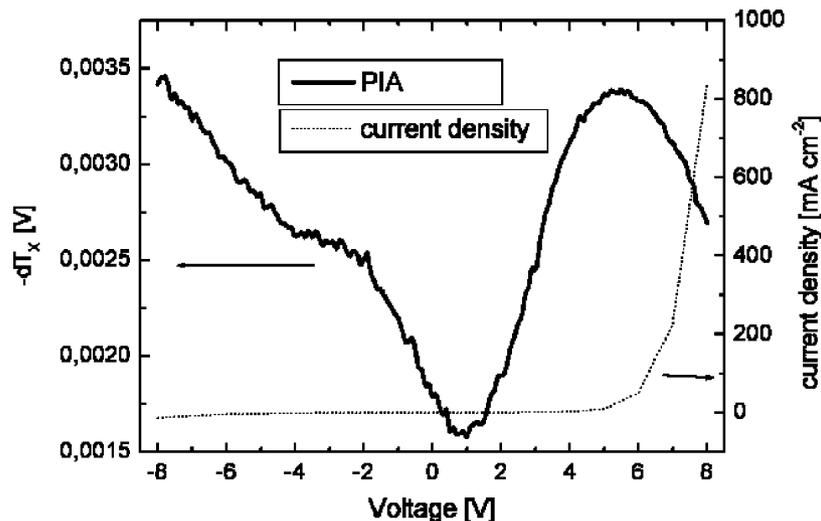


Fig. 2. PIA ( $-dT_x$ ) signal in reflection geometry at 1.3 eV and 80 K of the device with 60 nm Al back electrode, in comparison the dark current–voltage curves.

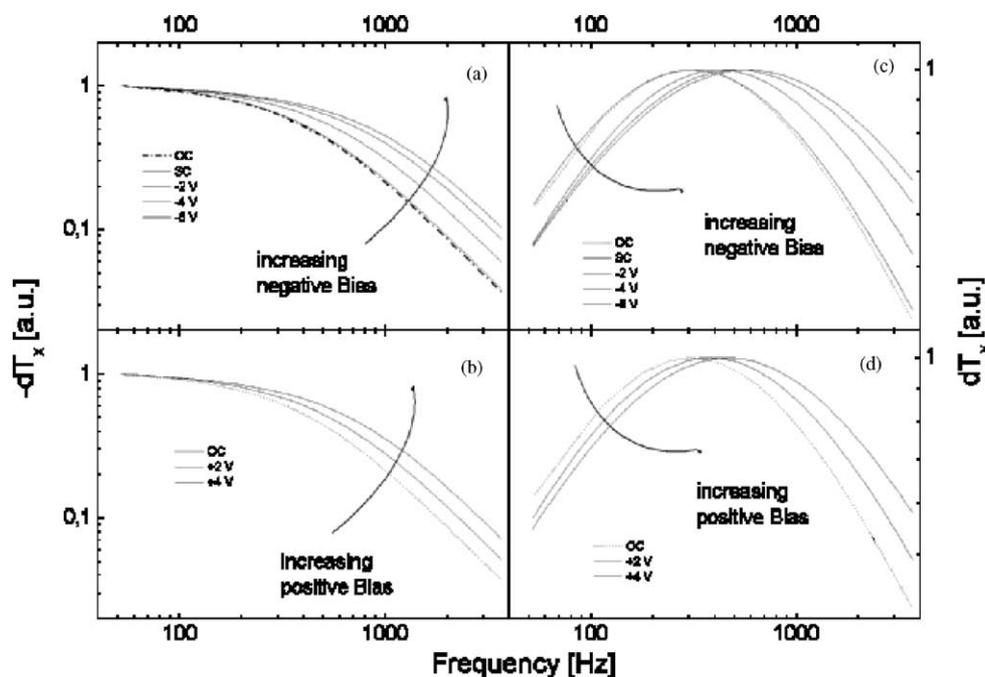


Fig. 3. Normalized frequency dependence of the PIA signal at 1.3 eV in transmission geometry, thin Au electrode; the OC case is shown for comparison (dash dot) (a) real part ( $-dT_x$ ) for increasing negative bias, (b) real-part ( $-dT_x$ ) for increasing positive bias, (c) imaginary part ( $dT_y$ ) for increasing negative bias, (d) imaginary part ( $dT_y$ ) for increasing positive bias.

polarons on the PPV backbone [11]. An increase of a factor 2–3 is observed when applying an external voltage on the device. No significant change of the spectrum was observed when applying a voltage.

Fig. 2 shows the PIA signal, in reflection geometry, at 1.3 eV, the maximum of the polaron peak of MDMO-PPV versus the applied voltage. For comparison, the current voltage curve of the device is shown. A minimum of the signal around the open circuit voltage at 0.91 V is observed. The spectrum is symmetric around this minimum for low voltages, but becomes asymmetric for higher voltages.

Fig. 3 shows the chopper frequency dependence, normalized to maximum, of the polaron signal at 1.3 eV, fitted after the dispersive relaxation model [12]. The measurements were done in transmission geometry with a thin LiF/Au electrode on top. Table 1 sums up the mean lifetimes  $\tau$  and dispersion factors  $\alpha$  at different voltages. The signal is divided by the lock in amplifier into a real ( $-dT_x$ ) and imaginary ( $dT_y$ ) part. For positive as well as negative voltages, the curves for the real part become flatter and the maximum of the imaginary part shifts to higher frequencies. Such frequency

dependences indicate a decrease of the mean lifetime when applying a voltage.

#### 4. Discussion

In steady state condition, the photoinduced signal is given by Eq. (1):

$$dT \sim \Delta n \sigma \tau \quad (1)$$

whereas  $dT$  is the photoinduced signal,  $\Delta n$  the number of photoinduced species created per time unit, in this case the number of positive polarons,  $\sigma$  the absorption cross-section and  $\tau$  is the polaron lifetime. Since the photoinduced charge transfer is known to be quantitative with efficiency near unity, we cannot expect any change in  $\Delta n$  upon applying a voltage. Also for  $\sigma$ , no significant change is expected.

The only factor for which we expect a change due to applying a voltage is the lifetime. The frequency dependence of the signal, Fig. 3 shows that the lifetime is decreasing by applying an external voltage. We assign the decrease of the lifetime to the charge collection at the electrodes under external field in addition to the recombination, which is the only relaxation pathway without electric field as it is at near to open circuit voltage.

But this decrease in lifetime is in contrast to the increased photoinduced signal.

The existence of very long living charge carriers, so called persistent charges, was shown by steady state light induced

Table 1  
Calculated mean polaron lifetimes and dispersion factors for different applied voltages

	-6 V	-4 V	-2 V	0 V	$V_{OC}$	+2 V	+4 V
$\tau$ (ms)	1.8	2.0	2.4	3.2	3.3	2.7	2.3
$\alpha$	0.62	0.64	0.69	0.70	0.72	0.69	0.66

electron spin resonance ESR [4,5]. These charge carriers cannot be detected by modulation spectroscopy, since their lifetime is much longer than the chopper cycle. Since the lifetime of the polaron on the conjugated polymer is changed, we assign the increase of the PIA signal to a change of the number of detectable photoexcited species. Therefore, we propose the increase of the photoinduced signal due to a detrapping of persistent charge carriers, which can now recombine within the frequency range of the chopper and can therefore be detected by modulation spectroscopy.

For high positive external voltage, a decrease of the photoinduced signal is observed. In Fig. 2, the current voltage curve for the same device is shown for comparison. The onset for current injection in forward bias corresponds with the quenching of the photoinduced absorption signal. We assign this decrease due to enhanced recombination of the photoexcitations with injected charge carriers.

## 5. Conclusion

We studied the behavior of the positive charge carriers in conjugated polymer/fullerene photovoltaic devices at low temperatures and operation conditions. Upon applying an external voltage, an increase of the photoinduced signal is observed around the open circuit voltage. We assign this increase to detrapping of persistent charge carriers under the influence of the electric field. In addition, a decrease of the mean lifetime is observed, what is due to the charge collection at the electrodes in addition to the recombination of the charge carriers. At higher positive bias, the photoinduced signal is decreasing again, which we assign to the enhanced recombination with injected charge carriers.

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