

Scientific Report

About an Exchange Grant

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Introduction

The utilization of SWCNT in polymer organic solar cells has gained significant interest during the last five years. However, the performance of this type solar cells has been tremendously disappointing; the contradictory results published in the literature raise the fundamental question: if the poor performance of SWNT in organic photovoltaic, is rather due to a fundamental mismatch between the energy levels involved or due to intrinsic defects from the production of SWNT (metallic catalyst, graphitic particle and bundle aggregation and oxidation [1]). For this reason, we chose to investigate the primary step of photo-generation, which is the **photo-induced charge transfer**. At the current stage of production, the purity of SWCNT remains an obstacle; consequently we would like to raise several issues concerning the SWCNT compared with standard C60 or PCBM. Assuming that SWCNTs may act as photoactive components, a similar signal like for PCBM cannot be expected for the following reasons:

- 1) C60 accepts 0.1 electron per carbon atom – the rate for SWNT is only 0,005 electron per carbon atom,
- 2) While the purity of PCBM reaches 99,5%, the purity of SWNT is today 90% in the best case. Among this 90% only the SWNT with a wide band gap will contribute (small diameter)
- 3) the presence of the catalysts and graphite might be source a of recombination for the photogenerated exciton
- 4) and on the other hand , the purification process induces defects, which might cause also recombination

For all this reasons we expect in these studies a signal with two orders of magnitude less than for what is observed with common C60. Therefore we took particular attention on the sample preparation – mainly the dispersion – in order to increase the

surface of interaction between the polymer and the SWCNT and reduced the influence of metallic nanotube, (noticed that presence of on metallic tube inside a bundle of semiconducting lower the possibility of a charge as well as the percolation threshold. The photo-induced charge transfer was studied by light-induced electron spin resonance and photo-induced absorption.

The purpose of the granted project is not to compete with the actual system P3HT:PCBM, but to understand the photo-physics of the processes at the SWNT-polymer interfaces

The experiments were carried out during the visit at Ilmenau University of Technology and completed at Würzburg University.

Experimental

Preparation of samples for ESR

100 μ liter of CNT/P3HT blend solution were drop casts from 1,4 di-chlorobenzene solutions on Teflon foil and have been slowly dried, then rolled to fit in an ESR sample-tube. The preparation took place in a glovebox with nitrogen-atmosphere. The top of the samples were sealed with a screw cap containing a PTFE septum, which should protect the samples at least for a few days from environmental degradation. The ESR-tube it was put on some double-sided tape and then rolled onto around a thin Teflon-hose, which was then put into the ESR-tube. A reference holding (Teflon, double tape, glass are ESR silent) was used for determining any background signals.

ESR Experimental conditions

The measurements were performed with a modified Bruker ESR200D machine at temperature at 100 K (using nitrogen flow cooling). The main magnetic field of 0,33 T

was overlapped with alternating field of 100 KHz allowing lock in detection of the microwave absorption in the first derivative. The g-factor was calibrated for every measurement in Bruker 035M NMR –Gaussmeter and EIP 28b frequency counter. Light excitation was done with a 150 W halogen cf Appendix

Materials investigated:

Sample	Polymer				SWCNT			Additive
	P3HT	Meh-PPv	1,6eV	1,8eV	HipCO	Comocat	KM1	PCBM
And where is sample 1?								
2			X					X
3			X		1%			X
4			X		1%			
5				X				X
6				X	1%			X
7				X	1%			
8		X						
9		X			1%			
10	X				1%			
11	X					1%		
12	X							
14					1%			
15	X						1%	

Materials

We decided to investigate 3 different type of SWCNT:

HipCO purchase from Inc company ,

ComCat (Swnte) purchase from <http://www.swentnano.com>

SWNT KM1 purchase from NanoCarbLab (MedChemLabs division) Russia (www.nanocarblab.com).

P3HT from Rieke Metals Inc. and a low bandgap polymer provided by F. Krebs [2]

Interpretation of common ESR-signals

For every sample at least three measurements @100K were performed

1. In the dark before first light-excitation. (Dark)
2. The measurement has been reproduced several times measured under illumination in order to confirm that the light induced signals is real additional signal .This signal will be called “illum”.
3. The dark after the illumination is to see if the signal returns to the pre-illumination size and shape. (after-dark)

If there is a signal before 1st light-excitation this is a sign of impurities or oxygen-influence. Pure fullerenes or polymers are not ESR-active in the dark. Even very small amounts of oxygen lead to a rising signal in most polymers. Impurities from the synthesis can also lead to those signals. Pure materials should even not give a signal under illumination, as there is no partner for charge transfer. But most polymers still show a very little signal, as always some minor impurities or oxygen are present. So very weak signals are not to be overrated. If the signal of a blend-material grows under illumination, it should do so within seconds. If the rise is slower than that, this is proof of slowly filled charge carrier traps and is also a hint of bad mobility. Only the fast rising component of the signal is interesting for charge carrier extraction in solar cells. The same applies for

the after-dark measurements. A good blend-material shows a low dark-signal, high illum-signal and the same low after-dark signal as before the illumination. It is often observed, that the after dark signal is only a little lower than the illum-signal and only slowly shrinking at 100K. This is also proof of unwanted charge carrier traps. The signals can usually be assigned to the used donor and acceptor by their g-factor and line-shape. Polymers tend to have a g-factor very close to that of the free electron 2.0023 or slightly higher and have a very symmetrical line-shape. C60-containing acceptors have always the same g-factor of 2.0002 and a very typical asymmetric line-shape, which facilitates identification. Measurements at different microwave-powers give additional help for identification of the peaks. Usually the peaks show different saturation-behaviour with rising power. A non-saturating signal should grow proportional to the root of the used μ -wave-power. Usually polymer-peaks saturate at low μ -wave-powers (\sim mw) and fullerenes don't. If both signals show exactly the same saturation-behaviour, this is an indicator of incomplete CT with the charge carriers still being close to each other and having their spins interacting.

Results

A Polymer –SWCNT system, Polymer SWCNT-PCBM, and Polymer PCBM system for (1,6 eV and 1,8 eV polymer band gap)

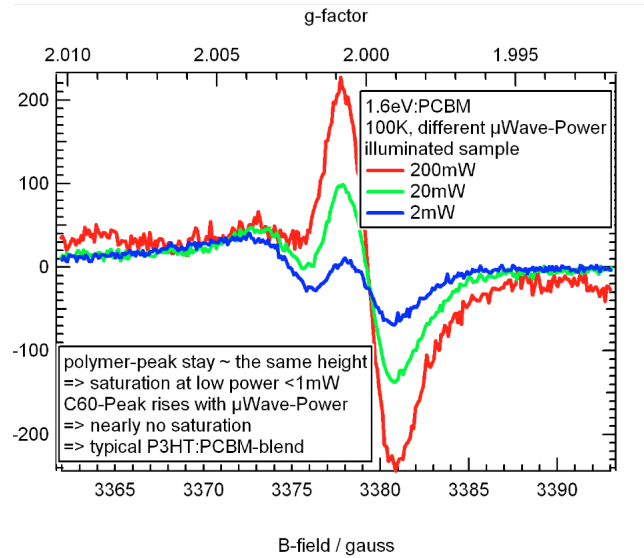


Figure 1 : ESR spectra of sample 2 (1.6eV polythiophene and PCBM)

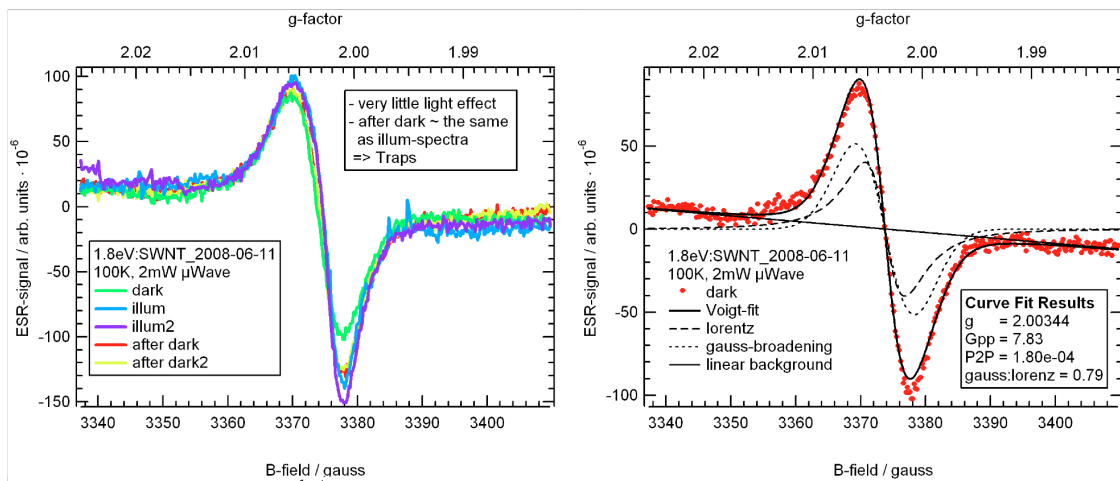


Figure 2 : ESR spectra of sample 7 (1,8 eV polythiophene derivative 1%SWCNT)

Sample 2 shows typical signals and behaviour of a charge transfer in a P3HT-PCBM blend. Except that the illum-signal is really weak, which indicates an inefficient CT (Regular P3HT:PCBM shows 10-100 times bigger signals.)

The amount of traps @100K (difference between dark and after-dark) contains most of the illum-signal.

The μ wave-saturation shows typical behaviour with the P3HT-peak saturating at low power and the C60-peak not saturating at all. The fit identifies the two components with typical g-factors and line-widths (Gpp).

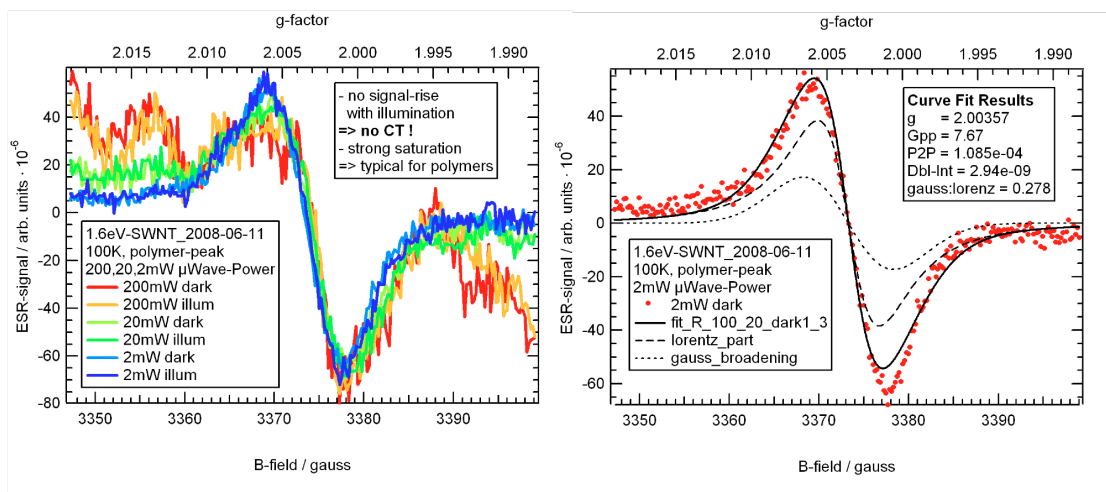


Figure 3 LESR spectra of sample 4 (1,6 eV polithiophene 1% SWCNT hipco)

Sample 4 shows no light-induced signals and therefore no CT. The small signal observed at $g=2.0036$ does not correspond to the polymer-signal found in illuminated sample 2 (1.6eV:PCBM), as it has different g-factor, line-width and shows no light-excitation. The origin of the signal is unknown, but it is comparable to the dark signal found in sample 5 (1.8eV:PCBM). It might be, that this signal is also present in sample 2, but so weak, that it is not obvious. It might also be, that signal is due to the SWNT. Similar signals have been described by Wang et al. [3] What does not speak in favour of this idea is, that this signal is not influenced by illumination. And Wang quotes, that there was no signal for dark measurements.

The more interesting signal in Sample 4 is the very broad line centred around $g=2.1$ with a line-width of 1000Gauss. This signal is also not influenced by illumination and shows no μ wave-saturation at high intensities (linear dependence in the log-log plot). The signal can also not be explained with the underlying background from the substrate (see sample 1). We expect that ferromagnetic residue from the synthesis is the source of this signal, as has been described by Wang et al [3]

Sample 5 shows three different ESR-signals. A dark signal of unknown origin and typical signals from the polymer and the charged C60-fullerene. The initial dark signal is very broad and cannot be assigned to the polymer or the fullerene, as it has different g -factor (2.00365) and line-width (7Gauss). It is also not influenced by light. A possible source of this signal might be broken polymer or other impurities, which lead to charged traps in the blend.

The difference between the dark and the illuminated signals is shown in the lower two graphs. These signals behave again typical for P3HT:PCBM-blends. The signal-intensity is about twice as high as for the 1.6eV:PCBM blend in sample 2, indicating more CT.

The after-dark signal is about the same, as the dark signal, which indicates a lower trap concentration compared to sample 2. Only on the C60-part of the spectrum some residual signal can be observed.

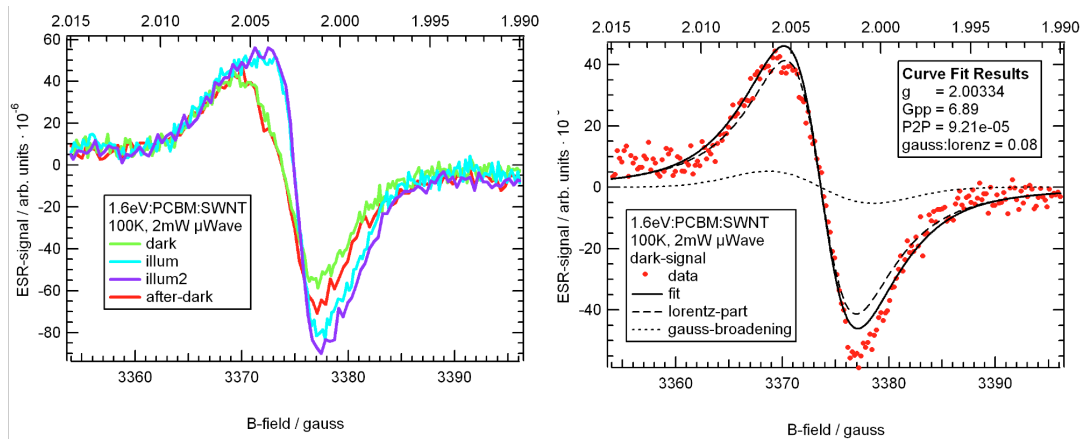


Figure 4 : LESR spectra of sample 3 (1,6 eV polythiophene derivative, PCBM 1 % SWCNT hipco)

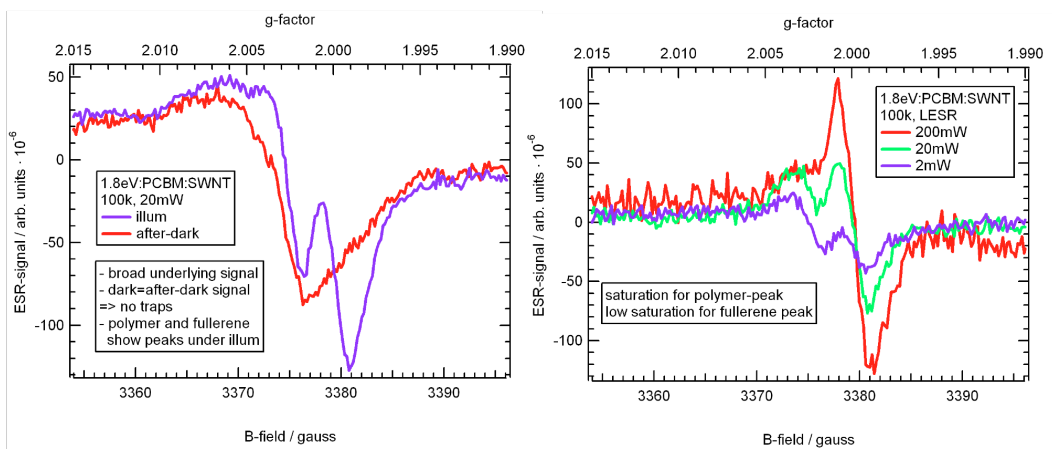


Figure 5 : LESR spectra of sample 6 (1,8eV polythiophène derivative and PCBM and 1% SWCNT hipco)

Sample 7 shows a similar spectrum as sample 4. A broad dark signal at $g=2.0034$, that is not influenced by light and a very broad signal of ferromagnetic impurities. The saturation-behaviour is the same: strong saturation for the dark signal (not shown) and no saturation for the giant signal. However this huge signal shows a different slope and different features, as the giant signal in sample 4 or the background from the substrate. If in both blends the same nanotubes with the same impurities have been used, this signal should be the same as well. The interesting feature of the spectra is the very faint light-effect, which might be due to charge transfer CT. The light-induced part of the spectrum can be fitted with similar parameters as for the 1.8eV-polythiophene signal in sample 5 (1.8eV:PCBM). The question is: where is the negative charge? Why doesn't it give a signal in the ESR? However this light-induced signal is very faint and should not be overrated. In many “pure” polymers a light-induced signal like this can be found, which

indicates CT from the polymer to some impurities from the synthesis or a small amount of molecular oxygen (air) in the sample-tube. This last assumption looks for me as the most probable explanation

Polymer SWCNT for P3HT and MeH PPV polymer

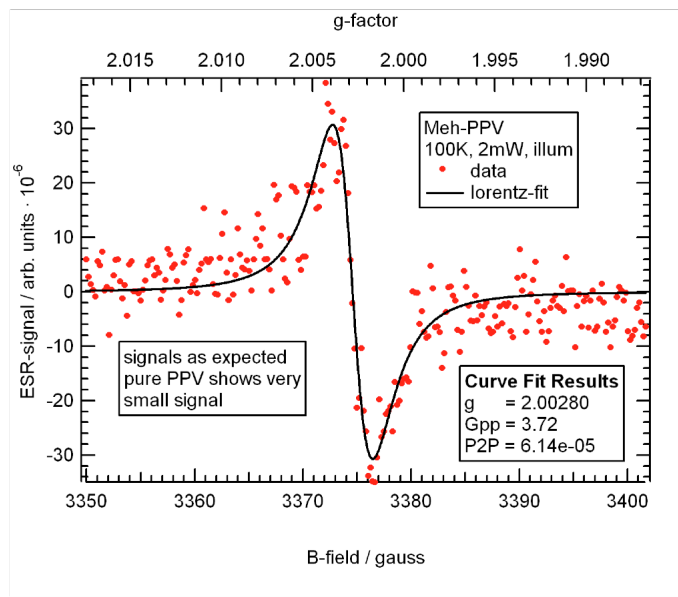


Figure 6 LESR fitting of the sample 8 spectra MEH-PPV

Sample 8 shows no dark-signal and a very faint illuminated signal. The after-dark signal is nearly a flat line again (not shown)

For sample 9 we also measures some additional spectra. The giant signal was recorded at 100, 200 and 300K and the Teflon substrate and the empty cavity were also measured again at 200K. As shown in the upper left graph, the contribution of the substrate and the cavity is only a low drift in the spectrum. The giant signal shrinks with temperature, which is expected for ferromagnetic impurities. The polymer-part of the spectrum however behaves unexpected for different temperatures. There is always a small dark signal, but its g-factor rises with temperature. The LESR-signal (illum-dark) is intense at

300K, but weak at 100K and even weaker at 200K, which is completely unexpected. This might have to do with different traps of different activation energies, but this is speculation.

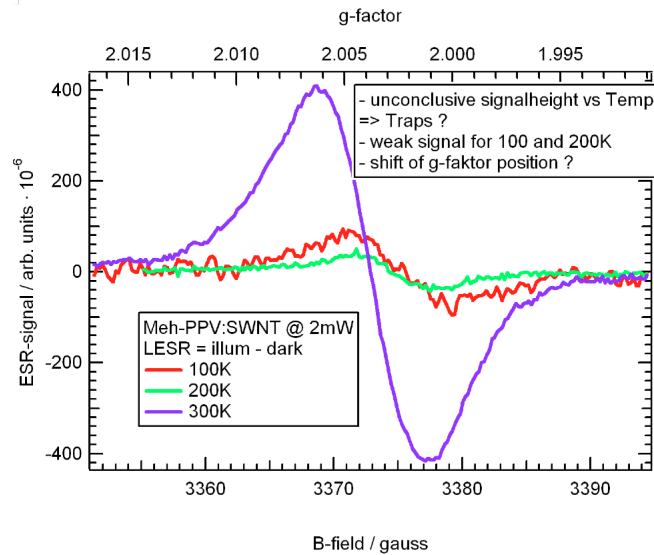


Figure 7 : LESR spectra of sample 9 (Meh-PPV 1% SWCNT hipco)

As pure MEH-PPV in sample 8 showed no relevant signal, these signals are rather interesting for further investigation. But if this should be interpreted as CT, the negative charge is still missing in the spectra. Oxygen-doping from improper sample-handling is also a possible explanation. Air could have diffused into the sample during the first cooling because of the lower pressure at falling temperatures

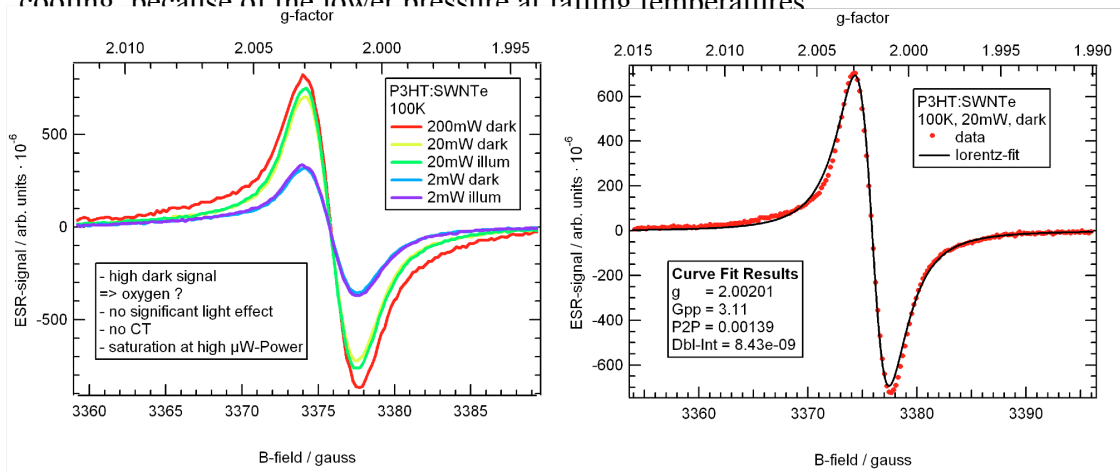


Figure 8: Sample 11 (P3HT 1% SWCNT comocat)

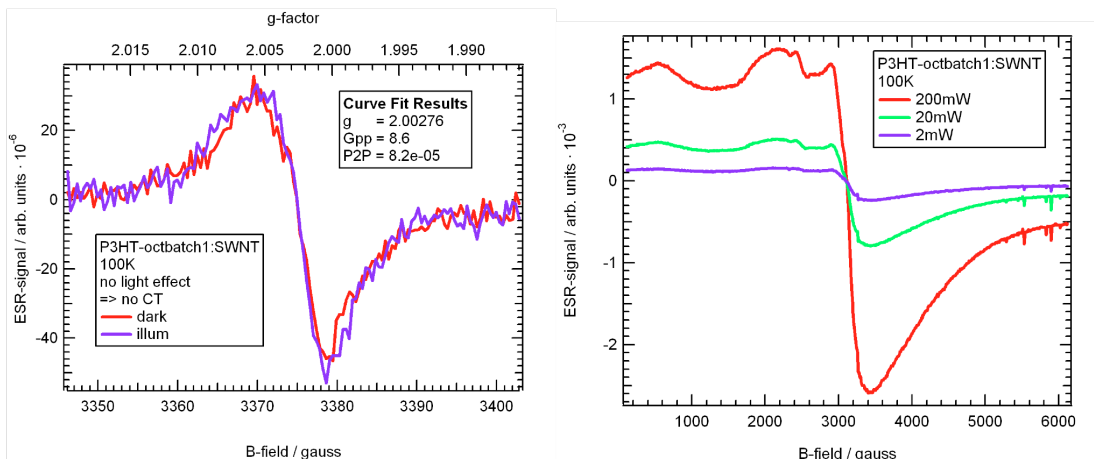


Figure 9 : LESR spectra of sample 10 (P3HT-1% SWNT Hipco)

Sample 11 shows a strong and narrow dark- signal: $g=2.002$, Width=3.1Gauss. These are typical values for polarons on P3HT. As there are not light-induced signals, they most likely are due to oxygen-influence. Under illumination the signal grows less than the fluctuation between measurements. Thus there is no CT in sample 11. Besides the signal seems to have a shoulder at $g>2.005$ which was previously noticed to be a sign of old degenerated P3HT. The signal of the ferromagnetic impurities is less intense in the lower field part (<3000 gauss) and can be assigned to the substrate and the cavity. However the higher field part shows a bigger shoulder, than can be explained with the background. This nanotube sample (SWNTe) should have lower impurity-concentrations, which fits well to the observed spectra.

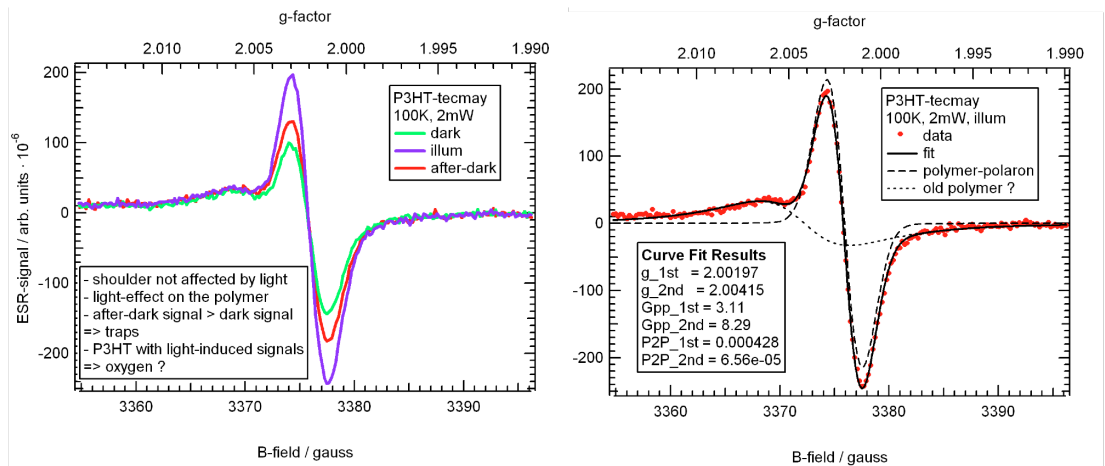


Figure 10: LESR spectra of sample 11 (P3HT old batch)

Sample 12 shows a large signal at $g=2.002$ with a shoulder at $g>2.005$, very similar to sample 11. I noticed those signals earlier in other P3HT-samples that I prepared. The signal and the shoulder can probably assigned to old oxygen-doped polymer.[4-6]

The illuminated spectra support this assumption. The P3HT(older batch) shows a signal increase under illumination, which stays partly as after-dark signal. Pure fresh P3HT does not give rise to any signals

Conclusions and further works

In this work, we investigated the photoinduced charge transfer between carbon nanotubes and various conjugated polymers via Light-Induced Electron Spin Resonance. The purity of the SWCNT material remains to be an obstacle. At this stage of development we show untreated well dispersed nanotubes in MEH-PPV, P3HT and a low band gap polymer do not exhibit a measurable light induced charge transfer by LESR. The quenching of photoluminescence observed in different SWCNT/ P3HT composites is indeed an energy transfer. Several other experiments need to complete those first preliminary results. However the understanding of the active role of SWCNT in organic solar cells need to be continued. In the future, we would like to realize LESR and photoconductivity of treated CNT (free of catalyst) in the same polymers. The goal will be to understand where an improvement of solar cell performance by including CNT might come from. Although the LESR experiment has shown that SWCNT (untreated and well dispersed) do not contribute significantly to the photo induced charge transfer. Furthermore the addition of SWCNT in Polymer /PCBM system is tremendously disturbing the LESR signal where solar cells behaviour remains unchanged or slightly improve.[7] Those observations can lead to answer for the remaining question whereas the presence of SWCNT in bulk heterojunction solar cells is doping the P3HT for the hole conduction or helping for the electron conduction?

This work was presented as a poster at Warwick Excitonic solar cells conference 2008

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References

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Appendix

Spectrum of the used halogen lamp with IR Cut-Off at 700nm:

