Supporting Information

Degradation kinetics in different polymer-fullerene blends investigated by electron spin resonance

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**Rise and decay kinetics of light induced ESR signals**

Figure S1 shows normalized rise and decay curves of the LESR signal monitored on the polymer peak for annealed and not annealed P3HT/PCBM blends. Upon light exposure, the signal increases quickly. For the annealed sample the signal saturates while the signal for the not annealed samples continues to grow with a moderate rate after the first rapid increase. Switching the light off results in a prompt drop of the ESR signal followed by a very slow decay. Although the signals have been normalized, the long-lived component of the decay of annealed and the not annealed samples appear to be different. This effect is caused by the dark signal present in the not annealed sample and leads to some complications when performing a quantitative analysis of the decay curves.



Figure S1: Example of rise and decay LESR measurements of P3HT:PCBM in a vacuum sealed tube at 60K in a pristine and annealed sample. The traces for pristine and annealed sample are normalized (0,1) showing a substantial difference in decay curve offset (black and red). The subtracted curve depicts the difference in the dynamics in the pristine and annlealed sample (green). The sharp spikes are caused by the temporal misalignment and do not reflect the real effect. In order to demonstrate the effect of the signal increase during the „light on“ phase in pristine sample containing oxygen traces on the decay curve offset we shifted the pristine curve by Δx (blue) which corresponds to the initial difference in the spectra offset which can be seen in the differential spectrum.

It was suggested that by monitoring of the peak evolution after illumination one can estimate (based on the decay kinetics) the trap distribution in the sample.[[1]](#endnote-1) Other works explain the observed kinetics based on nongeminate recombination of randomly distributed carriers which recombination rate depends only on the tunneling process and therefore on the intrapair distance between the photoexcited carriers.[[2]](#endnote-2) We show here factors which can dramatically influence the decay kinetics and disable any correct evaluation.

**Which peak should be chosen for the measurement?**

The fullerene peak is typically much narrower and higher than the polymer peak. It offers much higher aspect ratio and therefore higher resolution for a given modulation amplitude in rise and decay LESR measurements. The fullerene peak overlaps with the polymer peak, therefore any measurement done on this peak will contain also the dynamics from the polymer peak. Proper evaluation of any measurement done on the fullerene peak has to take into account the dynamics of the polymer peak. It is therefore advisable to record any peak dynamics preferably on the polymer peak where the overlap of both peaks is minimal. Schultz et al.[2] did their measurements on the fullerene peak, Carati et al. [1] and other authors reported their measurements on the polymer peak. Figure S2 illustrates the rise and decay measurements done for two samples prepared from the same polymer-fullerene blend. The decay of the polymer peak after the normalization shows the same behavior for both samples but a huge difference is observed in the case of the fullerene peak dynamics.



Figure S2: Example of rise and decay LESR spectra of P3HT:PCBM in vacuum sealed tubes at 60K measured for two different samples prepared from the same P3HT:PCBM blend.

**Power and modulation levels for the ESR measurement**

In order to get a reasonable signal-to-noise ratio of the LESR signal the power level has to be adjusted properly. The saturation effects should be possibly avoided. On the other hand due to a very low carrier concentration in the sample one wants to maximize the detected signal. Therefore the power level as high as 200 μW (30 dB), which corresponds with the polymer saturation maximum (maximum admissible power without saturation effects), is a good choice. Another source of artefacts which causes further broadening of the narrow peaks is the excessive modulation amplitude. In order to prevent this unwanted broadening the modulation amplitude should be kept below 1 G.

**Temperature and its influence on the recombination dynamics**

Low temperature is essential for increasing of the carrier lifetimes for the successful detection of the LESR spectra. Monitoring the peak dynamics under the constant illumination while sweeping the temperature can improve our insight into the studied problem. Figure S3 shows that different polymer fullerene blends show essentially the same kinetics when the temperature is swept from low to higher temperatures. This also supports the idea that the recombination processes in the samples are caused by tunneling rather than defects or traps. We believe that in the case of oxygen-free samples the spectra follow the model suggested by Schultz et al. based on the tunneling. In this model the recombination probability depends only on the spatial distance among the carriers and the energy barrier.11



Figure S3: Temperature dependence of the LESR spectra („light on“) of different polymer-fullerene blends measured on fullerene peak for thin semitransparent films. The spectra show virtually no difference for different blends favoring the tunneling model against the trap model.

**Thickness dependence**

Figure S4 shows a thickness dependences of the LESR signals and the rise and decay LESR curves in P3HT:PCBM and ZZ115:PCBM films. We have started with a semitransparent film in the tube and increased the film thickness subsequently by adding more material into the tube. The rise and decay LESR curves show a clear increase in the persistent part of the signal for thicker samples. This illustrates another serious problem for the “defect and trap” model because of the different decay behavior for different thicknesses. The bigger persistent part represents “deep traps” in this model and therefore one may “tune” the number of deep traps in the model based on the sample thickness. More favorable explanation for this type of behavior represents the tunneling model where we can see a transition from a quasi 2D type tunneling (semitransparent sample) to a 3D type tunneling with a clear saturation at higher thickness.



Figure S4: LESR and rise and decay LESR spectra of P3HT:PCBM (a, b) and ZZ115:PCBM (c, d) in flame-free suprasil EPR low pressure tubes for different thicknesses of films in vacuum measured at 60 K. The material was added into the tube in nitrogen filled glove box after each measurement cycle increasing the film thickness. Increasing the film thickness results in increase of the persistent part of the rise and decay LESR.

**g-factor shift and its influence on the recorded spectrum**

Temperature-dependent recombination spectra show some deviation at low temperature (below 50 K). This is obviously caused by the g-factor shift at those low temperatures in some of the polymer fullerene blends. The apex of the peak drifts whereas the static magnetic field stays constant during the whole measurement which causes the decrease of the signal at low temperature.

**Degradation pathway**

We show the evidence that in the properly evacuated and sealed tubes no degradation occurs when the samples are exposed to the visible or/and ultraviolet light even for a prolonged period of time. Conversely, the samples in which the vacuum was broken due to improper melting, defects in the quartz walls, or by intentional breaking of the tubes, show a significant increase of the polymer LESR peak and simultaneous disappearance of the fullerene LESR peak when exposed to the visible or ultraviolet light (Figure S5 and Figure S6).

 

Figure S5: Example of LESR spectra of the samples in leaky ESR tubes exposed to light from the sun simulator and UV lamp for different time intervals measured at 60 K. a) P3HT:PCBM, b) ZZ115:PCBM



Figure S6: a) Example of LESR spectra of the ZZ115:PCBM in a flame-free suprasil EPR low pressure tube before and after oxygen injection measured at 60 K. b) Room temperature LESR on the same sample showing that the progress in the sample degradation can be easily seen also without use of cryogenic temperatures which provides a very useful, fast and cheap method for the sample quality and stability evaluation.

LESR and rise and decay LESR spectra recorded for different polymer fullerene blends

 



Figure S7: LESR and rise and decay LESR spectra of P3HT:PCBM (a, b), PBDTT-CT:PCBM (c, d), PTB7:PCBM (e, f), ZZ50:PCBM (g, h). All these samples were proven to be leak-tight and the vacuum was preserved for the whole period of the investigation. Samples were measured at 60 K as prepared (t0), after 10 days under SS (t0+10) , after 25 days under SS (t0+25), after 33 days under SS (t0+33) and after additional 4 days under UV lamp (the sample with P3HT:PCBM followed slightly different but comparable light treatment). Samples were cooled during this simulated light degradation by a fan in order to prevent any heating degradation effects. No significant changes above the noise and error level in LESR spectra or in rise and decay LESR curves were observed in any of the investigated samples. This result shows that light itself without the presence of oxygen does not cause any degradation of the investigated samples. Due to a high number of labels and essentially overlapping spectra we decided not to include them in figures.

References

1. Carati, C., Bonoldi, L. & Po, R. Density of trap states in organic photovoltaic materials from LESR studies of carrier recombination kinetics. Phys. Rev. B 84, 245205 (2011). [↑](#endnote-ref-1)
2. Schultz, N., Scharber, M., Brabec, C. & Sariciftci, N. Low-temperature recombination kinetics of photoexcited persistent charge carriers in conjugated polymer/fullerene composite films. Phys. Rev. B 64, 245210 (2001). [↑](#endnote-ref-2)