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Transport-related triplet states and hyperfine couplings in organic tandem solar cells probed by pulsed electrically detected magnetic resonance spectroscopy

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ABSTRACT

Tandem solar cells constitute the most successful organic photovoltaic devices with power conversion efficiencies comparable to thin-film silicon solar cells. Especially their high open-circuit voltage – only achievable by a well-adjusted layer stacking – leads to their high efficiencies. Nevertheless, the microscopic processes causing the lossless recombination of charge carriers within the recombination zone are not well understood yet. We show that advanced pulsed electrically detected magnetic resonance techniques such as electrically detected (ED)-Rabi nutation measurements and electrically detected hyperfine sublevel correlation (ED-HYSCORE) spectroscopy help to understand the role of triplet excitons in these microscopic processes. We investigate fully working miniaturised organic tandem solar cells and detect current-influencing doublet states in different layers as well as triplet excitons located on the fullerene-based acceptor. We apply ED-HYSCORE in order to study the nuclear spin environment of the relevant electron/hole spins and detect a significant amount of the low abundant ^{13}C nuclei coupled to the observer spins.

1. Introduction

The power conversion efficiencies of organic solar cells (OSC) have steadily increased during the past decade, recently reaching efficiencies beyond 13% [1]. These record efficiencies, which are comparable to those of thin-film silicon solar cells [2], have so far only been achieved with multi-junction solar cells, i.e. two or more solar cells monolithically stacked on top of each other. Their elaborated architecture comprises a multitude of different absorbers, contact and recombination layers—even for tandem solar cells comprising only two subcells. The electrical transport in these devices with various layers and interfaces is rather complex and can be strongly influenced by localised states and defects through recombination and transport-limiting processes. Identifying and understanding the charge generation and extraction mechanisms as well as loss pathways will be the basis for developing strategies towards further efficiency enhancements.

The spin of the photo-excited states in organic tandem solar cells may be used to elucidate transport and excitation transfer pathways. In particular, the spin can be used to probe excitons at the internal interfaces as well as their influence on electrical transport in these devices.

For example, the formation of triplet excitons within the recombination zone plays a crucial role for the charge separation in tandem solar cells. The recombination zone fosters lossless recombination of opposite charge carriers from both absorber layers and thus attain the addition of the subcell voltages. So far, the influence of the spin statistics on the recombination process has not been investigated. Yet, it would be intriguing to see whether the formation of any triplet excitons influence the recombination process and hence the performance of the tandem solar cell.

On the other hand, triplet excitons can promote energy losses in OSC. Their binding energy, which is typically much larger than for singlet excitons, can lead to an open-circuit voltage (V_{OC}) drop and to a reduced device performance [3,4]. It was also reported that triplet excitons can open up a loss channel for intermediate charge transfer states via back electron transfer [5–9]. However, triplet excitons have a longer lifetime than singlet excitons and therefore may, in principle, exhibit larger diffusion lengths. Hence, the probability of exciton migration to a dissociation interface may be higher than for singlet excitons.

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Electrically detected magnetic resonance (EDMR) spectroscopy is the method of choice to investigate triplet excitons in OSC. EDMR provides the opportunity to identify triplet states based on their signatures known from electron paramagnetic resonance (EPR) spectroscopy [10–13,9,14,15] and hence allows to probe their influence on the photocurrent of the OSC. It was already reported that EDMR is a powerful tool for studying charge carrier transport and recombination in single junction inorganic [16,17] and organic solar cells [18–22].

Here we investigate organic tandem solar cells using pulsed (p) EDMR spectroscopy. Their advanced device architectures result in rather complicated EDMR spectra with many spectral contributions from various layers. Field-sweep pEDMR in combination with more advanced EDMR techniques helps us to understand these complex spectra and to draw conclusions on spin-dependent processes influencing the efficient charge separation in tandem solar cells.

In order to disentangle the pEDMR spectra, we performed electrically detected Rabi nutation (ED-Rabi) measurements to separate the pEDMR spectrum into sub-spectra stemming from paramagnetic centres associated with different spin states ($S = 1/2$ and $S = 1$). In a second step, we investigated the current-influencing paramagnetic states with regard to their microscopic nuclear environment using electrically detected hyperfine sublevel correlation (ED-HYSCORE) spectroscopy. We demonstrate that these two sources of information (ED-Rabi nutations and ED-HYSCORE) can usefully complement the picture of fundamental processes in organic tandem solar cells.

2. EDMR background information

EDMR spectroscopy is a well-established technique to investigate the influence of spin interactions on the macroscopic photocurrent of solar cells and light emitting diodes [23,24]. It probes the resonant current change (resulting from resonant microwave absorption) and hence directly detects conductivity-influencing paramagnetic centres. The first continuous wave (cw) EDMR experiments, in which microwave (mw) radiation is continuously applied to the sample, was already applied to silicon-based devices in 1966 [25,26]. This cwEDMR technique can provide information about the *g*-values (microscopic fingerprint of a paramagnetic centre) and spectral signatures of current-influencing paramagnetic centres.

In analogy to pulsed EPR, also pEDMR experiments using short mw-pulses instead of continuous irradiation for the spin manipulations were developed. The pEDMR technique can be used to explore the microscopic environment of the paramagnetic centres by sensing the coupling between two electron spins (exchange and dipolar) and electron-nuclear (hyperfine) interactions. Further, it provides insight into the dynamics of the spin-dependent processes [17]. Also, a direct correlation between polaron pair states detected by transient EPR spectroscopy [27,28] and their influence on the photocurrent was recently demonstrated by transient (tr) EDMR spectroscopy [20].

In order to quantify the hyperfine (hf) interaction between current-influencing electron spins and nuclear spins in their vicinity, advanced pEDMR techniques such as ED-electron spin echo envelope modulation (ED-ESEEM) [29,30], ED-electron nuclear double resonance (ED-ENDOR) [31], and ED-HYSCORE [32] were adapted from pEPR with slight modifications, making them compatible with the electrical detection scheme. It was shown that these techniques are useful to explore the nuclear environment of the current-influencing spin states.

In ED-ENDOR experiments, radio-frequency pulses, selective for nuclear spins, are applied in addition to mw-pulses to probe the influence of nuclear spin manipulations on the electron spins. The advantage of this method is its capability to detect strong isotropic hf-couplings [31].

In contrast, ED-ESEEM and ED-HYSCORE experiments do not use direct nuclear spin manipulation. They use sequences of short mw-pulses exciting forbidden transitions within the electron-nuclear spin system. They are especially sensitive to weak and anisotropic hf-couplings. The two-dimensional HYSCORE experiment is an advancement of the one-dimensional ESEEM technique, which allows a better separation of the hf-spectrum of nuclei with comparable nuclear Larmor frequencies. In particular, it provides the opportunity to distinguish between the influence of isotropic and anisotropic hf-interactions and to identify contributions of weakly coupled (first quadrant) and strongly coupled (second quadrant) nuclei in the two-dimensional spectrum. Additional information about the HYSCORE technique can be found in the literature [33,34]. A detailed description of the EDMR equivalent, ED-HYSCORE, and of the used pulse sequences are given in Ref. [32].

ED-Rabi nutation experiments are, in general, very useful preparation measurements for all pEDMR echo experiments. They allow us to deduce the lengths of mw-pulses with well-defined flip angles $\pi/2$ or π ($t_{\pi/2}$ or t_{π}). Furthermore, Rabi nutations can be used to determine the spin-multiplicity of the observed spin state by evaluating the nutation frequency ω [35,36]. The nutation frequency depends on the following relation between the total spin quantum number S and the mw-magnetic-field strength B_1 at the position of the sample:

$$\omega_{m_s,m_{s\pm1}} = \Omega\sqrt{S(S+1) - m_s(m_s \pm 1)} \tag{1}$$

with $\Omega = \gamma_i B_1 = g_i \mu_B B_1/\hbar$ (in resonance), γ_i being the gyromagnetic ratio and g_i the *g*-value of the *i*-th spin, S the total spin quantum number and m_s indicating the spin sublevels. The frequencies ω of a spin-1 (triplet) is by a factor of $\sqrt{2}$ larger than that of a spin-1/2 (doublet). This difference can be used to separate doublet and triplet states in a pEDMR measurement. This is particularly helpful if the spectra of weak triplet signals overlap with stronger doublet signals.

An EDMR measurement probes the interaction between two or more spins. In the case of a two-dimensional Rabi nutation experiment, probing two weakly coupled doublets with the same or similar *g*-values, the FFT spectrum consists of a main signal centered at Ω and a Rabi parabola (B_0 in off-resonance) described by

$$\Omega(B_0) = \sqrt{(\gamma B_1)^2 + (\omega_{mw} - \gamma B_0)^2} \tag{2}$$

with ω_{mw} being the angular frequency of the mw and γB_0 being the Lamor frequency of the probed spin. This equation describes the relation between the oscillation frequency Ω and the amplitude B_1 of the oscillatory mw magnetic field [37–39]. In addition, a signal can occur at 2Ω, if the excitation bandwidth of the mw-pulse is sufficiently broad to flip both contributing spins at the same time. This phenomenon is called spin-locking [18,19]. Spin-locking was also reported for an organic solar cell originating from a positive and negative polaron with different *g*-values [21].

3. Materials and sample preparation

The organic tandem solar cells were fabricated on fused silica glass substrates (2.5×57.5 mm^2 to fit into the mw-resonator used in the experiment) carrying a prepatterned indium-doped tin oxide (ITO) electrode ($< 20\ \Omega/\square$). After ultrasonication in acetone and 2-propanol (10 min each), all substrates were transferred into a nitrogen filled glovebox for subsequent layer deposition following a procedure published before [40]. To enable spin coating of homogeneous layers on such narrow substrates, they were fixed