



## Light-induced electron spin resonance study of galvinoxyl-doped P3HT/PCBM bulk heterojunctions



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### ABSTRACT

We report the effects of doping of P3HT/PCBM layers with spin 1/2 radicals of galvinoxyl (Gx) based on light-induced electron spin resonance (LESR), photoluminescence-detected magnetic resonance (PLDMR), and post-annealing experiments.

LESR showed both a P3HT<sup>+</sup> and PCBM<sup>-</sup> signal for undoped P3HT/PCBM; however, as Gx doping increased (above ~1 wt%), only the P3HT<sup>+</sup> signal was evident in the LESR spectra, with no PCBM<sup>-</sup> signal.

The PLDMR exhibited a strong narrow signal at  $g = 2.002$  that originates from nongeminate polaron pairs; no triplet PLDMR signal has been observed throughout the whole range of Gx concentrations ( $x = 0, 0.1, 1, 2, 4, 12$  wt%). Adding Gx to ~3 wt% led to a decrease of the PL-enhancement.

There was big difference between the slow-dried P3HT/PCBM samples and the post-annealed samples. For the slow-dried samples, efficiency monotonously decreased with Gx additives. When post-annealed, however, an enhancement in  $\eta$  was observed at ~2 wt% for P3HT/PCBM(1:2) samples.

The LESR spectra for post-annealed samples revealed disappearance of Gx spin signals, and thus no spin interactions with PCBM<sup>-</sup> spins. It is unlikely that the increase of efficiency after Gx doping of P3HT/PCBM solar cell is due to an increase of triplet states.

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### 1. Introduction

Energy conversion of a bulk heterojunction photovoltaic device depends critically on photoinduced charge transfer, charge separation, and charge carrier collection at the electrodes. Upon light absorption by the polymer/fullerene blend of regio-regular poly(3-hexylthiophene-2,5-diyl) (P3HT) (donor–D) and phenyl-C61-butyric acid methyl ester (PCBM) (acceptor–A), excitons are

initially photogenerated in the P3HT polymer chains [1]. These excitons diffuse first towards D–A interfaces within ~10 ps [2–4], where upon arrival, they form charge transfer excitons [5,6]. Fast charge transfer effectively prevents the primary excitons from recombination and, thus, establishes the basis for quantum efficiencies close to unity.

Charge transfer is succeeded by the formation of an intermediate charge transfer complex (CTC) at the heterojunction [5–8], whose dissociation finally yields separated polarons – a positive polaron in the polymer and a negative polaron in the electron-accepting material [8]. It is generally assumed that the CTC resembles hybrid states at the heterojunction, formed by polymer highest occupied molecular orbital (HOMO) and fullerene lowest unoccupied molecular orbital (LUMO) levels that are occupied by P<sup>+</sup> and P<sup>-</sup>, respectively [8]. Coulombically-bound polaron pairs

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( $P^+P^-$ ) are intermediate species at D–A domain interfaces that have relatively long lifetimes (namely, a few microseconds) [1]. At a later time, the  $P^+P^-$  species may separate into ‘free’ electrons and hole polarons available for charge transport via the A and D domains, and can be collected at the anode and cathode, respectively.

Recently, Zhang et al. presented a method to improve the efficiency ( $\eta$ ) of organic photovoltaic solar cells that involves doping the device active layer with spin 1/2 radical galvinoxyl (Gx) [1]. As Gx is a spin 1/2 radical, photogenerated polaron–polaron ( $P^+P^-$ ) pairs are converted from spin singlets to triplets via spin exchange interactions, thus enhancing the lifetime of  $p^+p^-$ , which facilitates polaron–polaron ( $p^+p^-$ ) pair separation at P3HT/PCBM interfaces.

The shape of the light-induced electron spin resonance (LESR) spectrum of P3HT:PCBM bulk heterojunctions has usually been understood as the superimposition of signals from radical cations (P3HT $^+$ ) and anions (PCBM $^-$ ) [9]. To see the P3HT $^+$  and PCBM $^-$  signals, strongly bound neutral excitons must break down into two spin-carrying charged counterparts, P3HT $^+$  and PCBM $^-$  [10].

Here we report a LESR, photoluminescence detected magnetic resonance (PLDMR), and post-annealing study of spin 1/2 radical Gx-doped P3HT:PCBM blends. The results are discussed in relation to Zhang et al.’s model [1] that describes the increase of photocurrent in P3HT/PCBM blend by doping of Gx.

## 2. Experiments

To make standard P3HT/PCBM organic photovoltaics (OPV) samples, P3HT (Rieke Metal Inc.) and PCBM (Nano-C Inc.) were mixed with 1,2-dichlorobenzene (*o*-DCB; Aldrich) solution. The donor-acceptor (D–A) weight ratio was set at 1:0.8.

To make galvinoxyl-doped P3HT/PCBM samples, galvinoxyl powder (Aldrich) was mixed with 1,2-dichlorobenzene (*o*-DCB; Aldrich) solution (1.0 ml) at the weight ratio of 0.1, 1, 2, 4, 8, and 12 wt% to P3HT/PCBM (24 mg:19.2 mg), then stirred at 450 rpm at 40 °C for 12 h in N $_2$ .

After filtering P3HT and PCBM solution mixed with galvinoxyl through a PTFE 0.45  $\mu$ m filter, the solution was spin-coated on a transparent indium tin oxide (ITO) coated glass substrate at 400 rpm for 60 s and then 2000 rpm for 3 s, and then slowly dried at room temperature for an hour in a N $_2$  glove box, then capped with LiF/Al cathode. The thickness of the active blend layers was  $\sim$ 220 nm. If needed, some P3HT/PCBM samples were post-annealed at 150 °C/20 min in N $_2$ .

The current density-voltage ( $J$ – $V$ ) curves of the OPV cells were measured under the solar irradiation of 100 mW/cm $^2$  at the condition of AM 1.5 global. The light intensity of solar simulator was calibrated with a standard Si photodiode.

To make LESR samples, the P3HT/PCBM active layer was prepared in the same way on PET substrate. The samples were cut into small pieces in the air for a few minutes and then placed in N $_2$ -sealed ESR quartz tubes to protect them from moisture and oxygen.

ESR measurements were taken using a Bruker EMXplus apparatus. ESR spectra were recorded for samples in standard ESR quartz tubes. Samples were excited by a laser diode (Toptica Photonics AG; 515 nm) through an optical fiber that terminated at the cover of the cavity. The exciting light entering the cavity was unfocused and estimated to be 50 mW. Low-temperature (4 K–150 K) measurements were carried out. These measurements were performed at low microwave powers, at which both magnetic resonance signals are in a nonsaturated regime. ESR intensities of the signals were calculated by double integration of the first derivative spectra.

For PLDMR, the same setup as in X-Band ESR was used, with a frequency synthesizer (Wiltron 69137A) as the microwave source. The microwaves amplified by a solid state amplifier arrive in the

cavity with a power of  $\sim$ 60 mW. Instead of the microwave absorption, the variation of PL intensity ( $\Delta$ PL) due to resonant microwave irradiation was recorded. The measurements were performed with a lock-in amplifier, referenced by switching the microwave radiation on/off in the kHz range. All PLDMR measurements shown here were recorded at T = 10 K.

## 3. Results and discussion

LESR spectra of an P3HT/PCBM(1:0.8) film are shown in Fig. 1a. Illumination was provided by a 515 nm laser ( $\sim$ 50 mW). To better observe the light-induced ESR signal, a temperature of 50 K was used. Under photoexcitation, an intense LESR signal (designated ‘‘L’’) with two peaks was found ( $g = 2.002$  and  $g = 1.999$ ), confirming earlier results [11–13]. The broader signal at lower magnetic fields was ascribed to positive polarons (P3HT $^+$ ) on the polymer chain, and the narrow signal at higher fields was ascribed to electrons on PCBM (PCBM $^-$ ) [9,14]. P3HT/PCBM samples showed a dark ESR signal (designated ‘‘D’’) before illumination with light. The dark ESR signal is usually attributed to deep trapped carriers [11] related to oxygen or moisture. In Fig. 1b, we defined the term ‘‘net LESR’’ (‘‘L–D’’) as the light-on signal corrected for the dark signal. The net LESR originated from the already dissociated charge carriers, P3HT $^+$  and PCBM $^-$ . The intensity of the L–D spectrum is in general proportional to the amount of light-induced charges. If light is turned off, part of the net-LESR disappears promptly, while some of the net-LESR remains persistently (‘‘P’’). The prompt component of LESR (‘‘L–P’’) disappears as light is switched off. The transient L–P signal vanishes through P3HT $^+$  PCBM $^-$  bipolar recombination. L–P corresponds to light-induced mobile carriers. The prompt component of LESR (L–P) disappears as the light is switched off, because the two photoinduced mobile charges

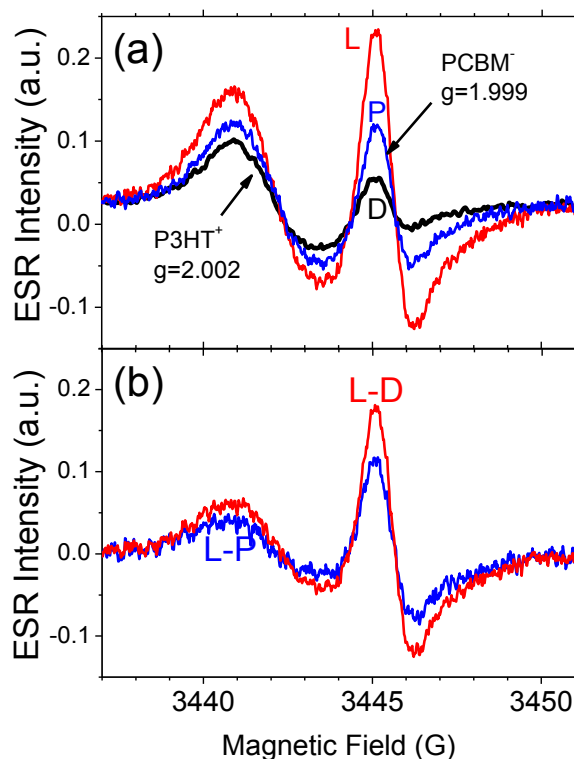


Fig. 1. (a) LESR spectra for an undoped P3HT/PCBM(1:0.8) sample. ESR spectra were recorded at 50 K and 0.1 mW of microwave power. Illumination was provided by a 515 nm laser at 50 mW. The P3HT/PCBM solution was stirred in N $_2$ . (b) L–P and L–D spectra for the (a) sample.

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