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Abstract A variation of the electron spin echo (ESE) signal caused by laser pulse in a blend of [6,6]-phenyl C₆₁ butyric acid methyl ester and poly(3-hexylthiophene) (P3HT:PCBM) was detected. This variation was attributed to light-generated paramagnetic species in P3HT:PCBM blend, with non-equilibrium spin polarization. The echo-detected electron paramagnetic resonance (EPR) spectrum of these species closely resembles the time-resolved EPR spectrum of spin-correlated polaron pair PCBM⁻/P3HT⁺ (Behrends et al. in Phys. Rev. B 85:125206, 2012) and was assigned to this pair. The characteristic times for polarization and coherence decay (9 ± 1 and 1.0 ± 0.2 µs, respectively) were measured for the PCBM⁻/ P3HT⁺ pair at 77 K. These times are long enough, which shows the possibility of the application of the ESE technique for studying spin evolution of light-generated charge transfer intermediates in composites of fullerenes and conductive polymers.

1 Introduction

Composites of fullerenes and conductive polymers are promising materials for plastic solar cells [1, 2]. Since bulk heterojunction is formed in these composites, they are widely used as an active layer in photovoltaic devices. While the light to electricity power conversion efficiency of such devices continues to increase, its presently achieved maximum value is about 7% [3, 4], which is below the commercially interesting level.

Understanding the nature of the intermediates of light-driven charge separation in polymer/fullerene composites is crucial for optimization of their composition and morphology, which is the main way of increasing power conversion efficiency of

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plastic solar cells [5, 6]. In polymer/fullerene blends, the light-generated excitons dissociate within a few picoseconds [7], resulting in the formation of polaron pairs, with each of them consisting of a delocalized cation radical of the polymer and an anion radical of the fullerene. Since these polarons are paramagnetic, electron paramagnetic resonance (EPR) is a method of choice for the study of post-nanosecond intermediates of light-driven processes in polymer/fullerene composites [8, 9]. The most widely used technique for such studies is continuous-wave (CW) EPR [10–14] under stationary light illumination of the sample. However, it lacks temporal resolution and thus does not allow one investigation of polaron pair evolution.

Recently, time-resolved (TR) EPR signal was detected for the polaron pair in the blend of [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3HT), Fig. 1, the most popular polymer/fullerene composition at present [15]. The TR EPR had emissive and absorptive components, and the spectral shape was characteristic for geminate spin-correlated radical pair (for the case of polymer/fullerene blends it is usually called "polaron pair"). It was concluded that for small values of delay after flash (DAF), the majority of the polarons are coupled in these pairs (charge transfer complexes) and experience magnetic interaction (exchange and/or dipolar) within the pair. For more detailed determination of the type and magnitude of magnetic interactions between the components of polaron pair the electron spin echo (ESE) experiments are needed. Especially desired is the observation of the out-of-phase ESE [16–19], which provides direct information about the magnitude of magnetic interactions and the interspin distance in the spin-correlated radical pair.

However, up to now no ESE signals were reported for the polaron pairs of polymer/fullerene composites generated by laser flash in their non-equilibrium spin state. This is caused mainly by small volume of the blend effectively illuminated in the ESE experiment, and by a relatively low sensitivity of the ESE technique, as compared to CW EPR. In the present paper, the polarized ESE signal of spin-correlated polaron pair PCBM⁻/P3HT⁺, appearing upon laser excitation of the P3HT:PCBM blend is observed for the first time. The spin relaxation times for this pair are determined.

Fig. 1 Chemical structures of [6,6]-phenyl C_{61} butyric acid methyl ester (*PCBM*) and poly(3-hexylthiophene) (*P3HT*)



OCH₃

PCBM

98

2 Experimental

2.1 Sample Preparation

The solution of 400 µl toluene and 0.5 mg PCBM (Aldrich) and 0.5 mg P3HT (Aldrich) was prepared using ultrasonic bath. The solution was put in the quartz EPR tube of 4.5-mm outer diameter, and three freeze–pump–thaw cycles were performed. Toluene was evaporated in vacuum of about 0.1 torr, which resulted in the formation of the P3HT:PCBM blend on the inner wall of the EPR sample tube. The sample was annealed at 450 K during 20 min and the tube was sealed. The thickness of P3HT:PCBM blend was slightly inhomogeneous over the sample, with estimated thickness of 2 µm. Since the typical absorption coefficient of the P3HT:PCBM blend at 532 nm is about 10^5 cm^{-1} [20], the thickness of the blend ensures complete absorption of the laser light in our setup.

2.2 Experiments with Stationary Light Illumination

CW EPR and ESE measurements were carried out on an X-band ELEXSYS ESP-580E EPR spectrometer equipped with an ER 4118 X-MD-5 dielectric cavity inside an Oxford instruments CF 935 cryostat.

The following parameters of CW EPR experiments were set: microwave power (mw), 63 μ W; magnetic field modulation frequency, 100 kHz; magnetic field modulation amplitude, 1 G.

ESE signal was obtained using a two-pulse mw pulse sequence $\pi/2-\tau-\pi$ -echo, where the $\pi/2$ and π pulses were of 24 and 48 ns duration, respectively, and the τ delay was 120 ns. The whole echo signal in the time domain was integrated within an integration time window 80 ns centered at the echo maximum.

Samples were illuminated by continuous light irradiation of an Xe lamp, equipped with a filter transmitting light in the range between 350 and 700 nm. The estimated light power reaching the sample was about 10 mW. Temperature was kept at 80 K by cold nitrogen gas flow.

2.3 Experiments with Laser Pulse Illumination

ESE experiments were carried out on an X-band Bruker ESP-380E FT EPR spectrometer equipped by a homebuilt rectangular resonator [21] with a circular hole of 4-mm diameter in the center of the front wall. A refractive lens was mounted on this wall, with its optical axis passing through the center of the hole. The sample was placed in the quartz Dewar vessel filled with liquid nitrogen, so the sample temperature was 77 K. The vessel was fixed in the resonator, with the sample positioned at the center of the resonator. Illumination from Nd-YAG laser Surelite I-10 was used, with wavelength 532 nm, pulse duration 10 ns, and pulse repetition rate 10 Hz. The laser light was directed to the refractive lens along its optical axis. After passing through the lens and the hole in the resonator wall, the laser pulse illuminated 0.4×1 cm² of the sample area with about 5 mJ/cm² density of energy per flash. Such geometry of the experiment allows nearly complete illumination of

polymer/fullerene blend in the sample with easily controlled light intensity. The contact of the sample with liquid nitrogen is also important for successful observation of ESE signal of laser-generated polaron pair. Such contact ensures better heat sink from the sample than nitrogen gas flow. This allows the use of a higher laser flash intensity and to produce higher polaron concentration without sample degradation caused by overheating.

For the ESE detection, the sequence flash DAF $-\pi/2-\tau-\pi$ -echo was used, where the $\pi/2$ and π pulses were of 24 and 48 ns length, respectively, and the τ delay was 320 ns. Such a long τ delay was used because of the resonator ringing, which made the detection of a relatively weak ESE signal at shorter τ delays problematic. The whole echo signal in the time domain was integrated within an integration time window 160 ns centered at the echo maximum.

Quadrature detection was used. The phase for the echo (in-phase) was adjusted by the dark ESE signal of accumulated polarons in the P3HT:PCBM blend (see below). All the ESE signals presented in this paper refer to the in-phase component of ESE.

3 Results and Discussion

CW EPR spectra of the P3HT:PCBM blend before and during the stationary light illumination are shown in Fig. 2a as solid and dashed lines, respectively. The spectrum obtained under illumination is similar to that obtained previously for the P3HT:PCBM blend [22] and is composed of the signals of PCBM⁻ and P3HT⁺ polarons at stationary concentration. A small dark signal was obtained before the illumination. It probably originates from residual P3HT⁺ polarons [10].

Figure 2b shows the echo-detected (ED) EPR spectrum of the P3HT:PCBM blend under the stationary light illumination. As expected, its shape is close to the integrated CW EPR signal (Fig. 2a), although some broadening can be noticed for ED EPR spectrum. This broadening is probably caused by a relatively large excitation bandwidth of the mw pulses compared to that of the continuous mw irradiation of CW EPR. Integration over the echo signal is known to reduce this effect. However, at our experimental conditions, the excitation bandwidth broadening of ED EPR spectra is not canceled completely.

It is well known that some fraction of photogenerated polarons in the P3HT:PCBM blend has a relatively long lifetime at cryogenic temperatures (in the order of min) [23]. In our experiments, they are accumulated under the action of the laser flashes and their electron spins relax to Boltzmann equilibrium with the longitudinal electron spin relaxation time T_1 in the order of tens to hundreds microseconds (see below). The ED EPR spectrum of the accumulated polarons in the P3HT:PCBM blend is shown as dotted line in Fig. 3. This spectrum was recorded with synchronization between the laser pulses and mw pulses switched off. Since the repetition time of the laser flashes in our experiment (100 ms) is much longer than T_1 of the polarons in the P3HT:PCBM blend, one can assume that they are at thermal equilibrium at the conditions described. As expected, this spectrum (dotted line in Fig. 3) is similar to the ED EPR spectrum of the P3HT:PCBM under



Fig. 2 a CW EPR spectra of the P3HT:PCBM blend. *Solid line* before illumination. *Dashed line* under stationary illumination. **b** ED EPR spectrum of the P3HT:PCBM blend under stationary illumination. The magnetic field differs between **a** and **b** because of the difference in mw frequency

stationary illumination (Fig. 2b). Some dark background contributes to the wings of the spectrum of the accumulated polarons in Fig. 3. It is probably caused by paramagnetic centers in the quartz Dewar and quartz sample tube.

The dashed line in Fig. 3 shows the ED EPR spectrum obtained after the laser flash with DAF = 0.1 μ s. All the experimental conditions (except the synchronization between laser and mw pulses) for this spectrum are the same as for the previously described spectrum of the accumulated polarons in Fig. 3. However, these spectra are clearly different. The difference between the ED EPR spectrum obtained for DAF = 0.1 μ s and the ED EPR spectrum of the accumulated polarons in the P3HT:PCBM blend is shown as a solid line in Fig. 3. We assign it to paramagnetic intermediates, generated by the laser flash in the P3HT:PCBM blend.



Fig. 3 *Dashed line* ED EPR spectrum of the P3HT:PCBM blend obtained after laser flash with DAF = $0.1 \ \mu$ s. *Dotted line* ED EPR spectrum of the polarons accumulated under the action of laser flashes in the P3HT:PCBM blend without synchronization of laser pulse with the echo-forming mw pulse sequence. *Solid line* flash-induced ED EPR spectrum of the PCBM⁻/P3HT⁺ pair (the difference between the spectra is shown by *dashed* and *dotted lines*; see text). The *horizontal line* indicates zero signal level

Hereinafter, the spectra obtained by this procedure will be referred to as "flashinduced ED EPR" spectra. Such spectra are an ESE analog of TR EPR spectra: in both methods the laser flash-induced change of the mw absorption is measured.

The flash-induced ED EPR spectra obtained for different DAF values in the P3HT:PCBM blend are shown in Fig. 4. For small DAF values, these spectra demonstrate strong non-equilibrium spin polarization, with low-field emissive and high-field absorptive components. This spectral shape is very similar to that of TR EPR spectra, obtained for the P3HT:PCBM blend [15]. Also, g values of the characteristic spectral features in Fig. 4 (2.003 \pm 0.001 for the low-field minimum and 2.000 \pm 0.001 for the high-field maximum) are close to those previously obtained. Therefore, we assign the flash-induced ED EPR spectra in Fig. 4 to the geminate spin-correlated polaron pair PCBM⁻/P3HT⁺.

With DAF increase, the flash-induced ED EPR spectra of the PCBM⁻/P3HT⁺ pair change. Again, this evolution is similar to that obtained for the TR EPR spectra of the PCBM⁻/P3HT⁺ pair [15]. On the timescale of several microseconds, the low-field emissive component disappears. At DAF = 30 μ s, the whole flash-induced ED EPR spectrum becomes weakly absorptive.

Despite an overall similarity between the present flash-induced ED EPR spectra of the PCBM⁻/P3HT⁺ pair and the TR EPR spectra obtained in Ref. [15], there are some differences between them. First, at small DAF the ED EPR spectrum has *EA* polarization pattern, in contrast to *EAEA* polarization pattern of TR EPR spectrum, i.e., a narrow weak *AE* feature is absent in the ED EPR spectrum (here A = absorption, E = emission). This is probably caused by an mw excitation bandwidth broadening of the flash-induced ED EPR spectra, similarly to the above



Fig. 4 Flash-induced ED EPR spectra obtained for different DAF values in the P3HT:PCBM blend. $DAF = 0.1, 3, 10, 30 \ \mu s$ from *bottom* to *top*

case of the ED EPR spectra of the P3HT:PCBM blend under continuous light illumination. Due to this effect, narrow spectral features are smeared out in the ED EPR spectra. Second, the polarization pattern of the ED EPR spectra at intermediate DAF values 3 and 10 μ s is still *EA*, in contrast to *AEA* and *AA* patterns for the TR EPR spectra at the DAF values 3.5 and 10 μ s, respectively [15]. This can be explained by a slower dissociation of the polaron pair PCBM⁻/P3HT⁺ into free polarons and/or slower spin–lattice relaxation of the polarons of 77 K (temperature at which the ED EPR spectra were recorded in the present work) than at 100 K (temperature at which the TR EPR spectra were recorded in Ref. [15]).

The DAF dependence of the flash-induced ESE signal at the low-field component $(B_0 = 3371 \text{G})$, see Fig. 4) is shown as a thin line in Fig. 5. It can be approximated by a single exponential decay with the characteristic time $9 \pm 1 \,\mu\text{s}$ (thick line in Fig. 5). Solid and dashed lines in Fig. 6a show the two-pulse ESE decay traces for the P3HT:PCBM blend under stationary illumination, obtained for $B_0 = 3459.5 \,\text{G}$ and $B_0 = 3456 \,\text{G}$, respectively. Since g factors of PCBM⁻ and of P3HT⁺ are different, the former signal originates mainly from PCBM⁻, while the latter is caused mainly by P3HT⁺ [8] (see Fig. 1). Both curves can be perfectly approximated by a single exponential decay, with the characteristic times $T_2 = 2.4 \pm 0.3 \,\mu\text{s}$ for PCBM⁻ and $T_2 = 1.8 \pm 0.3 \,\mu\text{s}$ for P3HT⁺ (data not shown).

The thin line in Fig. 6b shows the decay of the two-pulse flash-induced ESE with τ increased for the low-field component of the PCBM⁻/P3HT⁺ pair spectrum ($B_0 = 3371$ G) for DAF = 0.1 µs. This curve can be reasonably well approximated by a single exponential decay with the characteristic time $T_2 = 1.0 \pm 0.2$ µs (thick line in Fig. 6b).



Fig. 5 *Thin line* DAF dependence of flash-induced ESE signal at low-field component ($B_0 = 3371$ G). *Thick line* approximation of this DAF-dependence by single exponential decay

Due to the complexity of the studied system, the spin relaxation times are not easy to interpret. The inversion-recovery curves for PCBM⁻ and P3HT⁺ under stationary illumination at 80 K (data not shown) are markedly non-exponential, with characteristic times in the range from about 10 to several hundred microseconds for both PCBM⁻ and P3HT⁺. The observed time of the flash-induced ESE decay with DAF increase at 77 K is close to the lower edge of this range and thus may reflect the spin–lattice relaxation of the PCBM⁻ and P3HT⁺ spins in the PCBM⁻/P3HT⁺ pair from spin-correlated state to thermal equilibrium. A smaller value of T_2 for the spin-correlated polaron pair PCBM⁻/P3HT⁺, as compared to that of accumulated polarons, may be caused by increased polaron mobility at the initial stage of the PCBM⁻/P3HT⁺ pair evolution. While the detailed analysis of the spin relaxation mechanisms in this system is beyond the scope of the present paper, the obtained data clearly show that T_1 and T_2 times of the spin-correlated polaron pair PCBM⁻/ P3HT⁺ are long enough, which allows studying its spin dynamics by the ESE technique.

For more detailed characterization of the geometry of spin-correlated polaron pair PCBM⁻/P3HT⁺, an observation of the out-of-phase ESE for this pair would be very helpful. However, the out-of-phase component of the flash-induced ED EPR spectrum was very weak and can be hardly found in the experimental noise. It is established that for generating of the out-of-phase ESE in spin-correlated radical pairs, the electron spins of both components of the pair should be excited by mw pulses, i.e., these pulses should be non-selective [24, 25]. A possible reason of our failure to observe the out-of-phase ESE for the PCBM⁻/P3HT⁺ pair is incomplete mw excitation of the EPR spectrum of this pair in our setup. An indication of partial selectivity of the mw excitation in our experiment is the pronounced emissive/ absorptive polarization of the in-phase flash-induced ED EPR spectrum of the PCBM⁻/P3HT⁺ pair. This is in marked contrast with the absence of the *in-phase* ESE signal in photosynthetic spin-correlated radical pair at the conditions of nonmw excitation, predicted theoretically [16, 17] selective and observed



Fig. 6 a Solid and dashed lines two-pulse ESE decay traces for the P3HT:PCBM blend under stationary illumination, obtained for $B_0 = 3459.5$ G and $B_0 = 3456$ G, respectively. **b** Thin line decay of the two-pulse flash-induced ESE with τ increase for low-field component of the PCBM⁻/P3HT⁺ pair spectrum ($B_0 = 3371$ G) for DAF = 0.1 µs. Thick line approximation of this decay by a single exponential

experimentally [18, 26]. Another expected difficulty for observing the out-of-phase ESE of the PCBM⁻/P3HT⁺ pair is the possible distribution of the effective interspin distances between the polarons in the pair and the corresponding distribution of the parameters of dipolar and exchange interaction. This leads to a faster decay of the out-of-phase ESE with the increase of the interval between the mw pulses, as compared to the in-phase ESE decay [27].

4 Conclusion

In the present work, the ESE signal of spin-correlated polaron pair the PCBM^{-/} P3HT⁺, generated by laser flash irradiation of the P3HT:PCBM blend is detected for the first time. The shape of the ED EPR spectrum of this pair and its evolution with the increase of DAF are surprisingly similar to those of the TR EPR spectrum

obtained for such a blend. The characteristic times for polarization and coherence decay (9 and 1.0 μ s, respectively) were measured for PCBM⁻/P3HT⁺ at 77 K. Only the in-phase component of ESE of the spin-correlated polaron pair PCBM⁻/P3HT⁺ was detected clearly in the present work. An optimization of the experimental setup with an aim of detecting the out-of-phase ESE in this system is in progress now.

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