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Photoinduced charge carriers in conjugated polymer–fullerene composites studied with light-induced electron-spin resonance

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Detailed studies on photoinduced spins in conjugated polymer/fullerene composites using (cw) light-induced electron-spin-resonance (LESR) technique are reported. Two overlapping LESR lines are observed, from positive polarons on the polymer chains and negative charges on the fullerene moieties. Microwave power saturation studies show different relaxation times for these two spins, ruling out spin-exchange correlations, giving clear evidence of independent spins. The unusually high relaxation rate of the fullerene monoanionic spins is of intrinsic origin, and discussed in terms of a splitting of the T_{1u} level by a Jahn-Teller-type distortion as proposed in the literature. Further, we observed two distinct contributions to LESR signals: a prompt one and a persistent one. The excitation light intensity dependence of the prompt contributions into the P^+ and $C_{60}{}^-$ ESR signals is of bimolecular type ($I^{0.5}$), and implies mutual annihilation within the created ($P^+ \ldots C_{60}{}^-$) pair. The persistent contribution is found to be excitation intensity independent, and is proposed to originate from deep traps due to disorder. [S0163-1829(99)0112-X]

INTRODUCTION

Photoinduced electron transfer in solid-state composites of semiconducting conjugated polymers and fullerenes has recently attracted considerable scientific and technological attention.[1–12] The possibility of utilizing this effect for photovoltaic energy conversion,[5,8,13–17] as well as for nonlinear optical devices such as optical limiters and transient holographic systems, has been demonstrated.[18–21] The photoinduced forward electron transfer occurs within a picosecond time scale[22,23] and the charge-separated state is long lived (milliseconds at 80 K).[1,24] Indeed, by doping the conjugated polymer matrix with a few wt % fullerenes, a strong quenching of the photoluminescence[1,6,24] and an increase of photoconductivity of nearly two orders of magnitude[7,25,26] has been observed.

Preliminary light-induced electron-spin-resonance (LESR) studies on conjugated polymer/fullerene composites have been reported, and revealed the appearance of two LESR signals.[1,4,27–29] These signals were attributed to radical anions on the fullerene molecule and positive polarons on the polymer chain. For composites of fullerenes and thiophene oligomers, similar results have been obtained.[27] The LESR spectrum of conjugated polymer/fullerene composites, however, is not clearly understood. An exact analysis of the line shapes is difficult due to the strong spectral overlap of the two LESR signals. Assignment of the particular LESR signal to radical anions or radical cations requires a knowledge of g factors. Dark ESR and LESR signals in undoped polyphenylene-vinylene (PPV) were observed by Murata *et al.*[30] They were attributed to positive polarons, which are trapped on defect states and photogenerated, respectively. The g factor was found to be anisotropic, and was larger than 2 ($g = 2.004$ and 2.0023) for both signals. ESR studies on fullerene radical anion salts[31–35] revealed the g factor for $C_{60}{}^-$ as 1.999x, i.e., smaller as 2. We did not find dark ESR or LESR in the vacuum-sealed, pristine, conjugated polymer components used in our work. A strong dark ESR signal appears, however, in the presence of ambient atmosphere. On the other hand, highly sensitive photoluminescence-detected magnetic resonance[9,36,37] and magnetic-field spin-effect experiments[38] indicate the photoinduced formation of oppositely charged polarons in pairs in the conjugated polymers even without the addition of fullerenes. With the addition of C_{60} into the conjugated polymer matrix, the primary photoexcitation of the conjugated polymer undergoes an ultrafast electron transfer, and the resulting state may also be a weakly bound charge-transfer pair which can be separated by an external field. However, in previous studies on these conjugated polymer/fullerene composites, the results were understood as a complete separation of the photoinduced charges without any further correlation effects. To attack these open questions and to reveal a closer look to photoexcitations in conjugated polymer/fullerene composites, we performed systematic LESR studies.

The two LESR lines observed in conjugated polymer/fullerene composites were found to have different relaxation times, which allowed us to separate the two overlapping ESR signals clearly by utilizing microwave power saturation. This is clear evidence of completely independent photoinduced spins without detectable spin-exchange type correlation effects. The high-spin-lattice relaxation rate on the fullerene anion moiety may result from a splitting of the T_{1u} level by a Jahn-Teller-type distortion, as proposed in the literature.[33] Very low intensities of exciting light are enough to generate LESR signals. Two contributions to the LESR spectrum are observed: a prompt, reversible one and a persistent one. Excitation light intensity dependence of the prompt contribution to the P^+ and $C_{60}{}^-$ ESR signals is of bimolecular type ($I^{0.5}$), and implies the mutual annihilation within the created ($P^+ \ldots C_{60}{}^-$) pair. The persistent contribution is found to be excitation intensity independent, and is proposed to originate from deep traps due to disorder on the polymer.

EXPERIMENT

We used a Bruker EMX (X-Band) ESR spectrometer with Oxford variable temperature cryostats, allowing measurements in the range 4–300 K. α,α'-diphenyl-β-picrylhydrazyl (DPPH) has been used for g-factor calibration, utilizing a NMR gaussmeter for obtaining the static magnetic-field strength. An Ar^+-ion laser was used for light excitation without focusing through a 50% transmission grid on the cavity.

The LESR experimental procedure consisted of the following sequence: (i) scan the ESR spectrum of the nonilluminated sample; (ii) scan the ESR spectrum under light illumination (P_{exc} between 1 and 100 mW/cm^2); (iii) turn off the illumination and scan the ESR spectrum; and (iv) warm the sample up to the room temperature, cool it down to working temperature, and scan the ESR spectrum again. These ESR signals will be referred to as: ‘‘dark,’’ ‘‘light-on,’’ ‘‘light-off,’’ and ‘‘annealed’’ signals, respectively. As discussed below, the switching off of the excitation light does not lead to the disappearance of the ESR signal at low temperatures. To eliminate the ESR spectrum completely, the sample had to be warmed up to room temperature (annealing). This step was performed every time while measuring the microwave power and excitation light intensity dependencies. As default definition of the term LESR we choose the light-on signal corrected for the dark signal. Finally, we distinguish between the prompt LESR signal (light-on minus light-off), and the persistent one (light-off minus dark, or light-off minus annealed).

Previously we used a set of different conjugated polymers and their composites with pure and functionalized C_{60} in the photoinduced spectroscopic studies.[1–4] The polymer reported here was poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) which is soluble in xylene at elevated temperatures (Fig. 1). The preparation and characterization of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} [denoted as PCBM (Fig. 1)] was described elsewhere.[39] C_{60} (99.5%) was purchased from MER Corp. We studied films made of following composites: MDMO-PPV/PCBM (1:3 weight ratio) and MDMO-PPV/C_{60} (3:1). The ultrasonically treated PCBM solution was filtered before mixing with polymer through the 0.2-μm recycled cellulose (RC) filter. The xylene solutions of the composites were poured into quartz tubes, and dried by dynamic vacuum. To avoid the diffusion of the ambient air into the samples, the tubes were also pumped during the measurements.

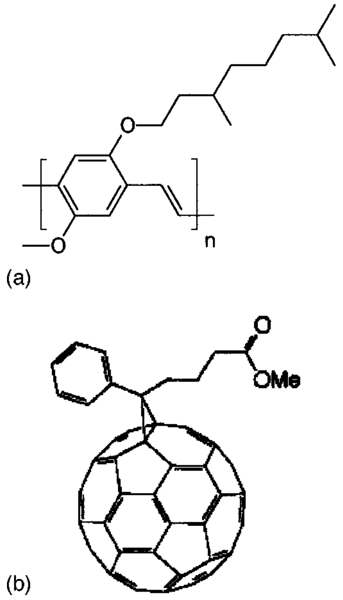

FIG. 1. Structural formula of the (a) MDMO-PPV and (b) PCBM.

RESULTS

Pristine MDMO-PPV, PCBM, and MDMO-PPV/PCBM composite

Neither ‘‘dark’’ ESR signals nor LESR signals have been found in films of pure MDMO-PPV in the temperature range of 77–300 K and at excitation power between 0.5 and 100 mW/cm^2. No dark ESR signal can be found in the PCBM film either. Pure PCBM shows a weak LESR signal with two lines [Fig. 2(a)], as discussed previously.[29] Even though these lines show a resemblance to the LESR features in conjugated polymer/PCBM composites, they are much weaker in intensity (see the microwave power used). The origin of these LESR spectra in a pure PCBM film is unknown, as discussed below.

A dramatic enhancement of the LESR is observed when mixing both substances together in a weight ratio of 1:3 (MDMO-PPV:PCBM) [Figs. 2(b) and 2(c)]. Two overlapping LESR lines with microwave-power-dependent intensities are observed in qualitative agreement with the previous preliminary reports.[1,4,27,28]

Figure 3 shows the microwave power dependence of the two LESR peaks in a MDMO-PPV/PCBM film measured at $T = 90\,\mathrm{K}$. Plotted is the double integral value of the LESR signal, which is proportional to the number of spins excited as a function of the microwave power. As noted above, an annealing of the sample up to room temperature was performed before each measurement. A four-decades variation of the microwave power allows one to distinguish the region where both LESR signals are not in saturation, i.e., at micro-

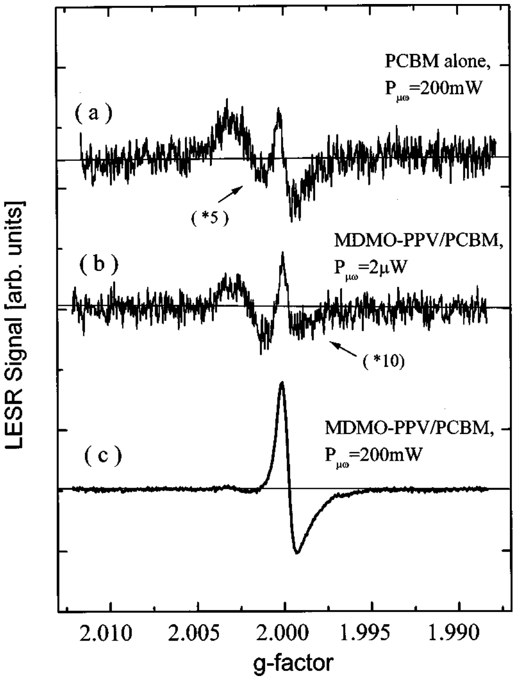

FIG. 2. (a) LESR spectrum of pristine PCBM. $P_{\mu\omega} = 200$ mW; (b) LESR spectrum in a MDMO-PPV/PCBM composite (weight ratio 1:3) at $P_{\mu\omega} = 2\ \mu$W. (c) LESR spectrum of MDMO-PPV/PCBM, $P_{\mu\omega} = 200$ mW, $T = 100$ K, $\lambda_{\mathrm{exc.}} = 488$ nm, and $P_{\mathrm{exc.}} = 20$ mW/cm^2.

wave powers below 30 μW. One can clearly separate these LESR lines by measuring them at different microwave powers.

MDMO-PPV/C_{60} composites

The film of MDMO-PPV/C_{60} composite (weight ratio 3:1) does not show any dark ESR signal. Figure 4 shows LESR spectra of MDMO-PPV/C_{60} for three values of the microwave power—200 mW, 20 mW, and 20 μW, respectively—at $T = 100$ K. At a microwave power of 200 mW one can almost suppress the low-field LESR line due to microwave saturation (see the upper curve in Fig. 4). In contrast, the intensity of the high-field LESR signal vanishes to zero at 20 μW. Thus the different saturation behavior enables us to separate the two overlapping LESR lines from different paramagnetic species, and to determine the individual g values as $g = 2.0025$ and 1.9995.

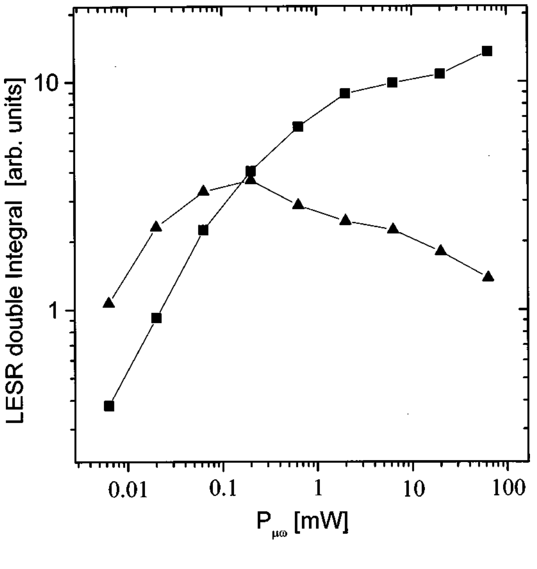

FIG. 3. Microwave power dependence (in $\log_{10}$ base) of two LESR signals (double integral) in MDMO-PPV/PCBM. $T = 90$ K, $\lambda_{\mathrm{exc.}} = 488$ nm, and $P_{\mathrm{exc.}} = 20$ mW/cm^2. Squares are for the high-field LESR line and triangles are for the low-field one.

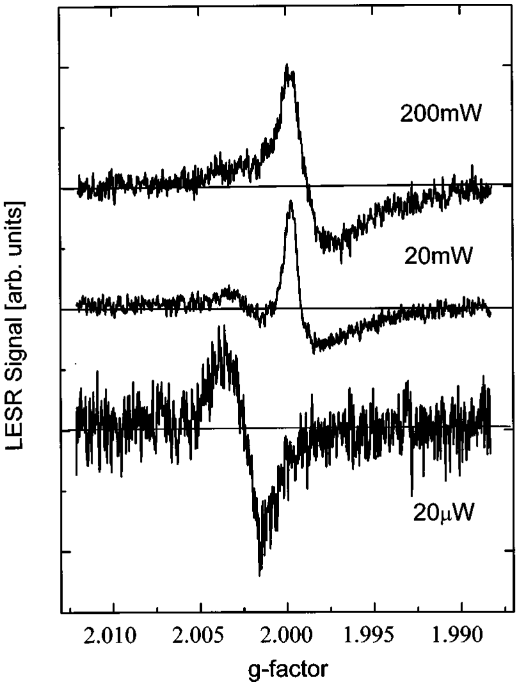

FIG. 4. LESR spectrum of MDMO-PPV/C_{60} composites at different values of microwave power. $T = 100$ K, $\lambda_{\mathrm{exc.}} = 488$ nm, and $P_{\mathrm{exc.}} = 20$ mW/cm^2.

Microwave saturation of LESR in MDMO-PPV/PCBM composites at different temperatures

The microwave power dependence of the LESR signal intensity (double integral of the measured signal as a measure of the number of spins) at five temperatures from 90 to 200 K, for the two paramagnetic species (a) $g = 2.0025$ and (b) $g = 1.9995$, is plotted in Fig. 5. The LESR signals show different saturation behaviors. The low-field LESR signal [Fig. 5(a)] measured at 90 K (squares) reaches its maximum at microwave power around 0.2 mW (Note that the curves in this figure are shifted along the y axis for clarity). At $T = 100$ and 120 K (circles and up triangles), the maximum is reached at microwave powers of 0.3 and 0.7 mW, respectively. At higher temperatures, $T = 150$ and 200 K, the saturation maximum cannot be reached with the microwave power available [Fig. 5(a); down triangles and diamonds, respectively).

The high-field LESR signal [Fig. 5(b)] exhibits no saturation maximum even at the highest microwave power available. The shape of the saturation curve does not change with the temperature, but the LESR double integral decreases by a factor of 20 when warming up the sample from 90 to 200 K [at $T = 200$ K, only one point (the diamond) is shown].

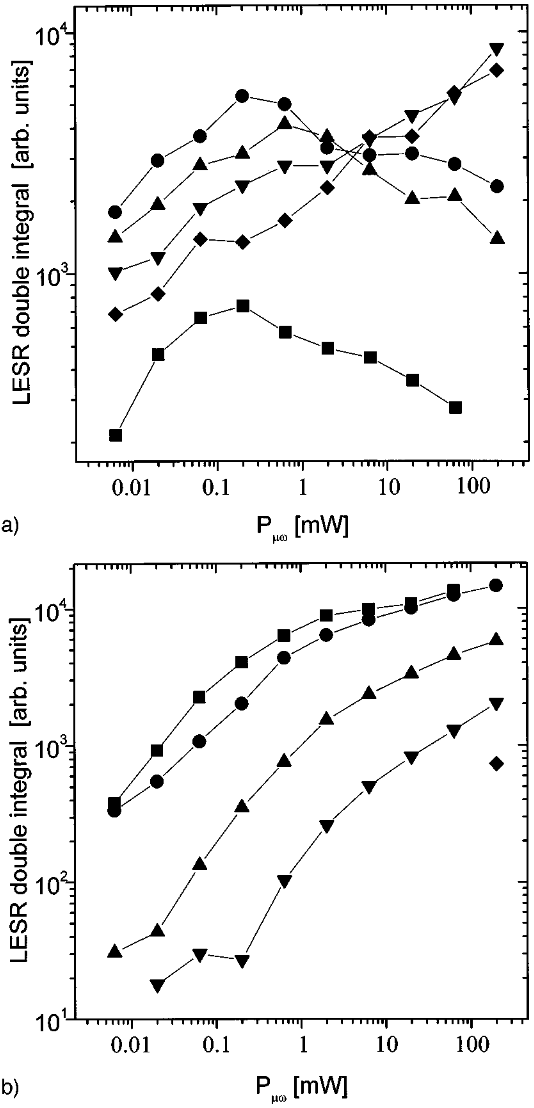

FIG. 5. Microwave power dependency (in $\log_{10}$ base) of doubly integrated LESR signals of a MDMO-PPV/PCBM composite at $T = 90\,\mathrm{K}$ (squares), 120 K (circles), 150 K (up-triangles), 180 K (down triangles), and 200 K (diamonds) for two species: (a) $g = 2.0025$ and (b) $g = 1.9995$. Spectra are placed arbitrary along the y axis. $\lambda_{\mathrm{exc.}} = 488\,\mathrm{nm}$ and $P_{\mathrm{exc.}} = 20\,\mathrm{mW/cm^2}$.

Dependence of LESR in MDMO-PPV/PCBM composites on the light excitation intensity

When the excitation light is switched off, the intensity of the ESR signals in conjugated polymer/fullerene composites decrease significantly, but does not disappear completely. Therefore, we distinguish between the prompt component of LESR, which disappears as the light is switched off, and the persistent component, which remains for hours at low temperatures after the illumination is off. The persistent component, however, can be eliminated by heating the films in the dark up to room temperature for several minutes (annealing).

The prompt and persistent components of the two LESR signals are plotted in Figs. 6(a) and 6(b), respectively, as a function of the intensity of the excitation light. The prompt LESR component, which is the difference between ESR spectra with light on and light off, shows almost equal amounts of spins (i.e., almost equal doubly integrated ESR intensities) and a $I^{\alpha}\,(\alpha \approx 0.5)$ power dependence on the intensity of excitation light for both low- and high-field LESR lines [see Fig. 6(a)]. These measurements were performed at 100 μW, when both magnetic resonance signals are in a nonsaturated regime, to make the comparison of the amount of spins possible. The persistent component, which is the difference between ''light-off'' ESR spectrum and the ''dark'' ESR spectrum, or ESR in the annealed sample, is nearly independent on the intensity of the previously applied light within the light power range 1–50 mW/cm^2 [see Fig. 6(b)]. It is seen that the integrated low-field ESR signal (squares) is much larger than the high-field ESR signal (circles). We found no difference in the line shape and saturation behavior between the prompt and persistent components of each LESR line.

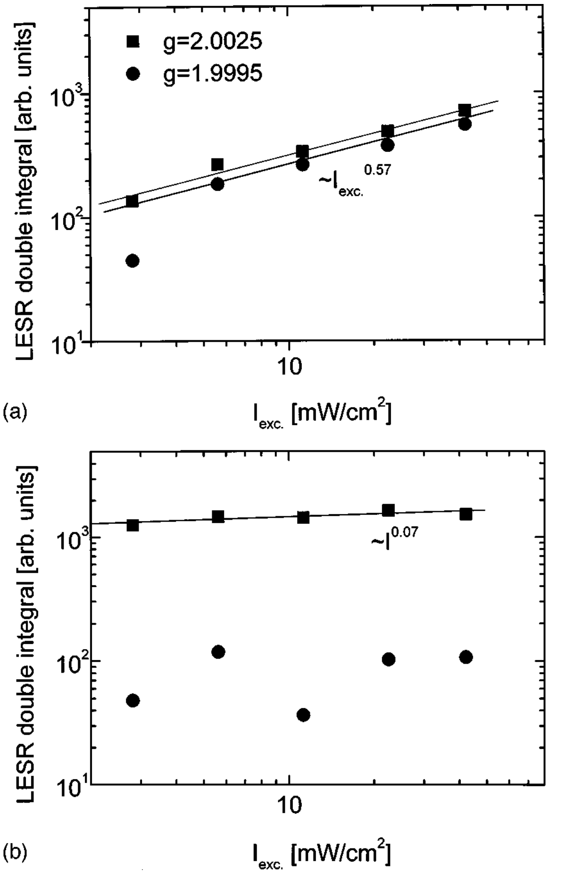

FIG. 6. Dependencies of the magnitude (in $\log_{10}$ base) of the LESR of a MDMO-PPV/PCBM composite on the intensity of the exciting light: prompt (light-on minus light-off) components (a), and persistent (light-off minus dark) components (b).

DISCUSSION

It is known from ESR studies on fullerene-based salts that the radical anion of C_{60} has a g factor below 2 both in solutions and in the solid state.[31–35,40–43] This is a distinct ESR feature of this molecule: the shift of the g factor toward values less than 2 is attributed to spin-orbit coupling. Therefore, the LESR signals at $g = 1.9995$ observed in all composites studied in this work were assigned to the $C_{60}{}^{-}$ radical. The two main difficulties in the calculation of the g value of the fullerene anion are (i) the asymmetric shape of the ESR line, and (ii) the overlap with the low-field LESR signal. The LESR line with $g=2.0025$ is attributed to the positive polaron P^+ on the conjugated polymer backbone.

It is quite possible that in the radical pair of type ($P^+ \ldots C_{60}{}^-$) the two unpaired spins ($\frac{1}{2}$ each) are interacting. If the radicals were related by a strong exchange interaction, the g factors of the coupled system should be affected. This is apparently the case in a number of fullerene-containing salts, such as tetrakis-dimethylamino-ethylene (TDAE)-C_{60}, where one ESR signal with a mean value of the g factor is observed instead of two ESR signals.[33,43–45] In conjugated polymer/fullerene composites, we did not find any difference in the line shapes and g factors despite the large variation of the relative concentrations of conjugated polymers and fullerenes from 1:3 to 3:1. Also, a significant dipolar interaction of the photoinduced spins such as triplet pair formation is not observed.[46]

Our result of two decoupled spins is quite intriguing. Since the electron transfer between donor and acceptor moieties which are close to each other will occur much more likely (for orbital overlap as well as tunneling mechanisms), the vast majority of the photoinduced spins are created as geminate pairs in close proximity which should interact with each other, either by exchange or by dipolar mechanisms. Assuming that the major part of the observed LESR signal is related to these photoinduced spin pairs, and since we do not see any of these interactions, it is safe to conclude that the spins diffuse spatially away from each other on a time scale much faster than spin-exchange times ($10^8-10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$). As discussed below, the diffusion of fullerene anion spins by a hopping mechanisms of the type

$$C_{60}{}^- + C_{60} \rightarrow C_{60} + C_{60}{}^-$$

is not the dominating relaxation channel for the high-spin-lattice relaxation rate.[32,33] Therefore, we conclude that *the mobile polarons on the conjugated polymer backbone move away from the fullerene anions* on a time scale faster than the above-mentioned exchange times (assuming an average configuration of interacting spins like in a $1M$ solution, i.e., $t < 10^{-8}$ s). This rapid spatial separation of the photoinduced charges is proposed to be responsible for the unusual long lifetime of the charge-separated state in these systems.[1] We cannot rule out a very large polaron on the conjugated polymer which does not move but is vastly spread out; this object would not show any significant spin density close to the fullerene anion (which may be approximated as a point charge and localized spin), and thus explain the undetectable interaction of the spins. However, it is very unlikely that there will be such a large polaron due to limitations of the conjugation lengths down to 5–10 unit cells due to disorder. Furthermore, the strongly enhanced photoconductivity in these conjugated polymer/fullerene composites suggest mobile polarons.[25]

The LESR signals in conjugated polymer/fullerene composites originate from a photoinduced electron-transfer reaction, which creates equal amount of spins (holes on the polymer chain, electrons on the fullerene molecule). Hence one can expect equal areas under the integrated LESR curves (i.e., almost the same value of the doubly integrated LESR signal). In any case the sample should remain charge neutral, with equal amounts of photoinduced positive and negative charges. Taking the difference in the relaxation behavior into account, one may only compare the number of photogenerated spins during which both systems are away from the saturation condition, as shown in Fig. 6(a). We observe nearly equal amounts of prompt LESR spins for the two different signals. Hence we may conclude that the two photoinduced charges annihilate each other with bimolecular dynamics. This is confirmed by the $I^{0.5}$ variation of LESR intensity with the excitation light power [see Fig. 6(a)]. However, a slightly larger amount of spins for the low-field ($g>2$) signal is observed. This can have several origins.

(a) It is proposed from a photoluminescence-detected ESR (PLDMR) study on pure PPV films that absorption of light by the polymer is followed by the formation of interchain polaron pairs of $P^+ \ldots P^-$ type. However, the PLDMR spectrum of such a state consists of a single slightly asymmetric line. One may speculate that the presence of the negative polaron ESR is hidden by the P^+ ESR signal due to their overlap. Formation of P^- cannot be excluded in the composites. In this case the area under the $g=2.0025$ LESR signal consists also of photogenerated negative polarons on the polymer.

(b) Furthermore, pure (6,6) PCBM already shows two weak LESR lines [see Fig. 2(a)] which contribute to the net intensity of the LESR signal. The origin of these two LESR signals in pure PCBM remains unclear. A straightforward suggestion would be an intramolecular charge transfer from the side groups onto fullerene. However, no LESR was found in glassy solutions of PCBM in MeTHF, which clearly shows that an intramolecular electron-transfer reaction is unlikely, and the aforementioned effect probably arises from the solid state effects of a pure PBCM film. Further studies on this effect are underway.

After switching off the exciting light, the intensities of both LESR signals decrease dramatically but do not vanish completely. The line shapes and g factors of the ''light-off'' persistent LESR signals are similar to the prompt LESR. Furthermore, the fullerene anion LESR line is much less persistent compared to the conjugated polymer polaron LESR signal. The fraction of the persistent LESR components is temperature dependent, but is nearly independent on the intensity of previous light excitation [see Fig. 6(b)]. The persistent spins can be completely removed from the sample after thermal annealing up to 300 K. This result puts up the question of electrical neutrality, i.e., for every positive polaron created by incident light there must be also a corresponding fullerene anion radical observable. Therefore, we imply the existence of deeply trapped photoexcited polarons of both signs on the polymer backbone. Exciton dissociation induced by charged fullerenes creates negatively charged polarons in the composite medium. Upon migration, the mobile charged polarons on the polymer are more likely to become trapped on the disorder-induced deep traps compared to the photoinduced electrons on the molecular fullerenes.

Unusually high relaxation of the fullerene anions compared to polymer polarons

It is remarkable that the LESR line for the fullerene anions does not saturate within the experimentally available microwave power range. The absorbed microwave power P_a per unit sample is given by

$$P_a \propto \frac{H_1^2}{1+\gamma_e^2 H_1^2 \tau_1 \tau_2},$$

where H_1 is the excitation field amplitude at the sample, γ_e is the electronic magnetogyric ratio, and τ_1 and τ_2 are spin-lattice and transverse relaxation times, respectively. As long as $\gamma_e H_1^2 \tau_1 \tau_2 \ll 1$, the saturation terms can be neglected.

In Fig. 5 it is clearly demonstrated that the polymer polaron LESR can be saturated at around 0.2 mW (90 K), whereas the fullerene anion signal does not saturate under same conditions up to powers which are 100 times higher. The field for saturation maximum is related to the spin-lattice relaxation times by

$$\tau_1 = \frac{1}{2\tau_2 \gamma_e^2 H_{1\,\max}^2},$$

where $H_{1\max}$ is the excitation field amplitude at the sample where the maximum in the saturation studies occur. We then conclude that the fullerene anion radical τ_1 is approximately ten times shorter than the τ_1 for the positive polaron P^+.

This interesting issue already attracted attention in previous studies.[31–35,40–43] It cannot originate from spin-exchange and/or electron-transfer mechanisms (the hopping mechanism as denoted above) because it was also observed in diluted frozen solutions.[32] With the studies presented here we can also rule out environmental as well as phonon effects for this effect. Boltzmann distribution of phonons for the spin-lattice relaxation cannot be very different in these two photoinduced spins, since both moieties consist of unsaturated carbon-carbon backbone with similar vibrational energies. Thus the lattice temperature for the two kinds of spins in these conjugated polymer/fullerene solid-state composites is expected to be quite similar. The environment in an homogenous composite is also expected to be similar for the two spins. Therefore we conclude that the *high relaxation rate of the fullerene anion spin is an intrinsic property*. A Jahn-Teller-type distortion on the fullerene ball would split the T_{1u} level, and result in two closely spaced energy levels available for the anion.[32,33] Thermal averaging over such states would provide a dominant relaxation channel for the spin, and would account for the linewidth effects[32,33] as well as the nonsaturation in our studies.

CONCLUSION

In this work we performed comparative studies of the photoinduced charge transfer in conjugated polymer/fullerene composites as well as in pure components by using the light-induced electron spin resonance. Light-induced charge transfer from the polymer into the fullerene in the composites results in the appearance of two LESR signals (i) $g=2.0025$ and (ii) $g=1.9995$, which are attributed to positive polarons on the conjugated polymer backbone, P^+ and fullerene anions, $C_{60}{}^-$, respectively. The microwave saturation studies clearly demonstrate that the different paramagnetic species contributing to the LESR spectrum have different spin-lattice relaxation times. From the absence of any exchange and/or correlation effects between these two photoinduced spins, we conclude that the mobile polarons on the conjugated polymer backbone are moving away from the fullerene anions on a time scale faster than the spin-exchange times. We further distinguish between a fast decaying, reversible, contribution to P^+ and $C_{60}{}^-$ LESR signals (prompt), and a slowly decaying (persistent) one. Excitation light intensity dependence of the prompt contributions into P^+ and $C_{60}{}^-$ LESR signals is of bimolecular type ($I^{0.5}$), and implies the mutual annihilation within the created ($P^+ \ldots C_{60}{}^-$) pairs. The persistent contribution is found to be excitation intensity independent, and is related to deep trap defect states due to disorder in the polymer backbone. The unusually high relaxation rate of the fullerene anion spins is attributed to an intrinsic property, possibly arising from a Jahn-Teller type distortion on the fullerene ball splitting the T_{1u} level.

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