Optical- and photocurrent-detected magnetic resonance studies on conjugated polymer/fullerene composites

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X-band photocurrent- and photoluminescence-detected magnetic resonance spectra of films of MDMO-PPV [poly(2-methoxy,5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] with different concentrations of PCBM [1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61}] are described and discussed. Magnetic resonance at $g \approx 2$ is found to reduce the photocurrent and increase the photoluminescence. Upon increasing the fullerene concentration, the intensity of the photocurrent-detected magnetic resonance (PCDMR) spectrum decreases. Compared to the pure polymer sample, the resonance position shifts to a smaller g value and the line shape changes from one Lorentzian line to a line with a pronounced shoulder at smaller g values. This is attributed to different free-charge-carrier generation processes in the polymer and polymer-fullerene mixtures. In the pristine material at the magnetic resonance condition the recombination of polymer anion-cation pairs (polaron pairs) increases, while in the mixture the polymer cation-fullerene anion pair recombination is enhanced. Both species are precursors for free charge carriers. At high PCBM concentrations free charge carriers are no longer created via a precursor, but free charges are formed immediately after photoexcited charge transfer from polymer onto fullerenes. Adding small amounts of PCBM to MDMO-PPV, both the narrow (polaron) resonance at $g \approx 2$ and the triplet resonances are enhanced in the photoluminescence-detected magnetic resonance spectra. Similar to the PCDMR experiment, the position of the polaron resonance shifts to smaller g values and the line shape changes from one Lorentzian line to a line with a shoulder at lower g values. Increasing the fullerene concentration in the polymer matrix, the triplet resonance is quenched, while the polaron resonance amplitude is almost constant up to the highest PCBM concentrations investigated. The observed polaron resonance line shape suggests that the observed radicals result from photoinduced charge transfer.

I. INTRODUCTION

The discovery of metastable photoinduced charge transfer from π-conjugated polymers onto C_{60} has attracted widespread interest due to possible applications in low-cost photovoltaic devices and photodetectors.[1–7] While C_{60} does not act as a dopant in the ground state, photoinduced absorption (PIA) experiments have demonstrated that the PIA spectrum of a composite film of a conjugated polymer/C_{60} mixture has an entirely different spectrum to that of pristine polymer or fullerenes.[8] Light-induced electron spin resonance (LESR) studies have clearly identified two long-living photoexcitations in mixtures of conjugated polymers with fullerenes, which have been attributed to positive polarons on the polymer and fullerene anions.[2,9] Another manifestation of the charge transfer is the quenching of the polymer photoluminescence (PL) and a strong increase in the photoconductivity (PCo). In composite films PL quenching and a PCo enhancement by three orders of magnitude and a significant reduction of the PL lifetime have been observed.[9] The change in PL lifetime can be used to estimate the charge transfer time, and values of <100 fs can be deduced from experiments.[9]

In this paper, mixtures of the conjugated polymer MDMO-PPV [poly(2-methoxy,5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] and the highly soluble methanofullerene PCBM [1-(3-methoxycarbonyl)-propyl-1-

phenyl-(6,6)C_{61}] are investigated. The chemical structure of these compounds is shown in the upper part of Fig. 1. In mixtures of these two components the charge transfer was found to occur within 45 fs.[10] Light-induced ESR studies identified two light-induced features: namely, positive polarons at $g = 2.0025$ and the PCBM anion at $g = 1.9995$.[11,12] Using MDMO-PPV and PCBM, efficient photovoltaic devices (plastic solar cell) can be prepared. Shaheen *et al.* demonstrated an energy conversion efficiency of 2.5% under AM1.5 illumination for this system.[13] To improve the understanding of charge generation and recombination processes in the plastic solar cell mixture, photocurrent- (PC-) and PL-detected magnetic resonance studies have been performed. Previous studies[14–18] on pristine conjugated polymers have exhibited a narrow PC decreasing and a PL enhancing resonance at $g \approx 2$ due to spin-$\frac{1}{2}$ polarons and PL-enhancing full-field ($\Delta m_s = 1$) and half-field ($\Delta m_s = 2$) triplet exciton powder patterns. The reduction of the photocurrent is associated with resonant-microwave-transition-enhanced recombination of polaron pairs.[19] Polaron pairs are intermediate states, which contribute to the photocurrent by dissociation. The influence of the resonant microwave transitions on the photoluminescence is based on indirect processes. One model assumes that charges (polarons) and also triplet excitons are quenchers for singlet excitons.[14,16,20] Magnetic resonance reduces the number of polarons and triplet excitons, and there-
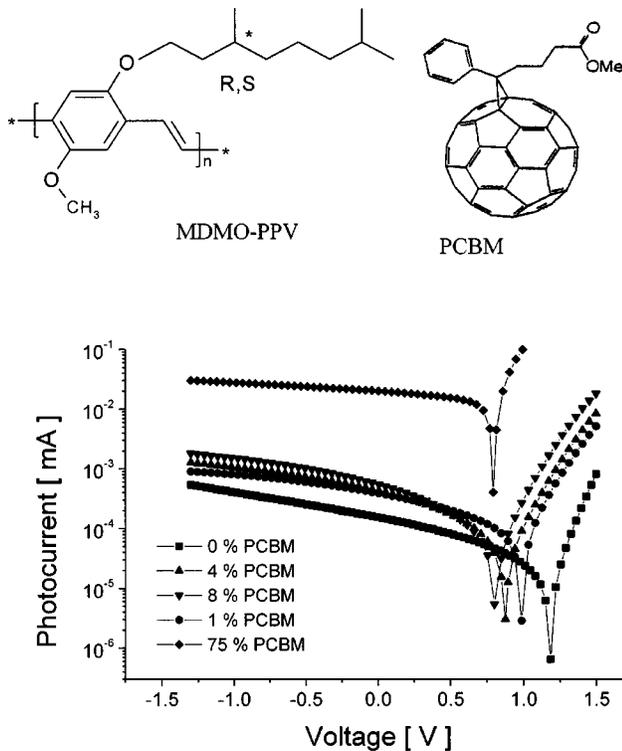
FIG. 1. Chemical structure of poly(2-methoxy,5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} (PCBM). Current-voltage curves of diodes with different concentrations of PCBM recorded under white light 60 mW/cm^2 illumination.

fore PL increases. Frankevich and co-workers suggested that triplet-triplet annihilation (TTA) is responsible for all features in the PLDMR spectrum.[17,21] The resonance at $g \approx 2$ increases the number of triplet excitons, resulting in more singlet exciton generated by TTA. The full-field and half-field triplet exciton resonances redistribute the population of triplets and enhance the TTA rate. Both models have been supported by recent publications suggesting the quenching of singlet excitons by charges[22] and triplet excitons,[20] but also TTA,[23,24] are possible processes in conjugated polymers. Lane et al.[25] investigated the influence of C_{60} on the PLDMR spectrum of different π-conjugated polymers. Following their studies, they conclude that conformational defects, which are induced by admixture of C_{60}, are responsible for the increase of the PLDMR resonance. At higher fullerene concentrations they find that direct photoinduced charge transfer is responsible for quenching of the PLDMR signal.

In this study we report a systematic experimental analysis of the effect of mixing of PCBM into MDMO-PPV by photoluminescence-detected magnetic resonance (PLDMR) as well as in photocurrent-detected magnetic resonance (PCDMR) supported by optical excited-state spectroscopy. The results clearly indicate the creation of intermolecular radical pairs where the radical cation is on the polymer and the radical anion is on the fullerene at small concentrations of fullerenes in the polymer matrix. The higher loading of fullerenes into the polymer matrix results in a strong quenching of both the triplet PLDMR as well as the PCDMR signal.

II. EXPERIMENT

MDMO-PPV has been purchased by COVION, and the synthesis of this polymer has been described elsewhere.[26] PCBM was provided by J. C. Hummelen, and its synthesis has been described in Ref. 27. Solutions for film preparation were prepared in such a way that materials were separately dissolved in the same organic solvent (toluene). The polymer solution was stirred for several hours at elevated temperatures. The fullerene solution was first put into an ultrasonic bath for ~15 min and then stirred for another hour at room temperature. As a last step, both solutions plus pure solvent were mixed to achieve solution holding a concentration of 3 mg/ml MDMO-PPV and the desired concentration of PCBM. All concentrations are given in weight percent (wt %).

For PLDMR experiments films were prepared by spin-coating the solutions on a plastic substrate. Up to ten pieces, each with an approximate size of 2 mm×3 cm, were cut from the substrate and put into an ESR-grade quartz tube and sealed in helium atmosphere. Photocells for the PCDMR measurements were prepared in the following way: poly(ethylene dioxythiophene doped with polystyrene sulfonic acid) (PEDOT:PSS) and the photoactive material were deposited with a thickness of ~100 nm consecutively by the spin-coating technique on a cleaned indium-tin-oxide- (ITO-) coated substrate. As a last step, a 60-nm aluminum layer was evaporated as top electrode. The active area of the devices was about 6 mm^2. Samples were contacted with thin copper wires and sealed in an ESR quartz tube in an Ar atmosphere. The tubes were placed in a rectangular TE$_{102}$ cavity with two windows for optical access inside a magnet of a commercial X-band ESR spectrometer (Bruker EMX). The microwave power, which was 200 mW in all measurements presented, was modulated with a home-built p-i-n modulator. The microwave frequency was locked to an additional cylinder cavity, and the resonance condition was controlled using an external microwave diode. α, α'-diphenyl-β-picrylhydrazyl (DPPH) has been used for g-factor calibration. All g values are given with an accuracy of ±0.0003. Photodiodes were excited by spectrally dispersed light $\lambda = 476$ nm, 10 mW/cm^2 coming from a xenon arc lamp. For the photoexcitation in PLDMR experiments an Ar$^+$ laser was employed ($\lambda = 476$ nm). The samples were excited through an optical fiber terminating inside the optical window of the cavity (50 mW/cm^2). A combination of two lenses collected the PL of the samples. Long-pass filters blocked stray light from the laser. A lock-in amplifier was used to detect the synchronous changes of the photocurrent produced by the silicon diode (PLDMR) or by the polymer photodiode (PCDMR) on the square-wave-modulated microwave power while gradually sweeping the magnetic field. Due to the rather slow response of the electrical signal of the polymer diode on the modulation of the microwave irradiation, all the PCDMR experiments were carried out at low microwave power modulation frequencies (<300 Hz). The PCDMR experiments presented here were performed at room temperature, while PLDMR experiments were carried out at 10 K. A schematic setup of the PLDMR experiment is shown in Fig. 2. For photoinduced absorption (PIA) an Ar$^+$ laser beam at 476 nm served
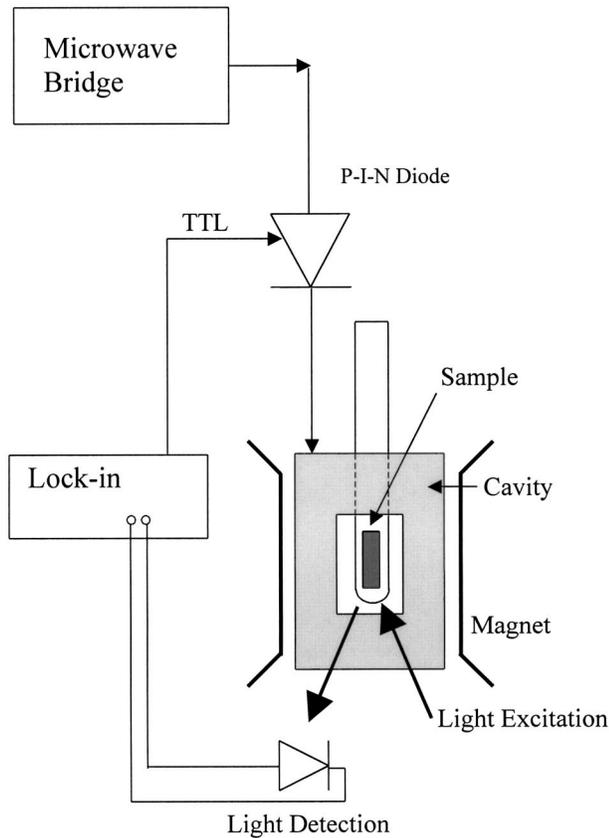
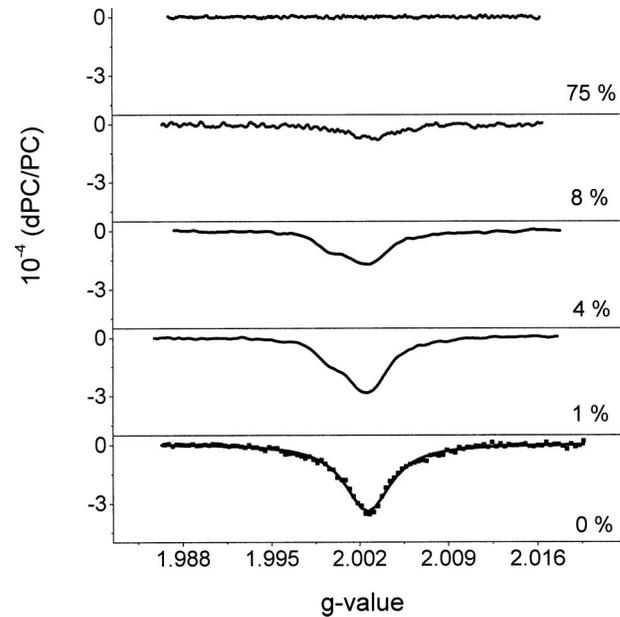FIG. 2. Schematic experimental setup of the PLDMR experiment.

FIG. 3. Photocurrent-detected magnetic resonance spectra of MDMO-PPV photodiodes holding different concentrations of PCBM. Measurements were performed at room temperature and 200 mW modulated microwave power. Diodes were illuminated by 10 mW/cm^2 at 476 nm.

as an excitation source. The pump beam was mechanically modulated at a frequency of 173 Hz, and changes in the white light (120-W tungsten-halogen lamp) probe beam transmission ($-\Delta T$) were detected, after dispersion with a 0.3-m monochromator, in the range from 0.55 to 2.15 eV with a Si-InGaAsSb sandwich detector. The detector signals were recorded phase sensitively with a dual-phase lock-in amplifier. The probe light transmission (T) was recorded separately using the same chopper frequency. The PIA spectra ($-\Delta T/T$) were obtained after correction for the sample luminescence and normalization on the probe light transmission. For the PIA experiments, the samples were mounted in an Oxford CF204 continuous-flow cryostat allowing measurements down to 19 K.

III. RESULTS

In Fig. 1 typical current-voltage characteristics of the investigated photodiodes are shown. Samples were illuminated by white light (60 mW/cm^2). Adding fullerenes to the conjugated polymer, the open circuit voltage (V_{oc}) of the diodes is reduced and saturates at approximately 750 mV. Liu *et al.* observed something similar for MEH-PPV$-$C$_{60}$ diodes.[28] The origin of the shift of V_{oc} upon the addition of PCBM is still subject to debate.[28,29] In Fig. 3, PCDMR spectra of diodes with different fullerene contents are plotted. A reduction of the photocurrent at magnetic resonance conditions is clearly observed. For the pure polymer diode without

fullerenes the signal is found to be largest. The PCDMR resonance has a Lorentzian line shape and a g value of 2.0028, $\Delta B_{1/2} = 7.3$ G, with an amplitude dPC/PC of -3.4×10^{-4}. Adding small amounts of fullerenes, the maximum of the PCDMR resonance is weakened systematically, slightly shifted to smaller g values, and a new shoulder at lower g values is observed. For 1% of PCBM a signal amplitude dPC/PC of -2.8×10^{-4} is found. Adding more fullerenes, the resonance weakens further; however, the line shape does not change significantly at a concentration of 4% PCBM. For 4% of PCBM a signal amplitude dPC/PC of -1.7×10^{-4} is found. For the diode with 8% PCBM content the PCDMR signal is already very small (dPC/PC$=-7 \times 10^{-5}$) and the weak resonance does not allow determining the exact position and line shape of the spectrum. For the fullerene concentrations used in the plastic solar cell (75% PCBM) the influence of microwave modulation on the photocurrent is below the detection limit of our experiment ($\sim 1 \times 10^{-5}$). PCDMR results for $g \sim 2$ are summarized in Fig. 4. The amplitude of the relative change of the photocurrent (dPC/PC) and the amplitude of the photocurrent change dPC are plotted versus the fullerene concentration. In all PCMDR experiments we also checked the possibility of triplet-type excitations with signals half field ($\Delta m_s = 2$), but no signal could be observed for all reported concentrations of fullerenes. In Fig. 5, PLDMR spectra of thin films of MDMO-PPV mixed with various concentrations of PCBM are compared. The pure polymer shows a PL-enhancing magnetic resonance signal with Lorentzian line shape (solid line in Fig. 5) at $g = 2.0028$, $\Delta B_{1/2} = 11.6$ G, with an amplitude dPL/PL of 1.6×10^{-4}. This resonance is comparable in intensity to that observed in typical PPV's and other conju-
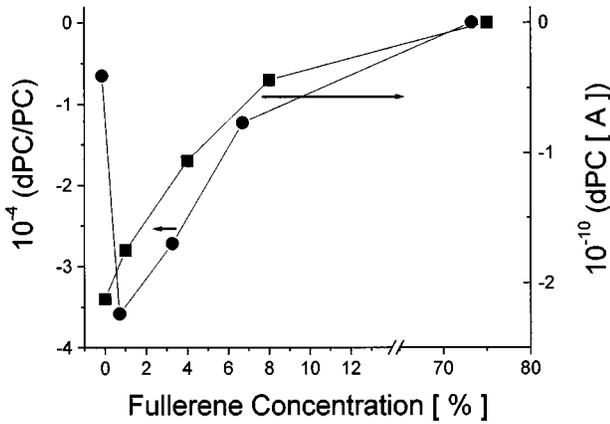
FIG. 4. Change of the photocurrent dPC (circles) and the relative photocurrent dPC/PC (squares) plotted vs the fullerene concentration.

FIG. 6. Maximum amplitude of all spectra shown in Fig. 3 plotted vs the PCBM concentration. The inset show the first derivative of the sample MDMO-PPV plus 1% PCBM.

gated polymers. Adding 1% of PCBM, the resonance increases by a factor of 8 (dPL/PL$=1.2\times10^{-3}$), the g value of the maximum shifts to a lower value, and an additional shoulder is observed. At higher fullerene concentration the resonance increases further, reaches an amplitude of $\sim3.25\times10^{-3}$ at 5% PCBM content, and remains approximately constant up to 10% PCBM (Fig. 6). The strong quenching of PL by PCBM does not allow a further increase of the fullerene concentration in our experiments. In the inset of Fig. 6 the first derivative of the PLDMR spectrum of the sample holding 1% of PCBM is shown. It clearly indicates the presence of two features in the magnetic resonance spectrum. Small amounts of fullerene also increase the resonance at half field ($\Delta m=2$) $g\sim4.0$ in the PLDMR spectrum (Fig. 7). At 1% PCBM doping also a weak full-field triplet powder pattern could be observed (Fig. 7). At higher fullerene concentrations the half-field resonance decreases significantly and can no longer be distinguished at the higher PCBM load. In Fig. 8, PIA spectra of MDMO-PPV and MDMO-PPV with 1% PCBM are compared. Both films have the same optical density at 476 nm and were investigated under the same experimental conditions. Pure MDMO-PPV shows one photoinduced absorption located at around 1.35 eV, which
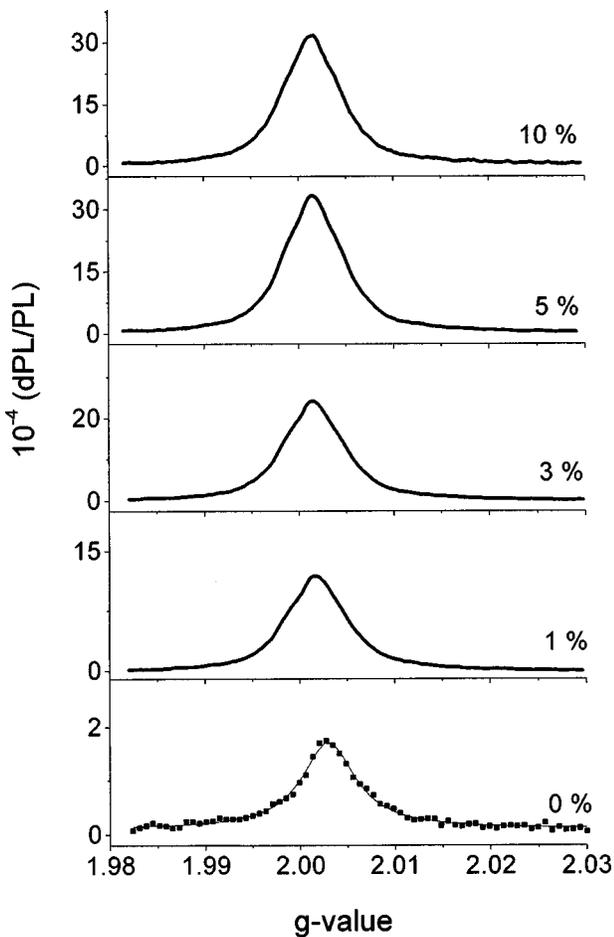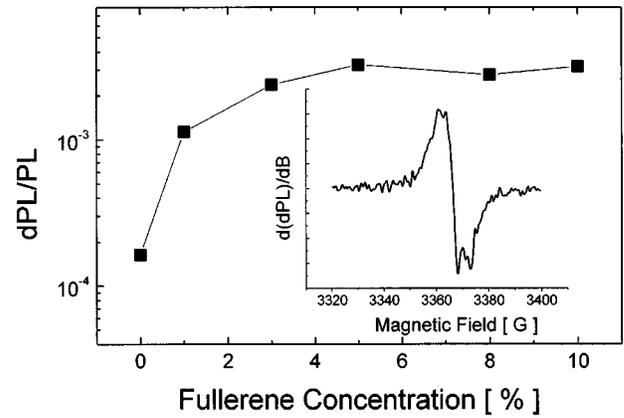

FIG. 5. Photoluminescence-detected magnetic resonance spectra of MDMO-PPV with different concentrations of PCBM. Measurements were performed at $T=10$ K and 200 mW modulated microwave power. Samples were excited by 50 mW/cm^2 at 476 nm.
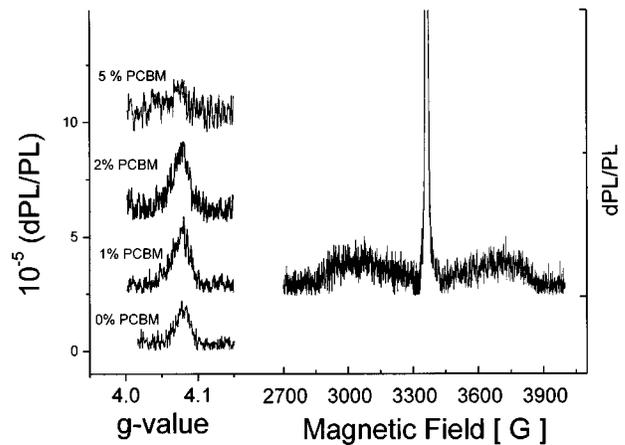

FIG. 7. Comparison of the half-field PLDMR spectra for various concentrations of PCBM in the MDMO-PPV film (left-hand side). On the right-hand side full-field triplet powder pattern and the polaron resonance of the sample MDMO-PPV plus 1% PCBM is shown. Measurements were performed at $T=10$ K. Samples were excited by 50 mW/cm^2 at 476 nm.
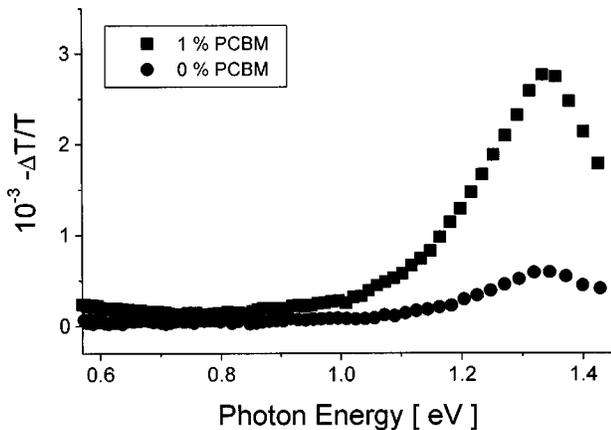
FIG. 8. Comparison of PIA spectra recorded for a thin film of MDMO-PPV and a film with the same optical density in the visible range of MDMO-PPV plus 1% PCBM. Both spectra were measured at $T = 19$ K. Samples were excited by 5 mW/cm^2 at 476 nm.

has been attributed to a triplet-triplet absorption.[30] Adding 1% of PCBM to the polymer, the PIA signal at 1.35 eV increases. In addition, a weak absorption at 0.6 eV is observed, indicating the presence of polarons.[30]

IV. DISCUSSION

A. Photocurrent-detected magnetic resonance

The observation of a reduction of the photocurrent in conjugated polymer diodes is usually explained by microwave-enhanced recombination of polaron pairs.[19] A polaron pair consists of a positive and a negative polaron, which can be localized on different conjugated segments as described by Dyakonov and Frankevich.[21] After their formation, pairs can recombine or contribute to the photocurrent by dissociating into free charge carriers. Under magnetic resonance conditions the number of pairs decreases, and in this way their contribution to the photocurrent is reduced. In the pure MDMO-PPV diode positive and negative polarons are created by charge transfer to a neighboring chain or chain segment or by dissociation of singlet excitons. In the PCDMR experiment a single line with Lorentzian-like line shape at a g value of $g = 2.0028$ is observed. This suggests that the g values of the positive and negative polarons are similar. This is in contrast to observations in electrochemically induced polarons in derivatives of polythiophenes.[31] From light-induced ESR experiments, the g value of the positive polaron in these PPV derivatives is known to be around 2.0025.[11] Assuming a slightly higher g value for negative polarons, which are weakly exchange coupled to the positive counterparts, the observed common g value can be rationalized by merging the resonance into one at the arithmetic average of the two g values.[32]

The PCDMR spectrum changes by adding PCBM in several ways. The resonance intensity decreases, indicating that the free-charge-carrier generation via pairs, which can be influenced by magnetic resonance, is getting less important. At the same time the position of the resonance and the line shape is changing. The spectra for 1% PCBM and 4% PCBM

can be reconstructed by one Lorentzian line at $g = 2.0025$ and a Gaussian line at $g = 2.0003$. The g value of the positive polaron on MDMO-PPV is around $g = 2.0025$, and the g value of the PCBM anion is around $g = 1.9995$.[11] This suggests that the main contribution to this observed resonance comes from positive polarons on the polymer and negative charges on the fullerene. This also displays a polaron pair as defined above, but now in two different species consisting of the donor cation radical (positive polaron on the chain) and the acceptor anion radical. Increasing the fullenene content further, the fraction of charges created from intermediate pairs is becoming smaller and smaller and no influence of microwaves on the photocurrent is observed for the highly loaded polymer mixtures as used in the plastic solar cell (75% PCBM). From these results one may conclude that the photogeneration of free charges is influenced in the pure conjugated polymer by the dissociation of polaron pairs, which are formed upon photoexcitation. Adding small amounts of fullerenes, photoinduced electron transfer produces pairs of polymer$^+$-fullerene$^-$ radicals, which contribute to the photocurrent by dissociation into free charge carriers. At high fullerene concentrations, photoexcitation produces dominantly free charge carriers, which results, in the high incident photon, the electron conversion of this system up to 70% quantum efficiency.[13]

B. Photoluminescence-detected magnetic resonance

The PLDMR spectrum of a thin film of MDMO-PPV shows one $g \approx 2$ PL-enhancing feature. The resonance has a Lorentzian line shape and is positioned at $g = 2.0028$ and has also been ascribed to the microwave-enhanced recombination of polaron pairs.[16–21] There are two opposing models describing the influence of the enhanced polaron pair recombination on the PL. One is based on a strong interaction between polarons or polaron pairs and singlet excitons. Singlet excitons, which are the primary source for PL, are quenched by polarons or polaron pairs.[14–16,21] In almost all conjugated polymers PL and the absorption of the positive polaron overlap. Therefore it is quite natural to consider quenching singlet excitons by these charges. Reducing the number of polarons by magnetic resonance should therefore increase PL. The second model is based on the well-known process of triplet-triplet annihilation.[17,21,23] Magnetic resonance increases the number of triplet excitons, which are formed by recombination of triplet polaron pairs. These triplet excitons are mobile species, and they form with a probability of 1/9 a singlet exciton when two triplet excitons annihilate.[23] Increasing the number of triplet excitons also increases the probability for triplet-triplet annihilation, and therefore PL should increase under magnetic resonance. Adding a small amount of fullerene to the polymer increases the PL-enhancing resonance. The position of the signal maximum is shifted to smaller g values, and a line shape similar to the PCDMR (compare Fig. 3) experiment is observed. The PLDMR spectrum of the film holding 1% of PCBM can be reconstructed by a Lorentzian line and a Gaussian line centered at $g = 2.0025$ and $g = 1.9995$, respectively. The appearance of a component at $g < 2$ indicates that

the PCBM$^-$ radical contributes to the observed spectrum since this unusually low g value for the fullerene radical has been identified earlier.[33] By adding more fullerenes, dPL is gradually diminishing due to the strong luminescence quenching which makes signal analysis unreliable.

Lane *et al.* observed a similar increase of the PLDMR signal in various conjugated polymer C_{60} mixtures.[25] In addition, they were able to use very high C_{60} concentrations and they find that the signal is decreasing again at high C_{60} loads. Because they observed no changes in the resonance line shape, they conclude that in the systems they investigated, the increase of the PLDMR at low fullerene concentrations does not result from photoinduced electron transfer, but explains the increase of the PLDMR intensity by fullerene-induced structural changes of the polymer. Only at high C_{60} loads does charge transfer reduce the PLDMR intensity.

In the study presented in here an increase of half-field PLDMR is found upon light fullerene doping, in agreement with earlier studies.[25] The position and shape of the half-field signal do not change from the pure polymer to doped samples. In addition, the sample with 1% PCBM shows a very weak full-field triplet powder pattern, which could not be observed in the pure polymer or at higher PCBM concentrations. In Ref. 25 the increase of the triplet resonance was ascribed to fullerene-induced structural changes. We propose in this work a different process yielding a higher triplet exciton population on the conjugated polymer: Considering the energy level diagram of the investigated materials, a backtransfer of the electron on the PCBM to the polymer directly followed by the formation of a triplet exciton seems to be energetically possible. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of MDMO-PPV and the LUMO level PCBM were determined by electrochemistry to be -5.3, -3, and -4 eV versus vacuum, respectively.[34] The energy difference between the ground state and the first triplet excited state, $S_0 - T_1$, of MDMO-PPV is not known, but this quantity has been measured for poly(2-methoxy,5-(2'-ethyl-hexoxy)-p-phenylenevinylene) (MEH-PPV), a polymer very similar to MDMO-PPV, to be 1.27 eV.[35] Using these numbers, one can estimate the energetic positions of the T_1 level of the polymer and the LUMO level of the fullerene to be quite similar. Therefore the formation of triplet excitons on the polymer via an electron backtransfer from fullerene could be possible and this process could also explain the increase of the half-field PLDMR.

With increasing PCBM concentration the half-field resonance decreases in intensity and cannot be observed for the sample with 10% PCBM. The reduction of the triplet resonance has been attributed to the quenching of triplet excitons by charges.[25] Another indication of the increase of the triplet exciton concentration is found in the photoinduced absorp-

tion experiments. Although there is a contribution of the polaron PIA in weakly fullerene doped samples, the net increase of the PIA feature at 1.35 eV (triplet-triplet absorption) indicates a net increase of the triplet yield on the polymer by addition of small amount of fullerene. This also supports our proposal that additional triplets could be produced by a recombination of MDMO-PPV$^+$ and PCBM$^-$ as described above. At high fullerene concentration no triplets as well as no photoluminescence are observed in the PIA spectrum as photoinduced-absorption-detected magnetic resonance spectra have demonstrated.[36]

V. SUMMARY

The photophysics of fullerene-doped conjugated polymers were studied by PCDMR and PLDMR. The introduction of PCBM into the polymer matrix quenches PL and increases PC. PCDMR shows a negative signal that decreases in magnitude upon the addition of fullerene. This is attributed to a change of the free-charge-carrier generation process. While dissociation of polaron pairs is important in pure MDMO-PPV, photoinduced electron transfer is the dominating process in the presence of PCBM. At high fullerene concentrations free charge carriers are formed without an intermediate pair. PLDMR magnetic resonance is positive in sign, and small fullerene doping enhances its intensity. We propose for this enhancement an increase of triplet excitons on the polymer via recombination of the charge-separated state between polymer and fullerene. The resonance spectra (both PLDMR and PCDMR) show a shoulder at lower g values when small amounts of PCBM are present, which demonstrates that the products of the charge transfer (MDMO-PPV$^+$ and PCBM$^-$) are manipulated by the microwave radiation. This indicates an intermolecular radical pair formation between the polymer and fullerene at these small fullerene concentrations. At higher fullerene concentrations free charge carriers are formed with no luminescence detectable. Furthermore, photocurrent-detected resonance effects are fully quenched at high fullerene concentrations.

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