

Light-Induced EPR Study of the Effect of Coumarin Trace Additives on Spin Dynamics in the P3DDT/PC₆₁BM Polymer Composite

E. I. Yudanov^{a, *}, V. I. Krinichnyi^{a, **}, and N. N. Denisov^a

^aInstitute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

*e-mail: yudan@icp.ac.ru

**e-mail: kivi@cat.icp.ac.ru

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Abstract—The paper presents the results of an EPR study of the magnetic, relaxation, and dynamic parameters of spin charge carriers photogenerated by light in photovoltaic polymer composites, based on poly(3-dodecylthiophene) (P3DDT) and 6,6-phenyl-C₆₁-butyric acid methyl ester (PCBM), in the presence of coumarin admixed to the system. It has been shown that the concentration of polarons and fullerene radical anions is characterized by a nonmonotonic dependence on the energy of incident photons with extrema at 1.9 and 2.7 eV. The largest increase in the concentration of mobile charge carriers was observed in composites with a coumarin content of 3 or 6 wt %. A significant slowdown of the carrier recombination process in the composites containing 3–6 wt % coumarin was observed after switching off the light. The temperature dependences of the concentrations of mobile and localized charge carriers for P3DDT/PCBM samples with a coumarin content of 3 wt % showed enhancement of the exchange interaction between charge carriers. The data obtained lead to the conclusion that coumarin affects spin interactions in the polymer composite.

Keywords: bulk heterojunction (BCJ), light-induced EPR (LEPR), methanofullerene, polaron, charge transfer, charge recombination, spin relaxation

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Organic polymer semiconductors with unique electronic properties have attracted much attention from researchers because of the promise of their use as active matrices of various molecular devices, for example, field effect transistors, photodiodes, sensors, and solar cells [1]. A significant advantage of organic electronic devices, along with increased functionality and efficiency, is the simplicity of their manufacture and a low cost. The efficiency of converting solar energy into electrical energy by organic photovoltaic cells based on composites of polymers and fullerenes currently reaches 10–17% [1–3]. Light photons in bulk heterojunctions (BHJs) of such cells generate coupled singlet excitons [4], the subsequent dissociation of which leads to the formation of spin charge carriers. The fundamental problem of photovoltaic elements based on organic polymers is the possibility of the formation of energetically deep spin traps in them due to the disordering of their matrices. Such traps capture the corresponding charge carriers, ultimately leading to a significant decrease in the effective rate of their transport. There are several stages of energy conversion in BHJs [4]: (1) generation of excitons upon absorption of light photons; (2) diffusion of excitons to the boundary of the donor and acceptor phases; (3) formation of a coupled electron–hole pair at the

interface of these phases, and its subsequent dissociation into a pair of free carriers; and, finally, (4) transport of charge carriers in the direction of the corresponding electrodes. At each of these stages, bimolecular geminate or unimolecular non-geminate recombination of charge carriers can occur, which is substantially determined by the properties of spin charge carrier traps present in the polymer.

One of the important tasks of organic photovoltaics is to optimize the morphology of composites for achieving balanced transport of both charge carriers and increasing the efficiency of solar energy conversion. It was shown [5] that the addition of 1–3 wt % diiodoctane to a polymer photovoltaic cell improves the morphology of the composite and reduces the population of electron traps, thereby ultimately reducing the carrier recombination probability. Doping with low-molecular-weight compounds not only can improve the mixing of the components of polymer composites at the molecular level, but also can accelerate the electronic processes of photogeneration and charge transfer in BHJs. It is known that coumarin, having a relatively small molecule, is a good dispersant, anticoagulant, and photophysical activator of electronic-excitation energy transfer in luminescent devices with a high quantum yield [6]. Coumarin

derivatives, due to their photochemical characteristics, stability, good solubility, and relative simplicity of synthesis, have been extensively studied with the aim of creating various electronic and photonic devices, such as solar energy batteries, nonlinear optical elements, fluorescent probes, sensors, and other functional materials [7–9]. This stimulated us to study the effect of coumarin on the dynamic and relaxation parameters of spin charge carriers in photovoltaic devices. The spin nature of the charge carriers generated by light photons in polymer–fullerene composites predetermined the use of the direct method of light-induced electron paramagnetic resonance (LEPR) spectroscopy for this purpose. In this work, we studied by the LEPR technique the photovoltaic polymer composite BHJ poly-(3-dodecylthiophene)/methanofullerene (P3DDT/PC₆₁BM) doped with trace amounts of coumarin.

EXPERIMENTAL

The chemicals used in the study were the regioregular polymer poly(3-dodecylthiophene) (P3DDT) purchased from Sigma-Aldrich (the United States), 6,6-phenyl-C₆₁-butanoic acid methyl ester (PC₆₁BM) manufactured by Solenne BV (the Netherlands), and commercial coumarin C₉H₆O₂ available from Sigma-Aldrich. All the substances were used without further purification. The chemical structures of these components are shown schematically in Fig. 1. The polymer and methanofullerene in a mass ratio of 1 : 1 were dissolved in chlorobenzene to have a concentration of 1 wt %. Samples of 6 mg P3DDT and 6 mg PC₆₁BM were dissolved in 1.1 mL of chlorobenzene, and treated for 10 min with 50-W ultrasound in a DADI DA-968 ultrasonic cleaner, heated for 30 min at 333 K, and sonicated again for 10 min. Since coumarin is poorly soluble in chlorobenzene, it was dissolved in dichlorobenzene (2.6 mg coumarin in 1 mL of dichlorobenzene). Then, by adding appropriate amounts of the coumarin solution to the P3DDT/PC₆₁BM solution, the following solutions were prepared: **1**, additive-free P3DDT/PC₆₁BM; **2**, P3DDT/PC₆₁BM + 3 wt % coumarin; **3**, P3DDT/PC₆₁BM + 6 wt % coumarin; **4**, P3DDT/PC₆₁BM + 9 wt % coumarin; and **5**, P3DDT/PC₆₁BM + 21 wt % coumarin. The resulting solutions were applied dropwise onto ceramic plates to form a thin layer gradually by one drop of a volume $V = 5 \mu\text{L}$ on each side of the plate, as it dried. In total, 75 μL of each composite solution was applied to each plate to obtain samples in the form of double-sided films.

LEPR measurements were carried out using a PS-100X 3-cm radiospectrometer (9.7 GHz) with a maximum microwave power of 150 mW and an RF synchronous/phase detection frequency of 100 kHz. The LEPR spectra of the composites were recorded at 77 K using a quartz dewar filled with liquid nitrogen, as well

as in the range of 90–340 K using a BRT temperature attachment and a flow-through quartz dewar (Special Design Bureau at the Institute of Organic Chemistry, Russian Academy of Sciences). These devices excluded the contact of the samples with atmospheric oxygen over the entire range of temperatures used. The LEPR spectrum of the composites was determined as the difference between the light and dark EPR spectra. The signal-to-noise ratio of the LEPR spectra was increased by signal accumulation using multiple scanning. The EPR spectra were processed and simulated using the programs EasySpin and OriginLab. The contributions of unpaired electrons of various charge carriers to the effective susceptibility of the sample were determined by deconvoluting the LEPR spectra according to the procedure described in [10–12]. The paramagnetic susceptibility of individual charge carriers, proportional to the concentration of spins, was determined by double integration of the absorption spectra of their spin packets far from the conditions of their microwave saturation.

The samples were illuminated directly in the cavity of the EPR spectrometer through a quartz light guide using achromatic, white light sources with color temperatures of $T_c = 15000, 5500, \text{ and } 3300 \text{ K}$, as well as monochromatic light with photon energies varying in the range of $h\nu_{\text{ph}} = 1.33\text{--}3.40 \text{ eV}$ from powerful light emitting diodes, as described in [13].

Samples for optical measurements were prepared from composite solutions **1–5** in chlorobenzene in a proportional ratio by applying onto a quartz substrate and the subsequent removal of the solvent. Ultraviolet/visible/near infrared (UV/VIS/IR) absorption spectra of composite films were recorded with a Specord 250 spectrophotometer (Analytik Jena) at $T = 298 \text{ K}$.

RESULTS AND DISCUSSION

One of the first photovoltaic systems in which the photogeneration of spin charge carriers was studied was the P3DDT/PC₆₁BM composite. Figure 1 shows the LEPR spectra of this compound and the structure of its ingredients. The polymer P3DDT without illumination exhibits an EPR signal, which is created by polarons localized on impurities and is characterized by an effective g -factor of 2.0025 in the temperature range of 77–340 K [14]. When the composites are illuminated with visible light, the light-induced EPR spectrum is recorded in the samples, which is a superposition of the spectra of individual spin charge carriers. The UV/VIS/IR absorption spectra of composites **1–5** at $T = 298 \text{ K}$ are shown in Fig. 2. The resulting UV/VIS/IR spectra are a superposition of the spectra of the polymer, the fullerene, and coumarin. All components of composites **1–5** have absorption bands in the visible and ultraviolet regions of the spectrum. It is known [15, 16] that coumarin has absorption bands at 280 and 320 nm and a broad peak in the vis-

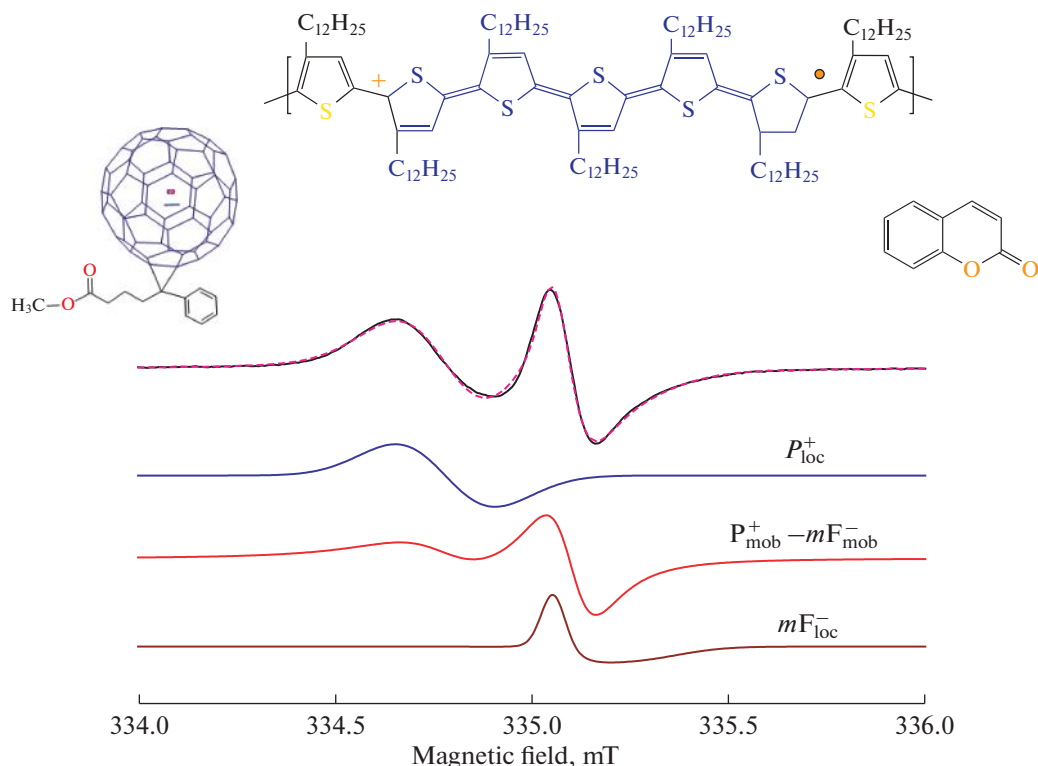


Fig. 1. Experimental LEPR spectrum of the P3DDT/PC₆₁BM composite irradiated at 77 K with a 1.89-eV light source. The dashed lines show the theoretically calculated effective spectrum and its contributions due to the spins of localized polarons and fullerene radical anions, as well as pairs of mobile polarons and fullerene radical anions.

ible region at 522 nm is due to the HOMO π –LUMO π^* transition in P3DDT [17]. The bands at 213, 257, and 329 nm (5.82, 4.82, and 3.77 eV) belong to the fullerene C₆₀ molecular moiety [18]. With an increase in the coumarin concentration in composites 1–5, the intensity of the UV absorption bands increases in proportion to the coumarin concentration and the absorption bands of the polymer moiety of the composite remain almost unchanged. An analysis of the spectra shows that there is no pronounced effect of coumarin on the structure of the absorption spectra of the polymer–fullerene composite. Figure 1 also shows the spectra of individual spin charge carriers as obtained by deconvolution of the total spectrum with allowance for the unresolved structure of individual lines and their main values of g -tensors determined in [14]. All the components of the LEPR spectra due to mobile and localized spins in the composite were determined, both for P_{mob} and P_{loc} polarons and methanofullerene radical anions F_{mob}[–] and F_{loc}[–]. Simulation of the effective LEPR spectrum and each of its contributions made it possible to separately determine the EPR line widths, spin susceptibilities χ , spin concentrations, and other magnetic resonance parameters for P_{mob}, P_{loc}, mF_{mob}[–], and mF_{loc}[–], as well as to monitor the change in these parameters with changing experimental conditions. Thus, the dependence of the number of spin charge carriers on the temperature and frequency of incident photons

was revealed. Figure 3 shows the ratios of the concentration of mobile charge carriers R_{mob}^{mF} to the concentration of polarons R_{loc}^P localized in spin traps of composites 1–5 with different coumarin concentrations, depending on the energy of incident photons E_{ph} at $T = 77$ K. The maxima of spin concentration R_{mob}^{mF} in the case of photonic excitation are observed at 1.9 and 2.8 eV for all the investigated composites. As can be seen from Fig. 3, the relative concentrations of generated mobile spins were 1.5–2 times higher in samples 2 and 3 than in parent sample 1, whereas the number of generated mobile charge carriers in samples 4 and 5 was two times lower than in the initial composite 1. It is known [6] that coumarin is a good dispersant and improves the morphology of the composites when added in an amount of 3 or 6 wt % (samples 2 and 3), but coumarin molecules at high concentrations form domains, deteriorating the morphology of the polymer composite. The energy of 1.9 eV, at which the first extremum in the dependence is observed, is close to the energy gap of the P3DDT polymer. Earlier [19, 20] in the composites of methanofullerene with the narrow-gap copolymers poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)], poly[2,7-(9',9'-dioctylfluorene)-alt-4',7'-bis(thiophen-2-yl)benzo-2',1',3'-thiadiazole], poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)], we observed similar frequency

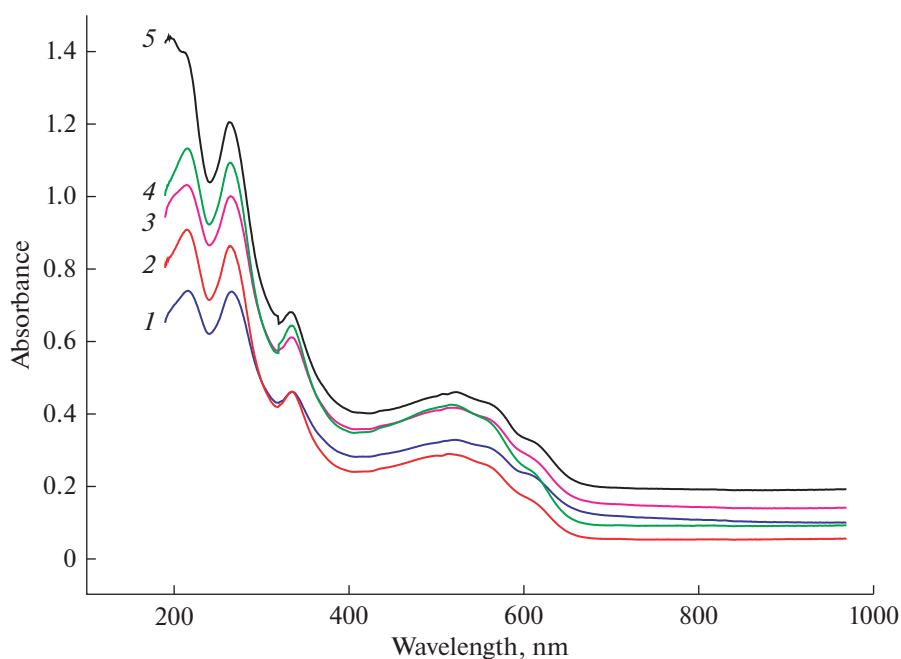


Fig. 2. UV/VIS/IR absorption spectra of composites 1–5, as measured at $T = 298$ K.

dependences for localized polarons with characteristic maxima near 1.8 and 2.7 eV. This was explained by the predominant formation of localized polarons in the matrices of these copolymer composites with specific 2D morphology, the concentration of which turned out to be more sensitive to photon energy in the studied composites than the concentration of mobile polarons and fullerene radical anions. However, the addition of coumarin to composites 1–5 under study leads to an increase in the concentration of mobile charge carriers in them. This difference is apparently associated with the 3D morphology of the P3DDT/PC₆₁BM composite and the effect of trace coumarin additives. When the light is turned off, the intensity of the LEPR spectra begins to decrease monotonically with time because of the recombination of charge carriers. From the dependences shown in Fig. 4, it follows that the signal from the mobile methanofullerene radical anions F_{mob} in systems 2 and 3 decays much slower after turning off the light than in initial sample 1, whereas the recombination of mobile spin charge carriers F_{mob} and P_{mob} in samples 4 and 5 even becomes faster compared with initial sample 1. It is important to note that mobile charge carriers in samples 2 and 3 were detected for at least 7 h after turning off the light, which is due to stabilization of the concentration of mobile carriers in composites in the presence of 3–6 wt % coumarin in modified samples. It is likely that as a result of doping with coumarin and a change in the morphology of the P3DDT/PC₆₁BM composite, the pseudorotation of fullerene molecules is hindered, as was the case with pyrene additives in [21]; on the other hand, the number, spatial scatter, and energy depth of spin traps decrease, similar to the case observed for diiodooctane-modified

polymer photovoltaic cells [5]. The result of these changes is a decrease in the probability of recombination of mobile carriers F_{mob} and P_{mob} , an increase in their concentration, and acceleration of dynamics in P3DDT/PC₆₁BM bulk heterojunctions.

The temperature dependence of spin susceptibility χ , which is determined by the concentrations of spins of polarons R^P and methanofullerenes R^{mF} , is also important for revealing the interaction of mobile and localized spins in the modified composites. An increase in the number of spin carriers in the BHJ enhances the exchange interaction between them, which is characterized by the exchange integral. According to the model of spin charge carriers interacting in disordered systems [22, 23], pairs of spins randomly distributed in the polymer matrix can interact with a spin exchange constant J_{ss} . This constant decreases upon spin capture in deep energy traps formed in a disordered matrix and increases upon overlapping wave functions of more mobile spin pairs. Figure 5 shows the temperature dependences of the concentration of localized polarons R^P_{loc} , the concentration of mobile fullerene radical anions R^F_{mob} (equal to the concentration of mobile polarons R^P_{mob}), and the ratio of mobile charge carriers R^{mF}_{mob} to the number of localized polarons R^P_{RT} detected at $T = 300$ K in the initial sample 1 and modified sample 2. It can be seen from these data that the concentrations of all spin charge carriers decrease with heating of the samples and are characterized by a peak in the region of $T \approx 110$ K. A decrease in the paramagnetic susceptibility with increasing temperature can be interpreted as

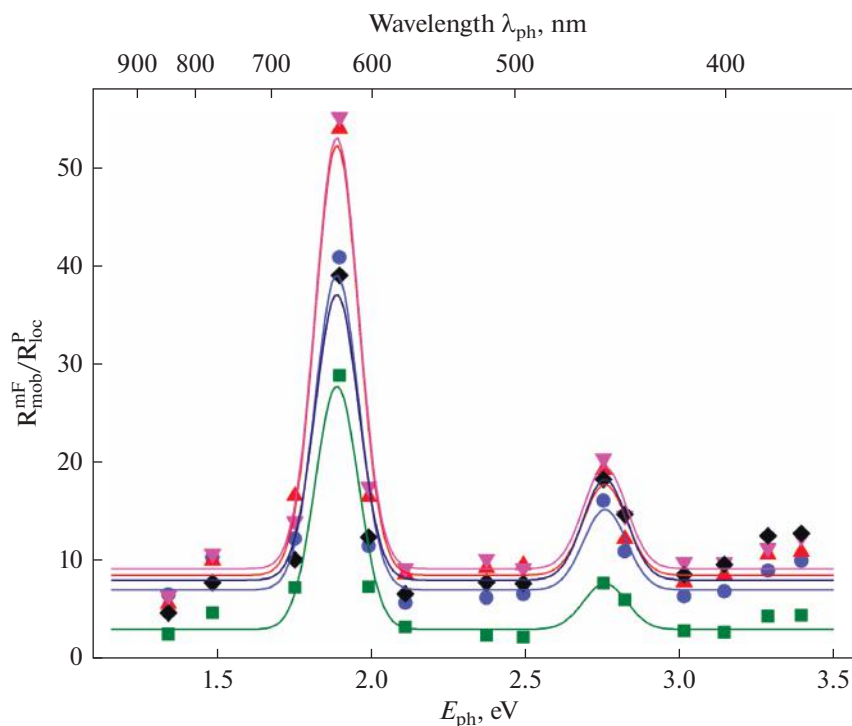


Fig. 3. Dependence of the concentration ratio of mobile charge carriers to localized polarons captured by spin traps on the energy of incident photons E_{ph} at 77 K for composites with different coumarin concentrations: (●) 1, (▲) 2, (▼) 3, (■) 4, and (◆) 5.

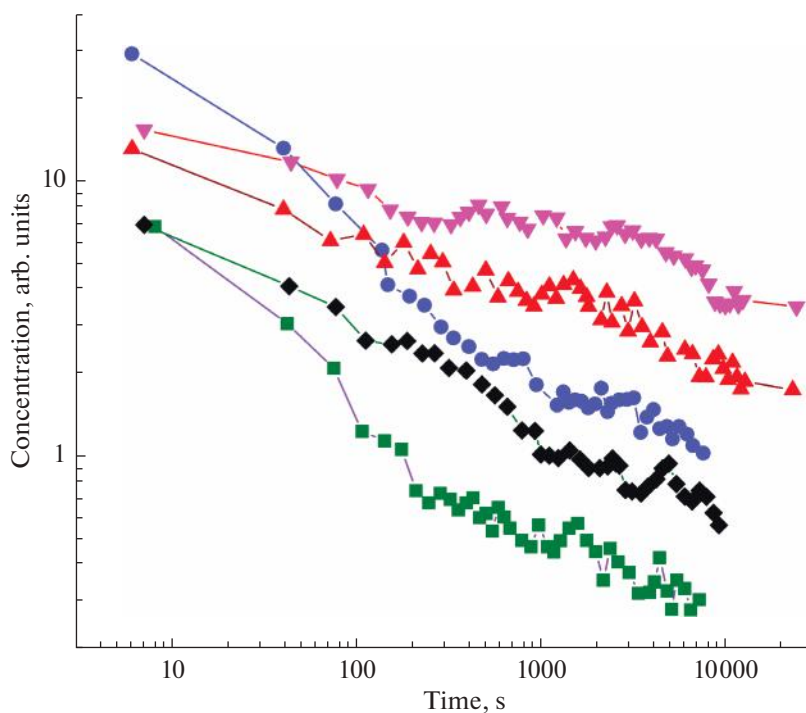


Fig. 4. Dependence of the concentrations of mobile charge carriers of methanofullerenes R_{mob}^{mF} and polarons R_{mob}^P in coumarin-modified P3DDT/PC₆₁BM composites on time after switching off the 1.89-eV light source at 77 K for samples with different additive concentrations: (●) 1, (▲) 2, (▼) 3, (■) 4, and (◆) 5.

Table 1. Values for χ_1 , χ_2 (arb. units), ω_0 , ΔE_{ij} , E_{ss} , and J_{ss} calculated by Eqs. (1) and (2) for localized polarons and mobile fullerene radical anions generated by 1.8-eV photons in initial sample **1** ($P_{loc}^{+\bullet}$ and $mF_{mob}^{-\bullet}$) and coumarin-modified sample **2** ($P_{loc}^{+\bullet}/3c$ and $mF_{mob}^{-\bullet}/3c$)

Spin packets	χ_1	χ_2	ω_0, s^{-1}	$\Delta E_{ij}, eV$	E_{ss}, eV	J_{ss}, eV
$P_{loc}^{+\bullet}$	2.02×10^{-5}	3.73×10^8	8.82×10^7	0.089	0.041	0.124
$mF_{mob}^{-\bullet}$	4.94×10^{-9}	1.31×10^8	4.64×10^8	0.148	0.051	0.201
$P_{loc}^{+\bullet}/3c$	1.67×10^{-6}	8.45×10^8	1.85×10^8	0.114	0.048	0.126
$mF_{mob}^{-\bullet}/3c$	1.97×10^{-8}	4.34×10^9	2.76×10^8	0.149	0.056	0.078

resulting from acceleration of charge recombination due to an increase in the mobility of spin carriers, which can be described in terms of the Miller–Abrahams concept [24] of polaron diffusion between the i th and j th junctions of the polymer matrix, whose energy differs by ΔE_{ij} . In analysis of the changes in paramagnetic susceptibility, the exchange interaction between spin charge carriers diffusing in the polymer matrix with a relative frequency ω_0 should also be taken into account. The probability p of this interaction is defined by the following relationship [25, 26]:

$$p = \frac{1}{2} \frac{\alpha^2}{1 + \alpha^2}, \quad (1)$$

where $\alpha = (3/2)2\pi J_{ss}/\hbar\omega_0$, J_{ss} is the constant of spin–spin exchange interaction, and \hbar is the Pauli constant. The interaction of this kind can significantly vary with temperature and should be the cause of the appearance of the term responsible for the nonmonotonic behavior of the temperature dependences presented above. As a result, the temperature dependence of the effective paramagnetic susceptibility can be written as the sum of the diffusion and exchange terms [25, 26]:

$$\chi = \chi_1 \exp(\Delta E_{ij}/k_B T) + \chi_2 2(1 + \alpha^2)/\alpha^2, \quad (2)$$

where χ_1 and χ_2 are constants. Table 1 presents the concentration and energy parameters of the BHJ of composites **1** and **2**, obtained from a comparison of the temperature dependences of their paramagnetic susceptibility measured experimentally and calculated by Eq. (2). As can be seen, the model calculations provide good agreement with the experimental data obtained for these samples, indicating the applicability of this model to the description of these spin-dependent processes in the systems under study. Earlier, we recorded similar temperature dependences of spin susceptibility in the study of multispin photovoltaic systems based on P3DDT/PC₆₁BM and doped polyaniline [27, 28]. The increase in susceptibility χ in [27, 28]

was associated with an enhancement of spin exchange by introducing of additional polyaniline spins into P3DDT/PC₆₁BM, which shifted the transition between the limits of strong and weak exchanges in this multispin system. The addition of coumarin to the P3DDT/PC₆₁BM composite improves the morphology of the samples and increases the number of mobile spin charge carriers, thereby enhancing the exchange interaction between the spins of mobile and localized charge carriers.

CONCLUSIONS

For the first time, the processes of generation, separation, transport, and recombination of spin charge carriers in the bulk heterojunctions of the initial and coumarin-modified P3DDT/PC₆₁BM composites have been studied using the LEPR method over a wide range of photon energies and temperatures. By the action of light, both positively charged polarons on chains of the polymer matrix of the samples and radical anions of methanofullerene are photogenerated and part of the charge carriers are captured of high-energy spin traps, which substantially depend on the amount of coumarin added. The contributions of localized and mobile spin charge carriers were determined by deconvoluting the total LEPR spectrum. The temperature dependences of the concentrations of mobile and localized charge carriers for the modified samples revealed an enhancement of the exchange interaction between charge carriers. The modification of the initial composite with the optimal amount of coumarin leads to an increase in the concentration of mobile charge carriers due to partial detrapping of the localized carriers and to a decrease in the probability of their recombination. This significantly increases the efficiency of light conversion by the composite and, thus, predetermines the promise of its use as a prototype of an organic energy storage.

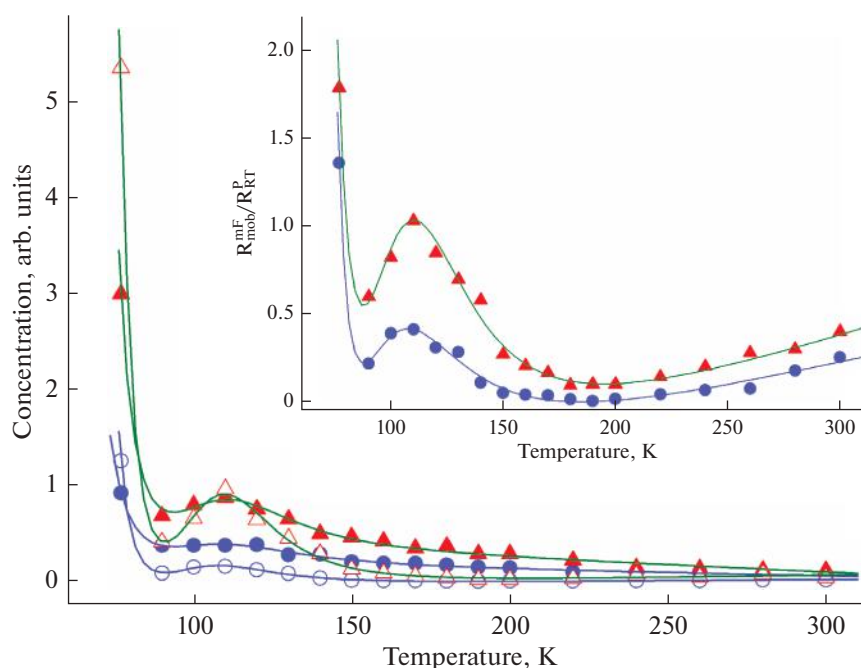


Fig. 5. Temperature dependence of the concentration of spins of localized (closed symbols) and mobile (open symbols) charge carriers in composites (●, ○) **1** and (▲, △) **2** with different additive concentrations, irradiated with 1.89-eV photons. Inset: temperature dependence of the ratio of the number of mobile spin charge carriers R_{mob}^{mF} to the number of localized polarons R_{RT}^P , determined at $T = 300$ K.

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