

EPR Study of Photogeneration of Spin Charge Carriers in Fullerene-Free Polymer Composites PBDB-T : IT-M

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Abstract—The paper presents the results of an EPR study of a new organic photovoltaic composite with a nonfullerene acceptor PBDB-T : IT-M. The parameters of the EPR spectra of all photogenerated spin charge carriers, both trapped and mobile, have been determined, which are in good agreement with previously reported data. The dependences of the spin concentration of all trapped and mobile charge carriers on the photon energy demonstrate an extreme increase in the region of 2.37 eV, which coincides with the band gap of the PBDB-T : IT-M polymer composite. The introduction of 2,5-diphenyloxazole (PPO) as a photoactivator into the system of trace additives improves the composite morphology as a result of more intense π – π interaction between the components, which enhances the exchange interaction between them and stabilizes the amount of spin charge carriers, mainly localized in the energy traps of the polymer matrix. The exchange interaction between polymers and diphenyloxazole in the composite leads to a twofold increase in the number of spins in the energy region close to the band gap of the composite.

Keywords: fullerene-free organic solar cells, polarons, light-induced EPR (LEPR), charge transfer, charge recombination, spin relaxation

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The problem concerning the synthesis and study of organic composites is central to the creation of next-generation electronic [1, 2] and spintronic [3] devices. Fullerene derivatives are commonly used as electron acceptors in photovoltaic polymer composites. However, fullerene acceptors are characterized by weak absorption of photons in the infrared and red regions of the optical spectrum, which significantly limits the energy-converting properties of such molecular devices. The use of nonfullerene electron acceptors based on small molecules with a conjugated system of π -bonds turned out to be more promising. Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-B:4,5-B']dithiophene))-*alt*-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T) has appeared as one of the most effective electron donors in polymer composites with a high-power conversion efficiency of bulk heterojunctions (BHJs) [4]. Based on this polymer and 3,9-bis(2-methylene((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithien[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-M), it was possible to create a fullerene-free composite, in which the photovoltaic conversion efficiency exceeded 12% [5]. This enhancement of the efficiency is due to better exciton dissociation and less bimolecular recombination of charge carriers in the BHJs of the PBDB-T : IT-M composite [5]. Similar parameters

were achieved in other solar cells based on the PBDB-T polymer with the inverted architecture and the ITIC and IT-M nonfullerene acceptors [5, 6]. These devices were distinguished by good thermal stability required for the long service life of organic photovoltaic systems. The PBDB-T polymer can also be used as a hole transporter in widely known perovskite solar cells due to the optimal combination of energy levels of its highest occupied molecular orbital (HOMO) and the valence band of perovskites.

Charge carriers (holes and electrons) generated in donor–acceptor polymer systems by the action of light are paramagnetic. This property permits the successful use of the method of light-induced EPR (LEPR) for studying the processes occurring in these composites with the participation of spin charge carriers of this kind [7, 8]. For example, the PBDB-T : ITIC composite was studied in [9] by the LEPR method at a recording frequency of 94 GHz. Thus, it was possible to obtain the main weakly anisotropic magnetic resonance parameters of spin ensembles arising in PBDB-T and ITIC under the action of light. The IT-M acceptor used in this work has a complementary PBDB-T structure and a high light conversion efficiency, which is a consequence of the planar conformation of the components, which leads to more intense π – π interactions between them. However, detailed EPR studies of this and other fullerene-free

composites have not yet been carried out. Therefore, the influence of the structural, electronic, and magnetic parameters of the constituents of such composites on their effective performance characteristics remains unclear.

Previously, we have demonstrated the possibility of a significant improvement in the electronic properties of organic solar cells based on polymer : fullerene BHJs by doping with the 1,2-benzopyrone (BP) and 2,5-diphenyloxazole (PPO) small-molecule organics, which exhibit the quasi-2D photoactivator or scintillator properties [10, 11]. It was shown that the addition of BP or PPO to the P3DDT/PCBM composite improves the morphology of the samples, thereby enhancing exchange interaction between the spins of mobile and trapped charge carriers and, as a result, increasing the effective concentration of mobile spin charge carriers. A study of colloidal perovskites CsPbA_3 (A: Cl, Br, I) by Cho et al. [12] revealed a significant increase in the radioluminescence quantum yield in the system after the addition of PPO. The cited authors proposed a mechanism according to which PPO plays a key role in increasing the radioluminescence of CsPbA_3 nanocomposites in octane due to surface hybridization of halide perovskite nanocomposites with PPO in a nonpolar liquid solvent medium. However, the mechanisms of interaction of polymers with 2D photoactivators in polymer composites require further study.

This work is devoted to a detailed EPR study of the magnetic resonance, relaxation, and electronic properties of the spins of charge carriers, generated by light of different frequencies in a PBDB-T : IT-M copolymer composite with a nonfullerene acceptor, and an analysis of the effect of trace additives of the 2D photoactivator PPO on these properties.

EXPERIMENTAL

We used PBDB-T and IT-M from Ossila® (the United Kingdom) and PPO from Aldrich® (the United States). The energies of the higher occupied (HOMO) and lower unoccupied (LUMO) molecular orbitals for PBDB-T are -5.33 and -3.53 eV, respectively, and the band gap of this copolymer is $E_g = 1.8$ eV. These energies for IT-M are -5.50 and -3.35 eV, respectively, and $E_g = 2.15$ eV [5]. The organic photoactivator/scintillator 2,5-diphenyloxazole (PPO) with $E_g = 3.79$ eV and $E_{\text{LUMO}} = -3.31$ eV was used as a small additive [13].

The chemical structures of these components are shown schematically in Fig. 1.

Samples for EPR measurements were prepared as follows. A weighed 10-mg portion of PBDB-T was dissolved in 1 mL of chlorobenzene. The resulting solution was sonicated at a power of 50 W for 10 min in a DADI DA-968 ultrasonic bath and heated for 10 min at $T = 50^\circ\text{C}$ for better dissolution. Then, a solution of

IT-M in chlorobenzene was prepared to have a concentration of $C = 10$ mg/mL, and the PBDB-T and IT-M solutions were combined so that the ratio of the components PBDB-T : IT-M was 1 : 1 and the concentration was 10 mg/mL. Sample 1 was an additive-free composite solution (PBDB-T : IT-M). Sample 2 (PBDB-T : IT-M/PPO) was prepared by adding a PPO solution in chlorobenzene to a solution of composite 1 so that the PPO/polymer ratio was 6 wt %. The resulting solutions of 1 and 2 were gradually poured dropwise with a droplet volume of $V = 5$ μL onto ceramic substrates until complete drying. The total volume of the sample applied onto each substrate was 25 μL . The finished samples on the ceramic substrates were additionally heated for 30 min at 160°C . For optical measurements, 5 μL of solutions of 1 and 2 were applied onto fused silica plates, followed by removal of the solvent. Ultraviolet/visible/near infrared (UV/VIS/NIR) absorption spectra of the composite films were obtained on a Specord 250 spectrophotometer (Analytik, Jena) at $T = 298$ K.

EPR measurements were carried out using a PS-100X X-band (9.7 GHz) spectrometer with a maximum microwave power of 150 mW and an RF synchronous/phase detection frequency of 100 kHz. The EPR spectra of the samples were recorded at 77 K by immersion in a quartz cell filled with liquid nitrogen. The signal-to-noise ratio of the LEPR spectra was increased by accumulating signals via multiple scanning. The EPR spectra were processed and simulated using the EasySpin and OriginLab programs. The contributions of unpaired electrons of different charge carriers to the effective susceptibility of the sample were determined by deconvolution of LEPR spectra as described in [14–16]. The paramagnetic susceptibility χ of the sample was determined by double integration of the absorption spectra of individual spin packets far from the microwave saturation conditions. The samples were illuminated directly in the spectrometer cavity using a quartz light guide and Luxeon® 5-W achromatic white light sources with a color temperature of $T_c = 5000$ K, as well as almost monochromatic light with a photon energy of $h\nu_{\text{ph}} = 1.32, 1.46, 1.61, 1.88, 1.97, 2.10, 2.34, 2.48, 2.64, 2.95,$ or 3.14 eV.

RESULTS AND DISCUSSION

Unlike fullerene derivatives as acceptors, which have an absorption maximum at 400 nm, nonfullerene acceptors of the IT-M type have a narrow energy gap in the spectrum and begin to absorb at 700 nm in solution. Figure 2 shows the absorption spectra of films of individual samples studied in this work. IT-M has absorption bands in the ultraviolet region (198 and 227 nm) and also exhibits strong absorption in the VIS–IR region of 500–800 nm, which is attributed to the HOMO–LUMO π – π^* transition [5, 17]. PBDB-T exhibits absorption bands at 250, 360, 580, and 612 nm [18]. Obviously, the absorption spectra of

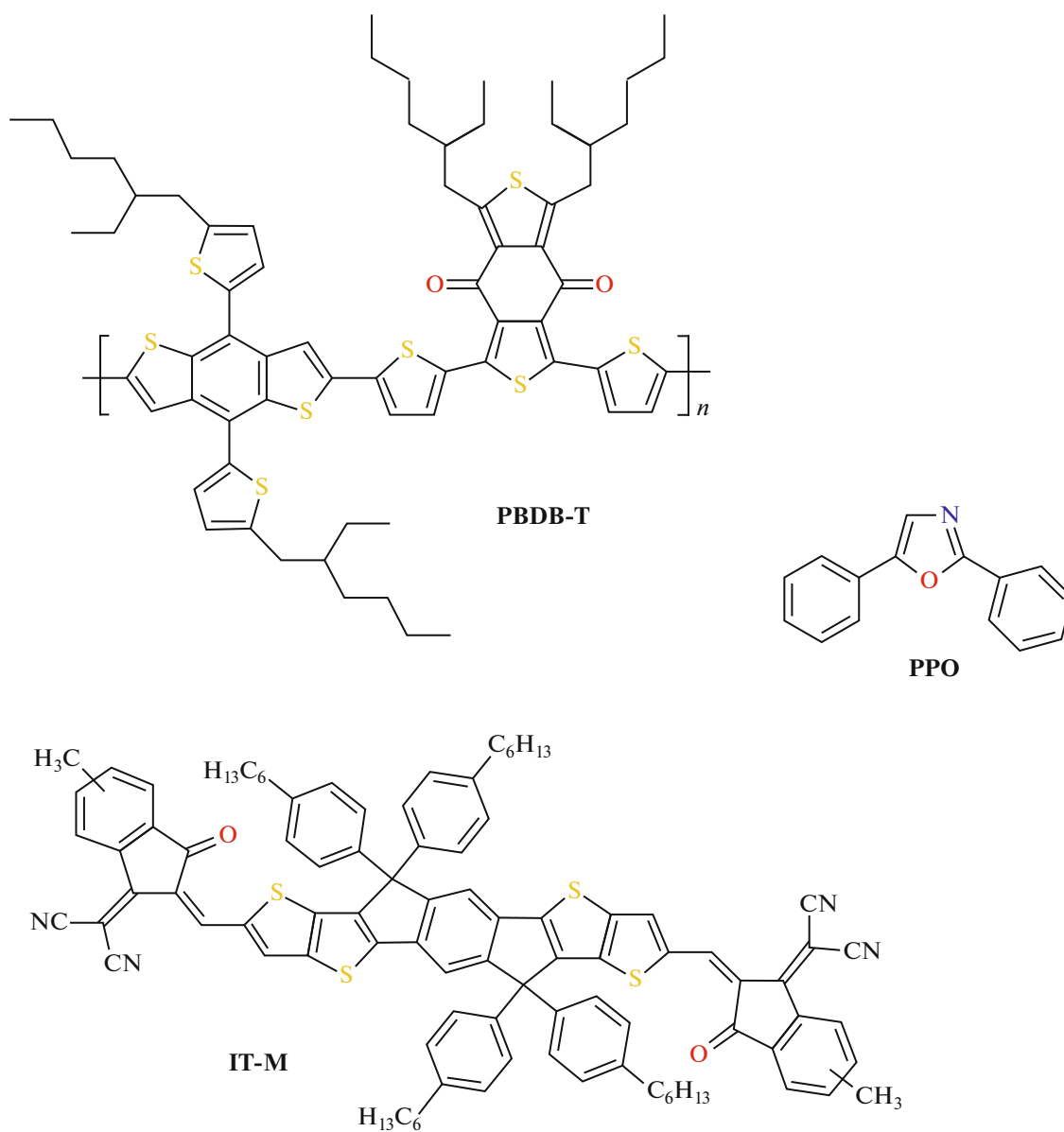


Fig. 1. Chemical structures of PBDB-T, IT-M and PPO.

PBDB-T and IT-M overlap significantly in the visible region and are complementary to each other. The absorption maximum for PPO appears at 303–305 nm (~4.1 eV) [13]. It can be seen from Fig. 2 that the absorption spectra of composites **1** and **2** differ slightly

from each other, with a slight bathochromic shift of the peaks from PBDB-T and IT-M in composite **2** as a result of PPO addition being worth noting.

In the case of illumination of composites **1** and **2** with visible light, the recorded EPR spectrum of the

Table 1. Parameters of LEPR spectra of $P^{+\cdot}$ polaron spins in the PBDB-T polymer and the $IT-M^{\cdot-}$ radical anions in composite **1**; the third row presents the parameters for the $IT-M^{\cdot-}$ radical anion in composite **2**

Charge carriers	g_{zz}	g_{yy}	g_{xx}	g_{iso}	ΔB_{pp}^X	ΔB_{pp}^Y	ΔB_{pp}^Z	ΔB_{pp}^{iso}
Polarons in PBDB-T	2.00327	2.00224	2.00146	2.00232	1.42	1.58	1.42	1.47
IT-M radical anions	2.00401	2.00304	2.00170	2.00292	1.56	1.70	1.56	1.61
PBDB-T : IT-M/PPO	2.00403	2.00299	2.00176	2.00293	1.57	1.73	1.57	1.62

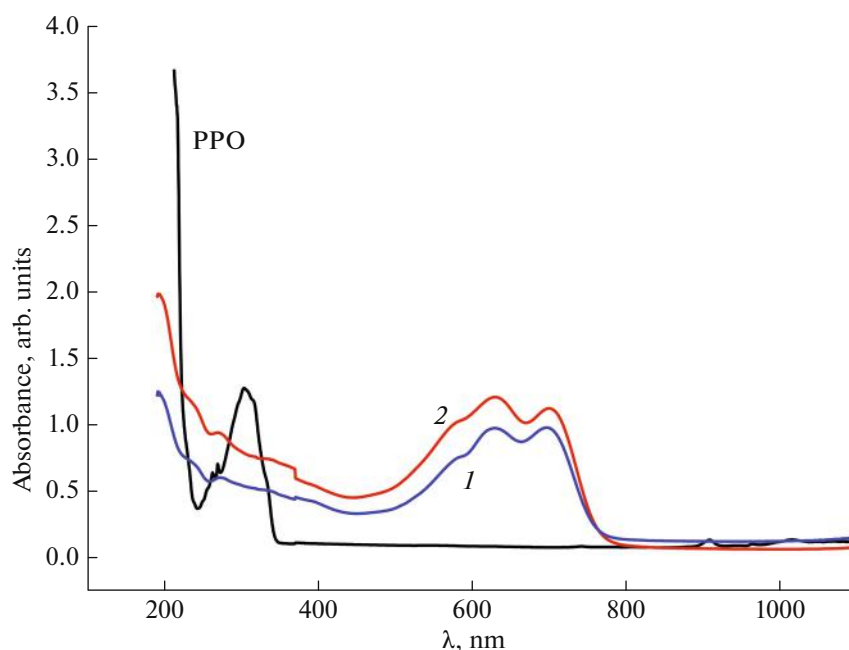


Fig. 2. UV/VIS/NIR absorption spectra of composites **1** and **2**, as recorded at $T = 298$ K.

samples (Fig. 3) is a superposition of the spectra of individual spin charge carriers, namely, positive polarons $P^{+\bullet}$ on PBDB-T and radical anions $IT-M^{\bullet-}$. Deconvolution of the apparent EPR spectra made it possible to separately obtain the values of g -factors and EPR line widths ΔB_{pp} from the components of the spectral contributions of polarons and IT-M radical anions in the composites under study. These parameters are given in Table 1. It should be noted that the EPR parameters determined in this study are in good agreement with the values of $g_{zz} = 2.0032$, $g_{yy} = 2.0022$, and $g_{xx} = 2.0019$ obtained earlier in [6] for polarons trapped in the PBDB-T polymer, as well as $g_{zz} = 2.0044$, $g_{yy} = 2.0034$, and $g_{xx} = 2.0025$ reported for radical anions. All the EPR components due to mobile and localized spins of polarons P_{mob} and P_{loc} and IT-M radical anions in the composites were distinguished. Simulation of the apparent EPR spectrum and each of its contributions made it possible to separately determine the EPR line widths, spin susceptibilities χ , and the spin concentration for P_{mob}/P_{loc} and $IT-M_{loc}/IT-M_{mob}$ (Fig. 3). The relative values of the spin concentration of charge carriers were calculated from the spin susceptibilities of the individual components of the simulated spectrum. Figure 4 shows the dependences of the spin concentration of charge carriers at different energies of photoexcitation of samples **1** and **2**. These dependences are characterized by a peaked maximum of the concentration for all constituent spins at 522 nm (2.37 eV), which is close to the value of the band gap of the polymer composite PBDB-T : IT-M. A characteristic concentration peak appears for all spin carriers,

both mobile and trapped, but the greatest increase is observed for spins localized on the polymer. When PPO is added to composite **2**, the number of localized polarons increases more than twofold compared to sample **1** without PPO, while the number of mobile polarons and $IT-M^{\bullet-}$ radical anions changes only slightly. The mechanism of the effect of the 2D photoactivator PPO on the formation of spins in the composite is not yet entirely clear; therefore, its identification requires further research. In this regard, it should be noted that the study of colloidal perovskites $CsPbA_3$ (A: Cl, Br, I) with PPO additives revealed a significant increase in the radioluminescence quantum yield in the system [12], which was reportedly attributed to surface hybridization of dopant PPO nitrogen (N) atoms and Pb atoms of perovskite due to exchange interaction. The same exchange interaction could be expected between PPO and PBDB-T and IT-M molecules in composite **2**. Indeed, the PPO molecule has a planar structure and an extended π -system. It can easily be incorporated between polymer chains and the IT-M molecule from solution during the preparation of composites, increasing the overlap of energy bands and forming van der Waals bonds between them. The position of the energy level of the lowest unoccupied molecular orbital (LUMO) of the PPO molecule is $E_{LUMO} = -3.31$ eV, close to the LUMO values for IT-M and PBDB-T of -3.35 and -3.53 eV, respectively. However, in the PPO nitrogen atom N, a significant contribution to the energy transfer is also made by the LUMO, LUMO+1, and LUMO+4 levels [12], which are positioned higher in energy than the levels of the PBDB-T and IT-M molecules and can

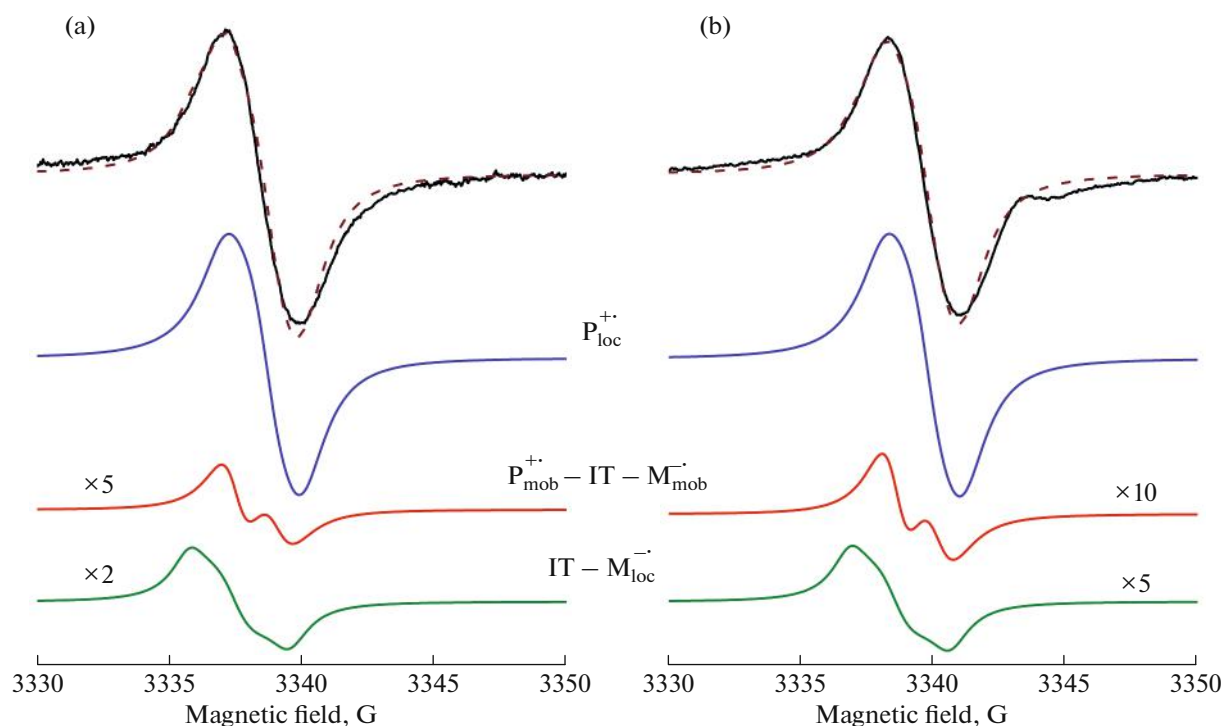


Fig. 3. LEPR spectra of composites (a) **1** and (b) **2**, as obtained experimentally under continuous illumination with white light of $T_c = 5000$ K at $T = 77$ K and calculated using the magnetic resonance parameters given in Table 1. The solid curves refer to spectral contributions of spin-trapped polarons P_{loc}^{++} and radical anions $IT-M_{loc}^{-}$, as well as mobile pairs of these charge carriers $P_{mob}^{++} - IT - M_{mob}^{-}$.

effectively induce photon transfer from PPO to PBDB-T and IT-M via the mechanism of nonradiative energy transfer. For more substantiated conclusions about the interaction of molecules in the composites, we plan to carry out density functional theory calculations in the future. The exchange interaction between PPO and the composite leads to an increase in the number of spins in the energy region close to the band gap of the composite by more than a factor of 2. In addition, doping with PPO molecules improves the composite morphology, as shown in [11]. Thus, the introduction of PPO trace additives into the composite promotes an increase in the number of spin charge carriers in the system, which are mainly localized in energy traps on the polymer.

Figure 5 shows the recombination kinetics of mobile and localized spins in test photovoltaic composites **1** and **2** when the light is turned off. This process is determined by the number and spatial distribution of spin traps formed in BHJ composites as a result of disordering of their polymer matrices. As in the case of other composites [4, 5], the process can be described in terms of the theory of multiple trapping–detrapping of mobile charge carriers involving high-energy traps [19]. According to this model, the interaction of charge carriers with such traps should lead to

a change in their concentration with time according to the relation:

$$n(t) = n_0 \frac{\pi\kappa\delta(1+\kappa)v_d}{\sin(\pi\kappa)} t^{-\kappa}, \quad (1)$$

where $\kappa = k_B T / E_0$, E_0 is the trap energy dispersion, δ is the gamma function, and v_d is the frequency of the hopping diffusion of a polaron after its detrapping. Figure 5 illustrates the dependences calculated from Eq. (1). The experimental data obtained for polarons localized in the matrices of the initial and PPO-doped samples **1** and **2** are described well by Eq. (1) with energies $E_0 = 0.0566$ and 0.0690 eV, respectively. Consequently, the recombination of long-lived spin charge carriers photogenerated in test composites **1** and **2** can be described in terms of the above model. An increase in the trap energy dispersion E_0 of the composite by doping with PPO should also indicate a change in the morphology of its polymer matrix. Note that after switching off the light source, the residual EPR signal with trapped charge carriers remained almost unchanged for a day at $T = 77$ K. This effect of slowing down photodegradation can improve the performance of energy conversion and storage devices based on polymer composites.

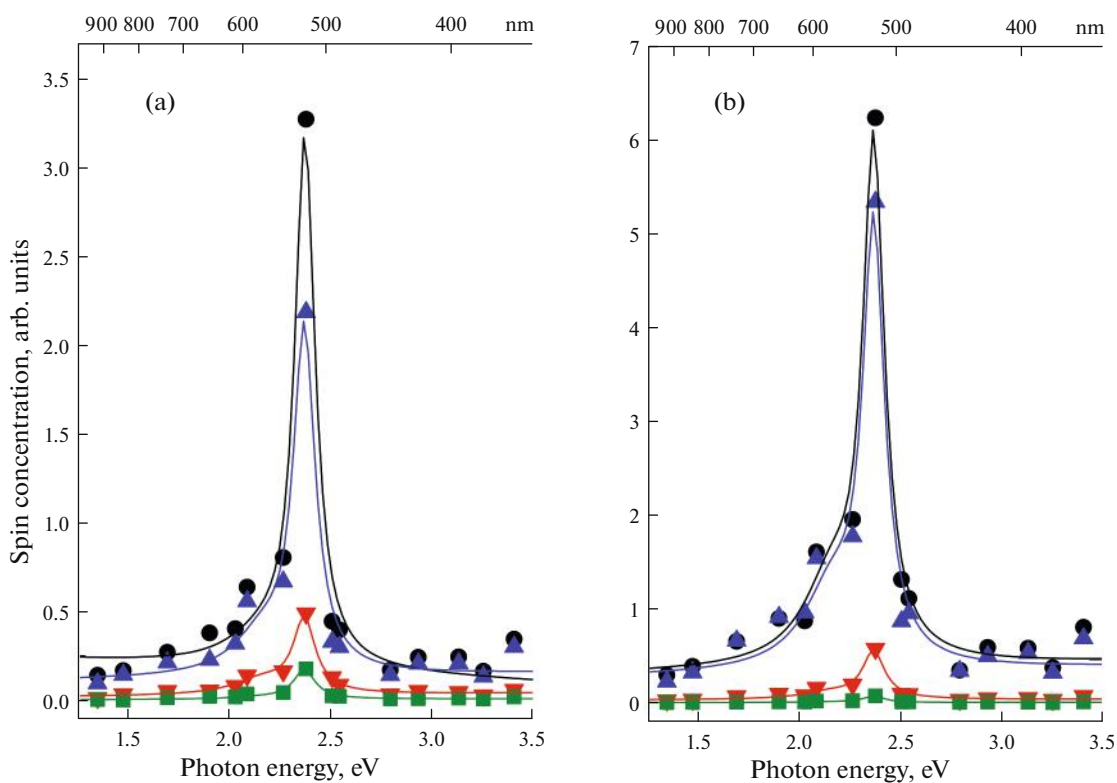


Fig. 4. Dependences of the spin concentration of charge carriers in composites (a) **1** and (b) **2** at $T = 77$ K on the energy of light sources: (●) total number of spins, (▲) polarons P_{loc}^{++} localized on the PBDB-T polymer, (▼) mobile polarons P_{mob}^{++} -IT- M_{mob}^{-} , and (■) trapped radical anions IT- M_{loc}^{-} .

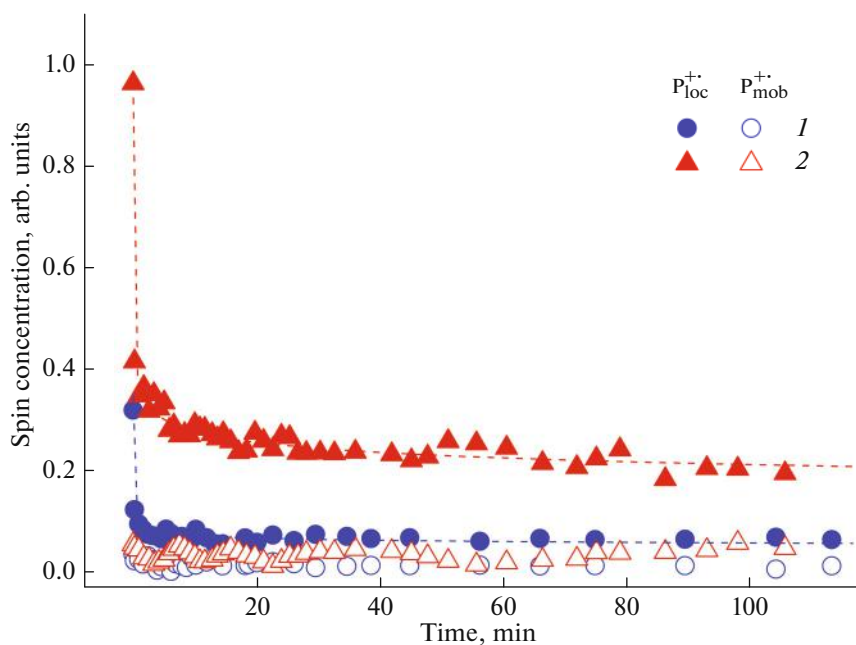


Fig. 5. Kinetics of recombination of localized (closed symbols) and mobile (open symbols points) polarons in composites **1** and **2** at $T = 77$ K after switching off the source of white light with $T_c = 5000$ K. The upper and lower curves show the dependences calculated using Eq. (1) with $E_0 = 0.0566$ and 0.0690 eV, respectively.

CONCLUSIONS

A photoinduced LEPR study of a new organic photovoltaic composite with a PBDB-T : IT-M nonfullerene acceptor has been carried out. The EPR parameters determined for all spin charge carriers generated in the composite are in good agreement with the published data. The dependence of the EPR magnetic resonance parameters of samples **1** and **2** on the incident photon energy is shown. The dependences of the spin concentration of trapped and mobile charge carriers on the photon energy demonstrate an extreme increase in the region of 2.37 eV (522 nm), which is close to the band gap of the PBDB-T : IT-M polymer composite. The introduction of PPO trace additives into the PBDB-T : IT-M composite improves the composite morphology due to the more intense π - π interaction between them, which enhances the exchange interaction between the composite components and stabilizes the amount of spin charge carriers in the composite, which are mainly localized in energy traps of the polymer matrix. The exchange interaction in composite **2** leads to a twofold increase in the number of spins in the energy region close to the band gap of the composite.

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