



Influence of spin–spin exchange on charge transfer in PANI-ES/P3DDT/PCBM composite



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ARTICLE INFO

Article history:

Received 18 April 2013

Received in revised form 13 July 2013

Accepted 16 July 2013

Keywords:

Light-induced EPR
Conducting polymers
Fullerene
Relaxation

ABSTRACT

The first results of the light-induced EPR study of magnetic, relaxation and dynamic parameters of charge carriers stabilized in emeraldine salt form of polyaniline (PANI-ES) highly doped with sulfuric (SA) and *para*-toluenesulfonic (*p*TSA) acids, spin pairs background photoinitiated in bulk heterojunctions formed by poly(3-dodecylthiophene) with [6,6]-phenyl-C₆₁-butyric acid methyl ester (P3DDT/PCBM) as well as charge carriers in appropriate PANI-ES/P3DDT/PCBM composites are described. Main magnetic resonance parameters for positively charged polarons in both polymer backbones and negatively charged methanofullerene ion-radical in the P3DDT/PCBM bulk heterojunctions were determined separately from deconvoluted LEPR spectra. These parameters were shown to be governed by the conformation of the PANI-ES chains which determines insulating and conducting forms of the PANI-SA and PANI-*p*TSA samples, respectively. The effective absorption peak-to-peak line width was described in terms of the exchange interaction of the polarons hopping along the neighboring solitary PANI and P3DDT nanoparticles. Paramagnetic susceptibility of such charge carriers was interpreted in the framework of the model of exchange coupled spin pairs differently distributed in parental polymer matrices. Exchange interaction increases dramatically as the PANI-SA network is replaced by the PANI-*p*TSA one in the triple composite. This deepens overlapping of wave functions of polarons in both polymer matrices and leads to the increase in the energy barrier which they overcome crossing a bulk heterojunctions and acceleration of spin–lattice relaxation in PANI-*p*TSA. Polaron diffusion in P3DDT was shown to govern spin susceptibility of methanofullerene anion radicals rotating between its chains.

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1. Introduction

Over the past decades organic polymer semiconductors attract great attention as promising active matrices in molecular devices, e.g., field-effect transistors, light-emitting diodes and solar cells [1]. In such systems charge is transferred by weakly spin-orbital coupled carriers, solitons and polarons [2]. This gains particular interest because the existence of a spin charge carriers in such organic semiconductors allows one to construct more efficient molecular electronic devices than using spineless ones [3]. For instance, a unique capability of spin orientation in external magnetic field and its very weak interaction with own environment in semiconductors open an undoubted imperative to developing new spin electronic (magneto-electronic, spintronic) devices simultaneously exploiting both charge and spin of electrons in the same device and appropriate cutting-edge spectroscopic methods suitable for

registration of spin polarization and its controlled manipulation [4].

Electron spin plays a crucial role in organic semiconductor devices. Injection of charge carriers into light-emitting diodes or light illumination of polymer/fullerene solar cells leads to the formation of excitons in these organic semiconductors. Excitons can be transformed into polaron pairs or donor–acceptor complexes which then can collapse into radical pairs, positively charged polarons on polymer chains and negatively charged fullerene anion radicals. Moreover, the triplet state of fullerene characterized by high electron spin polarization can also be easily photoexcited in bulk heterojunction which it forms with a polymer backbone. However, these processes themselves are not trivial phenomena whose microscopic details still remain unknown. For example, one would not necessarily expect the recombination of a charge carrier with the first opposite charged carrier. Because both the charge carriers exchangeable spin-flip, their further recombination becomes dependent on their dynamics, number, polarization and mutual separation. For large separations, when thermal energy exceeds the interaction potential, the charges can be considered as non-interacting. Once the carriers become nearer than

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the inverted Coulombic interaction potential, their wave functions overlap and exchange interactions become non-negligible. This can lead to the formation of singlet or triplet excitons in organic semiconductors. Introduction of galvinoxyl radical into polymer/fullerene bulk heterojunctions allowed one to suppress recombination of photoinduced charge carriers and thereby to improve of light conversion efficiency of such solar cells [5]. Such effect was explained by resonant exchange interaction of charged acceptors with spin adducts, which converts the bipolaronic spin state from singlet to triplet. However, direct experiments analyzing spin interactions in such systems were not been made.

Such excited states can be detected in organic systems using optical (fluorescence and phosphorescence) and/or magnetic resonance [6]. However, other absorbing species are generally present in such systems, namely polaronic charge carriers, which themselves introduce efficient subgap optical transitions. Thus, a clear assignment to triplet excitations is not always possible. Electron paramagnetic resonance (EPR) was proved to be the most effective direct tool able to reveal the underlying nature of spin carriers excited in such systems [6]. This method allows one to study various materials with weak spin–orbit coupling, where the differences in lifetime between the three excited-state triplet sublevels give rise to a spin-dependent buildup of macroscopic polarization [7], including spin charge carriers stabilized in conjugated polymers [8,9] and photoinduced in their fullerene-based compositions for photovoltaic applications [10,11]. The interaction between polarons and excitons increases under paramagnetic resonance [12]. Thus, singlet excitons are quenched to promote non-radiative decay to the ground state. However, there is no simple picture which would clarify spin resonance-assisted processes in organic semiconductors governed by spin-dependent exciton–charge interactions and consistent with the spin-dependent polaron pair recombination model [13]. Besides, we proved [11,14] that such processes are also governed by the energy of initiating photons. This can be attributed to inhomogeneous distribution of polymer and fullerene domains with different ordering (and, hence, spin trap depth and band gap energy) in their bulk heterojunction. It should also be noted that only very few data are published on molecular magnetic resonance spectroscopy related to actual problems in organic electronics.

The interaction between spin charge carriers should also affect electronic properties of organic polymers with spin charge carriers. PANI-ES seems to be one of the most suitable systems for the study of spin-assisted charge transfer in organic semiconductors. PANI-ES highly doped with, e.g., *para*-toluenesulfonic acid (PANI-*p*TSA) becomes Fermi glass with high density of states near the Fermi energy level ε_F [15,16], DC conductivity of PANI-ES follows the 3D Mott's variable range hopping (VRH) model [17]. The dispersion treatment of this system changes significantly its structure and improves its main electronic properties [18]. We showed [19] the existence in PANI-ES of two types of paramagnetic centers, namely, polarons trapped on chains in amorphous polymer phase and polarons diffusing along and between polymer chains. Polarons diffusing along polymer chains appeared to be accessible for triplet excitations injected into the polymer bulk. For the first time, EPR method has evidenced and quantified it. Spin exchange interaction leads to collision of domestic and guest spins dramatically changing their magnetic, relaxation and electron dynamics parameters. Such effect was not registered in PANI-ES highly doped by sulfuric acid (SA) [9,20] and some other [21] dopants. The magnetic field effect can be used for more detailed EPR study of electronic states and their handling/manipulation in organic semiconductors. Such principal difference can probably be explained by the increase in a PANI-*p*TSA matrix ordering under its dispersion treatment. Similarly to PANI-ES doped with camphor sulfuric acid [22], PANI-*p*TSA can also be considered as disordered metal on the boundary

of the metal–insulator transition, while PANI-SA is Fermi glass in which the electronic wave functions are localized. So-called Anderson localization arises from the severe disorder observed in the latter initiating in such a system electron VRH between exponentially localized states with energies near ε_F . However, PANI-*p*TSA demonstrates better material quality and therefore more metallic behavior with extended states near ε_F . Thus, PANI-*p*TSA is disordered metal on metallic side of the metal–insulator boundary in contrast to PANI-SA characterized as Fermi glass, in which electronic states at ε_F are localized due to disorder. This predestined the use of both these PANI-ES as reservoirs of stabilized spins in our comparative experiments.

Poly(3-alkylthiophene) (P3AT) can be used as another spin ensemble. Illumination of bulk heterojunction formed by P3AT and fullerene derivative, e.g., [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) provokes the turnover exciton to the donor–acceptor complex which collapses into positively charged polaron and a methanofullerene radical anion. Since the former shows high mobility along a polymer backbone, the radicals are scattered in this radical pair in such a way that two respective non-interacting spins are stabilized in bulk heterojunction. A long spatial distance lowers the probability of their collision and recombination that provides longer lifetime. Earlier we showed [11] that the rate, anisotropy and mechanism of charge transfer photoinitiated in different polymer/fullerene composites are governed by structure, nanomorphology and concentration of their ingredients. Therefore, we selected poly(3-dodecylthiophene) (P3DDT) previously used as an effective polymer matrix of organic solar cells [14,23,24] as a second spin reservoir.

EPR study of PANI-ES/P3DDT/PCBM composites and their ingredients is expected to provide a good framework for understanding the underlying nature of exchange interactions among spins in such system with two polaron lattices. In this work we report the first results of the LEPR study of main magnetic resonance parameters of polarons stabilized in highly doped PANI-*p*TSA, polarons and fullerene radical anions photoinduced in the P3DDT/PCBM composite under background illumination by white light, as well as these charge carriers stabilized in the PANI-*p*TSA/P3DDT/PCBM composite in a wide temperature range. To emphasize these results, we also investigated the PANI-SA and PANI-SA/P3DDT/PCBM composite. We demonstrated evident exchange interaction of polarons stabilized in PANI-ES and photoinitiated in P3DDT strongly governing by the structure of counter ions and properties of their microenvironment. This will allow to schedule the strategy of spin handling in organic semiconductors for the further construction of novel molecular devices with spin-assisted electronic transport.

2. Experimental

Powder-like emeraldine salt form of polyaniline (PANI-ES) highly doped with sulfuric and *para*-toluenesulfonic acids (PANI-SA and PANI-*p*TSA, respectively) using the described procedures [16,17,25] was used. DC conductivity of the samples was measured at room temperature to be 23.5 and 7.1 S/cm, respectively. Soluble regioregular poly(3-dodecylthiophene) (P3DDT) purchased from Aldrich and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) purchased from Solenne BV were also used to produce bulk heterojunctions, in which hole and radical anion charge carriers were photoinitiated. These ingredients are shown schematically in Fig. 1.

For the analysis of spin properties of the initial PANI-ES samples, they were comminuted to decrease characteristic size of their individual particles down to ca. 30 μm , mixed with pure MgO powder (1:5) and then placed into a quartz capillary with the internal diameter of ca. 2 mm. Such polymer dilution by an insulating matrix allowed one to prevent possible interaction between

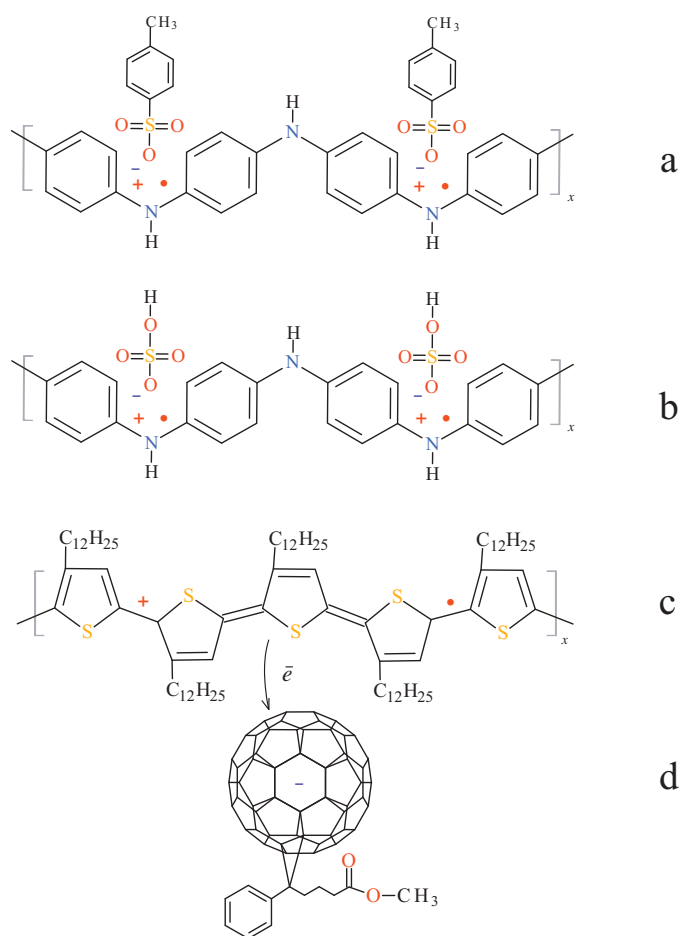


Fig. 1. Schematic structure of emeraldine salt of polyaniline in the polaron lattice state fully doped with sulfuric (a) and *para*-toluenesulfonic (b) acids, regioregular poly(3-dodecylthiophene) (c), and [6,6]-phenyl-C₆₁-butyric acid methyl ester (d). The appearance of positive charged polaron in the P3DDT backbone due to photoinitiated charge separation and transfer to the fullerene globe is shown.

powder particles. Quartz capillaries with so-prepared samples were filled with dry argon and closed before further EPR experiments. The chlorobenzene solution of P3DDT and PCBM taken at a 1:1 wt. ratio with concentration ca. 1 wt.% was placed into ceramic plate and dried. Therefore, the P3DDT/PCBM composite was formed as film with the size of ca. $4 \times 8 \text{ mm}^2$ and thickness of ca. 0.1 mm. Bulk heterojunctions of so prepared polymer/fullerene bulk heterojunctions employing P3DDT as an electron donor and PCBM as an electron acceptor were used for individual photonic analysis in nitrogen atmosphere. Finally, PANI-ES powders were mixed with the above chlorobenzene solution of the latter composite at a 1:1 wt. ratio, placed into similar ceramic plates and dried in nitrogen atmosphere before EPR experiments.

Magnetic resonance experiments were performed using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with 100 kHz field ac modulation for phase-lock detection. The “dark” (EPR) and light-induced (LEPR) spectra of the initial samples and their respective composites were measured in the 90–340 K temperature range in dry nitrogen atmosphere using a BRT SKB IOH temperature controller and at 77 K in a quartz Dewar filled with liquid nitrogen. LEPR spectra were measured at background illumination of the composites directly in a microwave cavity of an EPR spectrometer using a LP5W-80F320CW solid-state white light source with the intensity of ca. 5400 Lux measured by Luxmeter CT312 and 5500 K color temperature. Total paramagnetic susceptibility of the samples was determined using double integration of their EPR spectra obtained

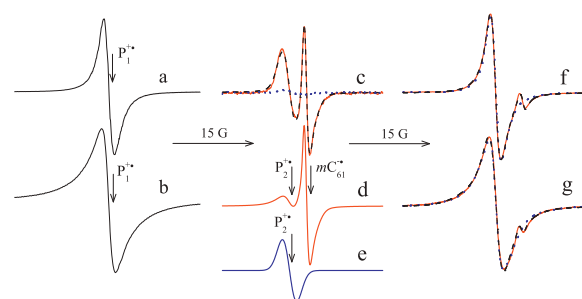


Fig. 2. X-Band EPR spectra of polarons $P_1^{\bullet+}$ stabilized in PANI-SA (a) and PANI-*p*TSA (b), P3DDT/PCBM bulk heterojunctions illuminated by white light (c) with contributions due to mobile polaron-methanofullerene radical pairs $P_2^{\bullet+}$ - $mC_{61}^{\bullet-}$ (d) and localized polarons $P_2^{\bullet+}$ pinned by deep traps (e) as well as PANI-SA/P3DDT/PCBM (f) and PANI-*p*TSA/P3DDT/PCBM (g) composites illuminated by white light at 77 K. Dashed line in (c) and deconvoluted lines (d and e) show EPR spectra calculated using $\Delta B_{pp}^p = 2.67 \text{ G}$, $\Delta B_{pp}^p = 1.17 \text{ G}$, and $[P_2^{\bullet+}]/[mC_{61}^{\bullet-}] = 2.0$. In (c), (f) and (g), dotted lines exhibit “dark” EPR spectra of paramagnetic centers stabilized in appropriate composites, whereas the spectra calculated at their illumination by white light at 77 K are shown by dashed lines. The positions of paramagnetic centers and their terms are shown as well.

with and without light illumination far from MW saturation conditions. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) single microcrystal was used as standard for estimation of spin concentration and *g*-factors. The *g*-factor, absorption amplitude, peak-to-peak linewidth and energy parameters were determined with $\pm 1 \times 10^{-4}$, $\pm 1.2\%$, $\pm 1 \times 10^{-2} \text{ G}$, and $\pm 5\%$ accuracy, respectively. The spin-lattice relaxation time T_1 was measured by saturation method [26]. All the spectra were simulated numerically using the Bruker Simfonia and OriginLab software.

3. Results and discussions

3.1. EPR and LEPR spectra

To analyze the nature of all paramagnetic centers in both the PANI-SA/P3DDT/PCBM and PANI-*p*TSA/P3DDT/PCBM composites, first related study of spin properties of their ingredients should be done.

Initial PANI-SA and PANI-*p*TSA samples shown in Fig. 1a and b exhibit single 3-cm waveband EPR spectra presented in Fig. 2a and b, attributed to polarons $P_1^{\bullet+}$ with effective *g*-factor equal to 2.003₁ (PANI-SA) and 2.002₈ (PANI-*p*TSA) stabilized in their backbones. These values remain almost unchanged within all temperature range used during long time that is characteristic of paramagnetic centers in crystalline high-conductive solids [9,20,27]. As-prepared P3DDT/PCBM sample does not demonstrate any EPR spectrum without light irradiation (Fig. 2c). When illuminated by visible light, positively charged polaron is formed on a polymer backbone due to electron transfer to methanofullerene (see Fig. 1). Various experimental methods have shown the reversibility of this process and its stability over time [10,11]. Thus, two partly overlapping LEPR lines are observed at low temperatures (Fig. 2c). As in our previous studies [14,24], this spectrum was attributed to radical pairs of positively charged diffusing polarons $P_2^{\bullet+}$ with isotropic (effective) $g_{iso} = 2.0018$ and negatively charged radical anions $C_{61}^{\bullet-}$ with effective $g_{iso} = 1.9997$ rotating about the main axis. These values are close to those obtained for spin charge carriers photoinduced in other polymer/fullerene bulk heterojunctions [11,28]. The EPR line shape due to dipole or hyperfine broadening is normally Gaussian. Due to spin 3D motion in metal-like crystallites of PANI-ES or exchange of different spin packets, the line shape becomes close to Lorentzian shape, corresponding to an exponential decay of transverse magnetization. The effective LEPR spectrum presented in Fig. 2c shows mainly a Lorentzian doublet of mobile

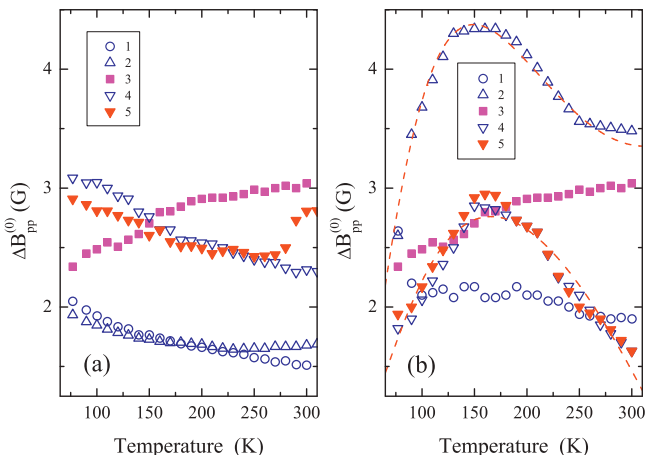


Fig. 3. Temperature dependence of peak-to-peak line width $\Delta B_{pp}^{(0)}$ determined for domestic polarons $P_1^{\bullet+}$ stabilized in the initial PANI-ES backbones (1), PANI-ES/P3DDT/PCBM composites (2), polarons $P_2^{\bullet+}$ background photoinitiated by white light in the P3DDT/PCBM bulk heterojunctions (3), as well as polarons $P_2^{\bullet+}$ stabilized in the darkened (4) and irradiated by white light (5) PANI-ES/P3DDT/PCBM composites with SA (a) and *p*TSA (b) counter-ions. The upper (O) symbol in $\Delta B_{pp}^{(0)}$ implies this parameter to be measured far from the spectrum microwave saturation. Dashed lines show the dependences calculated from Eq. (1) with $\omega_{hop}^0 = 1.2 \times 10^9 \text{ s}^{-1}$, $E_b = 6.3 \text{ meV}$ (above line), $\omega_{hop}^0 = 1.3 \times 10^9 \text{ s}^{-1}$, $E_b = 11.6 \text{ meV}$ (below line), $J_{ex} = 110 \text{ meV}$, and $n_p = 1.2 \times 10^{-4}$. The error margins are of the order of symbol size.

radical pairs $P_2^{\bullet+} - mC_{61}^{\bullet-}$, shown in Fig. 2d as a sum of equally contributed mobile polarons $P_2^{\bullet+}$ and fullerene methanofullerene radical anions $mC_{61}^{\bullet-}$ as well as a Gaussian contribution of the former charge carriers pinned by deep traps appeared in a polymer matrix under its illumination (shown in Fig. 2e). Both mobile charge carriers recombine with the probability increasing with temperature, and their effective spectrum shown in Fig. 2d becomes too weak to be registered at $T \geq 200 \text{ K}$ at a reasonable signal/noise ratio. Captured polarons $P_2^{\bullet+}$ are characterized by higher stability, and their spectrum can be observed for several hours even at high temperatures. Nevertheless, these carriers indirectly participate in collective charge transfer through bulk heterojunctions.

It is evident that LEPR spectra of both PANI-SA/P3DDT/PCBM and PANI-*p*TSA/P3DDT/PCBM composites presented in Fig. 2f and g, respectively, can be considered as a sum of P3DDT/PCBM and appropriate PANI-ES contributions. As an illumination is turned off, the spectra originated from the polarons $P_1^{\bullet+}$ stabilized in PANI-ES (shown in Fig. 2a and b) and polarons $P_2^{\bullet+}$ pinned in P3DDT/PCBM (shown in Fig. 2e) can only be registered (see Fig. 2f and g). In study charge-separated states and spin–spin interactions in these systems more precisely, their spectra should be tentatively deconvoluted, as it was successfully done for analogous spin-modified systems [14,29,30]. This allowed to obtain separately magnetic resonance parameters of all paramagnetic centers stabilizing in initial polymers and appropriate composites and analyze their interaction in bulk heterojunctions.

3.2. EPR line width

Fig. 3a shows temperature dependences of effective absorption peak-to-peak line width ΔB_{pp} of polarons $P_1^{\bullet+}$ stabilized in the PANI-SA, $P_2^{\bullet+}$ photoinitiated in P3DDT/PCBM bulk heterojunctions, and these values obtained for darkened and illuminated PANI-SA/P3DDT/PCBM composite. It is seen that the EPR line width for both polarons stabilized in these systems depends on structure of a polymer matrix. Indeed, the heating of the initial PANI-SA samples is accompanied by a monotonic decrease in ΔB_{pp} of polarons $P_1^{\bullet+}$ stabilized on their chains. However, this parameter for polarons

$P_2^{\bullet+}$ photoinitiated in the P3DDT/PCBM bulk heterojunctions evidences an opposite temperature dependence as compared with that for polarons $P_1^{\bullet+}$ (Fig. 3). This effect can be explained by different interaction of these polarons with appropriate polymer lattice (see below). The formation of the PANI-SA/P3DDT/PCBM composite does not noticeably changes the line width for paramagnetic centers $P_1^{\bullet+}$. However, this originates the change in the temperature dependence of $P_2^{\bullet+}$ charge carriers photoinitiated in the P3DDT matrix (see Fig. 3a).

Spin properties of both polaronic reservoirs in the PANI-ES/P3DDT/PCBM composites are strongly governed by the conformation of PANI-ES chains which determines its main electronic properties [18]. As the PANI-SA matrix is replaced by the PANI-*p*TSA one, both polarons $P_1^{\bullet+}$ and $P_2^{\bullet+}$ start to demonstrate extreme temperature dependent line widths characterized by appropriate critical point $T_{ex} = 150 \text{ K}$. A similar effect was observed in the EPR study of exchange interaction of polarons with guest oxygen biradicals $\cdot O - O \cdot$ in PANI-ES highly doped with hydrochloric acid [31] and *p*TSA [19]. This effect was identified as exchange interaction in quasi-pairs formed by guest spins with domestic mobile polarons hopping between sites of polymer chain with rate ω_{hop} across energy barrier E_b . Such interaction is characterized by the exchange integral or the constant of spin exchange interaction J_{ex} . Thus, the data, presented in Fig. 3b can perfectly be described in terms of the spin–spin exchange interaction of polarons $P_1^{\bullet+}$ and $P_2^{\bullet+}$ hopping in the nearby located solitary polymer chains. The collision of both type spins should additionally broaden the absorption term of EPR line by the value [32]

$$\delta(\Delta\omega) = p\omega_{hop}n_p = \frac{1}{2}\omega_{hop}n_p \left(\frac{\alpha^2}{1+\alpha^2} \right), \quad (1)$$

where p is flip–flop probability during a collision of both spins, $\omega_{hop} = \omega_{hop}^0 \exp(-E_b/k_B T)$, n_p is a number of guest polarons per each aniline ring, $\alpha = (3/2)2\pi J_{ex}/\hbar\omega_{hop}$ and $\hbar = h/2\pi$ is the Plank constant. According to spin exchange fundamental concepts $\delta(\Delta\omega) \sim 1/2n_p\omega_{hop}$ at strong interaction [32], whereas $\delta(\Delta\omega) \sim n_p/\omega_{hop}(J_{ex}/\hbar)^2$ holds as such interaction becomes weaker. If these conditions can be realized in a spin system at $T \leq T_c$ and $T \geq T_c$, respectively, the line width should be characterized by the extreme temperature dependence. In particular, it is an evidence of a stronger interaction of polarons with own microenvironment in P3DDT as compared with PANI-ES.

Assuming activation character of polaron motion in both polymer matrices and $n_p = 1.2 \times 10^{-4}$ obtained for P3DDT/PCBM bulk heterojunctions [14], the line width of the polarons $P_1^{\bullet+}$ and $P_2^{\bullet+}$ can be fitted by Eq. (1) with $E_b = 6.3$ and 11.6 meV , respectively, at $J_{ex} = 110 \text{ meV}$ (see Fig. 3b). J_{ex} is less than that (360 meV) determined for air-filled PANI-*p*TSA [19] due probably to less number of guest radical and higher inter-polaron distance.

3.3. Spin susceptibility

The temperature dependence of spin susceptibility χ is also important to reveal mobile or localized character of spins and their possible interaction. For non-interacting and localized (or slightly delocalized) electrons in disordered phase, susceptibility follows the Curie law $\chi_C \propto 1/T$, whereas polarons delocalized in the conduction band of ordered crystallites cause temperature-independent Pauli behavior, χ_p . However, such simple picture has been questioned especially for polyaniline and other conducting polymers because most of the spins are expected to be localized [8,33]. Disorder localizes electron spins and conducting polymer systems exhibit significant disorder. Therefore, we used an exchange coupled pairs (ECP) model [34,35]. According to this approach, $N_s/2$ spin pairs randomly distributed in a polymer matrix can interact

Table 1

The values of C , a_d , and J determined for effective paramagnetic susceptibility χ of polarons $P_1^{\bullet+}$ stabilized in the initial PANI-SA and PANI-*p*TSA matrices and polarons $P_2^{\bullet+}$ photoinduced in the P3HT network of respective PANI-ES/P3DDT/PCBM composites fitted using Eq. (2) and the data of Fig. 4.

	Parameter	$P_1^{\bullet+,a,c}$	$P_1^{\bullet+,b,c}$	$P_2^{\bullet+,c,d}$	$P_2^{\bullet+,d,e}$
PANI-SA	C , emu/mol 2Ph	2.3×10^{-6}	2.2×10^{-6}	1.1×10^{-9}	1.5×10^{-9}
	a_d	0.041	0.039	0.965	0.966
	J , meV	3.8	5.6	11	6.4
PANI- <i>p</i> TSA	C , emu/mol 2Ph	5.8×10^{-6}	9.8×10^{-7}	1.1×10^{-8}	1.0×10^{-8}
	a_d	0.88	0.98	0.92	0.98
	J , meV	3.4	9.8	20	15

^a Polarons in initial PANI-ES.

^b Polarons in PANI-ES embedded into the PANI-ES/P3DDT/PCBM composite.

^c Polarons in the darkened samples.

^d Polarons initiated in P3DDT network of the PANI-ES/P3DDT/PCBM composite.

^e Background illuminated by white light.

with the exchange coupling coefficient J . A small value of J corresponds to spin localization in a strongly disordered matrix. Higher value of J arises at overlapping of wave functions of spin pairs in more ordered regions. In this case effective spin susceptibility of such interacting spins should depend on temperature as [34]

$$\chi(T) = \frac{Ca_d}{k_B T} \left[3 + \exp\left(-\frac{2J}{k_B T}\right) \right]^{-1} + C(1 - a_d) \left\{ \frac{J}{3k_B T} + \ln \left[3 + \exp\left(-\frac{2J}{k_B T}\right) \right] \right\}, \quad (2)$$

where $C = N\mu_B^2 g^2 S(S+1)$ is a constant, μ_B is the Bohr magneton, g is the Lande factor, and a_d is a fraction of spin pairs interacting in disordered polymer regions.

Fig. 4a and b shows the temperature dependence of spin susceptibility χ with contributions due to polarons $P_1^{\bullet+}$, $P_2^{\bullet+}$ and methanofullerene radical anions $mC_{61}^{\bullet-}$ forming spin pairs in the P3DDT/PCBM bulk heterojunctions stabilized in the darkened and background illuminated PANI-SA/P3DDT/PCBM and PANI-*p*TSA/P3DDT/PCBM composites. The analysis of the above data was performed using an ensemble of $N_s/2$ spin pairs with an uniform distribution of intrapair exchange characterized by coefficient J . It is seen that the model calculations provide excellent fits to all the experimental data sets within all temperature range used. The C , a_d , and J values determined for polarons carrying a charge in the initial PANI-ES and respective PANI-ES/P3DDT/PCBM composites are summarized in Table 1. Spin susceptibility obtained for $P_1^{\bullet+}$ is close to that obtained for PANI highly doped by sulfonic [15] and hydrochloric [36] acids. The latter parameter is normally a function of distance. When polymer chains vibrate, J for polarons diffusing along neighboring chains would oscillate and should be described by a stochastic process [37]. However, such effect appears at low temperatures, when $k_B T \ll J$. Thus, it can be neglected within all temperature range used. Nevertheless, this constant increases as polarons $P_1^{\bullet+}$ start to interact with polarons $P_2^{\bullet+}$ and, on the side, SA counter ions are replaced by *p*TSA ones (see Table 1). This is additional evidence of strong interaction of polarons stabilized in both PANI-ES and P3DDT matrices. When the Fermi energy ε_F is close to the mobility edge, the temperature dependence of spin susceptibility gradually changes from Curie-law behavior $\chi_C \propto 1/T$ to temperature-independent Pauli-type behavior with increasing temperature. Corresponding density of states $n(\varepsilon_F)$ for both spin directions per monomer unit at ε_F can be determined from the analysis of the $\chi(T)T$ dependence for all polarons stabilized in both polymers (see inserts in Fig. 4). It is seen that the *p*TSA-treated system is characterized by higher $n(\varepsilon_F)$ as compared with PANI-SA. This can be explained by the difference in their above mentioned metallic properties and also by on-site electron–electron interaction [38].

Spin susceptibility obtained for methanofullerene radical anions $mC_{61}^{\bullet-}$ in both composites demonstrates sharper temperature dependence (Fig. 4). This can be explained by fast recombination of the polaron–methanofullerene radical pairs $P_2^{\bullet+} - mC_{61}^{\bullet-}$. The spectrum is shown in Fig. 2d. During background illumination of the P3DDT/PCBM bulk heterojunctions, two processes are realized simultaneously, namely, photoinitiation and recombination of spin pairs. As a result, we detected only net (effective) spin concentration. Therefore, effective paramagnetic susceptibility of both charge carriers photoinitiated in P3DDT/PCBM bulk heterojunction should inversely depend on the probability of their recombination. Such process is also governed by multi-stage activation one-dimensional (1D) polaron hopping between polymer units [39].

Positive charge on a polaron is not required to be recombined with the first negatively charged methanofullerene radical anion. Activation traveling of a polaron near such a center localized near a polymer chain should interact with its unpaired electron with the above probability p [40]. In this case, effective spin susceptibility of such interacting spin sub-pairs can finally be written as [11,14,30,41]

$$\chi = \chi_0 \frac{2(1 + \alpha^2)}{\alpha^2} \exp\left(\frac{E_b}{k_B T}\right). \quad (3)$$

The dependences calculated from Eq. (3) with $E_b = 24$ and 50 meV are also presented in Fig. 4. The latter value is higher than $E_b = 11.6$ meV obtained from Eq. (1) for polaron diffusion in the respective system. It can probably be explained by more complex exchange interaction of methanofullerene radical anion with polarons in both the PANI-*p*TSA and P3DDT backbones. Eq. (3) fits well the experimental data presented in Fig. 4. Therefore, the decay of long-lived charge carriers originated from initial spin pairs photoinduced in the PANI-ES/P3DDT/PCBM composites can successfully be described in terms of the above model in which the low-temperature recombination rate is strongly governed by temperature and the width of energy distribution of trap sites. This process is also determined by structure and morphology of radical anion and its environment in a polymer backbone. The use, for example, of poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) instead of P3DDT and C_{70} -based methanofullerene instead of $PC_{60}BM$ should facilitate the excitation to reach the polymer/fullerene interface for charge separation before it becomes spatially self-localized and bound within an exciton [42]. Therefore, the main properties of an exciton are irrelevant to ultrafast charge transfer and do not limit effective charge transfer in such composite.

It is seen from Fig. 4 that spin susceptibility of polarons $P_1^{\bullet+}$ stabilized in both initial PANI-ES samples is characterized by weak temperature dependence without any anomaly. This also holds for polarons $P_2^{\bullet+}$ photoinitiated in the PANI-SA/P3DDT/PCBM composite. The shape of $\chi(T)$ changes dramatically as SA counter ions are replaced by *p*TSA ones. Such a replacement provokes extremal χ vs. T dependence obtained for polarons $P_1^{\bullet+}$ and $P_2^{\bullet+}$ (see Fig. 4b). This is evidence of the above mentioned exchange interaction between these polarons formed on neighboring PANI and P3DDT chains. Such interaction increases the overlapping of their wave functions (which, however, slightly decreases at further light flashing) and the energy barrier which overcomes the polaron crossing a bulk heterojunction. This affects the polaron intrachain mobility and, therefore, probability of its recombination with fullerene anion. However, the character of the $mC_{61}^{\bullet-}$ quasi-rotation changes weakly under such a replacement (see Fig. 4).

3.4. Spin relaxation

Spin–lattice, T_1 , and spin–spin, T_2 , relaxation times can get important information about spin localization, matrix

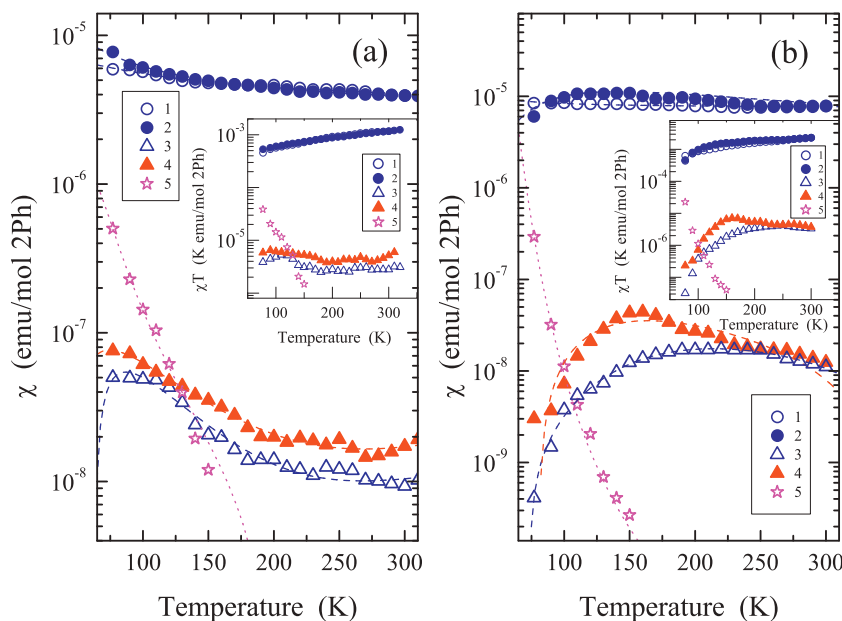


Fig. 4. Temperature dependences of spin susceptibility χ and χT product (inserts) obtained for domestic polarons P_1^{*+} stabilized in the initial PANI-ES network (1) and respective PANI-ES/P3DDT/PCBM composite (2), polarons P_2^{*+} stabilized in the darkened (3) and illuminated by white light (4) PANI-ES/P3DDT/PCBM composites, as well as methanofullerene radical anions mC_{61}^{*-} (5) photoinitiated in these composites with SA (a) and pTSA (b) counter-ions. The error margins are of the order of symbol size. Dashed lines show the dependences calculated from Eq. (2) with C , a_d , and J presented in Table 1. The dotted lines show the dependences calculated from Eq. (3) with $E_b = 24$ (a) and 50 (b) meV.

dimensionality and spin-assisted electronic processes carrying out in the system under study. There are several relaxation and dynamic processes, for example, dipole–dipole, hyperfine, exchange interactions between paramagnetic centers of different spin-packets, etc., which cause the shortening of spin relaxation times and hence the change of the shape of an EPR line. Above, it was demonstrated with the EPR linewidth term $\delta(\Delta\omega)$ which is opposite proportional to the spin–spin relaxation time. Spin–lattice relaxation shortens the lifetime of a spin state and broadens the line as well. If we, represent all the other relaxation processes by a time T_2^l , we can write the half-linewidth of a Lorentzian line at half power, $\Delta B_{1/2}$, as [43]

$$\Delta B_{1/2} = \gamma_e^{-1} T_2^{-1} = \gamma_e^{-1} \left(\frac{1}{T_2^l} + \frac{1}{2T_1} \right), \quad (4)$$

where γ_e is the gyromagnetic ratio for electron. Earlier, we have showed that spin relaxation of spin charge carriers stabilized in, e.g., PANI-SA [20,44], PANI-pTSA [19,45], and P3DDT [14,23,24] is strongly defined by structural, conformational and electronic properties of their microenvironment. So, it would be important to analyze also how spin exchange affect spin–lattice relaxation. The interaction of polarons P_1^{*+} stabilized in the PANI-SA matrix was appeared to be depending weakly on the presence of guest spins. They dominantly contribute in an effective spin susceptibility of the composites under study. So, a spin–lattice relaxation of these charge carriers in the PANI-pTSA and PANI-pTSA/P3DDT/PCBM bulk heterojunctions can be analyzed with more degree of certainty.

Fig. 5 exhibits temperature dependencies of T_1 and T_2 values for polarons P_1^{*+} stabilized in shadowed PANI-pTSA and PANI-pTSA/P3DDT/PCBM samples. Spin–spin relaxation was shown above to be governed by the spin–spin exchange interaction. Spin–lattice relaxation time of the samples was measured at room temperature to be 0.45×10^{-7} and 0.33×10^{-7} s, respectively. These values are in good agreement with $T_1 = 0.98 \times 10^{-7}$ s obtained by Wang et al. [46] for polyaniline highly doped by hydrochloric acid. It is seen, that spin–lattice relaxation of P_1^{*+} stabilized in the

initial polymer changes weakly as the temperature increases up to ~ 180 K that is typical for organic ordered systems. This process accelerating suddenly near $T \sim 210$ K possibly to a phase transition and then plateaus at higher temperatures. The latter value differs from T_c introduced above because they characterize different processes. As P_1^{*+} start to interact with other paramagnetic centers in the PANI-pTSA/P3DDT/PCBM composite, their spin–lattice relaxation strongly accelerates and becomes more temperature-dependent (Fig. 5). It is once more evidence of the exchange between polarons stabilized in neighboring polymer chains. Fig. 5 demonstrates that T_1 tends to T_2 at high temperatures. This is typical for organic systems of low dimensionality and can be explained by the defrosting of macromolecular dynamics.

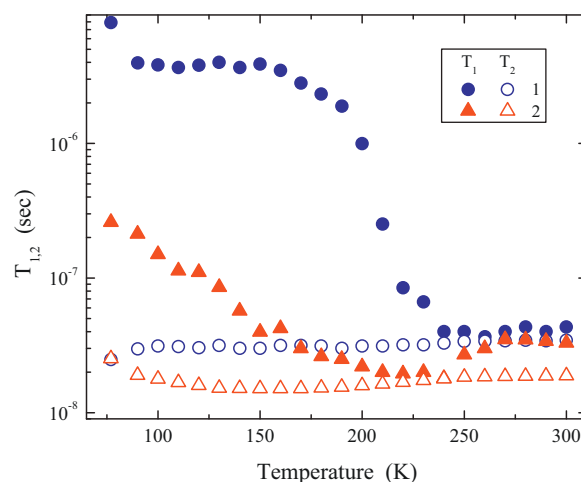


Fig. 5. Temperature dependence of spin–lattice, T_1 , and spin–spin, T_2 , relaxation times determined for polarons P_1^{*+} stabilized in the PANI-pTSA backbone (1) and respective PANI-pTSA/P3DDT/PCBM composite (2) without light illumination. The error margins are of the order of symbol size.

4. Conclusions

Light excitation of P3DDT/PCBM bulk heterojunctions in the PANI-ES/P3DDT/PCBM composites leads to charge separation and transfer from a P3DDT chain to a methanofullerene molecule. This is accompanied by the excitation of two paramagnetic centers with clearly resolved LEPR spectra, namely, the positively charged polaron $P_2^{*\bullet}$ on the polymer backbone and the negatively charged radical anion $mC_{61}^{\bullet-}$ located between polymer chains. Both radicals are spatially separated due to fast 1D diffusion of the former, so that they become non-interacting. Polarons $P_2^{*\bullet}$ moving in P3DDT solitary chains interact with $P_1^{*\bullet}$ stabilized on neighboring PANI-ES chains due to overlapping of their wave functions. Such interaction is governed mainly by nanomorphology of PANI-ES subdomains and defines insulating and conducting forms of PANI-SA and PANI-pTSA, respectively. Spin exchange and transverse relaxation of polarons is governed by 1D activation hopping $P_2^{*\bullet}$ along P3DDT chains and strongly increase as PANI-SA polymer is replaced by PANI-pTSA one in the triple composite. Spin-lattice relaxation of polarons stabilized in PANI-pTSA is also accelerated by their exchange interaction with guest spin ensemble. Paramagnetic susceptibility of these polarons is realized according to the model of exchange coupled spin pairs differently distributed in appropriate polymer matrices. This deepens overlapping of wave functions of these charge carriers and leads to the increase in the energy barrier which overcomes the polaron under its crossing through a bulk heterojunction. It is evident that separate EPR investigation of spin properties of domestic and photoexcited paramagnetic centers in the polymer/polymer/fullerene composite and its ingredients may give a possibility to control its texture and other structural properties over the entire range of temperatures studied. The data obtained for such model system can contribute to open new horizon in creation of flexible and scalable organic molecular devices with spin-assisted electronic properties. Our results suggest an important role played by interchain coupling of different spin charge carriers on a handling of charge transfer in bulk heterojunction. PANI-ES/P3DDT/PCBM. Photoinitiation of additional spins allows making such handling more delicate that is a critical strategy in creating systems with spin-assisted charge transfer. The correlations established between dynamics, electronic and structural parameters of these systems can be used for controllable synthesis of various organic spintronic devices with optimal properties. Since coherent spin dynamics in organic semiconductors is anisotropic, our strategy seems to make it possible obtaining complex correlations of anisotropic electron transport and spin dynamics for the further design of progressive molecular electronics. Electronic properties of such devices seem to be improved by the use of more ordered composites. This will be covered in detail elsewhere.

Acknowledgments

The authors are thankful to Dr. N.N. Denisov for the assistance in LEPR experiments. The work was partly supported by the Russian Foundation for Basic Research (Grant No. 12-03-00148).

References

- [1] (a) A.J. Heeger, N.S. Sariciftci, E.B. Namdas, *Semiconducting and Metallic Polymers*, Oxford University Press, London, 2010; (b) X. Yang (Ed.), *Semiconducting Polymer Composites: Principles, Morphologies, Properties and Applications*, Wiley VCH, Weinheim, 2012.
- [2] Y. Lu (Ed.), *Solitons and Polarons in Conducting Polymers*, World Scientific, River Edge, NJ/Singapore, 1988.
- [3] V.A. Dediu, L.E. Hueso, I. Bergenti, C. Taliani, *Nature Materials* 8 (2009) 707–716.
- [4] S. Maekawa (Ed.), *Concepts in Spin Electronics*, Oxford University Press, Oxford, 2006.
- [5] (a) Y. Zhang, T.P. Basel, B.R. Gautam, X.M. Yang, D.J. Mascaro, F. Liu, Z.V. Vardeny, *Nature Communications* 3 (2012) 1043–1010–1043–1041; (b) Y. Zhang, B.R. Gautam, T.P. Basel, D.J. Mascaro, Z.V. Vardeny, *Synthetic Metals* 173 (2013) 2–9.
- [6] J.M. Lupton, D.R. McCamey, C. Boehme, *Chemical Physics Chemistry* 11 (2010) 3040–3058.
- [7] M. Kinoshita, N. Iwasaki, N. Nishi, *Applied Spectroscopy Review* 17 (1981) 1–94.
- [8] K. Mizoguchi, S. Kuroda, in: H.S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, 3, John Wiley & Sons, Chichester/New York, 1997, pp. 251–317 (Chapter 6).
- [9] V.I. Krinichnyi, *Synthetic Metals* 108 (2000) 173–222.
- [10] C. Brabec, U. Scherf, V. Dyakonov (Eds.), *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*, 1, Wiley-VCH, Weinheim, 2008.
- [11] V.I. Krinichnyi, in: M. Lechkov, S. Prandzheva (Eds.), *Encyclopedia of Polymer Composites: Properties, Performance and Applications*, Nova Science Publishers, Hauppauge, NY, 2009, pp. 417–446 (Chapter 11).
- [12] M.K. Lee, M. Segal, Z.G. Soos, J. Shinar, M.A. Baldo, *Physical Review Letters* 94 (2005) 137403–137406.
- [13] D.R. McCamey, K.J. van Schooten, W.J. Baker, S.Y. Lee, S.-Y. Paik, J.M. Lupton, C. Boehme, *Physical Review Letters* 104 (2010) 017601–017604.
- [14] V.I. Krinichnyi, E.I. Yudanov, N.G. Spitsina, *Journal of Physical Chemistry C* 114 (2010) 16756–16766.
- [15] P.K. Kahol, *Physical Review B* 62 (2000) 13803–13804.
- [16] B. Wessling, D. Srinivasan, G. Rangarajan, T. Mietzner, W. Lennartz, *European Physical Journal E* 2 (2000) 207–210.
- [17] A. Kapil, M. Taunk, S. Chand, *Journal of Materials Science-Materials in Electronics* 21 (2010) 399–404.
- [18] B. Wessling, *Polymers* 2 (2010) 786–798.
- [19] (a) V.I. Krinichnyi, H.K. Roth, M. Schrödner, B. Wessling, *Polymer* 47 (2006) 7460–7468; (b) V.I. Krinichnyi, S.V. Tokarev, H.K. Roth, M. Schrödner, B. Wessling, *Synthetic Metals* 156 (2006) 1368–1377.
- [20] V.I. Krinichnyi, *Russian Chemical Bulletin* 49 (2000) 207–233.
- [21] (a) V.I. Krinichnyi, S.D. Chemerisov, Y.S. Lebedev, *Physical Review B* 55 (1997) 16233–16244; (b) A.L. Kon'kin, V.G. Shtyrlin, R.R. Garipov, A.V. Aganov, A.V. Zakharov, V.I. Krinichnyi, P.N. Adams, A.P. Monkman, *Physical Review B* 66 (2002) 075203/1–075203/75203; (c) V.I. Krinichnyi, A.L. Konkin, A. Monkman, *Synthetic Metals* 162 (2012) 1147–1155.
- [22] K. Lee, A.J. Heeger, *Synthetic Metals* 84 (1997) 715–718.
- [23] (a) V.I. Krinichnyi, *Acta Materialia* 56 (2008) 1427–1434; (b) V.I. Krinichnyi, *Solar Energy Materials and Solar Cells* 92 (2008) 942–948; (c) V.I. Krinichnyi, E.I. Yudanov, *Journal of Renewable and Sustainable Energy* 1 (2009) 043110/1–043110/43110.
- [24] V.I. Krinichnyi, A.A. Balakai, *Applied Magnetic Resonance* 39 (2010) 319–328.
- [25] F. Lux, G. Hinrichsen, V.I. Krinichnyi, I.B. Nazarova, S.D. Chemerisov, M.M. Pohl, *Synthetic Metals* 55 (1993) 347–352.
- [26] C.P. Poole, *Electron Spin Resonance*, Int. Sci. Publ., London, 1967.
- [27] V.I. Krinichnyi, *Russian Chemical Reviews* 65 (1996) 521–536.
- [28] (a) R.A.J. Janssen, D. Moses, N.S. Sariciftci, *Journal of Chemical Physics* 101 (1994) 9519–9527; (b) K. Marumoto, Y. Muramatsu, N. Takeuchi, S. Kuroda, *Synthetic Metals* 135 (2003) 433–434.
- [29] (a) K. Takeda, H. Hikita, Y. Kimura, H. Yokomichi, K. Morigaki, *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* 37 (1998) 6309–6317; (b) V.V. Yanilkin, N.V. Nastapova, V.I. Morozov, V.P. Gubskaya, F.G. Sibgatullina, L.S. Berezhnaya, I.A. Nuretdinov, *Russian Journal of Electrochemistry* 43 (2007) 184–203; (c) O.G. Poluektov, S. Filippone, N. Martín, A. Sperlich, C. Deibel, V. Dyakonov, *Journal of Physical Chemistry B* 114 (2010) 14426–14429.
- [30] (a) V.I. Krinichnyi, E.I. Yudanov, *Solar Energy Materials and Solar Cells* 95 (2011) 2302–2313; (b) V.I. Krinichnyi, E.I. Yudanov, *Journal of Physical Chemistry C* 116 (2012) 9189–9195.
- [31] E. Houze, M. Nechtschein, *Physical Review B* 53 (1996) 14309–14318.
- [32] Y.N. Molin, K.M. Salikhov, K.I. Zamaraev, *Spin Exchange*, Springer, Berlin, 1980.
- [33] A. Raghunathan, P.K. Kahol, J.C. Ho, Y.Y. Chen, Y.D. Yao, Y.S. Lin, B. Wessling, *Physical Review B* 58 (1998) R15955–R15958.
- [34] P.K. Kahol, M. Mehring, *Synthetic Metals* 16 (1986) 257–264.
- [35] W.G. Clark, L.C. Tippie, *Physical Review B* 20 (1979) 2914–2923.
- [36] Z.H. Wang, A. Ray, A.G. MacDiarmid, A.J. Epstein, *Physical Review B* 43 (1991) 4373–4384.
- [37] F.J. Adrain, L. Monchick, *Journal of Chemical Physics* 71 (1979) 2600–2610.
- [38] J.M. Ginder, A.F. Richter, A.G. MacDiarmid, A.J. Epstein, *Solid State Communications* 63 (1987) 97–101.
- [39] B. Yan, N.A. Schultz, A.L. Efros, P.C. Taylor, *Physical Review Letters* 84 (2000) 4180–4183.
- [40] J. Nelson, *Physical Review B* 67 (2003) 155209/1–155209/155209.
- [41] V.I. Krinichnyi, E.I. Yudanov, *AIP Advances* 1 (2011) 022131/1–022131/22131.
- [42] J.S. Moon, J. Jo, A.J. Heeger, *Advanced Energy Materials* 2 (2012) 304–308.
- [43] J.E. Wertz, J.R. Bolton, *Electron Spin Resonance*, McGraw-Hill, New York, 1972.
- [44] V.I. Krinichnyi, H.K. Roth, G. Hinrichsen, F. Lux, K. Lüders, *Physical Review B* 65 (2002) 155205/1–155205/155205.
- [45] V.I. Krinichnyi, S.V. Tokarev, H.K. Roth, M. Schrödner, B. Wessling, *Synthetic Metals* 152 (2005) 165–168.
- [46] Z.H. Wang, E.M. Scherr, A.G. MacDiarmid, A.J. Epstein, *Physical Review B* 45 (1992) 4190–4202.