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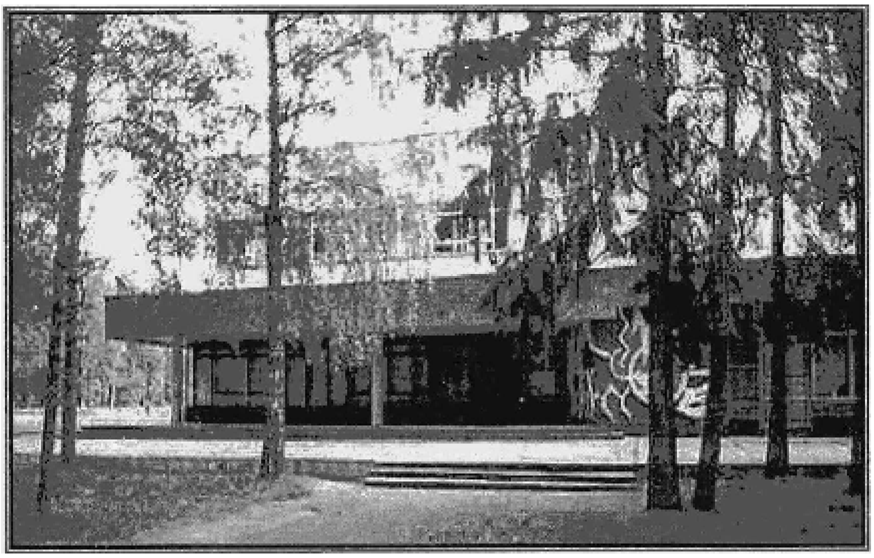

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LEPR Study of Photoinduced Charge Transfer in Poly(3-Dodecylthiophene)/Fullerene Solar Cells

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Conjugated polymers and their composites with fullerenes are interesting materials for various molecular electronic applications, e.g. light-emitting diodes, thin film field effect transistors and flexible plastic solar cells [1].

Earlier we shown [2] that the irradiation of a bulk heterojunctions between poly(3-dodecylthiophene) (P3DDT) and fullerene derivative, [1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61}] (PCBM) photoinduces electron transfer from a polymer chain to a fullerene molecule accompained by the formation of the non-linear polaron excitation $P^{+\bullet}$ and fullerene ion-radical C_{61}^{-}. Except the above charge transport, a charge is transferred by polaron along (Q1D) and between (Q3D) polymer chains and a rotational motion of fullerene molecules are also realized in such polymer/fullerene system. The understanding of the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials. These molecular and electronic processes should undoubtedly be correlated in the P3DDT/PCBM solar cells. However, such correlations have not been studied so far.

Each paramagnetic centers (PC) in radical pairs photoinduced in the P3DDT/PCBM bulk heterojunctions possess unpaired electron with spin S = ½, therefore the Light-Induced EPR (LEPR) seems to be powerful method for the study of electronic processes occuring in plastic solar cells. This method was used in the study of magnetic, relaxation and dynamic parameters of polarons and fullerene anion-radicals photoinduced in the P3DDT/PCBM composite by a beam of solid-state lasers with photon energy of $h\nu_{ph}$ = 1.88, 2.22, and 2.75 eV (here $h = \mathbf{h}/2\pi$ is the Plank constant and ν_{ph} is a photon frequency) in wide temperature region.

As the compound P3DDT/PCBM is irradiated by laser at $T \leq 200$ K, two overlapping LEPR lines with temperature dependent intensities are observed (Fig. 1). Sum spectrum was attributed to radical pairs of positively charged diffusing polarons $P^{+\bullet}$ and rotating round main axis negatively charged anion-radicals $C_{61}^{-\bullet}$. These radicals recombine at 180 – 200 K and the recombination rate was revealed to be governed by the laser photon energy. Taking into account anisotropic character of PC in poly(3-alkylthiophenes) [3] and PCBM [4] the main values and traces of the $\boldsymbol{g}$-tensors of the $P^{+\bullet}$ and $C_{61}^{-\bullet}$ PC were determined to be respectively g_{xx} = 2.00320, g_{yy} = 2.00225, g_{zz} = 2.00145, $\langle g \rangle$ = 2.00230 and g_{xx} = 2.00061, g_{yy} = 2.00030, g_{zz} = 1.99941, $\langle g \rangle$ = 2.0001. The sum spectra calculated with the fitting magnetic parameters are shown in Fig. 1 as well.

Figure 2 depicts the Arrhenius dependence of spin susceptibility of both PC in 77 – 200 K region derived from their double-integrated spectra registered at non-saturated conditions. This value should inversely depend on the probability of recombination of PC in radical pairs. Assuming that polaron diffuses by tunneling between initial site i to final site j with the energy spending ΔE_{ij}, so then the rate of the PC recombination can be written as [5]

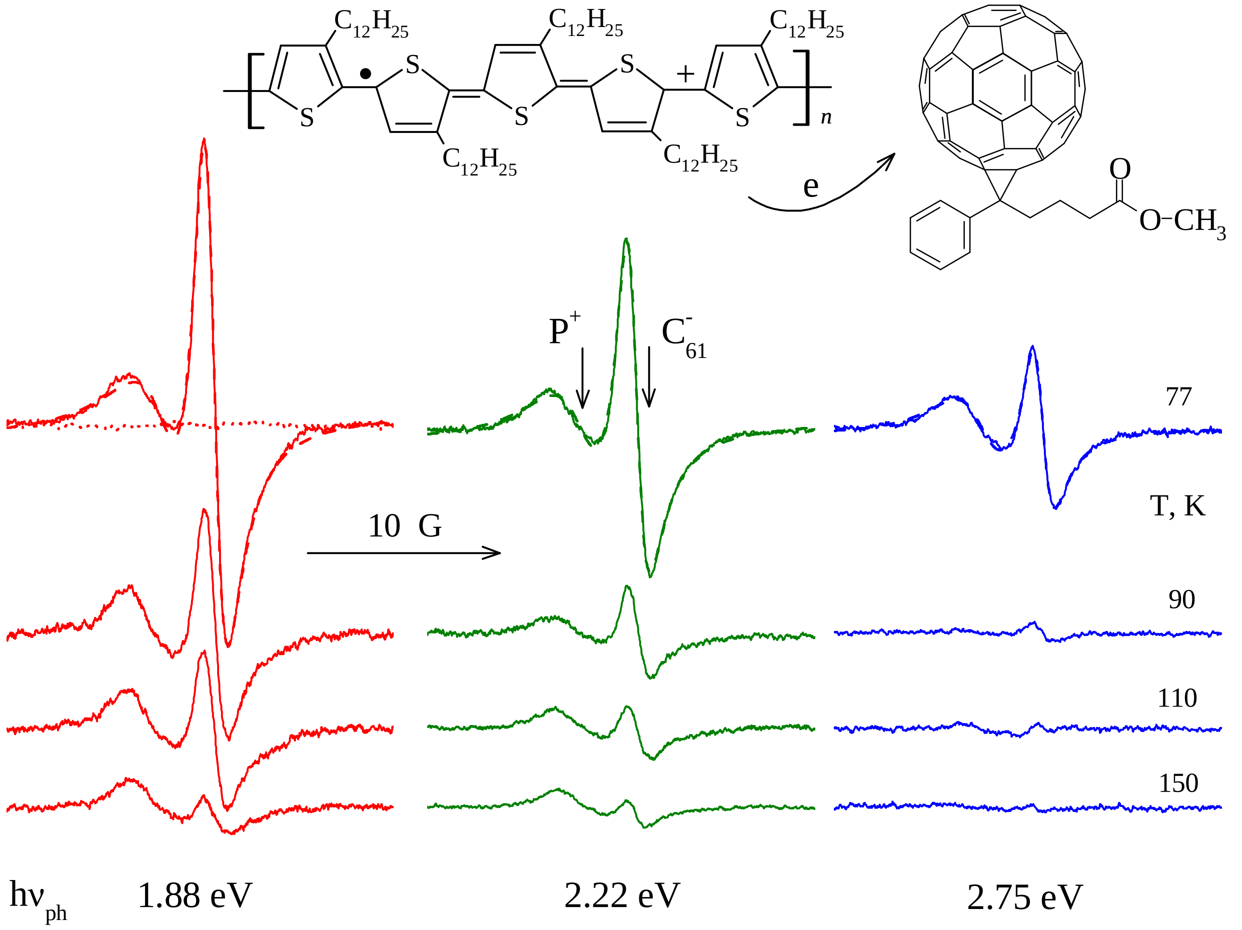

FIGURE 1. LESR spectra of the radical pairs photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different laser photon energy $h\nu_{\mathrm{ph}}$ and registered at different temperature. The dashed lines show calculated spectra. The "dark" spectrum is shown by dotted line.

$$\nu(\Delta E_{ij}) = \nu_0 \exp\left(-\frac{\Delta E_{ij}}{k_{\mathrm{B}}T}\right) \tag{1}$$

Figure 2 shows that the polaron charge carriers are characterized by $\chi(T) \propto T^{-1}$ temperature dependence in the P3DDT/PCBM system, whereas spin susceptibility of fullerene anion-radicals excited by photons with $h\nu_{\mathrm{ph}} = 1.88$ and 2.22 eV at $77\ \mathrm{K} \leq T \leq 160$ K and with $h\nu_{\mathrm{ph}} = 2.75$ eV at $77\ \mathrm{K} \leq T \leq 110$ K follows the Arrhenius law. The values of ΔE_{ij} in Eq.(1) determined for fullerene anion-radical from the slopes of appropriate curves are presented in Table 1. It is seen that ΔE_{ij} increases by factor of forth with the $h\nu_{\mathrm{ph}}$ growing from 1.88 eV up to 2.75 eV. The annihilation of radical pairs in the P3DDT/PCBM compound follows the thermally activated bimolecular process of non-interacting PC that stipulates their long life. The ratio of spin concentrations was obtained to be near to unit at the irradiation of the P3DDT/PCBM by light with $h\nu_{\mathrm{ph}} = 1.88$ eV and 2.22 eV that is in agreement with fundamental principle of photoinduced charge separation in radical pair. This value, however, increases at $h\nu_{\mathrm{ph}}$=2.75 eV due, probably, to appearing of additional channel

Table 1. The ΔE_{ij} in Eq.(1) determined for spin susceptibility for fullerene anion-radical and activation energy in Eq.(3) determined for rotational and translation diffusion of the fullerene anion-radicals $E_{\mathrm{a}}^{\mathrm{C61}}$ and polarons $E_{\mathrm{a}}^{\mathrm{P*}}$ photoinduced by laser with different photon frequency $h\nu_{\mathrm{ph}}$ (all in eV).

$h\nu_{\mathrm{ph}}$	$\Delta E_{ij}^{\mathrm{C61}}$	$E_{\mathrm{a}}^{\mathrm{C61}}$	$E_{\mathrm{a}}^{\mathrm{P*}}$
1.88	0.014	0.017	0.048
2.22	0.023	0.010	0.038
2.75	0.058	0.012	0.094

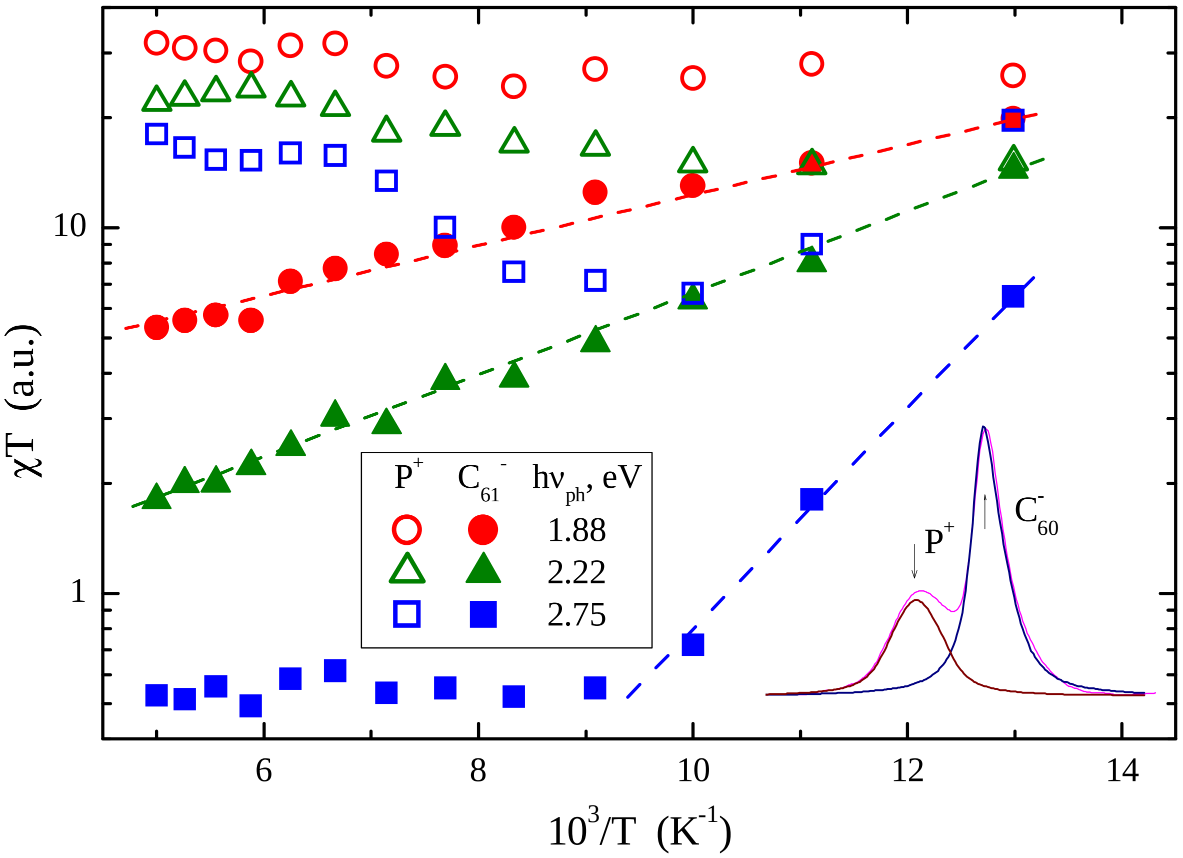

FIGURE 2. Arrhenius dependence of paramagnetic susceptibility of the polarons $P^{+\bullet}$ and fullerene anion-radicals $C_{61}^{-\bullet}$ photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different photon energy. Dashed lines show the dependences calculated using Eq.(1) with ΔE_{ij} presented in Table 1. Low-temperature integral contributions of these PC to sum spectrum are shown in the insert as well.

for the electron moving away the fullerene molecule. LEPR study of poly(3-alkylthiophenes) / fullerene at $h\nu_{ph} \leq 4.1$ eV shown [6] that a remarkable enhancement of prompt LEPR signal is registered at near 1.8 eV, which is consistent with the enhancement of the photoconductivity. The same tendency seems to be realized in our case as well.

It was shown that the linewidth $\Delta B_{pp}^{(0)}$ of non-saturated spectrum of polarons changes monotonically with the temperature, whereas this parameter of fullerene radicals demonstrate more complex dependence on the temperature and photon energy. Extrapolation to room temperature gives 1.4 – 2.0 G for $P^{+\bullet}$. The spectral linewidth should reflect different processes occurring in the P3DDT/PCBM composite. One of them is the association of mobile PC with the counter charges. Another reason is the dipole-dipole interaction between mobile and trapped polarons and fullerenes that broadens the line by $\Delta B_{dd} = \mu_B / R_0^3 = 4/3\pi\mu_B n_P$, where μ_B is the Bohr magneton, R_0 is the distance between dipoles proportional to the polaron concentration n_P on the polymer chain. Extrapolating temperature dependences to the lower temperature limit, *i.e.* when the temperature tends to zero, one obtains $\Delta B_{pp}^{(0)} \approx 0.7 – 0.8$ G for polarons and $\Delta B_{pp}^{(0)} \approx 0.5 – 0.6$ G for fullerene anion-radicals and, therefore, $R_0 \approx 2.3 – 2.5$ nm for the dipolar distance in the P3DDT/PCBM system.

At the increase of the microwave power in the cavity the intensity of both the PC spectra first linear increases, plateaus and then decrease. Such a process is accompanied by these spectra broadening that can be explained by saturation of PC in the plastic solar cells. This allows to

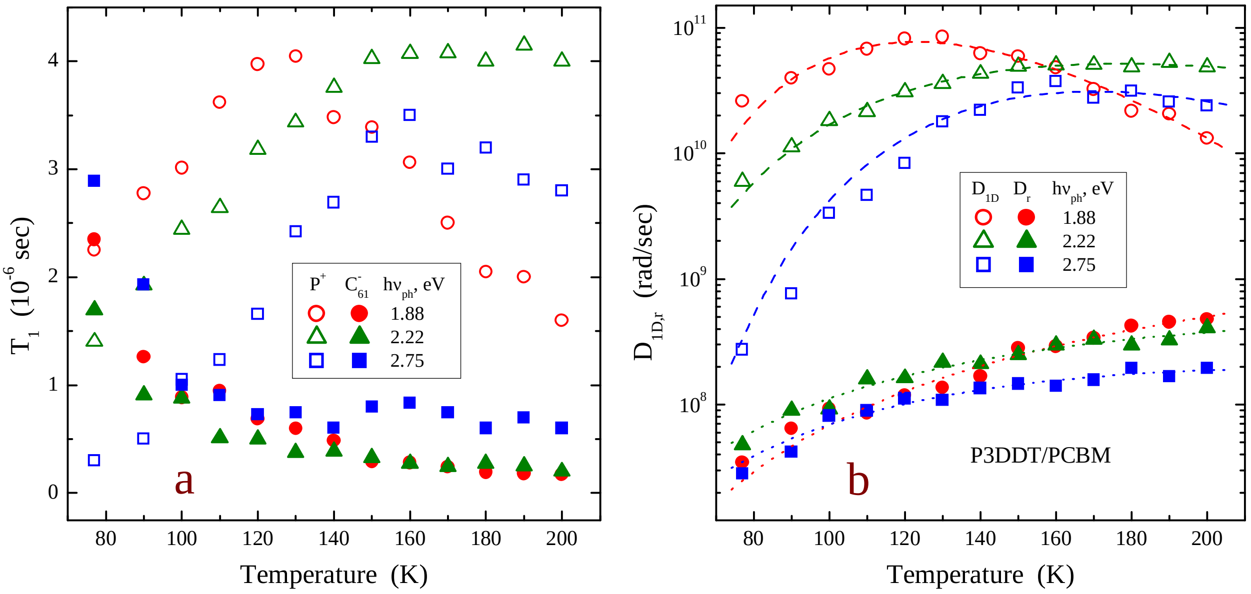

FIGURE 3. The spin-lattice relaxation times (*a*) and the rates of the polaron diffusion along polymer chains D_{1D} and of the $C_{61}^{-\bullet}$ rotation D_r (*b*) in the P3DDT/PCBM system irradiated by laser with different photon energy. Top to down right lines show the dependences calculated from Eq.(3) with $\alpha = 1.2$ and $E_a^{P*} = 0.048$ eV, $\alpha = 0.45$ and $E_a^{P*} = 0.038$ eV, $\alpha = 2.2$ and $E_a^{P*} = 0.094$ eV (dashed lines) and with $\alpha = 0.04$ and $E_a^{C61} = 0.010$ eV, $\alpha = 0.03$ and $E_a^{C61} = 0.017$ eV, $\alpha = 0.06$ and $E_a^{C61} = 0.012$ eV (dotted lines).

determine separately spin-lattice T_1 and spin-spin T_2 relaxation times for both PC from their spectra registered at different microwave power [7].

Figure 3a depicts relaxation parameters determined separately for polarons and fullerene anion-radicals from their LEPR spectra as function of temperature. The analysis of the Figure shows that the interaction of anion-radicals $C_{61}^{-\bullet}$ with the lattice is characterized by monotonic temperature dependence, whereas spin-lattice relaxation time of polarons $P^{+\bullet}$ demonstrates extremal temperature dependence with maximum at critical temperature $T_c \approx 130 - 160$ K. The latter value depends on the photon energy (Fig. 3a). Spin-spin relaxation of both PC was expected to be accelerated nearly monotonically at the temperature increase.

PC-aided dynamic processes occurring in the P3DDT/PCBM system, *e.g.* Q1D polaron diffusion with coefficient D_{1D}, rotational diffusion of fullerene anion-radical around main molecular axis with coefficient D_r should induce an additional magnetic field in the whereabouts of electron (and nuclear spins) and, therefore, lead especially to the acceleration of electron relaxation of both spin ensembles. As the relaxation of the whole spin reservoir is defined mainly by a dipole-dipole interaction between electron spins, the following equation can be written for spin-lattice relaxation rate at resonant frequency ω_e [8]

$$T_1^{-1}(\omega_e) = \langle\omega^2\rangle\left[2J(\omega_e) + 8J(2\omega_e)\right] \qquad (2)$$

where $\langle\omega^2\rangle = 1/10\,\gamma_e^4 \mathbf{h}^2 S(S+1)n\Sigma ij$ is the constant of a dipole-dipole interaction for powder, n is a number of polarons per each monomer, Σ_{ij} is the lattice sum for powder-like sample, $J(\omega_e) = (2D_{1D}\omega_e)^{-1/2}$ (at $D_{1D} >> \omega_e >> D_{3D}$) or $J(\omega_e) = \tau_c/(1+\tau_c^2\omega_e^2)$ is a spectral density function respectively for Q1D longitudinal or rotational diffusion with correlation time τ_c.

The dynamic parameters calculated from Eq.(2) for both PC in photoinduced radical pairs using the appropriate spectral density functions are presented in Fig. 3b as function of temperature. To account for the LEPR mobility data obtained, the Elliot model [9] based on a hopping of carrier over barrier E_a has been used. This model predicts a frequency dependent carrier diffusion rate, so then

$$D_{1D,r}(\omega_e T) = D_{1D,r}^0 T^2 \omega_e^s \exp\left(\frac{E_a}{k_B T}\right) \tag{3}$$

where $s = 1 - \alpha k_B T/E_a$ is the exponent reflecting the dimensionality of the system and α is a constant.

The energies E_a required for activation of the polaron longitudinal and fullerene rotational diffusion in P3DDT/PCBM are also summarized in the Table 1. It is seen in Fig. 3b that the temperature dependences calculated from Eq.(3) with the E_a presented approximate well experimental data.

Therefore, light excitation of the bulk heterojunction in the P3DDT/PCBM composite leads to a charge transfer from a polymer chain to a fullerene molecule. This is accompanied by the formation of two photoinduced rhombic symmetric paramagnetic centers with clearly resolved LEPR spectra, namely the positively charged polaron $P^{+\bullet}$ on the polymer backbone and the negatively charged fullerene anion-radical $C_{61}^{-\bullet}$ situated between polymer chains. Both radicals are spatially separated due to high mobility of a polaron charge carrier. This decreases a probability of recombination of PC which become non-interacting. Photoinduced charge is transferred by polaron along polymer chain near the position of a fullerene anion-radical where they can recombine. The probability of the collapse of photoinduced radical pairs follows the activation law and depends on the energy of initiating photons. Weak interaction of PC in the radical pair stipulates for a difference in their interaction with own microenvironment and, therefore, in their magnetic and relaxation parameters. Spin dynamics induces an additional magnetic field in the whereabouts of another spins that accelerates the electron relaxation of both spin ensembles. This allowed to calculate separately all dynamic parameters of polarons and fullerene anion-radicals in the system under study. Q1D diffusion of polarons and rotation of fullerenes are realized in frames of the activation mechanism and re governed by laser photon energy. This allows to conclude the independence of dynamics of photoinduced spins taking part in a charge transfer in the P3DDT/PCBM composite.

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1. *Organic Photovoltaics: Mechanisms, Materials, and Devices*, edited by S.-S. Sun and N.S. Sariciftci, CRC Press, Boca Raton, 2005.
2. S. Sensfuss, A. Konkin, H.-K. Roth, M. Al-Ibrahim, U. Zhokhavets, G. Gobsch, V.I. Krinichnyi, G.A. Nazmutdinova, and E. Klemm, Synth. Met. 137, 1433-1434 (2003).
3. V.I. Krinichnyi and H.-K. Roth, Appl. Magn. Reson. 26, 395-415 (2004).
4. J. De Ceuster, E. Goovaerts, A. Bouwen, J.C. Hummelen, and V. Dyakonov, Phys. Rev. B 64, 195206-1-195206-6 (2001).
5. B. Yan, N.A. Schultz, A.L. Efros, and P.C. Taylor, Phys. Rev. Lett. 84, 4180-4183 (2000).
6. K. Marumoto, Y. Muramatsu, N. Takeuchi, and S. Kuroda, Synth. Met. 135, 433-434 (2003).
7. Ch.P. Poole, *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, John Wiley, New York, 1983.
8. F. Carrington and A.D. McLachlan, *Introduction to Magnetic Resonance with Application to Chemistry and Chemical Physics*, Harrer & Row, Publishers, New York, London, 1967.
9. A.R. Long and N. Balkan, Philos. Mag. B 41, 287-305 (1980).