



Photo-induced charge separation process in (PCBM-C₁₂₀O)/(M3EH-PPV) blend solid film studied by means of X and K-bands ESR at 77 and 120 K

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ABSTRACT

The new fullerene dimer adduct PCBM-C₁₂₀O was studied as an electron acceptor by light-induced ESR (LESR) when blended with the electron donor-conjugated polymer M3EH-PPV in a thin solid film. ESR parameters for the PCBM-C₁₂₀O anion radical and the M3EH-PPV polaron (triaxial $g_{x,y,z}$ factors) were determined by X- and K-band ESR techniques at temperatures of 77 and 120 K. It was found that isotropic g_0 of PCBM-C₁₂₀O anion radical ESR spectra obtained in this blend under illumination is close to g -factors of electrochemically reduced (C₁₂₀O)^{-•} and does not coincide with the analogous parameter of (C₁₂₀O)^{2-••} (reported in literature). Spin relaxation parameters (T_1 and T_2) of the PCBM-C₁₂₀O anion radical and M3EH-PPV positive polaron are similar to T_1 , T_2 for light-induced ion radicals in the P3HT/PCBM blend.

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1. Introduction

The search for and study of new effective donor/acceptor compounds for photovoltaics continues to be one of the most important goals for the application and understanding of the fundamental aspects of electron transfer in solid organic semiconductors. Mono-fullerene anion radicals and their various mono-adducts exhibit good properties as electron acceptors in mediums with conjugated polymers. The photovoltaic properties of the most effective fullerene derivatives for solar cell applications, including the mono-fullerene adduct 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methano fullerene (PCBM), have been widely introduced in numerous literature sources (for example, discussed in [1a,b]); this is, however, not the case for the fullerene dimer composites. The unique possibility of mono-fullerene and its derivatives to accept not only one, but several electrons and create poly-anions C₆₀⁽ⁿ⁻⁾ where $n=2$ through 5 (theoretically $n=6$) has already been established experimentally by electrochemical methods (partly with the use of ESR). This has been reported in the references sum-

marized in review [2a] and also in some other recently published works [2b,c]. However, the above properties for $n \geq 2$ have not been demonstrated in any experiments where the photo-induced charge separation processes (CSP) is expected in the donor-acceptor composites medium. Regarding the most stable poly-anion radical, C₆₀⁽²⁻⁾, one can see that an alternative for the di-anion of mono-fullerene and its derivatives could be is the di-anion of di-fullerene and its derivatives. The study of di-fullerene reduction/oxidation properties has already been performed [3a,b]. The reduction of C₁₂₀O to (C₁₂₀O)⁶⁻ was successfully demonstrated electrochemically [3a] and the reduction to (C₁₂₀O)^{4-•} and (C₁₂₀OS)^{3-•} was recorded by ESR in [3a] and [3b], respectively. Concerning ESR, it should be pointed out that its application to the electrochemical reduction/oxidation process study can give unique information about the spin states of di-fullerene ions (doublet, triplet states [3a,b]). Nevertheless, it should be noted that contrary to the electrochemical method in previous ESR and LESR studies, the number of charges cannot be established reliably from the ESR spectra in all cases. Therefore, from now on only the sign of charge will be denominated for the anion radical in this report. Although an example of CSP with di-fullerene has already been demonstrated for solar cell applications [4a], we report here what is most likely one of the first experiments of photo-induced CSP registration by LESR in (fullerene dimer)/(conjugated polymer) blends.

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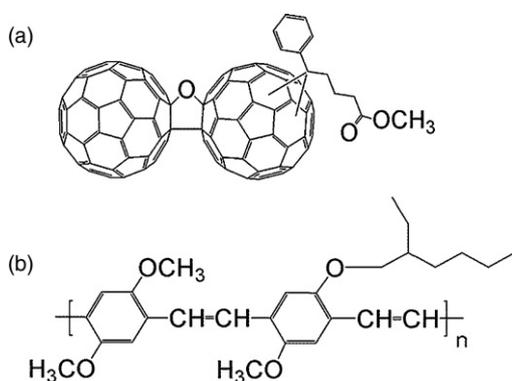


Fig. 1. Composite structures: (a) PCBM-C₁₂₀O (from now on referred to as {1}), (b) M3EH-PPV copolymer.

2. Experimental

The PCBM-C₁₂₀O fullerene dimer and M3EH-PPV (poly[2,5-dimethoxy-1,4-phenylene-1,2-ethynylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylenevinylene-1,2-ethynylene)]) copolymers have been synthesised by the methods described in [4b] and [5a,b], respectively, and their chemical structures are shown in Fig. 1. Copolymers M3EH-PPV and PCBM-C₁₂₀O were combined with a weight ratio of 1:1 w.r. and diluted in chlorobenzene. As a comparison composite for the spin relaxation parameters, a film consisting of the regioregular poly(3-hexylthiophene) (P3HT)/PCBM blend was used with the same weight ratio of components but in a chloroform solution. The composite films ($d = 0.55 \pm 0.05 \mu\text{m}$) were prepared via drop casting using polyester foil as the substrate. The samples were dried under ambient conditions or inert N₂ gas atmosphere (for comparison) at room temperature. ESR experiments were carried out with the films 4–5 h after preparation. At the above experimental conditions, observable differences for the ESR parameters for both drying variants were not found. The ESR spectra were recorded using a Bruker X- and K-band spectrometer ELEXYS E500 operated at frequencies of 9.4 and 24 GHz, respectively, with and without illumination from a Xe-lamp. An optical transmission resonator, ER 4104OR (Bruker BioSpin), provided a simple approach for Xe-lamp illumination in the X-band experiments, contrary to the K-band where an optical fibre was used for this purpose. All X-band ESR measurements have been performed at both 77 and 120 K while K-band were only performed at 120 K. This temperature (120 K) is close to the lower extreme for the K-band temperature attachment and is close to the high extreme value for the interval at which photo-induced anion radicals of PCBM and PCBM-C₁₂₀O were reliably registered under low Xe-lamp power density ($<1 \text{ mW/cm}^2$). This is due to the essential decrease of light intensity when using the optical fibre method. Spectra simulations were carried out in the same way as in [6] for the completely and partly disordered systems.

3. Results and discussion

Two separate (well resolved) anion/cation radicals were found under Xe-lamp illumination and their light-induced K- and X-band ESR spectra are shown in Fig. 2(a) and (b), respectively. To increase the experimental spectrum resolution, the K-band ESR attachment was also employed (parallel to the X-band experiments) in order to obtain the spectral parameters with better accuracy (g_i and ΔB_i , $i = x, y, z$) and to establish the frequency dependent part of ΔB_i (the linewidth at half-height of individual Lorentzian lines were used in simulation). The resulting extracted “light-dark”

experimental spectrum and the complete simulation spectra are displayed in Fig. 2(a) and (b). The extracted spectrum after simulation, S₃, corresponds to the anion radical of PCBM, which is presented in the product {1} (see Fig. 1(a)) as the impurity after synthesis. This conclusion is also supported by the results of the mass-spectroscopy analysis of the PCBM-C₁₂₀O initial product [4a]. The parameters for the positive polaron of the M3EH-PPV and PCBM-C₁₂₀O anion radicals (or di-anion di-radicals without substantial interaction between two electrons) obtained by both X- and K-band ESR techniques at 77 and 120 K, as well as for P3HT and PCBM for comparison, are collected in Table 1. The isotropic parameter value for the light-induced radical {1}•• (from here on L{1}••) $g_o = 1/3(g_x + g_y + g_z) = 1.9996$ does not coincide (differences as great as $\delta g_o = 0.0034$ were observed) with the reported radicals [C₁₂₀-O]^{2-••} ($g_o = 2.003$ for the triplet spin state and $g_o = 2.0016$ for the doublet state [3a]), but is close to $g_o \approx 1.999$ of [C₁₂₀-O]^{-•} radical ESR spectra [3b,c]. The comparison of PCBM-C₁₂₀O/M3EH-PPV radical products spin relaxation data with the analogous data for

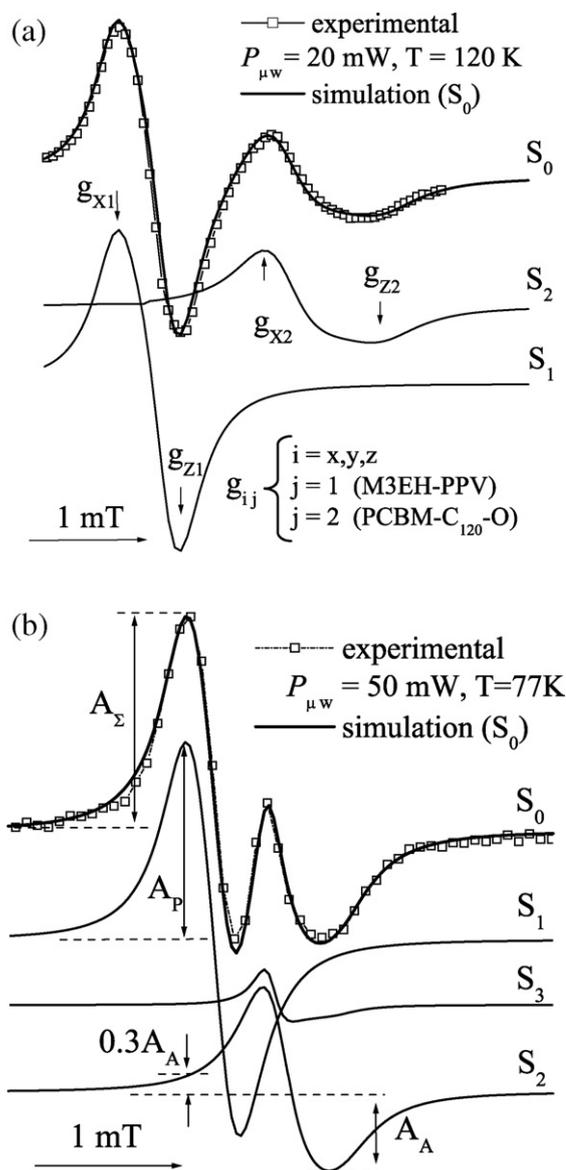


Fig. 2. “Light-dark” LESR spectra: [a: 24 GHz; b: 9.4 GHz]; experimental-({1})/(M3EH-PPV) (1:1) blend film, S₀-experiment simulation. Spectra extracted from S₀ spectrum: S₁ – (M3EH-PPV) positive polaron, S₂ – {1}•• anion radical, S₃: PCBM anion radical (was not observed under the weak illumination using optical fibre).

the P3HT/PCBM blend (the latter is one of the perspective blends for photovoltaic applications) was one of the goals of this study.

The preliminary comparison of $\Delta B_i \sim 1/T_2$ was performed in experiments using a higher resolution version of the K-band technique ($T=120$ K). It should be pointed out that contrary to the M3EH-PPV polymer, which did not display any visible orientation ordering in thin films in these experiments, the poly(3-alkylthiophene) (P3AT) type polymer exhibits some dominant molecular orientation in films. In contrast to randomly orientated paramagnetic molecules, partially orientated ones have a primary orientation with the distribution function $P(\delta, \xi)$, where ξ is the angle between the direction of the external magnetic field and the chosen primary orientation, which in our case coincides with the direction normal to the film plain (this approach with complete angle description is discussed in detail in [6] and its references). Therefore, P3HT/PCBM spectra have been simulated according to the method discussed in [6]. Experimental and simulated K-band spectra of the above blends are shown in Figs. 3 and 4 and the results of the simulation are gathered in Table 1. In Fig. 4 the higher resolution (relative to the X-band) K-band LESR spectra of the P3HT/PCBM film, recorded using two film plane orientations relative to the external magnetic field, visually demonstrate the essential angular ESR spectral line dependences due to the partial ordering of molecular chains. As a result, the dominant orientation of polymer chains should be taken into consideration during the computation of ESR parameters for P3AT type polymers. In Ref. [6] it was found that the polaron ESR spectral linewidth for P3HT essentially depends on the preparation conditions as well as the external exposure. In our experience the ESR linewidth deviation of the polaron in un-doped P3AT type polymers can vary up to 40%. A slight difference for the P3HT polaron effective transverse relaxation $T_2 \sim 1/\Delta B_j$ was expected from this work based on previously reported results [6], however the deviation does not exceed 40% and therefore can be used for the preliminary comparison with M3EH-PPV data (Table 1). Regarding $L\{1\}^{*}$, the preliminary conclusion for T_2 of PCBM-C₁₂₀O and PCBM is reported below. Contrary to the P3HT polarons, the PCBM anion radical exhibits more stable relaxation parameters which are not as sensitive to the preparation and experimental conditions. ΔB_i values obtained in this work correlate well with the same data for PCBM found in PPV-PPE/PCBM

Table 1
The ESR spectra parameters.

Ion radicals of:	$g_x, g_y, g_z^{a,b}$	$\Delta B_x, \Delta B_y, \Delta B_z^c$ (mT)
M3EH-PPV (K-band)	2.0034, 2.0025, 2.0024	0.22, 0.265, 0.275
(X-band)	2.0036, 2.0024, 2.0023	0.205, 0.24, 0.25
PCBM-C ₁₂₀ O (K-band)	2.0004, 2.0002, 1.9984	0.36, 0.36, 0.44
(X-band)	2.0004, 2.0003, 1.9982	0.25, 0.24, 0.32
P3HT ^d (K-band)	2.003, 2.0021, 2.0011	0.16, 0.15, 0.16
PCBM (K-band)	2.0005, 2.0004, 1.9988	0.12, 0.11, 0.29
(X-band)		0.11, 0.10, 0.19

^a The error in g_i – values is approximately 1.5×10^{-4} .

^b g -Factor temperature deviation around interval 77–290 K (for polymer radical) and 77–140 K (for fullerenes) does not exceed the error in g_i values. The preliminary estimated average g -factor temperature gradient ($-dg_i/dT$) in the above intervals for both compounds is around $(1 \pm 0.12) \times 10^{-6}$, and cannot essentially influence the spectroscopic data obtained here.

^c The error in ΔB_i for the M3EH-PPV, P3HT, PCBM ion radicals is ~ 0.015 mT, for PCBM-C₁₂₀O one is ~ 0.02 mT. The average ΔB_x temperature gradient ($-dB/dT$) of the studied blends for 77–180 K is about $(0.5 \pm 0.1) \times 10^{-3}$ mT.

^d g_i components values are similar to the same obtained in [6] and near the $+2 \times 10^{-4}$ difference for the reported light-induced polarons obtained in [7] at 4 K using W-band (94 GHz) ESR spectrometer.

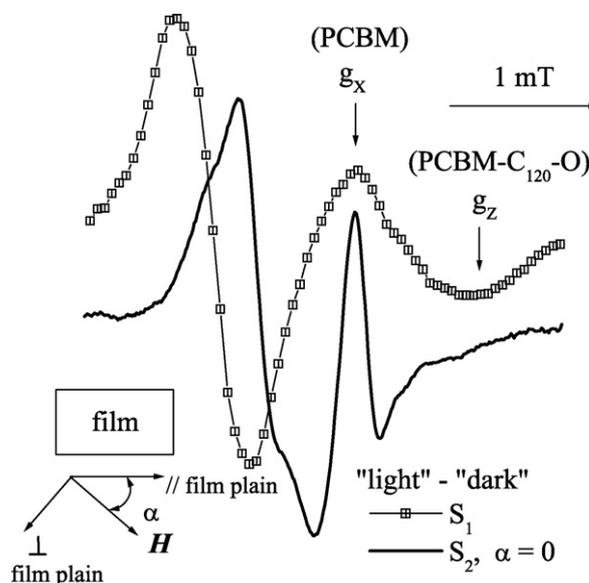


Fig. 3. K-band LESR spectra: S_1 -experimental results of (P3HT)/M3EH-PPV blend film (is taken from Fig. 2(a)) and S_2 -experimental results of P3HT/PCBM (1:1) blend film recorded in the orientation of the external magnetic field $H \parallel$ to the film plane $\alpha = 0$ rad.

composites obtained previously using X-band LESR [8]. Moreover, the parameters enumerated above in Table 1 exhibit good correlation with the approach found in [9] for linear contribution to ESR frequency dependence for ΔB_j components ($j = x, y, z$):

$$\Delta B_j = \delta_0 + k \cdot \Delta g_{jy} \cdot \nu \quad (1)$$

where δ_0 is the frequency independent part of ΔB_j , $\Delta g_{jy} = |g_j - g_y|$, ν is the linear ESR frequency and k is constant and differs for the various radicals. The poly-empirical equations system (1) often satisfactorily describes experiments performed at the X-band [9], however the deviation from experimental parameters increases with increasing ν . This deviation can be connected with the addi-

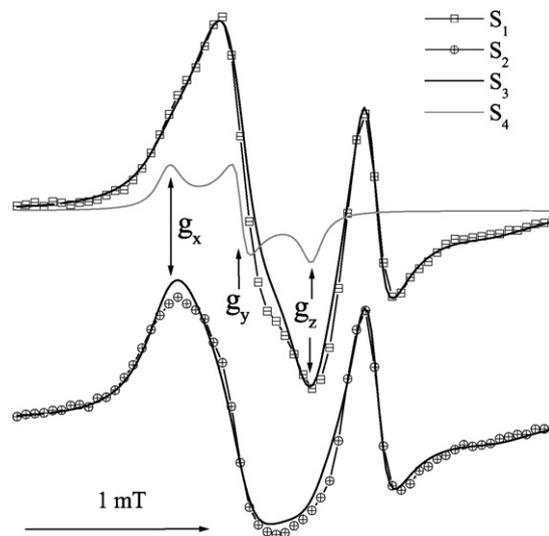


Fig. 4. K-band LESR spectra: S_1 -experimental results of P3HT/PCBM blend film (is taken from Fig. 3) and S_2 -experimental data of the same film recorded in the orientation $\alpha = (3/4)\pi$, S_3 – simulated spectra for the orientations $\alpha = 0$ and $(3/4)\pi$ rad and $a_{02} = 2.1$ for the ordered/disordered composites constructed by the approach discussed in [6], S_4 – spectrum simulated for the completely disordered system using the P3HT polaron $g_{x,y,z}$ components obtained after S_3 simulation (to establish the correct position of g_j spectral components by increasing the resolution, values of $\Delta B_x = \Delta B_y = \Delta B_z = 0.05$ mT have been used for the simulation).

tional $\delta_{x,y,z}(\nu)$ line broadening which is responsible for the other ν -dependent mechanisms (see below). Eq. (1) can therefore be rewritten as

$$\Delta B_j = \delta_0 + k \cdot \Delta g_{jy} \cdot \nu + \delta_{x,y,z}(\nu) \quad (2)$$

It was established in [8] that PCBM anion radical ESR spectroscopy at 9.5 GHz exhibits the dependences of ΔB_x and ΔB_z on the value of parameters Δg_{xy} and Δg_{zy} , respectively, however the dependence $\Delta B_j \sim f(\nu)$ could not be confirmed at the single ESR frequency. In the presented work this correlation has been demonstrated reliably by ESR operated at $\nu = 24$ GHz. In addition, according to the data shown in the Table 1, one can see that the above examination for PCBM may be expanded and valid for the same consideration of P3HT, M3EH-PPV polarons as well as $L\{1\}^{-\bullet}$. Therefore, one additional available ν ESR should be sufficient to begin correctly fitting the procedure of system (2) in order to estimate the different probable broadening mechanisms of $\delta_{x,y,z}(\nu)$ (W-band (94 GHz) should be preferred to Q-band (36 GHz)). The possibility of multi-frequency ESR experiments (using the same sample) would be beneficial, as expected, due to the essential difference of the origins as well as the mathematical descriptions of expected contributions to the effective T_2 relaxation: (a) the slow/ultra-slow radical orientation (rotational) diffusion motion $\sim \nu^{1/2}$ [10], and (b) polaron diffusion dynamics – the important line broadening mechanism responsible for the conductive polymer photovoltaic characterisation. This mechanism (b) is due to the Q1D (quasi-one-dimensional) polaron diffusion $\sim d_1 \nu^{-(1/2)}$ when $\nu d_2 \gg 1$ and the ν -independent contribution (included in δ_0) when $\nu d_2 \ll 1$, where d_1, d_2 are the coefficients of spin diffusion along a polymer chain (1D) and between the chains (3D), respectively [11a]. According to the suggested line broadening mechanism and data for polymers included in Table 1, one can see that 1D diffusion under the condition $\nu d_2 \gg 1$ cannot be dominated by $\sim \nu^{-(1/2)}$ since the line broadening has been recorded in all experiments with increasing ν , however the search for its contribution, and also of the case $\nu d_2 \ll 1$, should be a goal of study for multi-frequency ESR. In addition to the previously mentioned mechanisms, the polaron diffusion, including the $\sim \nu^2$ linewidth dependence considered recently for some oligothiophenes in [11b], may also require data found utilizing the third ESR frequency. However, the choice of ν (ESR spectrometers; L/S-bands (1/3.5 GHz, respectively) or Q/W-bands) depends on the goal of the experiment, i.e. what kind of frequency dependent contribution should be studied. One can expect that, in the above experiments, utilization of the pulse ESR technique would be preferable since both variants of experimental results: (a) FT spectrum for simulation and (b) the direct T_1 and T_2 measurements, are available.

The relaxation dynamic with regard to the search for saturation conditions (longitudinal relaxation time- T_1 determination) was studied using the X-band technique at 77 K since, in this case, there are no limitations for the input light intensity and the temperature is sufficiently low for reliable anion radical stabilisation. A LESR spectrum of $L\{1\}^{-\bullet}$ shows the beginning of weak saturation of the signal only after increasing the microwave power ($P_{\mu w}$) to 100 mW. Contrary to $L\{1\}^{-\bullet}$ the M3EH-PPV positive polaron ($P_M^{+\bullet}$) exhibited a stronger saturation effect in this blend in a range near 20 mW microwave power (Figs. 5 and 6). The effective T_2 can be obtained directly by $T_2 = 2/(\gamma \Delta B_i)$, where γ is the electron gyro magnetic ratio. In order to estimate T_1 , the ESR line amplitude curve can be utilized with dependence on $P_{\mu w}$ [12,13]. In the case of saturation, both variants of T_1 calculation (note that T_2 is already calculated)

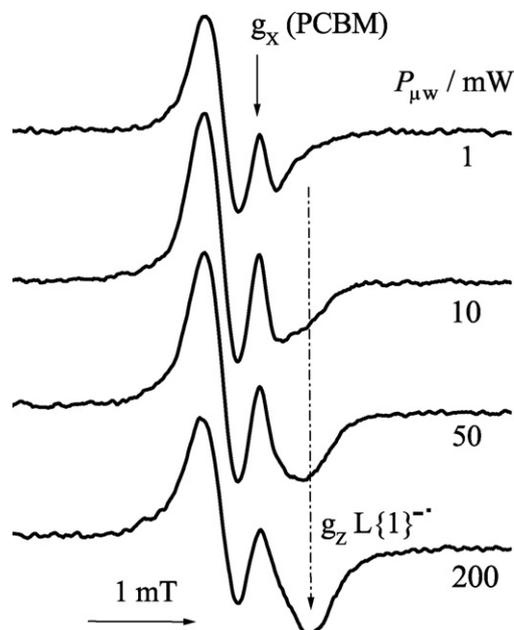


Fig. 5. Several X-band LESR spectra of $(\{1\})/(\text{M3EH-PPV})$ blend (film) recorded at various microwave powers ($P_{\mu w}$) under 0.1 W/cm^2 Xe-lamp illumination.

are available: (a) computation by $A \sim f(P_{\mu w})$ curve fitting:

$$A \sim \frac{|\gamma| P_{\mu w}^{0.5} T_2^2}{(1 + \gamma^2 P_{\mu w} T_1 T_2)^{1.5}} \quad (3)$$

and (b) using

$$T_1 = \frac{1}{2\gamma^2 P_{\mu w}^M T_2} \quad (4)$$

which is obtained by differentiating (3) with the condition $-dA/dP_{\mu w} = 0$, where $P_{\mu w}^M$ is the $P_{\mu w}$ value corresponding to the

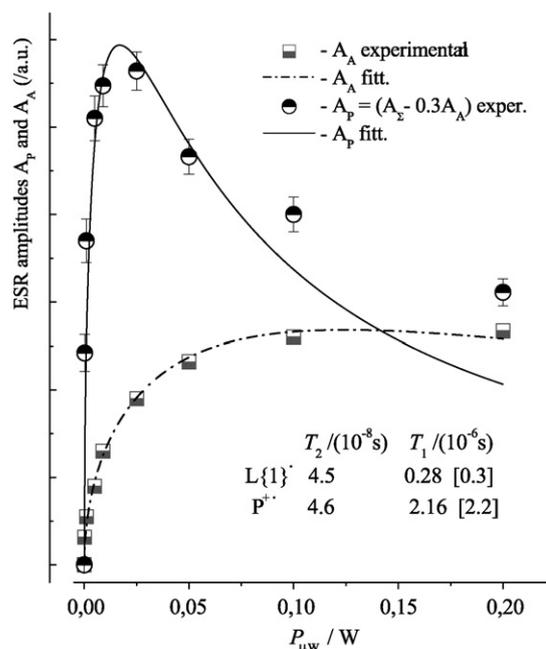


Fig. 6. X-band ESR amplitudes A_A and A_P dependence on microwave power (graphically A_A and A_P denominations are given in Fig. 2(b)). Calculated average effective values for $T_2 = 2/(\gamma \Delta B_{x,y})$ and T_1 by Eqs. (3) and (4) are shown in the inset table (by (4) in square brackets).

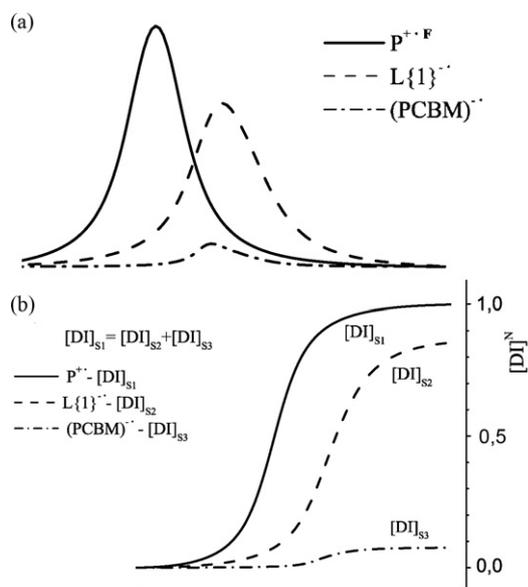


Fig. 7. (a) The constructed absorption spectra of the simulated S_1 , S_2 , S_3 introduced in Fig. 2(b). (b) Normalised DI of S_1 , S_2 , S_3 .

maximum A (start of saturation). In Fig. 6 experimental curves and those computed/fitted by Eq. (3) $A_{A,P}$ for $L\{1\}^{\bullet-}$ and $P_M^{\bullet+}$ are shown. Computed relaxation parameters demonstrate that T_2 for $P_M^{\bullet+}$ of M3EH-PPV are similar to T_2 values of the P3HT polaron in the P3HT/PCBM blend and T_1 of $L\{1\}^{\bullet-}$ is several factors shorter than T_1 of the M3EH-PPV polaron. The same tendency for the magnitude of T_1 (relative to T_2) was reported for the other blends, for example in poly(3-dodecylthiophene) P3DDT/ C_{60} [14] and poly[(2-methoxy-5-(3',7'-dimethyloctyloxy))-1,4-phenylenevinylene] MDMO-PPV/PCBM [15]. In addition, the parameters calculated by (4) are also included in the inset table of Fig. 6. In accordance with the data of the experimental spectrum simulation and the double integral (DI) calculation of S_1 , S_2 , S_3 spectra (see Fig. 2), one can estimate the efficiency of CSP in the mixed composites medium – donor/two acceptors – at around 100% with certainty taking into consideration the accuracy of the experimental spectra simulation ($\sim 6\%$):

$$| + Q^{\text{polar}} | \approx | - Q^{(\text{PCBM}-C_{120}O)} - Q^{(\text{PCBM})} |$$

The constructed absorption spectra of S_1 , S_2 , S_3 and their DI values (normalized to the DI maximum of the polaron spectrum) are shown in Fig. 7.

4. Conclusion

In this work the principal g component values of the M3EH-PPV positive polaron ($P_M^{\bullet+}$) and PCBM- $C_{120}O$ anion radical ($L\{1\}^{\bullet-}$)

spectra registered during photo-induced CSP are reported. Based on the data of g -factor parameters and taking into account that in $L\{1\}^{\bullet-}$ ESR spectra no traces of the triplet spin state features were found, one can make the preliminary conclusion that $L\{1\}^{\bullet-}$ can be corresponded to the mono-anion radical. In addition, $P_M^{\bullet+}$ and $L\{1\}^{\bullet-}$ spin dynamic data, in regard to their essential difference in T_1 , demonstrate low probability for fast electron spin exchange interaction between them and as a result decrease the opportunity of the fast intermolecular charge recombination process, at least at low temperatures. From this point of view this blend is similar to P3HT/PCBM. Therefore, in light of the ESR results (PCBM- $C_{120}O$)/(M3EH-PPV) composite blends should be verified as a working medium for the photovoltaic devices (solar cells).

References

- [1] (a) D.F. Kronholm, J.C. Hummelen, in: C. Brabec, U. Scherf, V. Dyakonov (Eds.), Organic Photovoltaics Materials, Wiley-VCH, Weinheim, 2008, pp. 155–178; (b) H. Hoppe, N.S. Sariciftci, in: S.R. Marder, K.-S. Lee (Eds.), Photoresponsive Polymers II, Series: Advances in Polymer Science, vol. 214, Springer, Berlin, 2008, pp. 1–86.
- [2] (a) C.A. Reed, R.D. Bolskar, Chem. Rev. 100 (2000) 1075–1118; (b) D.V. Konarev, S.S. Khasanov, R.N. Lyubovskaya, Russ. Chem. Bull. 56 (2007) 371–392; (c) V.V. Yanilkin, N.V. Nastapova, V.I. Morozov, V.P. Gubskaja, F.G. Sibgatullina, L.Sh. Berezhnaja, I.A. Nuretdinov, Russ. J. Electrochem. 43 (2007) 184–203.
- [3] (a) A.L. Balch, D.A. Costa, W.R. Fawcett, K. Winkler, J. Phys. Chem. 100 (1996) 4823–4827; (b) L. Dunsch, P. Rapta, A. Gromov, A. Stasko, J. Electroanal. Chem. 547 (2003) 35–43; (c) P. Paul, R.D. Bolskar, A.M. Klark, C.A. Reed, Chem. Commun. (2000) 1229–1230.
- [4] (a) L. Weber, S. Sensfuss, U. Ritter, P. Scharff, Fuller Nanotechnol. Carb. Nanostruct. 17 (2009) 187–207; (b) L. Weber, M. Reinmoller, U. Ritter, Carbon Sci. Technol. 1 (2008) 9–12.
- [5] (a) T. Kietzke, D.A.M. Egbe, H.-H. Hörhold, D. Neher, Macromolecules 39 (2006) 4018–4022; (b) D.A.M. Egbe, T. Kietzke, B. Carbonnier, D. Mühlbacher, H.-H. Hörhold, D. Neher, T. Pakula, Macromolecules 37 (2004) 8863–8873.
- [6] A. Konkin, H.-K. Roth, P. Scharff, O. Ambacher, A. Aganov, S. Sensfuss, Sol. State Commun. 149 (2009) 893–897.
- [7] A. Aguirre, P. Gast, S. Orlinskii, I. Akimoto, E.J.J. Groenen, H. El Mkami, E. Goovaerts, S. Van Doorslaer, Phys. Chem. Chem. Phys. 10 (2008) 7129–7138.
- [8] A.L. Konkin, S. Sensfuss, H.-K. Roth, G. Nazmutdinova, M. Schroedner, M. Al-Ibrahim, D.A.M. Egbe, Synth. Met. 148 (2005) 199–204.
- [9] G.M. Zhidomirov, Y.S. Lebedev, S.N. Dobryakov, N.I. Steinsneider, A.K. Chirkov, V.A. Gubanov, Interpretation of Complicated EPR Spectra, Nauka, Moscow, 1975.
- [10] S. Lee, S.-Z. Tang, Phys. Rev. B 31 (1985) 1308–1317.
- [11] (a) K. Mizoguchi, S. Kuroda, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, Wiley, Sussex, 1997, p. 251 (and references therein); (b) K. Kanemoto, K. Furukawa, N. Negishi, Y. Aso, T. Otsubo, Phys. Rev. B 76 (2007) 155205(1–7).
- [12] C.P. Poole, Electron Spin Resonance, Interscience, John Wiley & Sons, New York, 1967.
- [13] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Paramagnetic Resonance: Elementary Theory and Practical Applications, John Wiley & Sons, New York, 1994.
- [14] S. Sensfuss, A. Konkin, H.-K. Roth, M. Al-Ibragim, U. Zhokhavets, G. Gobsch, V.I. Krinichnyi, G.A. Nazmutdinova, E. Klemm, Synth. Met. 137 (2003) 1433–1435.
- [15] V. Dyakonov, G. Zorinians, M. Scharber, C.J. Brabec, Phys. Rev. B 59 (1999) 8019–8025.