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Magnetic-field-controlled charge transport in organic polymer composites



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ABSTRACT

Spin properties of charge carriers photoexcited in the P3HT:PC₆₁BM and PCDTBT:PC₆₁BM composites were studied at X-band EPR spectroscopy. Light-induced EPR spectra were deconvoluted and the contributions of all spin charge carriers were determined. The main magnetic resonance parameters of charge carriers obtained were compared with those determined at millimeter EPR wavebands and analyzed as a function of electron precession frequency. The linewidth of spin charge carriers was established to originated mainly due to the weak anisotropy of their *g*-factors. The external magnetic field significantly affects dynamics, electron relaxation and recombination of spin charge carriers.

1. Introduction

Recently, much attention has been paid to the development of functional polymer materials due to the great potential of their use in molecular electronic [1,2] and spintronic [3] devices. The functionality of such devices is achieved by introducing into the polymer matrix fullerene derivatives, carbon tubes, other suitable additives that become as an electron donor (hole transporter, p-type material) and an acceptor (electron transporter, *n*-type material), respectively. The transfer of free electron from the donor to the additive is accompanied by the appearance of a polaron on polymer chain. As a result of charge separation in the donor and acceptor phases of such a system, two spin ensembles are formed. The spin nature of charge carriers leads to the specificity of the basic properties of such systems in comparison with traditional semiconductors. This also determines the predominant applicability of various magnetic resonance methods for detailed study of organic molecular devices, e.g., polymer:fullerene composites [4–7]. For example, the light-induced cw EPR (LEPR) method allows to study in details the separation, transfer, and recombination of charge carriers photoexcited directly in EPR cavity. Because g-factors of these charge carriers are close to g-factor of free electron, $g_e = 2.00232$, their spectral lines are overlapped partially or completely at relatively low frequency of spin precession, $\omega_e = 2\pi\nu_e$. An analysis of the main magnetic resonance parameters (paramagnetic susceptibility, linewidth, g-factor) of spin ensembles becomes more accurate and detailed at millimeter wavebands LEPR [8–10]. Deconvolution of effective spectra of multispin system increases additionally the efficiency of the method at different experimental conditions [6,7,10-12].

After the formation of charge carriers some their quantity tends to recombine, whereas their other part fills energetically deep spin traps formed in disordered polymer backbone, so only small number of carriers able to transfer a charge to respective electrodes. This determines spin-assistance of the main processes carrying out in organic polymer: fullerene composites with paramagnetic additives [6,7,13,14]. They depend on the structure and morphology of composites, the density, energetic depth and spatial distribution of spin traps formed in its disordered matrix, and also on the energy of exciting photons. So, the efficiency and functionality of the above systems are governed mainly by spin-assisted separation, dynamics and recombination of free charge carriers formed in their bulk heterojunctions (BHJ).

In order to wider functionality of such systems and use them not only for a direct conversion of energy but also in spintronics, it would be important to organize independent channels for flexible handling their electronic properties. They may be manipulated, e.g., by changing the density and energy of the initiating light photons. Another handling channel for charge carriers can be organized by changing their electron relaxation, which reflects spin-assisted processes occurring in spin donor-accepter systems. Because both the charge carriers exchangeable spin-flip [14], their recombination becomes dependent on spin dynamics, concentration, polarization, and mutual separation [15]. The interaction of the nearest spin ensembles was shown [14] to play an important role in charge transport. Analyzing the character of this process, it would be possible intended to use the interaction of solitary charge carriers with their own microenvironment and other spin ensembles to change the direction of spin precession during their characteristic spin-lattice and spin-spin relaxation times, T_1 and T_2 ,

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respectively. These parameters of spin charge carriers photoinitiated in some photovoltaic systems are shown [6,7] to depend on the energy of initiating photons and Zeeman splitting. The structural disordering of the donor–acceptor composites should also cause the dependence of the above processes on the cross-relaxation of spin charge carriers occurring within a characteristic time T_{12} . However, the influence of the frequency of electron precession on spin-exchange and spin-dynamic processes in polymer:fullerene composites has not yet been analyzed.

Herein, we analyze the processes of photoinitiation and recombination of charge carriers in BHJ of exemplary composites formed by regioregular poly(3-hexylthiophene) (P3HT) and poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) with [6,6]-phenyl-C₆₁-butanoic acid methyl ester (PC₆₁BM) additive at X-band ($\omega_e/2\pi = 9.7$ GHz, $B_0 = 345$ mT) LEPR in comparison with those determined at K- ($\omega_e/2\pi = 24$ GHz, $B_0 = 862$ mT) [11], W- ($\omega_e/2\pi = 95$ GHz, $B_0 = 3356$ mT) [12], and D- ($\omega_e/2\pi = 130$ GHz, $B_0 = 4650$ mT) [10] wavebands LEPR. The data obtained by the direct magnetic resonance method in combination with spectral simulations allowed us to obtain the correlation of the balance of these processes and the frequency of spin precession.

2. Experimental details

2.1. Materials

In the work, regioregular poly(3-hexylthiophene) (P3HT), poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzo-thiadiazole)] (PCDTBT), distributed by Rieke Metals®, and [6,6]-phenyl-C₆₁-butanoic acid methyl ester (PC₆₁BM), distributed by Solenne BV®, were used as electron-donating and accepting photovoltaic sub-systems, respectively. The samples were prepared as double-sided films formed on a ceramic plate, both with the size of ca. $4 \times 8 \text{ mm}^2$ and thickness of ca. 0.1 mm as described earlier [16,17]. CW EPR measurements were performed at the X-band ($\omega_e/2\pi = 9.7 \text{ GHz}, B_0 = 345 \text{ mT}$) using PS-100.X spectrometer with a maximum microwave power of 150 mW and 100 kHz phase detection. Both the samples were steady-state illuminated by the LED-based light source (10 W Luxeon® 2.38 eV/522 nm) through the quartz cylindrical light guide directly in the MW cavity of the spectrometer.

2.2. Methods

Darkened and photoinduced X-band LEPR spectra of the samples were obtained at 77 K being inserted into a quartz Dewar filled with liquid nitrogen and placed into the EPR spectrometer cavity. At other wavebands experiments were carried out at 50 K $\leq T \leq$ 120 K. Taking into account that the structural-conformational transitions in organic conjugated polymers occur only at T > 160 K, one could expect the compliance of all the results obtained. To avoid instrumental and fast passage linewidth effects, all spectra were obtained in a regime sufficiently below their microwave saturation. The signal-to-noise ratio of signals was improved by their accumulation during multiple scanning of LEPR spectra. Spectral lines and concentration of different spin ensembles were determined by using deconvolution of effective LEPR spectra as described earlier [7,10,18]. Landé g-factors of spin charge carriers were determined using the DPPH standard demonstrating symmetrical single line at $g = 2.0036 \pm 0.0002$ [19]. The accuracy of estimating the intensity I, g-factor and the distance between its positive and negative spectral peaks of the line, ΔB_{pp} , was determined to be 5%, $\pm 2 \times 10^{-4}$ and $\pm 2 \times 10^{-3}$ mT, respectively. The simulation of experimental spectra obtained at X-band in the present work as well as at K- ($\omega_e/2\pi = 24$ GHz, $B_0 = 862 \text{ mT}$) [11], W- ($\omega_e/2\pi = 95 \text{ GHz}$, $B_0 = 3356 \text{ mT}$) [12], and D- $(\omega_e/2\pi = 130 \text{ GHz}, B_0 = 4650 \text{ mT})$ [10] wavebands LEPR were performed using the EasySpin [20] and OriginLab programs.

3. Results and discussion

3.1. Composition of spin charge carriers

Figs. 1 and 2 show LEPR spectra of paramagnetic centers photoinduced in the P3HT:PC₆₁BM and PCDTBT:PC₆₁BM composites, respectively, by the source of visible light at various wavebands and $T \leq 120$ K. As in the case of other similar compounds [6,7], the low- and high-field spectral components were assigned to polarons, P⁺⁺, excited on polymer chains and methanofullerene radical anions, mF_{61}^{-} , situated between them. Both these charge carriers are characterized by weakly anisotropic magnetic resonance parameters, *g*-factor, and peak-to-peak linewidth, $\Delta B_{\rm pp}$, which is mostly manifested for localized polarons, P⁺⁻_{loc}, and radical anions, $mF_{\rm loc}^{-}$, at millimeter wavebands EPR. These parameters depend on spin relaxation, dynamics, and precession frequency [10–12] that should be taken into account upon the deconvolution of effective LEPR spectra.

It is seen from the Figures how change the shape of these spectra with the increase in spin precession frequency, $\nu_e = \omega_e/2\pi$. Such transformation occurs mainly due to a manifestation of the above-mentioned anisotropy of magnetic resonance parameters as well as to concentrations of mobile and localized charge carriers. The main values of *g*-factor of polarons photoinitiated in the P3HT:PC₆₁BM and PCDTBT:PC₆₁BM composites were precisely measured at D-band LEPR to be $g_{xx}^P = 2.0032$, $g_{yy}^P = 2.0023$, $g_{zz}^P = 2.0012$ and $g_{xx}^P = 2.0032$, $g_{yy}^P = 2.0024$, $g_{zz}^P = 2.0018$, respectively, whereas methanofullerene radical anisotras are characterized by the main tensor values $g_{xx}^{mF} = 2.0006$, $g_{yy}^{mF} = 2.0005$, $g_{zz}^{mF} = 1.9985$ [21]. Once these carriers start to move, their anisotropic spectra become single and are registered at $g_{iso}^P = 2.0024$, 2.0025, and $g_{iso}^{mF} = 1.9999$, respectively (see the contribution due to the respective mobile pairs $P_{mob}^{+-} \leftrightarrow mF_{mob}^{--}$ shown in Figs. 1 and 2).

3.2. Linewidth of spin charge carriers

Except the positions of both spectral contributions of photoinitiated charge carriers photoinitiated in the systems under study, the deconvolution of effective LEPR spectra of polymer:fullerene composites allowed also to determine and control separately a linewidth of their contributions. Because these magnetic resonance parameters are weakly anisotropic and depend on electron relaxation, dynamics and precession frequency of spin charge carriers [10-12], that should be taken into account upon such procedure. The interaction between these carriers with other spin systems changes their spin-spin relaxation rate, $T_2^{-1} =$ $\sqrt{3}\gamma_e\Delta B_{pp}/2$ [22], where γ_e is the gyromagnetic ratio of electron spin. The main terms of the linewidth tensors of localized charge carriers obtained from the fitting of the P3HT:PC_{61}BM and PCDTBT:PC_{61}BM LEPR spectra are summarized in Table 1. When the motion of these paramagnetic centers is accelerated, this and other magnetic resonance parameters of charge carriers are averaged. Fig. 3 shows the variation of the averaged linewidth $\Delta B_{\rm pp}$ of mobile charge carriers photoinitiated in the P3HT:PC₆₁BM composite with the spin precession frequency $\nu_e = \omega_e/\omega_e$ 2π of their spins. It may consist of some contributions, e.g.,

$$\Delta B_{pp} = \Delta B_{pp}^{hfi} + \Delta B_{pp}^{vib} + \Delta B_{pp}^{QID} + \Delta B_{pp}^{g} \tag{1}$$

The first term of the right-side Eq. (1) is secular width originated due to hyperfine interaction (hfi) of solitary spins with neighboring paramagnetic centers which it does not change with the electron precession frequency ω_e and external magnetic field B_0 . Extrapolation of such parameter to $\omega_e \rightarrow 0$ allows one to obtain $\Delta B_{pp}^{hfi} = 0.101$ and 0.066 mT for isotropic linewidth of polarons and methanofullerene radical anions, respectively, photoinitiated in the P3HT:PC₆₁BM BHJ. The other terms are frequency-dependent, they describe LEPR lifetime widths which are introduced to consider radical vibration (libration) and quasi-one-dimensional (Q1D) dynamics as well as g-strain of radicals in a real



Fig. 1. Effective X- (a), K- (b), -W (c) and D- (d) wavebands LEPR spectra of the P3HT:PC61BM composite background illuminated by visible light at $T \leq 120$ K (the above solid lines). Calculated sum spectra (the above dashed lines) and their contributions caused by localized polarons P_{loc}^+ . methanofullerene anion radicals $mF_{loc}^$ and mobile radical pairs $P_{mob}^{+} \leftrightarrow mF_{mob}^{-}$ are shown as well. The orientation of the principal axes of the polaron's g-tensor is given. The charge transfer from polymer chain to methanofullerene molecule accompanied by the formation on the former of polaron with an elementary positive charge and spin $S = \frac{1}{2}$ is shown schematically. Reconstructed K-, W-, and D-band spectra are presented with permission from Phys. Chem. Chem. Phys. 10 (2008) 7129-7138; Copyright (2008) Royal Society of Chemistry, Synth. Met. 160 (2010) 485-489; Copyright (2010) Elsevier, and Adv. Energy Mater. 7 (2017) 1602226; Copyright (2017) John Wiley & Sons.

disordered polymer system. Let the influence of these reasons on the LEPR linewidth be analyzed.

Assume a rotational small-angle vibration of methanofullerene molecules between polymer chains near own main molecular axis with correlation time τ_c unaltered at any ω_e . According to the Redfield theory [23], fast vibrations of spins with $S = \frac{1}{2}$ and a spectral density function $J(\omega) = 2\tau_{\rm c}/(1+\tau_{\rm c}^2\omega_{\rm e}^2)$ [24] should to broaden spectral lines by the value $\Delta B_{pp}^{\gamma ib}=4/\sqrt{3}\gamma_e^3\hbar^2S(S+1)\pi^{mF} au_c\Sigma_{ij}$ (here $\hbar=h/2\pi$ is the Planck constant, n^{mF} is the number of mobile and immobilized methanofullerene radical anions per each polymer unit, and Σ_{ii} is a lattice sum for powderlike sample), similar to that as it occurs in some other organic systems [25,26]. If this were the case, then the linewidth of these radicals would depend linearly on the ratio $n_{\rm mob}^{\rm mF}/n_{\rm loc}^{\rm p},$ where $n_{\rm loc}^{\rm p}$ is the number of localized polarons per polymer unit. However, Fig. 3a shows a strongly non-linear dependence of these parameters. Relaxation of charge carriers in a Q1D polymer system may also depend on spin dynamics along and between polymer chains with the rates $\nu_{||} \gg \omega_e$ and $\nu_\perp \ll \omega_e,$ respectively. In this case, a respective spectral density function would depend on ω_e as $J(\omega_e) = (2\nu_{||}\omega_e)^{-1/2}$ [27,28]. Fig. 3b shows the linewidths of both charge carriers as function of $\omega_e^{-0.5}$. It is seen from the data presented that spin dynamics still cannot cause a sufficient spectral field-dependent line broadening. Finally, g-strain should additionally broaden the line by the value $\Delta B_{pp}^g = (2/15\sqrt{3})B_0^2 \sum_i \Delta g_i^2 (\mu_B/h)^2 \tau_c$ [29], where B_0 is the external magnetic field, $\sum_i \Delta g_i^2$ is the sum of squares of deviations of the principal values of the g-tensor from g_e equal to $2.03{\times}10^{-6}$ and $2.09{\times}10^{-5}$ for polarons and PC_{61}BM, respectively, excited in the P3HT:PC₆₁BM composite [21], and μ_B is Bohr magneton. Fig. 3c demonstrates nearly linear broadening of both the charge carriers with the $\nu_e^2 \propto B_0^2$. So, the analysis made evidence that spectral lines of charge carriers photoinitiated in the sample under study are broadened mainly as a result of the g-strain effect due to their distribution in the disordered sample. However, the weaker effect of spin fast hopping vibration on small angles and Q1D polaron diffusion should be also taken in consideration of spin-assisted processes carrying out in disordered systems.

3.3. Concentration of spin charge carriers

A part of mobile spin pairs is disunited into non-interacting charge carriers, scatter and reach the corresponding electrodes, while their residual part tends to recombine. So, two oppositely directed processes of the appearance and pairing of spins occur simultaneously. The balance of such processes depends on the spatial density and energy depth of the spin traps formed in the disordered polymer backbone and determines the number of free charge carriers reaching respective electrodes. It is proportional to the ratio of the number of mobile polarons to the number of those captured by spin traps, $n_{\rm mob}^{\rm p}/n_{\rm loc}^{\rm p}$ (or the above-mentioned $n_{\rm mob}^{mF}/n_{\rm loc}^{\rm p}$ because a priory $n_{\rm mob}^{mF} \equiv n_{\rm mob}^{\rm p}$), per each polymer unit. This parameter was shown [13,14] to depend minimally on the sample history and, therefore, be most suitable for adequate control of electronic and energy converting properties of photovoltaic composites. Such concentration ratio is frequency-dependent. Assuming the availability of cross-interaction between respective spin ensembles occurs within an appropriate time interval $T_1 > T_{12} > T_2$ [30], the probability, *p* \equiv (2 T_{12})⁻¹, of an interaction between individual spin ensembles in such system should follow the law [31]

$$p = p_0 \sqrt{M_2} \exp\left(-\frac{g_e^2 \mu_B^2 B_0^2}{2h^2 M_2}\right)$$
(2)

where p_0 is a constant and M_2 is the second momentum of a resonant line (in $s^{-2})$ at $B_0 \to 0$ limit.

Fig. 4 depicts the dependence of concentration ratio $n_{\text{mob}}^{\text{P}}/n_{\text{noc}}^{\text{P}}$ determined for the sample P3HT:PC₆₁BM at various EPR wavebands. The data presented evidence strongly decrease in the number of mobile charge carriers with the ν_{e} and, therefore, B_0 rising. They can well be fitted by the law $n_{\text{mob}}^{\text{P}}/n_{\text{loc}}^{\text{P}} = n_{\text{mob}}^{\text{mF}}/n_{\text{loc}}^{\text{P}} = k_1 \exp\left(-\omega_{\text{c}}^2/8\pi^2k_2^2\right)$ with $k_1 = 9.52 \times 10^{-5}$ and $k_2 = 3.45 \times 10^4 \text{ s}^{-1}$. It is seen from the Figure, that the above ratio obtained for the PCDTBT:PC₆₁BM at X-band EPR is less at least four times compared to that measured for the P3HT:PC₆₁BM. It can be explained, e.g., by the lamellated/layered morphology of the former composite, other copolymer BHJ with extended π -system. This increases the interchain and interlayer interaction between adjacent spin charge



Fig. 2. Effective X- (a) and D- (b) wavebands LEPR spectra of the PCDTBT:PC61BM composite background illuminated by visible light at T < 77 K (the above solid lines). Calculated sum spectra (the above dashed lines) and their contributions caused by localized polarons $\mathbf{P}_{loc}^{+ \star},$ methanofullerene anion radicals $mF_{loc}^{-\cdot}$, and mobile radical pairs $P_{mob}^{+\cdot} \leftrightarrow$ mF_{mob}^{-} are shown as well. The orientation of the principal axes of the polaron's g-tensor is given. The charge transfer from copolymer chain to methanofullerene molecule accompanied by the formation on the former of polaron with an elementary positive charge and spin $S = \frac{1}{2}$ is shown schematically. Reconstructed D-band spectrum is presented with permission from Adv. Energy Mater. 7 (2017) 1602226; Copyright (2017) John Wiley & Sons.

Table 1

Main values of tensors of the peak-to-peak Linewidth of polarons and methanofullerene radical anions photoinitiated in P3HT:PC₆₁BM and PCDTBT: $PC_{61}BM$ composites used for calculation of their LEPR spectra at different LEPR wavebands.

Parameter	X-Band	K-Band	W-Band	D-Band
	P3HT:PC ₆₁ BM			
$\Delta B_{\rm P}^{\rm x}$, mT	0.146	0.324	0.709	2.010
$\Delta B_{\rm P}^{\rm y}$, mT	0.113	0.208	0.423	0.676
$\Delta B_{\rm P}^{\rm z}$, mT	0.140	0.265	0.590	0.652
$\Delta B_{\rm F}^{\rm x}$, mT	0.102	0.103	0.296	0.363
$\Delta B_{\rm F}^{\rm y}$, mT	0.121	0.174	0.342	0.574
$\Delta B_{\rm F}^{\rm z}$, mT	0.160	0.289	1.293	3.282
	PCDTBT:PC ₆₁ BM			
$\Delta B_{\rm P}^{\rm x}$, mT	0.153	_	_	0.682
$\Delta B_{\rm P}^{\rm y}, {\rm mT}$	0.217	_	-	1.002
$\Delta B_{\rm P}^{\rm z}, {\rm mT}$	0.180	_	_	0.534
$\Delta B_{\rm F}^{\rm x}$, mT	0.113	_	-	0.378
$\Delta B_{\rm F}^{\rm y}$, mT	0.129	_	_	0.610
$\Delta B_{\rm F}^{\rm z}$, mT	0.169	_	_	2.337

carriers, which, in turn, accelerates corresponding charge transfer [14]. Despite the small number of experimental points obtained for the PCDTBT:PC₆₁BM sample (see Fig. 4), one can nevertheless assume a similar trend for this composite as well as higher likely for another organic disordered systems with mobile spin charge carriers. This should indicate a decrease in spin cross-relaxation and, as a result, a decrease in the number of charge carriers released from deep spin traps upon light irradiation of the samples in high magnetic fields. Such effect, however, may also be caused by the lower sensitivity of the pulse method to the mobile charge carriers [32–34] that should be taken into consideration.

Taking into account a formation of spin-correlated ion pairs of opposite charges, one can also interpret the above-mentioned simultaneous recombination and braking of spin charge carriers in the external magnetic field in terms of the Chemically Induced Dynamic Electron Polarization (CIDEP) approach [35]. Indeed, pairs of singlet spin-correlated polarons and radical ions with opposite charges are formed as a result of the dissociation of photoinitiated excitons. The spin state of these carriers remains singlet even after their separation within BHJ. Polarons walking along the polymer chains do not recombine with the first radical anions. A part of such carriers, therefore, acquires triplet state as a result of singlet–triplet conversion. Such polarons become unable to recombine with singlet counterions. The precession frequency of singlet and triplet spins with unequal Landé splitting g-factors become different. As a result, only the fourth part of the initially photoexcited polarons becomes field-dependent and potentially able to recombine



Fig. 3. Averaged linewidth of mobile polarons and methanofullerene radical anions photoinitiated in the P3HT:PC₆₁BM bulk heterojunctions as a function of the relative concentration of mobile spins (*a*), $\nu_{\rho}^{-0.5}$ (*b*) and ν_{ρ}^2 (*c*). The dashed and dash-dotted lines are drawn arbitrarily only for illustration to guide the eye.



Fig. 4. The dependence of the n_{mob}^p/n_{loc}^p ratio as a function of the spin precession frequency $\nu_e = \omega_e/2\pi$. The dashed line shows the dependence calculated from Eq. (2) for the P3HT:PC₆₁BM sample. The dash-dotted line is drawn arbitrarily only for illustration to guide the eye.

with singlet counterions. Therefore, it is quite obvious that all these effects should be taken into account when creating new molecular devices with field-light-controlled electronic properties.

4. Conclusion

In summary, we have presented a first analytic LEPR study of charge transfer through different polymer:fullerene BHJ at the wide variation of spin precession frequency. Under light illumination of the composites, two spin charge carriers are excited in their BHJ, polarons (holes) fast diffusing along polymer chains and methanofullerene radical anions vibrating at small angles inside the polymer backbone. The widths of individual spectral contributions of these charge carriers are mainly determined by a weak anisotropy of their magnetic resonance parameters. A part of these carriers is captured by energetically deep traps formed in the polymer matrices due to their disordering. So immobilized carriers also participate in the charge transfer process, however, indirectly. When an external magnetic field is applied to the sample, the cross-relaxation of spin charge carriers slows down and they become independent. This accelerates the transfer of charge carriers through BHJ and stipulates their recombination. Such a process should depend not only on the structure, the order of the polymer composite and the state of spin charge carriers but also on the energy of light photons, temperature, other experimental factors. Appropriate further research is planned to be carried out elsewhere. The approach proposed can be used in the study of systems with other polymer/copolymer electron donors and fullerene electron acceptors. The data obtained can be used to construct molecular electronic and spintronic devices with light and magnetic-field controlled properties.

CRediT authorship contribution statement

Victor I. Krinichnyi: Conceptualization, Investigation. Evgeniya I. Yudanova: Methodology, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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