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Dynamics of Hot Exciton Relaxation in Conjugated Polymer Chain

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Abstract

Hot excitons are formed after photoexcitation of conjugated polymer chains. Hot excitons relax and convert into cold excitons with the aid of vibrational modes. In this study, the dynamics of such conversion is studied within the strong coupling regime. It has been found that the magnitudes of electronic coupling integrals for hot exciton relaxation are mostly due to exchange interactions between the interacting units. During relaxation, hot excitons oscillate back and forth between two different sites until they lose their extra energy. The time step for each oscillation has been found as small as 0.3 fs. It has also been found that photoexcited states in conjugated polymer chains do not necessarily localize at their initial location formed. Monte-Carlo simulations show that hot excitons can sustain their coherent motion along the conjugated backbone to some extent before total relaxation.

1. Introduction

The electronic energy transfer between chromophores is generally studied in the strong and weak coupling regimes [1]. Coherent energy transfer is usually seen in the strongly coupled chromophores with significant exchange correlations among the clouds of the interacting units [2, 3]. When the chromophores are well separated in space with negligible overlap of wavefunctions, incoherent energy transfer then becomes the major mechanism for energy transfer through Coulombic interactions [4, 5]. One of the famous examples in the weak coupling limit is Förster energy transfer, which assumes that energy transfer rate from a donor chromophore to an acceptor chromophore occurs in a time scale much shorter than relaxation rate of acceptor site. Thus, there is a little chance of energy transfer back to donor chromophore from acceptor chromophore [6]. On the other hand, strong coupling of donor and acceptor chromophores causes oscillation of photoexcited energy between the donor and the acceptor sites. Thus, the system can be seen as single pair with well delocalized wavefunctions, which does not allow distinguishing the donor chromophore from the acceptor chromophore [7]. Strong coupling between the chromophores causes energy level splitting. One of the well-known examples of energy transfer in the strong coupling regime is observed in the energy transfer interaction of chromophores in H- and J-aggregates of conjugated small molecules [6].

Upon photoexcitation in conjugated systems, hot excitons are formed [8]. Such excitons lose their energy to bath and form cold excitons from where emission is observed in luminescent materials. The relaxation dynamics of hot excitons in conjugated materials in ultrafast time scales are difficult to study both theoretically and experimentally [9]. The reason stems from the fact that expensive instrumentation is needed to analyze the excitonic decay mechanisms by using indirect methods [10-12]. Theoretical background that describes relaxation dynamics of highly energetic excitons is not adequately developed yet [13-15]. Since there is significant wavefunction overlap anticipated among interacting units,

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the use of Förster type energy transfer mechanism for strongly coupled systems is not appropriate. As a consequence, more advanced theories and approaches need to be utilized for simulation of hot exciton relaxation dynamics. There are numerous methods in the literature that examines energy transfer processes in the weak coupling regime [13, 16, 17]. Strong coupling regime studies are mostly focused on systems with significant wavefunction overlap between two different chromophores [7]. In this article, an attempt has been made to understand the relaxation dynamics of hot excitons in a conjugated polymer chain by using theoretical methodologies developed for strongly coupled chromophores [18]. The results indicate that exchange interactions are the dominant type of interactions when hot excitons oscillate between different sites during cooling process.

2. Theoretical Methods

An electronically excited chromophore may transfer its energy to a nearby non-excited chromophore due to Coulombic interaction and exchange correlations. Since the nearest chromophores next to the initially excited chromophore should be considered, exchange correlations become important part of excitonic dynamics along a polymer chain. An isolated two-level chromophoric system (a donor (D) and an acceptor (A)) is the starting point to describe the hot exciton relaxation dynamics through energy transfer to lower energy sites. In such dual system, $|D_0A_0\rangle$, $|D_1A_0\rangle$, $|D_0A_1\rangle$, and $|D_1A_1\rangle$ represents ground state, singly excited states, and doubly excited state, respectively. Since there are four states, the interaction between the donor and the acceptor chromophores should ideally be investigated in a 4 × 4 matrix. Although strong coupling regime is operative in such situation, it is assumed that inter-chromophoric coupling is not involved in the mixing of the ground state and the doubly excited state. Therefore, there are two states left, $|D_1A_0\rangle$ and $|D_0A_1\rangle$, that describes energy transfer from a donor chromophore to an acceptor chromophore. Then, after following Harcourt model [19] the electronic coupling between these two states can be represented as:

$$V \cong \langle D_1A_0|\hat{V}|D_0A_1\rangle \cong 2\langle dd'|aa'\rangle - \langle d'a'|ad\rangle \cong 2J - K \qquad (1)$$

where $\hat{V}$ is the Hamiltonian, d and d' are the highest occupied and the lowest unoccupied molecular orbitals on donor chromophore involved in the excited state formation. Similarly, a and a' are the highest occupied and the lowest unoccupied molecular orbitals on acceptor chromophore. J is the Coulombic coupling term whereas K is the exchange coupling term which includes ionic configurations and can be regarded as the charge-transfer or polarization character of the state.

Electronically excited state is on the donor chromophore initially, thus the system is in $|D_1A_0\rangle$ state. The hot exciton then relaxes and migrates to an acceptor chromophore, which can be deduced as $|D_0A_1\rangle$ state. The wavefunction for this two level system is $|\psi_i\rangle = c_D\,|D_1A_0\rangle + c_A\,|D_0A_1\rangle$. The eigenvalues can be obtained by solving the equations for the following matrix: [20]

$$\begin{bmatrix} E_D & V \\ V & E_A \end{bmatrix}\begin{bmatrix} c_D \\ c_A \end{bmatrix} = E\begin{bmatrix} c_D \\ c_A \end{bmatrix} \qquad (2)$$

Here, $E_D = E(D_1) - E(D_0)$ and $E_A = E(A_1) - E(A_0)$. For this special case, E_D corresponds to the excitation energy that eventually leads to the formation of hot exciton. The eigenvalues of the secular determinant can be calculated as:

$$E_{\pm} = \frac{E_D + E_A}{2} \pm \sqrt{\Delta^2 + V^2} \qquad (3)$$

with $\Delta = \frac{E_D - E_A}{2}$. It is important to note that in the strong coupling regime, hot exciton relaxes to the neighboring acceptor sites for which $E_D \cong E_A$ and Δ is quite small in comparison to V. Therefore, the wavefunctions of the coupled states are found to be as:

$$\psi_{\pm} = \frac{1}{\sqrt{2}}(|D_0A_1\rangle \pm |D_1A_0\rangle) \qquad (4)$$

Since time evolution of coupled donor-acceptor pair is of interest, the time dependent wavefunction can be written as $|\psi(t)\rangle = \hat{U}(t,t_0)|\psi(t_0)\rangle$ and in the basis set of $|\psi_+\rangle$ and $|\psi_-\rangle$ as: [20]

$$|\psi(t)\rangle = c_+ e^{-iE_+(t-t_0)/\hbar}|\psi_+\rangle + c_- e^{-iE_-(t-t_0)/\hbar}|\psi_-\rangle \qquad (5)$$

The hot exciton is located on the donor chromophore first, therefore one can easily notice $|\psi(t_0)\rangle = |D_1A_0\rangle$. However, hot exciton moves to acceptor chromophore at time t. To reveal the dynamics of exciton relaxation, it is vital to find the probability of excited state relaxation on acceptor chromophore by calculating the overlap between $|\psi(t)\rangle$ and $|D_0A_1\rangle$. After solving overlap based equations, the probability of occupation on acceptor site and the corresponding rate equation are found as: [20]

$$P_A(t) = |\langle D_0A_1|\psi(t)\rangle|^2 = \frac{|V|^2}{\Delta^2 + |V|^2}\sin^2\frac{\sqrt{\Delta^2 + |V|^2}\,t}{\hbar} \qquad (6)$$

$$k_{DA} = \frac{dP_A(t)}{dt} = \frac{|V|^2}{\hbar\sqrt{\Delta^2 + |V|^2}}\sin\frac{2\sqrt{\Delta^2 + |V|^2}\,t}{\hbar} \qquad (7)$$

According to Eq. (7), $|V|$ and Δ parameters must be evaluated in order to calculate the time dependent rate value for hot exciton relaxation. $|V|$ can be estimated by using Eq. (1) for which Coulombic and exchange integrals need to be calculated explicitly. The energy difference between the donor and the acceptor sites, Δ, is quite small; as will be discussed below. Thus, hot exciton for the most part oscillates back and forth between the donor and the acceptor chromophores until total relaxation.

As a model conjugated polymer, a short segment of polythiophene with 20 α-linked fully planar thiophene rings (th20) is chosen for this study. Both ground and excited states geometries are obtained using 3-21G basis set with Hartree-Fock (HF) and spin restricted configuration interactions with single excitations (RCIS) methods, respectively. Excitonic absorption and emission energies were obtained by employing time dependent density functional theory (DFT) with B3LYP functional and 6-31G(d) basis set on HF and RCIS optimized geometries. All calculations were performed with Gaussian 09 software package [21]. 3D transition density plots for the lowest excitonic transitions were constructed by using the formula below: [4, 8]

$$\rho_{\mu 0}(r) = \sum_{h,l} C_{\mu hl}\phi_h\phi_l \tag{8}$$

where $C_{\mu hl}$ is the configuration interaction coefficients of the transition between occupied (ϕ_h) and unoccupied (ϕ_l) molecular orbitals.

The dynamics of relaxation has been carried out with Monte-Carlo methods. Monte-Carlo simulations start at the location where the photoexcitation occurs. Two rates are calculated with Eq. (7), one for self-localizing (k_{self}) exciton (hopping distance = 0 Å) and the other for hopping exciton (k_{hop}) to either the left or right direction of conjugated chain (hopping distance = 3.93 Å, one thiophene unit migration). One of the rates is chosen on the basis of their weighted probabilities for the hopping process. The hopping time is estimated based on the following equation: [22]

$$\tau = \frac{-\ln(rand)}{k_{self}+k_{hop}} \tag{9}$$

where $rand$ is a random number between 0 and 1. The Monte-Carlo simulation runs until the formation of cold exciton. 10,000 Monte-Carlo runs are found to be sufficient to get converged results.

3. Results and Discussion

Hot exciton relaxation mechanism through various potential energy surfaces is illustrated in Figure 1. In the model presented in this work, hot exciton strongly couples with the nearby excited states, which act as acceptor chromophores. Such chromophores have very similar potential energy surfaces and resemble very much initially excited state chromophore with slight deviations in the reaction coordinate. The movements in the reaction coordinate are facilitated by vibronic modes coupled to the excited states. After relaxation of hot exciton to the lowest energy site, a cold exciton forms, which decay to the ground state either radiatively (by emitting photon) or non-radiatively [23]. In order to reveal the dynamics of hot exciton relaxation, one needs to exploit those intermediate excited states and figure out the main vibrational mode(s) that transform hot exciton into cold exciton.

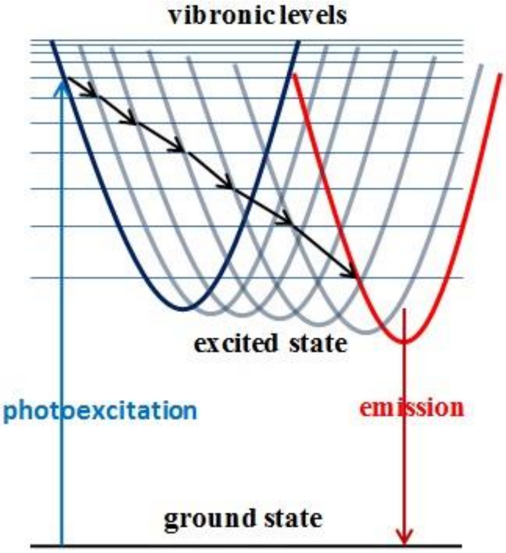

Figure 1. The relaxation mechanism of hot exciton to cold exciton through intermediate excitonic states with the use of vibrational modes.

The size and location of hot and cold excitons can be best visualized by transition density plots [8]. Figure 2 shows that hot exciton on th20 oligomer is much more delocalized than cold exciton, as one might expect. It has been shown in many different studies that relaxation of hot exciton is accompanied by structural changes over the chromophoric unit [8, 11, 24]. The major change in thiophene based systems is lengthening of C=C double bonds while shortening of C-C single bonds along the conjugated backbone. Such structural change is achieved by involvement of C-C stretching modes around 1,600 cm^{-1}. Indeed, C-C stretching modes are the major players of vibrational modes that transform hot exciton into cold exciton in conjugated materials [11]. Therefore, it is assumed that the timescale of motion for this vibrational mode determines the timescales of hot exciton relaxation. In addition, there is experimental evidence that indicates photoexcited states relax in timescales less than 100 femtoseconds (fs), mainly limited by the sensitivity of utilized equipment [10, 12, 25]. The stretching motion at 1,600 cm^{-1} is completed at 30 fs. Half of the periodic motion should, in principal, give adequate room for hot exciton to structurally convert into cold exciton in a perfectly planar system that does not possess any kind of defects, kinks, torsional degrees of freedom, and possible interchromophoric migration sites for exciton hopping.

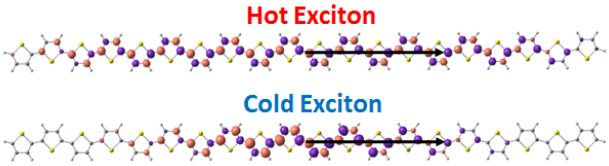

Figure 2. 3D transition density plots (isovalue surface: 0.0004 au) of hot exciton and cold exciton on th20 oligomer. Blue color represents negative and red color represents positive transition density coefficients. Black arrows show the direction of transition dipole moments.

The minimum energy required for formation of hot exciton is 2.09 eV, according to time dependent DFT calculations (Table 1). Vibrationally coupled relaxation of hot exciton yields cold exciton, which has emission energy of 1.70 eV. The symmetries of both transitions are the same and both transitions are mostly dominated by HOMO to LUMO transitions. It is important to note that the calculated transition energies are very similar to those of poly(3-hexylthiophene), implying the accuracy of calculations in predicting polymeric properties from relatively large oligomer derivatives [26]. The Stokes shift, 0.39 eV, is the energy hot exciton loses via vibronic modes through relaxation.

Table 1. Photoexcitation / emission transition energies, involved molecular orbitals, transition dipole moments (μ), oscillator strengths (f), and symmetry of transitions are given below.

structure	**transition (eV)**	**orbital transitions**	**μ (D)**	**f (a.u.)**	**symmetry**
hot exciton	2.09 ($S_0 \rightarrow S_1$)	H - 2 → L + 2 (4%) H - 1 → L + 1 (24%) H → L (72%)	11.40	6.66	^1B_u
cold exciton	1.70 ($S_1 \rightarrow S_0$)	H - 1 → L + 1 (5%) H → L (95%)	11.85	5.83	^1B_u

Table 2 lists the calculated J and K coupling integrals for hot exciton relaxing to various acceptor sites. The relative dielectric constant of the medium in the relevant integral calculations is assumed to be 3, which is a typical number for organic semiconductor thin films [22]. In small molecules, hot exciton is expected to relax to its own location due to presence of well delocalized wavefunctions that cover the whole molecule. However, in supramolecular materials such as in conjugated polymers, the excitons might find an opportunity to move extra dimensions due to available sites for exciton migration. Such migration is well-known and experimentally measured for relaxed excitons (cold excitons) in the weak coupling regime. Cold excitons in conjugated polymers can diffuse an average of 10 nm before decaying either radiatively or non-radiatively [17]. Nonetheless, the effect of hot exciton relaxation on exciton diffusion is neglected or unknown for two major reasons. One of them is the experimental difficulties in working on the timescales of such dynamics due to very fast relaxation of hot excitons over the photoexcited chromophore as mentioned above. The second reason is due to fact that excitons are neutral quasiparticles and they are hard to observe experimentally and therefore their dynamics can only be investigated using indirect methods. Therefore, hot excitons might cover some distances before relaxing into a cold exciton and such possible migration needs to be studied in the simulation methods.

Table 2. The magnitude of *J* and *K* coupling integrals for hot exciton relaxation to various acceptor sites for relative dielectric constant of 3.

Donor / Acceptor	***J* (eV)**	***K* (eV)**	**|V| (eV)**	**Covered Distance (Å)**
hot exciton / hot exciton	1.69	41.59	38.21	0
hot exciton / shifted hot exciton	-1.55	-11.63	8.53	3.94
hot exciton / shifted cold exciton	-1.47	-15.60	12.66	3.93
cold exciton / cold exciton	2.97	38.76	32.82	0
cold exciton / shifted cold exciton	-2.75	-21.89	16.39	3.92

Two possible cases are considered for hot exciton relaxation during simulations. In the first case, exciton relaxes at the location it is formed and therefore the center of transition density does not move. In the second case, exciton can move to the nearest acceptor site along the chain. For polythiophene chain, this can be thought of shifting of transition density coefficients one thiophene unit along the conjugated backbone as long as the symmetry and phase of the electronically excited state is preserved.

The donor / acceptor pairs for excitonic motion are listed in Table 2 along with the calculated coupling integrals. Hot exciton gradually decreases in size and transforms into cold exciton; therefore, hot exciton / hot exciton coupling integrals have initially been used to calculate the rate between the donor and the acceptor for exciton relaxing at its initial position. One will notice that Coulombic coupling integral (1.69 eV) is much smaller than the exchange coupling integral value (41.59 eV). All these calculated coupling integrals are quite large numbers in comparison to the electronic coupling integrals used in the weak coupling regime [27]. The reason stems from the fact that there is huge overlap between the wavefunctions of the donor and the acceptor sites. Consequently, much strong coupling integrals emerge from the calculations. It is important to note that exchange correlations are much stronger than Coulombic interactions and relaxation of hot exciton to low energy sites are driven by exchange mechanism. This observation is valid for all the donor / acceptor pairs studied in this work.

In the presented model, many intermediate excitonic transition densities participate in the gradual formation of cold exciton. The basis of such assignment will be further discussed below. As those intermediate excitonic states lose energy, cold exciton / cold exciton coupling integral becomes the last coupling integral that has to be included in the simulation in the strong coupling regime. After formation of cold exciton, intermediate or weak coupling regimes prevail in the migration of exciton to the other sites [9].

The gradual decrease in the value of electronic coupling element from hot exciton / hot exciton pair into cold exciton / cold exciton pair has been taken as a guide to simulate the time dependent hot exciton cooling rate according to Eq. (7). Afterwards, the probability of exciton occupying acceptor site is estimated according to Eq. (6). The upper panel in Figure 3 shows the rate dependence as a function of time. Since the rate equation has sine function, one also gets negative rate, which corresponds to back exciton transfer to donor site. Therefore, the absolute value of the rate for exciton relaxation has been used in the relevant graph in Figure 3. The average rate for each oscillation has been found as 3.75×10^{15} s^{-1}, which is much faster than typical rate constants predicted for incoherent motion of cold excitons in the weak coupling regime. The time step for exciton motion between intermediate excitonic states (see Figure 1) is predicted to be ~0.3 fs. This is rather short due to the extremely fast relaxation dynamics. $P_A(t)$ values in Figure 3 shows that while exciton relaxing, it can occupy both donor and acceptor site with almost similar probability. That is, hot exciton oscillates back and forth between donor and acceptor chromophores at ultrafast speeds. Due to very short time steps involved, the hot exciton gradually visits many intermediate excitonic states before forming cold exciton. That is why many intermediate states are needed to explain the relaxation dynamics in conjugated materials. As hot exciton relaxes to lower energy excitonic states, the magnitude of $|V|$ has been predicted to quadratically decrease (due to typical parabolic shape of potential energy surface) after each hop until cold exciton forms along the backbone.

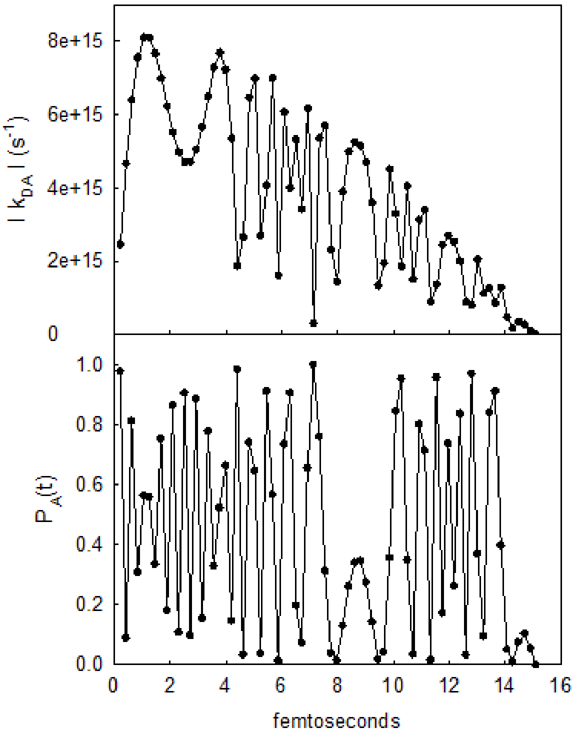

Figure 3. The time dependent rate values for hot exciton relaxation in the strong coupling regime (upper panel) and the occupation probability of acceptor site (lower panel).

In the simulation, $|V|$ has been found to be much larger than Δ, which is estimated as 0.39 eV divided by the number of hops between the donor and the acceptor sites. Due to extremely large electronic coupling integrals involved, exciting the polythiophene chain at the band edge or at higher energies would not yield very different hot exciton relaxation dynamics based on the model presented here. Indeed, Banerji et al. showed that the initial anisotropy decay profile for hot exciton relaxation is independent of chosen excitation wavelength in PCDTBT samples, supporting the conclusions given in this work [12].

Since conjugated polymers can be viewed as multi-chromophoric systems with varying sizes, then there is room for exciton hop to the nearest acceptor sites and this diffusion must be accounted for proper evaluation of hot exciton dynamics. If one assumes that hot exciton hops to the nearest site instead of localizing at its initial location, then $|V|$ is calculated as 8.53 eV (Table 2). From Eq. (7), one can estimate that the initial rate is six times faster when hot exciton relaxes at the original position (k_{self}) than jumping to the next chromophore (k_{hop}). In addition, when exciton starts hopping from one site to another, the geometrically relaxed exciton needs certain amount of energy for each hop [24]. Such energy loss for each excitonic hop limits the number of hops and hence distance an exciton can travel along the chain. Keeping all these considerations at hand, a Monte-Carlo simulation has been carried out for hot exciton formed by band edge excitation. Figure 4 shows the histogram plot of 10,000 exciton hopping trajectories on polythiophene chain. It is clear that hot exciton relaxes at its current position most of the time but can also travel distances as long as 2 nm. However, the root-mean-squared displacement of exciton hopping is calculated as 0.41 nm, corresponding to roughly one unit thiophene shift of the center of transition density within the duration of relaxation in the strong coupling regime. Thus, one can easily conclude that hot excitons can also migrate to some extent over the chain during the relaxation process.

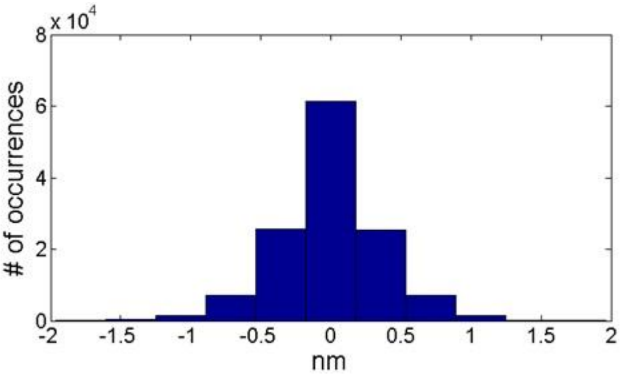

Figure 4. The histogram plot of hot exciton migration trajectories on conjugated polymer chain with band edge excitation after 10,000 Monte-Carlo runs.

4. Conclusions

In this work, hot exciton relaxation dynamics is studied for a conjugated polymer chain. Hot exciton on a perfectly linear polymer polythiophene chain relaxes at femtosecond time scale with the aid of vibrational modes, in accordance with experimental observations. During relaxation, hot exciton oscillates between the donor and the acceptor site until it cools down. Exchange coupling integrals dominate the total electronic coupling integral with only limited contribution coming from Coulombic interactions between the donor and the acceptors sites. Presented model predicts that it is possible for hot exciton to gain same mobility along the conjugated backbone over polythiophene chain during relaxation. Nonetheless, the extent of such mobility might differ from one conjugated polymer to another and more research is needed to unravel the dynamics of hot exciton migration among various types of conjugated materials.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of 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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