Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2023, **33**, 869–871

Mendeleev
Communications

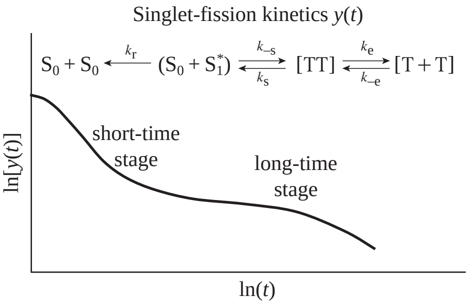
Specific features of time-dependent effects of triplet–triplet annihilation on the kinetics of singlet fission in molecular semiconductors

Anatoly I. Shushin

N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: shushin@chph.ras.ru

DOI: 10.1016/j.mencom.2023.10.044

The characteristic properties of the effects of migration-controlled triplet–triplet annihilation on the kinetics of singlet fission (the splitting of an excited singlet state S_1^* into a pair of triplet excitons) in molecular semiconductors are thoroughly analyzed. The analysis assumes that the short-time and long-time parts of the kinetics, *i.e.*, the kinetics of fluorescence *I*(*t*) from the S_1^* state, are governed by the corresponding short-time (geminate) and long-time (bulk) annihilation stages. Within the analysis, a simple formula is proposed that accurately describes the experimental singlet-fission kinetics over a wide range of times.



Keywords: singlet fission, triplet excitons, triplet–triplet annihilation, diffusion, fluorescence.

Photophysical processes in molecular semiconductors are of great importance for many applications and, especially, for the development of highly efficient solar energy conversion technologies. The mechanisms of these processes have been very actively studied for a long time.[1–3] It has been established, in particular, that a significant manifestation of photophysical processes is usually a consequence of highly efficient energy transfer in the systems under study and, for example, efficient migration and interaction of singlet (S) and triplet (T) excitons.[1–3]. Efficient energy transfer, for example, essentially controls the fluorescence kinetics as well as important accompanying phenomena such as up- and down-conversion.[1–13]

In this work we consider the specific kinetic features of a very important type of these processes, singlet fission (SF), *i.e.*, the spontaneous splitting of an excited singlet state S_1^* into a pair of T-excitons. It is assumed that the resulting T-excitons either diffuse back and merge through geminate TT-annihilation (g-TTA) or dissociate, thus generating a pair of free T-excitons, which can also merge through bulk bimolecular-type TT-annihilation (b-TTA). Note that, in the realistic limit of a low concentration of T-excitons, the short-time g-TTA and long-time b-TTA stages are well separated in time, which leads to a good separation of the corresponding short-time g-SF and long-time b-SF stages.

SF kinetics is traditionally studied according to the kinetic scheme[1–3]

$$S_0 + S_0 \xleftarrow{k_r} (S_0 + S_1^*) \underset{k_s}{\overset{k_{-s}}{\rightleftarrows}} [TT] \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} [T + T]. \qquad (1)$$

The first SF stage is the transition of a pair of coupled T-excitons from the S_0+S_1^* state to the [TT] state (called the c-state) at a rate of k_{-s}. The evolution of TT pairs in the [TT] state is controlled by TT fusion at a rate of k_s, as well as dissociation into a pair of free T-excitons in the [T + T] state (or e-state) and its recombination into the [TT] state at rates k_e and k_{-e}, respectively. The SF process is also accompanied by radiative deactivation of the S_1^* state at a rate of k_r.

Within this scheme, the g-SF kinetics is described in terms of the time-dependent fluorescence $I_g(t)$ from the excited state S_1^* at the short-time g-SF stage. The long-time b-SF fluorescence $I_b(t)$, resulting from the radiative decay of the S_1^* state, is generated in the reversible bimolecular TTA in the [T + T] state. The experimental SF kinetics is usually analyzed in terms of normalized fluorescence from the S_1^* state:[1,2]

$$y_\nu(t) = I_\nu(t)/I_g(0) = n_\nu(t)/n_g(0), \quad (\nu = g, b). \qquad (2)$$

In equation (2), $I_\nu(t) = k_r n_S^\nu(t)$ is the observed fluorescence intensity, $n_S^\nu(t)$ is the S_1^* concentration at stage ν (ν = g, b), $n_S^g(0) = n_{S_i}$ is the initial S_1^* concentration, and $y_\nu(t)$ is the population of the S_1^* state. Normalization of equation (2) implies that $y_g(t) = 1$ at $t = 0$.

Our work is devoted to the analysis of the kinetic properties of the SF process [equation (1)] in a wide range of times. The analysis was performed within the two-state model (TSM),[11,12,14,15] which makes it possible to accurately describe the effect of the diffusive migration of the T-exciton on the TTA and, thus, on the SF kinetics. In the TSM, migration effects are considered as transitions between kinetically coupled states: the [TT] state of interacting TT pairs and the [T + T] state of excitons that undergo isotropic relative diffusion in three-dimensional (3D) space.

The proposed approach allows us to derive expressions for the kinetic functions $y_g(t)$ and $y_b(t)$ for the stages g-SF and b-SF, respectively, which are combined into an interpolation formula for the kinetics *y*(*t*), which accurately describes the SF kinetics for both short and long time. In particular, this formula makes it possible to accurately describe, over a wide range of times, the SF kinetics recently measured in films formed by rubrene-based nanoparticles (NPs) dispersed in poly(vinyl alcohol) (PVA).[13] The obtained expression for *y*(*t*) predicts a noticeable effect of diffusion-assisted TTA on the shape of the SF kinetics profile, which manifests itself in a smoothed changeover of kinetics from $y_\mathrm{g}(t)$ to $y_\mathrm{b}(t)$.

First of all, consider the kinetics $y_\mathrm{g}(t)$ of the short-time g-SF. Within the proposed TSM, the kinetics of TTA-assisted g-SF, *i.e.*, the population of the S_1^* state $y_\mathrm{g}(t)$,[4,14,15] is determined by the spatiotemporal evolution of TT pairs in two states: in the intermediate [TT] state (c-state) of coupled T-excitons localized at a distance l, and in the [T + T] state (e-state) of non-interacting excitons undergoing isotropic relative 3D diffusion. The evolution of TT in these two states is described by the evolution functions $y_\mathrm{c}(t)$ and $y_\mathrm{e}(r, t)$, respectively. Naturally, the function $y_\mathrm{e}(r, t)$ determines the evolution of diffusing excitons in the [T + T] state not only in time t, but also in space, which is described by the dependence of this function on the distance $r = |\boldsymbol{r}|$ between T-excitons.

It is noteworthy that $y_\mathrm{c}(t)$ and $y_\mathrm{e}(r,t)$ are usually assumed to be spin matrices describing the effects of TT spin evolution on the SF kinetics. In our work, however, we will restrict ourselves to the analysis of SF processes in amorphous organic semiconductors, in which the T-exciton migration, which leads to strong fluctuations of the zero-field-splitting interaction in T-excitons, results in very fast spin-lattice relaxation in the excitons, which greatly reduces the effects of TT spin evolution.[11] In this case, the SF kinetics can be analyzed in terms of the approach that assumes that $y_\mathrm{c}(t)$ and $y_\mathrm{e}(r, t)$ are spin-operator-independent functions rather than matrices.[11]

These functions $y_\mathrm{g}(t)$, $y_\mathrm{c}(t)$ and $y_\mathrm{e}(r, t)$, describing the geminate TTA-assisted SF processes, satisfy the kinetic equation[4,11,12]

$$\mathrm{d}\boldsymbol{Y}_\mathrm{g}/\mathrm{d}t = \hat{\boldsymbol{K}}\boldsymbol{Y}_\mathrm{g}, \tag{3}$$

where $\boldsymbol{Y}_\mathrm{g} = (y_\mathrm{g}, y_\mathrm{c}, y_\mathrm{e})^\mathrm{T}$ is the transposed vector of populations of states ($\mathrm{S}_0 + \mathrm{S}_1^*$), [TT] and [T+T], respectively, whose time evolution is determined by the rate matrix

$$\hat{\boldsymbol{K}} = -\begin{bmatrix} k_\mathrm{r} + k_{-\mathrm{s}} & -k_\mathrm{s} & 0 \\ -k_{-\mathrm{s}} & k_\mathrm{s} + K_- & -(S_\mathrm{l}K_+)\hat{I}_\mathrm{l} \\ 0 & -S_\mathrm{l}^{-1}K_- & \hat{L}_\mathrm{r} + K_+\delta_{\mathrm{r}-\mathrm{l}} \end{bmatrix}. \tag{4}$$

In this matrix, k_α ($\alpha = -\mathrm{s}, \mathrm{s}, \mathrm{r}$) are the rates defined in equation (1), $S_\mathrm{l} = 4\pi l^2$ is the area of the spherical surface of the [TT] state localized at $r = l$, $\hat{\boldsymbol{L}}_\mathrm{r} = -Dr^{-2}\partial_\mathrm{r}(r^2\partial_\mathrm{r})$ is the radial part of the operator of relative 3D diffusion of T-excitons with diffusion coefficient D, and $\hat{\boldsymbol{I}}_\mathrm{l}$ is the operator defined by the formula $\hat{\boldsymbol{I}}_\mathrm{l}y_\mathrm{e} = \int_0^\infty \mathrm{d}r\,\delta_{\mathrm{r}-\mathrm{l}}y_\mathrm{e}(r) = y_\mathrm{e}(l)$, where $\delta_{\mathrm{r}-\mathrm{l}} \equiv \delta(r - l)$ is the Dirac delta function. The parameters $K_\mp \equiv K_\rightleftarrows$ are the rates of transitions $[\mathrm{TT}] \rightleftarrows [\mathrm{T + T}]$ satisfying the relation[11,14,15] $K_-/K_+ = l^2/Z_\mathrm{c} \sim e^{-\varepsilon_\mathrm{c}/(k_\mathrm{B}T)}$, in which Z_c is the partition function of a TT pair in the [TT] state, determined by the TT coupling ε_c in that state.[4,14,15]

Note that equation (4) should be solved with the initial conditions $y_\mathrm{g}(0) = 1$ and $y_\mathrm{c}(0) = y_\mathrm{e}(r, 0) = 0$, and the boundary conditions $\partial_\mathrm{r}y_\mathrm{e}|_{\mathrm{r}=\mathrm{l}} = 0$ and $y_\mathrm{e}(r \to \infty, t) = 0$.

The solution of equation (4) yields[11] the g-SF kinetics, *i.e.*, the population $y_\mathrm{g}(t)$:

$$y_\mathrm{g}(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty}\mathrm{d}\epsilon\left[\epsilon + k_\mathrm{rs} - \frac{k_{-s}k_s}{\epsilon + k_\mathrm{s} + K_\mathrm{e}(\epsilon)}\right]^{-1} e^{\epsilon t}, \tag{5}$$

where $k_\mathrm{rs} = k_\mathrm{r} + k_{-\mathrm{s}}$ and $K_\mathrm{e}(\epsilon) \approx k_\mathrm{e} + \xi_\mathrm{e}(k_\mathrm{e}\epsilon)^{1/2}$ is the effective rate of escape of T-excitons from the [TT] state, in which[11,14,15] $k_\mathrm{e} = 4\pi D_\mathrm{r}l/Z_\mathrm{c}$ and $\xi_\mathrm{e} = l(k_\mathrm{e}/D_\mathrm{r})^{1/2}$. Note that the expression for $K_\mathrm{e}(\epsilon)$ used in equation (5) was obtained in the realistic limit of fairly large rates $K_\mp$, assuming,[11,14,15] in particular, that $K_\mathrm{e}(0) = k_\mathrm{e} \ll K_-$.

It is important to point out that equation (5) predicts the anomalous long-time dependence $y_\mathrm{g}(t \to \infty) \sim \xi_\mathrm{e}t^{-3/2}$, resulting from the non-analytical behavior[11] of $K_\mathrm{e}(\epsilon) - k_\mathrm{e} \sim \xi_\mathrm{e}\epsilon^{1/2}$, which leads to some specific features of the g-SF kinetics $y_\mathrm{g}(t)$ and, thus, the total kinetics $y(t)$, which are clearly manifested, however, only in the limit of small initial S_1^* concentration $n_{\mathrm{S}_\mathrm{i}}$ (see below).

In the second part of the work, we consider the kinetics $y_\mathrm{b}(t)$ of long-time b-SF. It is assumed that the long-time bulk bimolecular stage of the SF kinetics is the result of diffusion-assisted bimolecular TTA, which can be quite accurately described by the conventional equation for bimolecular reactions:[16]

$$\mathrm{d}n_\mathrm{T}/\mathrm{d}t = -k_\mathrm{d}n_\mathrm{T} - 2K_\mathrm{a}n_\mathrm{T}^2. \tag{6}$$

In this equation, $n_\mathrm{T}(t)$ is the concentration of freely diffusing T-excitons, k_d is the triplet decay rate, and $K_\mathrm{a} = 4\pi Dl_\mathrm{a}$ is the b-TTA rate, which is essentially determined by the TTA effective radius l_a.[16] Equation (6) should be solved with the initial condition $n_\mathrm{T}(0) = n_\mathrm{T}^0$, where n_T^0 is the initial concentration of T-excitons, *i.e.*, the concentration of excitons generated during the short-time g-SF stage of the SF process [see equation (1)].

It is important to note that the T-exciton decay, the effect of which is described by equation (6), is assumed to manifest itself only at long times, *i.e.*, only in b-TTA at the kinetic stage of b-SF, due to the low characteristic value of the decay rate k_d.

It is worth noting that the radius l_a and thus the rate constant K_a, can be determined from the solution of equation (3) with the functions y_g, y_c and y_e replaced respectively by three others, x_g, x_c and x_e, obtained for the boundary conditions $\partial_\mathrm{r}x_\mathrm{e}|_{\mathrm{r}=\mathrm{l}} = 0$ and $x_\mathrm{e}(r \to \infty, t) = 1$, as well as the initial conditions $x_\mathrm{g}(0) = x_\mathrm{c}(0) = 0$ and $x_\mathrm{e}(r, 0) = 1$. More precisely, the radius l_a can be found from the analysis of the r-dependence of the function $x_\mathrm{e}(r, t \to \infty)$ for large r:[16] $x_\mathrm{e}(r, t \to \infty) \sim 1 - l_\mathrm{a}/r$.

Analysis of the solution of equations (4) obtained in this way for $x_\mathrm{g}(t)$, $x_\mathrm{c}(t)$ and $x_\mathrm{e}(t)$ yields

$$K_\mathrm{a} = (4\pi Dl)\frac{k_\mathrm{r}k_\mathrm{s}}{(k_\mathrm{r} + k_{-\mathrm{s}})(k_\mathrm{e} + k_s) - k_{-\mathrm{s}}k_\mathrm{s}}. \tag{7}$$

In our discussion of the long-time b-SF kinetic stage, we analyze the specific features of the kinetics at fairly long times $t \gg \tau_\mathrm{g}$, where $\tau_\mathrm{g} \sim l^2/D$ is the characteristic time of the short-time g-SF kinetics. Note that at low concentrations of T-excitons $n_\mathrm{T}^0 \lesssim n_{\mathrm{S}_\mathrm{i}} \ll l^{-3}$ the time τ_g is much shorter than that of the b-SF kinetic stage $\tau_\mathrm{b} \sim (K_\mathrm{a}n_\mathrm{T}^0)^{-1}$: $\tau_\mathrm{g} \ll \tau_\mathrm{b} \sim \tau_\mathrm{g}/(n_{\mathrm{S}_\mathrm{i}}l^3)$.

Under this condition, the kinetics of b-SF, *i.e.*, the time evolution of the S_1^* state population, $y_\mathrm{b}(t)$, is governed only by the bimolecular b-TTA process. In such a case at long times $t \gtrsim \tau_\mathrm{b}$, the function $y_\mathrm{b}(t)$ can be obtained in the framework of a simple quasi-stationary approach by equating the radiative S_1^* depopulation flux, $J_\mathrm{r} = k_\mathrm{r}n_{\mathrm{S}_\mathrm{i}}y_\mathrm{b}$, and the diffusion-assisted b-TTA population flux, $J_\mathrm{s} = K_\mathrm{a}n_\mathrm{T}^2$, resulting in the relation $y_\mathrm{b} = (K_\mathrm{a}n_\mathrm{T}^2)/(k_\mathrm{r}n_{\mathrm{S}_\mathrm{i}})$. Using this relation and the expression $n_\mathrm{T}(t) \approx n_\mathrm{T}^0[e^{k_\mathrm{d}t}(1 + q) - q]^{-1}$ obtained by solving equation (6) under the condition that $n_\mathrm{T}^0 = n_{\mathrm{S}_\mathrm{i}}Y_\mathrm{T}$ [see equation (10)] and $q = 2K_\mathrm{a}n_\mathrm{T}^0/k_\mathrm{d}$, we finally arrive at the equation

$$y_\mathrm{b}(t) = y_\mathrm{b}^0/\sigma_\mathrm{t}^2 \text{ with } \sigma_\mathrm{t} = \varepsilon_\mathrm{t}(1 + q) + 1, \tag{8}$$

where $y_\mathrm{b}^0 = q(k_\mathrm{d}/2k_\mathrm{r})Y_\mathrm{T}$,

$$q = 2K_\mathrm{a}n_\mathrm{T}^0/k_\mathrm{d} \text{ and } \varepsilon_\mathrm{t} = e^{k_\mathrm{d}\mathrm{t}} - 1. \tag{9}$$

In equation (8), y_b^0 is the initial value $y_\mathrm{b}^0 = y_\mathrm{b}(0)$, in which

$$Y_\mathrm{T} = 2Y_\mathrm{e} = \frac{2k_\mathrm{e}k_{-\mathrm{s}}}{k_\mathrm{r}(k_\mathrm{e} + k_\mathrm{s}) + k_\mathrm{e}k_{-\mathrm{s}}} \tag{10}$$

is the yield of T-excitons in the SF-process, naturally related to the yield Y_e of escaped TT-pairs.

We now have everything we need to derive the interpolation formula for the total SF kinetics. The above-mentioned significant difference in the values of the g-SF and b-SF kinetic times, $\tau_\mathrm{g} \ll \tau_\mathrm{b}$, allows us to combine the g-SF and b-SF functions, $y_\mathrm{g}(t)$ and $y_\mathrm{b}(t)$, into an interpolation formula for the total SF function $y(t)$. When deriving the formula, we take into account that in the considered low exciton concentration limit, $n_{\mathrm{S}_\mathrm{i}}l^3 \ll 1$, at short times $t \lesssim \tau_\mathrm{g}$, the amplitude of the g-SF function $y_\mathrm{g}(t)$ is much

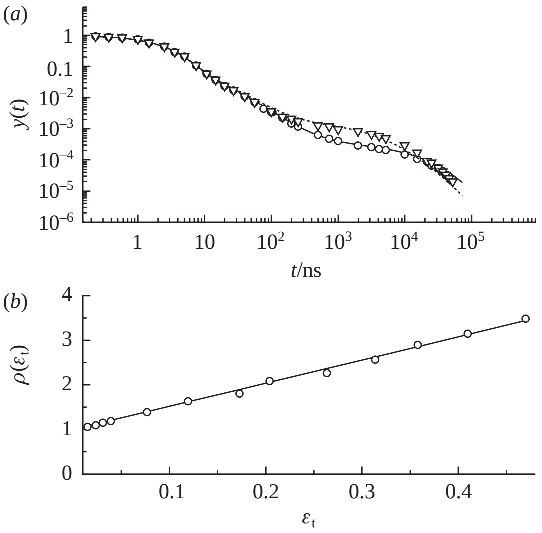


Figure 1 (*a*) Comparison of the experimental SF kinetics[13] $y_{exp}(t)$ (solid lines) in rubrene-based NP films measured at EPEs of 9 and 88 μJ cm^{-2} (circles and triangles, respectively) with the theoretical SF-kinetic functions $y(t)$ [equation (11)] (dashed lines) calculated using the fitting parameters of the initial S_1^* concentration $\bar{n}_{S_i} = n_{S_i} l^3$ and the T-decay rate k_d (ns^{-1}). (*b*) Comparison of experimental (circles) and theoretical (solid line) functions $\rho(\varepsilon_t) = [\bar{y}_t/y(\varepsilon_t)]^{1/2}$, where $\varepsilon_t = e^{k_d t} - 1$ [see quation (11)], at EPE of 9 μJ cm^{-2} and $[\bar{n}_{S_i}, k_d] = [3.2\times10^{-4}, 2.0\times10^{-5}]$.

greater than that of the b-SF function $y_b(t)$; in particular, $y_b(0) \sim y_g(0)(n_{S_i} l^3) \ll y_g(0)$. In this case, ensuring high accuracy of the interpolation formula for the SF kinetics $y(t)$, this formula can be written in two equivalent forms:

$$y(t) = \bar{y}_t/\sigma_t^2 \quad \text{and} \quad \sqrt{\bar{y}_t/y(t)} = \sigma_t \;, \qquad (11)$$

in which $\bar{y}_t = y_g(t) + y_b^0$, and $\sigma_t \equiv \sigma_t(\varepsilon_t)$ is defined in equation (8).

Note that equation (11) correctly reproduces the limiting behavior of $y(t)$ at short and long times.

In the final part, we will demonstrate the fairly high accuracy of the derived formulas by applying them to the description of the recently measured SF kinetics in rubrene-based spherical NPs with an average diameter of 220 nm, dispersed in PVA films, which were obtained according to the published method.[13]

The SF kinetics in NPs was measured fairly accurately over a wide time range from 10^{-1} to 10^5 ns and various excitation intensities. The NP size turns out to be quite large and does not manifest itself in the SF kinetics in the analyzed time range.[13] This makes it possible to interpret the SF processes in NPs as processes in a homogeneous (amorphous) rubrene film, which means that the proposed model can be safely applied to describe the SF kinetics.[11]

Figure 1(*a*) displays a comparison of two experimental SF-kinetic functions $y_{exp}(t)$ measured[13] at excitation pulse energies (EPEs) of 9 and 88 μJ cm^{-2} with the calculated functions $y(t)$. The comparison shows a quite good accuracy of formula (11).

The theoretical functions $y(t)$ were calculated by formula (11) using two fitting parameters: the dimensionless initial concentration of singlet excitons $\bar{n}_{S_i} = n_{S_i} l^3$ and the T-decay rate k_d (ns^{-1}), whose values are conveniently represented as a vector $[\bar{n}_{S_i}, k_d]$. In this representation, the most appropriate values of the parameters used to describe the experimental SF kinetics for the above EPEs can be written as $[3.2\times10^{-4}, 2.0\times10^{-5}]$ and $[1.1\times10^{-3}, 1.0\times10^{-5}]$. Note that the applied values of k_d turn out to be close to the value $k_d = 10^{-5}$ ns^{-1} estimated earlier experimentally.[13]

As for other parameters that determine the short-time SF kinetics $y_g(t)$, we used their values obtained in an earlier work[11] on a similar analysis of the SF kinetics $y_{sf}(t)$, measured in rubrene films[8] at short times $0.1 \lesssim t \lesssim 10^2$ ns. The use of these values is safe, since the observed[8] dependences $y_{sf}(t)$ are in good agreement with the measured $y_{exp}(t)$ in rubrene-based NP films.[13] The parameter values found in the cited work[11] can be given through the vector $\mathbf{z} = (z_{-s}, z_s, z_r, z_e)$, in which $z_\alpha = k_\alpha/k_{rs}$ ($\alpha = -$s, s, r, e), and two extra parameters k_{rs} and ξ_e [see equation (5)]: $\mathbf{z} = (0.8, 0.16, 0.2, 0.14)$, $k_{rs} = 0.37$ ns^{-1} and $\xi_e = 1.7$.

The fairly high accuracy of formula (11) is also illustrated in Figure 1(*b*) by comparing the experimental and theoretical SF kinetics at EPE of 9 μJ cm^{-2}, presented as dependences of $\rho(\varepsilon_t) = [\bar{y}_t/y(\varepsilon_t)]^{1/2}$ on $\varepsilon_t = e^{k_d t} - 1$. The comparison clearly shows good agreement between these dependences at long times $t \gtrsim 10^3$ ns.

In conclusion, it should be noted that this work have demonstrated a fairly good accuracy of the proposed interpolation formula for the kinetics of TTA-assisted SF processes in molecular semiconductors in a wide range of times corresponding to the geminate and bulk bimolecular stages of the TTA kinetics. The analysis shows that the developed interpolation approach can significantly simplify the description of the processes under study. It is important to emphasize that the proposed approach is quite general and can be applied for the analysis of many other physicochemical diffusion-assisted processes, such as recombination of radical pairs, triplet radical quenching, *etc.*, which can be observed for a long time.

This work was carried out within the framework of the State Assignment no. 0082-2019-0001 (State Registration no. AAAA- A19-119012890064-7).

References

1 M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd edn., Oxford University Press, New York, 1999.
2 M. B. Smith and J. Michl, *Annu. Rev. Phys. Chem.*, 2013, **64**, 361.
3 K. Miyata, F. S. Conrad-Burton, F. L. Geyer and X.-Y. Zhu, *Chem. Rev.*, 2019, **119**, 4261.
4 A. I. Shushin, *J. Chem. Phys.*, 2019, **151**, 034103.
5 N. Kh. Petrov, *Mendeleev Commun.*, 2023, **33**, 103.
6 A. Ryasnyanskiy and I. Biaggio, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 193203.
7 S. W. Eaton, S. A. Miller, E. A. Margulies, L. E. Shoer, R. D. Schaller and M. R. Wasielewski, *J. Phys. Chem. A*, 2015, **119**, 4151.
8 G. B. Piland, J. J. Burdett, D. Kurunthu and C. J. Bardeen, *J. Phys. Chem. C*, 2013, **117**, 1224.
9 G. B. Piland, J. J. Burdett, R. J. Dillon and C. J. Bardeen, *J. Phys. Chem. Lett.*, 2014, **5**, 2312.
10 G. B. Piland and C. J. Bardeen, *J. Phys. Chem. Lett.*, 2015, **6**, 1841.
11 A. I. Shushin, *Chem. Phys. Lett.*, 2017, **678**, 283.
12 A. I. Shushin, *J. Chem. Phys.*, 2022, **156**, 074703.
13 D. G. Bossanyi, Y. Sasaki, S. Wang, D. Chekulaev, N. Kimizuka, N. Yanai and J. Clark, *J. Mater. Chem. C*, 2022, **10**, 4684.
14 A. I. Shushin, *J. Chem. Phys.*, 1991, **95**, 3657.
15 A. I. Shushin, *J. Chem. Phys.*, 1992, **97**, 1954.
16 S. A. Rice, *Diffusion-Limited Reactions*, Elsevier, Amsterdam, 1985.

Received: 1st June 2023; Com. 23/7178