Kinetics of Triplet-Triplet Annihilation in Organic Glasses

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In the present paper, the results of the investigation of the decay kinetics of delayed luminescence of organic glasses are presented. A strong deviation of the decay of both phosphorescence and annihilation delayed fluorescence from the exponential law is observed. This effect is shown to be due to the relaxation process of electronic excitation energy in the system with large energetic disorder. At the same time, the presence of two time intervals in which the rate coefficient for triplet-triplet annihilation (TTA) reaction shows different dependence on time is observed. On a short time scale the classical behavior is observed, i.e., the reaction is well described by the second-order equation with a time-independent rate coefficient. At the limit of long times, we have strong dependence of rate coefficient on time, i.e., the electronic excitation energy transport is dispersive. It is shown that behavior observed for the rate coefficient for TTA reaction is due to the relaxation process (on short time scale) and the equilibrium energy migration (in long time limit).

INTRODUCTION

The kinetics of excitation transport in disordered or heterogeneous condensed phases is playing an increasingly important role in a number of fields, such as heterogeneous catalysis and *in vivo* biological reactions [1]. Disorder arises if (1) a fraction of the sites of a perfect crystal lattice is occupied randomly by molecules different from those constituting the host (substitutional disorder, isotopically mixed molecular crystals) [2], (2) asymmetric molecules occupy orientationally different yet energetically equivalent positions of a periodic lattice (orientational disorder, amorphalline solid) [3], (3) or lattice periodicity is abandoned (amorphous structure, organic glasses) [4]. The situation is more complex in the two last types of disorder. Because the environment of a given site is site specific, there is a fluctuation of the resonant and nonresonant energy terms contributing to the total site energy. Positional disorder therefore causes energetic disorder, as is well documented by the inhomogeneous broadening of optical spectra.

The wide practical use of such disordered systems as amorphous organic and inorganic semiconductors, polymers, and organic glasses in photoelectronic devices stimulated fundamental research on relaxation phenomena in non-equilibrium media in general. Except for the absolute time scale, the relaxation patterns are expected to carry common features, although individual processes may be quite different. The rationale behind this notion is that on passing from a crystalline to a glassy system, discrete quantities such as the lattice binding energy of molecules or the energy of an electronic excitation become subject to distribution. Relaxation dynamics should then be determined by the statistics of the transitions between the distribution of energy levels characterizing a specific property of the glass-forming elements. Similarity in the distribution functions should translate into similarity of relaxation patterns.

There is a powerful method of investigation of the energy transport kinetics. It is the method of triplet-triplet annihilation (TTA). In this case, it is possible to continu-

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ously in time monitor not only the concentration of triplet excitation, by recording the phosphorescence, but also the reaction product concentration (reaction rate) by recording the annihilation delayed fluorescence. This provides the possibility of finding the rate coefficient for the TTA reaction and analyzing its time dependence in the required time interval.

This paper presents the results of investigation of the effect of disorder on the kinetics of triplet excitations annihilation in an organic solid, for example, disordered chrysene, phenanthrene, and carbazole.

EXPERIMENTAL

Chrysene and carbazole were purified by liquid chromatography. Phenanthrene was zone refined. For investigations, substances were placed in a deairated quartz cell. The samples of disordered organic solids were obtained by fast cooling their melts.

The delayed luminescence spectrum was registered on the SDL-2 spectrometer by means of a disc phosphoroscope. To study the decay kinetics of delayed luminescence, a second harmonic of a ruby laser (λ_r = 347 nm) was used as the source of excitation. The decay luminescence was recorded photoelectrically with the aid a FEU-118 PM tube, a SRM-2 monochromator, and an analog-digital transducer connected to a computer. The kinetics given in this paper resulted from the averaging over 50 pulses. The processing of experimental curves was carried out with the help of a graphic package "Origin 5.0".

Theory

The reaction under consideration is the fusion (annihilation) of two triplet excitations to form a higher excited singlet, which very rapidly decays to the first excited singlet:

$$T_1 + T_I \rightarrow S^* \rightarrow S_1. \qquad (1)$$
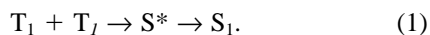
Because of the short singlet life time, the S_1 state rapidly decays. This decay is characterized by the emission of a photon. Delayed fluorescence arises. The time scale of delayed fluorescence is determined by the time required for two triplet excitations to meet via migration in the media.

The intensity of the delayed fluorescence at any time, t, $I_{df}(t)$, is proportional to the number of annihilation events, $n_{df}(t)$:

$$I_{df}(t) \propto n_{df}(t) \propto (dp/dt)_{ann}, \qquad (2)$$

here $p(t)$ is the triplet excitation density.

Classically, the triplet-triplet reaction rate coefficient is independent of time. The standard, classical second-order rate law gives

$$(dp/dt)_{ann} \propto P^2. \qquad (3)$$

However, in spatially heterogeneous and low-dimensional media, the rate coefficient ceases to be constant and becomes function of time [1]. Therefore, for the reaction of TTA, we can write:

$$(dp/dt)_{ann} \propto k(t)_{ann} \, p^2. \qquad (4)$$

In such systems, the TTA reaction rate has been explained in terms of the number of distinct sites, $S(t)$, visited by a random walker in equivalent media [5]. The time dependence of S is given by [6]:

$$S(t) \propto t^f, \, 0 \leq f \leq 1. \qquad (5)$$

The TTA reaction rate coefficient is related to $S(t)$ by the relation [7]

$$k(t)_{ann} \propto d \, S(t) \, / \, d \, t \propto k_0 \, t^{-h}, \, 0 \leq h = 1 - f \leq 1, \qquad (6)$$

where h measures the degree of local heterogeneity of media. The lower limit, $h = 0$, expresses motion in locally homogeneous environments or environments that are effectively homogeneous for the time scale of the experiment. The upper limit, $h = 1$, corresponds to "motion" in zero dimensions. The value $h = 0.5$ also corresponds to the motion in 1-dimensional filaments [1] and $h = 4/3$ corresponds to migration on percolation cluster at critical point [6].

The time dependence of $k(t)_{ann}$ can be obtained from

$$k(t)_{ann} \propto I_{df}/I_p{}^2. \qquad (7)$$

The plot of $\log(I_{df}/I_p{}^2)$ versus $\log t$ is expected to be linear with slope $-h$.

This approach is applicable to solid disordered media as well. The absence of order leads to a large inhomogeneous broadening of energy levels. At low temperature, when the quantity kT is much smaller than the spread of energy levels, energy disorder inevitably leads to the fact that the molecules on which equilibrium migration of excitation occurs prior to the moment of their annihilation form a system whose topology does not coincide with that of the entire medium as a whole. The geometry of this subsystem of molecules depends on the relationship between kT and the value of energetic disorder which shows up as inhomogeneous broadening of luminescence spectra. It can be expected that this system's topology will significantly affect the TTA kinetics. Depending on the temperature, the transport dimensionality can vary between zero, when both annihilating triplets are local-

ized on immobile traps, and a 3-dimensional one when free excitons annihilate.

RESULTS AND DISCUSSION

Figure 1 shows the delayed luminescence spectra of disordered organic solids at T = 77 K. The long-wavelength part of the spectra corresponds to their phosphorescence. In the short-wavelength part, luminescence coinciding, as to the spectrum, with its fluorescence is observed. This luminescence corresponds to delayed fluorescence arising from the TTA.

At the temperature of liquid nitrogen decay, both of phosphorescence and annihilation delayed fluorescence is non-exponentional. For example, Fig. 2 shows the curves of phosphorescence and annihilation delayed fluorescence decay of disordered phenanthrene registered in the first maximum of the spectra corresponded. The decay of phosphorescence can be described by power law $I(t) \propto t^{-\beta}$ with a exponent $\beta \approx 0.5$. The decay of delayed fluorescence is characterised by value of exponents $\beta \approx 1.0$ on short time scale and $\beta \approx 1.7$ in long time limit. The same behavior is also observed for the sample of disordered chrysene [8].

It was shown [9–13] that non-exponential decay of phosphorescence of organic solid is due to the energy relaxation in the system of energetically disordered centres, which is represented by the samples under study. At temperatures at which the kT value is much smaller than the value of the spread in energy levels immediately after excitation, the system is in non-equilibrium conditions. Therefore, on short times, directional electronic excitation energy transfer from the molecules with higher energy levels to the molecules with low excited-state energies should occur. The number of accessible hopping sites will decrease with time, and transport must be slowed until eventually dynamic equilibrium is attained. So the time dependence of the diffusivity of the excitation on a short time scale is a consequence of energy relaxation.

Figure 3 shows the dependence of $\log(I_{df}/I_p^2)$ on $\log t$. It is seen that we can speak about the presence of two time intervals in which the rate coefficient for TTA reaction shows different dependence on time. On a short time scale (till 3–4 ms) the classical behavior is observed ($h = 0$, $I_{df} \propto I_p^2$). At the limit of long times, there is a strong dependence of rate coefficient on time. The same situation is also observed for disordered chrysene [14,15].

The value of parameter h obtained on a long time scale can be connected with the equilibrium energy transport in a system with a large inhomogeneous broadening of the levels. At a low temperature, after the system
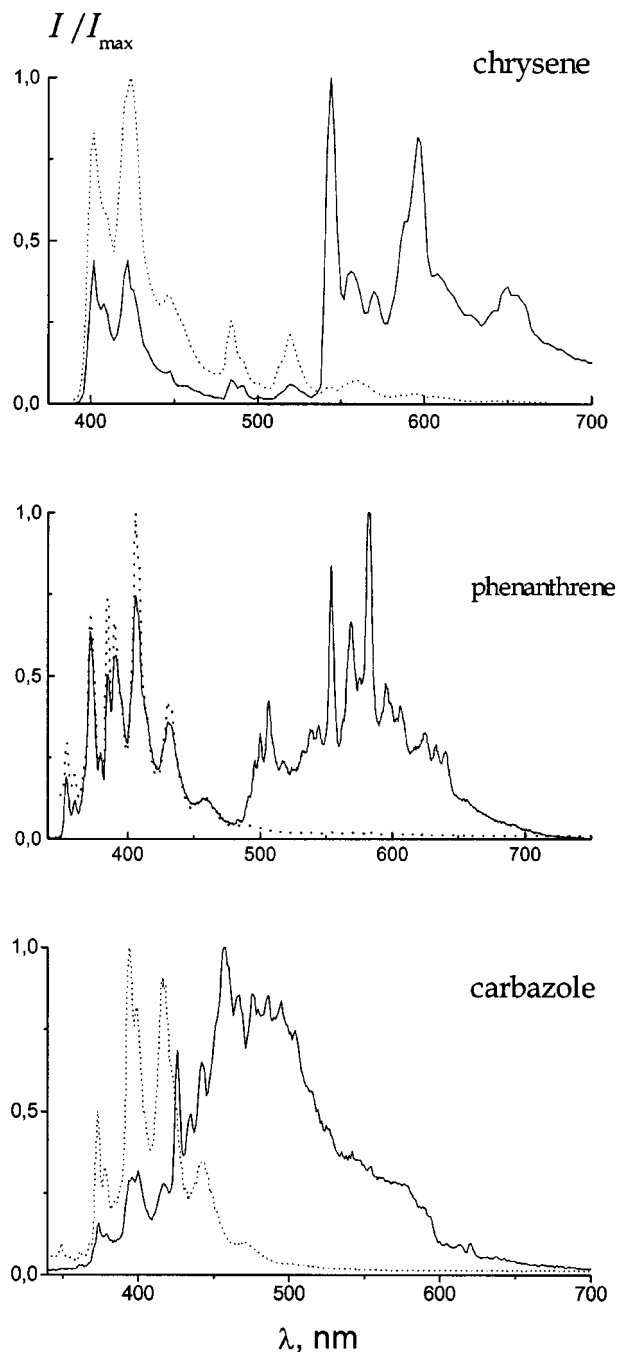

Fig. 1. Spectrum of steady-state luminescence (dots) and of delayed luminescence (solid line) of organic glasses at 77 K.

attains dynamic equilibrium, the geometry of the cluster of molecules over which equilibrium migration of energy occurs differs considerably from the geometry of the entire system as a whole. This difference is stronger, the lower the temperature and the higher the degree of energetic disorder. It is this subsystem's topology that
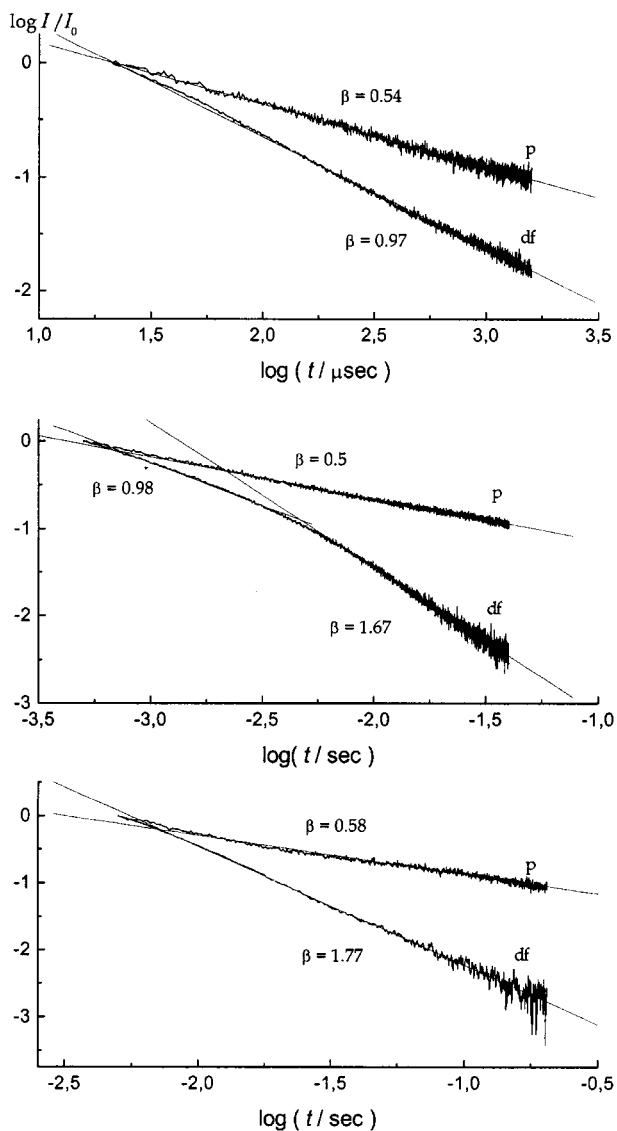
Fig. 2. The decay curves of phosphorescence and delayed fluorescence of disordered phenanthrene for different time scales. T = 77 K.

Fig. 3. The dependence of $\log(I_{df}/I_p^2)$ on $\log t$ for different time scales for sample of disordered phenanthrene. T = 77 K.

determines the energy transport kinetics. From the point of view of the fractal model, this value coincides with the value of h obtained for the chrysene solution in the polystyrene matrix at concentrations less than the critical one [16]. It can be concluded that the sample subsystem in which energy transport and annihilation take place is extremely restricted. It makes sense to assume that the surface of excited state energy molecules can include fractal-like canyons on which the triplet excitation migration occurs before the annihilation process [17]. The geometry of these canyons is close to that of chrysene molecule clusters in a low-concentration solution.
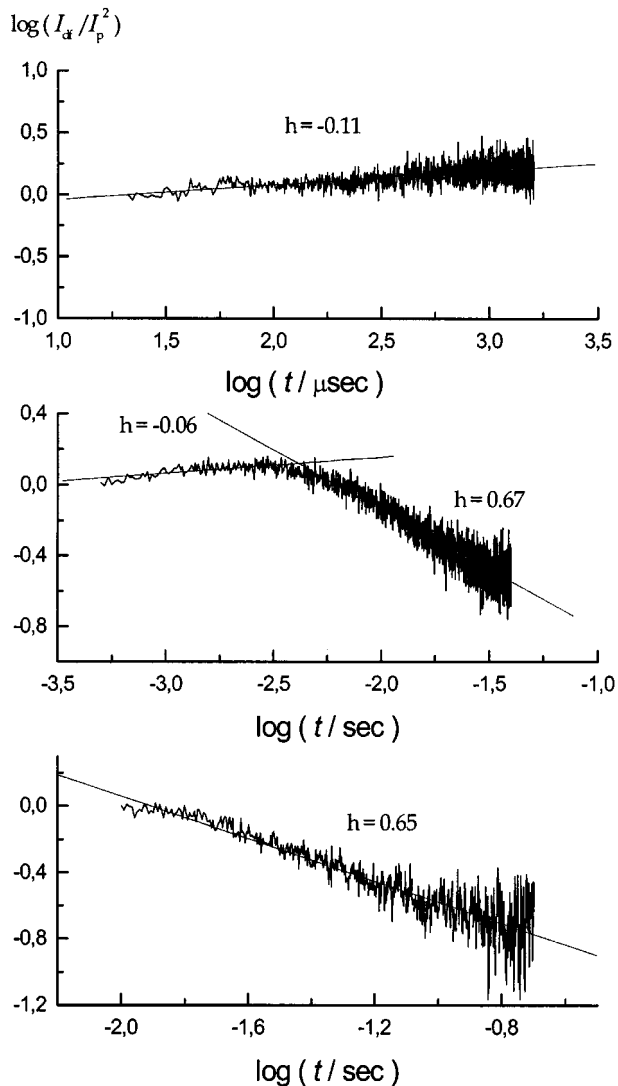
The zero value of the parameter h observed on a short time scale corresponds to the classical behavior when the excitations migrate in a locally homogeneous space. From the point of view of the results obtained within the range of large times, when the transport kinetics is determined by the geometry of the subsystem of molecules on which equilibrium energy transport occurs, the observed h value could be explained as follows. From the viewpoint of the model of low-dimension transport it has been shown that in systems with restricted geometry a non-zero value is only observed when the migration radius of excitation during the observation time is at least comparable to the size of the space limitation [18,19]. Otherwise, the behaviour characteristic of a homogeneous

space is observed [20,21]. It may be expected that at such short times the shift value of triplet excitation is less than the width of fractal-like canyons that form the surface of excited state energies of chrysene molecules in disordered solids. In this case, however, the decay kinetics of delayed luminescence should be exponential if, of course, the triplet annihilation does not make a great contribution to the decay of triplet excitations. In reality, a strongly non-exponential decay of phosphorescence is observed, and this decay does not depend on the exciting light intensity, which points to a low annihilation efficiency in the system under study.

In our opinion, the behavior observed on short times may be due to the relaxation process of electronic excitation energy in the system with large energetic disorder. Although the migration of triplet excitations under non-equilibrium conditions features pronounced energetic directivity (jumps occur mainly in places with a lower energy), this process is in no way limited spatially (every step leads to occupation of a new site that is characteristically for a homogeneous 3-dimensional space). Because the probability of annihilation is determined by relative motion of excitations, the delayed fluorescence resulting from the annihilation of two triplet excitations cascading down on the system of energetically disordered centres demonstrates the behavior typical of homogeneous media.

In the case of chrysene and carbazole, the samples obtained by crystallization from solution in the process of purification were investigated. On the short time scale, these samples show the same behavior as the samples obtained by fast cooling of melt [8]. Figure 4 shows the dependence of $\log(I_{df}/I_p^2)$ on $\log t$ for two type of samples of disordered carbazole once long time scale. It is seen that these dependencies differ strongly. The values of parameter h obtained in the limit of a long time scale for all samples investigated are presented in the Table I. From our point of view, this dependence is due to the difference in degree of the spatial correlation of energy of the excited state of molecules forming the system. The topology of the subsystem of molecules in which equilibrium energy transport takes place depends on the method of obtaining the samples of disordered organic solid (the microscopic properties of a medium). The higher degree of correlation
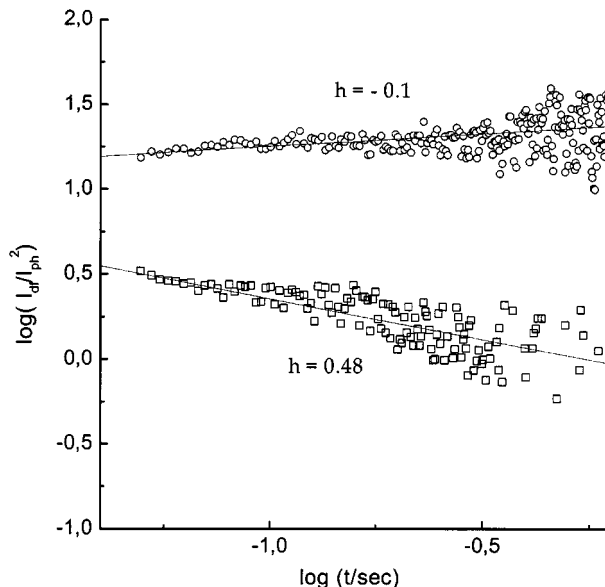
Fig. 4. The dependence of $\log(I_{df}/I_p^2)$ on $\log t$ for samples of disordered carbazole obtained by crystallization from solution (circles) and by fast cooling of melt (squares). $T = 77$ K.

(e.g., in the case of a polycrystalline sample obtained by crystallization from solution) leads to the more connected subsystem of molecules in the medium. As a result, the energy transport is more extended and the value of h is closer to 0.

In any case, the dispersive character of energy transport in disordered media is due to the structural and, consequently, energetic disorder characteristic of such a systems. It is obvious that as the temperature is increased, transition must take place to a homogeneous, classical behavior when the rate coefficient is no longer time dependent [22,23]. The data given in Fig. 5 demonstrate a good agreement with this proposition. The increase of temperature leads to decrease of value of h. It points to extension of the aria of triplet excitations migration in the system.

CONCLUSION

The investigation of the delayed luminescence of disordered organic glasses at 77 K has shown that its

Table I. The Value of Parameter h Obtained on a Long Time Scale

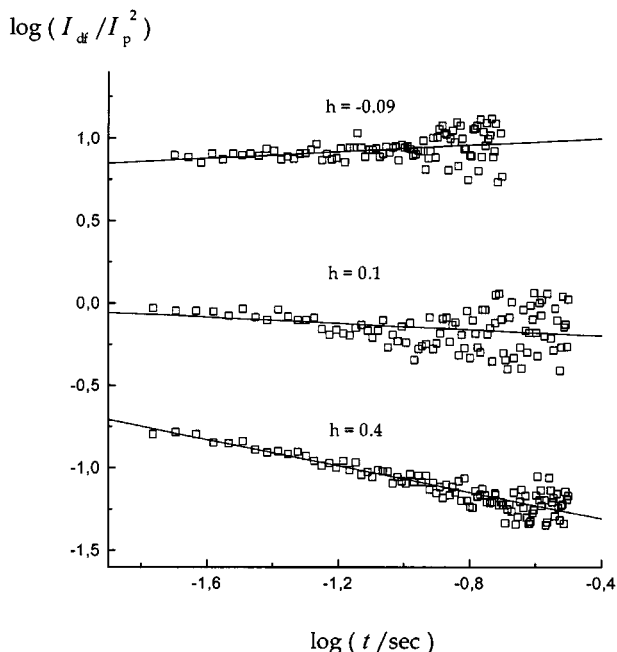| Sample	Polycrystalline chrysene	Fast cooled melt of chrysene	Fast cooled melt of phenanthrene	Polycrystalline carbazole	Fast cooled melt of carbazole
h	0.14	0.5	0.67	−0.1	0.48

$\log (I_{df} /I_{p}{}^{2})$

Fig. 5. The dependence of $\log(I_{df}/I_p{}^2)$ on $\log t$ for disordered phenanthrene at different temperatures. Top to bottom: 150, 120, and 90 K.

decay is non-exponential, especially on a short time scale. The deviation of the phosphorescence decay from the exponential law is due to the energy relaxation in the system of energetically disordered centres that is represented by the samples under study.

At the same time, the presence of two time intervals in which the rate coefficient for TTA reaction shows different dependence on time is observed. On the short time scale the classical behavior is observed. At the limit of the long time scale, there is a strong dependence of rate coefficient on time, i.e., the electronic excitation energy transport is dispersive. The behavior observed on short times may be due to the relaxation process of electronic excitation energy in the system with large energetic disorder. Although the migration of triplet excitation under non-equilibrium conditions features pronounced energetic directivity, this process is in no way limited spatially. Because the probability of annihilation is determined by the relative motion of excitations, the delayed fluorescence resulting from the annihilation of two triplet excitations cascading down on the system of energetically disordered centres demonstrates the behavior typical of homogeneous media.

For long times, the decay kinetics of delayed luminescence is determined by the effective geometry of the subsystem of molecules on which equilibrium migration of excitations occurs prior to the moment of their annihilation. The geometry of this subsystem of molecules depends on the relationship between kT and the value of energetic disorder, which manifests as inhomogeneous broadening of luminescence spectra. The topology of subsystem of molecules in which equilibrium energy transport takes place also depends on the method of obtaining the samples of disordered organic solid (the microscopic properties of a medium). Depending on the temperature, the transport dimensionality can vary between zero, when both annihilating triplets are localized on immobile traps, and a 3-dimensional one when free excitons annihilate.

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