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Electronic excitation energy transfer in solid solution of 7-diethylamino-3,4-benzophenoxazine-2-one (Nile Red dye) in bis[*N*-2-(oxybenzylidene)-4-*tert*-butylaniline]zinc

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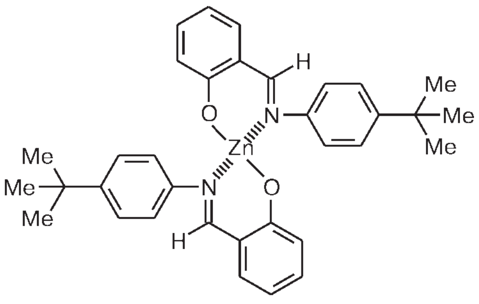
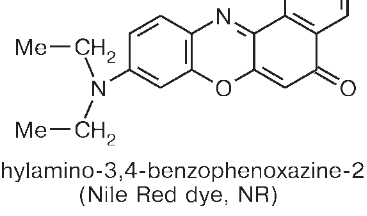
Transfer of electronic excitation energy from the host material to guest molecules was studied taking the solid-phase system bis[*N*-(2-oxybenzylidene)-4-*tert*-butylaniline]zinc + 7-diethylamino-3,4-benzophenoxazine-2-one (the guest compound) as an example. The luminescence excitation spectra and the concentration quenching of green fluorescence of the host compound and the excitation of sensitized red fluorescence of the guest molecules were studied. Among the exciton mechanism of energy migration and Förster´s long-range, single-jump mechanism, the former dominates. The number of jumps (m) and the mean diffusion length of the singlet exciton (l), calculated in the framework of the model of partially delocalized, randomly hopping exciton, were estimated at $\approx 1.5 \cdot 10^3$ and ≈ 450 Å, respectively.

Key words: electronic excitation, energy transfer, luminescence.

Transfer of electronic excitation energy belongs to fundamental problems of solid state chemistry.[1] Energy transfer manifests itself, in particular, in the form of quenching and sensitization of luminescence. Recently, these phenomena have been used for efficient transformation of the frequency of the emitted light in electroluminescent systems based on organic materials[2,3] by adding small amount of fluorescing molecules to the active electroluminescent layer. The authors of this work developed a new system based on the solid solution of the Nile Red (NR) dye in the organometallic matrix of bis[*N*-2-(oxybenzylidene)-4-*tert*-butylaniline]zinc (ZG) complex, which is an efficient electroluminescent material emitting in the red spectral region.[4]



Bis[*N*-2-(oxybenzylidene)-4-*tert*-butylaniline]zinc (ZG)



7-diethylamino-3,4-benzophenoxazine-2-one (Nile Red dye, NR)

According to the results of preliminary studies, this system is characterized by (i) efficient quenching of green fluorescence of the zinc complex and (ii) the excitation of sensitized red fluorescence of NR as a result of transfer of electronic excitation energy from the ZG host molecules to the guest molecules of NR.

This work reports the results of a detailed study on the transfer of electronic excitation energy in a solid solution of NR in ZG. To this end, we measured the photoluminescence spectra of this system and studied how the quenching of ZG fluorescence and the excitation of NR fluorescence depend on the concentration of the latter compound. Possible energy transfer mechanisms considered in this work were the diffusion of excitons and the single-step jumpwise energy transfer by the long-range, dipole-dipole inductive-resonance mechanism.[1]

Experimental

Absorption spectra were recorded on a Specord M-40 spectrophotometer. Luminescence spectra were recorded using a setup comprised of a grid-type monochromator for recording the spectra and an MDR-2 double prismatic monochromator for the separation of monochromatic exciting radiation.

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A DRSh-500M high-pressure mercury lamp and a DKSSh-500 xenon lamp attached to a stabilized DC power supply were used as the sources of exciting light. Luminescence spectra were recorded using the emitted light, at an angle of 30° with respect to the direction of the exciting light. Luminescence excitation spectra were recorded on both the luminescence setup in the wavelength region from 200 to 800 nm and on the Specord M-40 spectrophotometer equipped with a special fluorescence accessory for studies in the 300—800 nm wavelength region.

The spectral sensitivity of the luminescence setup was determined using the known procedure[5] from measurements of the luminescence spectra of the solutions of the compounds with known quantum distributions. In addition, the luminescence setup was also used for measuring the emission spectra of the filament lamp and the DKSSh-500 xenon lamp for which the quantum distributions were preliminarily established using the monochromator and a nonselective radiation detector (a thermopile). The calibration curve of the spectral sensitivity of the luminescence setup (S_λ) was calculated using the known procedure.[6] All luminescence spectra were corrected for the spectral sensitivity of the setup, S_λ, and expressed in the relative quantum units (quantum (nm s)$^{-1}$).

The ZG complex used in this work was synthesized following the known procedure[4] and purified by precipitation from the benzene solution. Nile Red dye (Aldrich) was used as received. Solvents were dried over metallic Na and blown with argon to remove oxygen.

Films were prepared by casting or spinning the benzene solutions of ZG with NR admixture on non-luminescent quartz plates. The benzene solutions of ZG are highly sensitive to trace amounts of moisture and oxygen. The films prepared from benzene solutions of NR exhibit rather low stability. However, the films prepared from a mixture of pure ZG and ZG containing an admixture of NR exhibit long-term stability in air, which is confirmed by retention of the parameters of their absorption and luminescence spectra. In this connection the true concentration of NR in the ZG films prepared was determined from the absorbances (D) at the maxima of the long-wavelength absorption band of NR (λ = 552 nm).

The thicknesses (d) and the refractive indices (n) of the ZG films with $D \geq 1$ were determined from the interference spectra in the wavelength region from 500 to 1000 nm. The parameters of the ZG films with $D_{410} = 1$ were $d = 8.3 \cdot 10^{-5}$ cm and $n = 1.1$. The thicknesses of the thinner films were determined from the absorbance at λ = 410 nm using the formula $d = 8.3 \cdot 10^{-5} \cdot D_{410}$ cm. The extinction coefficients (ε) in the absorption spectra were determined in the experiments with the ZG films with the known concentrations of ZG.

The quantum yields of luminescence for the films studied in this work were calculated following the known procedure[7] as the ratios of the integrated intensities of ZG and NR luminescence to the integrated intensity of luminescence of anthracene films.

Results and Discussion

The absorption spectrum of the ZG film (Fig. 1, curve *1*) exhibits three bands at λ = 410 ($\varepsilon = 1.13 \cdot 10^4$), 311 ($\varepsilon = 1.06 \cdot 10^4$), and 235 nm ($\varepsilon = 1.72 \cdot 10^4$ L mol^{-1} cm^{-1}). In the spectral region 280—500 nm this spectrum qualitatively coincides with the absorption spectrum of ZG in the benzene solution (λ = 405 nm ($\varepsilon = 2.4 \cdot 10^4$) and 308 nm ($\varepsilon = 2.3 \cdot 10^4$ L mol^{-1} cm^{-1})). The differences between them consist in a slight (3—5 nm) red shift of the absorption bands, which points to a weak interaction of the ZG molecules in the amorphous film, and a nearly halved extinction coefficient.

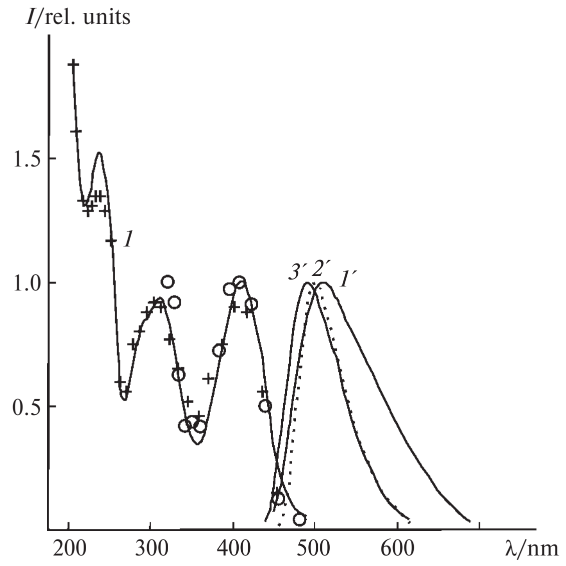

Fig. 1. Absorption, luminescence, and luminescence excitation spectra of ZG: absorption spectrum of ZG film with D_{410} = 0.2 (*1*) and fluorescence excitation spectra recorded on the Specord M-40 spectrophotometer (crosses) and on the luminescence setup (open circles); fluorescence spectra of ZG in amorphous film (*1′*), solid polycrystalline powder (*2′*), and benzene solution (*3′*).

The fluorescence spectrum of the ZG film (see Fig. 1, curve *1′*) is independent of the wavelength of the exciting radiation and represents a broad structureless band with a maximum at λ = 510 nm and a halfwidth, $\Delta\lambda_{1/2}$, of 115 nm, which is twice as large as that of the long-wavelength absorption band (λ = 410 nm, $\Delta\lambda_{1/2}$ = 57 nm). The fluorescence band of the ZG film is 1.6 to 1.9 times broader than the corresponding fluorescence bands of the polycrystalline ZG powder (λ = 500 nm, $\Delta\lambda_{1/2}$ = 62 nm) and its solution in benzene (λ = 490 nm, $\Delta\lambda_{1/2}$ = 71 nm) (see Fig. 1, curves *2′* and *3′*, respectively).

The absorption spectrum of the ZG film containing 0.02 mol L^{-1} NR (Fig. 2, curve *1*) coincides with the absorption spectrum of the undoped ZG film in the spectral region λ < 500 nm. However, beyond this spectral region (λ > 500 nm) the spectrum exhibits a new long-wavelength band at λ = 552 nm ($\Delta\lambda_{1/2}$ = 87 nm, $\varepsilon = 4.1 \cdot 10^{-4}$ L mol^{-1} cm^{-1}) originated, apparently, from the absorption of NR. An analogous band is also observed in the spectra of NR solutions in ethanol (λ = 552 nm, $\Delta\lambda_{1/2}$ = 88 nm, see Fig. 2, curve *2*), chloroform (λ = 538 nm, $\Delta\lambda_{1/2}$ = 81 nm), and benzene (λ = 529 nm, $\Delta\lambda_{1/2}$ = 78 nm). The excitation of the film doped

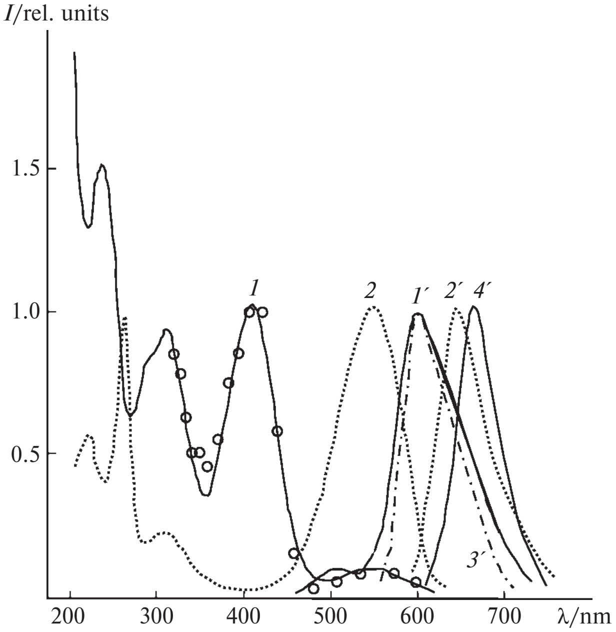

Fig. 2. Absorption, luminescence, and luminescence excitation spectra of NR. Amorphous ZG film ([NR] = 0.02 mol L^{-1}): absorption spectrum (*1*, solid line), luminescence excitation spectrum (*1*, open circles), and fluorescence spectrum (λ_{exc} = 406 nm) (*1′*). Nile Red solution in ethanol: absorption spectrum (*2*) and fluorescence spectrum (*2′*). Nile Red solution in chloroform: fluorescence spectrum (*3′*). Polycrystalline NR powder: fluorescence spectrum (*4′*).

with 0.02 mol L^{-1} NR with monochromatic light at λ = 405 nm leads to fluorescence. Here, the fluorescence spectrum exhibits two structureless bands, a weak band at 510 nm and a more intense band at 600 nm with $\Delta\lambda_{1/2}$ = 84 nm (see Fig. 2, curve *1′*). Only one fluorescence band at 600 nm ($\Delta\lambda_{1/2}$ = 84 nm) appears upon the excitation of this film in the spectral region $\lambda > 500$ nm. The band at 510 nm can be assigned to the fluorescence of ZG (see Fig. 1, curve *1′*), while the intense band at 600 nm can be assigned to the fluorescence of NR. Analogous fluorescence bands are observed in the NR solutions in chloroform (λ = 602 nm, $\Delta\lambda_{1/2}$ = 70 nm), ethanol (λ = 645 nm, $\Delta\lambda_{1/2}$ = 66 nm), and in polycrystalline NR powder (λ = 665 nm, $\Delta\lambda_{1/2}$ = 54 nm) (see Fig. 2, curves *2′—4′*). The fluorescence bands of the NR molecules incorporated into the ZG matrix are 1.2 to 1.6 times broader than the corresponding bands observed in the spectra of NR solutions and polycrystalline NR powder. This broadening is much smaller than the corresponding broadening of the ZG fluorescence bands. The fluorescence band of the NR molecules in the ZG film exhibits no broadening compared to the long-wavelength fundamental absorption band and is symmetric (on the wavelength scale), which is appreciably different from the absorption and luminescence spectra of the host ZG molecules. The Stokes shift between the absorption and luminescence bands of the NR molecules in the ZG film is 48 nm, or 1449 cm^{-1}, which is 2 or 3 times smaller than the corresponding values for the ZG film (100 nm, or 4790 cm^{-1}). Position of the maximum of the NR fluorescence band strongly depends on the nature of the solvent for both liquid and solid solutions.

In addition to absorption and fluorescence spectra, we studied the fluorescence excitation spectra. Generally, the luminescence intensity (I) can be written as $I = \eta_0 J_\lambda(1 - 10^{-D\lambda})$, where η_0 is the quantum yield of luminescence and D_λ and J_λ are the absorbance of the sample and the intensity of the exciting monochromatic radiation at the wavelength λ, respectively. At low D_λ, the luminescence intensity (I) is given by the formula $I = 2.3\eta_0 J_\lambda D_\lambda$; if the quantum yield of luminescence (η_0) is independent of λ, we get $I/J_\lambda = \mathrm{const} \cdot D_\lambda$. The spectral dependence of the I/J_λ ratio is called the luminescence excitation spectrum, or the action spectrum. The fluorescence excitation spectrum of the undoped ZG film (see Fig. 1, curve *1*, crosses and the open circles) satisfactorily matches the absorption spectrum of the same film (D_{410} = 0.2) (see Fig. 1, curve *1*). This points to the fact that the fluorescence band at 510 nm does originate from fluorescence of the host ZG molecules and that the quantum yield of fluorescence of the ZG films is independent of the wavelength of the exciting light in the spectral region 200—500 nm (*i.e.*, the Vavilov law holds). However, the NR luminescence excitation spectrum of the ZG film containing 0.02 mol L^{-1} NR (see Fig. 2, curve *1*, open circles) coincides with the net absorption spectrum of this film in the spectral region 300—400 nm (see Fig. 2, curve *1*). Therefore, the intensity of the NR fluorescence from the doped ZG film upon the excitation of the ZG molecules is much higher than that observed upon selective excitation of the NR molecules. For instance, the intensity of the NR fluorescence excited at λ = 410 nm (*i.e.*, at the absorption maximum of the host compound) is an order of magnitude higher than in the case of direct excitation of the NR molecules by light near the fundamental absorption band at λ = 552 nm. According to calculations, reabsorption of light of the green fluorescence of the matrix (λ = 510 nm) in the doped film by the NR molecules in the spectral region 500—600 nm followed by sensitized fluorescence of the NR molecules (λ = 600 nm) can increase the intensity of red NR fluorescence by several per cent only. Bright fluorescence of NR in the doped ZG film observed upon photoexcitation of ZG immediately points to effective nonradiative transfer of electronic excitation energy from the host ZG molecules to the guest NR molecules.

To study the nonradiative energy transfer mechanism, we measured the dependences of the intensities of the green and red luminescence bands for the NR-doped ZG films on the concentration of NR. Figure 3 presents the

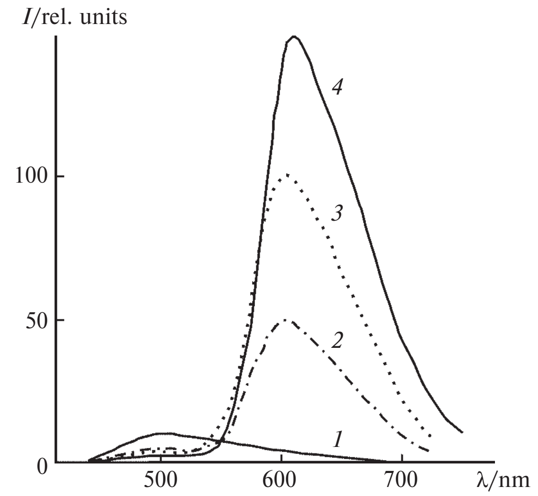

Fig. 3. Fluorescence spectra of NR-doped ZG films ($D_{410} = 0.3$, λ_{exc} = 406 nm). Undoped films (*1*) and films doped with $0.8 \cdot 10^{-3}$ (*2*), $1.4 \cdot 10^{-3}$ (*3*) and $2.6 \cdot 10^{-3}$ (*4*) mole NR per mole ZG.

fluorescence spectra of the doped ZG films at different concentrations of NR. As the concentration of NR increases, the intensity of the green fluorescence band of the host ZG molecules at 510 nm decreases while the intensity of the band of sensitized red fluorescence of NR molecules at 610 nm increases. An increase in the NR concentration in the film leads to slight broadening of the fluorescence band of NR and to a red shift of this band due to reabsorption. Calculations with inclusion of reabsorption effects show that the spectral patterns of sensitized NR fluorescence and non-quenched ZG fluorescence in the amorphous film are independent of the NR concentration. This indicates that concentration quenching of the green fluorescence of the host compound, ZG, and simultaneous excitation of the red fluorescence of NR molecules are due to photophysical energy transfer from the ZG molecules to the NR molecules rather than, *e.g.*, chemical interaction between them.

In Fig. 4 we present the concentration plots of the integrated intensities of the green fluorescence of ZG (I^{ZG}) and of the red fluorescence of NR (I^{NR}) in the form of their ratios to the fluorescence intensity of the undoped ZG film (I_0^{ZG}). As can be seen, an increase in the concentration of NR leads to quenching of the green fluorescence of the matrix and to excitation of the red fluorescence of the guest molecules, which reaches a maximum at the concentration $C \approx 10^{-2}$ mol NR per mol ZG and then decreases. A decrease in the NR fluorescence intensity at high concentrations is probably due to the concentration quenching (Q), which is typical of solutions and is accompanied by a drop of the quantum yield, shortening of the lifetime of the fluorescent molecules, and depolarization of radiation.[1] Near the spectral maximum, *e.g.*, at $C = 0.007$ mol NR per mol ZG, the fluorescence intensity of the host compound decreases by almost an order of magnitude, while the intensity of sensitized fluorescence of NR increases by a factor of nearly 13 as compared to the initial fluorescence intensity of the matrix, I_0^{ZG}. The quantum yield of the green fluorescence of the ZG film, η_0^{ZG}, is 0.07 and the quantum yield of the red fluorescence of NR molecules incorporated into the ZG film, η_0^{NR}, is 1. Thus, the system studied in this work is characterized by highly efficient transformation of the excitation energy of the host molecules into the sensitized red fluorescence of the guest molecules.

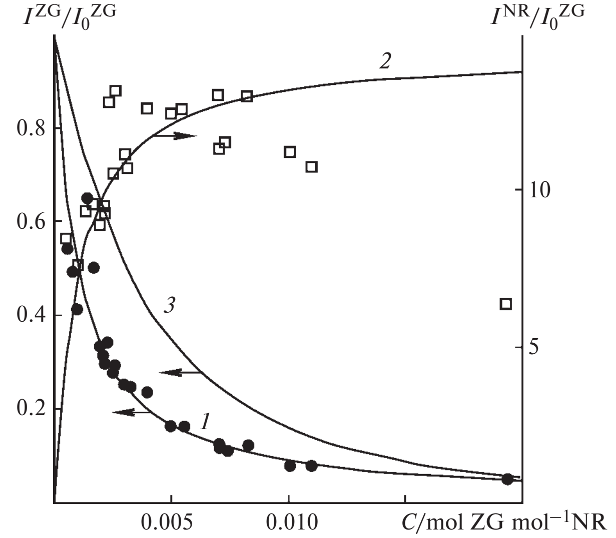

Fig. 4. Concentration quenching of green fluorescence of the host compound I^{ZG}/I_0^{ZG} (points — experiment, *1* — calculations using the exciton theory, *3* — calculations using the inductive-resonance mechanism) and excitation sensitized red fluorescence I^{NR}/I_0^{ZG} (squares — experiment, *2* — calculations using the exciton theory).

The experimental data shown in Fig. 4 are given in the form of the corresponding anamorphoses in Fig. 5. As can be seen, the concentration dependences of the quenching and excitation factors match each other and are linear.

Linear dependence of the quenching factor on the concentration of guest molecules is predicted by the model of partially localized, randomly hopping exciton. This model was used, in particular, for the description of energy transfer in solid solutions of organic molecules in a polymeric matrix.[8,9] The exciton was considered as an excited state that undergoes random migrations from one matrix molecule to another. Since such a partially delocalized exciton can "visit" a large number of matrix molecules during the lifetime of the excited state, a small amount of guest molecules that act as traps can favor both efficient quenching of matrix luminescence and sensitization of the fluorescence of the guest molecules. The concentration dependence of the quenching factor is linear: $Q = 0.66mC$,[8,9] where m is the number of exciton jumps between the matrix molecules during the lifetime.

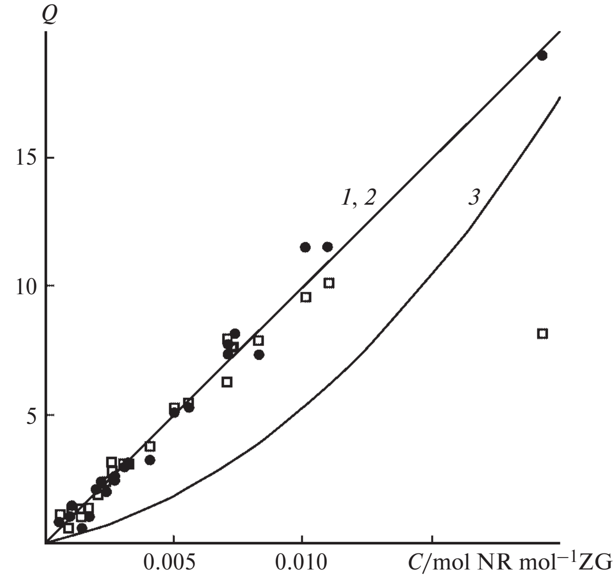

Fig. 5. Concentration plots of the quenching factor of green fluorescence of the host compound $Q = (I_0^{ZG} - I^{ZG})/I^{ZG}$ (points denote the experimental data; calculations using the exciton theory (*1*); calculations using the inductive-resonance mechanism (*3*)) and the excitation factor of sensitized red fluorescence of NR $Q = (I^{NR}/I^{ZG}) \cdot (\eta_0^{ZG}/\eta_0^{NR})$ (squares denote the experimental data; calculations using the exciton theory (*2*)).

Therefore, the experimentally determined linear dependence (see Fig. 5) is evidence for the exciton mechanism of the excitation energy transfer from the host ZG molecules to the guest NR molecules.

If the interaction between the molecules of the host compound is weaker than the interaction between the host and guest molecules, transfer of electronic excitation energy can follow Förster´s single-step, long-range, inductive-resonance dipole-dipole mechanism.[10] We also analyzed the results of our experiments in the framework of this mechanism. In this case, $I/I_0 = 1 - 2q\exp(q^2) \cdot \int\exp(-x^2)\mathrm{d}x$, [1,10] where I and I_0 are the donor fluorescence intensities in the presence and in the absence of acceptor; x is the integration variable; q is the dimensionless transfer parameter: $q = [2.36/(2\pi n)^2](\eta_0\alpha)^{1/2}C$, where 2.36 is the coefficient corresponding to random mutual arrangement of the donor and acceptor molecules; n is the refractive index of the medium; η_0 is the quantum yield of fluorescence of the donor molecules; C is the concentration of acceptor molecules (in molecule cm^{-3}); and α is the overlap integral of the fluorescence spectrum of the donor and the absorption spectrum of the acceptor (cm^6) ($\alpha = \int f(\lambda)\varepsilon(\lambda)\lambda^4\mathrm{d}\lambda$, where $f(\lambda)$ is the fluorescence spectrum of the donor, normalized to unity, *i.e.*, $\int f(\lambda)\mathrm{d}\lambda = 1$); and $\varepsilon(\lambda)$ is the absorption spectrum of the acceptor (cm^2 molecule^{-1}).

Curves *3* in Figs. 4 and 5 present the results of calculations carried out with $\eta_0 = 0.07$, $n = 1.1$, and $\alpha = 3.3 \cdot 10^{-34}$ cm^6. The experimentally observed quenching of fluorescence is 2 to 3 times more efficient than quenching by the Förster resonance mechanism which, moreover, predicts the nonlinear concentration dependence for Q.

Thus, the results of our experiments count in favor of the exciton mechanism of energy transfer in the system under study. The number of jumps of the exciton during the lifetime, m, was estimated at $1.5 \cdot 10^3$. The diffusion length of the singlet exciton can be estimated from the formula $l = a(n)^{1/2}$,[8] where a is the separation between the ZG molecules. Based on the mean intermolecular distance in the ZG film estimated from the volume per molecule at a concentration of 1.06 mol L^{-1} ($a = 11.6$ Å), we found that $l \approx 450$ Å. Studies on the migration of singlet excitons in various doped molecular crystals[1] showed that the m values lie between several tens and hundreds of thousands of jumps, while the l values span the range from several hundreds to thousands of nanometers. For instance, perylene-doped thin crystalline films of *N*-isopropylcarbazole are characterized by $m = 4 \cdot 10^4$ and $l = 1350$ Å.[8]

The results obtained in this work show that the singlet exciton can also migrate within the amorphous media (*e.g.*, the films under study); however, in this case the migration is less efficient than in organic molecular crystals. One can suggest that the amorphous media are also characterized by some short-range order.

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